Journal of Global Optimization **22:** 97–118, 2002.

Equivalent formulations and necessary optimality conditions for the Lennard–Jones problem

HONG–XUAN HUANG[1], PANOS M. PARDALOS[2,*] and ZUO–JUN SHEN[2]
[1]*Department of Mathematical Sciences, Tsinghua University, Beijing 100084, P.R. China;*
[2]*Department of Industrial and Systems Engineering, University of Florida, Gainesville, FL 32611, USA; *Corresponding author (E-mail: pardalos@cao.ise.ufl.edu)*

Abstract. The minimization of molecular potential energy functions is one of the most challenging, unsolved nonconvex global optimization problems and plays an important role in the determination of stable states of certain classes of molecular clusters and proteins. In this paper, some equivalent formulations and necessary optimality conditions for the minimization of the Lennard–Jones potential energy function are presented. A new strategy, *the code partition algorithm*, which is based on a bilevel optimization formulation, is proposed for searching for an extremal Lennard–Jones code. The convergence of the code partition algorithm is proved and some computational results are reported.

Key words: Global optimization, Potential energy function, Lennard–Jones problem, Extremal Lennard–Jones code, L–Points Pattern Lennard–Jones code, Code partition algorithm

1. Introduction

Global optimization problems, that is, finding the global minimum (or maximum) of a function with arbitrary number of independent variables that may be continuous or discrete, appear in almost all fields of science, technology and industry, ranging from hydrodynamics and protein folding to the design of VLSI circuits and optimal transportation routes. One of the most significant and challenging global optimization problems in molecular biophysics and biochemistry is that of computing the native three-dimensional conformation (folded state) of a protein given its amino acid sequence, possibly in the presence of additional agents (e.g., drugs). Systematic conformational search based on global optimization algorithms and heuristics is a powerful tool in modeling of biomolecules. The minimization of molecular potential energy functions plays an important role in the determination of ground states or stable states of certain classes of molecular clusters and proteins [1, 5, 24, 27, 34–37].

In almost all cases, the molecular potential energy function is nonconvex and therefore has many local minima. So far, significant progress in identifying appropriate energy functions has been made; the primary impediment is the lack of efficient global minimization methods for these large-dimensionality problems. How to find efficiently global minima of such nonconvex potential energy functions

This paper is dedicated to Professor Reiner Horst on the occasion of his 60th birthday.

is one of the most challenging, unsolved global optimization problems [13, 14, 16, 40].

The most important optimization methods for modeling biomolecular structures are discussed in the paper [32] and the special issues [34, 35]. A comprehensive survey of recent developments in global optimization can be found in the references [2, 7, 19, 20, 28, 30, 31].

Among the most commonly used potential energy functions, the simplest one is that of two-body central 'forces' between the component atoms [14, 18, 25]. Given a cluster of N atoms in the three–dimensional space, let the code $P_N = \{x_1, \cdots, x_N\}$ be the collection of centers of N atoms. The potential energy function of the cluster is defined as the summation of the two-body interatomic pair potentials over all of the pairs, i.e.,

$$V(P_N) = \sum_{1 \leqslant i < j \leqslant N} v(r_{ij}), \tag{1}$$

where $r_{ij} = \|x_i - x_j\|$ is the Euclidean distance of the points x_i and x_j, and $v(r_{ij})$ denotes the potential energy between atoms i and j with centers at x_i and x_j, respectively.

Many types of the function $v(r)$ may be used in physical models, but some necessary restrictions should be imposed on them in order to let the behavior of $v(r)$ reflect the configurations of molecular clusters. Usually, we are only interested in cases where $v(r)$ is a *well potential* satisfying the following conditions [32]:

1. $v(r) \to 0^-$ as $r \to +\infty$;
2. $v(r) \to +\infty$ as $r \to r_{\min}^+$ and $r_{\min} \geqslant 0$;
3. $v'(r_0) = 0$ for a unique r_0 with $r_{\min} < r_0 < +\infty$;
4. $v''(r_0) > 0$ and $v(r_0) < 0$.

During the last decade many attempts have been made to globally minimize potential energy functions [4, 6, 29, 33, 37, 40]. In particular, the Lennard-Jones potential energy function

$$\begin{aligned} V(P_N) &= \sum_{1 \leqslant i < j \leqslant N} v(\|x_i - x_j\|) \\ &= \sum_{1 \leqslant i < j \leqslant N} (\|x_i - x_j\|^{-12} - 2\|x_i - x_j\|^{-6}), \end{aligned} \tag{2}$$

where the code $P_N = \{x_1, \cdots, x_N\}$ and $v(r) = r^{-12} - 2r^{-6}$, has been studied by many optimization researchers [6, 15, 22, 26, 41, 42]. An equivalent form of the Lennard–Jones potential function (i.e., $v(r) = (\sigma r^{-1})^{12} - (\sigma r^{-1})^6$) is also used in some research papers [3, 8, 9, 10, 23, 39]. This is a simple case of the more general potential energy function with $v(r) = (m-n)^{-1}(nr^{-m} - mr^{-n})$ and $m > n$.

The general formulation of the Lennard–Jones problem in this paper is defined as follows:

$$(LJ - G)E_N \triangleq \min \sum_{1 \leqslant i < j \leqslant N} (r_{ij}^{-12} - 2r_{ij}^{-6}), \tag{3}$$

where $r_{ij} = \|x_i - x_j\|$ and each point $x_i \in \Re^3$. A globally optimal solution $P_N^* = \{x_1^*, \cdots, x_N^*\}$ of the Lennard–Jones problem (i.e., $V(P_N^*) = E_N$) is called *an extremal Lennard–Jones code*. Since we cannot prove the optimality of the best code that has been found except for a very small N, we should refer to the code with the lowest known energy as a *putative* extremal Lennard–Jones code, but for convenience in the following this adjective usually is dropped.

The Lennard–Jones problem is a very simple, yet reasonably accurate mathematical model of low temperature microclusters of heavy rare gas atoms such as argon, krypton or xenon. Since the objective function in (3) is non-convex and the number of distinct local minima in the potential energy surface of an N-atom Lennard–Jones cluster is about $O(e^{N^2})$ [16], the Lennard–Jones problem is considered to be a very difficult and challenging global optimization problem. Although many algorithms have been proposed during the past thirty years [6, 8–10, 12, 16, 17, 22, 23, 26, 41, 42] and good putative global optima are known for the Lennard–Jones problem, new better codes are still being found within the range of $2 \leqslant N \leqslant 147$. In fact, the Lennard–Jones problem has become a benchmark for any new global optimization algorithm.

The methods proposed to deal with the Lennard–Jones problem can be classified into two groups:

(i) Lattice methods [3, 15, 17, 26, 38, 41, 42]. The main idea of this class of methods is to use various lattices or structures as the basis of searching for an extremal Lennard–Jones code, such as polytetrahedral structures, the IC (the complete Mackay icosahedron) and FC (tetrahedrally bonded face sites which lie at stacking fault locations relative to IC lattice, together with the vertex sites) multilayer icosahedral lattices, face-centered cubic (FCC) lattice and so on. After a better structure of points is found, the algorithm relaxes the resulting configuration by using a nonlinear optimization method, such as the conjugate gradient algorithm, or the quasi-Newton method.

(ii) General purpose methods [4, 6, 11, 22]. This class of methods does not make any prior assumptions regarding the molecular configuration. It may integrate various global optimization ideas and approaches, including simulated annealing, genetic algorithm, smoothing and spatial averaging of the objective function and packet annealing [32].

Many valuable ideas are exploited and incorporated into these two kinds of methods, such as growth sequences and related forward greedy growth operator F (i.e., an extremal code with respect to $N + 1$ may be obtained from that of N by searching over a more extensive set of coordinates after adding a single atom and relaxing over all variables to a local minimum), reverse greedy growth operator

R (i.e., an extremal code with respect to $N-1$ may be obtained by removing the least tightly bound atom in the optimal conformation with respect to N and relaxing over all variables to a local minimum) [22]. Some other strategies, such as transforming the original objective function into another form having the same global minima, or using a new form instead of the original objective function at the beginning of algorithms, have been proved very successful in searching for an extremal Lennard–Jones code [8, 26].

In this paper, some properties, which are related to any extremal Lennard–Jones code, are studied and a new strategy to attack the Lennard–Jones problem is suggested. The paper is organized as follows: In Section 2, a property and some related equivalent formulations for the Lennard–Jones problem are explored. In Section 3, another equivalent formulation for Lennard–Jones problem based on the bilevel optimization model and a concept about the *L–points pattern Lennard–Jones code* are introduced. Necessary optimality conditions for the Lennard–Jones problem is also established. In Section 4, a new strategy, *the code partition algorithm*, to search for an extremal Lennard–Jones code is suggested and some computational results are reported.

2. Equivalent formulations for the Lennard–Jones problem

2.1. EQUIVALENT CONSTRAINED GLOBAL OPTIMIZATION

Let us consider the constrained global optimization problem:

$$(LJ-S)\quad \max \sum_{1\leqslant i<j\leqslant N} r_{ij}^{-6} \quad \text{or} \sum_{1\leqslant i<j\leqslant N} r_{ij}^{-12}, \tag{4}$$

$$\text{s.t.} \sum_{1\leqslant i<j\leqslant N} r_{ij}^{-12} = \sum_{1\leqslant i<j\leqslant N} r_{ij}^{-6}, \tag{5}$$

where $r_{ij} = \|x_i - x_j\|$.

It is clear that every feasible solution of the constrained global optimization problem (4)∼(5) corresponds to an upper bound of the unconstrained global optimization (3), i.e., the Lennard–Jones problem. We claim that the constrained global optimization problem (4)∼(5) is equivalent to the Lennard–Jones problem (3). In order to establish the equivalence of the two above formulations for the Lennard–Jones problem, it is sufficient to prove that every globally optimal solution P_N^* of (3) is a feasible solution of the problem (4)∼(5). In this case, P_N^* must be a globally optimal solution of the problem (4)∼(5). Therefore, the constrained global optimization problem (4)∼(5) is referred to as the special formulation of the the Lennard–Jones problem.

Given a real ϵ in a small neighborhood of zero and a code $P_N = \{x_1, \cdots, x_N\}$ in which points are mutually different, define the code $P_{N,\epsilon} = \{(1+\epsilon)x_1, \cdots, (1+\epsilon)x_N\}$.

In the following, we denote by

$$\omega_s(P_N) = \sum_{i<j} \|x_i - x_j\|^{-s},$$

for any real $s > 0$. From the Lennard–Jones potential function (2), we get

$$V(P_{N,\epsilon}) = (1+\epsilon)^{-12}\omega_{12}(P_N) - 2(1+\epsilon)^{-6}\omega_6(P_N). \tag{6}$$

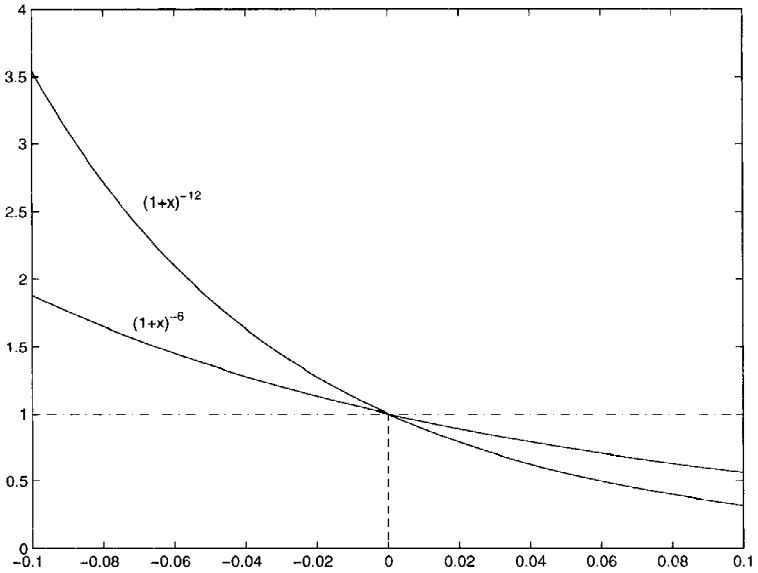

Figure 1. The functions $(1+x)^{-12}$ and $(1+x)^{-6}$.

Figure 1 plots the functions $(1+x)^{-12}$ and $(1+x)^{-6}$ for $x \in [-0.1, 0.1]$. Since $x = \epsilon$ is very close to zero, the following Taylor's expansions hold:

$$(1+\epsilon)^{-12} = 1 - 12\epsilon + 78\epsilon^2 + o(\epsilon^2)$$
$$(1+\epsilon)^{-6} = 1 - 6\epsilon + 21\epsilon^2 + o(\epsilon^2).$$

We substitute the above expressions into (6) and obtain

$$\begin{aligned} V(P_{N,\epsilon}) =& V(P_N) - 12(\omega_{12}(P_N) - \omega_6(P_N))\epsilon \\ &+ (78\omega_{12}(P_N) - 42\omega_6(P_N))\epsilon^2 + o(\epsilon^2). \end{aligned}$$

If the code P_N is a globally optimal solution of (3), $V(P_N)$ must be a locally minimal value of $V(P_{N,\epsilon})$ with respect to variable ϵ. Furthermore, the derivative of $V(P_{N,\epsilon})$ at $\epsilon = 0$ must be zero, i.e., $\omega_{12}(P_N) \equiv \omega_6(P_N)$. Therefore, we get the following theorem.

THEOREM 2.1. *For the general formulation of the Lennard–Jones problem, if the code* $P_N = \{x_1, \cdots, x_N\}$ *is a globally optimal solution of* (3)*, then it is a feasible solution of the special formulation* (4)∼(5)*, i.e., it satisfies*

$$\omega_{12}(P_N) \equiv \omega_6(P_N). \tag{7}$$

It is also a globally optimal solution of (4)∼(5)*. Furthermore, the general formulation of the Lennard–Jones problem is equivalent to the special formulation* (4)∼(5).

Proof. From above analysis, it is clear that P_N is a feasible solution of the special formulation (4)∼(5). If it is not a globally optimal solution of (4)∼(5), then there exists a code P_N^* such that

$$\omega_6(P_N^*) > \omega_6(P_N),$$
$$\omega_{12}(P_N^*) = \omega_6(P_N^*).$$

Therefore, we get a better code P_N^* than P_N for the problem (3) such that

$$V(P_N^*) = -\omega_6(P_N^*) < -\omega_6(P_N) = V(P_N).$$

Hence, P_N is not a globally optimal solution of the problem (3). This contradiction indicates that a global optimal solution of the problem (3) must be a globally optimal solution of (4)∼(5) and vice versa. □

REMARK 1. The special formulation (4)∼(5) of the Lennard–Jones problem can be expressed equivalently as

$$(LJ - SL) \max \omega_6(P_N) \text{ or } \omega_{12}(P_N), \tag{8}$$
$$\text{s.t.} \omega_{12}(P_N) \leqslant \omega_6(P_N), \tag{9}$$

where $P_N = \{x_1, \cdots, x_N\}$.

REMARK 2. Consider the following problem:

$$(LJ - SG) \min \omega_6(P_N) \text{ or } \omega_{12}(P_N), \tag{10}$$
$$\text{s.t. } \omega_{12}(P_N) \geqslant \omega_6(P_N), \tag{11}$$

where $P_N = \{x_1, \cdots, x_N\}$. Any optimal solution of (10)∼(11) is a feasible solution of the special formulation (4)∼(5) of the Lennard–Jones problem.

2.2. EQUIVALENT UNCONSTRAINED GLOBAL OPTIMIZATION

Let us consider the following unconstrained global optimization problem:

$$(LJ - GE) \min \ln(\omega_{12}(P_N)) - 2\ln(\omega_6(P_N)), \tag{12}$$

where $P_N = \{x_1, \cdots, x_N\}$. We claim that above unconstrained optimization problem (12) is equivalent to the general formulation (3) of the Lennard–Jones problem. For this equivalence, we have the following theorem:

THEOREM 2.2. *The following two conclusions hold:*

(1) *If P_N^* is an optimal solution of the problem* (3)*, then P_N^* is also an optimal solution of the problem* (12)*.*

(2) *If P_N^* is an optimal solution of the problem* (12)*,*

then $k \cdot P_N^* \triangleq \{k \cdot x_1^*, \cdots, k \cdot x_N^*\}$ is an optimal solution of the problem (3)*, where $k = (\omega_{12}(P_N^*)/\omega_6(P_N^*))^{1/6}$. The global minimum of the problem* (3) *is $-(\omega_6(P_N^*))^2/\omega_{12}(P_N^*)$.*

Proof. The first conclusion is a corollary of Theorem 2.1 based on the monotonic property of the logarithm function.

If P_N^* is an optimal solution of the problem (12), and let us denote

$$k := (\omega_{12}(P_N^*)/\omega_6(P_N^*))^{1/6},$$

then it is easy to check that $k \cdot P_N^*$ is a feasible solution of the special formulation (4)∼(5). The objective function value of the problem (12) with respect to $k \cdot P_N^*$ is the same as its globally minimal value and is also equal to $-\ln(\omega_6(k \cdot P_N^*))$. By the monotonic property of the logarithm function, $\omega_6(k \cdot P_N^*)$ must be the globally maximal value of the problem (4)∼(5), i.e., $k \cdot P_N^*$ is a globally optimal solution of the problem (4)∼(5). Using Theorem 2.1 again, we know that $k \cdot P_N^*$ is a globally optimal solution of the problem (3). Hence, the second conclusion also holds. □

REMARK 3. For the unconstrained formulation (12) of the Lennard–Jones problem, the objective function value with respect to a code P_N remains unaltered or invariant under similarity transformations (i.e., translation, rotation, reflection, dilation or dilatation of the entire configuration).

3. Necessary optimality conditions for the Lennard–Jones problem

In this section, we first present a bilevel optimization formulation for the Lennard–Jones problem. The main idea of the bilevel optimization formulation is to partition the whole code into a reference code and an active code, and then, to solve two optimization problems with respect to the active code and the reference code, respectively. In fact, partition patterns can be changed during iteration from a practical point of view. Theorem 3.1 states the relationship between a solution of the Lennard–Jones problem and that of its bilevel optimization formulation. By a particular partition, which leads to a one-point pattern Lennard–Jones code, Theorem 3.2 gives a necessary optimality condition for an extremal Lennard–Jones code.

Secondly, based on an idea similar to that used in Section 2, we obtain a general necessary optimality condition for an extremal Lennard–Jones code (i.e., Theorem 3.3), which can be referred to as extensions of Theorem 2.1 and Theorem 3.2.

Let $P_N = \{x_1, \cdots, x_N\}$ be a code in which points are mutually different. For any subset $U \subseteq I = \{1, \cdots, N\}$, any index $k \in I$ and any real $s > 0$, denote

$P_N(U) = \{x_k \mid k \in U\}$ and

$$\omega_s(P_N(U)) = \sum_{i,j\in U, i<j} \|x_i - x_j\|^{-s},$$
$$\omega_s^k(P_N) = \sum_{i\in I_k} \|x_i - x_k\|^{-s}.$$

where $I_k = I\backslash\{k\}$. We note that $\omega_s(\{x\}) = 0$ for any $x \in \Re^3$. If we partition the index set I into two disjoint subsets I^+ and I^- (i.e., $I^+ \cap I^- = \emptyset$ and $I^+ \cup I^- = I$), then the Lennard–Jones potential energy function (2) can be decomposed as follows:

$$\begin{aligned} V(P_N) &= \omega_{12}(P_N) - 2\omega_6(P_N) \\ &= \frac{1}{2}\sum_{k\in I} V^k(P_N) \\ &= V(P_N(I^+)) + V(P_N(I^+), P_N(I^-)) + V(P_N(I^-)), \end{aligned}$$

where

$$V^k(P_N) = \omega_{12}^k(P_N) - 2\omega_6^k(P_N),$$
$$V(P_N(I^\pm)) = \omega_{12}(P_N(I^\pm)) - 2\omega_6(P_N(I^\pm)),$$
$$V(P_N(I^+), P_N(I^-)) = \sum_{i\in I^+,\, j\in I^-} V(\{x_i, x_j\}).$$

Let us consider the bilevel optimization problem:

$$\min \quad \{V(P_N(I^-)) + \bar{V}(P_N(I^-))\}, \tag{13}$$
$$s.t. \quad x_i \in \Re^3,\ \forall i \in I^-, \tag{14}$$

where $\bar{V}(P_N(I^-))$ is the globally optimal value of the sub-problem:

$$\min \quad \{V(P_N(I^+)) + V(P_N(I^+), P_N(I^-))\}, \tag{15}$$
$$s.t. \quad x_j \in \Re^3,\ \forall j \in I^+. \tag{16}$$

The index subsets I^- and I^+ are called *the reference index set* and *the active index set*, respectively. $P_N(I^-)$ and $P_N(I^+)$ are referred as to *the reference code* and *the active code*, respectively. It is easy to obtain the following theorem, whose proof is omitted.

THEOREM 3.1. *A code P_N is a globally optimal solution of the problem* (3)*, if and only if, given any $I^- \subset I = \{1, \cdots, N\}$ as a reference index set, the active code $P_N(I^+)$ is a globally optimal solution of the problem* (15)∼(16)*, where $I^+ = I\backslash I^-$ is the corresponding active index set.*

DEFINITION 3.1. *Given an integer* $L \in [1, N]$, *a code* $P_N = \{x_1, \cdots, x_N\}$ *is called an L–points pattern Lennard–Jones code if, for any subset* $U \subset I = \{1, \cdots, N\}$ *with L elements,* $P_N(U)$ *is a globally optimal solution of the problem* (15)∼(16) *corresponding to* $U^c = I \backslash U$ *as its reference index set. In particular, a code* P_N *is called a one–point pattern Lennard–Jones code if,* $\forall i \in I$, $x_i \in P_N$ *is a globally optimal solution of the problem* (15)∼(16) *corresponding to* $I_i = I \backslash \{i\}$ *as its reference index set.*

For $k = 1, \cdots, N$, if we sequentially choose a reference index set $I^- = I_k$, then we obtain N similar three-dimensional global optimization problem (15)∼(16) where $V(\{x_k\}) = 0$ and $V(\{x_k\}, P_N(I_k)) = V^k(P_N)$. Based on this idea and the above notations, the following necessary optimality conditions for the Lennard–Jones problem can be proved.

THEOREM 3.2. *For the general formulation* (3) *of the Lennard–Jones problem, if a code* $P_N = \{x_1, \cdots, x_N\}$ *is an extremal Lennard–Jones code, then for any* $k \in I$, x_k *is a globally optimal solution of the corresponding optimization problem* (15)∼(16), *where* $I^+ = k$, $I^- = I_k$, *i.e.,* P_N *is a one–point pattern Lennard–Jones code. Furthermore,* $\forall k \in I$, x_k *is a solution of the following nonlinear equation:*

$$\sum_{i \in I_k} x_i (r_{ik}^{-14} - r_{ik}^{-8}) = x_k(\omega_{14}^k(P_N) - \omega_8^k(P_N)), \tag{17}$$

where $r_{ik} = \|x_i - x_k\|$, $i \in I_k$.

Proof. Suppose that $P_N = \{x_1, \cdots, x_N\}$ is a globally optimal solution of the problem (3). For any $k \in I$, if x_k is not a globally optimal solution of the corresponding problem (15)∼(16), then there exists $x_k^* \in \Re^3$ such that

$$\begin{aligned} V(\{x_k^*\}, P_N(I_k)) &= \sum_{i \in I_k} \|x_i - x_k^*\|^{-12} - 2\sum_{i \in I_k} \|x_i - x_k^*\|^{-6} \\ &< V(\{x_k\}, P_N(I_k)) = \sum_{i \in I_k} \|x_i - x_k\|^{-12} - 2\sum_{i \in I_k} \|x_i - x_k\|^{-6} \end{aligned}$$

Since Lennard–Jones potential energy function values, corresponding to codes $\{x_k^*\} \cup P_N(I_k)$ and P_N, are

$$\begin{aligned} V(\{x_k^*\} \cup P_N(I_k)) &= V(\{x_k^*\}, P_N(I_k)) + V(P_N(I_k)) \\ V(P_N) &= V(\{x_k\}, P_N(I_k)) + V(P_N(I_k)), \end{aligned}$$

respectively, we conclude that $V(\{x_k^*\} \cup P_N(I_k)) < V(P_N)$, i.e., P_N is not a globally optimal solution of the Lennard–Jones problem (3). This contradiction indicates that x_k is a globally optimal solution of the problem (15)∼(16), where $I^- = I_k$. Because the objective function (15) is differential, we get the following necessary

optimality condition that x_k must satisfies:

$$\begin{aligned}\nabla_k V(\{x_k\}, P_N(I_k)) &= \nabla_k \omega_{12}^k(P_N) - 2\nabla_k \omega_6^k(P_N) \\ &= 12\sum_{i\in I_k}(x_i - x_k) r_{ik}^{-14} - 2 * 6 \sum_{i\in I_k}(x_i - x_k) r_{ik}^{-8} \\ &= 0,\end{aligned}$$

where ∇_k is gradient operator with respect to x_k and $r_{ik} = \|x_i - x_k\|$. Hence, x_k satisfies equation (17). □

COROLLARY 3.1. *For the general formulation* (3) *of the Lennard–Jones problem, suppose that* $P_N = \{x_1, \cdots, x_N\}$ *is an extremal Lennard–Jones code. For any* $k \in I$, *denote* $x_k = r_k \overset{\circ}{x}_k$, *where* $r_k = \|x_k\|$ *and*

$$\overset{\circ}{x}_k = (\cos(\theta_k), \sin(\theta_k)\cos(\phi_k), \sin(\theta_k)\sin(\phi_k))^T.$$

Then, $\forall k \in I$, x_k *is a globally optimal solution of the problem* (15)∼(16), *where* $I^+ = k$, $I^- = I_k$, *and* (θ_k, ϕ_k, r_k) *is a solution of the following equations:*

$$\begin{aligned}&\sum_{i\in I_k}(r_{ik}^{-14} - r_{ik}^{-8}) x_i^T \ \nabla_{\theta_k} \overset{\circ}{x}_k = 0, \\ &\sum_{i\in I_k}(r_{ik}^{-14} - r_{ik}^{-8}) x_i^T \ \nabla_{\phi_k} \overset{\circ}{x}_k = 0, \\ &\sum_{i\in I_k}(r_{ik}^{-14} - r_{ik}^{-8}) x_i^T \ \overset{\circ}{x}_k \qquad = r_k(\omega_{14}^k(P_N) - \omega_8^k(P_N)),\end{aligned}$$

where $r_{ik} = \|x_i - x_k\|$, $i \in I_k$.

It is easily checked that, $\forall k \in I$, $x_k^T \ \nabla_{\theta_k} \overset{\circ}{x}_k = 0$, $x_k^T \ \nabla_{\phi_k} \overset{\circ}{x}_k = 0$ and $x_k^T \ \overset{\circ}{x}_k = r_k$. Using Theorem 3.2, we know that Corollary 3.1 holds.

Next, we give a general necessary optimality condition as an extension of Theorem 2.1. Let P_N be a code in which points are mutually different, I^- be a reference index set and I^+ be the corresponding active index set. Denote the corresponding reference code and active code by P_N^- and P_N^+, respectively. For any real ϵ in a small neighborhood of zero, let $P_{N,\epsilon}^+ = \{(1+\epsilon)x_i \,|\, i \in I^+)\}$. It is easy to check that

$$\begin{aligned}V(P_{N,\epsilon}^+) = V(P_N^+) &- 12(\omega_{12}(P_N^+) - \omega_6(P_N^+))\epsilon \\ &+ (78\omega_{12}(P_N^+) - 42\omega_6(P_N^+))\epsilon^2 + o(\epsilon^2).\end{aligned}$$

Then $\forall i \in I^+$ and $\forall j \in I^-$, the Taylor's expansion

$$\begin{aligned}\|(1+\epsilon)x_i - x_j\|^{-s} =& r_{ij}^{-s}(1+\frac{2\epsilon x_i^T(x_i-x_j)+\epsilon^2\|x_i\|^2}{r_{ij}^2})^{-s/2}\\ =& r_{ij}^{-s} - s\frac{x_i^T(x_i-x_j)}{r_{ij}^{s+2}}\epsilon\\ &+(-\frac{s}{2}\frac{\|x_i\|^2}{r_{ij}^{s+2}}+\frac{s(s+2)}{2}\frac{(x_i^T(x_i-x_j))^2}{r_{ij}^{s+4}})\epsilon^2+o(\epsilon^2)\end{aligned}$$

holds for any real $s > 0$, where $r_{ij} = \|x_i - x_j\|$. After we take the summation of the above expansion for every $i \in I^+$ and $j \in I^-$, we have

$$\begin{aligned}V(P_{N,\epsilon}^+, P_N^-) =& \sum_{i\in I^+, j\in I^-}(\|(1+\epsilon)x_i - x_j\|^{-12} - 2\|(1+\epsilon)x_i - x_j\|^{-6})\\ =& V(P_N^+, P_N^-) - 12\epsilon\sum_{i\in I^+, j\in I^-}(r_{ij}^{-14} - r_{ij}^{-8})x_i^T(x_i - x_j)\\ &- 6\epsilon^2\sum_{i\in I^+, j\in I^-}(r_{ij}^{-14} - r_{ij}^{-8})\|x_i\|^2\\ &+\epsilon^2\sum_{i\in I^+, j\in I^-}(84r_{ij}^{-16} - 48r_{ij}^{-10})(x_i^T(x_i - x_j))^2 + o(\epsilon^2).\end{aligned}$$

Therefore, we obtain the following necessary optimality condition of the Lennard–Jones problem:

THEOREM 3.3. *For the general formulation* (3) *of the Lennard–Jones problem, if* $P_N = \{x_k | k \in I\}$ *is an extremal Lennard–Jones code, then for any reference index set* $I^- \subseteq I$ *and its corresponding active index set* $I^+ = I \backslash I^-$, *the active code* $P_N^+ = P_N(I^+)$ *is a solution of the following nonlinear equation:*

$$\omega_{12}(P_N^+) - \omega_6(P_N^+) + \sum_{i\in I^+, j\in I^-}(r_{ij}^{-14} - r_{ij}^{-8})x_i^T(x_i - x_j) = 0, \tag{18}$$

where $r_{ij} = \|x_i - x_j\|$.

Proof. By Theorem 3.1, if P_N is a globally optimal solution of the Lennard–Jones problem (3), then, for any reference index set $I^- \subseteq I$ and a real ϵ, the active code P_N^+ must be a globally minimal solution of the function $V(P_{N,\epsilon}^+) + V(P_{N,\epsilon}^+, P_N^-)$, where the notations have the same meaning as above. Using the first necessary optimality condition with respect to variable ϵ, the conclusion follows. □

REMARK 4. Theorem 3.3 is an extension of Theorem 2.1. In fact, Theorem 3.3 implies the following conclusion:

$$\omega_{12}(P_N^-) - \omega_6(P_N^-) + \sum_{i\in I^+, j\in I^-} (r_{ji}^{-14} - r_{ji}^{-8}) x_j^T (x_j - x_i) = 0. \tag{19}$$

Notice that $r_{ij} = r_{ji}$ and $r_{ij}^2 = (x_i - x_j)^T (x_i - x_j)$. After summing (18) and (19), we know the formula (7) holds when P_N is an extremal Lennard–Jones code. In fact, Theorem 3.3 also implies the formula (17) in Theorem 3.2, which is a special conclusion of the following Corollary 3.2.

COROLLARY 3.2. *For the general formulation* (3) *of the Lennard–Jones problem, if $P_N = \{x_k | k \in I\}$ is an extremal Lennard–Jones code, then for any reference index set $I^- \subseteq I$ and its corresponding active index set $I^+ = I \backslash I^-$, the following equation holds:*

$$\sum_{i\in I^+, j\in I^-} (r_{ij}^{-14} - r_{ij}^{-8})(x_i - x_j) = 0, \tag{20}$$

where $r_{ij} = \|x_i - x_j\|$. In particular, since P_N is a one-point pattern Lennard-Jones code, the conclusion (20) *holds for the cases of $|I^-| = 1$ or $N - 1$.*

Proof. Because the (absolute) distance between two points in the three-dimensional space is invariant under any isometric transformation (i.e., translation, rotation, reflection), the transformed code from P_N must be an extremal Lennard–Jones code under any isometric transformation of the entire configuration. In particular, $\forall a \in \Re^3$, the code $P_N^* = P_N + a = \{x_k + a \,|\, x_k \in P_N\}$ is also an extremal Lennard–Jones code. By Theorem 3.3, we know that P_N^* satisfies equation (18). On the other hand, P_N also satisfies the same Eq. (18). Therefore, We have

$$\sum_{i\in I^+, j\in I^-} (r_{ij}^{-14} - r_{ij}^{-8}) a^T (x_i - x_j) = 0.$$

Since a is chosen arbitrarily, the nonlinear equation (20) holds for the extremal Lennard–Jones code P_N. □

4. The code partition algorithm and computational results

By Theorem 3.1 and Definition 3.1, we know any extremal Lennard–Jones code must be L–points pattern Lennard–Jones code, where L is any integer between 1 and N. In this section, a *code partition algorithm* (CPA) based on Theorem 3.1 is presented to search for a certain X–points pattern Lennard–Jones code as the approximation to an extremal Lennard–Jones code, where X is an unknown natural integer. CPA is described first and a proof of its convergence follows. Some details

and characteristics about CPA's implementation and some computational results are given in this section.

4.1. THE CODE PARTITION ALGORITHM (CPA)

Step 1. Set the error tolerance $\varepsilon > 0$. Input the parameter N and an initial molecular configuration code $P_N^{(0)}$. Set $k = 0$ and the strategy index $SI_k = 1$.

Step 2. At the beginning of kth iteration, perform a translation on the entire configuration such that the center of mass lies in the origin of a new coordinate system. We still denote the new configuration code as $P_N^{(k)}$. Choose an arbitrary partition $\{\triangle_i^{(k)} \mid i \in M_k\}$ of the index set $I = \{1, \cdots, N\}$, where $M_k = \{1, \cdots, t_k\}$ and $2 \leqslant t_k \leqslant N$. For each $i \in M_k$, denote the subcode $P_N^{(k)}(\triangle_i^{(k)})$ by $Q_i^{(k)}$.

Step 3. The exploratory code $\hat{P}_N^{(k)} = \bigcup_{i \in M_k} \hat{Q}_i^{(k)}$, where $\hat{Q}_i^{(k)} = \{\hat{x}_j^{(k)} \mid j \in \triangle_i^{(k)}\}$, is set by one of the following strategies. If $SI_k = 1$, then go to step 4; otherwise, go to step 5.

Step 4. **Strategy 1:**
For each $i \in M_k$, set the exploratory subcode $\hat{Q}_i^{(k)}$ to be a globally optimal solution of the problem (15)$\sim$(16), where the active index set $I^+ = \triangle_i^{(k)}$, its corresponding reference index set $I^- = I \backslash I^+$ and $P_N = P_N^{(k)}$. Go to step 6.

Step 5. **Strategy 2:**
For $i \in M_k$, let $M_{k,i}^- = \{j | j < i, j \in M_k\}$, $M_{k,i}^+ = \{j | j \geqslant i, j \in M_k\}$ and set the exploratory subcode $\hat{Q}_i^{(k)}$ to be a globally optimal solution of the problem (15)$\sim$(16), where the active index set $I^+ = \triangle_i^{(k)}$, its corresponding reference index set $I^- = I \backslash I^+$ and $P_N = \bigcup_{j \in M_{k,i}^-} \hat{Q}_j^{(k)} \cup \bigcup_{j \in M_{k,i}^+} Q_j^{(k)}$. Go to step 6.

Step 6. If $V(\hat{P}_N^{(k)}) < V(P_N^{(k)})$, find the value λ^* that minimizes the function $V(P_N^{(k)} + \lambda(\hat{P}_N^{(k)} - P_N^{(k)}))$. Let $P_N^{(k+1)}$ be the configuration code $P_N^{(k)} + \lambda^*(\hat{P}_N^{(k)} - P_N^{(k)})$ and set the strategy index $SI_{k+1} = 1$. Otherwise, let

$$i^* = \text{argmin}\{V(\hat{Q}_i^{(k)} \cup P_N^{(k)}(I \backslash \triangle_i^{(k)})) \mid i \in M_k\}.$$

Let $P_N^{(k+1)}$ be the configuration code $\hat{Q}_{i^*}^{(k)} \cup P_N^{(k)}(I \backslash \triangle_{i^*}^{(k)})$ and set the strategy index $SI_{k+1} = 2$.

Step 7. If $V(P_N^{(k+1)}) > V(P_N^{(k)}) - \varepsilon$, terminate CPA and output the configuration code $P_N^{(k+1)}$ together with its potential energy function value; otherwise, set $k \leftarrow k + 1$ and go to step 2.

From the code partition algorithm, we can see that $\{V(P_N^{(k)})\}$ is a strictly monotonic decreasing sequence as k becomes larger. It is easy to check that $-N(N-1)/2$ is

a lower bound of this potential energy sequence. We give the following conclusion about the convergence of the code partition algorithm as the error tolerance ε tends to zero.

THEOREM 4.1. *Let C_N be the set of all feasible codes with N points for the Lennard–Jones problem* (3)*. Let $V(P_N)$ be the Lennard–Jones potential energy function defined by* (2) *on C_N. Given a code $P_N^{(0)} \in C_N$ with the center of mass at the origin of the three–dimensional Cartesian coordinate system, let $\alpha = V(P_N^{(0)})$ and the level set*

$$S(V, \alpha) = \{P_N \mid P_N \in C_N, V(P_N) \leqslant \alpha\}.$$

Let $\{P_N^{(k)}\}$ be the sequence of codes generated by the code partition algorithm. For each $i \in I$, denote $V_i^{(k)} = \min_{x_i \in \Re^3} V(\{x_i\} \cup P_N^{(k)}(I \backslash \{i\}))$ and $\tilde{x}_i^{(k)}$ to be its globally optimal solution. If the following conditions hold:

(i) *For $k = 0, 1, \cdots$, $I^{(k)} = \{i \mid V_i^{(k)} < V(P_N^{(k)})\} \neq \emptyset$ implies that there exists a natural number $s(k) \in I^{(k)}$ such that $V(P_N^{(k+1)}) \leqslant V_{s(k)}^{(k)}$;*

(ii) $\lim_{k\to\infty} V_{s(k)}^{(k)} = \lim_{k\to\infty} \min\{V_i^{(k)} | i \in I^{(k)}\}$;

then every cluster point P_N^* of $\{P_N^{(k)}\}$ is at least a one-point pattern Lennard–Jones code. In particular, P_N^* satisfies the nonlinear equation (17)*.*

Proof. If $\{P_N^{(k)} | k = 0, 1, \cdots\}$ is a finite set, then CPA terminates at $P_N^{(K)}$, where K is the number of iterates. Clearly, $P_N^{(K)}$ is at least a one–point pattern Lennard–Jones code.

Without loss of generality, suppose that $\{P_N^{(k)} | k = 0, 1, \cdots\}$ is an infinite subset of $S(V, \alpha)$. Because $\{V(P_N^{(k)})\}$ is a monotonic decreasing sequence and is bounded below, it has a limit. Let P_N^* be any cluster point of the set $\{P_N^{(k)}\}$, that is, there exists a subsequence $\{P_N^{(k_m)}\}$ such that $\lim_{m\to+\infty} P_N^{(k_m)} = P_N^*$. We claim that P_N^* is at least a one–point pattern Lennard–Jones code.

If P_N^* is not a one–point pattern Lennard–Jones code, then there exists at least a natural number q such that

$$V(\{\tilde{x}_q^*\} \cup P_N^*(I_q)) = \min_{y\in\Re^3} V(\{y\} \cup P_N^*(I_q)) < V(\{x_q^*\} \cup P_N^*(I_q)),$$

where $I_q = I \backslash \{q\}$. We choose the integer p such that

$$p = \text{argmax}\{V(\tilde{x}_q^* \cup P_N^*(I_q)) \mid V(\tilde{x}_q^* \cup P_N^*(I_q)) < V(P_N^*)\}. \tag{21}$$

Denote $\{\tilde{x}_p^*\} \cup P_N^*(I_p)$ by $\tilde{P}_{N,p}^*$ and $\epsilon = V(P_N^*) - V(\tilde{P}_{N,p}^*) > 0$.

Based on continuity of the potential energy function $V(P_N)$ on $S(V, \alpha)$ and $\lim_{m\to+\infty} P_N^{(k_m)} = P_N^*$, we get

$$\lim_{m\to+\infty} V(P_N^{(k_m)}) = V(P_N^*)$$

$$\lim_{m\to+\infty} V(\{\tilde{x}_p^*\} \cup P_N^{(k_m)}(I_p)) = V(\{\tilde{x}_p^*\} \cup P_N^*(I_p)).$$

For sufficiently large k_m, the following inequality holds

$$\begin{aligned} V(\{\tilde{x}_p^*\} \cup P_N^{(k_m)}(I_p)) &\leqslant V(\{\tilde{x}_p^*\} \cup P_N^*(I_p)) + \epsilon/2 \\ &= V(P_N^*) - \epsilon/2 \\ &< V(P_N^{(k_m)}). \end{aligned}$$

By definition of $V_p^{(k_m)}$ and $\tilde{x}_p^{(k_m)}$, we can conclude that $V_p^{(k_m)} \leqslant V(\{\tilde{x}_p^*\} \cup P_N^{(k_m)}(I_p))$ and $p \in I^{(k_m)}$ for sufficiently large k_m. Thus, we get $I^{(k_m)} \neq \emptyset$. By the hypothesis (i), we know that, $\exists\ s(k_m) \in I^{(k_m)}$ s.t. $V(P_N^{(k_m+1)}) \leqslant V_{s(k_m)}^{(k_m)}$. By the hypothesis (ii), for the above ϵ and very large k_m, $V(P_N^{(k_m+1)}) \leqslant \min\{V_i^{(k_m)} | i \in I^{(k_m)}\} + \epsilon/4 \leqslant V_p^{(k_m)} + \epsilon/4$ also holds. Therefore, using the monotonicity of the sequence $\{V(P_N^{(k)})\}$, we have

$$V(P_N^*) < V(P_N^{(k_m+1)}) \leqslant V(\{\tilde{x}_p^*\} \cup P_N^{(k_m)}(I_p)) + \epsilon/4 \leqslant V(P_N^*) - \epsilon/4,$$

which is a contradiction. Hence, P_N^* is at least a one–point pattern Lennard–Jones code. From the proof of Theorem 3.2, it is easy to check that P_N^* satisfies the nonlinear Eq. (17). □

The code partition algorithm seems to solve t_k smaller size global optimization problems with respect to every subcode $Q_i^{(k)}$ ($i \in M_k$) at kth iteration. It is still difficult even to solve one of these smaller size problems with respect to a single point. In fact, during the process of searching for an extremal Lennard–Jones code, structure among atoms is more important than the exactly minimal value of potential energy function with respect to a certain subcode $Q_i^{(k)}$. Therefore, in order to find a one–point pattern Lennard–Jones code or better, we should pay more attentions to adjust the structure among atoms during the implementation of the CPA instead of finding a globally minimal solution for every subcode. Since the separation of any pair of points for the Lennard–Jones problem exists, the effect of one large change for a certain subcode is expected to be approximated by that of many small changes for all points or subcodes simultaneously. Hence, an effective method for adjusting the structure among atoms is to conduct a series of local optimizations or local searches for these subcodes.

In order to search for one of extremal Lennard–Jones codes, there are three important aspects: (i) How close is the initial molecular configuration $P_N^{(0)}$ to a certain extremal molecular configuration? (ii) How to get a better molecular configuration from $P_N^{(0)}$? (iii) How to find a better basin-hopping strategy to escape the attraction of a locally optimal configuration? In fact, the third aspect can be classified as a special case of the first aspect. In our experiments based on the code partition algorthim (CPA), we use the following approaches to deal with these aspects:

Approach 1: Use the hyperspherical coordinate system instead of the Cartesian coordinate system. That is, the code P_N is represented by the hyperspherical coordinates of N points in the three–dimensional space. Since it is observed that an extremal Lennard–Jones code corresponds to the points located on almost concentric spheres, it is convenient to adjust the position of a point on a certain sphere in the hyperspherical coordinate system.

Approach 2: The initial molecular configuration code is generated by the following two-step algorithm. At the first step, a configuration code is generated randomly under the condition of restricting N points to be located in a ball with the origin as its center and the radius less than 1.75 (For a large N, a larger radius may be preferred.) At the second step, a locally optimal configuration code is searched for by using the code partition algorithm with $\omega_{12}(P_N) - \omega_6(P_N)$ instead of $\omega_{12}(P_N) - 2\omega_6(P_N)$ as the objective function.

Approach 3: A special partition in which $\triangle_i^{(k)} \equiv \{i\}$ is adopted for every iteration of the code partition algorithm with respect to the two different objectives above. The exploratory code $\hat{P}_N^{(k)}$ is determined by a series of one step searching of the steepest descent method with respect to a single point while other points are fixed according to Strategy **1** or **2**. In particular, the movement along the radial direction during one step searching is adjusted so as not to excess the border of the ball mentioned in approach 2. Note that this special partition approach is similar to that used in the point balance algorithm for the spherical code problem [21], however, the code partition algorithm is not limited to this single point partition.

Approach 4: In order to accelerate the convergence of the code partition algorithm and correct the error in the configuration code caused by the initial constrained ball, the *Broyden-Fletcher-Goldfarb-Shannon* (BFGS) quasi–Newton method is used to relax the resulting configuration code of the code partition algorithm.

Approach 5: The following perturbation methods are used to adjust the structure of a locally optimal configuration code. For any of these perturbation methods, the resulting configuration code can be used as the initial input code, and then, the corresponding locally optimal configuration code is searched for by using the code partition algorithm together with the approches 1, 3 and 4. The perturbation methods which are used randomly include: (i) compressing the outer layer of the code closer to the origin or/and expanding the inner layer of the code further away from the origin; (ii) adjusting randomly the positions of points on the outer/inner layer of the code in their own neighborhoods; (iii) moving the point with the highest potential energy to the neighborhoods of the points on the outer layer of the code; (iv) adding randomly $m \in \{1, 2, 3\}$ points in the neighborhoods of the points on the outer layer of the code, and then, searching for the corresponding locally optimal code and deleting m points with higher potential energy from the optimal code.

The numerical experiments were conducted using *MATLAB 5.3* on a *PC* with AMD K6–2/300 CPU processor and 64M memory. The BFGS quasi–Newton accelerating approach can be implemented by calling the subroutine *fminu.m* in *MAT-*

Table 1. Computational results for the symmetric configurations, where $d_{\min} = \min_{i \neq j} r_{ij}$, $r_{\min} = \min_{i} \max_{j \neq i} r_{ij}$, $d_{\max} = \max_{i \neq j} r_{ij}$.

N	$-E_N$	Distances			Number of points on each layer	Radius of each layer
		$d_{\min}$	$r_{\min}$	$d_{\max}$		
2	1.0000000000	1	1	1	2	0.500
3	3.0000000000	1	1	1	3	0.577
4	6.0000000000	1	1	1	4	0.612
5	9.1038524157	0.998	1.002	1.627	3–2	0.578–0.813
6	12.7120622568	0.996	1.408	1.408	6	0.704
7	16.5053841680	0.994	1.023	1.620	2–5	0.511–0.852
13	44.3268014195	0.964	0.964	1.928	1–12	0–0.964
19	72.6597824544	0.922	1.875	2.828	2–5–10–2	0.461–0.861–1.224–1.414
23	92.8444724283	0.932	1.879	2.823	3–2–6–6–6	0.538–0.826–1.083–1.304–1.426
26	108.3156162317	0.941	1.883	2.822	4–4–6–12	0.576–1.011–1.181–1.434
29	123.5873714004	0.939	1.892	3.142	3–2–6–6–6–6	0.550–0.761–1.086–1.299–1.429–1.600
38	173.9284265906	0.978	2.199	3.117	6–8–24	0.691–1.202–1.559
55	279.2484704630	0.936	1.906	3.812	1–12–30–12	0–0.936–1.633–1.906

LAB 5.3. The tolerance for the code P_N and its corresponding potential energy $V(P_N)$ is set to 1.0e-5. The number N for the Lennard–Jones problem ranges from 2 to 56. Tables 1 and 2 contain some computational results for the Lennard–Jones problem. In order to demonstrate the multilayer structure of an extremal Lennard–Jones code, the longest distance between each point x_i and others, i.e., $r_i = \max_{j \neq i} r_{ij}$, is calculated. The minimal radius $r_{\min}$ of the balls that contain all points in the code P_N and refer to each x_i as its center equals to $\min_i r_i$. Let $d_{\min}$ and $d_{\max}$ denote the minimal and maximal distances among the points in P_N, respectively. Obviously, $d_{\max} = \max_i r_i$. For an extremal Lennard–Jones code, without loss of generality, we refer to the origin of the coordinate system as the center of mass of the points in the set $\{x_i | r_i \leqslant r_{\min} + 0.1, i \in I\} \subset P_N$, denoted by x_0. In our experiments, we have obtained all of putative global minima for the Lennard-Jones problem when $2 \leqslant N \leqslant 56$, which is similar to the well-known results reported in the reference [22]. The computational results with higher precision and its corresponding multilayer structural characteristics are presented in Table 1 and 2.

Table 1 presents some computational results related to the configurations with a certain symmetry, which include the number of points N, the globally optimal potential energy E_N, r_{min}, d_{min}, d_{max}, the number of points on each layer and the radius of each layer. The width of each layer is less than 1.0e-5.

Table 2 shows some computational results related to the configurations with less symmetry, which include the number of points N, the globally optimal potential

Table 2. Computational results for other less symmetric configurations, where $d_{\min} = \min_{i \neq j} r_{ij}$, $r_{\min} = \min_{i} \max_{j \neq i} r_{ij}$, $d_{\max} = \max_{i \neq j} r_{ij}$, $R = \max_{i \in I} \|x_i - x_0\|$.

N	$-E_N$	Distances			Radius	Number of points
		$d_{\min}$	$r_{\min}$	$d_{\max}$	R	on each layer
8	19.8214891922	0.990	1.020	1.971	1.020	1–7
9	24.1133604336	0.984	1.016	1.961	1.016	1–8
10	28.4225318934	0.978	1.008	1.948	1.008	1–9
11	32.7659700900	0.971	0.997	1.962	0.997	1–10
12	37.9675995624	0.963	0.978	1.935	0.978	1–11
14	47.8451567826	0.962	1.560	2.398	1.560	1–12–1
15	52.3226272618	0.961	1.552	2.398	1.552	1–12–2
16	56.8157417804	0.957	1.555	2.402	1.555	1–12–3
17	61.3179946601	0.957	1.554	2.449	1.554	1–12–4
18	66.5309494631	0.938	1.565	2.414	1.565	1–12–5
20	77.1770425683	0.921	1.873	2.824	1.416	2–2–3–6–7
21	81.6845711314	0.922	1.871	2.819	1.440	3–2–6–6–4
22	86.8097822593	0.925	1.872	2.837	1.432	3–2–6–6–5
24	97.3488151180	0.931	1.880	2.853	1.446	4–4–6–10
25	102.3726631996	0.934	1.877	2.839	1.442	4–4–6–11
27	112.8735842737	0.931	1.887	3.188	1.609	3–2–6–6–4–6
28	117.8224017240	0.930	1.887	3.169	1.605	3–2–6–6–5–6
30	128.2865707030	0.928	1.899	3.205	1.673	2–5–10–7–6
31	133.5864219194	0.948	1.907	3.404	1.714	3–2–5–6–6–6–3
32	139.6355237695	0.948	1.908	3.406	1.712	3–2–5–6–6–6–4
33	144.8427188405	0.948	1.907	3.405	1.767	2–5–10–7–6–3
34	150.0445284105	0.949	1.940	3.404	1.940	1–12–17–4
35	155.7566432787	0.946	1.909	3.422	1.763	2–5–10–7–7–4
36	161.8253626623	0.945	1.911	3.414	1.760	2–5–10–7–8–4
37	167.0336724866	0.944	1.943	3.426	1.943	1–12–19–5
39	180.0331852029	0.946	1.917	3.402	1.752	2–5–10–7–10–5
40	185.2498386151	0.945	1.948	3.426	1.948	1–12–21–6
41	190.5362772767	0.944	1.946	3.430	1.946	1–12–22–6
42	196.2775335080	0.940	1.945	3.834	1.945	1–12–22–7
43	202.3646635847	0.937	1.943	3.836	1.943	1–12–23–7
44	207.6887275110	0.937	1.941	3.836	1.941	1–12–24–7
45	213.7848623502	0.938	1.937	3.829	1.937	1–12–25–7
46	220.6803299098	0.937	1.936	3.828	1.936	1–12–25–8
47	226.0122561376	0.936	1.934	3.828	1.934	1–12–26–8
48	232.1995294445	0.935	1.928	3.821	1.928	1–12–27–8
49	239.0918642339	0.934	1.927	3.820	1.927	1–12–27–9
50	244.5499263274	0.934	1.925	3.821	1.925	1–12–28–9
51	251.2539640366	0.936	1.914	3.816	1.914	1–12–30–8

Table 2. Continued.

N	$-E_N$	Distances			Radius	Number of points
		$d_{\min}$	$r_{\min}$	$d_{\max}$	R	on each layer
52	258.2299910739	0.935	1.913	3.815	1.913	1–12–30–9
53	265.2030161435	0.934	1.911	3.814	1.911	1–12–30–10
54	272.2086309712	0.935	1.909	3.813	1.909	1–12–30–11
56	283.6431052963	0.935	2.306	3.992	2.306	1–12–30–12–1

energy E_N, $r_{\min}$, $d_{\min}$, $d_{\max}$, R and the number of points on each layer. R is the minimal radius of a ball that contains all points in an extremal Lennard–Jones code and refers to the origin as its center. The corresponding layers are classified under the following heuristic rules: (i) the multilayer structures should be similar to each other except that at least one sufficient evidence indicates that there is a difference between them; (ii) the minimal distance between two different layers is at least 0.05. Because of the more or less un-symmetry in the molecular configuration, the width of each layer may not be less than 1.0e-5. For most cases, the width of each layer is less than 0.02.

From Table 1 and Table 2, it is observed that the parameters $d_{\min}$, $r_{\min}$, $d_{\max}$ and R do not change significantly for molecular configurations with similar multilayer structure. The inner layer structure for an optimal configuration with a large N is similar to that of a certain optimal configuration with a small N. Although it has been proved that the minimal distance $d_{\min}$ can not be less that 0.5 [43], it is obvious from our computational results that the value $d_{\min}$ is not less than 0.9. Actually, the potential energy function $v(r) = r^{-12} - 2r^{-6}$ $(r > 0)$ between two points has a unique zero point $2^{-1/6} \approx 0.8909$. We conjecture that $d_{\min}$ should not be less than the value $2^{-1/6}$, i.e.,

> *For any $N \geqslant 2$, let P_N^* be one of its corresponding extremal Lennard–Jones codes, the potential energy between any two points in P_N^* is not greater than zero.*

5. Concluding remarks

The Lennard–Jones problem is a challenging and unsolved problem in the area of molecular conformation and protein folding. Some equivalent formulations and necessary optimality conditions for this problem are presented in this paper. A new strategy, *the code partition algorithm*, which is based on the bilevel optimization formulation, is proposed for searching for an extremal Lennard–Jones code. Its convergence is proved and some approaches for its implementation have been

presented. Some computational results related to the new strategy are reported, which indicate that a more efficient algorithm for the Lennard–Jones problem could be constructed by using the equivalent formulations, necessary optimality conditions and the multilayer structure appearing in any globally optimal molecular configuration.

6. Acknowledgements

The research of the first author was supported by the China Scholarship Council while the author was visiting the Department of Industrial and Systems Engineering, University of Florida, Gainesville FL, USA. The research of the second author was partially supported by NSF under Grants DBI 9808210 and EIA 9872509.

References

1. Baljon, A. and Robbins, M. (1996), Energy Dissipation During Rupture of Adhesive Bonds. *Science*, 271: 482–484.
2. Barhen, J., Protopopescu, V. and Reister, D. (1997), TRUST: A Deterministic Algorithm for Global Optimization. *Science*, 276: 1094–1097.
3. Barron, C., Gomez, S. and Romero, D. (1996), Archimedean Polyhedron Structure Yields a Lower Energy Atomic Cluster, *Applied Mathematics Letters*, 9: 75–78.
4. Byrd, R. H., Eskow, E., Van der Hoek, A. et al. (1996), Global Optimization Methods for Protein Folding Problems, In *'Global Minimization of Nonconvex Energy Functions: Molecular Conformation and Protein Folding'*, P. M. Pardalos, D. Shalloway and G. Xue (eds.), DIMACS Series Vol. 23, American Mathematical Society, pp. 29–39.
5. Chan, H.S. and Dill, K.A., The Protein Folding Problem, *Physics Today*, February, 1993, pp. 24–32.
6. Coleman, T., Shalloway, D. and Wu, Z. (1994), A Parallel Build-Up Algorithm for Global Energy Minimizations of Molecular Clusters Using Effective Energy Simulated Annealing, *Journal of Global Optimization*, 4: 171–185.
7. Cvijovic, D. and Klinowski, J. (1995), Taboo Search: An approach to the Multiple Minima Problem, *Science*, 267: 664–666.
8. Doye, J. P. K. (2000), Effect of Compression on the Global Optimization of Atom Clusters, *Physical Review E*, 62(6): 8753–8761.
9. Doye, J. P. K., Miller, M. A. and Wales, D. J. (1999), The Double-Funnel Energy Landscape of the 38-Atom Lennard-Jones Cluster, *Journal of Chemical Physics*, 111(18): 8417–8428.
10. Doye, J. P. K., Miller, M. A. and Wales, D. J. (1999), Evolution of the Potential Energy Surface with Size for Lennard-Jones Clusters, *Journal of Chemical Physics*, 111(18): 8417–8428.
11. Deaven, D. M., Tit, N., Morris, J. R. and Ho, K. M. (1996), Structural Optimization of Lennard-Jones Clusters by a Genetic Algorithm, *Chemical Physics Letters*, 256: 195–198.
12. Doye, J. P. K., Wales, D. J. and Berry, R. S. J. (1995), The Effect of the Range of the Potential on the Structures of Clusters, *Journal of Chemical Physics*, 103(10): 4234–4249.
13. Fisher, I. Z. (1964), *Statistical Theory of Liquids*, University of Chicago Press.
14. Floudas, C. A., Klepeis, J. L. and Pardalos, P. M. (1999), Global Optimization Approaches in Protein Folding and Peptide Docking, In *'Mathematical Support for Molecular Biology'*, M. F. Colton, F. S. Roberts, M. Vingron and M. Waterman (eds.), DIMACS Series Vol. 47, American Mathematical Society, pp. 141–171.

15. Gu, J. and Du, B. (1996), A Multispace Search Algorithm for Molecular Energy Minimization, In *'Global Minimization of Nonconvex Energy Functions: Molecular Conformation and Protein Folding'*, P. M. Pardalos, D. Shalloway and G. Xue (eds.), DIMACS Series Vol. 23, American Mathematical Society, pp. 65–87.
16. Hoare, M. R., Structure and Dynamics of Simple Microclusters, *Advances in Chemical Physics*, 40(1979), pp. 49–135.
17. Hoare, M. R. and Pal, P. (1971), Physical cluster mechanics: statics and energy surfaces for monatomic systems, *Advances in Physics*, 21: 161–196.
18. Hopfinger, A. J., *Conformational Properties of Macromolecules*, Academic Press, New York and London, 1973.
19. Horst, R. and Pardalos, P.M. (eds.), (1995), *Handbook of Global Optimization* , Kluwer Academic Publishers, Dorcrecht.
20. Horst, R., Pardalos, P.M. and Thoai, N.V. (2000), *Introduction to Global Optimization* (2nd edition), Kluwer Academic Publishers, Dordrecht.
21. Huang, H. X., Pardalos, P. M. and Shen, Z. J. (2001), A Point Balance Algorithm for the Spherical Code Problem, *Journal of Global Optimization*, vol. 19, No. 4: 329–344.
22. Leary, R. H. (1997), Global Optima of Lennard-Jones Clusters, *Journal of Global Optimization*, 11: 35–53.
23. Leary, R. H. and Doye, J. P. K. (1999), Tetrahedral Global Minimum for the 98-Atom Lennard-Jones Cluster, *Physical Review E*, 60(6): R6320–R6322.
24. Maranas, C.D. and Floudas, C.A., (1992), A Global Optimization Approach for Lennard-Jones Microclusters, *Journal of Chemical Physics*, 97: 7667–7678.
25. Maranas, C.D. and Floudas, C.A. (1994), Global Minimum Potential Energy Conformations of Small Moleculars, *Journal of Global Optimization*, 4: 135–170.
26. Northby, J. A. (1987), Structure and binding of Lennard-Jones Clusters: $13 \leqslant N \leqslant 147$, *Journal of Chemical Physics*, 87: 6166–6177.
27. Pain, R. H., (Editor), (1994), *Mechanisms of Protein Folding*, Oxford University Press, London.
28. Pardalos, P. M. (1994), On the passage from local to global in optimization, In *'Mathematical Programming: State of the Art'*, J.R. Birge and K.G. Murty (eds.), The University of Michigan, pp. 220–247.
29. Pardalos, P.M., Liu, X. and Xue, G. (1997), Protein Conformation of a Lattice Model Using Tabu Search, *Journal of Global Optimization*, 11(1): 55–68.
30. Pardalos, P.M., Phillips, A. and Rosen, J.B. (1992), *Topics in Parallel Computing in Mathematical Programming*, Science Press.
31. Pardalos, P.M. and Rosen, J.B. (1987), *Constrained Global Optimization: Algorithms and Applications*, Lecture Notes in Computer Science 268, Springer, Berlin.
32. Pardalos, P.M., Shalloway, D. and Xue, G. (1994), Optimization Methods for Computing Global Minima of Nonconvex Potential Energy Functions, *Journal of Global Optimization*, 4(2): 117–133.
33. Pardalos, P.M., Shalloway D. and Xue, G. (eds.), (1996), *Global Minimization of Nonconvex Energy Functions: Molecular Conformation and Protein Folding*, DIMACS Series Vol. 23, American Mathematical Society.
34. Pardalos, P. M. and Xue, G. (eds.), (1994), Special issue on Advances in Computational Chemistry and Protein Folding, *Journal of Global Optimization*, 4(2).
35. Pardalos, P. M. and Xue, G. (eds.), (1997), Special issue on Computer Simulations in Molecular and Protein Conformations, *Journal of Global Optimization*, 11(1).
36. Richards, F.M., The Protein Folding Problem, *Scientific American*, January, 1991, pp. 54–63.
37. Shalloway, D. (1991), Packet Annealing: A Deterministic Method for Global Minimization, Application to Molecular Conformation, In *Recent Advances in Global Optimization*, C. Floudas and P. Pardalos (eds.), Princeton University Press: Princeton, NJ, pp. 433–477.

38. Van de Waal, B. W. (1989), Stability of Face-Centered Cubic and Icosahedral Lennard-Jones Clusters, *Journal of Chemical Physics*, 90: 3407–3408.
39. Wales, D. J. and Doye, J. P. K. (1997), Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms, *Journal of Physical Chemistry A*, 101: 5111–5116.
40. Wales, D. J. and Scheraga, H. A. (1999), Global Optimization of Clusters, Crystals and Biomolecules, *Science*, 285: 1368–1372.
41. Xue, G. (1994), Molecular Conformation on the CM-5 by Parallel Two-Level Simulated Annealing, *Journal of Global Optimization*, 4: 187–208.
42. Xue, G. (1994), Improvement on the Northy Algorithm for Molecular Conformation: Better Solutions, *Journal of Global Optimization*, 4: 425–440.
43. Xue, G. (1997), Minimum Inter-Particle Distance at Global Minimizers of Lennard–Jones Clusters, *Journal of Global Optimization*, 11: 83–90.