Clever and Efficient Method for Searching Optimal Geometries of Lennard-Jones Clusters

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An unbiased algorithm for determining global minima of Lennard-Jones (LJ) clusters is proposed in the present study. In the algorithm, a global minimum is searched by using two operators: one modifies a cluster configuration by moving atoms to the most stable positions on the surface of a cluster and the other gives a perturbation on a cluster configuration by moving atoms near the center of mass of a cluster. The moved atoms are selected by employing contribution of the atoms to the potential energy of a cluster. It was possible to find new global minima for LJ_{506}, LJ_{521}, LJ_{536}, LJ_{537}, LJ_{538}, and LJ_{541} together with putative global minima of LJ clusters of 10−561 atoms reported in the literature. This indicates that the present method is clever and efficient for cluster geometry optimization.

INTRODUCTION

Global optimization is an important problem in chemical fields including prediction of the lowest-energy structures of proteins and clusters. In the fields, Lennard-Jones (LJ) clusters are well elucidated, and putative global minima of LJ clusters up to 1610 atoms are tabulated.[1−9] Therefore, LJ clusters are considered as a test problem for investigating performance of global optimization algorithms.

Many of the putative global minima are searched by biased methods,[2−7] and thus it is desired to perform global optimization of LJ clusters by unbiased methods in order to examine the putative global minima. In the literature,[1,10−26] unbiased optimization methods for LJ clusters have been reported. Deaven et al.[10] used a genetic algorithm to obtain the lowest-energy structures of LJ clusters of 2−100 atoms. Their algorithm yielded new structures whose energies were lower than the energies reported previously. Wales and Doye[1] applied a basin-hopping algorithm to LJ clusters up to 110 atoms and found new global minima for LJ_{69}, LJ_{78}, and LJ_{107}. Shao et al.[11] proposed a dynamic lattice searching (DLS) method, and global optimization of LJ clusters up to 309 atoms was successfully performed by the method. Pullan[12] found global minima for LJ_n in the range of $2 \leq n \leq 372$ by a population-based search (PBS) method. An adaptive immune optimization algorithm (AIOA)[14] and an energy-based perturbation combined with a simple greedy method (EP-SGM)[15] were developed by Cheng et al. and were applied to geometry optimization of LJ clusters up to 200 atoms. Krivov[18] proposed a hierarchical greedy algorithm (HGA) and found a new global minimum for LJ_{186}. A variant of the basin-hopping method, monotonic sequence basin-hopping (MSBH),[19] located a new global minimum for LJ_{98}. New global minima for LJ_{537}, LJ_{542}−LJ_{548}, LJ_{664}, and LJ_{813} were found by Barrón as shown in ref 9.

In the present study, an unbiased optimization method based on a heuristic algorithm is proposed, and the method is used for geometry optimization of LJ_{10} to LJ_{561} (a complete icosahedral cluster[4,7]). The obtained results are compared with the results reported in the literature in order to examine performance of the present method.

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METHOD

The potential energy of LJ_n is given in terms of the atom−atom interaction potential $V(i, j)$

$$E_{\mathrm{LJ}} = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} V(i,j) = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\left(\frac{1}{r_{ij}^{12}} - \frac{2}{r_{ij}^{6}}\right) \qquad (1)$$

where r_{ij} represents the distance between atoms i and j. The potential energy of the ith atom $E(i)$ is calculated by using the following equation:

$$E(i) = \sum_{j\neq i}^{n} V(i,j) \qquad (2)$$

The optimization procedure proposed in the present study starts with a cluster configuration randomly generated. The potential energy of the cluster is locally minimized by using a limited memory quasi-Newton method (L-BFGS[27]). Then, an atom or some atoms with the highest potential energy are moved to positions which are expected to decrease the potential energy of the cluster. We regard the surface of the cluster and neighborhood of the center of mass of the cluster as the positions. Therefore, surface and interior operators, S_m and I_m, are devised where m represents the number of moved atoms. By applying local optimization (the L-BFGS[27] method) to geometries created by using these operators, global minima are repeatedly searched. The details of the global optimization method are described below.

Atom Selection. The m atoms with the highest potential energy are selected as follows: (i) Create a list of atoms on the outer shell of the cluster. When the number of outer atoms exceeds 100, the 100 highest-energy atoms are taken into

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account to create the list. This is because of reducing computational time in the next step. (ii) For all combinations of m atoms in the list (numbering of m atoms is represented by k_1, k_2,...,k_m), calculate the contribution $E_{\text{select}}(k_1,k_2,...,k_m)$ of m atoms to the potential energy of the cluster by using a formula such as

$$E_{\text{select}}(k_1,k_2,\dots,k_m) = \sum_{i=1}^{m} E(k_i) - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} V(k_i,k_j) \quad (3)$$

In this step, therefore, ${}_{n_o}C_m$ evaluations of E_{select} are performed where n_o denotes the number of the outer atoms in the list. (iii) Select the m atoms with the highest potential energy $E_{\text{select}}^{\max}$ from all the combinations. The number m is a predetermined integer as described below.

Interior Operator. This operator moves the atoms selected above on spherical surface with the radius $r_e/2$ where r_e denotes the equilibrium distance, 1.0. The center of the sphere coincides with the coordinates of the atom which is the closest to the center of mass of the cluster.

Motivation for developing this operator is based on simple consideration. In general the number of atoms surrounding the atoms moved by using the I_m operator is larger than that surrounding the atoms at the original surface positions. Therefore, after local optimization is performed for the cluster modified by the I_m operator, the potential energy of the moved atoms is expected to be lower than that of the atoms at the original positions $E_{\text{select}}^{\max}$. This leads to a probability that the potential energy of the cluster is improved by using the I_m operator.

Surface Operator. Stable positions on the surface of the cluster are first examined, and the best positions are chosen from them as the positions of the moved atoms as follows: (i) Remove the moved atoms from the cluster and prepare the template cluster composed of the $(n - m)$ atoms. (ii) Add an atom on the surface of the template at random and optimize a position of the added atom. The obtained position P of the atom and the potential energy between the atom and the template $E_{\text{template}}(P)$ are stored. This is repeated $2n$ times to create a set of stable positions on the surface. The number of repetition was safely set to be $2n$ since the number of independent positions n_s was found to be smaller than n. (iii) Calculate the potential energy E_{surface} for all combinations of m independent positions by

$$E_{\text{surface}}(P_1,P_2,\dots,P_m) = \sum_{i=1}^{m} E_{\text{template}}(P_i) + \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} V(P_i,P_j) \quad (4)$$

where numbering of m positions is represented by P_1, P_2, ..., P_m and $E_{\text{template}}(P_i)$ is obtained in step (ii). If the positions P_1, P_2, ..., P_m are similar to the coordinates of the atoms removed in step (i), the positions are excluded in the calculation of E_{surface}. (iv) Select the positions with the lowest potential energy $E_{\text{surface}}^{\min}$ from all the combinations (the ${}_{n_s}C_m$ evaluations of E_{surface}).

The cases with $m \geq 2$ must be carefully treated by the following reason. If the distances between the selected positions are close to r_e, slight changes of the positions may introduce a large energy difference. Therefore, when $m \geq 2$, the following step is carried out after step (iv): for all the configurations with the potential energy less than $E_{\text{surface}}^{\min} + 0.2$, positions of m atoms are simultaneously optimized, and the positions giving the lowest energy are selected.

Since the number of moved atoms m limits the search space in optimization, it is preferable to use several values for m. However, a lot of computational time was needed for calculations of eqs 3 and 4 when values larger than six were adopted for m as noted by Shao et al.[11] From the results of preliminary calculations performed with different m values in the range of 1−6, the following condition was adopted in the present study: $m \leq 4$ for the S_m operator[28] and $m \leq 5$ for the I_m operator, respectively.

Optimization Algorithm. The following algorithm is used in this work:

(1) Generate an initial geometry. Atoms are randomly placed in a sphere having a radius of $R = (3n/4\pi)^{1/3} r_e$.[13] The geometry is optimized by the L-BFGS method.[27]

(2) Create a new geometry from the current geometry by using the I_m operator and optimize it by the L-BFGS method. The number m is randomly chosen from 1−5.

(3) If the potential energy of the cluster is not improved during the last 10 optimizations, go to step (4). Otherwise, update the cluster geometry if the energy of the cluster lowers and return to step (2).

(4) The lowest-energy geometry obtained by using the I_m operator is modified according to the S_m operator, and the modified geometry is optimized by the L-BFGS method. The value of m is initially 1 and increases up to 4 at an interval of 1 if the energy of the cluster is not improved. When energy-lowering is observed, initialize the m-value, update the cluster geometry, and repeat this step.

(5) If the S_4 operator does not improve the energy of the cluster, terminate calculation.

It was found that moving the second or third highest-energy atom by the S_1 operator improves performance of the method.[29] In step (4), therefore, if the energy of the cluster is not improved by moving the highest-energy atom, the second highest-energy atom and the third highest-energy atom are separately moved by the S_1 operator. The S_1 operator for the highest-energy atom is equivalent to the directed operator[17] proposed by Hartke. Therefore, the S_m operator proposed here can be considered as an extension of the directed operator.

The global-minimum structures of LJ_{542}, LJ_{543}, LJ_{546} LJ_{547}, and LJ_{548} take configurations without the center atom[9] (the atom at the center of the icosahedron in the cluster[30]). In the above algorithm, no configuration without the center atom is created because the central part of the cluster is used in the interior operator. Therefore, to examine the stability of clusters with no center atom, the center atom is moved to arbitrary positions on the surface, and the resulting cluster with the central vacancy is modified by the S_m operator. This is carried out after step (5). The stability of clusters with the central vacancy was examined for $n \geq 470$. The algorithm proposed in the present study is summarized in Figure 1.

The cycle shown in Figure 1 is repeated until putative global minima[1−9] of clusters are found. The program was written in FORTRAN, and calculations were finished when a global minimum was obtained five times for each cluster with $n \leq 350$. For clusters with $351 \leq n \leq 561$, calculations were continued until each global minimum was found twice.

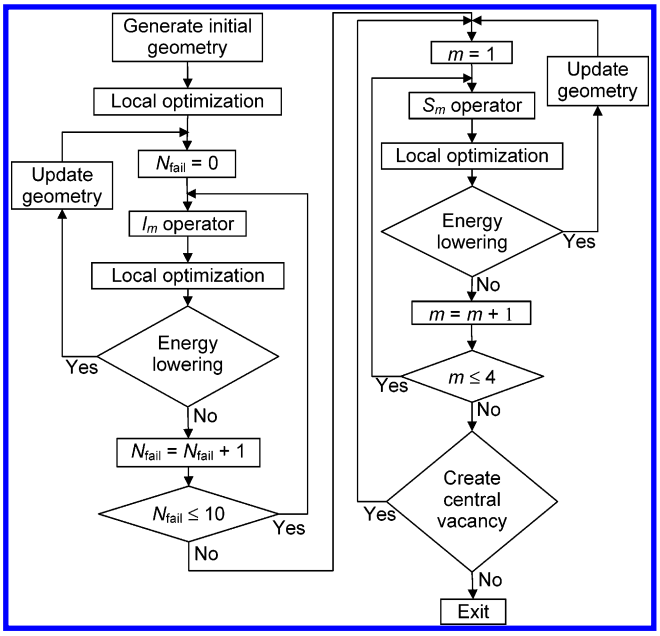

Figure 1. The flowchart for a global-optimization cycle proposed in the present study.

Table 1. Lowest Potential Energy of LJ_n

n	this work[a]	previous data	n	this work[a]	previous data
506	−3427.687517	−3427.621193[b]	537	−3659.821328	−3659.706286[c]
521	−3539.509777	−3539.331418[b]	538	−3668.751274	−3667.569346[b]
536	−3651.779047	−3651.645144[b]	541	−3691.231414	−3691.070873[b]

[a] Cluster without the center atom. [b] Reference 4. Cluster with the center atom. [c] Reference 9. Cluster with the center atom.

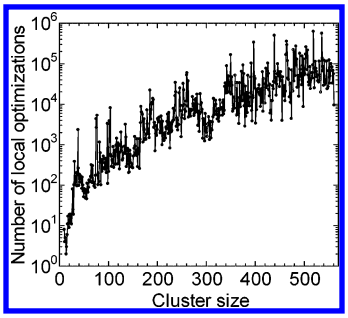

Figure 2. The number of local optimizations for LJ clusters of 10−561 atoms.

RESULTS AND DISCUSSION

All putative minima[1−9] of LJ clusters were obtained by the present method.[31] In addition, new global minima were also found for LJ_{506}, LJ_{521}, LJ_{536}, LJ_{537}, LJ_{538}, and LJ_{541}. The energies of the new global minima are compared with those of the minima found previously[4,9] in Table 1.

The clusters take the central vacancy, whereas the configurations found previously[4,9] takes no central vacancy. The fact that new global minima are obtained in this work indicates that the present method can explore the search space in optimization efficiently.

The number of local optimizations required for finding the global minimum has been used to examine the performance of unbiased optimization algorithms.[11,14,15,19] The present study also adopts this criterion as a property of the performance.[32] Figure 2 shows the dependence of the number of local optimizations on the cluster size. The number of local optimizations is smaller than 10^4 for all the clusters in the range of $10 \leq n \leq 184$ and is smaller than 10^5 for all the clusters with $n \leq 349$. The optimization of clusters with $n = 100$, 200, 300, 400, 500, and 561 takes mean times of 1.3, 16, 29, 1059, 2016, and 470 min on a single 3 GHz Pentium IV processor, respectively.

Table 2. Number of Local Optimizations Required for Obtaining the Global Minimum of LJ_n

n	this work[a]	EP-SGM[15]	DLS[11]	AIOA[14]	MSBH[19]	HGA[18]
30	102	132	43.5	360	739	
38[b]	2352	1739	3240	3046	2875	
50	51	264	270	537	460	
75[b]	4374	86000	2586	43000	152000	9259
98[b]	3312	27200	597	32000	180000	5660
100	844	2525	610	9304	9128	
102[b]	3881	13880	7733	31000	36028	
150	267	3230	1398			
188[b]	7320		12234			
200	2371	56550	4494	140000		
236[b]	16216		30875			
250	4611		11347			
300	2017		14875			
400	42600					
500	52462		70000			62000
561	9419					

[a] Average number of local optimizations. [b] Nonicosahedral clusters. Global optimization of these clusters is known to be more difficult than that of other clusters.

Table 2 compares the number of local optimizations of the present method with the results reported in the literature.[11,14,15,18,19] The numbers of local optimizations for LJ_{75}, LJ_{98}, and LJ_{102} obtained by the present method are much smaller than those of the EP-SGM,[15] AIOA,[14] and MSBH[19] methods. The numbers of optimizations for LJ_{75} and LJ_{98} given by the HGA[18] method are approximately twice larger than those of the present method. When $n \leq 100$ the number of local optimizations in the present study is comparable with that obtained by the DLS method[11] except for the case of LJ_{98}. For clusters with $n > 100$, however, our method reduces the number of local optimizations compared with the DLS method.

Pullan[12] performed geometry optimization of LJ clusters on 2-GHz Linux processors and reported processor times as the performance of the PBS method. According to the results of a single-processor version of the PBS method (optimized clusters are in the range of $2 \leq n \leq 200$), the average processor time for $n = 188-192$ is 3710 s and that for $n = 150$, 160, 170, and 180 is 1043 s. These values are comparable with the corresponding CPU times of the present method, 4187 and 747 s. Quantitative discussion is difficult because of the difference in computer and compiler used in calculation.

Figure 3 shows properties of a successful cycle where the global minimum for LJ_{200} was obtained. The I_m operator significantly decreases the energy of the cluster, but stagnation of the energy-lowering takes place at the 12th step. However, the global minimum is found by using the S_m operator.

The results of successful cycles for all clusters were analyzed to examine the performance of the I_m operator. Potential energies of clusters obtained by using the I_m operator are compared with those of initial geometries in Figure 4. Differences between the initial potential energies

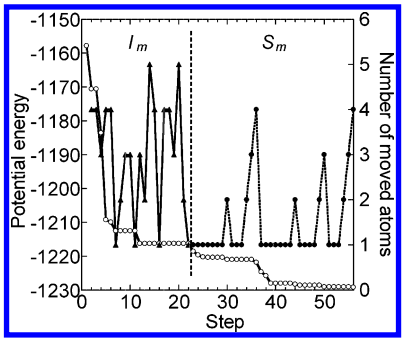

Figure 3. Global-optimization process for LJ_{200}. The open circles denote the potential energy obtained after local optimization. The closed circles and triangles denote the number of atoms moved by the S_m and I_m operators, respectively.

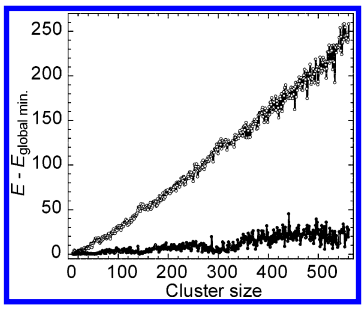

Figure 4. Differences of potential energies of initial geometries (open circles) and those of geometries optimized by using the I_m operator (closed circles) from the global-minimum energies $E_{\text{global min.}}$.

and the global-minimum energies are approximately proportional to the cluster size, but the I_m operator significantly improves the energy differences.

In 145 out of 230 successful cycles for LJ_{10} to LJ_{55}, the global minima were found by using the I_m operator alone. On the other hand, when $n > 55$ the S_m operator is also important for searching global minima: for example the 198 out of 225 successful cycles for LJ_{56} to LJ_{100} require this operator. Therefore, both the I_m and S_m operators separately play important roles for searching global minima.

CONCLUSION

The heuristic algorithm combined with the surface and interior operators yielded the global minima of LJ clusters of 10−561 atoms reported previously and the new minima for LJ_{506}, LJ_{521}, LJ_{536}, LJ_{537}, LJ_{538}, and LJ_{541}. This indicates that the present method is very efficient for global optimization. Therefore, the method is applicable to complicated chemical problems, i.e., structure prediction of molecular clusters and biomolecules. The study relating to geometry optimization of benzene clusters and model protein is in progress.

Supporting Information Available: Cartesian coordinates of new global minima of LJ_{506}, LJ_{521}, LJ_{536}, LJ_{537}, LJ_{538}, and LJ_{541}. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Stable positions on the surface of the cluster are also used in the DLS method.[11] However, the number of moved atoms in the DLS method ($N_{\text{move}} = 10-40$) is larger than that in the surface operator. In addition the number of evaluations of eq 4 in the surface operator is different from the corresponding number in the DLS method. For example, when $m = 4$, the number of evaluations of eq 4 is approximately 3×10^7 for LJ_{200} and much larger than the corresponding number in the DLS method ($N_{\text{try}} = 550$).

(29) For example, the geometry of LJ_{85} with the energy of $E^{85}_{\text{global min}} + 0.994$ changed to the global-minimum one by moving the third highest-energy atom where $E^{85}_{\text{global min}}$ denotes the global-minimum energy of LJ_{85}.

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(31) Energy values slightly lower than those reported in refs 1−9 were obtained for the following clusters: $E(LJ_{243}) = -1529.712151(5)$, $E(LJ_{358}) = -2348.782315(5)$, $E(LJ_{361}) = -2370.445427(10)$, $E(LJ_{362}) = -2377.676606(8)$, $E(LJ_{364}) = -2391.887487(4)$, $E(LJ_{365}) = -2398.871608(5)$, $E(LJ_{366}) = -2406.102774(5)$, $E(LJ_{407}) = -2704.203479(9)$, $E(LJ_{409}) = -2718.677731(10)$, $E(LJ_{410}) = -2725.907425(4)$, $E(LJ_{411}) = -2733.137602(3)$, $E(LJ_{413}) = -2747.363773(7)$, $E(LJ_{416}) = -2768.583578(9)$, $E(LJ_{417}) = -2775.814039(3)$, $E(LJ_{418}) = -2782.294096(6)$, $E(LJ_{552}) = -3777.120254(3)$, $E(LJ_{553}) = -3784.372712(7)$, $E(LJ_{554}) = -3791.625175(10)$, $E(LJ_{555}) = -3798.877768(9)$, $E(LJ_{557}) = -3813.382827(7)$, and $E(LJ_{558}) = -3820.635426(11)$, where numbers in parentheses denote differences from data in the above references referring to the last significant digit.

(32) Partial geometry optimizations used in the surface operator are not counted in the number of local optimizations because partial optimization is much faster than full geometry optimization.

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