Global Optimization by Basin-Hopping and the Lowest Energy Structures of 
Lennard-Jones Clusters Containing up to 110 Atoms

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We describe a global optimization technique using ‘basin-hopping’ in which the potential energy 
surface is transformed into a collection of interpenetrating staircases. This method has been designed 
to exploit the features which recent work suggests must be present in an energy landscape for efficient 
relaxation to the global minimum. The transformation associates any point in configuration space 
with the local minimum obtained by a geometry optimization started from that point, effectively 
removing transition state regions from the problem. However, unlike other methods based upon 
hypersurface deformation, this transformation does not change the global minimum. The lowest 
known structures are located for all Lennard-Jones clusters up to 110 atoms, including a number 
that have never been found before in unbiased searches.

I. INTRODUCTION

Global optimization is a subject of intense current interest. Improved global optimization methods could 
be of great economic importance, since improved solutions to travelling salesman type problems, the routing of 
circuitry in a chip, the active structure of a biomolecule, etc., equate to reduced costs or improved performance. In 
chemical physics the interest in efficient global optimization methods stems from the common problem of finding 
the lowest energy configuration of a (macro)molecular system. For example, it seems likely that the native 
structure of a protein is structurally related to the global minimum of its potential energy surface (PES). If this 
global minimum could be found reliably from the primary amino acid sequence, this knowledge would provide 
new insight into the nature of protein folding and save biochemists many hours in the laboratory. Unfortunately, this goal is far from being realized. Instead the development of global optimization methods has usually 
concentrated on much simpler systems.

Lennard-Jones (LJ) clusters represent one such test system. Here the potential is

\[ E = 4\epsilon \sum_{i<j} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right], \]

where \( \epsilon \) and \( 2^{1/6} \sigma \) are the pair equilibrium well depth and separation, respectively. We will employ reduced units, i.e. \( \epsilon = \sigma = 1 \) throughout. Much of the initial interest in LJ clusters was motivated by a desire to calculate 
nucleation rates for noble gases. However, as a result of the wealth of data generated, the LJ potential has 
been used not only for studying global optimization but also the effects of finite size on phase transitions such as 
melting. Through the combined efforts of many workers likely candidates for the global minimum of LJ \( N \) clusters 
have been found up to \( N = 147 \). This represents a significant achievement since extrapolation of Tsai and 
Jordan’s comprehensive enumeration of minima for small LJ clusters suggests that the PES of the 147-atom clus-
ter possesses of the order of \( 10^{60} \) minima.

Previous studies have revealed that the Mackay icosahedron provides the dominant structural motif for LJ clusters in the size range 10–150 atoms. Complete icosahedra are possible at \( N = 13, 55, 147, \ldots \) At most intermediate sizes the global minimum consists of a Mackay icosahedron at the core covered by a low energy overlayer. As a consequence of the phase behaviour of LJ clusters, finding these global minima is relatively easy. Studies have shown that in the region of the solid-liquid transition the cluster is observed to change back and forth between a liquid-like form and icosahedral structures. As a result of this ‘dynamic coexistence’ a method as crude as molecular dynamics within the melting region coupled with systematic minimization of configurations generated by the trajectory is often sufficient to locate the global minimum.

![Non-icosahedral Lennard-Jones global minima.](image-url)
However, there are a number of sizes at which the global minimum is not based on an icosahedral structure. These clusters are illustrated in Figure 1. For LJ\textsubscript{38} the lowest energy structure is a face-centred-cubic (fcc) truncated octahedron\cite{38} and for $N = 75, 76, 77, 102, 103$ and 104 geometries based on Marks’ decahedra\cite{33,30} are lowest in energy.\cite{42} For these cases finding the lowest minimum is much harder because the global minimum of free energy only becomes associated with the global potential energy minimum at temperatures well below melting where the dynamics of structural relaxation are very slow. For LJ\textsubscript{38}, the microcanonical temperature for the transition from face-centred cubic to icosahedral structures has been estimated to be about $0.12k^{-1}$, where $k$ is the Boltzmann constant, and for LJ\textsubscript{75} the estimate for the decahedral to icosahedral transition is about $0.09k^{-1}$\cite{13} (For comparison, melting typically occurs at about $T = 0.2 – 0.3k^{-1}$.)

The topography of the PES can also play a key role in determining the ease of global optimization.\cite{1} A detailed study of the LJ\textsubscript{38} PES has shown that there is a large energy barrier between the fcc and icosahedral structures which correspond to well-separated regions of the PES. Furthermore, fcc and decahedral structures have less polytetrahedral character than icosahedral structures, and hence they have less in common with the liquid-like state, which is characterized by disordered polytetrahedral packing.\cite{32,41}\cite{31} Since the vast majority of configuration space is dominated by ‘liquid-like’ configurations, it is therefore harder to find global minima based upon fcc and decahedral packing using unbiased searches.

These considerations explain why global optimization methods have only recently begun to find the truncated octahedron, and why, until now, the Marks’ decahedron has never been found by an unbiased global optimization method. The greater difficulty of finding the LJ\textsubscript{75} global minimum compared to LJ\textsubscript{38} can probably be explained by the slightly smaller transition temperature, the sharper transition and the much larger number of local minima.\cite{30} The global minimum of the deformed PES is then mapped back to the original surface in the hope that this will lead back to the global minimum of the original PES. The distinctions between the various methods of this type lie in the type of transformations that are used, which include applying the diffusion equation\cite{31} increasing the range of the potential,\cite{40} and shifting the position of the potential minimum towards the origin.\cite{41} The performance of hypersurface deformation methods has been variable: the potential shift approach managed to find the 38-atom truncated octahedron, but other workers report difficulties\cite{34} for the trivial cases of LJ\textsubscript{8} and LJ\textsubscript{9} where there are only 8 and 21 minima on the PES, respectively.

Although intuitively appealing, the problem with hypersurface deformation is that there is no guarantee that the global minimum on the deformed PES will map onto the global minimum of the original surface. This difficulty is clearly illustrated when we consider Stillinger and Stillinger’s suggestion of increasing the range of the potential:\cite{31} it has been shown that the global minimum may in fact depend rather sensitively on the range of the potential, with the appearance of numerous ‘range-induced’ transitions.\cite{30}

Other methods include those based on ‘annealing’. Such approaches take advantage of the simplification in the free energy landscape that occurs at high tempera-
turedes, and attempt to follow the free energy global minimum as the temperature is decreased. At zero Kelvin the free energy global minimum and the global minimum of the PES must coincide. Standard simulated annealing was used by Wille to find a few new minima at small sizes but does not appear to have been systematically applied to LJ clusters. More sophisticated variants of this technique include gaussian density annealing and analogues but again some appear to fail at small sizes.

The difficulty with the annealing approach methods is that, if the free energy global minimum changes at low temperatures where dynamical relaxation is slow, the algorithms will become stuck in the structure corresponding to the high temperature free energy global minimum. Such methods are therefore likely to experience difficulties in finding the global minima for LJ and LJ clusters. In the language employed in recent protein folding literature annealing will fail when $T_f < T_g$, where $T_f$ is the ‘folding’ temperature below which the global potential energy and free energy minima coincide, and $T_g$ is the ‘glass’ temperature at which the system effectively becomes trapped in a local minimum.

Another method which attempts to reduce the effects of barriers on the PES makes use of quantum tunnelling. The diffusion Monte Carlo approach is used to find the ground state wavefunction, which should become localized at the global minimum as $\hbar$ is decreased to zero. A more rigorous approach has been applied by Maranas and Floudas, who found upper and lower bounds for the energy of the global minimum. However, the computational expense of this method, which scales as $2^N$ with the number of atoms, means that it has only been used for small systems. Most of the above studies, along with the recently described ‘pivot method’ and ‘taboo search’, have yet to prove their usefulness by passing the first hurdle for LJ suggested above. However, this does not necessarily mean that these approaches should be discounted, since some authors have only applied their algorithms to smaller clusters and may not have run enough searches to achieve convergence.

In the present work we present the results of a ‘basin-hopping’ global optimization technique for Lennard-Jones clusters. All the known lowest energy structures up to $N = 110$ have been located successfully, including three minima not previously reported. (See Tables 1 and 2.) This method is also the first unbiased algorithm to find the global minima based on the Marks decahedron around LJ and LJ. For reference, we collect the rather scattered results previously reported for LJ clusters to provide a complete catalogue of the energies and point groups of the lowest energy minima that we know of. The results have been collected in the first entry of the Cambridge Cluster Database at http://brian.ch.cam.ac.uk.

II. METHOD

The present approach has been guided by previous work on energy landscapes which has identified features that enable the system to locate its global minimum efficiently. In particular, analysis of model energy landscapes using a master equation approach for the dynamics, has provided good evidence that such a surface should have a large potential energy gradient and the lowest possible transition state energies or rearrangement barriers. These results immediately suggest a simple way to transform the PES which does not change the global minimum, nor the relative energies of any local minima. We consider the transformed energy $\tilde{E}$ defined by:

$$\tilde{E}(\mathbf{X}) = \min \{ E(\mathbf{X}) \},$$

where $\mathbf{X}$ represents the $3N$-dimensional vector of nuclear coordinates and $\min$ signifies that an energy minimization is performed starting from $\mathbf{X}$. In the present work energy minimizations were performed using the Polak-Ribiere variant of the conjugate gradient algorithm. Hence the energy at any point in configuration space is assigned to that of the local minimum obtained by the given geometry optimization technique, and the PES is mapped onto a set of interpenetrating staircases with plateaus corresponding to the set of configurations which lead to a given minimum after optimization. A schematic view of the staircase topography that results from this transformation is given in Figure 2. These plateaus, or basins of attraction, have been visualized in previous work as a means to compare the efficiency of different transition state searching techniques.

![Energy Transformation](https://example.com/energy_transformation.png)

FIG. 2. A schematic diagram illustrating the effects of our energy transformation for a one-dimensional example. The solid line is the energy of the original surface and the dashed line is the transformed energy, $\tilde{E}$.

The energy landscape for the function $\tilde{E}(\mathbf{X})$ was explored using a canonical Monte Carlo simulation at a constant reduced temperature of 0.8. At each step all coordinates were displaced by a random number in the range $[-1,1]$ times the step size, which was adjusted to give an acceptance ratio of 0.5. The nature of the transformed surface allowed relatively large step sizes of between 0.36–0.40. For each cluster in the range considered
seven separate runs were conducted. Five of these each consisted of 5000 Monte Carlo steps starting from different randomly generated configurations of atoms confined to a sphere of radius 5.5 reduced units. The subsequent geometry optimizations employed a container of radius one plus the value required to contain the same volume per atom as the fcc primitive cell. The container should not be too tight. In the present work we required the root-mean-square (RMS) gradient to fall below 0.1 \( \epsilon \) between consecutive steps in the conjugate gradient search. The root-mean-square (RMS) gradient was satisfactory, but this was subsequently found to cause problems for clusters containing more than about 60 atoms. The lowest energy structures obtained during the canonical simulation were saved and reoptimized with tolerances of \( 10^{-4} \) and \( 10^{-9} \) for the RMS gradient and the energy difference, respectively. The final energies are accurate to about six decimal places.

Several other techniques were used in these calculations, namely seeding, freezing and angular moves. Here we used the pair energy per atom, \( E(i) \), defined as

\[
E(i) = 4 \epsilon \sum_{j \neq i} \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6}, \tag{3}
\]

so that the total energy is

\[
E = \frac{1}{2} \sum_i E(i). \tag{4}
\]

If the highest pair energy rose above a fraction \( \alpha \) of the lowest pair energy then an angular move was employed for the atom in question with all other atoms fixed. \( \alpha \) was adjusted to give an acceptance ratio for angular moves of 0.5 and generally converged to between 0.40 and 0.44. Each angular displacement consisted of choosing random \( \theta \) and \( \phi \) spherical polar coordinates for the atom in question, taking the origin at the centre of mass and replacing the radius with the maximum value in the cluster.

The two remaining runs for each size consisted of only 200 Monte Carlo steps starting from the global minima obtained for the clusters containing one more and one less atom. When starting from \( \text{LJ}_{N-1} \) the \( N - 1 \) atoms were frozen for the first 100 steps, during which only angular moves were attempted for the remaining atom, starting from a random position outside the core. When starting from \( \text{LJ}_{N+1} \) the atom with the highest pair energy, \( E(i) \), was removed and 200 unrestricted Monte Carlo moves were attempted from the resulting geometry.

The above basin-hopping algorithm shares a common philosophy with our previous approach in which steps were taken directly between minima using eigenvector-following to calculate pathways\(^{26}\). The latter method is similar to that described recently by Barkema and Mousseau\(^{27}\) in their search for well-relaxed configurations in glasses. Although the computational expense of transition state searches probably makes this method uncompetitive for global optimization, our study illustrated the possible advantage of working in a space in which only the minima are present. The basin-hopping algorithm differs in that it is applied in configuration space to a transformed surface, rather than in a discrete space of minima, and steps are taken stochastically. The genetic algorithms described by Deaven et al.\(^{28}\) and Niesse and Mayne\(^{29}\) used conjugate gradient minimization to refine the local minima which comprise the population of structures that are evolved in their procedure. Hence these authors are in effect studying the same transformed surface as described above, but explore it in a rather different manner. We suspect that the success of their methods is at least partly due to the implicit use of the transformed surface \( \tilde{E} \).

The transformation of the PES also reduces the barriers to dissociation. Therefore, to prevent evaporation either the cluster can be placed in a tight-fitting container or the coordinates of the current point in configuration space can be reset to that of the minimum after each successful step. In this paper we used the latter method and then the present approach is essentially the same as the Monte Carlo-minimization algorithm of Li and Scheraga\(^{30}\) who applied it to search the conformational space of the pentapeptide [Met\(^5\)]enkephalin. A similar method has recently been used by Baysal and Meirovitch\(^{31}\) to search the conformational space of cyclic polypeptides.

![FIG. 3. Lennard-Jones global minima that have not previously been reported.](image)

III. RESULTS

The basin-hopping algorithm has successfully located all the lowest known minima up to \( \text{LJ}_{110} \), including all the non-icosahedral structures illustrated in Figure 2 (sizes 38, 75, 76, 77, 102, 103 and 104) and three new geometries based upon icosahedra illustrated in Figure 3 (sizes 69, 78 and 107). We believe that this is the first time any of the six decahedral global minima have been located by an unbiased algorithm. The total number of searches was fixed in our calculations to provide a simple reference criterion. In fact, most of the global minima were...
found in more than one of the separate Monte Carlo runs. The global minima for the smallest clusters were located within a few steps in each of the seven runs. To give a better idea of how the algorithm performed we will provide some more details for the sizes with non-icosahedral or newly discovered icosahedral global minima.

For LJ$_{35}$ the truncated octahedron was found in four out of five of the longer unseeded runs; the first success occurred within a thousand Monte Carlo steps on average. Not surprisingly, the global minimum was not located in the shorter runs starting from the structurally unrelated global minima for $N = 37$ and 39. For LJ$_{75}$ the global minimum was found in just one of the longer Monte Carlo runs, and again in the short run from the global minimum for LJ$_{76}$. However, the latter minimum was only found in the short runs seeded from the LJ$_{75}$ and LJ$_{77}$ decahedra. Similarly, the LJ$_{77}$ global minimum was only found in the short run seeded from the LJ$_{76}$ decahedron. The decahedral global minimum for LJ$_{75}$ was found in four out of 100 Monte Carlo runs of 5000 steps each, a frequency which fits in quite well with our results for LJ$_{75}$, LJ$_{76}$ and LJ$_{77}$. A successful run requires an initial geometry which falls within the decahedral catchment area; all the other runs produce the lowest icosahedral minimum after which the decahedron is never found. It would obviously be possible to locate global minima based upon decahedra more efficiently by biasing the starting configuration, but our intention was to analyze the performance of an unbiased algorithm in the present work.

The pattern for LJ$_{75}$–LJ$_{77}$ is repeated for LJ$_{102}$–LJ$_{103}$. For LJ$_{102}$ the decahedral global minimum was located in one of the longer Monte Carlo runs and in the short run seeded from the global minimum of LJ$_{103}$. The decahedral minima for LJ$_{103}$ and LJ$_{104}$ were only found in short runs seeded from larger or smaller decahedra. The decahedral global minimum for LJ$_{102}$ was found in three out of 100 Monte Carlo runs of 5000 steps each.

The three new icosahedral global minima all have an atom missing from a vertex of the underlying Mackay icosahedron (Figure 3). This is a possibility that Norbury did not consider in his restricted search of the icosahedral configuration space. The new LJ$_{69}$ global minimum was found in three of the five longer Monte Carlo runs and in the short run seeded from LJ$_{70}$. The new global minimum for LJ$_{78}$ was only found in the short run seeded from LJ$_{75}$. The new minimum for LJ$_{107}$ was found in one of the longer Monte Carlo runs and in the short run seeded from LJ$_{108}$.

We also performed a few preliminary runs for LJ$_{192}$ and LJ$_{201}$, sizes at which a complete Marks decahedron and a complete truncated octahedron occur, respectively. For LJ$_{192}$ the Marks decahedron has energy $-1175.697144$. This structure was not found in 100 MC runs of 10000 steps each; instead the lowest minimum located had an energy of $-1174.919801$. For LJ$_{201}$ the truncated octahedron has energy $-1232.731497$. However, we located a structure of energy $-1236.124253$ which is based upon icosahedral packing. This minimum was found in three out of 50 MC runs of 10000 steps each. For these larger systems greater efficiency could probably be achieved by varying the temperature and other parameters of the MC search.

**IV. CONCLUSIONS**

We have presented the results of a ‘basin-hopping’ or ‘Monte Carlo-minimization’ approach to global optimization for atomic clusters bound by the Lennard-Jones potential containing up to 110 atoms. All the lowest known minima were located successfully, including the seven structures based upon fcc or decahedral packing and three new global minima based upon icosahedra. Of the latter ten structures, only the smallest has been located before by an unbiased algorithm, to the best of our knowledge.

The method is based upon a hypersurface deformation in which the potential energy surface (PES) is converted into a set of plateaus each corresponding to a basin of attraction of a local minimum on the original PES. This process removes all the transition state regions but does not affect the energies of the minima. On the original PES, most trajectories that approach the boundary between two basins of attraction are reflected back due to the high potential energy; only if the trajectory is along a transition state valley does passage between basins become likely. In contrast, on the transformed PES it is feasible for the system to hop between basins at any point along the basin boundary which dramatically reduces the time scale for interbasin motion. We speculate that the success of a previous genetic algorithm applied to the same clusters may be at least partly due to the fact that the same space is implicitly considered in that approach.

The efficiency of the present approach could doubtless be improved by combining it with various other techniques. The most obvious short-cut would be to start not from initial random configurations but from seeds with either decahedral, icosahedral or fcc morphologies. We have already checked that such biasing is indeed effective, but our aim in the present paper was to gauge the performance of the unbiased algorithm. The temperature at which our Monte Carlo runs were conducted was also not optimized systematically.

Finally, as we noted in the introduction, global optimization for Lennard-Jones clusters at most sizes is a relatively easy task. A more stringent and general test is provided by Morse clusters which exhibit different structural behaviour as a function of the range of the potential. At short range the task is particularly difficult because the PES is very rugged—the number of minima and the barrier heights increase as the range is decreased.
TABLE I. Global minima of LJ$_N$ for $N \leq 110$. The references in which each minimum was first reported (to the best of our knowledge) are given, and † indicates the present work. We intend to maintain an updated database of energies and coordinates for LJ and Morse clusters on our web site: http://brian.ch.cam.ac.uk.

| N  | Point group | Energy/ε | Ref. | N  | Point group | Energy/ε | Ref. |
|----|-------------|----------|------|----|-------------|----------|------|
| 2  | $D_{6h}$    | -1.000000 |       | 57 | $C_3$       | -288.342023 |       |
| 3  | $D_{3h}$    | -3.000000 |       | 58 | $C_{3v}$    | -294.378148 |       |
| 4  | $T_d$       | -6.000000 |       | 59 | $C_{2v}$    | -299.738070 |       |
| 5  | $D_{6h}$    | -9.103852 |       | 60 | $C_2$       | -305.875476 |       |
| 6  | $O_h$       | -12.712062|       | 61 | $C_{2v}$    | -312.008896 |       |
| 7  | $D_{5h}$    | -16.503584|       | 62 | $C_1$       | -317.353901 |       |
| 8  | $C_s$       | -19.821489|       | 63 | $C_1$       | -323.489734 |       |
| 9  | $C_{2v}$    | -21.133660|       | 64 | $C_3$       | -329.620147 |       |
| 10 | $C_{3v}$    | -24.422532|       | 65 | $C_2$       | -334.971532 |       |
| 11 | $C_{2v}$    | -32.765970|       | 66 | $C_1$       | -341.110599 |       |
| 12 | $C_{5v}$    | -37.967600|       | 67 | $C_{3v}$    | -347.252007 |       |
| 13 | $D_{3h}$    | -44.326801|       | 68 | $C_1$       | -353.394542 |       |
| 14 | $C_{3v}$    | -47.845157|       | 69 | $C_{5v}$    | -359.882566 |       |
| 15 | $C_{2v}$    | -52.22627 |       | 70 | $C_{5v}$    | -366.892521 |       |
| 16 | $C_s$       | -56.815742|       | 71 | $C_{5v}$    | -373.349661 |       |
| 17 | $C_2$       | -61.317995|       | 72 | $C_s$       | -378.637253 |       |
| 18 | $C_{5v}$    | -66.530949|       | 73 | $C_s$       | -384.789377 |       |
| 19 | $D_{5h}$    | -72.659782|       | 74 | $C_s$       | -390.908500 |       |
| 20 | $C_{2v}$    | -77.179043|       | 75 | $D_{5h}$    | -397.492331 |       |
| 21 | $C_{2v}$    | -81.684571|       | 76 | $C_s$       | -402.894866 |       |
| 22 | $C_s$       | -86.090782|       | 77 | $C_{2v}$    | -409.083517 |       |
| 23 | $D_{3h}$    | -92.844472|       | 78 | $C_s$       | -414.794401 |       |
| 24 | $C_s$       | -97.348815|       | 79 | $C_{2v}$    | -421.810897 |       |
| 25 | $C_s$       | -102.372663|      | 80 | $C_s$       | -428.083564 |       |
| 26 | $T_d$       | -108.315616|      | 81 | $C_{2v}$    | -434.343643 |       |
| 27 | $C_{2v}$    | -112.87584|       | 82 | $C_1$       | -440.550425 |       |
| 28 | $C_s$       | -117.822402|      | 83 | $C_{2v}$    | -446.924004 |       |
| 29 | $D_{3h}$    | -123.587371|      | 84 | $C_1$       | -452.657214 |       |
| 30 | $C_{2v}$    | -128.286571|      | 85 | $C_{3v}$    | -459.055799 |       |
| 31 | $C_s$       | -133.586422|      | 86 | $C_1$       | -465.384493 |       |
| 32 | $C_{2v}$    | -139.635524|      | 87 | $C_s$       | -472.09165 |       |
| 33 | $C_s$       | -144.842719|      | 88 | $C_s$       | -479.032630 |       |
| 34 | $C_{2v}$    | -150.044528|      | 89 | $C_{3v}$    | -486.053911 |       |
| 35 | $C_1$       | -155.756643|      | 90 | $C_s$       | -492.433908 |       |
| 36 | $C_1$       | -161.825363|      | 91 | $C_s$       | -498.811060 |       |
| 37 | $C_1$       | -167.033672|      | 92 | $C_{3v}$    | -505.185300 |       |
| 38 | $O_h$       | -173.928427|      | 93 | $C_1$       | -510.877688 |       |
| 39 | $C_{5v}$    | -180.033185|      | 94 | $C_1$       | -517.264131 |       |
| 40 | $C_s$       | -185.249839|      | 95 | $C_1$       | -523.640211 |       |
| 41 | $C_s$       | -190.536277|      | 96 | $C_1$       | -529.87146 |       |
| 42 | $C_s$       | -196.277534|      | 97 | $C_1$       | -536.681383 |       |
| 43 | $C_s$       | -202.364664|      | 98 | $C_s$       | -543.642957 |       |
| 44 | $C_1$       | -207.688728|      | 99 | $C_{2v}$    | -550.666526 |       |
| 45 | $C_1$       | -213.874862|      | 100| $C_s$       | -557.639820 |       |
| 46 | $C_{2v}$    | -220.680330|      | 101| $C_{2v}$    | -563.411308 |       |
| 47 | $C_1$       | -226.012256|      | 102| $C_{2v}$    | -569.363652 |       |
| 48 | $C_s$       | -232.199529|      | 103| $C_s$       | -575.766131 |       |
| 49 | $C_{3v}$    | -239.091864|      | 104| $C_{2v}$    | -582.086642 |       |
| 50 | $C_s$       | -244.549926|      | 105| $C_1$       | -588.266501 |       |
| 51 | $C_{2v}$    | -251.253964|      | 106| $C_1$       | -595.061072 |       |
| 52 | $C_{3v}$    | -258.229991|      | 107| $C_s$       | -602.007110 |       |
| 53 | $C_{2v}$    | -265.203016|      | 108| $C_s$       | -609.033011 |       |
| 54 | $C_{5v}$    | -272.208631|      | 109| $C_1$       | -615.411166 |       |
| 55 | $D_{3h}$    | -279.248470|      | 110| $C_s$       | -621.788224 |       |
| 56 | $C_{3v}$    | -283.643105|      |      |            |          |      |
TABLE II. Lowest energy icosahedral minima at sizes with non-icosahedral global minima.

| N  | Point group | Energy/ε | Ref. |
|----|-------------|----------|-----|
| 38 | C55v        | -173.252378 | 10  |
| 75 | C1          | -396.282249  | 1   |
| 76 | C1          | -402.384580  | 1   |
| 77 | C1          | -408.518265  | 1   |
| 102| C6          | -569.277721  | 1   |
| 103| C1          | -575.658879  | 1   |
| 104| C5          | -582.038429  | 1   |

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1 The magnitude of this interest can be gauged by, for example, the fact that there have been over 2600 citations of the classic simulated annealing paper by Kirkpatrick et al., cited below.
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