Eur. Phys. J. D **9**, 235–241 (1999)

THE EUROPEAN PHYSICAL JOURNAL D

EDP Sciences

Genetic algorithms for determining the topological structure of metallic clusters

R. Poteau and G.M. Pastor

Laboratoire de Physique Quantique, Unité Mixte de Recherche 5626 du CNRS, Université Paul Sabatier, 118 route de Narbonne, F–31062 Toulouse, France

Received: 1 September 1998 / Received in final form: 14 January 1999

Abstract. Genetic algorithms (GA) are applied for the optimization of the structure of metallic clusters by the calculation of the ground-state energies from a tight-binding (Hückel) Hamiltonian. The optimum topology or graph is searched by the use of the adjacency matrix A_{ij} as a natural coding. The initial populations for N-atom clusters are generated from a representative group of fit cluster structures having $N-1$ atoms by the addition of random connections or hoppings between the Nth atom and the rest of the cluster atoms ($A_{iN} = 0$ or 1). The diversity of geometries is enlarged by 20% with fully random structures. Several crossover strategies are proposed for the genetic evolution that combine the "parent" clusters while trying to preserve or transmit the physical characteristics of the parents' topologies. The performance of the different procedures is tested. For $N \leq 13$, the present GA yield topological structures that are in agreement with previous geometry optimizations performed using an enumerative search ($N \leq 9$) or simulated annealing Monte Carlo ($10 \leq N \leq 13$) methods. Limitations and extensions for $N \geq 14$ are discussed.

PACS. 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 36.40.Cg Electronic and magnetic properties of clusters – 02.60.Pn Numerical optimization

1 Introduction

Geometrical structure is one of a cluster's most fundamental properties. The large majority of physical properties that make clusters so unique depend crucially on the local environment of the atoms, and thus on the specific cluster geometry. For example, the reactivity of clusters in chemical reactions is sensitive to the availability of surface atomic sites with low coordination numbers. The electronic structure, as measured in photoemission or photoabsorption spectra, may be considered as a fingerprint of the symmetry and structure of the system. Magnetic properties such as local magnetic moments are enhanced significantly if the atoms have small local coordination numbers, and even the magnetic order may depend on structure (e.g., ferromagnetic or antiferromagnetic) because of different magnetic frustrations effects. Therefore, a precise knowledge of cluster geometry is often indispensable for the interpretation of experiments.

The determination of the ground-state structure of a metallic cluster remains an open problem in current cluster research. The lack of a direct means of determining the relevant geometries experimentally in a cluster beam complicates the comparison between theory and experiment and enhances considerably the interest in computer simulations in this area. Theoretically, the cluster structures are derived from an electronic property, the total energy, with the configurational entropy at finite temperatures taken into account. Within the Born–Oppenheimer approximation, the geometrical configuration at $T = 0$ is the one yielding the minimum energy. The problem of cluster structure prediction may be therefore viewed as consisting of two parts: The calculation of the ground-state energy (or free energy) for a given configuration of the atoms and the development of methods for searching the lowest-energy configuration. This paper is concerned with the determination of the structure of metal clusters by a new implementation of genetic algorithms (GA) [1–4] in the framework of a simple tight-binding or Hückel model. We begin with a brief introduction to the principles of GA, then describe our method of calculation, including the electronic model Hamiltonian and the specific implementation of the search procedure. Finally, we discuss some results of our simulations.

2 Genetic algorithms

Genetic algorithms are a general class of cooperative search methods that mimic the mechanisms found in nature's gene-based evolution [1]. The search is done for a *population* (ensemble of structures), not from a single individual, and can be therefore regarded as an evolution over successive *generations*. The population evolves from one generation to the next by means of three main operations on

its members: crossover, mutation, and selection. GA usually do not apply these operations directly to the actual variables of the problem (in structure prediction, the set of atomic coordinates) but to a *string coding*, a sort of genetic code which contains all the information on an individual in a compact, and often abstract, form. The coding is typically given by an integer in binary form (a succession of bits); this is conditioned by the practical implementation, and in some cases can be avoided [2, 4]. Besides being practical, string coding also contributes to the flexibility and robustness of GA, allowing a wide range of applications to very different problems which end up in similar codings.

The main steps in a GA optimization may be generally described as follows. An initial population Π_0 of trial solutions is established, represented by strings. Given the population Π_i at iteration i, the sequence of steps leading to the population Π_{i+1} starts with the creation of new strings by crossover operations. For example, two members of the population, or "parents", are selected randomly (eventually favoring the fittest strings), a breaking point in the string is chosen, and two new population members, or "children", are created by the interchange of the left and right portions of the parent strings. Mutations are introduced, usually with a small probability; for instance, one of the bits in the string may be changed. The fitness function is evaluated for the new individuals, which form, together with Π_i, an intermediate population Π_i'. Finally, the fittest members in Π_i' are selected so that a predefined size of the population is kept. This yields the population Π_{i+1}, of the next generation, and a new crossover sequence may be started.

There are obviously many details to be specified in an implementation of GA that are problem-specific and that have a strong influence on the performance of the method. This includes in particular the actual coding of the cluster structure and the associated crossover procedures, the generation of the initial population and its size, the type and probability of mutations, the total number of generations, and other convergence criteria. Various choices made in the present study are explained in the following section. The resulting performances are discussed in Sect. 4.

3 Method of calculation

The ground-state properties of the clusters are calculated through the use of the tight-binding or Hückel Hamiltonian, given by

$$H_0 = \sum_{\langle i,j\rangle,\sigma} t_{ij}\, c_{i\sigma}^{\dagger} c_{j\sigma}\,, \tag{1}$$

where, as usual, $c_{i\sigma}^{\dagger}$ ($c_{i\sigma}$) refers to the creation (annihilation) operator for an electron at site i with spin σ ($t > 0$). In this model, the hopping integrals t_{ij} take only two possible values, namely, $t_{ij} = -t$ if $R_{ij} = R_0$, and $t_{ij} = 0$ if $R_{ij} > R_0$, where R_{ij} refers to the interatomic distance and R_0 to the nearest-neighbor (NN) distance. Therefore, only the topological aspect of the structure is relevant for the calculation of electronic properties such as the ground-state energy E_0. In other words, it is enough to identify for each atom i the atoms j which are connected to i by a hopping element t. Taking into account only NN hoppings with fixed bond length results in a discretization of the configurational space. The geometry optimization can be performed within the set of graphs with N vertices [5], for example, by enumerative searches [6] or by simulated annealing Monte Carlo techniques [7]. It should be noted, however, that even with this simplification, the size of the configurational space n_g increases extremely rapidly with the number of atoms N (for example, $n_g = 11\,117$ for $N = 8$ and $n_g = 11\,716\,571$ for $N = 10$ [6]).

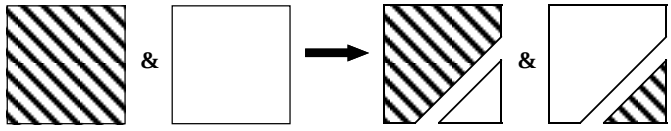


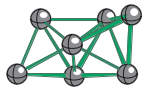
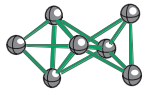
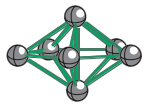
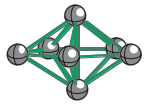
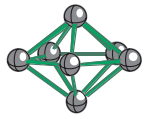
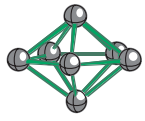
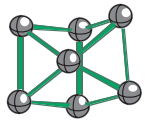
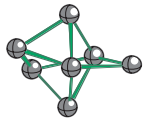
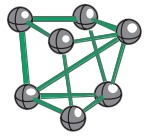
Fig. 1. Illustration of one of the crossover procedures used in the present paper, labeled by B in Fig. 2. The adjacency matrices A_{ij} corresponding to the "mother" (shaded), "father" (non-shaded), and "children" (mixed) are sketched (graph coding).

In order to perform the geometry optimization using GA, we consider the adjacency matrix A, which has the value $A_{ij} = 1$, if i and j are NN, and $A_{ij} = 0$ otherwise. A contains all the information necessary for defining the topology of the graph and thus provides a natural string coding. It may be efficiently stored on a computer in the form of the integer

$$\alpha(A) = \sum_{i>j} A_{ij}\, 2^{(i-1)(i-2)/2+j-1}\,. \tag{2}$$

The different bits in the binary notation of α correspond to the lower-diagonal entries of A ($A_{ij} = 0, 1$) [8]. The integer α may be used directly as a string coding, and the standard crossover method, consisting of the interchange of upper and lower parts of the parent strings, may be applied straightforwardly, as discussed in Sect. 2. This is one of the strategies used in our simulations. However, if alternative, more physical crossover procedures are sought, it is easier to work with the original matrix A, since it reflects more clearly the topologies of the parent clusters and the way they are combined in the children. We have used four different crossover strategies, denoted by A–D. In Fig. 1, one of these is illustrated (herafter labeled B). Given the atom k that defines the breaking point ($1 < k < N$), we observe that, when the two children are formed, the topology of the father (mother) within the subcluster containing the first k atoms (last $N - k$ atoms) is preserved. The hoppings t_{ij} between the two subclusters ($1 \le i \le k$ and $k < j \le N$) are taken from either one parent or the other. Additional crossover schemes may be constructed by analogy [9]. It should be noted that all the considered crossover procedures yield similar acceptance rates and that it is mainly the combination of several of them which is important for effi-

Table 1. Optimized energies and structures for clusters having $N = 7$ atoms and ν electrons. *a* refers to [10] and *b* to [6].

		previous works	this work		
N	ν	E_0	E_0	E_c	structure
7	3	-10.197^{a}	-10.197	< 0.1	
7	4	-11.458^{a}	-11.458	< 0.1	
7	5	-11.257^{a}	-11.257	< 0.1	
7	6	-11.875^{a}	-11.875	< 0.1	
7	7	$-11.105^{a,b}$	-11.105	0.4	
7	8	-11.105^{a}	-11.105	0.4	
7	9	-9.540^{a}	-9.540	0.2	
7	10	-8.910^{a}	-8.910	0.3	
7	11	-7.109^{a}	-7.201	0.8	

ciency. Mutation operators representing random changes in the connectivities of one atom are also easily obtained. An atom i is selected, and all its connections A_{ij} are redefined at random. In practice, mutations are introduced only with a small probability (typically in 5% of the generations).

At this point, the relation between the new string and the Cartesian coordinates of the atoms is lost, particularly since the numbering of atoms may be changed arbitrarily without resulting change in the actual topological structure. This would be of no importance if one were just interested in obtaining the *graph* with the lowest energy. However, for the study of clusters, we must consider only those graphs which can be represented as a true *structure* in space. A *graph* is mathematically acceptable as a cluster *structure* if a set of atomic coordinates $\mathbf{R}_i$ $(i = 1, \ldots, N)$ exists such that

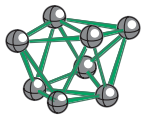
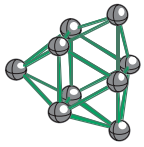
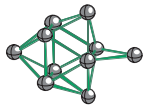
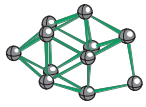
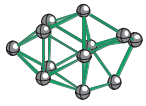
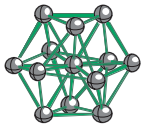
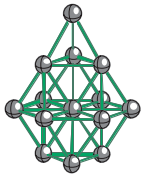
$$R_{ij} = R_0 \quad \text{if} \quad A_{ij} = 1\,, \tag{3}$$

i.e., the sites i and j are connected in the graph, and

$$R_{ij} > R_0 \quad \text{if} \quad A_{ij} = 0\,. \tag{4}$$

In practice, some flexibility has to be introduced because of the continuous distance dependence of the hopping integrals and the interactions between cores found in real systems. In fact, there are graphs which do not satisfy the previous conditions upon the interatomic distances, but which are *physically* acceptable as structures, since the conditions are violated only slightly. For example, in a pentagonal bipyramid ($N = 7$) it is reasonable – if the typical distance dependences of the hopping integrals are taken into account – to set $t_{ij} = -t$ for $R_{ij} \simeq 1.02R_0$ as well as for $R_{ij} = R_0$. Moreover, other graphs ($N \geq 7$) do satisfy the conditions on R_{ij}, and would thus be mathematically acceptable as cluster structures, but seem physically unrealistic, since in these cases one has $t_{ij} = 0$ for $R_{ij} \simeq 1.02R_0$, and $t_{ij} = -t$ for $R_{ij} = R_0$. In order to take this into ac-

Table 2. Optimized energies and structures for clusters having $N = 8 - 14$ atoms and $\nu = N$ electrons. *a* refers to [6] and *b* to [7]. The structures found in [7] for $N = 11$ and 12 are present in our final population, but they do not satisfy the conditions (3) and (4).

		previous works	this work		
N	ν	E_0	E_0	E_c	structure
8	8	-14.160[a]	-14.160	0.1	
9	9	-15.646[a,b]	-15.646	0.2	
10	10	-17.657[a] -18.056[b]	-18.056	0.3	
11	11	-19.240[a] -19.564[b]	-19.550	0.2	
12	12	-21.616[a] -21.984[b]	-21.837	0.2	
13	13	-24.000[a] -24.009[b]	-24.009	0.7	
14	14	-26.414[a] -26.523[b]	-26.414	0.2	

count, we calculate the ground-state energy E from

$$E = E_0 + E_c \,, \tag{5}$$

where E_0 refers to the sum of the occupied tight-binding eigenvalues and

$$E_c = t \sum_{ij} \left\{ A_{ij} \left| \frac{R_{ij}}{R_0} - 1 \right| + (1 - A_{ij}) \left(\frac{R_0}{R_{ij}} \right)^{12} \right\} \tag{6}$$

represents a phenomenological core–core interaction, which is weakly attractive if the sites are connected by the hoppings and repulsive if they are not. The minimum of E_c for a given graph A_{ij} provides a measure of the feasibility of satisfying the graph conditions in a three-dimensional structure. Moreover, including E_c in the calculation of the energy is a simple way of excluding unphysical graphs, which would otherwise dominate for $N \geq 8$.

For the generation of the initial population Π_0 for N-atom clusters, a representative group of fit cluster structures having $N - 1$ atoms (typically 80% of the optimized population of a previous GA evolution) is considered, and random connections or hoppings between the Nth atom and the rest of the cluster ($A_{iN} = 0$ or 1) are added. In order to enlarge the diversity of individuals, we also include 20% of the random structures, which are obtained by choosing $A_{ij} = 0$ or 1 with equal probabilities and by verifying that the graph is connected [5]. As expected, our simulations show that it is much more efficient to use the information on the fit structures of smaller sizes than to consider only randomly connected structures (see Sect. 4). It should be noted that in the present calculations, we never include in Π_0 any information from previous works or any reasonably expected structures, such as icosahedra or fcc cubooctahedra, since we are primarily interested in testing the performance of GA.

4 Results and discussion

First of all, we would like to discuss some technical aspects of the implemented GA in the light results of numerical simulations. The GA and its parameterization were tested on small clusters for which abundant results are available [6, 10]. For $N \leq 8$, the search of structures performed

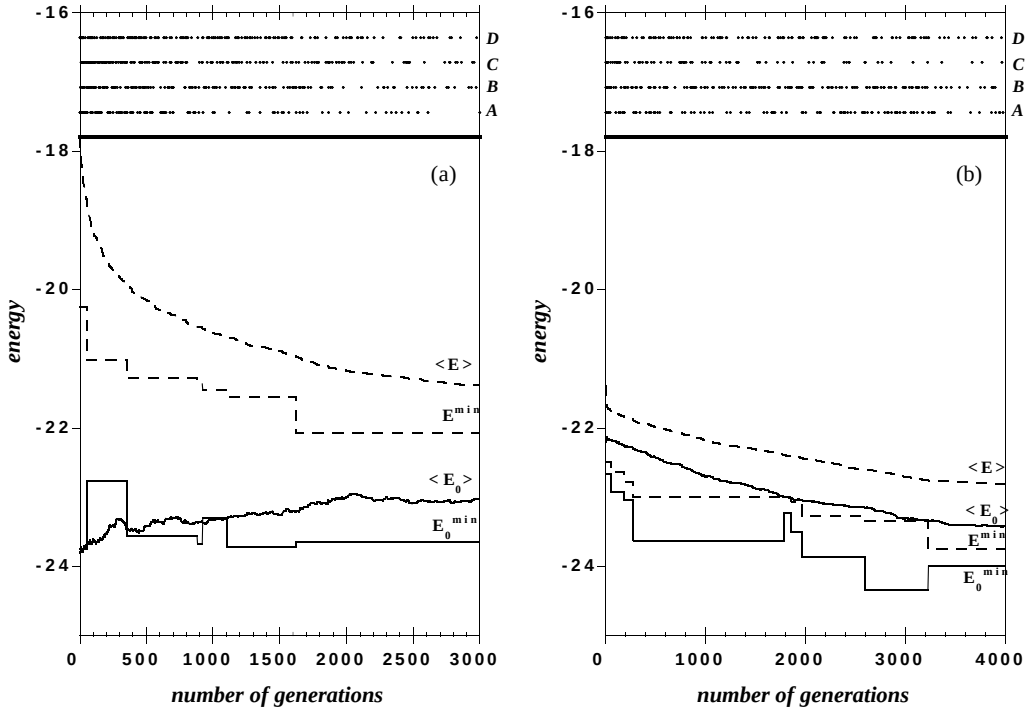


Fig. 2. Ground-state energies of clusters having $N = 13$ atoms and $\nu = 13$ electrons as a function of the number of generations i. $E_0^{\min}$ and $E^{\min}$ refer, respectively, to the optimum tight-binding and total energies. $\langle E_0 \rangle$ and $\langle E \rangle$ correspond to population averages. In (a), the initial population Π_0 is a set of randomly connected graphs, and in (b), it is derived from a fit population of 12-atom clusters. Notice that $E_0^{\min}$ and $\langle E_0 \rangle$ need not decrease with increasing i, since the acceptance criterion is based on E. In the upper part of the graphs, a dot indicates that a child has been retained at the generation i as a result of one of the proposed crossover procedures A–D (see Fig. 1).

in [10] is exhaustive, since all the physically acceptable graphs are investigated. We have thus particularly checked our algorithm on the 7-atom system with different fillings of the molecular orbitals (i.e., number of electrons ν). As a matter of fact, there is a strong link between cluster structure and band filling. For example, for $\nu = 4$, the structure is a prolate assembling of tetrahedrons, while it is an oblate pentagonal bipyramid for $\nu = 7$. Further details on the subtle differences between the various structures may be found in [10]. Notice, moreover, that $n_g = 853$ connected graphs have been recorded for $N = 7$. Therefore, already $N = 7$ is a nontrivial problem for a global optimization tool. As has been previously observed by several authors, in some cases it is necessary to apply mutation operators to members of the population in order to improve the convergence of the method [2–4]. The most spectacular effects related to mutations are found for larger systems. In any case, we observe that the mutation rate must be kept below 10%, otherwise the efficiency of the method decreases.

The optimized tight-binding energies E_0 of metal clusters in the range $N = 7$–14 (hereafter denoted as M_N) are given in Tables 1 and 2 together with the results of previous works. The size of the population was taken to be 50 individuals, and the mutation rate was fixed to 5%. For $N \leq 7$ and an arbitrary number of electrons ($3 \leq \nu \leq 11$), the present GA found the optimal structures reported in [10] in less than 1000 generations. In each case, the coordinates of the members of the initial population were created at random. Of course, structures issued from a previous run would be much more reasonable candidates for the initial population (e.g., the optimized population for $\nu - 1$ electrons). However, the purpose of these simulations was not to find the optimal structures with the best efficiency, but rather to test the robustness of the proposed GA. As is shown in Table 1, the agreement with previous works is excellent. The band-filling with $\nu = 11$ electrons deserves special attention. In this case, the structure reported in Table 1 has an energy E_0 which lies $0.1t$ below the optimal one of [10]. The graph of Table 1 is excluded from the optimization in [10], since it does not satisfy the conditions on the interatomic distances strictly. We find that it has a large E_c (poor physical character), and that in fact the structure of [10] yields the lowest E. In any case, both structures are found in the optimized GA population. The very good behavior of the algorithm encourages applications on larger systems.

In the following, the calculations concern clusters with half-filled molecular orbitals ($\nu = N$) which are isoelectronic to alkali clusters. Starting from a random initial population, the GA succeeded in finding the most stable structure for $N = 8$, but it could not reach the absolute minimum for $N \geq 9$. Increasing the number of generations up to 3000 and number of individuals in the population up to 100 does not yield significantly better results. The reason seems to be that as the number of atoms increases,

the large majority of the graphs generated at random are hardly physical. Many hundreds of generations are necessary for bringing the initial population Π_0 to low values of E_c. Moreover, the number of graphs becomes prohibitively large, and many graphs that are not physically acceptable have a Hückel energy E_0 that is lower than the optimal one for $N \geq 8$. Figure 2 illustrates this behavior in the case of M_{13}. Here we present results for the tight-binding energy of the minimum $E_0^{\min}$, the total energy $E^{\min}$, and the corresponding population averages $\langle E_0 \rangle$ and $\langle E \rangle$ as a function of the number of generations. If Π_0 contains only random graphs (Fig. 2(a)), the lowest-energy cluster after 3000 generations has a repulsive energy $E_c \simeq 1.6t$, while $\langle E_c \rangle = 1.7t$. The known optimal cluster is the fcc cubooctahedron with $E_0 = -24t$ and $E_c = 0.2t$. Typical values of E_c for physical graphs reported in Tables 1 and 2 lie around $0.5t$. We have checked that graphs with $E_c > t$ violate the conditions on the interatomic distances significantly, i.e., they have a very poor physical character. Consequently, if Π_0 is chosen at random, a long initial period is necessary before reasonable candidates emerge. This problem can be avoided by the creation of an initial population with fit cluster structures. A discussion of seeding strategies may be found in [4]. In our case, 80% of the initial clusters of size N are constructed by the addition of an atom to the previously determined structures having $N-1$ atoms. The remaining 20% of the initial population is created at random in order to enlarge the diversity of patterns. Figure 2b shows that in this way, the convergence of the algorithm is significantly improved. The optimal structure is attained before 4000 generations. Remarkably, as a result of the mutation operations, we obtain another structure that is quasi-degenerate with the perfect cubooctahedron. This is a distorted cubooctahedron with an additional bond and a Hückel energy $0.009t$ lower than the undistorted structure. The graph can still be considered as physically acceptable, since $E_c = 0.7t$. Comparing the molecular orbital spectra of the perfect and distorted cubooctahedron, we observe that the energy lowering is the result of a Jahn–Teller lifting of degeneracies. This distorted structure has been already reported by Yoshida *et al.* [7] but is not considered in [6].

For $N \geq 9$, the GA was started with the previously discussed growth method. We obtained the results presented in this paper by performing only one evolution or succession of generations. The size of the population was set at 150 members, and the number of generations was fixed to 5000. In many cases, only 2000 generations were necessary to find the best geometry. However, note that considering only one evolution is often not enough, neither for reaching the absolute minimum, nor for evaluating correctly the efficacy of a given strategy [4]. For $10 \leq N \leq 13$, our optimal cluster energies are often lower than those reported in [6], in agreement with more recent simulated annealing calculations [7]. For $N = 10$ we find a structure based on the bicapped square antiprism, with one square distorted into a rhombus and some associated recombinations of bonds (see Table 2). It is interesting that clusters with this type of geometry have been already found to have very low energies by a distance-dependent tight-binding Hamiltonian for alkali clusters [11]. Our structures for M_{11} and M_{12} are built around the M_{10} seed. In [7], other geometries have been found that show important distortions with respect to those reported in Table 2 and that have lower Hückel energies. In fact, these structures are present in our final population but have a higher total energy since the repulsion is too large. In other words, they violate the conditions (3) and (4) significantly.

The situation is different for $N = 14$. Using 13-atom clusters as seeds for generating the initial population, we obtain a unicapped cubooctahedron (see Table 2). In contrast, a clearly better topology has been found [7] that belongs to the family of optimal structures for $N = 9$–12. We have therefore repeated the calculations, including structures in the initial population that we obtained by adding sites randomly to the optima for $N = 9$–12. In this case, the agreement with [7] is recovered.

In conclusion, a new implementation of genetic algorithms for cluster structure prediction has been presented. In this approach, the topology of the cluster plays a central role in both string coding and the proposed crossover operations. The efficacy of the method in applications to metal clusters has been demonstrated by the use of the topological Hückel model. This is of interest since the efficiency of any implementation of GA (for example, choice of the initial population, crossover procedures, etc.) depends significantly on the specific problem under study. Useful methodological extensions, for larger clusters in particular, should take into account newly proposed mutation and seeding strategies [4] as well as symbiotic crossover methods [12]. Future applications include magnetism within the Hubbard model [10] and more complex distance-dependent Hamiltonians [11].

It is a pleasure to thank Professors K.M. Ho, U. Landman, and M. Manninen for helpful discussions and comments. Computer resources provided by IDRIS (CNRS) are gratefully acknowledged.

References

1. D.E. Goldberg: *Genetic algorithms in search, optimization and machine learning* (Addison-Wesley, Reading, Massachusetts 1989)
2. D.M. Deaven, K.M. Ho: Phys. Rev. Lett. **75**, 288 (1995)
3. See, for instance, S.K. Gregurick, M.H. Alexander, B. Hartke: J. Chem. Phys. **104**, 2684 (1996); W.J. Pullan: J. Comp. Chem. **18**, 1096 (1997) and references therein
4. M.D. Wolf, U. Landman: J. Phys. Chem. A **102**, 6129 (1998)
5. A graph $G = (V, E)$ is defined as a set V of sites or vertices $i = 1, \ldots, N$ and a set E of connections, bonds or edges (i, j) with $i, j \in V$. On physical grounds (see (1)) we restrict ourselves to graphs that are simple (i.e., there is no more than one connection between two given sites), connected (i.e., for all $i, j \in V$ there is a a sequence $\{i_1, i_2, \ldots, i_K\}$ with $i_1 = i$ and $i_K = j$ such that $(i_k, i_{k+1}) \in E$ for all $k < K$) and without on-site loops (i.e., if $(i, j) \in E$ then $i \neq j$)

6. Y. Wang, T.F. George, D.M. Lindsay, A.C. Beri: J. Chem. Phys. **86**, 3493 (1987); D.M. Lindsay, Y. Wang, T.F. George: J. Chem. Phys. **86**, 3500 (1987)
7. A. Yoshida, T. Døssing, M. Manninen: J. Chem. Phys. **101**, 3041 (1994)
8. For example, $\alpha = 7$ corresponds to a triangle and $\alpha = 3$, 5 or 6 to a linear chain ($N = 3$). Notice that there are different matrices A_{ij}, and integers $\alpha(A)$, which yield the same graph but with permuted site indices. However, a canonical form may be defined, for example, by the choice of the smallest α (among the equivalent ones). Physically, this yields a cluster where the atoms having the largest i have the smallest local coordination numbers, and vice versa
9. Further details will be published elsewhere
10. G.M. Pastor, R. Hirsch, B. Mühlschlegel: Phys. Rev. Lett. **72**, 3879 (1994); Phys. Rev. B **53**, 10 382 (1996)
11. R. Poteau, F. Spiegelmann: J. Chem. Phys. **98**, 6540 (1993)
12. K. Michaelian: Chem. Phys. Lett. **293**, 202 (1998)