Optimization of molecular clusters configurations using a Genetic Algorithm

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Abstract. We present a genetic algorithm developed (GA) to optimize molecular \( \text{AF}_6 \) cluster configurations with respect to their energy. The method is based on the Darwin’s evolutionary theory: structures with lowest energies survive in a system of fixed number of clusters. Two existing structures from a given population are combined in a special way to produce a new structure (child) which is kept if its energy is lower than the highest energy in the ensemble. To keep the population constant we reject the structure with the highest energy. This algorithm gives a better result than the optimization techniques used previously. Using the GA we have found a new structure corresponding to the (seemingly) global minimum. The most important result is that the new structure is detected only if the molecular cluster contains more than a critical number of molecules.

1. Introduction

Optimized structures give a detailed information about symmetry, phase transitions and we also can use them to calculate density of states of the studied substance. Every optimization algorithm tries to find the configuration with the lowest energy. Usually it minimizes the potential energy performing consecutive steps from one to another configuration by inspecting the local minima on the potential energy surface (PES). Molecular clusters made of octahedral molecules \( (\text{AF}_6, A = S, Se, Te, U) \) have rugged potential energy surface \( \mathbb{1} \). Attempts to use simulating annealing \( \mathbb{2} \) to find the global energy minimum in the systems often fail due to high-energy barriers (Fig. 7 in \( \mathbb{3} \)), which trap the simulated system in one of the innumerable metastable configurations. A cartoon can be seen in Fig. \( \mathbb{4} \). On such a surface, techniques like simulated annealing, quenching \( \mathbb{5} \), or the conjugate gradient method find the local ”global” (glocal) minimum, which might lie higher than the true global minimum if it is located in another basin \( \mathbb{6} \). Hence we need an algorithm, which would permit “jumps” from one basin to another and sample properly the phase space. Various techniques of global optimization have been proposed: basin hopping \( \mathbb{7} \), genetic algorithm \( \mathbb{8} \), adiabatic switching \( \mathbb{9} \).

In the present work we further elaborate GA originally developed of Deaven and Ho for atomic systems in order to make it applicable to molecular clusters. We implement the new algorithm for configuration optimization of \( \text{AF}_6 \) clusters, simulated with molecular dynamics \( \mathbb{10} \). A new structure has been found that has never been seen in our previous investigations \( \mathbb{11}, \mathbb{12} \).

2. A genetic algorithm for molecular clusters

In this section we describe our genetic algorithm in detail. Each molecule is defined with a pair of coordinates \( \{x, q\} = \vec{X}, x = \{x, y, z\} \) is the Cartesian coordinate of molecular center of mass, \( q = \{x, y, z\} \).
\{q_0, q_1, q_2, q_3\} is molecular orientation in quaternion representation. We denote a cluster configuration with \( N \) molecules with:

\[ \mathcal{G} = \{X_1, X_2, ..., X_N\} \]

The genetic algorithm uses a population of \( n \) structures \( \{\mathcal{G}\} \), \( n \) is kept constant during the optimization run. We define a mapping operator \( P : P(\mathcal{G}, \mathcal{G}') \rightarrow \mathcal{G}'' \), which performs the following action upon two parent geometries \( \mathcal{G} \) and \( \mathcal{G}' \) to produce a child \( \mathcal{G}'' \).

First we select parents from the population using the distribution Eqn. (1). Second, we choose planes that account for the parent clusters packing symmetry and pass through the center of mass of the parents. Then we cut the clusters in the chosen planes. We would like to underline that the choice of cutting planes is crucial for the proper work of the algorithm. In other words, it is very important to find out the packing symmetry of all clusters in the populations.

In the case of solid molecular clusters at a low temperature, the centers of the molecules hardly move but their orientations do. Hence, in the present version of Genetic Algorithm, we match centers of the parent clusters before searching for a suitable plane. After cutting the parents, we assemble the child \( \mathcal{G}'' \) from the molecules of \( \mathcal{G} \) which lie above the plane and the molecules of \( \mathcal{G}' \) which lie below the plane. If the child generated in this manner does not contain the correct number of molecules, we translate the plane until the child \( \mathcal{G}'' \) contains the correct number of molecules. Relaxation to the nearest local minimum is performed with a conjugate gradient minimization [3, 4].

We preferentially select parents with a lower energy from \( \{\mathcal{G}\} \). The probability \( p(\mathcal{G}) \) of an individual candidate \( \mathcal{G} \) to be selecting for mating is given by the Boltzmann distribution.

\[
p(\mathcal{G}) \propto \exp[-E(\mathcal{G})/K_bT_m] \tag{1}
\]

where \( E(\mathcal{G}) \) is the energy of the candidate \( \mathcal{G} \), \( K_b \) is the Boltzmann constant and \( T_m \) is the mating "temperature", chosen to be roughly equal to the range of energies in \( \{\mathcal{G}\} \). For a better performance we can apply mutations to some members (\( \mu \)) of the population. The mutation operator is defined as \( M : M(\mathcal{G}) \rightarrow \mathcal{G}' \) which performs two random actions with the same probability. First, \( M \) moves the coordinates of mass centers in a random direction with a random step. Second, \( M \) rotates the chosen molecule at a random angle. Such mutation can be applied to some molecules in a cluster \( \mathcal{G} \) or to all of them.

We create subsequent generations as follows. Parents are continuously chosen from \( \{\mathcal{G}\} \) with a probability given by Eqn. (1) and mated using the mating procedure described above. The fraction \( \mu \) of the children generated in this way are mutated; \( \mu = 0 \) means no mutation occurs. The (possibly mutated) child is relaxed to the nearest local minimum and replaced with a configuration with a higher energy in population \( \{\mathcal{G}\} \) if its energy is lower than the higher energy. This algorithm requires a great number of members \( (n) \) in the population in order to prevent a rapid convergence to a set of identical candidates.

3. Results for TeF\(_6\) clusters

To illustrate the method, we used configurations for TeF\(_6\) clusters obtained in MD simulations described elsewhere [5].
Figure 2. A population of $n=100$ clusters each containing 89 $TeF_6$ molecules finds the configuration with the lowest energy about 160 iteration steps. Fig. 2 shows the minimum energy found in an optimization of $n=100$ configurations (starting population) of 89-molecule $TeF_6$ clusters. During the first 100 iterations, the algorithm effectively and rapidly creates better children. Then the process is slowed after the 100th step. An important comment is that we start with a population of structures already optimized with conjugate gradient or simulated annealing methods. We underline that both techniques give the same optimized structures.

In the case of 89 and 137 $TeF_6$ clusters we have found a new local minimum on the PES which corresponds to quite a different structure with respect to the orientational order. Fig. 3 represents these orientational structures produced with two different minimization algorithms, e.g. the conjugate gradient and genetic algorithm.

We have found that in the case of $TeF_6$ clusters with 27 and 59 molecules such an orientation distribution can not be found as it is seen in Fig. 4. This is a pronounced size effect. For the case of 89 $TeF_6$ clusters we perform a sequential molecular dynamic run to check if this new structure is stable. Starting from a low temperature $\approx 0.5$ K, we increased the temperature up to 30 K and the structure is still stable.

4. Conclusion

Although the topography of the studied PES is very complicated, the newly developed algorithm has shown a great ability to find the "glocal" minimum. Mutations often boost this ability but in some cases
it becomes worst. One can optimize the mutation parameters (percentage of mutated-cluster, mutation operator $M$, etc.) to obtain better results [10]. Finally, we have found that the genetic algorithm can used to "clean" defects in structures optimized with techniques. For instance, the free molecular clusters have many surface molecules oriented improperly in comparison to the others even in the lowest energy configuration found with any other method. Such a procedure (cleaning) is very important if the density of states is needed. The general shortcoming of the method is its slowness, which makes its application limited.

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Density [a.u.] vs. \cos(\theta)
Potential energy

Configuration space
Density [a.u.] vs. \( \cos(\theta) \)
