Single-Parent Evolution Algorithm and the Optimization of Si Clusters

Ionel Rata,[1] Alexandre A. Shvartsburg,[2] Mihai Horoi,[1] Thomas Frauenheim,[3]
K. W. Michael Siu,[2] and Koblar A. Jackson[1]
[1]*Physics Department, Central Michigan University, Mount Pleasant, Michigan 48859*
[2]*Department of Chemistry and Centre for Research in Mass Spectrometry, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3*
[3]*Theoretische Physik, Universitat/GH, D33095 Paderborn, Germany*

(Received 9 March 2000)

We describe a novel method for the structural optimization of molecular systems. Similar to genetic algorithms (GA), our approach involves an evolving population in which new members are formed by cutting and pasting operations on existing members. Unlike previous GA's, however, the population in each generation has a single parent only. This scheme has been used to optimize Si clusters with 13–23 atoms. We have found a number of new isomers that are lower in energy than any previously reported and have properties in much better agreement with experimental data.

PACS numbers: 36.40.Mr, 36.40.Wa, 36.40.Qv

One of the most vexing problems in the theory of atomic clusters is the structural optimization of species containing more than a few atoms. This is a formidable task because the number of possible isomers increases explosively with the number of atoms. Once optimal geometries are found, their calculated properties can be compared with measured values to make structural assignments. This is of tremendous fundamental importance, since understanding any molecular system begins by elucidating its structure.

Recently, search strategies based on genetic algorithms (GA) have been used successfully to find the lowest-energy structures for several cluster systems, including Lennard-Jones (LJ) clusters [1], the buckyball [2], and, more recently, Si clusters [3]. GA approaches are conceptually modeled after biological evolution. Parent structures are combined to form offspring, which then compete with the parents and each other to remain in the population in a selection process which bases fitness on cluster total energy. Mating operations are chosen to introduce diversity into the offspring while preserving structural features of the parents. Occasional mutations further increase the diversity of the population. Over successive generations the population evolves to include increasingly optimal structures, ultimately containing the global minimum. To date, GA's developed for cluster systems have used populations containing multiple parents. Here we present an alternative approach involving only a single parent. While this is similar to Monte Carlo procedures, our method retains the critical elements of a GA. Namely, we employ operations that add diversity while preserving favorable attributes, and our lowest-energy structure evolves over successive generations in accordance with a fitness criterion.

At the heart of our method are the two geneticlike operations illustrated in Fig. 1, "piece reflection" and "piece rotation." In both, a cluster is cut by two randomly oriented parallel planes. These divide the cluster into three parts, such that the outer two pieces contain the same random number of atoms. In "reflection," one of the outer pieces is replaced by reflecting the other through a third parallel plane including the cluster center of mass. In "rotation," one of the outer pieces is simply rotated by a random angle about an axis normal to the cutting planes and passing through the cluster center of mass. After each of these transformations, a conjugate gradient relaxation is performed to take the newly formed cluster to the nearest local minimum, which is then defined as the offspring cluster. A lower energy offspring always replaces the parent cluster, while those with a higher energy replace the parent with a Boltzmann probability based on the energy difference between the parent and offspring. We use 1000 K as the temperature parameter in the Boltzmann factor. To institute a "mutation," an offspring is accepted regardless of its energy. Optimization runs begin with random initial configurations. Piece reflection and piece rotation operations are then applied in succession. Alternating the operations proved more efficient than using them at significantly different frequencies. This is continued until the cluster energy does not decrease for at least 100 generations. A

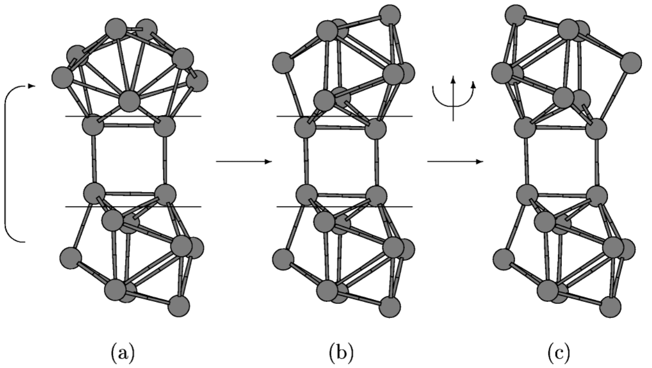

FIG. 1. Geneticlike operations used in our single-parent evolution scheme. The transformation taking cluster (a) to (b) is a piece reflection. That taking (b) to (c) is a piece rotation, in this example by $\pi/2$.

mutation is then used to move the calculation to a different part of the configuration space. The search is ended when several of these mutation cycles fail to result in a lower energy. Using the conjugate gradient minimizations to produce the offspring structures effectively transforms the true energy surface into a step like surface where the energy at any point is defined to be that of the nearest local minimum. The value of this transformation in the structural optimization problem has been discussed recently [4].

We have validated our single-parent method by finding all known global minima [5] for LJ clusters containing up to 105 atoms, including the nonicosahedral structures for $n = 75-77$ and $102-104$ that were not found in an earlier GA study [1]. Locating the LJ minima from unbiased starting points demonstrates the basic effectiveness of the method. However, a more severe test lies in finding optimal structures for Si clusters, a problem that has been the focus of tremendous experimental and theoretical effort. (Reference [6] provides a recent review of this work.) In contrast to the simple pair potentials used for LJ clusters, the covalent bonding in Si clusters can only be described adequately using quantum mechanical methods. We adopt a hierarchical approach in which the fast, but approximate, density-functional-based tight-binding (DFTB) [7] method is used in the GA to locate low-energy isomers. These are then relaxed using more accurate, but computationally more demanding, density functional theory (DFT) methods. The DFTB has proven reliable for Si clusters [8], as it produces local minima with the same bonding topologies as the DFT, and, for clusters with $n \leq 10$, gives the same ordering of the low-lying isomers [8]. However, all our energetics orderings are based solely on DFT values. Our DFT calculations [9] employ an all-electron formalism and extensive Gaussian orbital basis sets consisting of $6s$-, $5p$-, and $3d$-type orbitals on each atom. All calculations were performed using two generalized gradient approximation (GGA) functionals, the Perdew, Burke, and Ernzerhof [10] version and Perdew-Wang-Becke 88 (PWB). The two functionals give essentially identical results. We have chosen to quote the PWB cohesive energies below in order to facilitate comparison with previously published data [6,11,12].

The main focus of our calculations has been optimizing Si_n cations and anions, since most experiments study charged clusters. The energy surfaces for Si_n^+ and Si_n^- were surveyed directly by using the appropriate charge state in the DFTB calculations. This proved to be clearly superior to searching the neutral surfaces and then re-optimizing the resulting low-energy neutral structures for the cations and anions [6,12]. We made a number of GA runs for each cluster size and charge state studied. All structures coming within 50 meV/atom of the lowest one were relaxed in the GGA to reveal the global minimum. Applying this approach to charged Si clusters with $n \leq 20$, we have found for $n \geq 13$ several new morphologies (Fig. 2) that are lower in energy than any previously published [3,6,12].

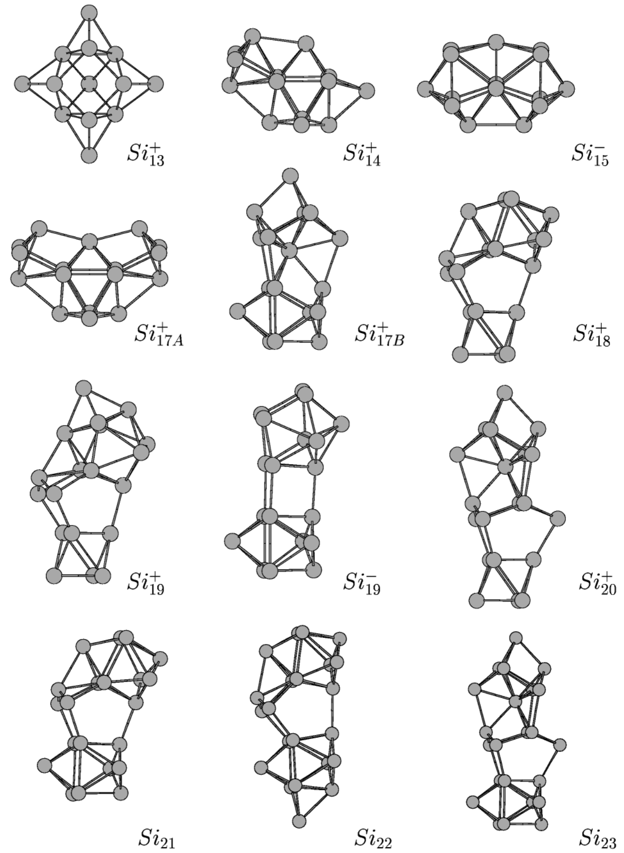

FIG. 2. Silicon clusters optimized using our single-parent evolution method. The structures for Si_{19} and Si_{20} neutrals are essentially identical to the cations depicted here.

Properties calculated for these new geometries are compared with measurements in Table I.

The cluster dissociation energy is a useful "depth gauge" for the minima on potential energy surfaces [11,13]. The dissociation energy is computed as the difference in cohesive energy between the precursor cluster and dissociation fragments along the lowest-energy pathway. The cohesive energies for the fragments are known. Thus, if the global minimum at a given size is missed, the calculated dissociation energy will fall short of the measured value. The results in Table I for cations up to Si_{20}^+ are in excellent agreement with experiment [14], establishing that they all must be at least very close to the respective global minima. For Si_{13}^+ and Si_{19}^+ the new dissociation energies are dramatic improvements over previous values [11], reflecting large gains in cohesive energies for these clusters. The dissociation energy computed for Si_{20}^+ is also significantly improved over the previous result [11], but still does not recover the measured value fully. Unfortunately, the dissociation energies of Si_n^- have not been measured.

The predicted lowest-energy dissociation channel is another crucial test of cluster energetics [11,13]. Previously calculated fragmentation pathways for Si_n^+ [11] match the results of collision-induced-dissociation experiments [15]

TABLE I. Properties calculated for the new Si cluster isomers in Fig. 2 and corresponding measurements. The second and third columns list the calculated cohesive energies (PWB) for our new geometries and the improvement this represents over the previous structures (based on calculations using the same code and basis sets) [3,6,12,19,20]. Measured mobilities are for the major peaks observed in Ref. [17]; measured dissociation energies are from Ref. [14].

	Cohesive energy (eV/atom)		Inverse mobility $(\mathrm{V\,s/m^2})$		Dissociation energy (eV)	
			Theory	Expt.	Theory	Expt.
$\mathrm{Si}_{13}^{+}\mathrm{C}_{2v}(\mathrm{II})$	3.132	+0.030	1675	1680	2.71	2.70
$\mathrm{Si}_{14}^{+}\mathrm{C}_{s}(\mathrm{III})$	3.188	+0.007	1756	1755	2.58	2.70
$\mathrm{Si}_{17A}^{+}\mathrm{C}_{2v}$	3.302	+0.004	1991	1985	2.01	2.10
$\mathrm{Si}_{17B}^{+}\mathrm{C}_{3v}(\mathrm{II})$	3.301	+0.003	1995	1985	1.99	2.10
$\mathrm{Si}_{18}^{+}\mathrm{C}_{s}$	3.345	+0.005	2107	2115	2.01	2.15
$\mathrm{Si}_{19}^{+}\mathrm{C}_{1}$	3.380	+0.011	2184	2200	2.62	2.70
$\mathrm{Si}_{20}^{+}\mathrm{C}_{3v}$	3.393	+0.005	2284	2245	1.80	2.15
$\mathrm{Si}_{15}^{-}\mathrm{C}_{2v}$	3.860	−0.002	1893	1915		
$\mathrm{Si}_{19}^{-}\mathrm{C}_{1}(\mathrm{II})$	3.871	+0.011	2258	2265		
$\mathrm{Si}_{19}\mathrm{C}_{1}$	3.719	+0.004				
$\mathrm{Si}_{20}\mathrm{C}_{3v}$	3.736	+0.014				
$\mathrm{Si}_{21}\mathrm{C}_{s}$	3.727	+0.043				
$\mathrm{Si}_{22}\mathrm{C}_{s}$	3.737	+0.009				
$\mathrm{Si}_{23}\mathrm{C}_{3v}$	3.747	+0.024				

in nearly all cases. One exception is Si_{23}^{+}, which decomposes into Si_{13}^{+} as the primary product and Si_{16}^{+} as the secondary one. However, previous calculations found the two channels to be degenerate [11]. The substantially lower energy Si_{13}^{+} geometry uncovered here renders the pathway leading to this product much more favorable than that yielding Si_{16}^{+}, in agreement with the measurement.

Ionic mobility in a buffer gas is an important structural probe, as the mobilities for various candidate geometries can be accurately predicted. Agreement between calculated and measured mobilities is a necessary (although generally not sufficient) criterion for a structural assignment. We have evaluated the room-temperature mobilities in He for the new Si_{n}^{+} and Si_{n}^{-} structures shown in Fig. 2 using the most accurate techniques available, trajectory calculations [16] and scattering on electron density isosurfaces [12]. The values for all new Si_{n}^{+} structures ($n = 13, 24, 17-20$) are in very good agreement with the measurements [17]. The situation for $n = 17-19$ is particularly interesting, since high resolution mobility data [17] indicate the coexistence of distinct isomers at these sizes. Previous lowest-energy structures for Si_{18}^{+} (C_{3v}) and Si_{19}^{+} (C_{2v}) do not match the mobility data for major peaks at 2115 and 2200 $\mathrm{V\,s/m^2}$, respectively, but fit secondary peaks at 2155 $\mathrm{V\,s/m^2}$ ($n = 18$) and 2075 $\mathrm{V\,s/m^2}$ ($n = 19$) [12]. However, the mobilities computed for the new geometries (Fig. 2) match the major peaks. Thus, in these cases we can now account for not only the major peaks, but also the origin and relative abundances of all features observed. For Si_{17}^{+}, the two new, nearly degenerate isomers (Fig. 2) have virtually identical mobilities that are closer to the major experimental peak at 1985 $\mathrm{V\,s/m^2}$ than that of the C_{3v} geometry found previously [6]. For Si_{20}^{+}, the mobility computed for the prolate structure shown in Fig. 2 agrees with experiment much better than that for the C_{s} near-spherical structure found earlier [6]; however, the predicted mobility remains somewhat too high (Table I). Considering also that the dissociation energy calculated for this structure is short of the measurement, the true global minimum for Si_{20}^{+} is probably still to be found.

For Si_{n}^{-} in the $n \leq 20$ range, we have found new ground states for $n = 15$ and 19 (Fig. 2). The new $\mathrm{Si}_{15}^{-}\mathrm{C}_{2v}$ is essentially degenerate with the previous C_{s} (III) geometry [12], but its mobility is much closer to the experimental value. For Si_{19}^{-} the agreement in mobility is dramatically improved over that of the previous best C_{2v} structure [12]. In addition, the photoelectron spectra simulated for both our new structures agree with experiment [18], while those for previously published geometries [12] do not.

The results in Table I show that our new Si_{n} cations and anions are lower in energy than all previously reported geometries. Furthermore, except for Si_{20}^{+}, their calculated properties are in excellent agreement with three independent experimental measures: ionic mobilities, dissociation energies and pathways, and photoelectron spectra. Taken together, this is strong evidence that the isomers observed in experiments are the global minima for sizes up to $n = 20$. It therefore appears that cluster growth in this size range is thermodynamically controlled. The results for Si_{17}^{+}, Si_{18}^{+}, and Si_{19}^{+} strongly support this picture, since the relative abundances of competing isomers observed in mobility measurements [17] are consistent with their calculated energetic ordering.

For neutral clusters with $n \leq 20$, we have found new lowest-energy geometries for both $n = 19$ and 20 (they are essentially identical to those of the cations in Fig. 2). For both sizes, the structures differ significantly from the previous best prolate geometries [3] that are stacks of Si_9 and Si_{10} units in the tricapped-trigonal-prism (TTP) motif. The energy gain for Si_{20} is substantial, in excess of 0.4 eV. Recently, Mitas *et al.* [19] proposed another Si_{20} isomer constructed from two Si_{10} TTP units. This geometry is competitive with the best previous structure [3] in GGA, and somewhat lower in high-level quantum Monte Carlo (QMC) calculations. However, it lies above the Si_{20} geometry found here by 0.3 eV (PWB). It would be interesting to compare the QMC energies of the two structures.

Considering all the new structures shown in Fig. 2, TTP subunits are still present, but less prevalent than in previously reported geometries for clusters in this size range [3]. To follow the structural trends, we used our GA for Si_{n} neutrals with 21–23 atoms. The species shown in Fig. 2 are lower in energy than the $n = 21$ stuffed cage of Pederson *et al.* [20] and the $n = 22$ and 23 stacked TTP structures of Ho *et al.* [3], respectively, the lowest energy isomers previously found for these sizes. While TTP units are conspicuous in the new clusters, they are not simply stacked as in earlier geometries [3]. Indeed, stable six- and eight-atom subunits can also be seen, as in Si_{20} (Fig. 2). In addition, a six-atom bridge unit appears as an important structural component in some of the larger clusters, for example, Si_{20}. This unit evidently resembles the six-atom "chair" in the diamond structure of bulk Si. A fundamental question regarding the evolution of cluster structure concerns the onset of bulklike properties. Present results indicate that the first structural elements of bulk Si may appear already at $n \leq 20$.

The use of a single parent in our evolution procedure versus multiple parents in genetic algorithms may seem to limit the diversity of searches. However, our findings for Si clusters clearly demonstrate the power of the method. To rationalize this effectiveness, we appeal again to biology. The evolution of a species represents a change in its genetic code over many generations. Yet the alterations from one generation to the next are quite modest, affecting only a small portion of the entire code. More dramatic changes, such as those occurring when the genes of different species are combined or a major mutation takes place, rarely produce viable offspring. In molecular optimization, the extensive structural changes wrought by joining pieces from different clusters may be analogous to profound genetic change and may therefore lead to a large fraction of unfavorable products. The changes invoked in the single-parent approach are, by comparison, less sweeping, and this may be a key to its efficiency.

From a more physical viewpoint, our method can be likened to the industrial technique of "zone refining," in which the crystallinity of a sample is improved by repeatedly dragging it through a narrow heating element. Structural defects are annealed out as slices that are systematically melted through the sample resolidify when the heating element recedes. The cuts made in our method may be functionally similar to these slices, since the adjacent regions are subject to the greatest rearrangements in the subsequent structural relaxations. It appears critical then that, over successive generations, cuts are made throughout the entire cluster and not just the center of mass.

To summarize, we have described a new evolutionary algorithm for molecular geometry optimization based on a single-parent population. Applying the method to Si clusters, we have found new Si_n cation, neutral, and anion geometries in the $n = 13-23$ range that are lower in energy than previously known structures. Ionic mobilities, dissociation energies/pathways and photoelectron spectra calculated for the new charged structures are all in excellent agreement with experiment. This indicates that the growth of Si_n species is thermodynamically controlled at least up to $n = 20$. Finally, the new structures reveal that the growth habit of prolate Si clusters features, in addition to TTP units, other significant structural motifs.

We are grateful to B. Liu, J. Müller, Dr. S. Ogut, Professor J. R. Chelikowsky, Professor G. Gantefor, and Professor K.-M. Ho for providing unpublished data and extensive discussions. We thank Dr. J. Grossman and Dr. L. Mitas for sending us their new Si_{20} geometry [19], and Dr. G. Jungnickel for the use of his Dylax DFTB code. This work has been supported by Research Corporation (K. A. J.), National Science Foundation Grant No. DMR-RUI9972333 (K. A. J.), and National Science and Engineering Research Council of Canada.

[1] D. M. Deaven *et al.,* Chem. Phys. Lett. **256**, 195 (1996).
[2] D. M. Deaven and K. M. Ho, Phys. Rev. Lett. **75**, 288 (1995).
[3] K. M. Ho *et al.,* Nature (London) **392**, 582 (1998).
[4] D. J. Wales and H. A. Scheraga, Science **285**, 1368 (1999); J. P. K. Doye and D. J. Wales, Phys. Rev. Lett. **80**, 1357 (1998).
[5] D. J. Wales and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997).
[6] B. Liu *et al.,* J. Chem. Phys. **109**, 9401 (1998).
[7] D. V. Porezag *et al.,* Phys. Rev. B **51**, 12 947 (1995); G. Seifert, D. Porezag, and Th. Frauenheim, Int. J. Quantum Chem. **98**, 185 (1996).
[8] A. Sieck *et al.,* Phys. Rev. A **56**, 4890 (1997).
[9] M. R. Pederson and K. A. Jackson, Phys. Rev. B **41**, 7453 (1990); K. A. Jackson and M. R. Pederson, Phys. Rev. B **42**, 3276 (1990).
[10] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[11] A. A. Shvartsburg *et al.,* Phys. Rev. Lett. **81**, 4616 (1998).
[12] A. A. Shvartsburg *et al.,* J. Chem. Phys. **112**, 4517 (2000).
[13] A. A. Shvartsburg *et al.,* Phys. Rev. Lett. **83**, 2167 (1999).
[14] M. F. Jarrold and E. C. Honea, J. Phys. Chem. **95**, 9181 (1991).
[15] M. F. Jarrold and J. E. Bower, J. Phys. Chem. **92**, 5702 (1988).
[16] M. F. Mesleh *et al.,* J. Phys. Chem. **100**, 16 082 (1996); A. A. Shvartsburg, G. C. Schatz, and M. F. Jarrold, J. Chem. Phys. **108**, 2416 (1998).
[17] R. R. Hudgins *et al.,* J. Chem. Phys. **111**, 7865 (1999).
[18] J. Müller *et al.* (to be published).
[19] L. Mitas *et al.,* Phys. Rev. Lett. **84**, 1479 (2000).
[20] M. R. Pederson *et al.,* Phys. Rev. B **54**, 2863 (1996).