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Binary Lennard-Jones atomic clusters: Structural features induced by large-sized atoms

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ABSTRACT

Global-minimum geometries of binary Lennard-Jones clusters (BLJ_N where N is the number of atoms) are previously elucidated when the size ratio of the large B atom to the small A atom is 1.05–1.3. In the present study, BLJ clusters for larger size ratios (1.4–2.0) are investigated to clarify the structural features. The heuristic method combined with geometrical perturbations and atom-type conversion is developed to search for the global minima of the BLJ clusters. In the lowest-energy geometries of the BLJ clusters ($N \leqslant 50$), A and B atoms form cores and outer shells, respectively. The existence of fairly large sized atoms induces complicated structural growth sequence patterns (including icosahedron, triangular orthobicupola, cuboctahedron, etc.). New global minima of BLJ_{59} for $s = 1.15$, BLJ_{68} for $s = 1.15$ and BLJ_{70} for $s = 1.2$ are also reported.

1. Introduction

Global optimization plays an important role in a field of computational chemistry including prediction of the lowest-energy structures of biomolecules, clusters, and crystals. However, it is a difficult problem since the optimal geometry of a system must be searched from enormous number of stable geometries. Hence a strategy to efficiently move from a local minimum to the global minimum on the potential energy surface of the system is indispensable.

For atomic and molecular clusters, many investigations on the structures and properties have been performed due to their importance. However, global optimization of the clusters is still challenging. In the field of atomic clusters, Lennard-Jones (LJ) clusters are well elucidated and putative global minima of the LJ clusters up to 1610 atoms are tabulated [1–9]. Accordingly the LJ clusters are considered as a test problem for investigating performance of global optimization algorithms. Previously the present author developed an efficient method for geometry optimization of Lennard-Jones clusters [10]. The method optimizes cluster geometries with two types of geometrical perturbations and yielded the global minima of LJ clusters with 10–561 atoms reported previously and the new minima for 6 LJ clusters. Then the method is improved to apply it to complicated clusters, molecular homoclusters where molecular orientations are further required as optimized parameters [11,12]. The first purpose of the present study is to improve the above optimization method for application to another type of complicated clusters, atomic heteroclusters.

For the heteroclusters, the composition of different atoms makes global optimization more difficult [13–23]. Since one of the simplest heteroclusters is the binary Lennard-Jones (BLJ) cluster, the putative global minima of the BLJ clusters have been examined [13–19]. For the N-atom BLJ clusters (BLJ_N), the potential energy is calculated using the atom–atom interaction potential $V(i,j)$:

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

Here r_{ij} represents the distance between atoms i and j, and α and β mean the atom types of atoms i and j (represented by A and B). The relation of $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB} = \varepsilon$ is used throughout the present study as adopted in the previous studies [13–19]. The values of σ_{AA} and σ_{BB} are set to be σ and $s\sigma$, respectively, and the σ_{AB} value is equal to $(\sigma_{AA} + \sigma_{BB})/2$ where the parameter s is a predefined constant of the system representing the size ratio of the B atom to the A atom. The BLJ clusters have been considered as an important model to study performance of optimization methods and structural properties of binary clusters.

The original investigation on the BLJ clusters was performed by Doye and Meyer [13] with basin-hopping (BH) algorithm. The study was aimed at finding the effect of the size of the B atom ($s = 1.05$, 1.1, 1.15, 1.2, 1.25, 1.3) on the global minima of the

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BLJ clusters with 5–100 atoms. The lowest energies and the corresponding geometries are tabulated in the CCD (Cambridge Cluster Database[7]). Cassioli et al. [14] confirmed a lot of the global minima with the population-based BH method and found 95 new minima. Marques and Pereira [15] proposed an evolutionary algorithm to search for global minima of the BLJ clusters and applied it to the BLJ clusters with 10–50 atoms. A new minimum was located for BLJ_{38} for $s = 1.05$ ($E_{38}/\varepsilon = -177.260697$). Kolossváry and Bowers [16] developed the hidden-force Monte Carlo (HFMC) algorithm. The results obtained for the geometries of BLJ_{90}–BLJ_{100} show that the HFMC method improved 17 global minima. In the study of Sicher et al. [17], the minima hopping method was applied to the clusters with $N = 5$–100 and yielded 17 new global minima. Most of the new minima were independently obtained with the HFMC algorithm [16]. Tao et al. [18] optimizes the geometries of the BLJ clusters with $N = 5$–100. Although 12 new global minima of the BLJ clusters were located, 15 global minima reported previously were missing. After the publication, Wenqi and Tao deposited following new minima in the CCD [7]; BLJ_{66} for $s = 1.15$ ($E_{66}/\varepsilon = -359.49937$), BLJ_{89} for $s = 1.15$ ($E_{89}/\varepsilon = -510.052009$), BLJ_{72} for $s = 1.2$ ($E_{72}/\varepsilon = -404.850951$), BLJ_{65} for $s = 1.25$ ($E_{65}/\varepsilon = -363.528091$) and BLJ_{99} for $s = 1.3$ ($E_{99}/\varepsilon = -597.679071$). Recently Rondina and Da Silva [19] developed a global optimization method based on the BH algorithm and applied it to several cases including the BLJ clusters with $N = 5$–100. Comparison of the results with the data taken from the above-mentioned studies shows that 2 new global minima are located with the method: BLJ_{38} for $s = 1.05$ ($E_{38}/\varepsilon = -177.260679$) and BLJ_{66} for $s = 1.15$ ($E_{66}/\varepsilon = -359.749940$). However, the global minima of BLJ_{99} and BLJ_{100} for $s = 1.3$ were not found with the method. To enhance the reliability of the global minima, it would be necessary to search for the global minima of the BLJ clusters with different methods.

In the previous study on the LJ clusters by the present author [10], two geometrical perturbations followed by local optimizations efficiently explore geometrical space. For the BLJ clusters, the atom types must be taken into account in the optimization algorithm. A simple way to optimize the type of the atom is to convert A into B or vice versa in the algorithm as performed in the literature [18]. In the present study, an optimization method was developed by combination of the two perturbations [10] with the atom-type conversion [18] algorithm. To evaluate the combined method, geometry optimization was performed for the BLJ_5–BLJ_{100} for $s = 1.05, 1.1, 1.15, 1.2, 1.25, 1.3$. Since these s-values were rather limited, the global-minima of BLJ_5–BLJ_{50} for $s = 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0$ were also calculated. The second purpose of the present study is to examine the structures, relative stability and growth sequence patterns of the BLJ clusters. The results of the present study complement the previous data of the BLJ clusters.

2. Calculation

The optimization procedure proposed in the present study starts with a cluster configuration randomly generated. The number of the A atoms N_A is randomly selected from zero to N. The atoms are placed within a sphere with the volume of $N_A\left(\sqrt[6]{2}\sigma_{AA}\right)^3 + (N - N_A)\left(\sqrt[6]{2}\sigma_{BB}\right)^3$. The geometry of the cluster is locally optimized with a limited memory quasi-Newton method (L-BFGS [24]). Then the type of an atom is converted from A to B or from B to A. After the conversion, the geometry of the cluster is optimized by the L-BFGS [24] method. If the potential energy of the cluster is improved, the cluster geometry and the type of the atom are updated. This procedure is repeated for every atom and thus the atom-type conversion is N times carried out.

After performing the above conversion operator, 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. The positions are selected from the surface of the cluster or neighborhood of the center of mass of the cluster. The above geometrical perturbations are called the surface and interior operations. By applying local optimization (the L-BFGS [24] method) to geometries created with these operators, new minima are repeatedly searched. The details of the operators are described below.

An atom or M atoms with the highest potential energy are selected as follows: (i) create a list of atoms on the outer shell of the cluster. (ii) the potential energy of an atom i in the list, $E(i)$, is calculated by using the following equation:

$$E_{\text{select}}(i) = \sum_{j \neq i}^{N} V(i,j) \tag{2}$$

For all combinations of M atoms (numbering of M atoms is represented by $k_1, k_2, \ldots, k_M$), the contribution of M atoms to the potential energy of the cluster $E_{\text{select}}(k_1, k_2, \ldots, k_M)$ is calculated by the formula:

$$E_{\text{select}}(k_1, k_2, \cdots, k_M) = \sum_{i=1}^{M} E_{\text{select}}(k_i) - \sum_{i=1}^{M-1} \sum_{j=i+1}^{M} V(k_i, k_j) \tag{3}$$

(iii) select the atoms with the highest energy contribution from all the combinations.

Many methods ignore the second term in the right-side of Eq. (3). This is mainly because the computation of the second term is time-consuming for large M values. The neglect of the second terms is a good approximation if the atoms are far from each other. According to our experience on the LJ clusters [10], the second term is often crucial to efficiently search for new minima. The following conditions are used for the BLJ clusters [10]: $M \leqslant 4$ for the surface operator and $M \leqslant 5$ for the interior operator, respectively.

The interior operator moves the selected atoms to the surface of the sphere whose center is coincident with the center of mass of the cluster. It takes the radius of $r_e/2$ where $r_e = \sqrt[6]{2}\sigma_{AA}$ for the A atoms and $r_e = \sqrt[6]{2}\sigma_{BB}$ for the B atoms. The number of atoms surrounding the atoms moved by using the interior operator usually increases compared with that surrounding the atoms at the original surface positions. Consequently the potential energy of the atoms obtained after local optimization is expected to be lower than that at the original positions. This leads to a probability that the potential energy of the cluster is improved with the interior operator. This is theoretical background on the development of the operator.

In the geometries created with the interior operator, some atoms are very close to each other. Hence displacement of them caused by local optimization (Δx, Δy, and Δz) is large, leading to the possibility of the evaporation. To avoid it, if the absolute values of Δx, Δy, and Δz are larger than σ, these are reduced to 0.1σ.

If the potential energy of the cluster is not improved during the last ten interior operations followed by local optimizations, the surface operator is carried out. In the 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 the position of the added atom. The surface is constructed by the spheres which have radii of $r_e/2$ and centers coincident with the positions of the template atoms. A vector generated randomly is used to show the direction from the center of mass of the cluster to the added atom; (iii) the obtained position P of the atom and the potential energy between the atom and the template $E_{\text{template}}(P)$ are stored; (iv) this is repeated $2N$ times to create a set of stable positions on the surface. The set of stable positions is separately