Forward and correct global optimization procedures for Lennard-Jones clusters

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Abstract

In this report some numerical results are presented for a special class of global optimization methods applied to molecular conformation problems. Following the results of a previously published method, in this report the authors show how some modifications to the basic structure of those algorithms enables us to obtain the optimal configuration for all clusters of Lennard-Jones atoms up to 80 atoms.

1 Problem definition

The problem we are facing is that of determining the configuration of minimum potential energy of a cluster of identical atoms with no charge in three-dimensional space. In this model all atoms are considered to be equal and only pairwise interaction is included in the definition of the potential energy. Let $N \geq 2$ be an integer representing the total number of atoms. The Lennard-Jones (in short L-J) pairwise potential energy function is defined as follows: if the distance between the centers of a pair of atoms is r, then their contribution to the total energy is defined to be

$$v(r) = \frac{1}{r^{12}} - \frac{2}{r^6} \tag{1}$$

and the L-J potential energy E of the cluster is defined as

$$E(X) = E(X_1, \ldots, X_N) = \sum_{i<j} v\left(\|X_i - X_j\|\right) \tag{2}$$

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where $X_i \in \mathbb{R}^3$ represents the coordinates of the center of the i–th atom and the norm used is the usual Euclidean one. An optimum L-J configuration $X^\star = \{X_1^\star, \ldots, X_N^\star\}$ is defined as the solution of the global optimization problem

$$LJ_N = E(X^\star) = \min_{X \in \mathbb{R}^{3N}} E(X). \tag{3}$$

In a recent paper [2] the authors have shown how with the addition of a penalty term in the potential energy all of the most difficult to find configurations have been obtained, through a simple Multistart-like method. However in that paper several cases which in the literature are considered to be easy, could not be discovered. In this sense the two phase approach might seem to be biased towards special classes of cluster conformations. We conjectured this is not the case and this report has been produced in order to fill this gap. It seems worthwhile to remind, however, that even if the approach would have been deemed as biased, in any case this hypotetical biasedness would have simply prevented the rediscovery of quite easy to find clusters, most of which follow into the class of icosahedral ones.

We recall briefly here that the idea of two phase methods in cluster optimization consists of using as a starting point for a local optimization of the Lennard-Jones potential a cluster which is obtained as the result of a local optimization, applied to a random configuration, of the following penalized potential function:

$$\sum_{i<j} h\left(\|X_i - X_j\|\right), \tag{4}$$

where

$$h(r) = \frac{1}{r^{2p}} - \frac{2}{r^p} + \mu r + \beta(\max\{0, r^2 - D^2\})^2, \tag{5}$$

where $p, \mu, \beta, D \geq 0$.

Using a small set of parameters it was possible, in the above cited paper, to obtain most of the putative optimum configurations for the Lennard-Jones problem. The only cases which, in the range of clusters with up to 80 atoms, the optimum could not be discovered with this approach and with the choice we made for the parameters where the cases $N = 62, 65, 66, 67, 68, 70, 71, 72, 73, 74, 78$. Also, in many cases in the range $61 - -74$, even if we could discover the optimum configuration, the rate of success was very low.

It is quite well known in the literature, however, that these are not considered as the most difficult to find configurations and it has been stated in [1] that "Any GO method 'worth its salt' should be able to find all the icosahedral minima and the truncated octahedron at $N = 38$. Success for the other non-icosahedral minima would indicate that the method has particular promise". The same author, referring to our approach, says that methods

like our own are often capable of "solving some 'hard' instances' while failing for 'easier' examples".

In this paper we would like to show that using the same basic idea of potential transformation alongside with more or less standard global optimization methods we could succeed in discovering also the "easy" cases.

Of course, in general, there is no interest in easy cases: but the fact that modifications of the standard method are able of discovering even the easy cases lets us assume that our class of methods is general enough to be applicable to all the instances of Lennard-Jones, or other similar potential minimization problems.

2 Two phase forward procedure

So called forward procedures are well known in the context of potential energy minimization. They rely on the fact that in many cases, given an optimal configuration for N atoms, the optimum configuration for $N+1$ has the same geometric structure. Of course, even if this is true in some cases, the assertion is false in particular for difficult configurations, which are indeed "difficult" because their structure impredictably changed when passing from N to $N+1$. The idea of forward methods is the following: given an optimum configuration of N atoms, a new atom is randomly placed in $\mathbb{R}^3$; the resulting cluster of $N+1$ atoms is then optimized. Optimization, in the literature, is either performed in two stages, first letting only the newly added atom vary and then re-optimizing the whole cluster ($3(N+1)$ variables). In our approach we decided to eliminate the first stage and to consider, from the start, all of the coordinates of the $N+1$ atoms as variables. However the local optimization procedure adopted was the two-phase method, with penalty terms added. In order to be able to obtain an optimum configuration it was observed that a beneficial effect could be obtained by "expanding" the N atom cluster prior to optimization. This was performed by centering the cluster at its center of mass and then multiplying each coordinate by a quantity greater than 1. In the experiments we introduced also a deformation by using a multiplier randomly generated between 1 and 1.3.

As the optimization in a forward method is generally quite fast, we decided to use a standard local optimization method interfaced to AMPL to perform our experiments.

The following is the AMPL source for the Lennard-Jones and the modified potential function:

```
param semilato;
```

```
param xopt {1..n};
param yopt {1..n};
param zopt {1..n};

param p;

param lowx {1..n} <= 0,default -semilato;
param hix {1..n} >= 0, default semilato;
param lowy {1..n} <= 0, default -semilato;
param hiy {1..n} >= 0, default semilato;
param lowz {1..n} <= 0, default -semilato;
param hiz {1..n} >= 0, default semilato;

param maxiter;
param mu >0;
param beta;
param R;
param alpha >0;

var x {i in 1..n} >= lowx[i], <= hix[i];
var y {i in 1..n} >= lowy[i], <= hiy[i];
var z {i in 1..n} >= lowz[i], <= hiz[i];
var dist3{i in 1..n, j in 1..n: j < i};
var dist2{i in 1..n, j in 1..n: j < i};
var dist1{i in 1..n, j in 1..n: j < i};

minimize lennard:
sum {i in 1..n} sum {j in 1..n: j < i}
        (1./dist3[i,j] - 2.)/dist3[i,j];

minimize lennard2:
sum {i in 1..n} sum {j in 1..n : j < i}
    ((1./dist2[i,j]^(p*0.5)-2.)/dist2[i,j]^(p*0.5)+mu*(dist1[i,j])
  + beta*max(0,dist2[i,j]-R*R)^2.);

s.t. defdist{i in 1..n, j in 1..n: j < i}:
     dist3[i,j] =
     ((x[i] - x[j])^2. +  (y[i] - y[j])^2. + (z[i] - z[j])^2.)^3.;

s.t. defdist1{i in 1..n, j in 1..n: j < i}:
```

```
     dist1[i,j] =
     sqrt((x[i] - x[j])^2. +  (y[i] - y[j])^2. + (z[i] - z[j])^2.);

s.t. defdist2{i in 1..n, j in 1..n: j < i}:
     dist2[i,j] =
     (x[i] - x[j])^2. +  (y[i] - y[j])^2. + (z[i] - z[j])^2.;
```

Here the objective `lennard` is the standard Lennard-Jones potential, while `lennard2` contains the definition of the modified potential. In order to run the forward procedure, the following command file was used:

```
option display_precision 20;
option display_width 100;
option display1_col 0;
option substout 1;

model lj.mod;

option solver lancelot;
let semilato := 4;
let p := 6.;
let mu :=  0.1 ;
let beta := 0;
let R := 0.;

param ottimoglobale;

let ottimoglobale := 0;

param nprove;

param xstart {1..n};
param ystart {1..n};
param zstart {1..n};
param barx;
param bary;
param barz;
param lowU;
param hiU;
let lowU := 1.0;
let hiU := 1.3;
```

```
data iniz.dat;

let barx := sum{i in 1..n-1} xstart[i]/(n-1);
let bary := sum{i in 1..n-1} ystart[i]/(n-1);
let barz := sum{i in 1..n-1} zstart[i]/(n-1);

let nprove := 0;

repeat while nprove < 20{
let nprove := nprove + 1;
display nprove;
let {i in 1..n-1} x[i] :=
   (xstart[i]-barx)*Uniform(lowU,hiU);
let {i in 1..n-1} y[i] :=
   (ystart[i]-bary)*Uniform(lowU,hiU);
let {i in 1..n-1} z[i] :=
   (zstart[i]-barz)*Uniform(lowU,hiU);

let x[n] := Uniform(-semilato,semilato);
let y[n] := Uniform(-semilato,semilato);
let z[n] := Uniform(-semilato,semilato);

###############
# PHASE I     #
###############

objective lennard2;
solve;
display lennard, lennard2;

###############
# PHASE II    #
###############

objective lennard;
solve;
display lennard, lennard2;

printf "n %d nprove %d lennard %30.25lg p %lg mu
%lg esp %f %f beta %f D %f\n", n, nprove, lennard,p,mu,lowU,hiU,beta,R ;
```

```
if (ottimoglobale > lennard) then {

display x,y,z > opt.dat;

let {i in 1..n} xopt[i] := x[i];
let {i in 1..n} yopt[i] := y[i];
let {i in 1..n} zopt[i] := z[i];

let ottimoglobale := lennard;
}

display lennard, ottimoglobale;
}

let {i in 1..n} xstart[i] := xopt[i];
let {i in 1..n} ystart[i] := yopt[i];
let {i in 1..n} zstart[i] := zopt[i];
printf "param " > iniz.dat;
display xstart, ystart, zstart >> iniz.dat;
display ottimoglobale;
```

This procedure performs 20 runs each of which consists in using as the starting configuration the coordinates contained in the file `iniz.dat`, adding a single molecule, displacing each atom by a random amount from the barycenter, and then optimizing using a two phase approach.

Using the modified potential function with $\mu = 0.1$ and $p = 6$, with no diameter penalization, we obtained the following success rate in 120 independent tests (where the column "succ" contains the number of runs which led to to global optimum configuration in 120 experiments and % contains the success rate):

N	succ.	%
61	4	3.33%
62	0	0.00%
63	8	6.67%
64	9	7.50%
65	0	0.00%
66	0	0.00%
67	3	2.50%
68	0	0.00%
69	0	0.00%
70	5	4.17%
71	3	2.50%
72	16	13.33%
73	0	0.00%
74	8	6.67%
75	0	0.00%
76	28	23.33%
77	2	1.67%
78	0	0.00%
79	4	3.33%
80	13	10.83%

It can be seen that some of the easy cases could be found with relatively small computational effort using this forward procedure.

3 Correction procedure

It can be seen that some cases which the standard two phase method could not discover are still lacking after running the forward method: we refer in particular to $N = 62, 65, 66, 68, 73, 78$. For these cases, and others, we tried with success the following correction procedure: after the two phase optimization, a correction procedure was adopted with success. The following AMPL commands report the core of the procedure:

```
fix x;
fix y;
fix z;

for {i in due} {
  unfix x[i];
  unfix y[i];
```

```
  unfix z[i];
};

objective lennard1;

solve;

unfix x;
unfix y;
unfix z;
for {i in 1..n} {
   let x[i] := x[i]*1.1;
   let y[i] := y[i]*1.1;
   let z[i] := z[i]*1.1;
};
objective lennard2;
solve;

objective lennard;
solve;
```

Here it is seen that a small subset of atoms is first considered as variable: this subset actually consists of a random pair of atoms chosen at random among the 20 atoms whose contribution to the total potential energy is maximum. Here the contribution of an atom to the potential is defined as

$$E_j(X) == \sum_{i \neq j} v\left(\|X_i - X_j\|\right) \tag{6}$$

and it is easily seen that

$$E(X) = 0.5 \sum_j E_j(X).$$

After randomly displacing two of the worst atoms, a phase I optimization, with modified potential function, was carried out; from the optimum configuration found, which corresponds to a very easy local optimization in only 6 variables, all of the coordinates where considered as variables and, after a slight expansion of 10% around the center of mass was imposed, again a complete two phase optimization was performed.

With this correction procedure all of the lacking configurations where successfully located in extremely short computational time

Conclusions

In this report we have shown how a standard two-phase method has been modified in order to be able to obtain a set of tools which are capable of discovering any known global optimum Lennard Jones cluster in the range $N \leq 80$. Indeed we extended our computations up to and found many optimal configurations also for larger clusters.

As a conclusion it can be safely stated that, in order to discover globally optimal Lennard-Jones clusters for a particular number N of atoms, the following approach could be adopted:

1. First, if available, start from the best known cluster of $N - 1$ atoms and apply the two-phase forward procedure;

2. then perform a few experiments with the correction method, randomly displacing two of the worst atoms and reoptimizing; if the forward procedure could not be used, the correction method could be applied to some of the best clusters obtained in the following point 3:

3. perform a standard Multistart-like two phase optimization, both with and without penalization terms on the diameter.

References

[1] J. P. K. Doye, *The physics of global optimization of atomic clusters*, in Selected Case Studies in Global Optimization, J. D. Pinter, ed., Kluwer, Dordrecht, 2000, p. in press.

[2] M. Locatelli and F. Schoen, *Fast global optimization of difficult lennard-jones clusters*, Computational Optimization and Applications, 21 (2002), pp. 55–70.