Cluster Energy Optimizing Genetic Algorithm

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ABSTRACT

Nanoclusters are small clumps of atoms of one or several materials. A cluster possesses a unique set of material properties depending on its configuration (i.e. the number of atoms, their types, and their exact relative positioning). Finding and subsequently testing these configurations is of great interest to physicists in search of new advantageous material properties. To facilitate the discovery of ideal cluster configurations, we propose the Cluster Energy Optimizing GA (CEO-GA), which combines the strengths of Johnston's BCGA [18], Pereira's H-C&S crossover [25], and two new mutation operators: Local Spherical and Center of Mass Spherical. The advantage of CEO-GA is its ability to evolve optimally stable clusters (those with lowest potential energy) without relying on local optimization methods, as do other commonly used cluster evolving GAs, such as BCGA.

Categories and Subject Descriptors

I.2.1 [**Artificial Intelligence**]: Applications and Expert Systems—*medicine and science*; J.2 [**Computer Applications**]: Physical Sciences and Engineering—*physics*

General Terms

Algorithms, design, performance, experimentation.

Keywords

Cluster energy optimization, Gupta potential, genetic algorithm, nanocluster, CEO-GA, global minimization

1. INTRODUCTION

In this paper, we introduce the Cluster Energy Optimization Genetic Algorithm (CEO-GA) derived from the Birmingham Cluster Genetic Algorithm (BCGA) [18]. The CEO-GA uses H-C&S crossover [25], atom permutation mutation, and incorporates two new operators: the Local Spherical mutation (Local-S) and the Center of Mass Spherical mutation (CoM-S). The CEO-GA, while not itself depending on local minimization like its predecessors, achieves results comparable to those previously obtained only via combining a GA with local optimization techniques.

Bulk solids typically have a periodic arrangement of atoms (unless they are amorphous), with well defined separations between the atoms (lattice constant) and characteristic geometry. For example, bulk Gold (Au) and Copper (Cu) are members of the so-called face-centered-cubic crystals. The percentage of atoms on the surface of a bulk material is negligible in relation to the total number of atoms in the bulk. Nanoclusters, on the other hand, are clusters of a few to a few hundred atoms that can be either homogeneous (composed entirely of atoms of a single material) or heterogeneous(containing atoms of two or more materials). A nanocluster is a unit in itself and decomposing it would alter its physical properties, effectively transforming it into several different clusters. The atoms on the surface of a nanocluster (which are responsible for any interactions with the environment) constitute a considerable percentage of the total cluster size. Since these surface atoms have lost some neighbors, they are under-coordinated and thus may serve as active sites for chemical reactions. Examples of Au, Cu, and Au-Cu nanoclusters are shown in figure 1.

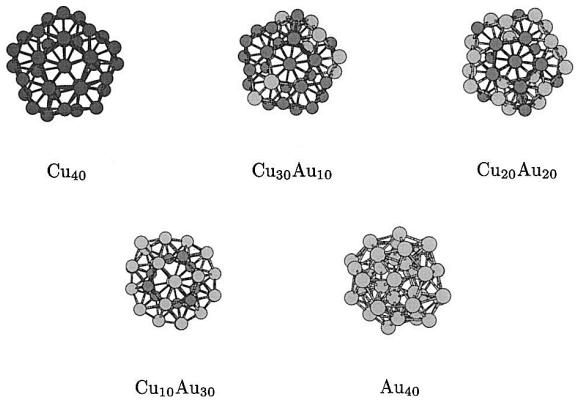


Figure 1: Examples of Au, Cu, and Au-Cu clusters. Dark and light sphere represent Cu and Au atoms, respectively.[1]

GECCO'13, July 6–10, 2013, Amsterdam, The Netherlands.

[1]Reprinted with permission from S. Darby, T. V. Mortimer-Jones, R. L. Johnson, and C. Roberts. Theoretical study of Cu-Au nanoalloy clusters using a genetic algorithm. *Journal of Chemical Physics*, 116(4):1536-1550, 2002. Copyright 2013, American Institute of Physics.

Materials science, which investigates the relation between the structure of a material and its physical properties, has in the past mostly dealt with bulk materials. Recent efforts have, however, turned to nanomaterials, which offer promising novel properties that could lead to technological advances such as stronger and lighter metals, self purifying liquids, or new catalysts. The variety of properties of metallic clusters can be drastically expanded through the creation of nanoalloy clusters, i.e. those formed by two or more metals [18]. One of the most interesting aspects of nanoalloys is the way their physical and chemical properties can be altered through varying the types of atoms in the cluster, their ordering, and their number [7]. Additionally, nanoalloys offer the opportunity to test properties of the combination of certain elements that are immiscible when combined in bulk [1].

So how do these special nanostructures behave? In order to answer this question we must first discover the most stable geometric configuration of atoms for a cluster of a specific size and composition. Clusters whose total energy corresponds to the global minimum for the given cluster composition (number and types of atoms) are more likely to be formed during a cluster experiment [12]. Once the optimal cluster has been evolved, we must construct this structure in a wet lab (by placing atoms onto a substrate, following the desired configuration). Finally, we must test the obtained structure so as to learn about its physical properties. In this paper we focus on the first step of this process, i.e. finding the exact relative atom locations for clusters with the lowest potential energy, given a specific number of atoms and their types. Starting with a search space of all possible cluster geometries, we use a GA to find those with minimal potential energy as calculated by the Gupta potential [5]. The Gupta potential has been previously shown to provide reasonably accurate results when assessing nanocluster energy [7], and thus has become a widely used heuristic employed to avoid computationally intensive ab initio calculations.

One of the difficulties with discovering lowest energy nanoclusters is the existence of "homotops", i.e. clusters that, despite being composed of the same number and types of atoms, and having identical cluster geometries, display different properties due to their atoms being arranged differently within said geometries [15]. Consequently, and although some research has been previously conducted through time consuming ab initio calculations [16], the majority of nanocluster formation research uses heuristics, such as genetic algorithms (GAs).

A GA will search for the optimum configuration of a cluster, given the desired composition (i.e. the number and types of atoms in the cluster), guided by an approximation of the interatomic interaction potential of each candidate cluster-configuration [18]. Examples of such interaction potentials are the Gupta potential ([5], [2], [21]) and the Lennard-Jones potential ([8], [12],[25]). Additionally, an energy-optimizing GA is generally combined with a local minimization method, such as the quasi-Newtonian conjugate gradient minimization L-BFGS (Limited-memory Broyden-Fletcher-Goldfarb-Shanno) [20].

Current cluster optimizing GAs rely heavily on local optimization techniques, being unable to successfully evolve low energy clusters when used without them. The purpose of a local optimization is to get from the current position to the nearest local optima. However, if diversity in the population is not maintained, a GA will be unable to continue exploring the search space for potentially better solutions, effectively getting stuck. The BCGA, proposed by Johnston [18], uses high selection pressure, causing the entire population to converge within a few generations, thus decreasing the chance of finding global optima.

In this work, the BCGA is stripped of its external local minimization procedure, L-BFGS [20], and subsequently augmented with a version of Deaven and Ho's C&S crossover developed by Pereira [25]: the H-C&S crossover. Additionally, the CEO-GA ensures population diversity by decreasing selection pressure, and incorporates two new mutation operators: Local-S mutation and CoM-S mutation. These improvements allow the CEO-GA to evolve clusters with energy values comparable to those obtained by the BCGA as reported by Darby et al. [7]. This represents a large improvement over the performance of cluster energy optimizing GAs without local optimization, as the CEO-GA is able to evolve the optimal known structures without local minimization (which may endanger the diversity of structures examined during the search process).

2. BACKGROUND

Below we review the history of cluster evolving GAs in general, as well as discuss the direct predecessor of the proposed CEO-GA: Johnston's BCGA [18]. In addition, we describe in detail Pereira's H-C&S crossover [25] and the Gupta many-body potential [5], both used in the CEO-GA.

2.1 History of cluster evolving methods

As the cluster size increases linearly, the number of minima increases exponentially. Ab initio methods for calculations of total energy, such as those based on density functional theory (DFT) [19], become increasingly computationally demanding. Approaches such as the Monte Carlo methods and Simulated Annealing for molecular dynamics have trouble finding global minima for certain types of interatomic interactions [23]. Random search algorithms also struggle to find the optimum even after thousands of searches [28]. As an alternative approach to cluster optimization, researchers have been turning to GAs, which have generally been able to evolve optimal clusters after a relatively small number of energy evaluations and local optimizations [28].

Hartke [11] and, independently, Xiao and Williams [31] conducted the first attempts to use GAs for the optimization of cluster geometries. The devised GAs used a binary encoding with corresponding genetic operators that modify the binary strings that represent each candidate cluster configuration. Zeiri improved this approach through the use of real-valued Cartesian coordinates to represent the location of each atom in the cluster [32]. Deaven and Ho further improved GA cluster optimization by using a gradient driven local minimization to optimize each configuration discovered by the GA during its run [8]. Yet another significant step pioneered by Deaven and Ho was to improve the crossover genetic operator by crossing the parents' phenotypes (the physical three dimensional cluster) instead of their genotypes (a string of Cartesian coordinates) [8]. The reason this change was so significant (leading them to discover numerous new minima [8]) is due to the fact that in 3D space, a section of the cluster would contain only neighboring atoms. In a string of numbers, consecutive coordinates do not neces-

sarily correspond to nearby atoms, and thus cutting a piece of such string would likely not correspond to cutting a continuous section of the cluster, thus leading to a less principled crossover recombination. Deaven and Ho's crossover is often referred to as "Cut and Splice" (C&S) [26] or "Cut and Paste" [13].

The BCGA is a well known and widely used cluster-optimizing GA designed by Johnston [18]. The BCGA has been used to optimize clusters of different types and sizes, and has been combined with different energy optimization methods over the years ([17], [24], [13], [14], [9], [4], [30], [6]). When it comes to bimetallic clusters, the lack of atom relocating mutations in the BCGA causes it to rely heavily on the L-BFGS local minimization procedure [20] to find the lowest energy clusters. The CEO-GA proposed in this paper (and detailed in section 3) borrows BCGA's atom permutation mutation [18], cluster energy calculation (Gupta potential), dynamic energy scaling (equation 4), and exponential fitness function (equation 5), while excluding BCGA's local optimization procedure (L-BFGS), and incorporating two new mutations operators (Local-S and CoM-S).

2.2 Gen-C&S and H-C&S crossovers

In the aforementioned Deaven and Ho's C&S, given two parent clusters, two random planes are chosen, each passing through the center of mass of one of the parents, and the clusters are split in half. A child is generated by combining the top half of one parent with the bottom half of the other. If the resulting child does not have the correct number of atoms, the parent clusters are translated by the same amount in opposite directions, perpendicular to their cutting plane, and splicing is repeated [8]. The BCGA uses a variation of C&S, where each parent cluster is randomly rotated about two perpendicular axis before being cut by a horizontal plane, and subsequently spliced to form a child cluster [18].

In 2008, Pereira proposed a modified version of C&S [8], named the Generalized Cut and Splice (Gen-C&S) crossover [26], and showed it to outperform the C&S when tested on a steady-state GA evolving Morse clusters [27]. Pereira also successfully applied this crossover to a generational GA [26]. The main advantage of Gen-C&S is that it removes an artificial constraint imposed by C&S: the cutting plane creates an arbitrary division between atoms, such that an atom that is further from some other atom might be grouped with it during crossover because a closer atom ended up on the opposite side of the dividing plane. Additionally, Gen-C&S does not require rotating the parents prior to crossover.

In Gen-C&S crossover for two clusters (P1 and P2) of size μ, a cut point (CP) is chosen as one of the atom locations in P1. A random number S (between 1 and $\mu - 1$) is chosen, and the S atoms in P1 closest to CP are copied into a child cluster. Then, the remaining $\mu - S$ atoms are copied into that child from P2, starting with those closest to CP. After all atoms in P2 have been considered for inclusion, if the child cluster still has less than μ atoms, it is completed with randomly placed atoms. For a graphic depiction of this operator, please refer to [26].

To adapt the Gen-C&S to bi-metallic clusters, Pereira devised the H-C&S crossover and used it to evolve Binary Lennard-Jones clusters [25]. H-C&S behaves almost identically to Gen-C&S with one distinction: after copying the first S atoms from P1, an atom from P2 is copied only if the child cluster still requires atoms of that type, thus maintaining the desired cluster composition [25].

Parameter	Cu-Cu	Cu-Au	Au-Au
A	0.0855	0.1539	0.2061
p	10.960	11.050	10.229
r_0	2.556	2.556	2.884
ζ	1.2240	1.5605	1.7900
q	2.2780	3.0475	4.0360

Table 1: Gupta potential parameters for Cu-Au clusters.

The minimum allowed inter-atomic distance is half of the ideal distance as defined by the r_0 Gupta potential value, provided in section 2.3. If any two atoms are much closer than their ideal distance, the potential repulsive energy becomes too large [27], which confounds the evolutionary process. Thus no atoms closer than $0.5 * r_0$ to any other atom already in the cluster can become part of said cluster. H-C&S crossover observes this rule when creating a child cluster, only allowing new atoms into the cluster if their location is further than $0.5 * r_0$ away from every atom already in the cluster [27].

2.3 Gupta Potential

As mentioned earlier, the Gupta many-body potential [5] is a widely used heuristic for modeling the inter-atomic interactions within a cluster and for calculating its potential energy in order to avoid the computationally expensive ab initio calculations. The Gupta parameters are strictly dependent on the types of atoms composing the cluster, and are derived empirically based on the second moment approximation to tight-binding theory [24].

The Gupta potential energy of a cluster, designated as (V_{clus}), is composed of a repulsive (V^r) and an attractive (V^m) terms, which are obtained via summing over the interactions of each pair of atoms in the cluster, as defined in equations 1, 2, and 3.

$$V_{clus} = \sum_{i}^{N} \{V^r(i) - V^m(i)\}, \tag{1}$$

$$V^r(i) = \sum_{j}^{N}{}' A(a,b) exp\left(-p(a,b)\left(\frac{r_{ij}}{r_0(a,b)} - 1\right)\right) \tag{2}$$

$$V^m(i) = \left[\sum_{j}^{N}{}' \zeta^2(a,b) exp\left(-2q(a,b)\left(\frac{r_{ij}}{r_0(a,b)} - 1\right)\right)\right]^{1/2} \tag{3}$$

$\sum'$ in equations 2 and 3 indicates that the summation is to be performed over all atoms j, except for $j = i$ [7] i and j are atoms and a and b are their types. N is the number of atoms in the cluster. The values of the Gupta parameters A, p, r_0, ζ, and q used in this work were obtained from [5], and are listed in table 1. Thus $A(Cu, Au)$, for example, is the value of the Gupta parameter A for the interaction between an atom of Copper and another of Gold, as experimentally fitted for the reference bulk structure.

3. CLUSTER ENERGY OPTIMIZING GENETIC ALGORITHM (CEO-GA)

The CEO-GA is derived from the BCGA, which (in conjunction with other techniques) has proven capable of correctly discovering previously known optimal energy configurations [18]. The CEO-GA makes use of the successful genetic operators present in the BCGA, while also improving upon some of BCGA's shortcomings. We aim to increase the efficacy of the underlying GA itself so as to decrease its dependence on potentially detrimental local optimization techniques.

The CEO-GA is a $(\mu + \lambda)$ generational GA, in which a population of μ parents generate λ children, which (alongside their parents) become candidates for the next generation. Only parent clusters are eligible for mutation. Newly generated offspring do not get mutated, thus allowing the GA to assess clusters generated by crossover before further alternation. Once all the candidate clusters are collected, the next population is chosen via modified roulette-wheel selection [10]: a cluster is chosen at random and accepted for mating if its dynamically scaled fitness (see equations 4 and 5 in section 3) is greater than a randomly generated value between 0 and 1. The same method is also used selecting parents for CEO-GA's H-C&S crossover [25]. The CEO-GA explicitly incorporates elitism by copying the best two candidate clusters into the next generation.

The bounding box is the legal area that atoms can occupy, i.e. any time an atom location is randomly generated, the new coordinate values are chosen between 0 and length of the box edge. Following Johnston's and Darby's work [7][18], for a cluster of N atoms, each edge of the bounding box is set to be $N^{1/3}$ scaled by the ideal distance between two atoms (Gupta Parameter r_0), ensuring that the volume of the box increases linearly with cluster size. Bimetallic clusters usually have three different values for r_0, one per each type of interaction (e.g. Cu-Cu, Cu-Au, Au-Au). Consequently, the bounding box in this work is set to $0.05N^{1/3} * largestR_0$, where $largestR_0$ is the maximum ideal distance between two atoms of the present types. In Cu-Au clusters, that distance is the r_0 between two atoms of Gold and is equal to 2.884 (view table 1). Following Pereira's work [27], all atoms in the first generation are ensured to be at least $0.5 * r_0$ away from each other. This rule is also observed when filling a cluster with random atom locations after an incomplete H-C&S crossover operation.

The CEO-GA uses a modified atom permutation mutation [18], which has been shown to lead to a higher chance of finding the global minimum and to increase the reproducibility of the obtained results [18]. The atom permutation mutation consists of swapping the types of one or more pairs of atoms. In CEO-GA, the number of atom-type swaps per mutated cluster corresponds to 20% of the cluster size, instead of BCGA's 30%. This change results in a more gradual evolution, allowing the GA to assess the value of smaller changes one at a time.

Additionally, the CEO-GA incorporates two new mutation operators inspired by the spherical nature of nanoalloy clusters: the Center of Mass Spherical mutation (CoM-S) and the Local Spherical mutation (Local-S).

1. The **Center of Mass Spherical mutation** (**CoM-S**) is designed to quicken the search for optimum configurations by rotating an atom about the cluster's center of mass (CoM). The CoM is calculated as the weighted sum of its atoms' coordinates, divided by the total mass of the cluster[2]. The vector from the CoM to the atom is calculated and converted to spherical coordinates (ρ, θ, ϕ)[3]. The distance between the atom and the CoM is preserved by keeping ρ constant, while selecting some combination of θ and ϕ angles to rotate the atom about the CoM. Once the new angles are obtained, the vector $(\rho, \theta_{new}, \phi_{new})$ is converted to its Cartesian equivalent and added to the CoM location. The atom is then relocated to this new position.

2. The **Local Spherical mutation** (**Local-S**) is designed to make small changes to the locations of 10% of a cluster's atoms. A small vector of spherical coordinates (ρ, θ, ϕ) is created, and its Cartesian equivalent is added to the current location of an atom. Angle θ can take on any value in the range of $0° - 180°$, ϕ can be $0° - 360°$, while distance ρ is the absolute of a random value obtained from a Gaussian distribution with a mean of 0 and a standard deviation equal to 5% of the side of the bounding box.

Given the spherical and fairly tight nature of Cu-Au cluster geometries (as can be seen in figure 1), ensuring that the "greater than $0.5 * r_0$" rule is observed can be difficult. A GA could get stuck repeatedly selecting new random coordinates, as most locations would be disqualified for being too close to pre-existing cluster atoms. To avoid re-selecting indefinitely, for a cluster of N atoms, we cap the number of tries at $N * 10$ per each newly generated location. Once the maximum tries have been exhausted, a Local-S mutation is repeatedly performed on each new atom that is too close to atoms already in the cluster, until the minimum distance is satisfied. Note that while the Local-S mutation uses the bounding box to calculate the increment ρ, it does not itself obey the boundaries of said box in order to quicken compliance with the minimum distance rule. Thus, the resulting atom coordinates may place the atom outside of $[0, N^{1/3} * largestR_0]$ range.

The CEO-GA mutation rates are as follows: for any given cluster of size N, an atom permutation mutation has a 10% chance to occur, in which case $0.2 * N$ label swaps are performed. The CoM-S mutation also has a 10% chance to occur, and causes each of the atoms to have a 10% chance to rotate about the CoM. The Local-S mutation has a 20% chance to happen, producing a 10% chance to cause a small spherical permutation of the location of each of the atoms in the cluster. A cluster can be mutated by all or none of these mutations. When a mutation does occur, each operator produces a separate mutant cluster, which becomes one of the candidates for the next generation. This ensures that the GA will be able to assess potential benefits of each mutation individually.

An optional cluster relocation mechanism was designed for the CEO-GA, such that the entire cluster is re-centered around the origin, i.e. the CoM of the cluster ends up at

[2]The atomic mass of Cu is 63.546, and the atomic mass of Au is 196.96655.

[3]In this paper, spherical coordinates (ρ, θ, ϕ) are used as is customary in the physics field: ρ indicates radial distance, θ indicates polar angle, and ϕ indicates azimuthal angle.

(0,0,0). While the mechanism did not provide any advantage for the tested clusters, it could be beneficial for more sparse cluster geometries that require more spacious bounding boxes. Re-clustering around the origin would ensure that atoms from parent clusters are combined in a principled and correlated manner during crossover.

Energy (V_{clus}) is calculated using the Gupta potential [5] as detailed in section 2.3. Energy is scaled dynamically according to equation 4, where ρ_i is the scaled energy of a cluster i, V_{min} is the lowest V_{clus} in the current population, and V_{max} is the highest.

$$\rho_i = (V_i - V_{min})/(V_{max} - V_{min}) \quad (4)$$

This results in a ρ value of 0 for the best cluster, and 1 for the worst cluster in the population.

The fitness of a cluster (f_i) is calculated using the exponential fitness function, as defined by Johnston [18] and provided in equation 5.

$$f_i = exp(-\alpha\rho_i) \quad (5)$$

Parameter α determines how fast fitness drops as energy increases, and is set to $\alpha = 3$ as in the original work [18].

4. EXPERIMENTAL SETUP

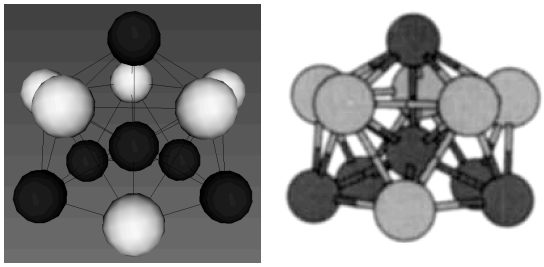
All experiments in this paper are performed on Cu-Au clusters. Ample data is available on the best known configurations of Cu-Au clusters ([7], [18], [9], [3], [22]), thus making them a suitable basis for comparison between cluster evolving GAs. Of particular relevance to this paper is the research conducted by Darby et al. [7], as it allows a direct comparison between Cu-Au clusters evolved with BCGA and those evolved with CEO-GA. However, as Pereira has already shown the Gen-C&S to outperform Deaven and Ho's C&S [27], the CEO-GA's performance is tested directly against our own implementation of the BCGA, from here forward referred to as BCGA$^-$: a BCGA without L-BFGS local optimization and augmented with Gen-C&S crossover. These modifications are made in order to verify that the CEO-GA offers benefits beyond the inclusion of Pereira's crossover.

Given the lack of location-changing mutations in the standard implementation of BCGA for bimetallic clusters [18], we also conducted tests on the BCGA$^-$ augmented with Pereira's Sigma mutation (from here forward referred to as the BCGA$^+$). In the Sigma mutation, the new position of an atom is the sum of its current position and a random value obtained from a Gaussian distribution with a mean of 0 and a standard deviation σ, which, following Pereira's example, is set to 5% of the length of any one of the edges of the bounding box (defined in section 3)[27].

In this work, the BCGA$^-$, BCGA$^+$, and CEO-GA are tested on their ability to evolve the best known pure ($Cu_{(N)}$, $Au_{(N)}$) and doped ($CuAu_{(N-1)}$, $Cu_{(N-1)}Au$) clusters. Following the example of [7] and [18], we also evolve stoichiometric nanoalloy clusters with the composition of common stable bulk Cu-Au alloy phases, i.e. those with Cu to Au atom ratios of 3, 1, and 1/3 [7]. The three GAs are tested with a population size μ=75 and a crossover rate of 0.8. The CEO-GA has a mutation rate of 0.1 for its atom permutation mutation as well as for its CoM-S mutation, and a mutation rate of 0.2 for its Local-S mutation. In order to provide an equal number of mutation children to both the CEO-GA and the BCGA$^-$, the BCGA$^-$'s atom permutation mutation rate was increased to 0.4. As the BCGA$^+$ incorporates an additional mutation type (sigma), its mutation rates were set to 0.2 for the atom permutation mutation and 0.2 for the sigma mutation. All experiments were subjected to 50 runs of 25000 generations each. The findings are presented in table 2 and consist of the best and average cluster energies for each of the three tested GAs, as well as their success rates. Success rate is defined as the percentage of the 50 runs that evolved a cluster whose energy is within 0.1 of the minimum cluster energy reported by Darby et al. [7], also presented in table 2 for ease of comparison.

5. RESULTS AND DISCUSSION

We summarize our results in table 2: BCGA$^-$ results are shown in columns 3, 4, and 5, BCGA$^+$ in columns 6, 7, and 8, and CEO-GA in columns 9, 10, and 11. Results from the original BCGA (with L-BFGS optimization) provided by Darby et al. in Table II of [7] are displayed in column 2 of table 2. In figure 2 we provide an example of a 3D visualization of the lowest potential energy clusters evolved by the CEO-GA, as well as the corresponding cluster evolved by the BCGA and reproduced from Darby et al. [7].



(a) CEO-GA Best (b) BCGA's Best [7]

Figure 2: Comparison of Cu_6Au_6 clusters evolved by the CEO-GA and the BCGA[4] Dark and light spheres represent atoms of Cu and Au, respectively. Both GAs evolved Cu_6Au_6 clusters with potential energy equal to -35.40, as can be seen in table 2. The depicted atomic radii are arbitrary, as only the atoms' centers are taken into account during the search.

As can be seen in table 2, the best structures reported by Darby et al. are consistently found accurate to two decimal places by the CEO-GA (column 9) within the span of 50 runs. Notice that since we are minimizing potential energy, lower (more negative) values are better. For example, for the Cu_3Au_9 cluster Darby reports the best found energy to be -37.725549, while the energy of the best cluster found by the CEO-GA is -37.724 (which is only 0.00155 away). Values that differ from the known minimum by up to 0.1 (and thus represent successful runs) were found by 26% of the CEO-GA runs. It is unknown, however, how often values near the optimum were found by Darby's implementation of the BCGA.

[4]Reprinted with permission from S. Darby, T. V. Mortimer-Jones, R. L. Johnson, and C. Roberts. Theoretical study of Cu-Au nanoalloy clusters using a genetic algorithm. *Journal of Chemical Physics*, 116(4):1536-1550, 2002. Copyright 2013, American Institute of Physics.

	BCGA	BCGA$^-$			BCGA$^+$			CEO-GA		
Cluster	Best	Best	AvgBest (stdv)	S.R.	Best	AvgBest (stdv)	S.R.	Best	AvgBest (stdv)	S.R.
Cu_{12}	-30.277969	-3.651	26.6296 (9.66)	0%	-30.233	-29.6094 (0.39)	24%	**-30.277**	-29.9218 (0.37)	50%
Au_{12}	-38.922569	110.389	190.2884 (30.76)	0%	-38.844	-38.5477 (0.19)	18%	**-38.921**	-38.6899 (0.18)	36%
$CuAu_{12}$	-	94.326	228.0147 (36.67)	0%	-43.055	-41.8591 (0.62)	14%	**-43.130**	-42.1157 (0.65)	20%
$Cu_{12}Au$	-	32.701	54.61392 (10.48)	0%	-34.973	-33.8937 (0.69)	22%	**-35.042**	-34.4089 (0.72)	52%
Cu_3Au_9	-37.725549	50.125	95.94986 (21.84)	0%	-37.671	-36.8992 (0.39)	10%	**-37.724**	-37.1537 (0.38)	26%
Cu_9Au_3	-33.112689	14.136	43.24580 (11.52)	0%	-33.080	-32.5323 (0.32)	14%	**-33.112**	-32.7186 (0.33)	38%
Cu_6Au_6	-35.402163	24.458	63.69496 (15.46)	0%	-35.341	-34.7210 (0.31)	8%	**-35.401**	-35.0093 (0.30)	28%

Table 2: GA performance comparison between BCGA (as reported by Darby et al. [7]), BCGA$^-$ (BCGA without L-BFGS and using Pereira's H-C&S crossover [25]), and BCGA$^+$ (BCGA without L-BFGS, using Pereira's H-C&S crossover and Sigma mutation), and the proposed CEO-GA. An evolved cluster is considered a success if by the end of a run its energy corresponds to BCGA's 'Best' energy (lowest cluster energy obtained by Darby et al. [7]) up to the first decimal place. Success rate (S.R.) represents a percentage of the 50 runs that evolved successful clusters (those with values within 0.1 of the minimum cluster energy reported by Darby et al. [7]) after 25000 generations of the GA. The best and average-best cluster potential energies, as well as standard deviation (stdv), are also reported out of 50 runs. Minimum energy values for doped clusters were not provided in the original work by Darby et al. [7]; therefore, the success cases for $CuAu_{12}$ and $Cu_{12}Au$ are estimated to be those within 0.1 of CEO-GA's best, given that in all other tested cases these values matched BCGA's 'Best' (column 2) up to the first two decimal places.

While not every run finds the known global optimum configurations, the CEO-GA success rates are much higher than those of BCGA$^-$ and BCGA$^+$, indicating that it approximates the global optimum significantly more frequently (1.4 to 3.5 times more), and the average best energies are closer to the known global optimum. The ability of the CEO-GA to accurately find global optima without the help of local optimization tools such as the L-BFGS is valuable because local optimization techniques can often cause premature convergence on a local optimum. GAs, on the other hand, are generally better suited for finding global optima. The CEO-GA relies solely on crossover and mutation for its search, lowering the risk of getting trapped in local optima (as can be seen by the higher success rates in table 2), while steadily approaching the global best, potentially paving the road for finding previously unknown global minima.

The BCGA$^-$ is included for reference only, as in absence of local minimization BCGA becomes unable to evolve even approximate solutions. This is a result of two of its characteristics: (1) the BCGA always picks the best μ solutions to become members of the next generation, which may cause premature convergence; (2) the BCGA does not itself possess the ability to make small adjustments to atom locations, and thus cannot narrow in specific coordinates, relying on H-C&S crossover for any atoms relocation away from its original randomly generated coordinates.

6. CONCLUSIONS

In this paper, a new cluster potential energy minimizing GA is presented: the Cluster Energy Optimization Genetic Algorithm. The CEO-GA is designed to improve upon the shortcomings of its predecessor, the BCGA, which requires a local minimization as it does not itself offer any atom relocating mutations. Additionally, the BCGA always picks the best μ solutions from amongst parent clusters, crossover offspring, and mutations, causing fast but often premature convergence such that every cluster in the population becomes identical to every other after just a few generations. These heavy-handed techniques cause high selection pressure, promptly pruning the population of all but the best-so-far cluster, making the BCGA highly susceptible to dangers of the low hanging fruit that is local optima. The CEO-GA combines BCGA's atom permutation mutation [18], Pereira's H-C&S crossover [25], and two new mutation operators designed to slowly move atoms closer to their idea location, thus paving a steady evolutionary path to the global optimum.

The CEO-GA is tested on pure, doped, and stoichiometric Cu-Au clusters, and is shown to outperform both the BCGA$^-$ (Johnston's BCGA without L-BFGS local minimization and with Devon and Ho's C&S crossover [8] replaced by Pereira's H-C&S crossover [25]) as well as the BCGA$^+$ (i.e. the BCGA$^-$ combined with Pereira's Sigma mutation [27]) in terms of success rate and ability to evolve the best known configurations. These results show that the CEO-GA, while not itself depending on local minimization, achieves results comparable to those previously obtained only via combining a GA with local optimization techniques. Since relying on local optimization can often lead to getting stuck on suboptimal clusters, a self-sufficient GA may not only possess a higher chance of finding global optima, but may also allow for the discovery of yet unknown lower energy cluster configurations. The CEO-GA's higher success rates (compared to other cluster evolving GAs without local optimization) also improve the reliability of finding a good cluster within fewer runs.

7. FUTURE WORK

Johnston devised an optional mechanism for maintaining diversity in BCGA's population through removing clusters whose energy was not sufficiently different from other clusters in the population [18], although it was unclear what effect this mechanism had on the GA's performance. CEO-GA could benefit from a similar diversity mechanism. However, we propose considering a clusters' geometric qualities as a measure of similarity instead of the clusters' potential energy. One approach could be to implement "speciation" based on clusters' atomic configuration, similar to that devised by Stanley for the NeuroEvolution of Augmenting Topologies (NEAT) algorithm for evolving structure [29]. Additionally it would be interesting to test the proposed optional relocation of the center of mass to the origin before

crossover-recombination on materials with less tight clusters. We hypothesize that having large empty sections of the bounding box could hinder crossover if the parents' centers of mass are distant.

It is possible that while the CEO-GA was able to find the known optima for the tested clusters, when evolving larger clusters, not using an external (to the GA itself) local optimization method such as the L-BFGS could prohibitively slow down evolution. On the other hand, using such local optimization combined with an improved base genetic algorithm could produce results quicker than previously used methods. To test this theory, the authors intend on applying the CEO-GA in conjunction with L-BFGS to clusters of sizes up to 50 atoms. It would also be interesting to compare the structures evolved with the CEO-GA with those obtained through ab initio calculations.

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