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Global Optimization of Binary Lennard-Jones Clusters Using Three Perturbation Operators

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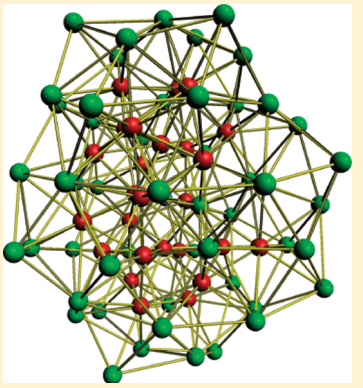
ABSTRACT: Global optimization of binary Lennard-Jones clusters is a challenging problem in computational chemistry. The difficulty lies in not only that there are enormous local minima on the potential energy surface but also that we must determine both the coordinate position and the atom type for each atom and thus have to deal with both continuous and combinatorial optimization. This paper presents a heuristic algorithm (denoted by 3OP) which makes extensive use of three perturbation operators. With these operators, the proposed 3OP algorithm can efficiently move from a poor local minimum to another better local minimum and detect the global minimum through a sequence of local minima with decreasing energy. The proposed 3OP algorithm has been evaluated on a set of 96 × 6 instances with up to 100 atoms. We have found most putative global minima listed in the Cambridge Cluster Database as well as discovering 12 new global minima missed in previous research.



INTRODUCTION

The study of binary clusters is very important both because alloy clusters play a fundamental role in catalysis and because the binary clusters allow us to tailor their property through the choice of atom types and composition, potentially leading to new properties which cannot be found on monatomic clusters.[1,2] However, binary clusters also present new challenges. Global optimization of binary clusters is significantly more difficult than that of monatomic clusters. We not only need to place the atoms to some suitable positions such that they form a low-energy geometrical structure but also have to assign an identity to each atom such that we can find out the lowest-energy solution among large amounts of homotops.

For the monatomic clusters, the Lennard-Jones (LJ) clusters are regarded as a standard benchmark system. Hundreds of papers have been published for this model. Various methods have been proposed, including basin hopping and its variant,[3−5] lattice methods,[6−10] population-based methods,[11−14] two-phase local search,[15,16] minima hopping,[17] funnel hopping[18] and so on. Using these methods, researchers have found putative global minima with up to 1610 atoms, which are now deposited in the Cambridge Cluster Database (CCD).[19]

For the binary clusters, the binary Lennard-Jones (BLJ) clusters are suggested to be a benchmark system.[1,2] However, compared with LJ clusters, there is much less work on the BLJ clusters. In 2005, Doye and Meyer first started a systematic exploration of the BLJ model.[1] Using the basin-hopping method, they published the putative global minima with up to $N = 100$ atoms for a range of LJ parameters. Later in 2009, Cassioli et al. reexamined the BLJ benchmark system using a method combining population basin hopping and two-phase local search and have found as many as 95 improved solutions.[20] According to the CCD, Pullan also found three improved solutions. Lately, Marques and Pereira[21] developed an evolutionary algorithm and discovered one new global minimum for $N = 38$ and $\sigma_{BB} = 1.05$. Very recently in August and September, 2010, Goedecker and Kolossvary, respectively, published 17 improved solutions on the CCD.[19]

This paper focuses on global optimization of BLJ clusters. To achieve this, we propose a heuristic algorithm (called 3OP) and test it on the BLJ benchmark system with up to 100 atoms. The computational results are compared with the results reported in the literature, showing the effectiveness of the proposed algorithm.

POTENTIAL

In BLJ clusters, each atom can be of two different types: A and B. And every two atoms i and j interact by a pair potential:

$$v(i,j) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right] \quad (1)$$

where α and β are the atom types of atoms i and j ($\alpha, \beta \in \{A, B\}$), $\varepsilon_{\alpha\beta}$ is the depth of the potential well, and $2^{1/6}\sigma_{\alpha\beta}$ is the equilibrium distance. The energy of the whole cluster is the summation of all pairwise potentials:

$$E = \sum_{i<j} v(i,j) \quad (2)$$

In this paper, we use the same settings adopted by previous researchers[1,2,20,21] and choose $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB} = \varepsilon_{BA} = 1$, $\sigma_{AA} = 1$,

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and $\sigma_{AB} = \sigma_{BA} = 0.5 \times (\sigma_{AA} + \sigma_{BB})$. Then, each problem instance is decided by two parameters: the number of atoms N and σ_{BB}. The whole BLJ clusters benchmark system consists of 96×6 instances with $5 \leq N \leq 100$ and $\sigma_{BB} \in \{1.05, 1.10, 1.15, 1.20, 1.25, 1.30\}$.

Note that, for global optimization of BLJ clusters, we have to determine both the atom type (A or B) and the coordinate position for each atom. Therefore, the number of local minima on the potential energy surface of a N-atom BLJ cluster is much larger than that of a N-atom LJ cluster. We can make a rough comparison as follows: For a specific stable configuration of a LJ cluster, we assign a certain atom type to each atom. Then, we locally optimize the configuration and obtain a stable configuration for the BLJ cluster. In total, there are 2^N different ways to choose atom types for N atoms. Thus, we can obtain up to 2^N different local minima for the BLJ cluster from one local minimum of a LJ cluster.

From the perspective of optimization, the BLJ clusters problem is very interesting because it is a mixture of continuous (determine atom positions) and combinatorial (determine atom types) optimizations.

■ ALGORITHM

The proposed 3OP algorithm is composed of three procedures: KNEAD, SMOOTH, and FLIP. The KNEAD and SMOOTH procedures are used to optimize the cluster's geometrical structure, and the FLIP procedure is used to choose identities for the atoms.

These three procedures share two common features: First, each of them starts from a locally optimal configuration and aims to improve it by repeatedly imposing some perturbations on it. Second, they have the same acceptance/rejection rule. That is to say, for the current locally optimal configuration X, they perturb it and locally optimize the perturbed X to obtain a new local minimum Y. Specifically, if $E(Y) < E(X)$, X is replaced by Y as the incumbent solution; otherwise, X is still kept as the incumbent solution. The difference among these three procedures is that they use different perturbation operators and have different stopping criteria. The details are described below.

The KNEAD Procedure. The KNEAD procedure aims to improve a locally optimal configuration by moving several high-energy atoms to the interior of the cluster. The energy of atom i is defined as[8,23]

$$E_i = \sum_{j=1, j\neq i}^{N} v(i,j) \qquad (3)$$

In the KNEAD procedure, we try to improve the current local minimum X by repeating the following three steps. First, we find out the top m (m is a random integer between 1 and $0.1 \times N$) highest-energy atoms in X and move each of them to a random position in the interior of the cluster, so that the distance between each moved atom and the mass center of the cluster is less than d ($d = 2$). Second, we locally optimize the perturbed configuration using the limited memory Broyden−Fletcher−Goldfarb−Shanno (LBFGS) algorithm[22] and obtain a new local minimum Y. Third, if $E(Y) < E(X)$, we accept Y; otherwise, we reject Y. The KNEAD procedure repeats the above three steps until 10 consecutive rejections appear.

Note that: (1) The high-energy atoms usually locate on the surface of the cluster, because they have a smaller number of nearest neighbors. By repeatedly moving the high-energy atoms to the interior of the cluster, the atoms tend to squeeze together, and the cluster becomes more uniform. (2) The perturbation operator of moving several high-energy atoms to the interior of the cluster was first introduced by Takeuchi with the name interior operator (IO).[23] It has become the main ingredient of some highly efficient algorithms for global geometry optimization.[10,23−26]

The SMOOTH Procedure. The SMOOTH procedure aims to improve a locally optimal configuration by moving a high-energy atom to a vacant site on the surface of the cluster. To find out the vacant sites on the surface of the cluster, we adopt the same method proposed by previous researchers.[8,23] We fix the N atoms at their respective positions and place an additional probe atom to a random place on the surface of the cluster. It is observed in our computational experiments and previous research that the atoms on the surface of the putative global minima are usually of type B. Therefore, we choose the probe atom to be a type-B atom. Being attracted or repelled by the fixed atoms, the probe atom will move from its initial position to a stable position. The obtained stable position is then regarded as a vacant site, and the energy of the probe atom is used to measure the degree of vacancy; lower energy implies a more vacant site. By repeating the above operations $2N$ times, we can find out almost all the vacant sites on the surface of the cluster.

In the SMOOTH procedure, we focus only on the top s ($s = 0.2 \times N$) highest-energy atoms and the top t ($t = 5$) most vacant sites. In the order of $i = 1, 2, ..., s$ and $j = 1, 2, ..., t$, we perturb the current local minimum X by moving the i-th highest-energy atom to the j-th most vacant site. Then we locally optimize the perturbed configuration and obtain a new local minimum Y. If Y is better than X, then Y is accepted as the incumbent solution, and the SMOOTH procedure is recursively used to further optimize Y. Otherwise, if we have tried all $s \times t$ moves but cannot find a better local minimum, then we terminate the SMOOTH procedure.

Note that: (1) Through repeatedly moving a high-energy atom to a vacant site, the surface of the cluster becomes smoother. (2) The perturbation operator of moving the "worst" atom to the "best" vacancy was first introduced by Northby[7] and has been adopted by many researchers for global geometry optimization.[6,8−10,13] (3) Prior to this work, the same technique of moving the worst element to the best site has been used for solving the packing equal circles in a square problem, producing very impressive results.[27]

The FLIP Procedure. The FLIP procedure aims to improve a locally optimal configuration by flipping the atom type of each atom. In the order of $i = 1, 2, ..., N$, we perturb the current local minimum X by flipping the atom type of atom i, i.e., changing its atom type from A to B or B to A. Then we locally optimize the perturbed configuration and obtain a new local minimum Y. If Y is better than X, then X is replaced by Y, and we continue to flip the next atom. The FLIP procedure terminates when each atom has been flipped once.

Note that: (1) One may ask why not keep flipping the atoms until we cannot obtain any improvement but only flip each atom once? In fact, we have tested this stopping criterion. Using this stopping criterion is significantly more time consuming, and the benefit is unclear. (2) The method of finding a better solution through iteratively flipping a variable has been widely used for solving the satisfiability (SAT) problem.[28]

Main Scheme of the Algorithm. The main scheme of the proposed 3OP algorithm is as follows:

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Table 1. Comparison between the Previously Best-Known Energy and the New Energy

N	σ_{BB}	previous energy	this work	N	σ_{BB}	previous energy	this work
78	1.10	−427.264722[a]	−427.333481	78	1.20	−444.822988[a]	−444.864069
79	1.10	−433.882967[a]	−433.956776	79	1.20	−451.342508[b]	−451.921407
73	1.15	−404.046888[b]	−404.095588	81	1.20	−464.422970[b]	−464.450846
83	1.15	−470.061091[b]	−470.064073	88	1.20	−511.429454[a]	−511.443323
76	1.20	−431.192388[b]	−431.281456	89	1.20	−517.713603[b]	−517.829589
77	1.20	−437.822083[a]	−437.832462	68	1.30	−387.691297[a]	−388.025204

[a] Found by Cassiolia et al.[20] [b] Found by Doye and Meyer.[1]

(1) Generate a random initial local minimum X by randomly scattering N atoms into a sphere of radius $R = 0.7 \times N^{1/3}$, randomly assigning atom type A or B to each atom and locally optimizing the initial configuration.
(2) X ← KNEAD (X).
(3) X ← FLIP (X).
(4) X ← SMOOTH (X).
(5) X ← FLIP (X).
(6) If X is improved in step (5), then go to step (4).

Note that: (1) Using the described three operators, we build up a complex neighborhood structure on the set of the local minima. Thus, the 3OP algorithm can be regarded as a local search method which starts from a randomly sampled local minimum and iteratively moves from the current local minimum to a better one. (2) There is much similarity between the proposed 3OP algorithm and the monotonic sequence basin hopping (MSBH) procedure proposed by Leary.[5] They both start from an initial local minimum and then iteratively move to a better local minimum. The main difference is that, in the MSBH algorithm, a locally optimal configuration is perturbed by randomly shifting each atom a small step, while in the 3OP algorithm, the perturbation of atoms is usually guided by some heuristic information. (3) It is usually not possible to locate the global minimum through one run of the 3OP algorithm. In computational experiments, we run the 3OP algorithm in a multistart fashion until the putative global minimum (or a new global minimum) has been found, or the elapsed CPU time has exceeded a predefined limit.

EXPERIMENTS

The proposed 3OP algorithm is programmed in C++ and compiled using GNU GCC. To evaluate its performance, we carry out 10 times of computational experiments. In each experiment, the 3OP algorithm is used to solve all the 96 × 6 problem instances without special tuning of parameters. On each problem instance, we run the 3OP algorithm in a multistart fashion and stop the search once the putative global minimum (or a new global minimum) has been found or the elapsed CPU time has exceeded 24 h. It should be noted that the best-known records used in this paper are contributed by Doye and Meyer,[1] Wayne Pullan,[19] Cassiolia et al.,[20] Marques and Pereira,[21] Stefan Goedecker,[19] and Istvan Kolossvary.[19] All experiments are done on a Linux cluster with multiple 2.33GHZ Intel Xeon CPUs. Though we have used up to 16 CPUs to solve all problem instances, no parallel computation has been performed.

Computational Results. After 10 times of computational experiments, we have found all the putative global minima except for the following instances:

- $\sigma_{BB} = 1.15$, $N = 59$
- $\sigma_{BB} = 1.20$, $N = 91, 93, 94, 99$
- $\sigma_{BB} = 1.25$, $N = 87, 91, 99, 100$
- $\sigma_{BB} = 1.30$, $N = 88, 89, 94, 97, 99, 100$

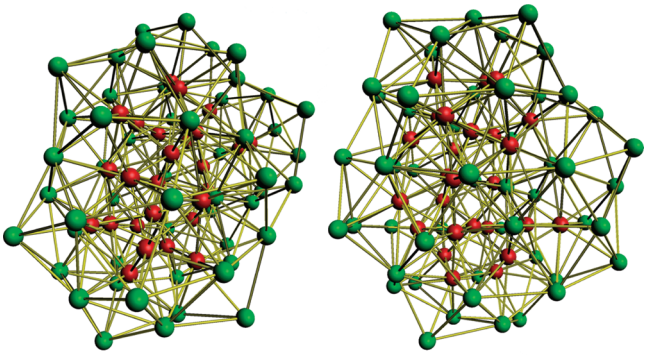

Figure 1. Comparison between the previous putative optimum and the new optimum for $N = 79$ and $\sigma_{BB} = 1.20$. The green balls denote the type-B atoms and the red balls type-A atoms. The previous configuration has energy −451.342508 and presents C_1 symmetry, while the new configuration has energy −451.921407 and presents C_{2v} symmetry. Both configurations have the same number of type-A and -B atoms ($N_A = 27$ and $N_B = 52$).

Observing the configurations of the undetected putative global minima, we find that most of them fall into two categories. For the first category, there are several type-B atoms which appear exceptionally in the interior of the cluster. These instances include $\sigma_{BB} = 1.20$, $N = 91, 99$; $\sigma_{BB} = 1.25$, $N = 87$; and $\sigma_{BB} = 1.30$, $N = 97$. Note that in most putative global minima, all type-B atoms locate on the surface of the cluster and type-A atoms in the interior. We therefore conjecture that it is the exceptional type-B atoms that makes the corresponding putative global minimum hard to detect. For the second category, the shape of the cluster is oblate or prolate. For example, the shape of the clusters for $\sigma_{BB} = 1.30$, $N = 88, 89$ is oblate, and the shape of the clusters for $\sigma_{BB} = 1.25$, $N = 99, 100$ and $\sigma_{BB} = 1.30$, $N = 99,100$ is prolate. The proposed 3OP algorithm disfavors oblate or problate clusters, because the KNEAD procedure tends to make the cluster spherical.

We also discover 12 new global minima missed in previous research. Table 1 presents a comparison between the previously best-known energy and the new energy that we find in this paper for all these 12 instances. The coordinate files of all the 12 new global minima have been sent to David J. Wales. They can now be openly accessed from the Cambridge Cluster Database. Figure 1 shows the configuration of the previous putative optimum and that of the new optimum for the instance of $N = 79$ and $\sigma_{BB} = 1.20$. The new configuration has lower energy and shows more symmetry than the old configuration. Both configurations have the same number of type-A and -B atoms.

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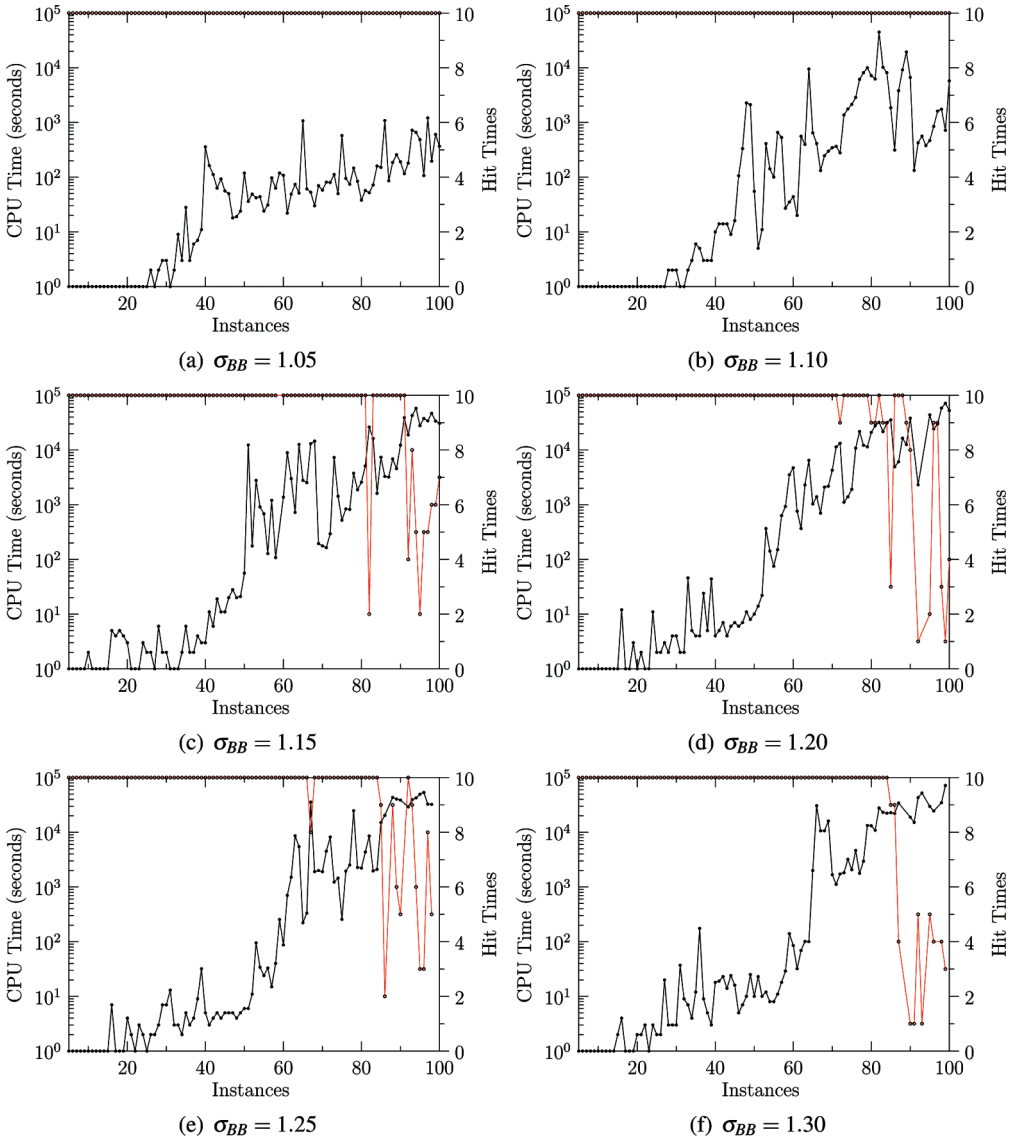

Figure 2. Computational statistics on the successful instances where the putative optima can be located within 24 h. The red lines indicate the hit times of the putative optima. The black lines denote the average CPU time over these multiple hits.

For the instances where the proposed 3OP algorithm can locate the putative global minima, we present in Figure 2 the detailed computational statistics, including the hit times of the global minima and the average CPU time over these multiple hits. From subfigures (a) and (b), one can observe that the first two sets of instances are relatively easy to solve; the 3OP algorithm can always locate all the putative global minimum within 24 h. The other four sets of instances with $N \geq 80$ are much more difficult; the 3OP algorithm can not always hit the putative global minima within 24 h.

Comparing with Previous Works. We find in previous literature that, prior to this work, there are only two groups (Doye and Meyer and Cassiolia et al.) who have systematically calculated all the instances in the BLJ benchmark system. Both of them did not present detailed computational statistics. However, the current best-known records reveal that Doye and Meyer[1] have missed more than 100 putative optima and Cassiolia et al.[20] have missed at least 29 putative optima. On the other hand, for the proposed 3OP algorithm, all initial configurations are randomly generated, and all parameters are kept constant for all tested instances. While in their works, some initial configurations are generated from lowest-energy structures of nearby N and σ_{BB}, and their algorithms usually use more parameters than the proposed 3OP algorithm.

Marques and Pereira[21] have calculated all the instances in the range of $5 \leq N \leq 50$. They are able to find all the putative global minima and one improved solution in this region. Compared with their evolutionary algorithm, the 3OP algorithm can also find all the current putative optima in this region. Moreover, one can observe from Figure 2 that the CPU time for locating the putative optima in this region is very short, in most cases less than 100 s.

Pullan, Goedecker, and Kolossvary also explored the BLJ benchmark system and reported several improved solutions on the CCD, respectively. We do not know about their methods and the detailed computational results. However, they have missed at least 12 new optima reported in Table 1.

Case Study. Due to the difficulty of the BLJ clusters problem and the proposed 3OP algorithm, it is impossible to analyze the

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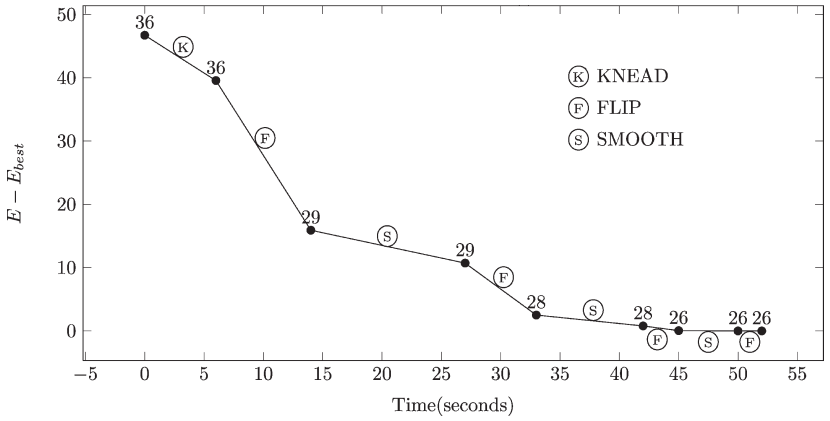

Figure 3. A typical search trajectory of the 3OP algorithm on the instance of $N = 85$ and $\sigma_{BB} = 1.15$.

3OP algorithm thoroughly at present. To demonstrate how the 3OP algorithm behaves, we present in Figure 3 a representative search trajectory of the 3OP algorithm on the instance of $N = 85$ and $\sigma_{BB} = 1.15$. The horizontal axis indicates the elapsed CPU time, and the vertical axis indicates the distance between the energy of the current local minimum (E) and that of the putative global minimum ($E_{best} = -483.671540$). The number above each dot denotes the number of the type-A atoms (N_A) in the current local minimum. At $t = 0$, the algorithm obtains a random initial local minimum with $\Delta E = E - E_{best} = 46.726$ and $N_A = 36$. After the KNEAD procedure ($t \in [0,6]$), the search reaches a local minimum with $\Delta E = 39.562$. Then, through the FLIP procedure ($t \in [6,14]$), the search arrives at a local minimum with $\Delta E = 15.913$ and $N_A = 29$. After that, the search performs three cycles of SMOOTH and FLIP procedures and finally finds the putative global minimum at $t = 52$. The computational test in this section is done on a PC with a 1.8 GHZ AMD Athlon CPU and 1G RAM.

CONCLUSION

This paper proposes 3OP, a heuristic algorithm for global optimization of BLJ clusters. The proposed algorithm makes extensive use of three perturbation operators: moving several high-energy atoms to the interior of the cluster, moving a high-energy atom to a vacant site on the surface of the cluster, and flipping the identity of each atom. Using these operators, the algorithm can efficiently search both the configurational and permutational spaces and detect the global minimum through a sequence of local minimum with decreasing energy. The effectiveness of the proposed 3OP algorithm has been shown by computational experiments. Even though several groups have searched the BLJ benchmark system using various methods, the 3OP algorithm can still find 12 better solutions than the best-known ones recorded in the Cambridge Cluster Database.

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