Global Optimisation of Molecular Clusters

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1 The Lennard-Jones Potential Function

All results presented here use the scaled Lennard-Jones potential such that the pair well depth and equilibrium distance are both unity

$$V_{LJ}(r) = \frac{1}{r^{12}} - \frac{2}{r^6}. \quad (1)$$

Thus all energies are given in units of the pair well depth, ϵ, and lengths are given in terms of the equilibrium distance σ. This means that for a dimer the potential and the separation are both one. Clusters of this type exhibit magic numbers corresponding to Mackay Icosahedra [10], at N=13,55,147,309,... etc. Most of the structures that are not magic numbers are built on variations of these icosahedra, but some (e.g. $N = 38$, $75 \leq N \leq 77$) are non-icosahedral, and as such are much harder to find. A good test of an unbiased algorithm is if it can find these structures [19, 2].

A lot of the early work in this area (e.g. [4]) used a seeding technique, as well as guessing an approximate structure and then feeding this in as the original cluster configuration. This method quickly begins to fail, especially as the minimum structures may be very different when an extra atom is added. Simulated Annealing has been successful for small to medium sized clusters; Genetic Algorithms have proved to be much more robust and consistent in terms of their ability to find the global minimum structures.

2 Simulated Annealing

2.1 Method

Simulated Annealing [9] is a relatively simple technique which is analogous to cooling the structure into the minimum state. The method consists of two loops, the first controls the temperature, and the second is a Metropolis loop [12]

Algorithm 1: ***Basic Simulated Annealing***

1: Begin with an initial temperature $T = T_i$ (cooling down to a final temperature T_f) and a trial structure of energy E
2: Start temperature loop
3: Start the Metropolis loop for a given number of steps
4: Generate a trial structure with energy E_{trial}
5: Set $\Delta E = E - E_{trial}$
6: **if** $\Delta E > 0$ **then**
7: $P = \exp(-\Delta E/k_B T)$
8: **else**
9: $P = 1$
10: **end if**
11: This value of P is then compared with a random uniform deviate $p\,\epsilon\,[0, 1]$
12: **if** $p < P$ **then**
13: then the new configuration is accepted
14: **end if**
15: End Metropolis loop
16: The temperature is then lowered by whatever cooling schedule is chosen
17: **if** $T = T_f$ **then**
18: a greedy run through the Metropolis loop is performed (only accept lower energy solutions)
19: then EXIT temperature loop
20: **end if**
21: End temperature loop

2.2 Improvements: Bouncing

Initial results were obtained by the basic method described above, however, a paper by Schneider *et al* described the use of temperature "bouncing" to improve the results a simulated annealing approach to the PCB442 problem [16]. This scheme was included so lines $16 - 21$ of the algorithm are altered to the following:

Algorithm 2: ***Bouncing Alteration***

16: The temperature is then lowered by whatever cooling schedule is chosen
17: **if** $T = T_f$ ***and*** $T_i/2 > T_f$ **then**
18: *a greedy run through the Metropolis loop is performed*
19: $T_i = T_i/2$
20: **else**
21: a greedy run through the Metropolis loop is performed
22: then EXIT temperature loop
23: **end if**
24: End temperature loop

It was found that these bouncing steps markedly improved the results

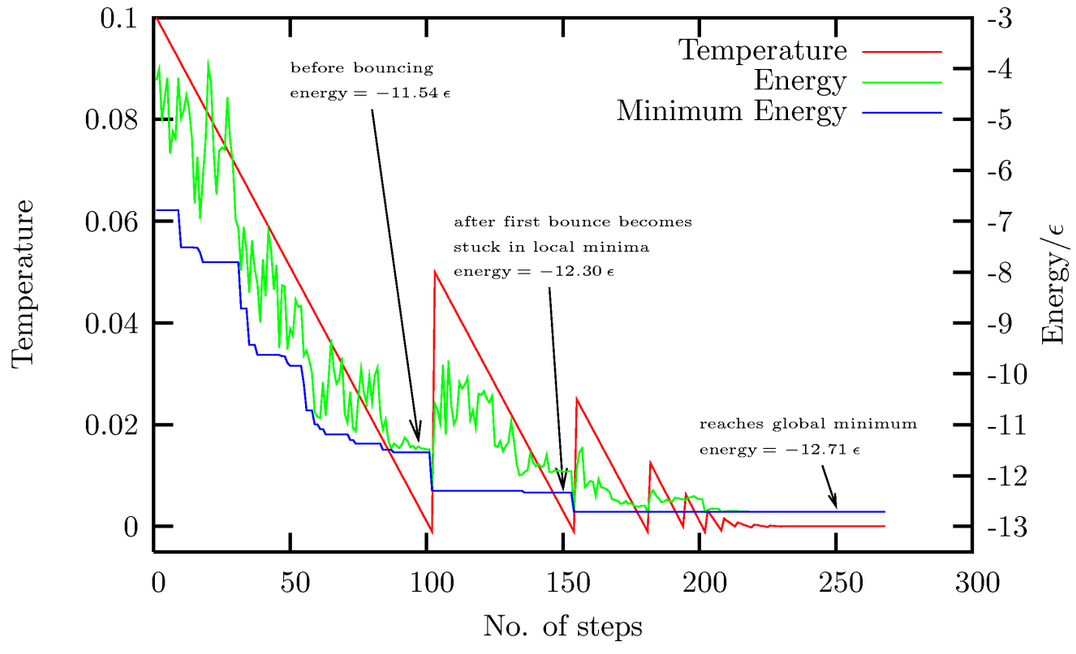

Figure 1: *The effects of temperature bouncing on energy for N=6 cluster*

2.3 Results

A difference plot between the results from our simulated annealing code and the accepted results (taken from the Cambridge Cluster Database [20]) is shown below. As can be seen, the results are fine for small numbers of atoms, but above 13 atoms the results begin to diverge. For 12 atoms only 1 out of 128 runs reached the global minimum. For 6 atoms, the global minimum of $-12.712\,\epsilon$ was found in $2.3\,\%$ of the runs performed, but the local minima at $-12.303\,\epsilon$ was found in $46.9\,\%$ of runs.

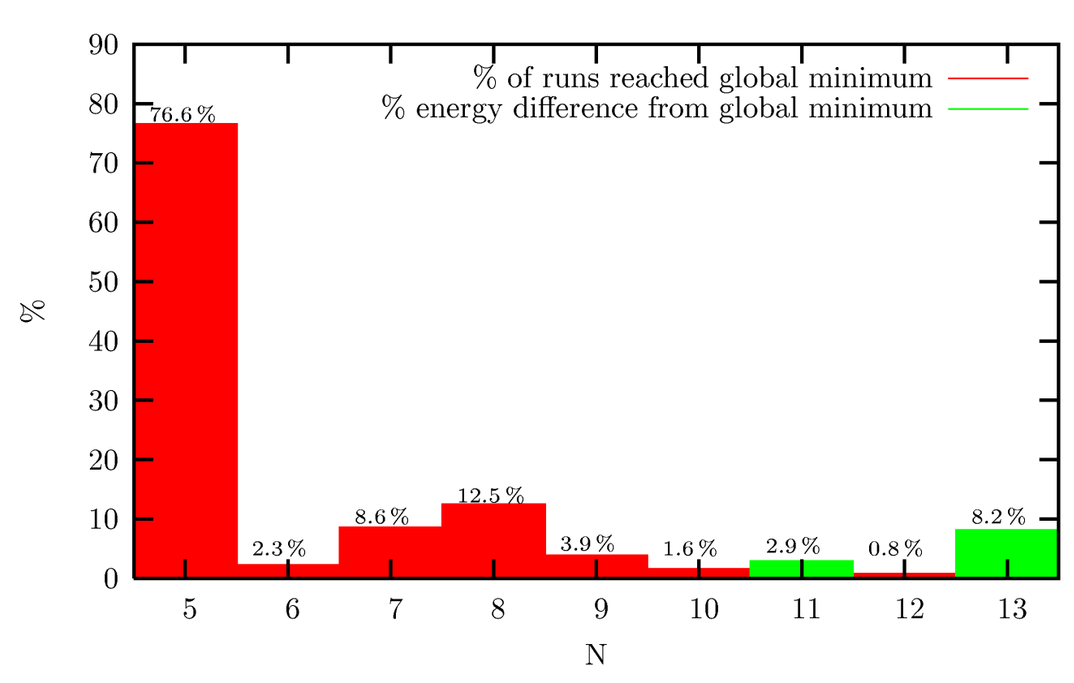

Figure 2: *Results from Simulated Annealing, comparing % of runs reaching global minimum with % deviation from global minimum if not acheived*

These results could be improved upon. Results from L.T. Wille give good results for $N \leq 25$ [22]. However, the cooling and Metropolis stepping scheme used was different from the one used here, and some modifications are required to implement them. Good results for $N \leq 25$ have also been found using modified SA methods, such as Gaussian density annealing [18].

Future plans include adding a local minimiser, such as a Polack-Ribière conjugate gradient method [15] to help improve the convergence of the results. Often SA will generate a structure from the global minimum well, but it will not be from the bottom of it. At the moment this is countered this by having a long run of greedy steps at the end of the temperature loop. However, this is very inefficient and is not always successful.

This minimiser will also be included in the genetic algorithm code. The reasons for this are included in the next section (figure 4).

3 Genetic Algorithms

3.1 Method

First proposed by John H. Holland in 1975 [5], the original idea behind GA's was to use a binary string to represent a member of a population, the encoding of which would contain sections which would give the population members different characteristics. The breeding of two strings, termed 'crossover' is done by swapping sections of string to produce offspring. However, this method of encoding and crossover is not practical for use with continuous variables such as the spatial positions used in the cluster problem. A solution to this was proposed by Deaven and Ho in 1995 [1], and is a much more physical way of dealing with the problem. The clusters are represented by an array of the atomic position vectors in *xyz* format, and crossover is done by taking a random plane through the centre of mass of the two parent clusters, and then swapping the halves. This is represented diagrammatically in figure 3.

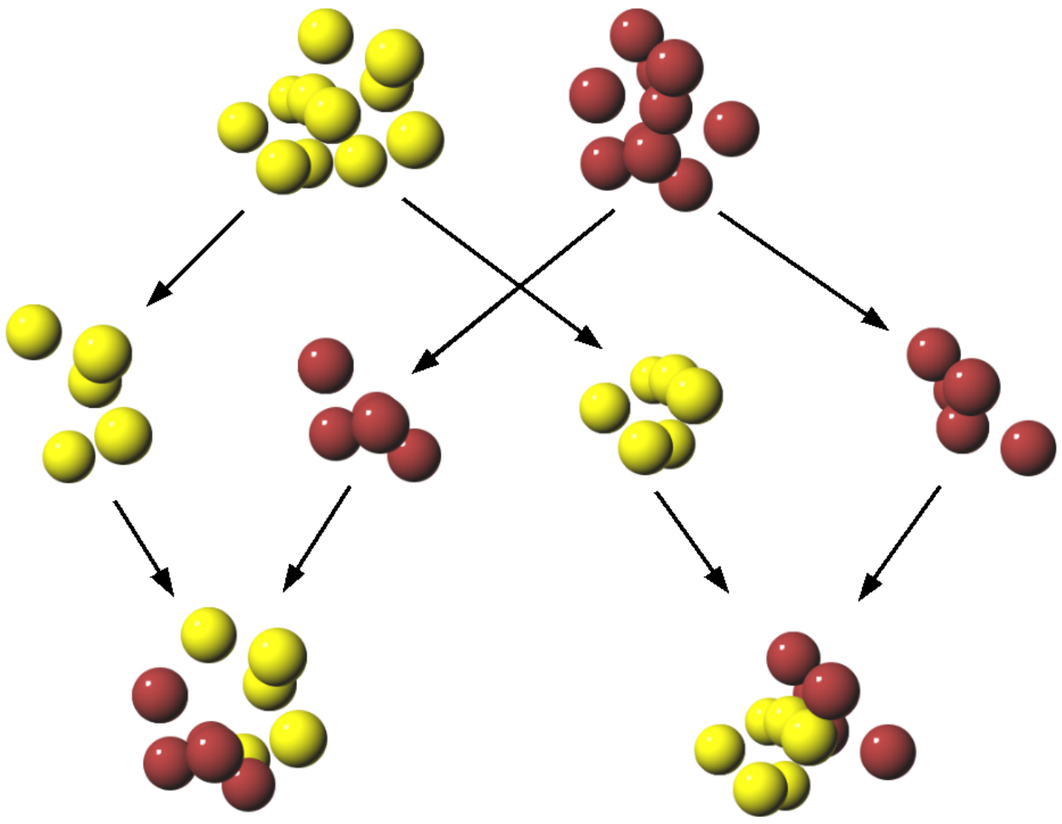

Figure 3: *Crossover*

The energy of each structure is calculated, which is then used to determine the fitness of each cluster. The fitnesses of the individuals in the population are then used to choose two parents for crossover, and then the offspring may or may not be mutated. Offspring are kept only if they are fitter than members of the original population. When the new population is decided upon, selection for crossover begins again.

Algorithm 3: ***Genetic Algorithm***

1: Generate initial population
2: calculate fitness of each member of the population
3: select population members for crossover
4: perform crossover
5: mutate offspring (typically 5-10 % mutation rate)
6: determine fitness of offspring
7: update the population
8: return to step 2.

There is a problem with this method as it stands. When one cluster is bred with another cluster two or more atoms may find themselves within $1\,\sigma$ of each other, and as such the offspring might have a large potential energy. A solution to this is to minimise every new structure that is generated *at any stage* into its basin of attraction, and as such all crossovers and mutations would produce viable structures [19, 6]. So after any mutation or crossover is performed, the cluster is minimised. This reduces the search space, and also means that if initially two unrelaxed clusters have different energies (and hence different fitnesses) they form the same relaxed cluster (although their absolute atomic positions may be different, their relative atomic positions will be the same) and should be given the same probabilities for crossover (see figure 4).

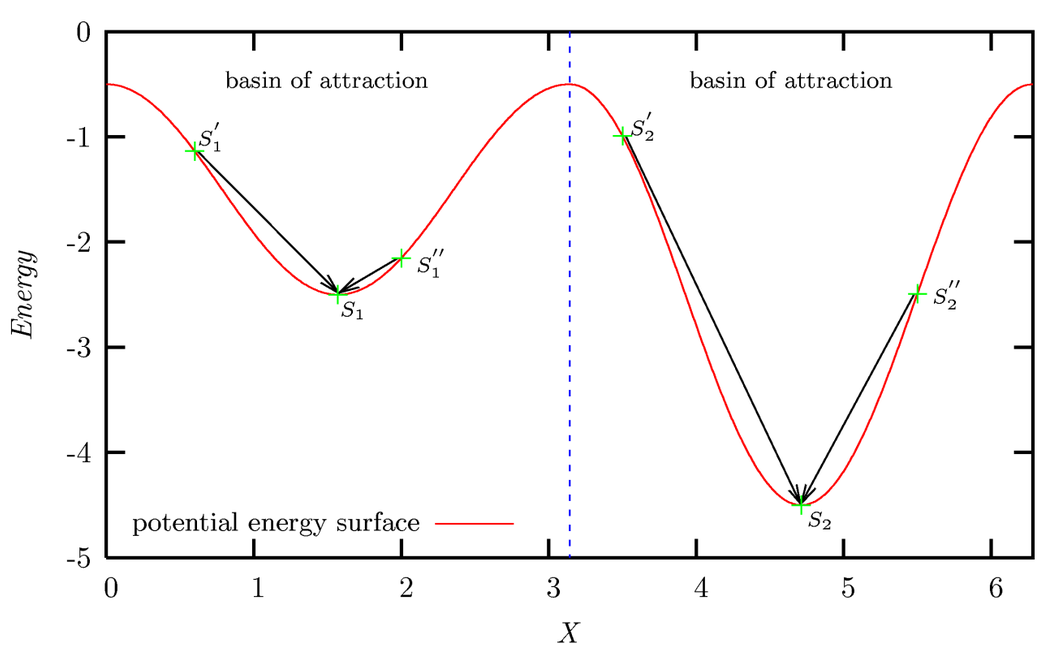

Figure 4: *Minimising structures into their basin of attraction simplifies the problem.*

However, this loop (algorithm 3) could technically go on indefinitely - so a convergence criterion must be included. This is again why some sort of local minimiser is needed. With no minimiser, the algorithm would bounce around in the bottom of the global minimum well, but might never reach the minimum structure. Genetic Algorithms are very good at homing in on the minimum well, but will have difficulty in getting to the bottom of it. Now convergence can be decided by the average energy of the whole population, or the length of time spent with a particular minimum energy.

3.2 Results

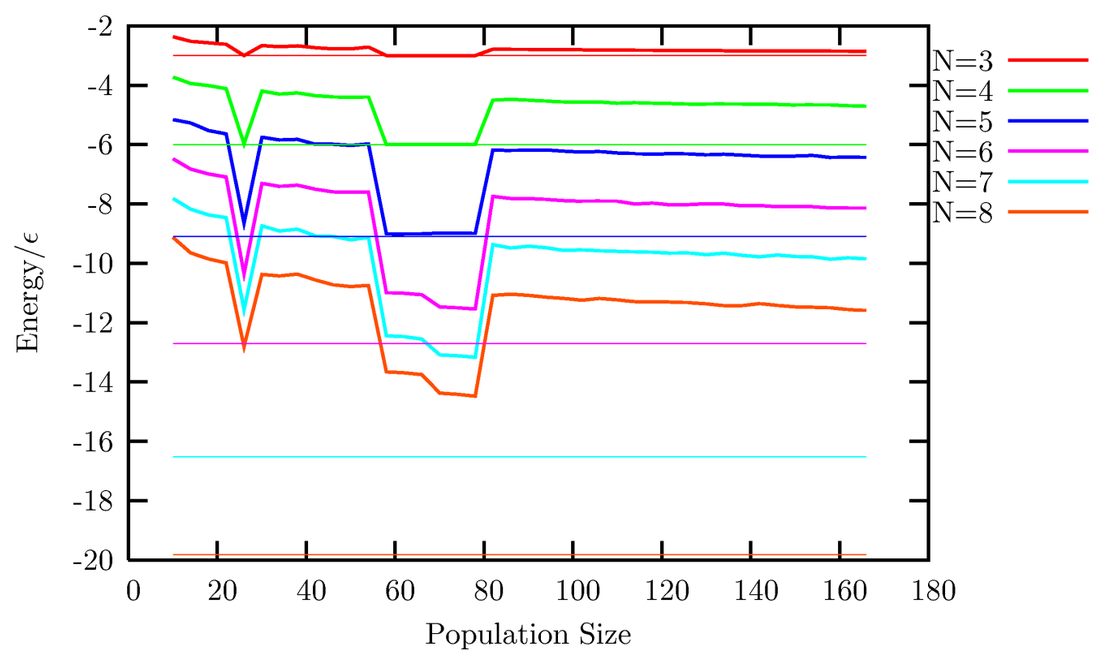

Figure 5: *Genetic Algorithm results for 3 to 8 atom clusters comparing energy with population size, without local minimiser, averaged over 640 runs. The bold lines show the results from our algorithm, the flat lines the global minimum energy*

Figure 5 shows the results of the program without a local minimiser present, which indicate that a population size of around $60 - 80$ clusters is optimum in this case. They also show that even without a local minimiser, the algorithm can find the global minimum structures for $N = 3 - 5$ atoms.

4 Molecular Clusters

Our main interest in developing these two techniques is to study the global minima of ice/water clusters. There have been a large number of papers published on this subject, using many different potentials, such as TIP3P [7] (e.g. [14, 8]) and TIP4P [7] (e.g. [21, 3]) as well as others, and some *ab initio* calculations [11]. TIP4P is a popular potential and gives some good agreement with *ab initio* results for small numbers of molecules. However, this potential has been shown to unrealistic around the freezing point [13], and hence might not be suitable for ice structures. Another feature of the small TIP4P clusters is that they are all cages, and except for $N = 19$ they have all the water molecules on the surface.

The clusters generated will the be used to simulate chemical reactions such as

$$\mathrm{ClONO_2}\ (g) + \mathrm{HCl}\ (ads) \xrightarrow{\text{ice}} \mathrm{Cl_2}\ (g) + \mathrm{HNO_3}\ (ads), \qquad (2)$$

which occurs on ice clouds in the stratosphere during the antarctic spring, by using an *ab initio* code such as CASTEP [17].

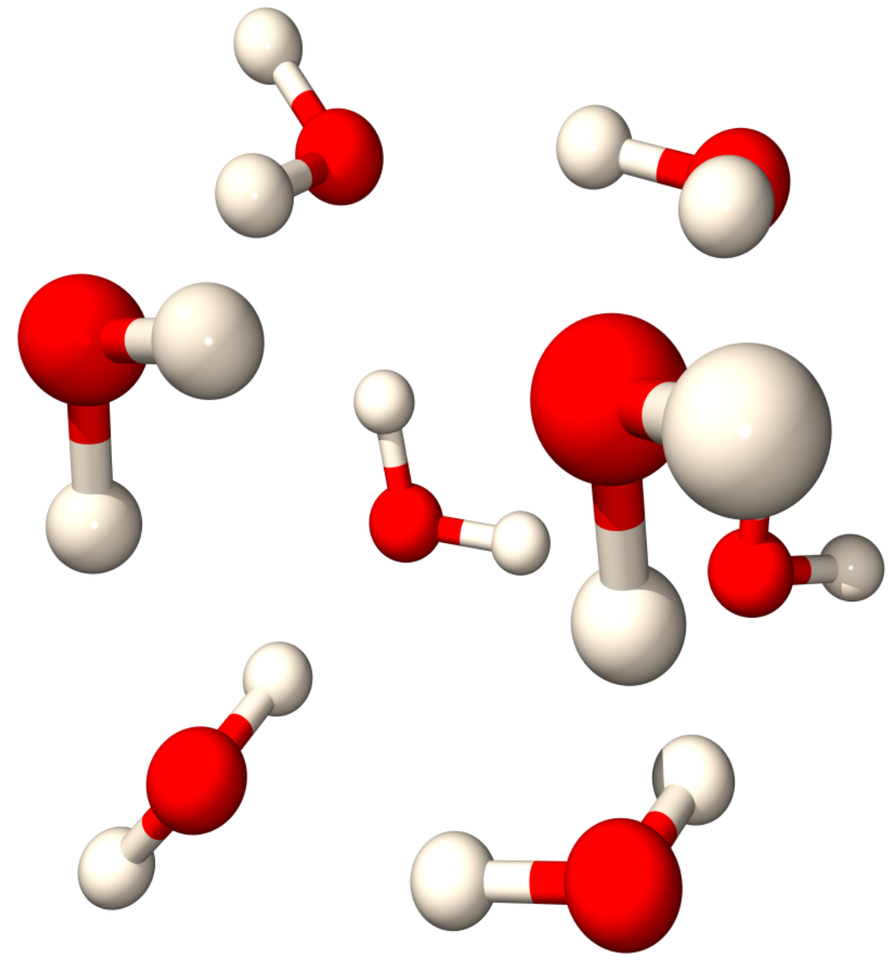

Figure 6: *The 8 molecule TIP4P cage structure. Co-ordinates from the Cambridge Cluster Database [20]*

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