Rules for the formation of initial approximations of the conformation of Morse atomic clusters on the basis of a geometrically grounded method

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Abstract. The paper presents a new method for the formation of initial approximations of Morse atomic clusters for the most complicated case, when the cluster stiffness is 14. The problem of structural optimization of conformations of Morse atomic clusters is stated. An algorithm for the structural optimization of the Morse atomic cluster is developed, which significantly reduces the algorithmic complexity of the problem being solved.

1. Introduction

Atomic or molecular clusters consist of a set of particles and may have new, completely different physical properties compared to a single molecule or bulk matter. The evaluation of their most important properties is used in many areas, ranging from protein structure prediction to studying the influence of stratospheric clouds on the ozone layer depletion. Moreover, the proper understanding of cluster properties has a tremendous value for nanotechnology.

Currently, there are no direct experimental methods that can identify the structure of free clusters by using molecular beams. The typical way is to evaluate the parameters that depend on the structure of an object, and to use the models with the predicted preferred geometries. The interactions between the particles that make up the cluster can be described by a multi-dimensional function denoted as a potential energy surface. It is essential to know it for the theoretical study of the cluster properties [1].

The energy of the Morse clusters is derived by summing up the Morse potentials describing all the pair interactions that occur in the cluster in their entirety [2], while the chemical bond between the atoms is neglected:

\[ v(r_{ij}) = \alpha(1 - e^{-\rho r_{ij}})(e^{\rho r_{ij}} - 2), \]

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \); \( \rho \) is the parameter that extends or narrows the potential “well” of pair interactions between the atoms in the Morse cluster [3]. Typically, \( \rho \) ranges from 3 to 14.

The interaction energy of all atoms in the cluster can be calculated as the sum of energies in pair interactions

\[ v(X) = \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1, j \neq i}^{m} v(r_{ij}), \]

where \( X = (x_1, ..., x_m)^T, \quad x_i \in \mathbb{R}^3 \) are the coordinates of atom centres in the cluster.
In the overwhelming number of papers devoted to this topic, the problem of finding optimal conformations in atomic clusters is associated with the global optimization (GO) of the potential function (2).

Currently, the GO tasks are used in many application fields of mathematics, computer science, physics, biology, chemistry and allied sciences. Recently researchers pay a special attention to the molecular conformation problems [4, 5, 6].

However, the problem of finding the optimal atomic cluster that corresponds to the lowest potential binding energy turned out to be an NP-hard problem [7], since the resulting objective function obtained by summing the energies of pair interactions is a nonconvex multimodal function of spatial coordinates of many atoms.

Naturally, the problem of global optimization of the potential function, which depends on a large number of variables, is the main difficulty in forming the optimal conformations of atomic clusters. Theoretical studies of global optimization methods do not presume that there may exist any practically beneficial direct GO methods for the functions with a number of variables greater than 30 [8]. Consequently, the existing practice of finding the optimal conformations is based on using stochastic algorithms for global optimization. The success in their application is explained by the use of a large number of heuristics on the properties of the object of study. At present, globally optimal conformations of Morse clusters have been constructed up to the clusters that contain 240 atoms [9]. However, the construction of large-size atomic Morse clusters (N>240) still presents serious difficulties due to significant computational costs.

This article deals with forming globally optimal conformations of large size atomic Morse clusters (N>240). The proposed approaches are based on searching for the rational heuristics to form the initial approximations of atomic Morse clusters and using the local methods to optimize the functions with a large number of variables.

2. Statement of the structural optimization problem

Various optimization methods are currently used to find the conformations that provide a global minimum of cluster energy. In one way or another, those methods use additional information on the properties of an atomic cluster. For example, it was observed that in Morse clusters the lattices, where the atoms are located in the conformation, tend to the symmetric spherical forms [10]. When applied, this information led to creating the geometric methods for global optimization of Morse clusters. The idea to consider the cluster's geometric structural properties to minimize its potential energy was often treated with distrust, but researchers repeatedly returned to it later on [5, 11, 12]. For example, icosahedral, decahedral or face-centred cubic structures were used as the cores of the initial cluster conformations in paper [11].

In this paper, we deal the most complex statement of the problem of finding optimal configurations in the Morse cluster: when \( \rho = 14 \) and the atoms can only touch each other. In such case, the problem of forming the atomic clusters with the minimal potential energy is actually associated with the close-packing of spheres [13]. It is assumed that the spherical shape of the conformation and the closer "packing" of atoms are the most important factors for the clusters.

For "rigid" spheres the closest packing is achieved in the face-centred cubic lattice. In this case, the spheres fill a little more than 74% of the space [14]. At the same time, for the "soft" atoms of the Morse cluster, where atoms can partially "squeeze" into each other, denser packages are formed in icosahedral and dodecahedral lattices [3, 11, 15, 16]. Work [17] based on the analysis of the globally optimal conformations of Morse clusters for \( \rho = 14 \), as presented in database [9], showed that it is always possible to find such a position of an axis, such as \( z \), when the atoms in the cluster will be located in layers, forming a fuzzy layered structure (table 1). In this case the expression "fuzzy" layer refers to such an arrangement of a group of atoms (spheres) that their centres are not on a plane, but in a sufficiently "thin" layer \( z_j \pm \Delta z_j \). The table shows that the conformations of the next generation clusters "inherit" the geometry of their predecessors. Thus, the cores in clusters N=196 and N=200 (like in the
other clusters with the number of atoms ranging from 193 to 199) coincide with the core of the symmetric icosahedron $N=192$. Changes occur only on the outer shells of the clusters.

However, at certain moments qualitative changes occur in the geometric structure of globally optimal conformations. Table 1 shows that a displaced icosahedral structure becomes optimal for $N=201$. In work [9] such a structure is referred to as "close-packed". However, in this case we may also observe the inheritance of parental properties in the descendants with a large number of atoms.

| Table 1. Layers of globally optimal Morse clusters $\rho = 14$. |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Layer       | $N=192$     | $N=196$     | $N=200$     | $N=201$     | $N=203$     | $N=209$     |
| 1           |             |             |             |             |             |             |
| 2           |             |             |             |             |             |             |
| 3           |             |             |             |             |             |             |
| 4           |             |             |             |             |             |             |
| 5           |             |             |             |             |             |             |
| 6           |             |             |             |             |             |             |
| 7           |             |             |             |             |             |             |
| 8           |             |             |             |             |             |             |
| 9           |             |             |             |             |             |             |
| 10          |             |             |             |             |             |             |
| 11          |             |             |             |             |             |             |
In certain cases, another kind of transformation of the cluster conformation may occur, when all atoms are located in the nodes of a face-centred grid. For example, the latter is true for the clusters with \( N = 38, 39, 40 \) and \( N = 223, 234, 235 \).

The analysis of the published globally optimal conformations of the atomic Morse clusters [9] shows that the choice of the optimal arrangements of the cluster atoms is made from a limited area of the compact arrangement of atoms in the icosahedral lattice (figure 1). Some of the atoms that form the group (the cluster core) are contained in all globally optimal clusters of the icosahedral type.

![Figure 1. Icosahedral lattice.](image)

In order to narrow the search area for the initial conformations of the cluster, we propose to select a group of atoms, "cutting" them out of the icosahedral lattice in regular geometric shapes, for example, as a cylinder. It is easy to predict the size of the cylinder, knowing the size of the cluster being formed. It is important that a sufficient number of atoms fits into the cylinder dimensions with a small reserve. In that case, the cylinder axis should be aligned with the icosahedral lattice axis in icosahedral clusters, while in close-packed clusters the cylinder axis is displaced (figure 1).

Let us introduce the set \( X_{seq} = \{X_1, X_2, \ldots, X_M\} \) - a subset of the icosahedral lattice, in which a globally optimal cluster conformation is being sought. Let \( X_{cor} = \{\tilde{X}_{i_1}, \tilde{X}_{i_2}, \ldots, \tilde{X}_{i_k}\} \) be the core of the cluster, i.e. the group of atoms that are unconditionally included in the globally optimal conformation (\( \forall k \tilde{X}_k \in X_{seq}, k = 1, \ldots M \)).

Let us define a subset of the set \( X_{seq} \) of free vertices \( X_{var} = X_{seq} \setminus X_{cor} \), in which the optimal conformation is being sought (with \( X_{seq} \) being its unchangeable part). Let us build graph \( G \) for \( X_{seq} \), taking into account the interconnectivity of atoms. This can be done by constructing the incidence matrix of graph \( G \) as follows:

\[
A_{seq} = \begin{cases} a_{ij} & i, j = 1, \ldots, M; \\
1 & \text{если} \ |X_i - X_j| \leq r_{min}, \\
0 & \text{иначе} \end{cases}
\]

(3)
where \( r_{\text{min}} \) is the minimal distance between the atoms that fixes their bond. The incidence matrix (3) actually defines the search graph \( G(X_{\text{seq}}, U, A_{\text{seq}}) \). Let us introduce the subgraph \( H(X', U', A') \subset G \) of graph \( G \), such that \( |X'| = N \), i.e. the number of vertices of the graph is equal to the size of the optimized conformation.

It is obvious that the number of such graphs in the set \( X_{\text{seq}} \) will be large, but enumerable. Let us denote them as \( H_\alpha \subset G \). Let us define the function \( \varphi(H_\alpha) \) for choosing the rational subgraph. The function will determine the utility of a given cluster configuration (subgraph). We may use the potential energy of pair interactions between atoms (2) or the sum of the degrees of the subgraph's vertices as such function.

\[
\varphi_1(H_\alpha) = \sum_{X' \in X'} \deg(X'_i)
\]

(4)

In such case, the structural optimization problem may be stated as follows:

\[
\min \left( \max \right) \varphi(H_\alpha) \quad \text{subject to} \quad \left| X' \right| = N
\]

(5)

Problem (5) belongs to the category of global optimization problems, but it has less complexity in comparison with the GO function problem (2), since it contains fewer optimized parameters (proportional to \( |X_{\text{var}}| \)) and is a discrete rather than a parametric optimization problem. In principle, for small cluster sizes problem (5) can be solved by using brute-force algorithms.

### 3. Stochastic algorithm for constructing the initial conformations of Morse clusters

The idea of the proposed algorithm (Table 2) is quite simple. It has been implemented in some way in the deterministic heuristic algorithm (DHA) described in [18]. The optimal conformation of the cluster is constructed by sequentially attaching atoms at rational positions to the previous configuration of the cluster. However, there are significant differences between the DHA and the proposed approach. In the new variant, the placement of atoms is not arbitrary, depending on the geometric configuration of the cluster. They are placed in the previously known spots of the icosahedral lattice, which guarantees a close packing of the Morse cluster atoms. In this case, the core of the cluster, i.e. the group of atoms contained in all globally optimal conformations of a certain series of sizes, acts as a kind of "ferment" for the conformation. Given the geometric relationships described in graph \( G \), the core determines the shape of the rational conformation, and problem (5) becomes an optimization problem on graphs that allows polynomial complexity algorithms. Let us examine that in more detail.

Since the "ferment" largely determines the "appearance" of the cluster's rational configuration, let us introduce some set of vertices out of the randomly generated \( X_{\text{var}} \). Let \( X_{\text{rnd}} = \{X_1, X_2, \ldots, X_r\} \) \( X_{\text{rnd}} \subset X_{\text{var}} \). Let us assume that

\[
X_{\text{var}}^{(1)} = X_{\text{var}}^{(0)} \setminus X_{\text{rnd}},
\]

\[
X_{\text{cor}}^{(1)} = X_{\text{cor}}^{(0)} \setminus X_{\text{rnd}},
\]

(6)

(7)

where \( X_{\text{var}}^{(0)} = X_{\text{var}}, \ X_{\text{cor}}^{(0)} = X_{\text{cor}} \).

| Table 2. Structural optimization algorithm. |
|--------------------------------------------|
| **Step 1. Preliminary operations:**        |
| - Calculating the incidence matrix \( A_{\text{seq}} \); |
| - Playing out the elements of the set \( X_{\text{rnd}} \); |
| - Initial settings: \( X_{\text{var}}^{(0)} = X_{\text{var}}^{(0)} \setminus X_{\text{rnd}} \) and \( X_{\text{cor}}^{(0)} = X_{\text{cor}}^{(0)} \setminus X_{\text{rnd}} \). |
Step 2. For each atom \(X_{\text{var}}^j \in X_{\text{var}}\) the value of the \(z_j = \varphi_1(X_{\text{var}}^j)\) criterion is calculated using the matrix \(A_{\text{seq}}\). The set of atoms \(X_{\text{var}}\) is ordered by the value of the \(z_j\) criterion in the descending order of \((z_1, ..., z_{m_{\text{var}}}) = \text{sort}(z_1, ..., z_{m_{\text{var}}})\).

Step 3. We consider the subset \(X_{\text{opt}} = \{X_{\text{var}}^j | z_j = z_1^j\}\) of the set \(X_{\text{var}}\); the subset forms the perspective conformations, if the corresponding atom is added to the core of the cluster \(X_{\text{cor}}^{(1)}\). If \([X_{\text{opt}}] = 1\), then the set \(X_{\text{opt}}\) is extended by the elements \(X_{\text{opt}} = \{X_{\text{var}}^j | z_j = z_2^j\}\).

Step 4. For each atom \(X_{\text{opt}}^j\) in the set \(X_{\text{opt}}\), the potential energy values of the clusters \(X_{\text{opt}}^j = X_{\text{opt}}^j \cap X_{\text{cor}} \ (X_{\text{opt}}^j \in X_{\text{opt}})\) are calculated as follows: \(v(X_{\text{opt}}^j)\). In addition, for each atom, the possible potential "contribution" of the atom is calculated, taking into account its short bonds, in the set \(X_{\text{seq}}\):
\[
\sum_{j=1}^{M} v(r_{jj})
\]
Step 5. In order to select the rational atom from the set \(X_{\text{opt}}\), a vector-valued objective function is formed with two components \(y_j = (v(X_{\text{opt}}^j), v(X_{\text{opt}}^j))\). The first component of the vector \(y_j\) directly estimates the efficiency of the cluster with the attached vertex \(X_{\text{opt}}^j\). The smaller \(v(X_{\text{opt}}^j)\), the better. However, it is often more useful to attach not the best vertex in the current iteration, but the vertex with a large number of connections to free vertices in the hope of getting more benefit in the future. The indicator \(v_2(X_{\text{opt}}^j)\) is applied for that purpose.

Step 6. A Pareto optimal set \([20]\) \(X_{\text{par}} \subset X_{\text{opt}}\) is constructed on the set \(X_{\text{opt}}\). If \([X_{\text{par}}] = 1\), then that is the desired "rational" atom \(X^* = X_{\text{par}}^k\). If not, the solution \(X^*\) is chosen randomly from the elements of the set \(X_{\text{par}}\).

Step 7. The core of the cluster is extended by one atom: \(X_{\text{cor}}^{(k)} = X_{\text{cor}}^{(k-1)} \cup X^*\) and the set \(X_{\text{var}}^{(k)} = X_{\text{var}}^{(k-1)} \setminus X^*\) is simultaneously reduced.

Step 8. If \([X_{\text{cor}}^{(k)}] < N\), then go to the next iteration (step 2), else complete construction of the optimal conformation.

The criterion \(\varphi_1(H_{\alpha})\) (4) turns out to be useful at the initial stage of the algorithm, to establish the search area of the most "successful" atom to be included into the cluster. The total degree of the subgraph determines the number of short bonds between the atoms, and the bigger is \(\varphi_1(H_{\alpha})\), the higher is the potential binding energy of atoms. It is natural to choose the cluster conformation among the variants with the highest values of this criterion. There is no difficulty in calculating the criterion \(\varphi_1(H_{\alpha})\) by using the previously established incidence matrix \(A_{\text{seq}}\).

In the proposed approach the globally optimal conformation is found due to a random enumeration of components in the set \(X_{\text{ind}}\) that determines the geometric shape of the initial optimal conformation.
of the Morse cluster, which is then completed to the desired size using the cluster optimization algorithm.

The cluster optimization algorithm described above has the polynomial complexity that can be estimated as \( O(N) \approx \frac{1}{4}(N-L-r-1)^2 \approx N^2 \). The stochastic Monte Carlo method of forming the set \( X_{\text{rand}} \) has a higher complexity. Given the full search, we have the exponential complexity \( O_1(N) \approx \frac{(M-L-r)!}{(r!(M-L)!)}. \)

However, the probability that a combination of atoms belonging to the globally optimal conformation may be chosen randomly is not too small.

\[
\Pr(N) = \sum_{j=0}^{L} \frac{N-L+j}{M-L-j}
\]

Besides, we can expect a relatively fast result, when randomly searching the globally optimal conformation of the Morse cluster by using the stochastic algorithm together with the structural optimization algorithm. In any case, the stochastic optimization algorithm is easily parallelized.

The proposed stochastic and structural optimization algorithms, when used jointly, allow us to form the geometric "appearance" of the initial conformation of the Morse cluster. The resulting intermediate product is processed further by means of the local optimization methods, and as a result, we get the final version of the Morse cluster. This strategy referred to as the local technique has been successfully used in many global optimization algorithms, including both exact methods \[19\] and the Morse clusters optimization methods.

4. Computational experiments
The efficiency of the proposed method for searching the globally optimal conformations of Morse atomic clusters for the most complex case \( \rho = 14 \) was verified on the known clusters of large sizes \( N = 210 \) and 211 from the database \[11\]. The proposed algorithms found the globally optimal conformations with the 210K and 211G codes with the potential binding energies \( v_{210K} = -994.8091 \) and \( v_{211G} = -1000.7765 \), respectively. The clusters with the potential energy values close to optimal \( v_{211F} = -1000.7757 \) and \( v_{211H} = -999.6763 \) were confirmed for a group of clusters of \( N = 211 \). Moreover, the test found the conformations, which have not been published in the database: their potential energy levels were comparable with the optimal values of \( v_{211-I} = -998.8049 \) and \( v_{211-II} = -997.8472 \). The experiments showed that the proposed method for the formation of globally optimal conformations of Morse atomic clusters generates a large number of geometric structures that are comparable in efficiency to the globally optimal variant.

5. Conclusion
In this paper, we present a new method for constructing the initial approximations of Morse atomic clusters in the most complicated case, when \( \rho = 14 \). The proposed approach applies the classical ideas of the Monte Carlo method, which is often used to address the increasing complexity of a problem. However, in this case the proposed cluster optimization algorithm disposes of a significant number of issues relating to the complexity of the problem being solved. It should be noted that the capacities of a modern personal computer proved to be sufficient for solving the task to construct globally optimal Morse clusters of sizes \( N = 210 \) and 211.

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