Alternative search strategy for minimal energy nanocluster structures: the case of Rh, Pd and Ag

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An alternative strategy to find global minima is presented and implemented. We use it to determine the structure of metallic clusters. It consists in a conformational space annealing (CSA) unbiased search in combination with many body phenomenological potential techniques to create a data bank of putative minima. Next, the clusters in this data bank are relaxed by DFT techniques to obtain their energies and geometrical structures. The scheme is successfully applied to magic number 13 atom clusters of rhodium, palladium and silver. We obtained minimal energy cluster structures not previously reported, which are different from the phenomenological minima. Moreover, they not always are highly symmetric, thus casting some doubt on the customary biased search scheme, which consists in relaxing with DFT global minima chosen among high symmetry structures obtained by phenomenological potentials.

Structure controls the behavior and characteristics of condensed matter systems, since mechanical, transport, optical, chemical and magnetic properties are determined by it. Thus, to establish the way the constituent atoms arrange spatially to form molecules, nanoclusters and crystals is the fundamental problem of solid state physics.[1] Nanoclusters are aggregates that contain up to a million atoms and constitute the building blocks of nanoscience. They can have properties that vary dramatically with size. As such they have been the focus of increasing attention by physicists, chemists and engineers during the past decade.[2,3] Finding the minimal energy structure of nanoclusters is the main objective of the present contribution.

Sophisticated global minimization techniques have been developed and implemented in order to find, among a huge number of local minima, the lowest energy configuration.[1,2,4–7] Given the complexity of the problem (for example, the potential energy surface of a 13 atom Lennard–Jones cluster has about a thousand minima[7]) it is not surprising that some degree of controversy and uncertainty is always present. In fact, most algorithms get stuck in some putative minimum that is not the global one. For example, recently Chang and Chou[8] reported that the buckled biplanar structure is slightly more favorable than the icosahedral one for 13 atom clusters of Tc, Rh, Pd, Ag and Cd. While differences between total cluster energies are of the order of 1 eV or less, previously the icosahedral structure had been assigned the minimum energy.[9]

In order to determine the minimum energy structure of a cluster a variety of techniques and strategies have been put forward, of which Monte Carlo, slow quenching, simulated annealing, basin hopping and the genetic algorithm, also called evolutionary algorithm,[2] are the most common examples. They are used in conjunction with phenomenological potentials and eventually followed by *ab initio* refinement. While the former tend to

get stuck in less favorable configurations the genetic algorithm (GA)[5,6] is quite efficient in locating the global minimum. Basin hopping is also quite successful, but has failed to find several[7] Lennard-Jones global minima by direct minimization. Without going into much detail one can classify the search strategies for minimum energy cluster configurations into three broad categories: i) search for the minima exploring the phenomenological potential energy surface (PES), a method that is especially suited for large clusters, where *ab initio* computations are either impractical or non feasible;[7,10] ii) adopt a certain structure and refine it *ab initio*, keeping the symmetry fixed,[11,12] or relaxing the symmetry entirely;[8,13] and iii) explore cluster structures, obtained by global optimization with a semiempirical potential; once a certain number of low energy configurations are identified reoptimize them via DFT.[3,14]

On the other hand, a novel and powerful global optimization method, called conformational space annealing (CSA), was put forward by Lee *et al.*[15] and applied extensively to the protein folding problem,[16,17] and more recently also to the global optimization of Lennard-Jones clusters.[18] The key feature that makes CSA advantageous is the fact that it yields a data bank of the low lying minima, while at the same time preserving diversity. GA instead, due to its notable efficiency, has a tendency to collapse most initial populations into a single global minimum. Our strategy tries to retain as much diversity as possible, which we achieve through a combination of CSA with genetic operations, and apply it to the cluster structure problem. More precisely, what we implement is the use of many body phenomenological potentials to obtain data banks via CSA; these data banks are then explored by *ab initio* computations. Thus, our strategy consists in first obtaining low lying minima by means of a fast, but rather coarse unbiased search, in order to generate a bank of putative minima. Next, all these minima are examined in detail by means of *ab initio* procedures. As will

be shown below, it is often the case that the lowest minimum obtained via GA, on the basis of phenomenological potentials, does not match the *ab initio* result, but with a very high likelihood the global minimum is contained in the CSA bank, thus decreasing the probability of missing it. The benchmark tests[15–17] have established that CSA is a very efficient algorithm and that the method, in some instances, provides previously overlooked global minima.[16,17] Moreover, CSA unifies the essential ingredients of three global optimization methods: i) Monte Carlo with minimization,[19] ii) genetic algorithm (GA)[4–6] and iii) simulated annealing (SA).[20]

We test our procedure on 13 atom clusters of Rh, Pd and Ag, but the main purpose of this paper is to validate the search method rather than obtaining the most precise, and thus also most computer time consuming, DFT verification of minimal energy structures.

The sampling diversity in CSA is directly controlled by introducing a measure of the distance $D(j,k)$ between configurations j and k of a single sample, which is given by[18]

$$D(j,k) = \sum_n n\left(2|H_j(1,n) - H_k(1,n)| + |H_j(2,n) - H_k(2,n)|\right)$$

(1)

where $H_j(1,n)$ $[H_j(2,n)]$ is the histogram of the number of atoms having n neighbors in the first [second] shell of the j-th configuration. To specify the shell radii we adopt the first and second neighbor distances of the respective bulk lattice, which in this particular instance is fcc. The distances $D(j,k)$ are compared with the parameter D_{cut}, which plays a role equivalent to the temperature in SA, following the procedure described in detail by Lee *et al.*[18] However, to enlarge the sampling we initially adopted $D_{\text{cut}} = D_{\text{ave}}$ instead of half the average distance. To generate a new trial configurations we modified the original procedure of Lee *et al.*[18] adopting the following genetic operators: four crossover operators (the arithmetic and geometric means, the N and the 2-point crossover) plus the inversion operator, as described by Niesse and Mayne,[21] to generate as large a diversity as feasible. Successive iterations are performed until all the bank configurations have been used as seeds.

As the genetic algorithm CSA starts with a set of configurations, denominated initial population in the GA context and *bank* in CSA; in our implementation a bank of 50 different configurations. Of them 20 are chosen at random as seeds to generate new configurations, which are incorporated into the data bank if they satisfy one of the following conditions: i) if the distance $D(j,k)$ between the trial and closest configuration in the bank is small, as evaluated with Eq. 1, the largest energy one is dropped; ii) if this distance is large then the highest energy configuration, including the trial, is removed from the bank. This way, diversity is improved as the bank is constantly being renewed until all its members have been used as seeds. For our initial bank the atomic coordinates are chosen at random within a cubic box of sides $a = 1.5 \times N^{1/3}$ [Å].

It is worth stressing the dynamic character of the bank, since new lower energy configurations are incorporated while the bank is being used to generate additional seeds. This way the number of seeds is, in general, significantly larger than the cluster replicas in the bank. In fact, for each seed CSA generates 30 trial configurations which are then minimized locally and compared, on the basis of the distance $D(j,k)$, with the closest configuration in the bank to decide whether or not it is incorporated. As usual[18] local minimizers were implemented, in our case a combination of Simplex and Monte Carlo, to obtain the local minimum configuration. Actually, after a maximum of three iterations deadlock is reached and the procedure is finalized.

For CSA to compute the energy of the different configurations in the bank a phenomenological potential has to be used, however the specific choice does not make much difference. Here we adopted the semi-empirical Gupta potential,[22,23] which was derived from Gupta's expression for the cohesive energy of a bulk material[22] and is based on the second moment approximation to tight binding theory. It is a potential that has a very simple analytical form, which depends on five parameters, and is written in terms of repulsive pair and attractive many-body terms which are obtained by summation over all atoms. The attractive many-body term (the band energy E_b) of atom i is given by

$$E_b^i = -\left[\sum_j \xi^2 \exp\left[-2q(r_{ij}/r_0 - 1)\right]\right]^{1/2}.$$

(2)

The stability of the system is ensured by adding a phenomenological core-repulsion term, of the Born-Mayer type, and given by

$$E_r^i = \sum_j A \exp\left[-p(r_{ij}/r_0 - 1)\right].$$

(3)

In these expressions r_{ij} is the spatial distance between atoms i and j; r_0 is the first-neighbor lattice distance, and A, ξ, p, and q are the parameters of the potential. For pure elements the parameters of the potential are fitted with bulk properties of the respective element (cohesive energy, lattice parameters, bulk modulus, independent elastic constants and the vanishing of the energy gradient at the equilibrium distance). The complete set of parameter values for Rh, Pd and Ag that we use in our calculations,[23] is given in Table I. We are fitting the parameter potentials to bulk properties, which constitutes a shortcoming of our method. At present we are working on a procedure to develop potentials that depend on cluster size, which we trust to conclude in the near future.[24]

The cohesive energy E_c of the system is given by

$$E_c = \sum_i (E_b^i + E_r^i).$$

(4)

Once CSA completes an iteration the data bank is updated. It includes a minimum energy configuration and

TABLE I: Parameters used in the implementation of Eqs. 2 and 3.

Element	Lattice	A (eV)	ξ (eV)	p	q
Rh	fcc	0.0629	1.660	18.450	1.867
Pd	fcc	0.1746	1.718	10.867	3.742
Ag	fcc	0.1028	1.178	10.928	3.139

49 additional geometries that correspond to local minima. While we did perform three CSA iterations the global minimum energy configuration, already obtained by other methods,[25] was always found in the first iteration.

We tested the efficacy of our scheme on 13 atom clusters of Rh, Pd and Ag. To do so all 50 lowest energy configurations obtained via CSA were relaxed *ab initio*, using a basis set of strictly-localized numerical pseudoatomic orbitals, as implemented in the SIESTA code.[26–28] The exchange-correlation energy was calculated within the local spin density approximation (LSDA) as parameterized by Perdew and Zunger.[29] We have used a double-ζ single-polarized (DZP) basis set.[27] Convergence tests have demonstrated that this basis yields reliable results in a variety of cases including covalent, ionic, and metallic systems.[30] Norm-conserving pseudopotentials,[31] in their non-local form, were used to describe the electron-ion interaction. Pseudopotentials of Rh, Pd and Ag have been generated for the $[Kr]4d^85s^1$, $[Kr]4d^{10}5s^0$ and $[Kr]4d^{10}5s^1$ configurations, respectively, including non-linear core corrections. While some controversy has emerged recently[32–34] on the use of SIESTA (with LDA) versus FP-LMTO (with GGA) in this context, the differences in bond length and energy between the different methods turn out to be rather small. Moreover, very similar results were obtained with VASP and WIEN2K.[33] The clusters were placed in a cubic supercell of 20 Å per side which ensures a minimum distance between cluster images of about 15 Å. Due to the large size of the supercell only the Γ point was used to sample the Brillouin zone (BZ). We have checked our results increasing to 18 k points the BZ sampling according to a $3 \times 3 \times 3$ Monkhorst-Pack mesh.[35] The difference in total energy between the Γ and 18 k-point calculations is less than 10^{-4} eV/cell. The cluster geometries previously obtained, from the CSA final data bank, were fully relaxed using the conjugate gradient method, without any symmetry constraint, until all the force components became smaller than 0.05 eV/Å. The geometry of each cluster was optimized for different spin multiplicities in order to find the corresponding spin that minimizes the total energy.

The 50 different lowest energies, obtained both phenomenologically (dashed lines) as well as *ab initio*, for Rh, Pd and Ag (full lines), are given in Fig. 1. The dashed line depicts the 50 lowest lying Gupta phenomenological energies. The solid line displays the SIESTA relaxed energies for the spin variable with the global minimum. A general tendency for the DFT energies to follow the
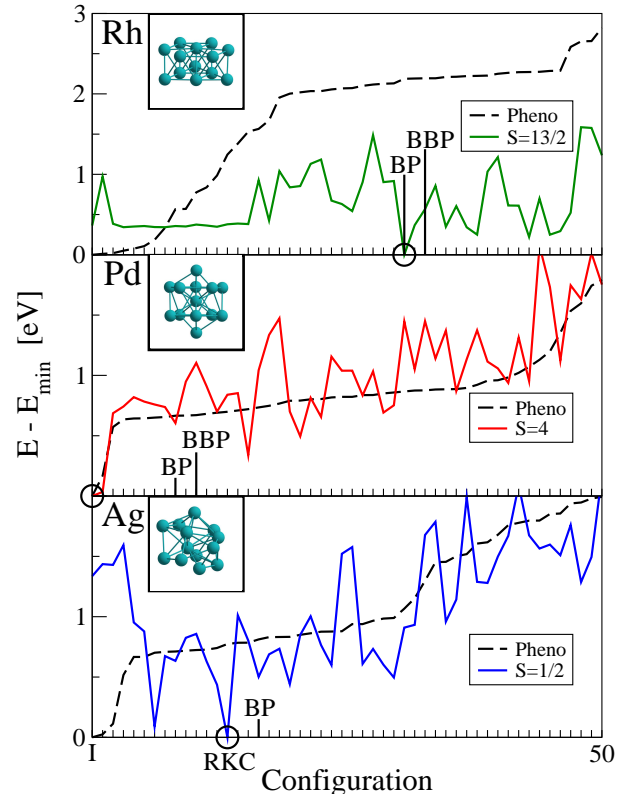

FIG. 1: (Color online) The energies of the 50 different lowest energy configurations for Rh, Pd and Ag, obtained with the Gupta phenomenological potential, are illustrated by the dashed lines. The solid line displays the SIESTA relaxed energies for the spin variable with the global minimum. The configuration labeled by I is ichosaheral; BP, BBP and RKC stand for biplanar, buckled-biplanar and relaxed Kumar cage, respectively. The inserts illustrate the structures that correspond to the gobal minimum configurations, which are denoted by circles.

phenomenological results is observed. Thus, it seems unlikely that global minimum energy structures could fall outside (to the right) of the ones we report. However, quantitatively we observe a much better agreement for Pd and Ag than for Rh, indicating that phenomenological results are quite dependent on the atomic species. In the understanding of Fig. 1 it is worth mentioning that the configurations are ordered according to growing energy along the abscissa, as obtained from a calculation using a phenomenological potential. Thus, for the different elements (Rh, Pd and Ag), the same configuration appears in the corresponding plot at a different position along the axis.

The minimal structures we obtain are the biplanar (BP), icosahedral (I), and relaxed Kumar cage (RKC), for Rh_{13}, Pd_{13} and Ag_{13}, respectively, as illustrated in Fig. 1. It is important to remark that for Ag the energy difference between the two lowest energy structures is very small indeed (of the order of 0.1 eV). Both minima correspond to rather irregular, low symmetry con-

figurations, like the one illustrated for Ag in the inset of Fig. 1. Our results differ from those of Chang and Chou[8] who reported as minimal the buckled biplanar (BBP) configuration for Rh_{13}, Pd_{13} and Ag_{13}. The reason is that biased search allows to discover overlooked structures and thus yields additional configurations to test. In fact, Chang and Chou[8] chose a different search procedure, which starts from high symmetry structures, obtained by molecular dynamics at 300 K and compares their energy at 0 K with previous results. Our results also differ with those of Bae *et al.*[13] for Rh_{13}.

As far as magnetic properties of the clusters is concerned our results indicate that the optimized Pd_{13} and Ag_{13} clusters exhibit spin multiplicities of S=4 and S=1/2, respectively. However, for the Rh_{13} cluster we find a rather large spin multiplicity (S = 13/2), implying a magnetic moment $m = 1$ μ_B/atom. Some time ago Reddy and Khanna,[36] obtained a magnetic moment of 1.61 μ_B/atom for Rh_{13}. Following this early theoretical suggestion Cox *et al.*[37] measured the magnetization of rhodium clusters, an element that is non-magnetic in the bulk, to find $m = 0.48 \pm 0.13$ μ_B/atom for Rh_{13}. Although the magnitude of this measured magnetic moment amounts to just one half of the theoretical value, it nevertheless confirms that small Rh clusters are magnetic. Our results for the magnetic moment of Rh_{13} are also compatible with more recent calculations.[13,38,39]

Thus, for Rh and Ag the minimum energy structures, selected by symmetry criteria from the bank obtained via CSA and phenomenological potentials, are different from the ones calculated by SIESTA. In consequence, the usual strategy of finding a minimum and refining it *ab initio*, is not always reliable. Of particular interest is the fact that the relaxed Kumar cage is the most favorable Ag_{13} structure, which we understand had not been reported before. Instead, for Pd the ichosaedral configuration is obtained both by phenomenological and *ab initio* methods, probably due to the fact that full atomic shells lead to better agreement of the two calculation procedures. For Rh we find a biplanar, rather than a buckled biplanar, configuration.

In conclusion, we have tested our unbiased search scheme and confirmed that it successfully handles the examples we studied, and even was able to find a new minimal energy configuration for the 13 atom Ag cluster. While we cannot exclude the possibility that the absolute minimum structure is missed by this unbiased CSA search, the likelihood of failing is quite small. Moreover, the strategy we put forward is quite insensitive on the choice of a specific phenomenological potential and/or a particular *ab initio* code.

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