Cluster optimization simplified by interaction modification

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Mathematics and the physical sciences harbor a large number of difficult nonlinear optimization problems. Some representative examples are the traveling salesman problem,[1] spin glass ground state configurations,[2] and the stable forms of folded proteins.[3] The chemical physics of clusters presents an equivalent challenge: even when the relevant interactions between the constituent particles are accurately known it can be difficult to determine the lowest energy configuration because of the large number of viable alternatives.[4] Most of these problems are classified as "NP complete," i.e., exponentially increasing in difficulty with the numbers of elements involved.[5]

Some general techniques are available for approximating optimal solutions to these problems, for example, the "simulated annealing" method which utilizes ideas from traditional statistical mechanics.[6] Another approach combines modification of the objective function with conventional minimization routines (such as steepest descent or the conjugate gradient method),[7] and has been named the "ant–lion strategy." It is the objective of this note to illustrate the latter for noble gas clusters. That such an approach might be successful is indicated by a recent paper on six- and seven-atom clusters by Braier, Berry, and Wales, showing how the complexity of potential energy surfaces for Morse pair potentials varies with the range of that function.[8]

For present purposes, we employ the Lennard-Jones interaction in reduced form:

$$v_p(r) = 4(r^{-2p} - r^{-p}). \tag{1}$$

To represent the noble gases Ar, Kr, and Xe one normally sets $p = 6$. We shall consider the effect of varying p. The minimum in the pair potential v_p occurs at r_e, where

$$r_e = 2^{1/p}, \quad v_p(r_e) = -1,$$
$$v_p''(r_e) = 2^{1-2/p}p^2. \tag{2}$$

Hoare[9] has made an exhaustive enumeration of the stable arrangements of N noble gas atoms, with $p = 6$ and $N \leqslant 13$. For $N = 13$ he reports 988 distinct arrangements, and for these the lowest potential energy is attained in the regular icosahedral structure. We have found that this icosahedron (one central atom surrounded symmetrically by 12 others) continues to be a mechanically stable configuration as p is reduced from the "physical" value 6. Table I reports values of the corresponding potential energies

$$\Phi = \sum v_p(r_{ij}), \tag{3}$$

and the radial distances r^* from the central atom to its neighbors, for various p choices.

Table I also contains a measure $S(p)$ of the dominance of the ground-state icosahedral structures over all other possibilities in the 39-dimensional cluster configuration space.

A Monte Carlo method has been used to evaluate $S(p)$. For each p value, 10^4 random initial positions of the 13 atoms within a $10 \times 10 \times 10$ cube were generated with uniform distribution. Each of these initial configurations was then mapped onto the relevant potential energy minimum by the steepest descent relaxation operation; this mapping to minima plays a central role in the inherent structure theory for condensed phases,[10,11] and has been employed previously to study cluster kinetics and thermodynamics,[12–14] The MINOP routine was employed to implement this mapping efficiently.[15] $S(p)$ is the success probability for capture at an icosahedral global minimum.

The last column in Table I shows that random sampling for $p = 6$ encounters icosahedral potential energy basins in only about 1% of the trials. In most instances the 13-atom system lodges at a higher-lying relative minimum. However this unfavorable probability improves dramatically as p declines. When $p = 1$ every one of the 10^4 random trials was found to occur within an icosahedral potential energy basin. Figure 1 presents the $S(p)$ results in graphical form.

It is obvious that reducing p below 6 causes the icosahedral basins to distend, and apparently to displace and annihilate most of the other, higher-lying, basins. This transformation can be described as changing the atoms from "sticky" to "slippery": instead of sticking in nonoptimal arrangements they slide unimpeded into the optimal icosahedral structure. Since decreasing p increases the range of the pair potential $v_p(r)$, this observation is consistent with those of Braier, Berry, and Wales for the Morse potential.[8]

Our simple example provides a clear-cut illustration of the ant–lion nonlinear optimization strategy. Starting from virtually any initial configuration of the 13 atoms, and with sufficiently small p, steepest descent minimization of the modified interaction

$$\Phi^* = \sum v_p[r^*(p)r_{ij}/r^*(6)] \tag{4}$$

will automatically place the cluster at the global minimum of the physical interaction $\Phi(6)$.

We suspect that the sticky to slippery atom transforma-

TABLE I. Characteristic properties for icosahedral 13-particle clusters.

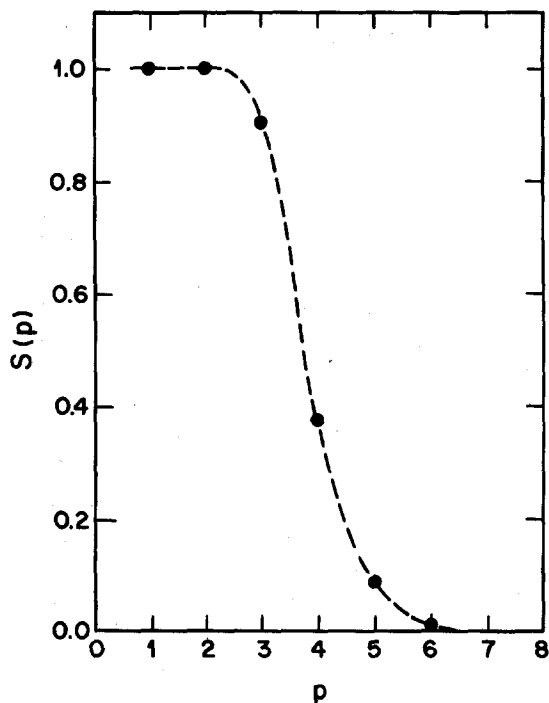| p	$r^*(p)$	$\Phi(p)$	$S(p)$
1	1.667 614	−73.356 631 01	1.0000
2	1.260 253	−64.222 222 22	0.9994
3	1.167 548	−56.107 493 96	0.9048
4	1.125 820	−50.420 749 28	0.3770
5	1.100 076	−46.720 639 44	0.0864
6	1.081 838	−44.326 801 42	0.0102

FIG. 1. Success probability S vs p for steepest-descent capture at the global icosahedral minimum. The dashed curve is included only for visual guidance.

tion may have computational utility outside of the cluster regime. In particular it may be a valuable optimization tool for the protein folding problem, in which one component of the overall potential function traditionally involves non-bonded atom–atom interaction.[16] This interaction modification (and others operating on the remaining components of the protein potential) can be expected to yield significant simplifications of that minimization problem.

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