Using Ant Colony Optimization to Find Low Energy Atomic Cluster Structures

Phillip Tomson
Dept. of Electrical & Computer Engineering
Portland State University
Portland, OR 97207
philtomson@gmail.com

Garrison W. Greenwood
Dept. of Electrical & Computer Engineering
Portland State University
Portland, OR 97207
greenwd@ece.pdx.edu

Abstract- Over the past 20 years atomic cluster structures have been intensively studied because of their importance in physics, chemistry and recently material science. Unfortunately finding the lowest energy structure, which is the most stable configuration, is NP-hard. In this paper we present preliminary results on an ant colony optimization algorithm used in conjunction with a Monte Carlo sampling method to find low energy configurations of small silicon atomic clusters.

1 Introduction

Atomic clusters are aggregates of atoms held together by the same forces that cause, for example, phase transition from vapor to liquid, formations of crystals, and so on. Cluster sizes range from as few as three atoms to more than several hundred atoms. In bulk material physical properties exist independent in size, but as things become sufficiently small, size does matter. The physical and chemical characteristics of a cluster often varies with its size. Indeed, even the addition of a single atom can result in an entirely different structure. How large does a cluster have to grow before the bulk properties prevail? At present this question remains unanswered.

Atomic clusters have been studied for some time, but the emergence of the nanotechnology field in recent years has made cluster research especially important. One of the most exciting research areas involves the role clusters play in the design of nano-scale systems. For example, researchers recently discovered 20-atom gold clusters have large energy gaps [1]. This means large amounts of energy are needed to induce any chemical reactions with them. Since the gold clusters are chemically inert, they could be used as insulators—even though bulk gold is an excellent electrical conductor! Moreover, their inertness suggests a potential use as a building block for new materials.

In this work we are interested in the cluster conformation (i.e., the 3-D structure) which is intimately related to the chemical and physical properties of the clusters. Among all possible atomic arrangements, the conformation with the greatest stability is the most important. The stability of any cluster conformation is determined, in part, by the total energy of the cluster. By exploiting the Born-Oppenheimer approximation [2], one can express the total energy of an atomic cluster as a function of the positions of the individual atoms[1]. That is,

$$E = E(\mathbf{r}_1, \ldots, \mathbf{r}_N) \qquad (1)$$

where E is the total energy, N is the number of atoms in the cluster, and $\mathbf{r}_i$ is the position of the i-th atom. Since the total energy is invariant with respect to the overall translation and rotation of the whole cluster, the total number of degrees of freedom is $3N - 6$.

The energy required to dissociate a conformation into isolated atoms is called the clusters *binding energy.* A lower total energy value corresponds to a higher binding energy magnitude. Consequently, conformations with minimum total energy are the most stable[2]. The problem of finding this minimum energy structure is therefore equivalent to optimizing E with respect to variations in all $3N - 6$ degrees of freedom. Our object is then to solve the following optimization problem:

> *Given an atomic cluster of N atoms which are subject to two-body central forces, find the conformation in 3-D Euclidean space that has the minimum total energy.*

One method of solving this optimization problem is to explore the potential energy surface (PES) composed of all possible cluster conformations. Unfortunately, as the cluster size increases, so does the number of degrees of freedom in the placement of the atoms. This characteristic produces a PES where the number of local optima grows exponentially with the cluster size [3]. Determining the ground-state energy level, which is the most energetically stable level, is extremely difficult. Wille and Vennik [4] proved this problem is NP-hard for homonuclear clusters (i.e., clusters with only one type of atom) and Greenwood [5] later proved

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[1] The Born-Oppenheimer approximation says atomic nuclei are stationary with respect to the electrons because they are so much heavier than the electrons are. Consequently, electron-nucleus interactions can ignore nuclei movements and need only consider potential energies.

[2] Stability is with respect to the internal energy of the cluster. Free energy is not considered in this paper.

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the same thing for heteronuclear clusters. Hence, heuristic search techniques are the only viable alternative.

Genetic algorithms (GAs) have been used to search for low energy cluster structures. The most comprehensive work in this area was conducted by Wolf and Landman where the GA searched for optimal structures in clusters with up to 100 atoms [6]. They modified the GA in special ways to improve its search capability. For instance, they added twinning mutations and seeded the population with structural motifs. Unfortunately, these modifications aren't universal because the PES topology depends on the potential energy function that was selected. Hence, the optimized GA proposed by Wolf and Landman—which was designed for a Lennard-Jones potential energy function—is not widely usable. Every time the energy function is changed, the GA must be re-optimized.

In this paper we describe a new search method that uses *ant colony optimization* (ACO) in conjunction with Monte Carlo sampling. What makes our method especially appealing is the search method is universal—i.e., no fine-tuning is needed if the energy function is changed. To our knowledge ACO has never been used for atomic cluster studies. Our preliminary results suggest ACO, augmented with Monte Carlo sampling, is a powerful combination capable of producing excellent results.

The paper is organized as follows. An overview of atomic clusters is provided in Section 2. Section 3 reviews the ACO approach and shows how it is used to search for low energy conformations. Section 4 presents some experiments conducted with small clusters of silicon atoms. Finally, Section 5 discuss some future work.

2 Homonuclear Clusters and Potential Energy Functions

The objective is to find the lowest energy conformation because it is the most stable conformation. But, how exactly does one quantify the energy of a conformation? In principle, one may obtain the total energy of a cluster in a given conformation using the most accurate *ab initio* methods. (*ab initio* calculations do not rely on experimental data. All calculations involve the electronic Hamiltonian used in Schrödenger's equation.) The methods required by these methods, however, scale typically as the 4th power of the number of electrons. They are therefore impractical even for a single large cluster conformation evaluation let alone global optimization. Practical alternatives to *ab initio* methods include density functional methods and simple force fields derived from fitting analytical function to empirical and/or *ab initio* data. In this work, we present preliminary results using the latter approach for the potential energy functions. In particular, we approximate the total energy as the sum of all the pairwise interactions between atoms:

$$E = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(\mathbf{r}_{ij}) \tag{2}$$

where $\mathbf{r}_{ij}$ is the Euclidean distance between atoms i and j, and $v(\mathbf{r}_{ij})$ is the pairwise potential energy function. Such approximations are adequate when quantum effects and many-body effects are negligible.

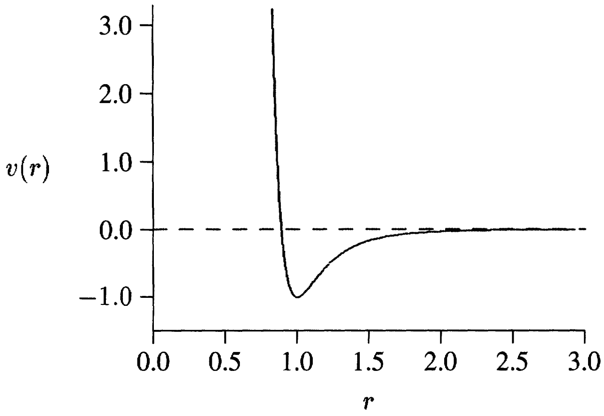

Figure 1: The scaled Lennard-Jones potential function.

A commonly used pairwise potential energy function for (1) is the scaled Lennard-Jones potential function

$$v(\mathbf{r}_{ij}) = \left(\frac{1}{\mathbf{r}_{ij}}\right)^{12} - 2\left(\frac{1}{\mathbf{r}_{ij}}\right)^{6} \tag{3}$$

The first term in (3) accounts for the repulsion between atoms and is the dominant interaction when atoms are only a short distance apart. The second term represents the attractive component between neutral atoms and this component dominates as the distance increases. This function is scaled in the sense that the globally potential energy level $v(\mathbf{r}_O) = -1.$ occurs with a bond distance of $\mathbf{r}_O = 1.$ Figure 1 shows this pairwise potential function.

Having defined a pairwise potential energy function one can now construct cluster conformations and compute their energy level using (3). Table 1 gives the globally minimum total energy conformations for small clusters using the scaled Lennard-Jones potential energy function.

3 Using ACO in Cluster Searches

3.1 ACO Overview

Ants are social insects with behaviors oriented towards the good of the colony they live in. Of particular interest is the way they forage for food. Ants keep track of the path

N	Conformation
2	linear chain separated by 1 unit
3	equilateral triangle each side 1 unit
4	tetrahedron, each side one unit
5	triangular bipyramid, slightly contracted along the symmetry and distended in the symmetry plane
6	regular octahedron with slightly contracted sides

Table 1: Optimal conformations for small clusters [7].

```
Initialize pheromone levels on each edge
while(termination condition not met)
    position each ant on a different node
    do
        each ant incrementally applies a state transition rule
            to construct a tour.
        Update pheromones on visited edges using a local
            update rule.
    until (all ants construct a tour)
    Update pheromones using a global updating rule
end while
```

Figure 2: Basic ACO algorithm for solving TSP instances.

from a colony to a food source by depositing a chemical *pheromone* on the trail. Other ants can detect this chemical and the stronger the concentration the more favorable the trail. Over time the shortest path will tend to have the strongest pheromone concentration.

Ant algorithms use multiple agents to search for the solution to difficult combinatorial optimization problems. (See [8] for a good introduction.) They conduct this search by emulating a colony of ants. Each agent represents an ant that explores the edges of a graph, thereby incrementally constructing a solution to the optimization problem. As the ant moves throughout the graph it deposits artificial pheromones on graph edges that are part of good solutions. Other agents can read these pheromone values. Hence, agents communicate with each other using a form of distributed memory. Ant algorithms are particularly well suited for optimization problems that involve paths in graphs such as routing in communications networks, vehicle routing and the well-known Traveling Salesman Problem (TSP).

The ACO algorithm does differ in several respects from real ants [8]:

- Ants are artificial agents that transition from one discrete state to another discrete state.
- Ants have an internal state that records previous movements.
- Ants deposit an amount of pheromone which reflects a solution's quality.
- Artificial ants can exhibit behaviors (such as backtracking) which real ants don't do.

The basic ACO algorithm is shown in Figure 2.

During each iteration of the ACO algorithm an ant moves across some edge to a new node. Let $\tau_{ij}(t)$ be the amount of pheromone on edge (i, j) of the graph at time t. (The more there is, the more favorable the edge.) As soon as an ant traverses an edge, the pheromone level is updated as follows

$$\tau_{ij}(t+1) \;=\; (1-\rho)\cdot\tau_{ij}(t)+\rho\cdot\tau_0 \qquad (4)$$

where ρ is a user-defined constant, and τ_0 is the initial pheromone level. ρ determines the pheromone evaporation level. We used $\rho = 0.1$ and $\tau_0 \approx 10^{-6}$.

After N iterations the ant will find a tour of length N. At that time the following global update rule is applied

$$\tau_{ij}(t+N) \;=\; (1-\alpha)\cdot\tau_{ij}(t)+\alpha\cdot\triangle\tau \qquad (5)$$

where α is a user-defined constant, and $\mathcal{E}$ is the total energy of the cluster

$$\triangle\tau \;=\; \begin{cases} \frac{1}{\mathcal{E}} & \text{if edge is in tour} \\ 0 & \text{otherwise} \end{cases}$$

The probability that an ant k on atom r will choose to move to atom s is given by a *random proportional rule*:

$$p_k(r,s) = \begin{cases} \dfrac{[\tau(r,s)]\cdot[\eta(r,s)]^{\beta}}{\sum_{u\in J_k(r)}[\tau(r,u)]\cdot[\eta(r,u)]^{\beta}} & \text{if } s\in J_k(r) \\ 0 & \text{otherwise} \end{cases} \qquad (6)$$

where τ is the pheromone level, $\eta = 1/((r)_{rs}+\varepsilon)$ with $\varepsilon = 1.000001$ to keep the denominator from going to zero. (Recall the Lennard-Jones energy function has a minimum value of -1.) $(r)_{rs}$ is the pairwise energy between atoms r and s computed using (3). $J_k(r)$ is the set of atoms that remain to be visited by ant k positioned on atom r. β is a user-defined positive parameter which determines the relative importance between the pheromone level and the energy level.

An ant located on atom r chooses the atom s to move to by applying a state transition rule given by

$$s = \begin{cases} \arg\max_{u \in J_k(r)} \{[\tau(r,s)] \cdot [\eta(r,s)]^{\beta}\} & \text{if } q \leq q_0 \\ \text{S} & \text{otherwise} \end{cases} \tag{7}$$

where q is a random number uniformly distributed between 0 and 1, q_0 is a constant ($0 \leq q_0 \leq 1$), S is a random variable selected according to the probability distribution given in (6).

The state transition rule given by (6) and (7) is a *pseudo-random proportional rule*. This rule tends to move atoms closer just like the random proportional rule does. Before choosing an atom to move to, the ant samples a random number q from the unit interval and compares it to a user defined constant q_0. This constant allows the user to trade-off exploitation and exploration. That is, as $q_0 \to 1$, the ant favors moving to an atom that lowers the energy. Conversely, as $q_0 \to 0$ lower energy moves are abandoned in favor of doing more exploration. If $q \leq q_0$, then (7) governs the ant's movement; otherwise, (6) is used.

3.2 Cluster Searching

Before the ants begin foraging the atoms must be placed in 3-D space. We used a Monte Carlo method where a large number of atoms are randomly scattered. The number of atoms should be at least $10N$ for a cluster of size N. The ants were then randomly placed on atoms. An ant must now visit exactly $N-1$ other atoms to complete a tour of length N. This process is shown in Figure 3 where two tours of length 4 are shown. Notice how the tour creates a cluster structure.

The Euclidean distance between two atoms in the tour is plugged into (3) to get the pairwise potential energy. The total energy for the entire cluster is found by summing the individual pairwise energies. After one interaction is complete the best (i.e., lowest energy) tour is kept and the remaining atoms are again randomly scattered in 3-D space. Another iteration is then run. This process continues until the termination criteria is met.

Finally, the Monte Carlo sampling we used in our experiments randomly distributed atoms uniformally around the origin. This is not a requirement. Indeed, if some knowledge about the atomic cluster structure is known *a priori*, the distribution can be modified accordingly. This should help control the number of iterations.

4 Experimental Results

Initially we randomly placed 100 atoms in a 3 dimensional space sized $10 \times 10 \times 10$. The optimal energy 7-atom cluster was then embedded among the randomly placed atoms in order to determine how well the algorithm would do at finding the embedded cluster. Ten ants were then randomly placed at random atom locations within the 3D space in each generation. Each run went for 20 generations. In eight of the ten runs the ants found the optimal configuration. (In the other two runs low energy configurations were found, but not the optimal one.) This performance is rather remarkable considering the ants have $\binom{100}{7}$ possible configurations to chose from. It also shows the efficacy of our approach. Figure 5 shows the optimal structure for the 7-atom Si cluster using the Lennard-Jones potential energy function[3]. This structure has an energy of -16.4353 eV.

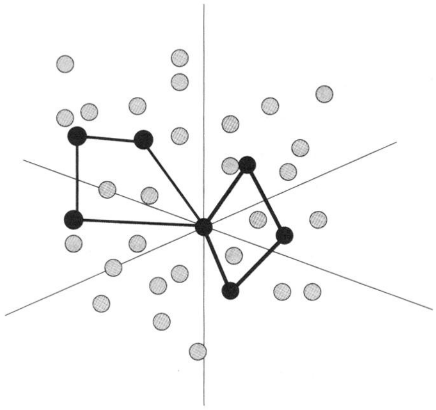

Figure 3: A Monte Carlo technique is used to position atoms in 3D space. Two tours of length 4 are highlighted. Each tour creates a 4-atom cluster. An atom may be in more than one tour.

The next experiment duplicates the first except that the known optimal energy cluster was not embedded with the randomly placed atoms. The best (lowest energy 7-atom cluster) found in five runs of the program had a cluster energy of -8.45925 eV, which is considerably higher than the optimal value. We attempted to improve on this result by "relaxing" the structure.

Relaxation refers to perturbing the final best structure to achieve a lower energy value. Once found, this perturbed structure replaces the old one, which is analogous to Lamarkian optimization sometimes used in GAs. Molecular dynamics (MD) is a common relaxation method. In this method each atom is treated as a point mass and simple Newtonian force equations simulate their interactions. Another method is gradient search that looks for low spots in the PES surface. Both of these methods are not trivial to implement, so we devised our own simple method, which uses simple hill-climbing in each dimension. Our relaxation method is shown in Figure 4.

Unfortunately, after relaxation the energy only reduced

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[3] All cluster graphics in the paper are produced by the RasMol software. See http://www.umass.edu/microbio/rasmol/ for further information.

```
Let $\delta r = 0.01$
foreach atom in cluster
    foreach dimension $(x, y, z)$
        $E_c$ = cluster energy
        $e1$ = cluster energy at atom location - $\delta r$
        $e2$= cluster energy at atom location + $\delta r$
        if ($e1 == \min(e1, e2, E_c)$)
            move atom to current location - $\delta r$
        else
        {
            if ($e2 == \min(e1, e2, E_c)$)
            move atom to current location + $\delta r$
        }
        else
            $E_c$ is best, so do nothing
        end if
    end foreach
end foreach
```

Figure 4: A simple relaxation routine. δr is a small constant used to perturb an atom's location in 3D-space.

slightly to -8.47173 eV. Obviously a more sophisticated method such as MD is needed. However, instead of taking that approach something simpler was tried first—and the improvement was surprizing. We simply increased the number of random atoms, which should improve the likelihood of optimally placing a subset of atoms. After randomly placed 1000 atoms in the $10 \times 10 \times 10$ 3D space the ant algorithm was re-run (but without using any relaxation). The result in this case was a cluster with an energy of -11.51—over a 26% improvement. This cluster is shown in Figure 6.

At first glance there is a noticeable difference between the optimal structure in Figure 5 and Figure 6, but a closer looks shows they are actually quite similar. If the far left atom in Figure 6 is rotated upwards it becomes planer with four other atoms. RasMol doesn't instantiate edges (representing chemical bonds) unless the atoms are within a certain minimum distance. After rotation this atom would be close enough to form a chemical bond between it and the upper, lower, and front atoms. If the far right atom is moved slightly inward, shortening the bond length with the front atom, this should put it within close proximity to the upper and lower atoms, which will add the two missing edges. (Silicon has a valence of 4, so these bonds form naturally.) A good relaxation method would identify these preferred atom positions.

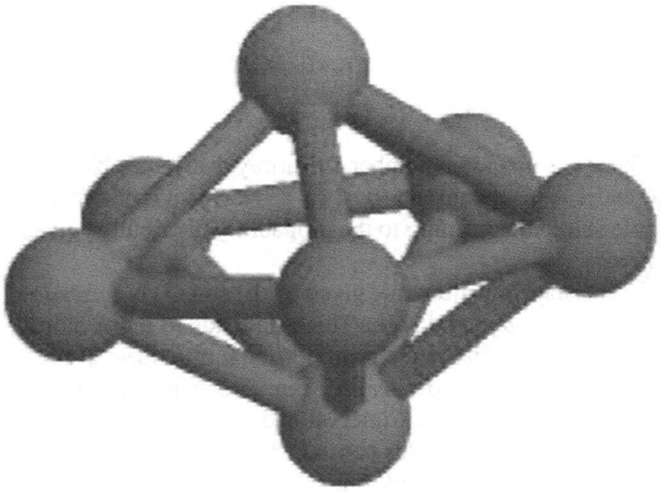

Figure 5: Optimal 7-atom Si structure for the Lennard-Jones potential energy. The spheres represent atoms and the edges represent chemical bonds.

5 Future Work

Algorithms that emulate what nature does have a real potential for finding good solutions to the clustering problem. Unfortunately, these algorithms perform a macro-search, making it difficult to find the lowest energy configuration in a highly multimodal PES. In all circumstances the algorithm must be augmented with some sort of relaxation in order to find really good low energy structures [9]. Our ACO algorithm is no exception. We intend to try a more sophisticated relaxation method. The bound constrained method proposed by Byrd et al. [10] is a good first choice because of its wide acceptance for these type of problems.

The Lennard-Jones PES is a generic energy function suitable for any type of atomic cluster (even heteronuclear ones.) There are PES designed specifically for Si atom clusters such as the Stillinger-Weber potential [11], which is designed to produce a diamond shape for solid-state silicon. We decided not to use these in a preliminary study because the Lennard-Jones energy function is trivial to incorporate while the 3-body potentials are not. (The Stillinger-Weber potential function requires angular information between atom triplets.) Of course now that we have shown what ACO can do, moving to a more sophisticated potential function is a logic next step.

It is worth repeating that switching from one potential function to a different one does not require any retuning of the ACO algorithm, but it will require retuning a GA. Each potential energy function creates a different PES topology. GAs must be re-optimized each time a change is made be-

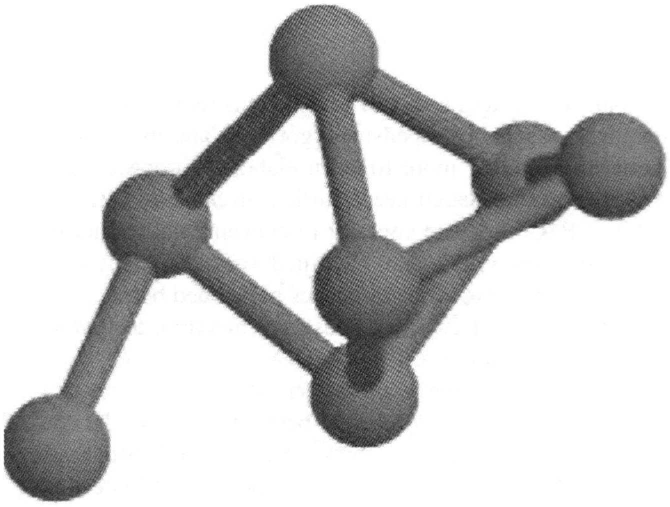

Figure 6: 7-atom Si structure for the Lennard-Jones potential energy found from a random placement of 1000 atoms (see text).

cause reproduction operators that work for one PES topology may not work well in another. Hence, our ACO method is better suited for finding homonuclear or heteronuclear atomic structures—especially when more than one potential function is likely to be used.

Bibliography

[1] J. Li, X. Li, H. Zhai, and L. Wang. Au_{20}: a tetrahedral cluster. *Science*, 299:864–867, 2003.

[2] M. Born and R. Oppenheimer. Zur quantentheorie der molekeln. *Ann. Physik*, 84:457–484, 1927.

[3] R. Berry. Potential surfaces and dynamics: what clusters tell us. *Chem. Rev.*, 93:2379–2394, 1993.

[4] L. Wille and J. Vennik. Computational complexity of the ground-state determination of atomic clusters. *J. Phys. A*, 18:L419–L422, 1985.

[5] G. Greenwood. Revisiting the complexity of finding globally minimum energy configurations in atomic clusters. *Z. Phys. Chem.*, 211:105–114, 1999.

[6] M. Wolf and U. Landman. Genetic algorithms for structural cluster optimization. *J. Phys. Chem. A*, 102:6129–6137, 1998.

[7] W. Pullan. Energy minimization of mixed argon-xenon microclusters using a genetic algorithm. *J. Comput. Chem.*, 18:1096–1111, 1997.

[8] M. Dorigo, G. Di Caro, and L. Gambardella. Ant algorithms for discrete optimization. *Artificial Life*, 5(2):137–172, 1999.

[9] J. Zhao and R. Xie. Genetic algorithms for the geometry optimization of atomic and molecular clusters. *J. Theo. Nanosci.*, 1:117–131, 2004.

[10] R. Byrd, P. Lu, and J. Nocedal. A limited memory algorithm for bound constrainded optimization. *SIAM J. Sci. & Stat. Comp.*, 16(5):1190–1208, 1995.

[11] F. Stillinger and T. Weber. Computer simulation of local order in condensed phases of silicon. *Phys. Rev. B*, 31:5262–5268, 1985.