

Global minima optimization via mirror-rotation transformation

Yi-Rong Liu^{1,*}, Yan Jiang,² Shuai Jiang,¹ Chun-Yu Wang,¹ and Teng Huang³¹School of Information Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China²School of Vanadium and Titanium, Panzhihua University, Panzhihua, Sichuan 617000, China³Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences, Hefei, Anhui 230031, China

(Received 16 July 2022; accepted 27 November 2022; published 16 December 2022)

Rapidly finding low-energy structures on high-dimensional potential energy surfaces remains a challenging problem for cluster science. We present a fast optimization method for structure prediction named mirror-rotation searching, which is inspired by the idea of symmetry and conservation. Our search algorithm can quickly converge to the minima of energy valley by continuously performing mirror-rotation transformation on the cluster, and we introduce the term *vaminima* to describe these minima. For the selected Lennard-Jones cluster of size $N \leq 150$, convergence to a *vaminima* on average takes 413 relaxations, and finding fullerene C_{60} from a random initial structure is 49-fold faster than the traditional genetic algorithm. The approach is general and flexible and can greatly improve the search efficiency of unbiased global optimization algorithms and be applied to different kinds of problems, such as molecular structure search, crystal structure prediction, and protein folding.

DOI: 10.1103/PhysRevResearch.4.L042045

Introduction. Exploration of the low-lying structures of atomic or molecular clusters remains a fundamental problem in nanocluster science. Nanocluster properties strongly depend on the size and shape of the nanocluster [1]. Unfortunately, the number of local minima on the potential energy surface (PES) increases exponentially with cluster size [2], and the PES can be visualized using disconnectivity graphs, which are based on samples of pathways that link local minima via transition states [3,4]. The global optimization of a cluster PES is a typical Non-Deterministic Polynomial (NP)-hard problem [5]. Therefore, one of the major challenges in cluster studies is how to quickly find the global minimum and other low-lying isomers on the PES. In the present work, we propose a fast and efficient optimization method different from previous methods to solve the global structure search problem [6–8].

To date, various types of algorithms have been developed to search for low-lying structures on complex PESs, such as genetic algorithms (GAs) [9], simulated annealing (SA) [10], and basin hopping (BH) [11], etc. [12–15]. These methods all involve two basic processes: (i) local geometry optimization and (ii) selection and movement. The main difference between the different methods is in the choice of new structure and how to move to the next local minima. The local optimization can transform the original PES into an energy staircase $f_o(S) \rightarrow$

S' , where S represents the original configuration space, $S' \subseteq S$ is the set of distinct local minima, and f_o is a geometry optimization method based on different tasks. The use of the f_o transformation operation can effectively remove the effect of the transition state regions without altering the global minima and greatly improve the search efficiency of the configuration space.

For structure prediction, extensive configuration searches are performed just to find a limited number of low-energy structures or global minima, while most structures are useless. We care more about these low-energy structures that lie at the bottom of the valleys of energy. For multicomponent materials research, Schebarchov and Wales *et al.* proposed *biminima* to describe these special local minima points related to coordinate space and permutation space for different atomic species [15]. Similar to *biminima*, we introduce the term *vaminima* to describe these lowest-energy configurations set of lying at the bottom of energy valleys on the PES. For general structure searching algorithms, most of the time is spent searching for local minima with high energy based on physical or biological laws. Therefore, how optimization algorithms can quickly and efficiently find the *vaminima* through finite search steps is a key issue in structure prediction. Here, we propose a fast structural optimization method called mirror ($\hat{M}$)-rotation ($\hat{R}$) search (MRS), where $\hat{M}$ and $\hat{R}$ represent the mirror and rotation operation matrices, respectively. By continuously performing mirror-rotation transformation on the S' configuration space based on the taboo strategy, the configuration energy sequences $\{E(S'_0) > E(S'_1) > E(S'_2) \cdots E(S'_n) > E(S'')\}$ can quickly converge to the bottom of the energy valley $f_o[\hat{M}\{\hat{R}(S')\}] \rightarrow S''$, where $S'' \subseteq S'$ represents the lowest-energy configuration in the energy valley and satisfies $\Delta E \geq 0$ for all S' configuration space within the energy valley, where $\Delta E = E(S') - E(S'')$. All S'' configurations form the *vaminima* set on the PES. We now present a detailed

*yrlu@ustc.edu.cn

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

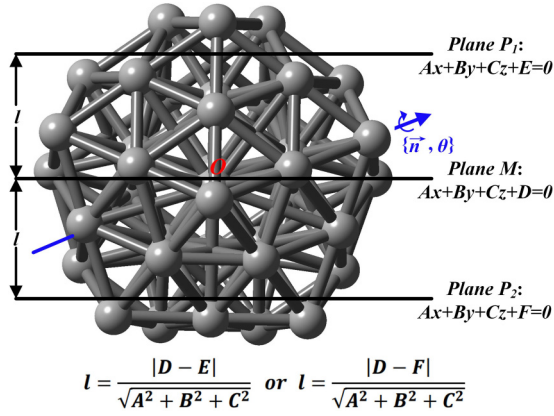


FIG. 1. Schematic diagram of mirror and rotation operations. Plane $M: Ax + By + Cz + D = 0$ represents the mirror plane, where A, B, C , and D are equation coefficients. Planes P_1 and P_2 are parallel to mirror plane M with different translation coefficients E and F , and they have the same distance to the mirror plane M . The variable l represents the distance between planes P_1 or P_2 and M and is calculated by plane equation coefficients. Red O represents the cluster centroid and is on plane M . The $\vec{n}$ is a random rotation vector through the centroid O , and θ is the rotation angle ($0 \sim \pi$).

description of this method and apply it to Lennard-Jones and fullerene atomic clusters.

For a system containing N atoms, its configuration energy is calculated by the function $E(X)$, where $X \equiv \{x_i, y_i, z_i\}_{i=1}^N$ is

the particle coordinates at d -dimensional space $X \in \mathbb{R}^d$. Our goal is to search for the lowest value of $E(X')$ in a space $S' = \{X'\}$ that is obtained by the f_o transformation function in the original S space, where $S = \{X\}$, $S' = f_o(S)$. For the general case, we focus on the local minima set, S' , if there exists a transformation matrix $\hat{F}$ such that $E(X'') \leq E(X')$ within limited loop steps of $X'' = f_o[\hat{F}(X')]$ for arbitrary $X' \in S'$, where $\{X''\} \subseteq \{X'\}$. Here, we propose mirror-rotation transformation $\hat{F} = \hat{M}_l \{\hat{R}_{\theta, \vec{n}}\}$ to sample S' space.

Figure 1 shows a schematic diagram of mirror ($\hat{M}_l$) and rotation ($\hat{R}_{\theta, \vec{n}}$) operations, where the $\hat{M}_l$ transformation matrix is related to the parameter l , which is the distance between the mirror plane M and P_1 or P_2 , and the $\hat{R}_{\theta, \vec{n}}$ transformation matrix is related to the random vector $\vec{n}$ and rotation angle θ ($0 \sim \pi$). Before performing the mirror transformation, the configuration first needs to be rotated $X'_R = \hat{R}_{\theta, \vec{n}}(X')$ by (1), where $X'_R \in S'$.

$$\begin{pmatrix} x'_R \\ y'_R \\ z'_R \end{pmatrix} = \hat{R}_{\theta, \vec{n}} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}. \quad (1)$$

Equation (2) represents the rotation matrix for all atoms, where $\vec{n} = (n_x, n_y, n_z)$ is a random unit vector $|\vec{n}| = 1$ through the centroid of the cluster. Note that the rotation operation on the S' space is symmetrical; it does not change the energy of the system, $E(X'_R) = E(X')$, but it will affect the number of atoms participating in the mirror transformation as follows.

$$\hat{R}_{\theta, \vec{n}} = \begin{bmatrix} \cos \theta + (1 - \cos \theta)n_x^2 & (1 - \cos \theta)n_x n_y - n_z \sin \theta & (1 - \cos \theta)n_x n_z + n_y \sin \theta \\ (1 - \cos \theta)n_x n_y + n_z \sin \theta & \cos \theta + (1 - \cos \theta)n_y^2 & (1 - \cos \theta)n_y n_z - n_z \sin \theta \\ (1 - \cos \theta)n_z n_x - n_y \sin \theta & (1 - \cos \theta)n_y n_z + n_x \sin \theta & \cos \theta + (1 - \cos \theta)n_z^2 \end{bmatrix}. \quad (2)$$

The key is to perform mirror transformation $X'_M = \hat{M}_l(X'_R)$ by Eq. (3), where $X'_R = \hat{R}_{\theta, \vec{n}}(X')$ is computed by the above rotation matrix transformation and $\hat{M}_l$ is the mirror operation with respect to parameter l .

$$\begin{pmatrix} x'_M \\ y'_M \\ z'_M \\ 1 \end{pmatrix} = \hat{M}_l \begin{pmatrix} x'_R \\ y'_R \\ z'_R \\ 1 \end{pmatrix} \quad \text{if } [|Ax'_R + By'_R + Cz'_R + D| / \sqrt{(A^2 + B^2 + C^2)}] \geq l. \quad (3)$$

Equation (4) represents the mirror transformation matrix, which maps S' space coordinates to mirror space S'' , $f_o[\hat{M}_l(X'_R)] \rightarrow X''$, and the matrix elements are determined by the mirror plane equation coefficients, where f_o is the geometry relaxation function.

$$\hat{M}_l = (A^2 + B^2 + C^2)^{-1} \begin{bmatrix} B^2 + C^2 - A^2 & -2AB & -2AC & -2AD \\ -2AB & A^2 + C^2 - B^2 & -2BC & -2BD \\ -2AC & -2BC & A^2 + B^2 - C^2 & -2CD \\ 0 & 0 & 0 & 1 \end{bmatrix}. \quad (4)$$

The above matrix transformation can be described as a mapping from S' to S'' space by (5), where $X' \in S'$ and $X'' \in S''$ and $d_i = |Ax_i + By_i + Cz_i + D| / \sqrt{(A^2 + B^2 + C^2)}$ is the distance between the i th atom and the mirror plane M .

$$X'' = f_o[\hat{M}_l\{\hat{R}_{\theta, \vec{n}}(X')\} + \hat{R}_{\theta, \vec{n}}(X')] \leftarrow \begin{cases} \hat{M}_l\{\hat{R}_{\theta, \vec{n}}(X')\} & \text{for } d_i \geq l \\ \hat{R}_{\theta, \vec{n}}(X') & \text{for } d_i < l \end{cases}. \quad (5)$$

To focus on the vaminima candidate set, we introduce a convergence criterion, denoted by $\Delta E_{X' \rightarrow Y'}(X') = E(Y') - E(X')$, which quantifies the change in energy due to mirror-rotation transformation, $f_o[\hat{M}_l\{\hat{R}_{\theta, \vec{n}}(X')\} + \hat{R}_{\theta, \vec{n}}(X')] \rightarrow Y'$. We now define a condition for a vaminima candidate that satisfies

$$\{\Delta E_{X' \rightarrow Y'}(X') \geq 0\}^M, \quad \text{continuously } M \text{ times mirror - rotation transformation.} \quad (6)$$

Algorithm I. Converging sequence of mirror-rotation transformation.

```

1  Initialization  $C \leftarrow \text{True}$ ,  $T \leftarrow 0$ ,  $I = \{X'\}$ , and  $X' \leftarrow$  a random structure in  $S'$  space
2  Set  $M = N$  (convergence threshold),  $K \leftarrow 0$  (quench count).
3  While ( $C$  is true) do:
4       $K = K + 1$ 
5      if ( $f_o[\hat{M}_l\{\hat{R}_{\theta,\bar{n}}(X')\} + \hat{R}_{\theta,\bar{n}}(X')\} \rightarrow Y' : E(Y') < E(X')$ ) then:
6          Update  $X' \leftarrow Y'$ , adding  $Y'$  to the  $I$  set.
7          Reset  $T \leftarrow 0$ 
8      else:
9           $T = T + 1$ .
10     if ( $T \geq M$ ) then:
11         Set  $C \leftarrow \text{False}$ .
12  Output  $I$  set sequence and quench count  $K$ .
```

In other words, (6) represents a continuous M times transformation for the X' configuration, and $\Delta E_{X' \rightarrow Y'}(X')$ is non-negative. The set of configurations X' satisfying this criterion defines a vaminima candidate.

Note that satisfying condition (6) will result in a set of candidate sets with reduced energy based on the taboo strategy, $\{X'_1, X'_2, X'_3, \dots, X'_{k-1}, X'_k, \dots, X'_n\}$, $\forall n, k \in \text{integer and } n > k$; there is $E(X'_k) > E(X'_n)$. Starting from a random structure X' in S' space, the transformation is performed by a mirror-rotation operation, $f_o[\hat{M}_l\{\hat{R}_{\theta,\bar{n}}(X')\} + \hat{R}_{\theta,\bar{n}}(X')\} \rightarrow Y'$. If $E(Y') < E(X')$, Y' will be accepted. For configuration X' , if a lower-energy configuration cannot be produced by mirror-rotation transformation within M times, the operation will be stopped.

We show the mapping $f_o[\hat{M}_l\{\hat{R}_{\theta,\bar{n}}(X')\} + \hat{R}_{\theta,\bar{n}}(X')\} \rightarrow Y'$ through mirror-rotation transformations to explore energy valleys on complex PESs. For our algorithm (Algorithm 1), each running from a random configuration contains a *while* loop, which will stop until the variable C changes from the initial value of True to False. This running will end only when (6) is satisfied, and the result contains a set of sequences with reduced energy.

Note that different from traditional methods, our algorithm only accepts lower-energy structures at each step within a cy-

cle and rejects transformation with $\Delta E_{X' \rightarrow Y'}(X') > 0$ to avoid jumping back, and this strategy is similar to previous studies [16]. Generally, accepting structures with higher energy will help the algorithm to climb from the current energy valley to another to explore unique structures. In the past, many algorithms have improved the climbing strategy to optimize the algorithm search efficiency, and this is a very efficient design for new structure predictions [17–19]. However, this will increase the invalid structure and time consumption. For structure prediction, the configurations at the bottom of the energy valley are very important for us.

For each cycle in Algorithm 1, the key mirror ($\hat{M}_l$) and rotation ($\hat{R}_{\theta,\bar{n}}$) operation on line five are controlled by the l , θ , and $\bar{n}$ parameters. However, for each *while* loop, the parameter l is fixed, and only the θ and $\bar{n}$ variables in the rotation matrix (2) change randomly. The parameter K represents the total quench count when the *while* loop ends.

Result and discussion. As a first test example, consider a Lennard-Jones potential:

$$E_{LJ} = 4 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (7)$$

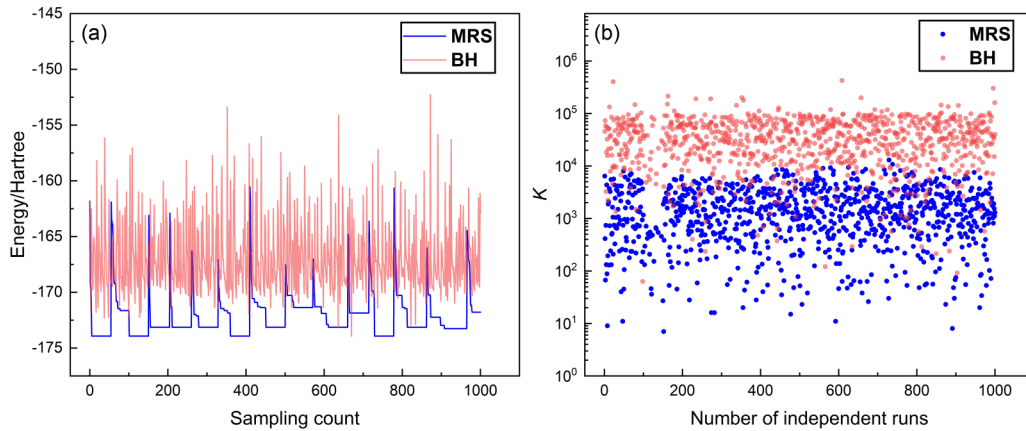


FIG. 2. (a) Comparison of the MRS (blue line) and BH (red line) methods regarding the sampled configuration energy versus the sampling count for the LJ_{38} cluster. The initial configuration is the same for the two methods. The blue horizontal line represents 14 loops in Algorithm 1 for MRS, and the blue vertical lines mark a random permutation. Red lines mark a BH search based on the Metropolis rule. (b) Number of quenches (K) required for finding the global minima (an fcc truncated octahedron for LJ_{38}) versus 1000 independent runs for MRS and BH. The initial structure is the same for each run.

TABLE I. Comparison of mean number of quenches required to find the global minimum of LJ₃₈ cluster for different revised basin-hopping and MRS methods. The statistics correspond to averages over 100 random starting points for LJ₃₈ cluster, which can be found on the GMIN website [21]. All jobs were run until the global minimum was located.

Sample size	Method	Average	Minimizations
100	Standard BH ^a	185493	1271
100	CO BH ^a	20655	142
100	CSMBH ^a	4369	34
100	MRS	1947	17

^aThese methods and data are from Ref. [20].

where $r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$ is the distance between atoms i and j , and the parameters ϵ (the well depth) and σ (atomic radius) are set to the same value ($\epsilon = \sigma = 1$).

To generate the energy-converged sequence by Algorithm 1, a random configuration X is first generated and then quenches X to the ground state. The prepared structure is then evolved by continuous mirror-rotation $\hat{M}_l\{\hat{R}_{\theta,\bar{n}}\}$ transformation and quenching. We compare our method with the basin-hopping (BH) method, which is one of the most powerful unbiased search methods [11]. For $N = 38$, the total energy of the system during this evolution is shown in Fig. 2(a) with 1000 sampling structures, and a total of 3957 and 11012 quenches are required for MRS (blue) and BH (red) searching, respectively. The total number of quenches required for BH search is three times that of MRS searching. For conventional BH, the atomic move step was set to 0.7 angstroms, and the temperature was adjusted to maintain a mean acceptance ratio of approximately 50%. The initial configuration is the same for both methods. It is obvious that the MRS method can quickly search from the high-energy random structure to the bottom of the energy valley and find the global minimum. For Fig. 2(a), we can see that starting from 14 independent random high-energy structures (blue vertical

line), the MRS searching can quickly obtain a candidate set of reduced energy. For MRS ($M = 50$), it takes an average of 95 quenches to find the lowest-energy structure for the LJ₃₈ system, but for the BH method, it will take 7370 quenches to find the global minima in our study. Table I shows the comparison of quench number for different revised BH methods and MRS to find the global minima of the LJ₃₈ cluster, and MRS takes fewer quenches than other methods [20]. Figure 1(b) shows the average quench number for finding the lowest-energy structure of the LJ₃₈ system by the MRS and BH methods, which contain 1000 independent searches with the same initial structure. This shows that MRS has a very high efficiency for the prediction of low-energy structures.

To further show the efficiency of mirror-rotation searching, we use the average quenches K in Algorithm 1 to denote the moving speed of the method from an arbitrary high-energy structure to an energy valley on the PES. The results of the configuration energy evolution for the LJ₉₈ system are presented in Fig. 3(a), showing that 22 randomly generated initial structures (blue arrows) by continuous $\hat{M}_l\{\hat{R}_{\theta,\bar{n}}\}$ transformation are quickly mapped into the bottom of the energy valley. The results in Fig. 3(a) show the average quenches $K = 324$ required before finding the global minima in the energy basin of the LJ₉₈ system, and the parameters l and M were set to 0.76 and 50, respectively. These vaminimas lying at the bottom of the energy basin will further help us narrow the scope of finding the global minima structure.

Therefore, the convergence criteria we propose based on the mirror-rotation transformation can help us reduce the structure exploration space and increase the probability of finding the global minima. Figure 3(b) shows that the average quenching increases with increasing atomic size (range from $N = 10$ to 150) except for atomic numbers $N = 50$ to 60, which form a V-shaped change trend with the lowest value $K = 82$ at $N = 55$. In general, the trend of changes is almost linear (red represents the fitted line), and an average of 413 quenches are required to converge to the lowest configuration in the energy valley for $N = 10$ to 150. Therefore, our proposed method will be very useful for large-scale structure searches because the number of quenches required to find

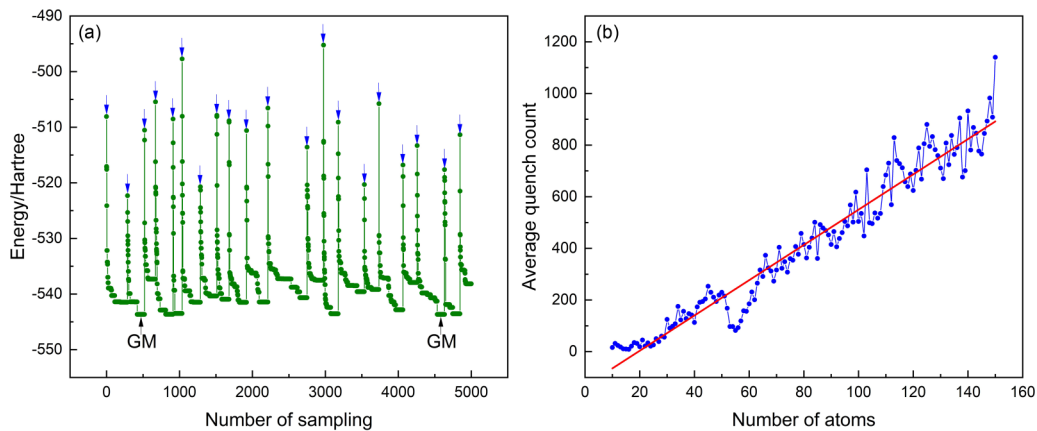


FIG. 3. (a) Sampled configuration energy versus sampling count for the LJ₉₈ cluster by MRS. The blue arrows represent the initial permutation configuration for the *while* loop in Algorithm 1, and green horizontal dots represent the lowest-energy configuration in the energy valley. Black arrows represent the global minima (GM) for the LJ₉₈ cluster. (b) Average quench count (K) versus number of atoms (N). Red represents the fitting line with a slope of 6.8 ± 0.1 .

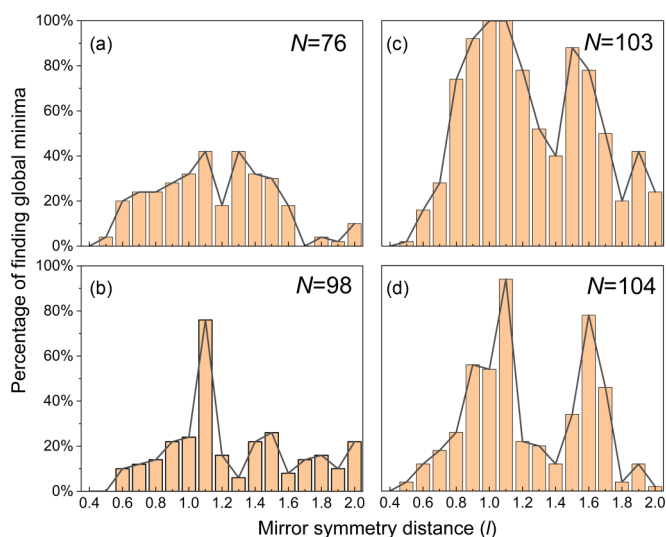


FIG. 4. Percentage of finding global minima (GMs) versus mirror symmetry distance (l) for nonicosahedral LJ_N ($N = 76, 98, 103, 104$) clusters.

the lowest-energy structure in the energy valley is almost linear.

To assess the effects of different parameters l in Algorithm 1, we now consider the percentage of finding global minima of double-funnel LJ_N ($N = 76, 98, 103, 104$) clusters at 100 independent runs for each fixed l . Due to the double-funnel feature of LJ_N ($N = 76, 98, 103, 104$) clusters, many algorithms have difficulty finding the global minima (GMs) for nonicosahedral LJ_N ($N = 76, 98, 103, 104$) clusters with strict competition between the nonicosahedral and icosahedral structural motifs [22–27]. Figure 4 shows that the percentage of four double-funnel LJ_N ($N = 76, 98, 103, 104$) clusters global minima found at different l values (range varies from 0.4 to 2.0 Å) has a similar change trend, first gradually increasing and then decreasing with a maximum value at $l = 1.1$ Å. Overall, it is easier to find the nonicosahedral configuration for LJ_{103} and LJ_{104} than for LJ_{76} and LJ_{98} for different l values. We infer that the nonicosahedral structures of LJ_{76} and LJ_{98} lie at the bottom of deep, very narrow energy valleys.

Finally, we illustrate how the mirror-rotation transformation can speed up the search efficiency of other optimization algorithms and find a unique lowest-energy structure for sulfuric acid (SA)-dimethylamine (DMA) molecular cluster system. Figure 5 shows that we use Metropolis Monte Carlo (MC) combined with mirror-rotation transformation to explore the fullerene (C_{60}) structure based on the density functional based tight binding (DFTB) method with a random initial configuration [28]. Note that using the Metropolis rule allows higher-energy structures to replace the previous structure according to a Boltzmann probability [29]. Starting with two random structures (blue arrow), the configuration energy during this search exhibits a nearly straight downward trend. The walk step before reaching the most stable fullerene structure in S' space requires 510 and 408 steps, which is almost 49-fold faster than traditional genetic algorithms [9]. This further demonstrates that our proposed method can greatly

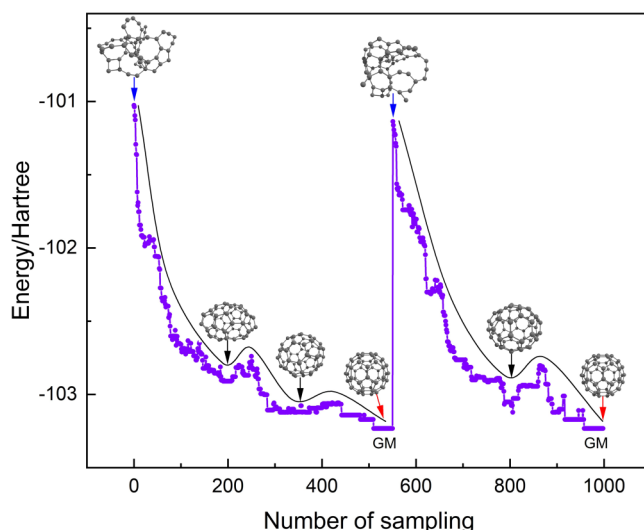


FIG. 5. Sampled configuration energy versus sampling number for the fullerene (C_{60}) cluster by Metropolis Monte Carlo (MC) combined with mirror-rotation transformation. Blue and red arrows represent random permutation configurations and global minima (GMs), respectively. Black arrows indicate local minima.

reduce the time cost of structure prediction. Another important application is that we use MRS to find different lowest-energy structures for the SA-DMA system than previous studies [30,31]. Especially for $(SA)_3(DMA)_2$, $(SA)_3(DMA)_2$, $(SA)_3(DMA)_2$, $(SA)_3(DMA)_2$, and $(SA)_3(DMA)_2$ molecular clusters, the lowest-energy structures found using MRS are 2.261, 1.102, 1.865, 3.443, and 4.256(kcal mol⁻¹) lower related to previous studies, respectively. The above calculation is based on the combination of wB97X-D/6-31++G(d,p) optimized geometries and frequency calculations with a DLPNO-CCSD(T)/aug-cc-pV(T+d)Z single-point energy calculation. All structure information can be found in the Supplemental Material [32].

Summary. In this work, we have presented the mirror-rotation transformation for structure search and defined the vaminima and convergence criteria on the PES. We show that exploring the local minima of the energy valley using the mirror-rotation method was faster and more effective in finding the low-energy structure of cluster molecules on the PES, and this approach is expected to be very efficient for improving the search efficiency of other unbiased global optimization algorithms. Due to the fast convergence of configuration energy using the mirror-rotation method, it is essentially more suitable for massively parallel searching on the PES. This method can be easily applied to different kinds of problems, such as molecular structure searching, crystal structure prediction, and protein folding.

Acknowledgments. The study was supported by grants from the National Natural Science Foundation of China (Grants No. 41775112 and No. 41877305). Part of the computation was performed at the Supercomputing Center of the Chinese Academy of Sciences and the Supercomputing Center of USTC.

- [1] A. R. Oganov, C. J. Pickard, Q. Zhu, and R. J. Needs, Structure prediction drives materials discovery, *Nat. Rev. Mater.* **4**, 331 (2019).
- [2] D. J. Wales, Structure, dynamics, and thermodynamics of clusters: Tales from topographic potential surfaces, *Science* **271**, 925 (1996).
- [3] D. J. Wales, M. A. Miller, and T. R. Walsh, Archetypal energy landscapes, *Nature (London)* **394**, 758 (1998).
- [4] C. L. Brooks, J. N. Onuchic, and D. J. Wales, Taking a walk on a landscape, *Science* **293**, 612 (2001).
- [5] G. Rossi and R. Ferrando, Searching for low-energy structures of nanoparticles: A comparison of different methods and algorithms, *J. Phys.: Condens. Matter* **21**, 084208 (2009).
- [6] J. Zhang and M. Dolg, ABCluster: The artificial bee colony algorithm for cluster global optimization, *Phys. Chem. Chem. Phys.* **17**, 24173 (2015).
- [7] Y. Wang, J. Lv, L. Zhu, and Y. Ma, Crystal structure prediction via particle-swarm optimization, *Phys. Rev. B* **82**, 094116 (2010).
- [8] C. Shang and Z. P. Liu, Stochastic surface walking method for structure prediction and pathway searching, *J. Chem. Theory Comput.* **9**, 1838 (2013).
- [9] D. Deaven and K. Ho, Molecular Geometry Optimization with a Genetic Algorithm, *Phys. Rev. Lett.* **75**, 288 (1995).
- [10] S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Optimization by simulated annealing, *Science* **220**, 671 (1983).
- [11] D. J. Wales and J. P. Doye, Global optimization by basin-hopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 atoms, *J. Phys. Chem. A* **101**, 5111 (1997).
- [12] U. H. Hansmann and L. T. Wille, Global Optimization by Energy Landscape Paving, *Phys. Rev. Lett.* **88**, 068105 (2002).
- [13] K. A. Jackson, M. Horoi, I. Chaudhuri, T. Frauenheim, and A. A. Shvartsburg, Unraveling the Shape Transformation in Silicon Clusters, *Phys. Rev. Lett.* **93**, 013401 (2004).
- [14] D. Cvijović and J. Klinowski, Taboo search: An approach to the multiple minima problem, *Science* **267**, 664 (1995).
- [15] D. Schebarchov and D. Wales, Structure Prediction for Multicomponent Materials Using Biminima, *Phys. Rev. Lett.* **113**, 156102 (2014).
- [16] R. H. Leary and J. P. K. Doye, Tetrahedral global minimum for the 98-atom Lennard-Jones cluster, *Phys. Rev. E* **60**, R6320 (1999).
- [17] A. Rapallo, G. Rossi, R. Ferrando, A. Fortunelli, B. C. Curley, L. D. Lloyd, G. M. Tarbuck, and R. L. Johnston, Global optimization of bimetallic cluster structures. I. Size-mismatched Ag-Cu, Ag-Ni, and Au-Cu systems, *J. Chem. Phys.* **122**, 194308 (2005).
- [18] G. Rossi, A. Rapallo, C. Mottet, A. Fortunelli, F. Baletto, and R. Ferrando, Magic Polyicosahedral Core-Shell Clusters, *Phys. Rev. Lett.* **93**, 105503 (2004).
- [19] S. Goedecker, W. Hellmann, and T. Lenosky, Global Minimum Determination of the Born-Oppenheimer Surface within Density Functional Theory, *Phys. Rev. Lett.* **95**, 055501 (2005).
- [20] M. T. Oakley, R. L. Johnston, and D. J. Wales, Symmetrisation schemes for global optimisation of atomic clusters, *Phys. Chem. Chem. Phys.* **15**, 3965 (2013).
- [21] Y. R. Liu, T. Huang, Y. B. Gai, Y. Zhang, Y. J. Feng, and W. Huang, Three-dimensional assignment of the structures of atomic clusters: an example of Au_8M ($M = \text{Si}, \text{Ge}, \text{Sn}$) anion clusters, *Sci. Rep.* **5**, 17738 (2015).
- [22] V. A. Mandelshtam, P. A. Frantsuzov, and F. Calvo, Structural transitions and melting in LJ(74-78) Lennard-Jones clusters from adaptive exchange Monte Carlo simulations, *J. Phys. Chem. A* **110**, 5326 (2006).
- [23] W. Pullan, An unbiased population-based search for the geometry optimization of Lennard-Jones clusters: $2 \Leftarrow N \Leftarrow 372$, *J. Comput. Chem.* **26**, 899 (2005).
- [24] J. Lee, I. H. Lee, and J. Lee, Unbiased Global Optimization of Lennard-Jones Clusters for $N \Leftarrow 201$ Using the Conformational Space Annealing Method, *Phys. Rev. Lett.* **91**, 080201 (2003).
- [25] J. P. Neirotti, F. Calvo, D. L. Freeman, and J. D. Doll, Phase changes in 38-atom Lennard-Jones clusters. I. A parallel tempering study in the canonical ensemble, *J. Chem. Phys.* **112**, 10340 (2000).
- [26] J. P. K. Doye, D. J. Wales, and M. A. Miller, Thermodynamics and the global optimization of Lennard-Jones clusters, *J. Chem. Phys.* **109**, 8143 (1998).
- [27] J. P. K. Doye, M. A. Miller, and D. J. Wales, The double-funnel energy landscape of the 38-atom Lennard-Jones cluster, *J. Chem. Phys.* **110**, 6896 (1999).
- [28] B. Hourahine *et al.*, DFTB+, a software package for efficient approximate density functional theory based atomistic simulations, *J. Chem. Phys.* **152**, 124101 (2020).
- [29] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, Equation of state calculations by fast computing machines, *J. Chem. Phys.* **21**, 1087 (1953).
- [30] J. Elm, An atmospheric cluster database consisting of sulfuric acid, bases, organics, and water, *ACS Omega* **4**, 10965 (2019).
- [31] I. K. Ortega, O. Kupiainen, T. Kurten, T. Olenius, O. Wilkman, M. J. McGrath, V. Loukonen, and H. Vehkamäki, From quantum chemical formation free energies to evaporation rates, *Atmos. Chem. Phys.* **12**, 225 (2012).
- [32] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevResearch.4.L042045> for the detailed coordinate information of SA-DMA system.