

Global optimization for molecular conformation problems

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Abstract

A primal-relaxed dual global optimization algorithm is presented along with an extensive review for finding the global minimum energy configurations of microclusters composed by particles interacting with any type of two-body central forces. First, the original nonconvex expression for the total potential energy is transformed to the difference of two convex functions (*DC transformation*) via an eigenvalue analysis performed for each pair potential that constitutes the total potential energy function. Then, a decomposition strategy based on the GOP algorithm [1–4] is designed to provide tight upper and lower bounds on the global minimum through the solutions of a sequence of relaxed dual subproblems. A number of theoretical results are included which expedite the computational effort by exploiting the special mathematical structure of the problem. The proposed approach attains ϵ -convergence to the global minimum in a finite number of iterations. Based on this procedure global optimum solutions are generated for small Lennard–Jones and Morse ($a = 3$) microclusters $n \leq 7$. For larger clusters ($8 \leq N \leq 24$ for Lennard–Jones and $8 \leq N \leq 30$ for Morse), tight lower and upper bounds on the global solution are provided which serve as excellent initial points for local optimization approaches.

1. Introduction

1.1. MICROCLUSTERS

Microclusters (or clusters) belong to an intriguing state of matter that encompasses different entities like microcrystallites, microdroplets, colloid nuclei, aerosol particles, grains, etc. Hoare [5] defined microclusters as aggregates of atoms, ions, or molecules, sufficiently small that a significant proportion of these units is present on their surfaces. They correspond to systems that are neither single entities nor continua composed of an infinite number of units, but lie somewhere in between, bridging the gap between single atoms or molecules and bulk matter. Typically, microclusters consist of two to several hundred atoms and pose the following questions that are central for disciplines like solid-state physics, chemistry, and the related field of material science:

- How small must an aggregate of particles become before the character of the substance they once formed is lost?

- How might the atoms reconfigure if freed from the influence of the matter that surrounds them?
- If the substrate is a metal, how small must its cluster of atoms be to avoid the characteristic sharing of free electrons that triggers conductivity?
- Do growing microclusters proceed gradually from one stable structure to another, largely through the simple addition of atoms, or do they undergo radical transformations as they grow?

Perhaps the first reference to clusters was made in 1661 by Boyle, in his *Skeptical Chymist*, which speaks of:

... minute masses or clusters that were not easily dissippable into such particles as composed them

Because of their minute size and typically large chemical reactivity, microclusters could not be studied with the techniques of traditional chemistry or even formed in the laboratory until the 1950's. In early efforts, an oven was used to vaporize a metal, which was precipitated as microclusters on a substrate. Since that time, chemists have developed a variety of methods of forming microclusters, each with advantages and disadvantages. For producing cluster beams of metals or semi-conducters a laser vaporization of the appropriate substances is performed within the flow of an helium carrier gas [6]. Another similar technique [7] called *multiple expansion cluster source* is used for producing microclusters of Cu, Ag, Au and Ni. In the *matrix isolation technique* microclusters are trapped in a solid environment by co-condensing the metal's vapor in the presence of rare gas on a cold surface [8]. The preparation of small microclusters involving quite uniform size distributions is based on well characterized metal-cluster complexes [9]. For the formation of microclusters supported on substates, the most widely used method is *vapor deposition* [10]. A different method [11] for producing colored powder-like microclusters is by growing them in solution until they reach the desired size, and then coating them with an organic outer layer that inhibits coalescence. Alternatively, the microclusters can be precipitated inside porous glasses or polymers resulting in a solid material that contains millions of isolated microclusters. Finally, other researchers form microclusters inside zeolites which are crystalline structures with relatively large empty spaces in which the clusters are grown. The major problem with all of these chemical methods is that they cannot produce microclusters of a unique size, but instead they tend to produce microclusters whose size is distributed around a mean value.

A key word pertaining to the novel features of microclusters is *size effects* [12]. The microscopic size of microclusters gives rise to unique properties in two ways. First, a large percentage of a cluster's atoms are on or close to the surface, and surface atoms do not arrange themselves in the same way as do atoms in bulk matter, but instead they tend to avoid being exposed on the surface. This effect

completely overwhelms the tendency of atoms to arrange themselves in a regular crystalline array as they normally do in bulk matter. For instance, the ordering of silicon atoms in the Si_{10} cluster is completely different from the ordering in the silicon crystalline structure. Clusters differ from bulk matter not only in the variation of the number of atoms or molecules that they contain, but also in the number of atoms or molecules that reside on the surface. Assuming a spherical shape, the fraction of the number of surface atoms is $4/n^{1/3}$. For $n = 10^2$ this number is 86%, for $n = 10^3$ it is 40% and for $n = 10^4$ it is still 20%. For example, in a cluster of 55 argon atoms at least 42 atoms are on the surface in some sense. Thus the structural, energetic and dynamic properties of the *microsurface* are of considerable interest.

Apart from the consequence on its geometry, a cluster's small size also affects its electronic structure. In bulk materials, electrons can move freely in any direction, but this is not the case in clusters since they are confined to a space that is only a few atoms width across. Presumably, the electronic structure is very sensitive to cluster size because the size determines how much room the electrons have to move around and consequently the possible energy of the electrons. It appears that clusters consisting of specific numbers of atoms are extremely stable, as they show up more prominently in the mass spectrum than neighboring cluster sizes. These numbers of particles that enhance stability are called *magic numbers* and they are substance specific [13]. For instance [14] xenium clusters consisting of $N = 13, 19, 23, 25, \dots$ are particularly stable, although for sodium clusters the magic numbers are $N = 8, 20, 40, 58, 92, \dots$.

Small clusters of atoms or molecules numbering from 4–5 to 100–200 can coexist as solids and liquids over a finite range of temperatures and have distinctly different melting and freezing points. This occurs because due to the interplay of internal energy and entropy the free energy function for these clusters has two distinct minima, one in the liquid phase and one in the solid. Between them lies a finite range of temperatures within which both phases are stable. In other words, the melting and freezing points are disconnected since nothing dictates that these transitions must occur at the same temperature. An example of clusters that display such phase coexistence is argon clusters of 7, 15 or 19 atoms [14]. These clusters exhibit a remarkable phenomenon; they randomly jump back and forth between the solid and the liquid state, staying for long periods of time in each one. It should be pointed out, however, that not all clusters exhibit two-phase coexistence. For example, argon clusters composed by 6, 8 or 17 do not phase coexist [14]. The allowed energies of a cluster are quantized, which restricts the energy of a cluster to a discrete set of levels. These levels are widely spaced at low energies but are close together at high energies. Solid clusters typically occupy deep potential wells but liquid clusters reside at shallow ones. Therefore, solid clusters have relatively widely spaced energy levels while liquid clusters have densely spaced ones. Most quantum size effects are case specific and depend on the nature of the specific elementary excitation.

The considerable progress achieved in this area of research stems from two directions. First, the advent of supersonic cluster beams has had a remarkable impact on the experimental progress in this field. Second, classical and quantum mechanical simulations have provided a conceptual framework for the understanding of structural, energetic, dynamic, and thermodynamic effects in clusters. These two factors have contributed to the unified description of the interrelationship between molecular, surface, and bulk phenomena in large finite systems.

1.2. APPLICATIONS

The importance of microclusters ranges from catalysis to astrophysics and crosses the boundaries of subjects such as nucleation, crystal growth and surface physics. The remarkable increase of interest in microcluster physics in the last few years has been catalyzed by the emergence of several fields of direct application in the study of cluster properties.

Perhaps the most promising application of microclusters is in industrial catalysis [11], which is central in petroleum refining for recovering of gasoline fractions from heavier distillates; in chemical industry for selectively favoring certain reactions; in pollution control for oxidizing or reducing pollutants; and in the synthesis of pharmaceuticals. The efficiency depends on its ability to attract reactants strongly enough for adsorption yet hold their products weakly enough for desorption. Critical for the entire process is the geometry of the active site, which remains an open problem for many catalytic reactions. Clusters are ideal for hosting active sites because their unfilled bonding capacity makes them adsorb readily, and their small size limits the number of possible adsorption geometries. These features make them likely to produce highly selective catalysts which are greatly valued in industry. Studies showed that cluster catalysis depends not only on the size and actual shape of the cluster, but also on its bond structure. The discovery that small changes in cluster size can produce large differences in adsorbing ability strengthens the notion that clusters represent a distinct state of matter. It also suggests that selectively adsorbing clusters can be chosen by size and deposited on a substrate for industrial catalysis, whereas unreactive clusters can form protective coatings.

Clusters of certain metals have a great ability to absorb light due to their high density of valence electrons and large surface to volume ratio. Based on a cluster's size and chemistry it is possible to predict which wavelengths of light it will absorb. Because certain clusters are so photoreceptive, if suspended in a transparent medium they can be used as efficient radiation detectors, wavelength-specific light filters or even elements in an optical-memory system. In photographic processes when a photographic film is exposed, photons convert a tiny portion of the silver halide crystals into silver metal clusters. More sensitive clusters will result in the production of faster films. Furthermore, smaller but equally sensitive clusters could lead to films that can resolve sharper images. The precise photon-emission patterns of clusters are also of value as a chemical fuel for lasers [11]. A rather exotic as well

as unexpected implication of microclusters occurs in the area of astrophysics [5]. Recent astrophysical theories have put increasing emphasis on the role of small interstellar grains as a factor in the generation of chemical species and the regulation of hydrogen equilibria in the galaxy. A main reason for the shift of interest towards grains in the microcluster size region is the realization that certain processes of adsorption and desorption may owe their character entirely to the small size of the particles, irrespective of the detailed physical chemistry of their surfaces.

Furthermore, microclusters correspond to a necessary vehicle for understanding nucleation processes in terms of atomistic rather than continuum models, explain crystal growth as a result of interactions between neighboring clusters, and account for the occurrence of condensation in supersonic flows.

1.3. MINIMUM POTENTIAL ENERGY PROBLEM

The study of the topography of the potential energy function of a microcluster in the internal configurational space was and still remains a central problem in this area of research [5, 15]. Even under simplifying assumptions about the interaction energy, the minimization of the potential energy is very difficult to solve because it corresponds to a nonconvex optimization problem involving numerous local minima. Hoare [5] claimed that the number of local minima of an n -atom microcluster grows as $\exp(n^2)$. In fact, Wille [16] has shown, that the complexity of determining the global minimum energy of a cluster of particles interacting via two-body forces belongs to the class NP. In other words, there is no known algorithm that can solve this problem in non-exponential time [17]. A geometrical, possibly topological proof that a local minimum is both unique and global is not likely to be found because there still exist unsolved problems in the theory of sphere packings where difficulties are undoubtedly less acute [18–21] than those in the minimization problem at hand.

Faced with these difficulties, current methods use physical intuition, approximation procedures, mimicking of physical phenomena, random searches, lattice optimization/relaxation, or local optimization approaches. Hoare in a series of papers [22–25, 15] proposed a method of finding minima of the total potential function of an $5 \leq N \leq 66$ particle LJ cluster based on a *growth scheme* involving the following steps: First, a particular compact *seed structure* involving a small number of atoms is selected which is likely to appear in the N -particle structure. At each iteration an extra particle is placed at all packing vertices and the resulting structures are tested for geometrical uniqueness. The distinct structures are then relaxed and a local optimization procedure locates and records the local minima involved. Each of the minima then serves as a new seed structure in repetition of the procedure. Finally, all of the generated distinct local minima are tabulated in decreasing order of binding energies. A number of "growth rules" are incorporated in the procedure that alleviates the computational effort. Using this method Hoare generated a large number of local minima for structures from 5 to 66 particles.

However, no claim for complete enumeration of all local minima, and thus detection of global minimum, can be made. In fact, it has been reported [26] that solutions of low-symmetry are not likely to be found with this method.

Piela's [27] method is based on the simple idea of smoothly deforming the potential energy hypersurface [28], in such a way as to make shallow potential wells disappear gradually, while the deeper ones grow at their expense. As the potential wells evolve they change their position and size. One then eventually ends up with a single potential well that has absorbed all the others which hopefully corresponds to the global minimum. A local optimization procedure then can easily find the single local minimum corresponding to the global one as well. The hypersurface is deforming using the diffusion equation, with the original shape of the hypersurface representing the initial concentration distribution. The main advantage of this method is that you do not have to explore the myriads of local optima, nor do you have to know their position beforehand. However, the approach depends on the conjecture that shallow potential wells disappear faster than deeper ones. In fact, it has been observed that when the global minimum lies on a narrow potential well of large depth, it might disappear faster than a wider, originally shallower, potential well.

Simulation studies are the most widespread method in the study of clusters. There are three basic simulation methods that have been used in cluster research: molecular dynamics, Monte Carlo simulations and statistics. In the molecular dynamics (MD) technique, the equation of motion is solved numerically for the set of N particles that form the cluster. Depending on the type of the system and on the form of the employed potential energy function, there is a variety of numerical algorithms available for this purpose [29, 30]. All methods generate a time-ordered series of particle coordinates representing the motion of every particle in the system. Kinetic energies are incorporated within the calculation sequence, and therefore temperature effects are intrinsically included in the result. In principle, if given a large enough number of iterations, molecular dynamics simulations can describe the evolution of any time-dependent system towards equilibrium.

Simulation calculations using the molecular dynamics technique were carried out by Heidi [31] and Jellinek [32] for studying the solid liquid changes in a 13-particle argon cluster. A systematic molecular dynamics simulation study of microclusters of 13–147 atoms was performed by Honeycutt and Andersen [33] using Lennard–Jones potential at constant temperature and constant energy calculations alternatively. Polymeropoulos and Brickmann [34] employed a molecular dynamics technique using two-body and three-body interactions calculating the stabilities of microclusters of various sizes and analyzing the effect of three-body interactions on the stability of the microcluster. In a more recent work Polymeropoulos and Brickmann [35] also analyzed ionized rare-gas clusters containing up to 26 atoms. Garzon et al. [36, 37] analyzed the effect of impurities on the structure and on the liquid–solid transition of Lennard–Jones and Van der Waals crystals respectively, using molecular dynamics simulations. Eroc and Katircioglu [38] investigated the energetics and the structural stability of gold microclusters containing 3–7 atoms. Molecular dynamics

were employed in the simulation, and the potential energy function used in the calculations included two as well as three-body interactions represented by Lennard–Jones and Axilrod–Teller functions respectively.

Monte Carlo techniques, employed in microcluster simulations, are in general based on the Metropolis procedure [39]. Starting from an initial random configuration, atoms are randomly displaced according to the Maxwell–Boltzmann distribution. After a sufficient number of Monte Carlo steps for sampling the phase space, the desired quantities are calculated as ensemble averages from position-dependent quantities estimated in every step. With this method any equilibrium quantity can be calculated as a function of temperature which is introduced via the Maxwell–Boltzmann factor. Tsai and Abraham [40], using a Monte Carlo simulation technique, calculated the structure and thermodynamics of binary Lennard–Jones microclusters as a function of cluster size, composition and temperature. Quirke and Sheng [41] studied the melting behavior of microclusters of atoms using a Monte Carlo method based on Lennard–Jones potentials. Bohmer and Peyerimhoff [42] analyzed the stability and structure of single-charged argon clusters of 3 to 27 atoms using Monte Carlo calculations in the temperature range between 10 and 40 K. Freeman and Doll [43] performed a quantum Monte Carlo study of the thermodynamic properties, homogeneous nucleation, and "magic numbers" distribution in argon clusters.

The static method is based on a simple minimization technique to find the configuration of a cluster corresponding to the nearest energy local minimum. It is a temperature-independent approach and can be regarded as the $T = 0$ case. Because of its simplicity and the moderate computational effort needed, it is often used to obtain local minima. However, depending on the initial configuration this method can provide only one energy local minimum associated with the cluster. Yang and Bambakidis [44] used the static method for finding the structural stability of small clusters by employing a two-body Morse interaction potential. Based on the static method, Halicioglu and White [45] solved for the most energetically stable structure of clusters consisting of up to 13 atoms interacting with two-body and three-body interactions.

The simulated annealing method is a variant of the Monte Carlo method. It has been widely used either alone, or in conjunction with some other method(s). The motivation of this method stems from the fact that each time a crystal is grown or a compound is synthesized, nature somehow seems to solve an energy minimization problem by what could be called an analog computation. It was this observation that led Kirkpatrick et al. [46] to develop the simulated annealing method for discrete combinatorial optimization problems. Vanderbilt and Louie [47] extended this method to problems with continuous variables.

Consider the potential energy to be minimized as a function of the position of the particles $V(r_1, r_2, \dots, r_N)$ where r_i , $i = 1, \dots, N$, are the positions of the particles. The simulated annealing method uses the Metropolis et al. [39] Monte Carlo prescription to decide whether or not to accept a random step Δr . If the associated energy change ΔE is negative, the step is accepted. If ΔE is positive, the

step is accepted with a probability $p = \exp(-\Delta E/T)$. The series of accepted steps generate a *random walk* on the potential energy surface attracted from the minima. The size of steps should be such that approximately half the steps are accepted. The parameter T plays the role of temperature; as T decreases the random walk becomes more likely to settle down to a minimum. By mimicking the process of annealing, the system is started in a random initial configuration at a sufficiently high temperature. After a number of steps M , which should be large enough that representative regions of the parameter space are sampled, the temperature is reduced by a constant factor χ_T (typically 0.75–0.90). This process is repeated until no further improvements are made over a number of iterations. Considerable reductions in the computational effort are achieved by switching to some gradient based local optimization procedure when the energy drops below a certain value in the last stages of the procedure. The collection of the points from which the same local minimum is obtained by this algorithm is called the *catchment region* of the local minimum. This whole procedure is repeated a number of times from many random initial points and produces a list of local minima, the smallest of which is taken to be the global minimum. Obviously there is no guarantee that the actual global minimum will be found in this manner. Particularly, if the catchment region of the global minimum is narrow, this method is likely to miss it. A large number of researchers have been using this method for finding the global minimum of the potential energy function. Wille [26, 48] solved the potential minimization problem for up to 25 particles, interacting under two-body Lennard–Jones forces and he found two new minima for $N = 24$ that were better than the one reported by Hoare and Pal [5]. Ballone and Milani [49] using a semiempirical many-body potential, solved for the ground-geometries of carbon clusters in the range $50 \leq M \leq 72$ and found that all the structures of low energy are hollow spheres with nearly graphitic atomic arrangement. Hohl and Jones [50] applied the same methodology also to phosphorus clusters P_2 to P_8 , arriving at a rather counter-intuitive most stable structure for P_8 . Navon et al. [51] used a combined simulated annealing and a quasi-Newton-like conjugate-gradient method for determining the structure of mixed argon–xenon clusters interacting with two-body Lennard–Jones forces. Vlachos et al. [52, 53] studied the binding energy of Ni Lennard–Jones clusters using the simulated annealing method in a canonical ensemble Monte Carlo technique.

The simulated annealing method can be viewed as a method for stochastically tracing the annealing process by Monte Carlo simulation. Shalloway [54, 55] presented a deterministic method for annealing the objective function by tracing the evolution of a multiple-Gaussian-packet approximation and using notions from renormalization group theory. This method has been applied to microcluster conformation problems and it appears that in most of the test problems was able to identify the global minimum.

It appears that lattice optimization techniques are the most efficient generating structures involving the lowest known potential energy. Farges et al. [56] proposed that the most energetically favored microclusters in the range $20 \leq N \leq 50$ are the

ones that involve interpenetrating icosahedra (polyicosahedra) or (PIC). For $N \leq 55$ a double icosahedral (DIC) growth was introduced [57] and for $55 \leq N \leq 147$ [58] a third layer icosahedral structure using two different surface arrangements was presented. Using these notions Northby [59] derived optimal configurations for LJ microclusters in the range $13 \leq N \leq 147$ based on a lattice optimization/relaxation algorithm. First a heuristic procedure is employed for finding a set of lattice local minimizers assuming icosahedral IC or face-centered FC arrangements. Then, the currently *best* lattice minimizers are relaxed by using a local optimization algorithm. Xue [60] improved on Northby's [59] method by reducing the time complexity of the algorithm. Furthermore, by relaxing *every* lattice local minimizer a number of better optimal configurations were found in the range $13 \leq N \leq 147$. However, it appeared that the best local lattice does not always relax to the structure involving the lowest total Lennard–Jones potential energy. A parallel implementation [61] allowed results on minimum energies for clusters of up to $N = 1000$ atoms. Also by employing a parallel version of a two-level simulated annealing algorithm [62] solutions for cluster sizes as large as $N = 100,000$ have been reported. Finally, Maranas and Floudas [64] transformed the initial nonconvex expression for the total potential energy of a Lennard–Jones microcluster into the difference of two convex functions through a convexification procedure. Then, a Primal-Relaxed Dual global optimization algorithm was implemented for finding the global minimum configuration of small LJ microclusters. For larger ones lower and upper bounds were derived by using a relaxation procedure.

2. Problem discussion

The problem which is to be addressed in this work can be stated simply as follows:

Given N particles interacting with two-body central forces, find their configuration(s) in the three-dimensional Euclidean space involving the global minimum total potential energy.

The employed simplifications in this work are the following:

- (1) Many-body and angle dependent interactions are not taken into account.
- (2) Quantum effects are not taken into consideration.
- (3) All particles are considered to be spherical and of the same size.

Assumption (1) restricts the applicability of the global optimization approach as developed to systems of particles interacting with two-body central forces. Although this model is certainly quite restrictive for some real systems because it ignores angle dependent force contributions and many-body force terms, it provides a valuable prototype for the study of microcluster mechanics. Furthermore, the proposed approach

can conceptually be extended to systems of particles interacting with many-body forces if an analytical expression for the total potential energy is given as a function of the Euclidean distances. Assumption (2) implies that the total potential energy is a continuously varying quantity, in other words it is not quantized. Any formulation of the problem that takes into account quantum effects must involve a number of discrete variables which further increase the already high complexity of the problem. Assumption (3) implies that all particles are identical and are of the same size. It has been introduced for the sake of simplicity and can be relaxed easily.

Under the aforementioned assumptions the potential energy of an N -particle cluster can be written as:

$$V = \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(r_{ij}),$$

where

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

and

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0.$$

Here V is the total potential energy of the microcluster as the summation of all two-body interaction terms, $v(r_{ij})$ is the potential energy term corresponding to the interaction of particle i with particle j , and r_{ij} is the Euclidean distance between i and j . Note that in the double summation, j spans from $i + 1$ to N so that we avoid doublecounting pair interactions and the interaction of a particle with itself. Furthermore, by specifying $x_1 = y_1 = z_1 = 0$, we fix the first particle at $(0, 0, 0)$, eliminating all three translational degrees of freedom of the microcluster. By further imposing $y_2 = z_2 = z_3 = 0$ we eliminate the rotational degrees of freedom as well.

Many different formulas for $v(r)$ have been used in physical models since there is no single, rigorously derived from first principles, expression for $v(r)$. In order for $v(r)$ to have satisfactory behavior in the entire configurational space, it must comply with the following requirements in $v(r)$ [5].

- (1) $v(r) \rightarrow 0^-$ as $r \rightarrow \infty$. (*No interaction at finite separation.*)
- (2) $v(r) \rightarrow \infty$ for $r < r_{\min}$ and $r_{\min} \geq 0$. (*Rigid core.*)
- (3) $v'(r_0) = 0$, $v''(r_0) > 0$ for a unique r_0 . (*Single stable state.*)

Pair potentials that have been used in cluster studies include the following [5]:

- (1) $v(r) = (n - m)^{-1} [nr^{-m} - mr^{-n}]$ (Mie).
- (2) $v(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}$ (Lennard-Jones).
- (3) $v(r) = [1 - e^{\alpha(1-r)}]^2 - 1$ (Morse).

$$(4) \quad v(r) = Ae^{-ar^2} - Be^{-br^2} \text{ (Gaussian).}$$

$$(5) \quad v(r) = z^\alpha z^\beta / r + Ae^{-r/\rho} \text{ (Born-Meyer).}$$

A necessary but not sufficient condition for local optimality is that all first order derivatives at the global minimum point must be zero [65]. Posing the problem on the x_i, y_i, z_i Cartesian coordinates we can write for any local minimum point:

$$\sum_{j=1}^N \frac{v'(r_{ij})}{r_{ij}} (x_i - x_j) = 0, \quad \forall i = 2, \dots, N;$$

$$\sum_{j=1}^N \frac{v'(r_{ij})}{r_{ij}} (y_i - y_j) = 0, \quad \forall i = 3, \dots, N;$$

$$\sum_{j=1}^N \frac{v'(r_{ij})}{r_{ij}} (z_i - z_j) = 0, \quad \forall i = 4, \dots, N.$$

Note that $v'(r_{ij})$ is the first order derivative of $v(r_{ij})$ with respect to the Euclidean distance r_{ij} . The points that conform with the above conditions are called stationary points, and their number increases more than exponentially with N [15]. However, only a fraction of the stationary points are indeed local minima, the rest of them are saddle points or local minima. The extra condition required in order to guarantee local minimality is that the Hessian matrix H must be positive definite at the point in question. The Hessian matrix contains the second order derivatives with respect to x_i, y_i, z_i of the total potential energy function. An equivalent condition with a positive definite Hessian matrix is requiring all eigenvalues λ , to be positive at the point in question. A physical interpretation of the eigenvalues of H is that at any point they give the principal radii of the curvature, and the corresponding eigenvectors define the principal axes and the set of normal coordinates in terms of which the Hessian is diagonal. Note that the positivity of the elements of H is not a sufficient condition for local minimality, since there might be *valleys* falling away from a stationary point parallel to the principal directions.

Since all particles are assumed to be identical, we must consider the multiplicity of configurations which differ only by permutations of the particles. In fact, for an N -particle cluster there $(N-3)!$ identical structures. These structures that differ only in labelling of particles are equivalent under proper symmetry operations in three-space, or they correspond to enantiomorphic configurations [5] and are called *geometrically equivalent*.

The main difficulty in solving this problem arises from the fact that the objective is a nonconvex function of many variables. Any local optimization technique is likely to find only a local minimum at best. Any attempt to exhaustively enumerate

all stationary points or local minima is unlikely to succeed not only because of their very large number but also because there is no way of guaranteeing the enumeration of all of them. In the next section, a procedure is introduced for transforming the initial nonconvex objective function to the difference of two convex functions (DC transformation). Note that a number of expressions describing the two-body interactions are considered. Then, by exploiting the acquired DC structure of the problem, a global optimization algorithm is proposed.

3. Eigenvalue analysis

The main difficulty in solving the minimization problem as it has been presented in the previous section arises from the presence of nonconvexities in the objective function. In fact, it will be shown that even the expression for a single pair interaction potential is a nonconvex function. Let $v(r_{01})$ be the general expression for the pair potential between particle (0) and particle (1). If now we pose the problem in the Cartesian coordinate space, $v(r_{01})$ becomes a function of six variables $x_0, y_0, z_0, x_1, y_1, z_1$. However, particle (0) can be arbitrarily fixed at (x_0, y_0, z_0) and thus $v(r_{01})$ is essentially a function of only three variables as shown in [64]. A necessary and sufficient condition for convexity is that all the eigenvalues of the Hessian matrix of $v(r_{01})$ must be positive. The first and second order derivatives of $v(r_{01})$ with respect to x_1, y_1, z_1 are the following:

$$h_x = \frac{v'(r_{01})}{r_{01}}(x_1 - x_0),$$

$$h_y = \frac{v'(r_{01})}{r_{01}}(y_1 - y_0),$$

$$h_z = \frac{v'(r_{01})}{r_{01}}(z_1 - z_0),$$

$$h_{xx} = \left(v''(r_{01}) - \frac{v'(r_{01})}{r_{01}} \right) \frac{(x_1 - x_0)^2}{r_{01}^2} + \frac{v'(r_{01})}{r_{01}},$$

$$h_{yy} = \left(v''(r_{01}) - \frac{v'(r_{01})}{r_{01}} \right) \frac{(y_1 - y_0)^2}{r_{01}^2} + \frac{v'(r_{01})}{r_{01}},$$

$$h_{zz} = \left(v''(r_{01}) - \frac{v'(r_{01})}{r_{01}} \right) \frac{(z_1 - z_0)^2}{r_{01}^2} + \frac{v'(r_{01})}{r_{01}},$$

$$h_{xy} = \left(v''(r_{01}) - \frac{v'(r_{01})}{r_{01}} \right) \frac{(x_1 - x_0)(y_1 - y_0)}{r_{01}^2},$$

$$h_{xz} = \left(v''(r_{01}) - \frac{v'(r_{01})}{r_{01}} \right) \frac{(x_1 - x_0)(z_1 - z_0)}{r_{01}^2},$$

$$h_{yz} = \left(v''(r_{01}) - \frac{v'(r_{01})}{r_{01}} \right) \frac{(y_1 - y_0)(z_1 - z_0)}{r_{01}^2}.$$

Here $v'(r_{01})$, $v''(r_{01})$ correspond to the first and second derivative of $v(r_{01})$ with respect to the Euclidean distance r_{01} . The three eigenvalues λ_1 , λ_2 , λ_3 can then be calculated from the following equation.

$$\det \begin{pmatrix} h_{xx} - \lambda & h_{xy} & h_{xz} \\ h_{xy} & h_{yy} - \lambda & h_{yz} \\ h_{xz} & h_{yz} & h_{zz} - \lambda \end{pmatrix} = 0.$$

By expanding the determinant we obtain:

$$\begin{aligned} & -\lambda^3 \\ & + \lambda^2(h_{xx} + h_{yy} + h_{zz}) \\ & + \lambda(h_{xy}^2 + h_{xz}^2 + h_{yz}^2 - h_{xx}h_{yy} - h_{xx}h_{zz} - h_{yy}h_{zz}) \\ & + (h_{xx}h_{yy}h_{zz} - h_{xy}^2h_{zz} - h_{yz}^2h_{xx} + 2h_{xy}h_{xz}h_{yz}) = 0. \end{aligned}$$

After substituting the expressions for h_{xx} , h_{yy} , h_{zz} , h_{xy} , h_{xz} , h_{yz} , the above equation becomes:

$$-\lambda^3 + \lambda^2 \left(v''(r_{01}) + 2 \frac{v'(r_{01})}{r_{01}} \right) - \lambda \frac{v'(r_{01})}{r_{01}} \left(v''(r_{01}) + 2 \frac{v'(r_{01})}{r_{01}} \right) + v''(r_{01}) \left(\frac{v'(r_{01})}{r_{01}} \right)^2 = 0.$$

By factoring the above equation we obtain the following simple formula,

$$\left(\lambda - \frac{v'(r_{01})}{r_{01}} \right)^2 (\lambda - v''(r_{01})) = 0,$$

which yields the following expressions for the three eigenvalues:

$$\lambda_{1,2} = \frac{v'(r_{01})}{r_{01}},$$

$$\lambda_3 = v''(r_{01}).$$

COROLLARY 1

$v(r_{01})$ is convex if and only if $v'(r_{01})$ and $v''(r_{01})$ are nonnegative for every r_{01} in (r_{\min}, r_{\max}) .

$v(r_{01})$ is convex in

$$(r_{\min}, r_{\max}) \Leftrightarrow v'(r_{01}) \geq 0, v''(r_{01}) \geq 0, \quad \forall r_{01} \in (r_{\min}, r_{\max}).$$

It is worthwhile to note that the above result is valid for any type of potential describing the interaction of two particles with central forces since no assumptions for the functionality between r_{01} and $v(r_{01})$ have been made. Furthermore, convexity of $v(r_{01})$ in the r_{01} space is not a sufficient condition for convexity in the x_1, y_1, z_1 Cartesian coordinate space. If $v(r_{01})$ is convex in r_{01} then $v''(r_{01})$ will be indeed positive; however, $v'(r_{01})$ might not be. Because the expression for $v(r_{01})$ must comply with the requirements set by [5], $v'(r_{01})$ is negative for $r \leq r_0$ and $v''(r_{01})$ is negative for $r \geq r_1$. Thus, $v(r_{01})$ stays convex only within the narrow interval (r_0, r_1) . Here r_0 corresponds to the value of r_{01} which zeroes the first derivative of $v(r_{01})$ and r_1 to the value of r_{01} which zeroes the second derivative of $v(r_{01})$. For different pair potential models table 1 summarizes the expressions for the eigenvalues $\lambda_{1,2}, \lambda_3$ and table 2 the analytical formulas (if they exist) for r_0, r_1 .

The very important property of convexity of $v(r_{01})$ can be maintained by augmenting $v(r_{01})$ with the addition of a "strongly" convex term. This term may have the following form:

$$\alpha_{01}(x_0^2 + y_0^2 + z_0^2 + x_1^2 + y_1^2 + z_1^2).$$

Note that α_{01} is an arbitrary large positive number. The effect of this extra term in the Hessian matrix is to add the term $2\alpha_{01}$ to all the diagonal elements of the matrix which, given a sufficiently large α_{01} , forces all the eigenvalues to become non-negative by overpowering the original convexity characteristics of $v(r_{01})$. Let $\phi(r_{01})$ be the summation of $v(r_{01})$ and the extra term $\alpha_{01}(x_0^2 + y_0^2 + z_0^2 + x_1^2 + y_1^2 + z_1^2)$.

$$\phi(r_{01}) = v(r_{01}) + \alpha_{01}(x_0^2 + y_0^2 + z_0^2 + x_1^2 + y_1^2 + z_1^2).$$

It is quite straightforward to find that the eigenvalues of the Hessian which corresponds to $\phi(r_{01})$ are:

$$\lambda_{1,2} = \frac{v'(r_{01})}{r_{01}} + 2\alpha_{01},$$

$$\lambda_3 = v''(r_{01}) + 2\alpha_{01}.$$

Table 1
Eigenvalues $\lambda_{1,2}$, λ_3 for different potential models.

Potential	$v(r)$	$\lambda_{1,2}$	λ_3
Coulomb	$\frac{z^\alpha z^\beta}{r}$	$-\frac{z^\alpha z^\beta}{r^3}$	$\frac{2z^\alpha z^\beta}{r^3}$
Scaled LJ	$\frac{1}{r^{12}} - \frac{2}{r^6}$	$12\left(\frac{1}{r^8} - \frac{1}{r^{14}}\right)$	$12\left(\frac{13}{r^{14}} - \frac{7}{r^8}\right)$
LJ	$4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right\}$	$\frac{24\epsilon}{\sigma^2}\left[\left(\frac{\sigma}{r}\right)^8 - \left(\frac{\sigma}{r}\right)^{14}\right]$	$\frac{24\epsilon}{\sigma^2}\left[26\left(\frac{\sigma}{r}\right)^{14} - 7\left(\frac{\sigma}{r}\right)^8\right]$
Mie	$-\frac{1}{n-m}\left[\frac{n}{r^m} - \frac{m}{r^n}\right]$	$-\frac{nm}{n-m}\left[\frac{1}{r^{n+2}} - \frac{1}{r^{m+2}}\right]$	$-\frac{nm}{n-m}\left[\frac{(m+1)}{r^{m+2}} - \frac{(n+1)}{r^{n+2}}\right]$
Morse	$\left[1 - e^{a(1-r)}\right]^2 - 1$	$\frac{2a}{r}e^{a(1-r)}\left[1 - e^{a(1-r)}\right]$	$2a^2e^{a(1-r)}\left[2e^{a(1-r)} - 1\right]$
Gaussian	$Ae^{-ar^2} - Be^{-br^2}$	$2\left(bBe^{-br^2} - aAe^{-ar^2}\right)$	$4r^2\left(a^2Ae^{-ar^2} - b^2Be^{-br^2}\right)$
Born-Meyer	$\frac{z^\alpha z^\beta}{r} + Ae^{-r/\rho}$	$\frac{-z^\alpha z^\beta}{r^3} - \frac{A}{\rho r}e^{-r/\rho}$	$\frac{2z^\alpha z^\beta}{r^3} + \frac{A}{\rho^2}e^{-r/\rho}$

Table 2
Convex interval (r_0, r_1) for different potential models.

Potential	$v(r)$	r_0	r_1
Scaled LJ	$\frac{1}{r^{12}} - \frac{2}{r^6}$	1	$\left(\frac{13}{7}\right)^{1/6} \approx 1.108683$
LJ	$4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right\}$	$2^{1/6}\sigma$	$\left(\frac{26}{7}\right)^{1/6}\sigma$
Mie	$-\frac{1}{n-m}\left[\frac{n}{r^m} - \frac{m}{r^n}\right]$	1	$\left(\frac{n+1}{m+1}\right)^{1/(n-m)}$
Morse	$\left[1 - e^{a(1-r)}\right]^2 - 1$	1	$\frac{\ln 2}{a} + 1$

Since we want all the eigenvalues to be nonnegative, we have the following inequality constraints for α_{01} .

$$\begin{aligned}\alpha_{01} &\geq 0, \\ \alpha_{01} &\geq -\frac{v'(r_{01})}{2r_{01}}, \\ \alpha_{01} &\geq \frac{v''(r_{01})}{2}.\end{aligned}$$

The minimum value of α_{01} that will maintain all eigenvalues of $\phi(r_{01})$ nonnegative can then be derived as the solution of the following optimization problem:

$$\alpha_{01} = \max_{r_{01}} \begin{cases} \frac{v'(r_{01})}{2r_{01}} & \text{if } r_{\min} \leq r_{01} \leq r_0, \\ 0 & \text{if } r_0 \leq r_{01} \leq r_1, \\ \frac{v''(r_{01})}{2} & \text{if } r_1 \leq r_{01} \leq r_{\max}. \end{cases}$$

Note that at the global minimum all interparticle distances are never significantly less than one, because otherwise the corresponding pair potential resumes a large positive value which cannot occur at the global minimum. In [64] rigorous lower bounds on the minimum interparticle distances are given for different cluster sizes. A sufficient value of r_{\min} for all practical purposes is about 0.9. If we define $\psi(r_{01})$ to be equal to

$$\psi(r_{01}) = \alpha_{01}(x_0^2 + y_0^2 + z_0^2 + x_1^2 + y_1^2 + z_1^2),$$

then the initial nonconvex expression for the pair has been transformed to the difference of two convex functions, more specifically:

$$v(r_{01}) = \phi(r_{01}) - \psi(r_{01}).$$

By applying the same analysis to every pair potential interaction, the total potential energy expression can be written as the difference of two convex functions (DC structure).

4. Problem formulation

The problem of finding the global minimum energy of N particles interacting with central two-body forces can be formulated as the following nonlinear optimization problem NLP:

(P1)

$$\begin{aligned} \text{minimize } V = & \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(x_i, y_i, z_i, x_j, y_j, z_j) \\ \text{subject to } & x_i^L \leq x_i \leq x_i^U, \quad i = 2, \dots, N, \\ & y_i^L \leq y_i \leq y_i^U, \quad i = 3, \dots, N, \\ & z_i^L \leq z_i \leq z_i^U, \quad i = 4, \dots, N, \\ & x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0, \end{aligned}$$

where $x_i^L, y_i^L, z_i^L, x_i^U, y_i^U, z_i^U$ define the box constraints for the x_i, y_i, z_i variables. In formulation (P1) the objective function is nonconvex so no guarantee for convergence to the global minimum can be made. In view of the transformation presented in the previous section, (P1) can be reformulated as the following (DC) programming problem.

(P2)

$$\begin{aligned} \text{minimize } V = & \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(x_i, y_i, z_i, x_j, y_j, z_j) + \alpha_{ij} (x_i^2 + y_i^2 + z_i^2 + x_j^2 + y_j^2 + z_j^2) \right\} \\ & - \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N \alpha_{ij} (x_i^2 + y_i^2 + z_i^2 + x_j^2 + y_j^2 + z_j^2) \right\} \\ \text{subject to } & x_i^L \leq x_i \leq x_i^U, \quad i = 2, \dots, N, \\ & y_i^L \leq y_i \leq y_i^U, \quad i = 3, \dots, N, \\ & z_i^L \leq z_i \leq z_i^U, \quad i = 4, \dots, N, \\ & x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0, \end{aligned}$$

where

$$\alpha_{ij} = \max_{r_{ij}} \begin{cases} -\frac{v'(r_{ij})}{2r_{ij}} & \text{if } r_{\min} \leq r_{ij} \leq r_0, \\ 0 & \text{if } r_0 \leq r_{ij} \leq r_1, \\ -\frac{v''(r_{ij})}{2} & \text{if } r_1 \leq r_{ij} \leq r_{\max}, \end{cases}$$

and

$$r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}.$$

In this work an approach for finding the global minimum based on the global optimization algorithm GOP developed by Floudas and Visweswaran [1–4] is presented. The GOP algorithm can be applied to optimization problems that have or can be transformed to the following form, and it guarantees ε -convergence to the global minimum in a finite number of steps:

$$\begin{aligned} & \underset{x,y}{\text{minimize}} && f(x,y) \\ & \text{subject to} && g(x,y) \leq 0, \\ & && h(x,y) = 0, \\ & && x \in X \in Y. \end{aligned}$$

Here X , Y are non-empty, compact, convex sets and $f(x, y)$, $g(x, y)$ and $h(x, y)$ are continuous, piecewise differentiable, and analytical functions over $X \times Y$. The initial variable set is partitioned to the sets X and Y in such a way that $f(x, y)$ and $g(x, y)$ are convex in x for every fixed y , and convex in y for every fixed x . And also, $h(x, y)$ is linear in x for every fixed y , and linear in y for every fixed x .

If these conditions cannot be satisfied with only partitioning of variables, transformation of variables can be employed. The GOP algorithm has been applied to optimization problems involving bilinear, quadratic, polynomial, or rational polynomial terms in the objective function and/or constraints [1–4].

In view of the GOP requirements for convergence to the global minimum, the following transformation of variables is performed on formulation (P2). The coordinate set of variables x_i, y_i, z_i (x -type) is "mirrored" to X_i, Y_i, Z_i (y -type) so $x_i = X_i, y_i = Y_i, z_i = Z_i, \forall i = 1, \dots, N$. Then, for each pair-potential, we add the term $\alpha(X_i^2 + Y_i^2 + Z_i^2 + X_j^2 + Y_j^2 + Z_j^2)$ to the total potential energy function. The purpose of these added terms is to "convexify" each pair potential by transferring the nonconvexities to the terms that we subtract from each pair-potential contribution. The terms that we subtract have the following form; $\alpha_{ij}(x_i X_i + y_i Y_i + z_i Z_i + x_j X_j + y_j Y_j + z_j Z_j)$. Note that they are linear in x_i, y_i, z_i for fixed X_i, Y_i, Z_i and vice-versa. The values of α_{ij} 's are selected so that they are the minimum ones that guarantee convexification of each pair-potential term with the addition of the extra terms. Based on the above analysis formulation (P2) can be reformulated as follows:

(P3)

$$\begin{aligned} \text{minimize } V = & \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(X_i, Y_i, Z_i, X_j, Y_j, Z_j) + \alpha_{ij} (X_i^2 + Y_i^2 + Z_i^2 + X_j^2 + Y_j^2 + Z_j^2) \right\} \\ & - \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N \alpha_{ij} (x_i X_i + y_i Y_i + z_i Z_i + x_j X_j + y_j Y_j + z_j Z_j) \right\} \end{aligned}$$

$$\begin{aligned}
\text{subject to} \quad & x_i = X_i, & i = 2, \dots, N, \\
& y_i = Y_i, & i = 3, \dots, N, \\
& z_i = Z_i, & i = 4, \dots, N, \\
& x_i^L \leq x_i \leq x_i^U, & i = 2, \dots, N, \\
& y_i^L \leq y_i \leq y_i^U, & i = 3, \dots, N, \\
& z_i^L \leq z_i \leq z_i^U, & i = 4, \dots, N, \\
& x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0, \\
& x_i^L \leq X_i \leq x_i^U, & i = 2, \dots, N, \\
& y_i^L \leq Y_i \leq y_i^U, & i = 3, \dots, N, \\
& z_i^L \leq Z_i \leq z_i^U, & i = 4, \dots, N, \\
& X_1 = Y_1 = Z_1 = Y_2 = Z_2 = Z_3 = 0.
\end{aligned}$$

Note that if we fix X_i, Y_i, Z_i and let x_i, y_i, z_i vary, formulation (P3) corresponds to a linear programming problem. If now we fix x_i, y_i, z_i and let X_i, Y_i, Z_i vary (P3) becomes a convex NLP programming problem. Thus, all GOP requirements are satisfied. Let us now consider a more restrictive version of (P3), where all y -type variables are fixed, namely, $X_i = X_i^K, Y_i = Y_i^K, Z_i = Z_i^K$,

(P4)

$$\begin{aligned}
\text{minimize } V = & \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(X_i^K, Y_i^K, Z_i^K, X_j^K, Y_j^K, Z_j^K) \right\} \\
& + \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N \alpha_{ij} \left[(X_i^K)^2 + (Y_i^K)^2 + (Z_i^K)^2 + (X_j^K)^2 + (Y_j^K)^2 + (Z_j^K)^2 \right] \right\} \\
& - \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N \alpha_{ij} (x_i X_i^K + y_i Y_i^K + z_i Z_i^K + x_j X_j^K + y_j Y_j^K + z_j Z_j^K) \right\} \\
\text{subject to} \quad & x_i = X_i^K, & i = 2, \dots, N, \\
& y_i = Y_i^K, & i = 3, \dots, N,
\end{aligned}$$

$$\begin{aligned}
z_i &= Z_i^K, & i &= 4, \dots, N, \\
x_i^L &\leq x_i \leq x_i^U, & i &= 2, \dots, N, \\
y_i^L &\leq y_i \leq y_i^U, & i &= 3, \dots, N, \\
z_i^L &\leq z_i \leq z_i^U, & i &= 4, \dots, N, \\
x_1 &= y_1 = z_1 = y_2 = z_2 = z_3 = 0.
\end{aligned}$$

Problem (P4) is called the *primal problem* and its solution provides an upper bound to the solution of (P3) since it corresponds to a more restricted form of it. It is clear that (P4) is always feasible and its solution corresponds to a single function evaluation. By applying the KKT conditions [65] we obtain for the Lagrange multipliers λ_{xi} , λ_{yi} , λ_{zi} associated with the equality constraints in (P3):

$$\begin{aligned}
\lambda_{xi} &= \left(\sum_{j=1}^N \alpha_{ij} \right) X_i^K, & i &= 2, \dots, N, \\
\lambda_{yi} &= \left(\sum_{j=1}^N \alpha_{ij} \right) Y_i^K, & i &= 3, \dots, N, \\
\lambda_{zi} &= \left(\sum_{j=1}^N \alpha_{ij} \right) Z_i^K, & i &= 4, \dots, N.
\end{aligned}$$

Problem (P3) can also be viewed as a two-level optimization problem, where the minimization over x_i , y_i , z_i and X_i , Y_i , Z_i occurs separately. By projecting in the space of the X_i , Y_i , Z_i variables [66], we can reformulate (P3) as an inner optimization problem over x_i , y_i , z_i and an outer optimization problem over X_i , Y_i , Z_i .

(P5)

$$\text{minimize}_{X_i, Y_i, Z_i} \xi(X_i, Y_i, Z_i)$$

subject to

$$\begin{aligned}
\xi(X_i, Y_i, Z_i) &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(X_i, Y_i, Z_i, X_j, Y_j, Z_j) + \alpha_{ij} (X_i^2 + Y_i^2 + Z_i^2 + X_j^2 + Y_j^2 + Z_j^2) \\
&+ \inf_{x_i, y_i, z_i} \left\{ - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \alpha_{ij} (x_i X_i + y_i Y_i + z_i Z_i + x_j X_j + y_j Y_j + z_j Z_j) \right\}
\end{aligned}$$

$$\begin{aligned}
x_i &= X_i, & i &= 2, \dots, N, \\
y_i &= Y_i, & i &= 3, \dots, N, \\
z_i &= Z_i, & i &= 4, \dots, N, \\
x_i^L &\leq x_i \leq x_i^U, & i &= 2, \dots, N, \\
y_i^L &\leq y_i \leq y_i^U, & i &= 3, \dots, N, \\
z_i^L &\leq z_i \leq z_i^U, & i &= 4, \dots, N, \\
x_1 &= y_1 = z_1 = y_2 = z_2 = z_3 = 0, \\
x_i^L &\leq X_i \leq x_i^U, & i &= 2, \dots, N, \\
y_i^L &\leq Y_i \leq y_i^U, & i &= 3, \dots, N, \\
z_i^L &\leq Z_i \leq z_i^U, & i &= 4, \dots, N, \\
X_1 &= Y_1 = Z_1 = Y_2 = Z_2 = Z_3 = 0, \\
\forall X_i &\in \mathcal{X}, \quad \forall Y_i \in \mathcal{Y}, \quad \forall Z_i \in \mathcal{Z}.
\end{aligned}$$

$\mathcal{X}, \mathcal{Y}, \mathcal{Z}$ are the subsets of (x_i^L, x_i^U) , (y_i^L, y_i^U) , (z_i^L, z_i^U) for which the outer optimization problem is feasible for some value of x_i, y_i, z_i . Note that the inner optimization problem is a parametric in X_i, Y_i, Z_i so the set of values that $v(X_i, Y_i, Z_i)$ attains is known only implicitly. By dualizing the equality constraints in formulation (P5) we obtain the following dual representation.

(P6)

$$\begin{aligned}
\xi(X_i, Y_i, Z_i) &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(X_i, Y_i, Z_i, X_j, Y_j, Z_j) + \alpha_{ij} (X_i^2 + Y_i^2 + Z_i^2 + X_j^2 + Y_j^2 + Z_j^2) \\
&+ \sup_{\lambda_{x_i}, \lambda_{y_i}, \lambda_{z_i}} \left\{ - \sum_{i=2}^N \lambda_{x_i} X_i - \sum_{i=3}^N \lambda_{y_i} Y_i - \sum_{i=4}^N \lambda_{z_i} Z_i \right. \\
&+ \inf_{x_i, y_i, z_i} \left[- \sum_{i=1}^{N-1} \sum_{j=i+1}^N \alpha_{ij} (x_i X_i + y_i Y_i + z_i Z_i + x_j X_j + y_j Y_j + z_j Z_j) \right. \\
&\left. \left. + \sum_{i=2}^N \lambda_{x_i} x_i + \sum_{i=3}^N \lambda_{y_i} y_i + \sum_{i=4}^N \lambda_{z_i} z_i \right] \right\}
\end{aligned}$$

$$\begin{aligned}
x_i^L &\leq x_i \leq x_i^U, & i = 2, \dots, N, \\
y_i^L &\leq y_i \leq y_i^U, & i = 3, \dots, N, \\
z_i^L &\leq z_i \leq z_i^U, & i = 4, \dots, N, \\
x_1 &= y_1 = z_1 = y_2 = z_2 = z_3 = 0, \\
\forall X_i &\in \mathcal{X}, \quad \forall Y_i \in \mathcal{Y}, \quad \forall Z_i \in \mathcal{Z}.
\end{aligned}$$

We can further relax (P6) by dropping the last implicit constraint on X_i, Y_i, Z_i , and not considering the maximization over $\lambda_{xi}, \lambda_{yi}, \lambda_{zi}$. Instead, we substitute the values for $\lambda_{xi}, \lambda_{yi}, \lambda_{zi}$ evaluated from the KKT conditions. By taking advantage of the fact that (P6) is separable in x_i, y_i, z_i we obtain the relaxed dual (RD) formulation. Clearly, the solution of this problem provides a lower bound to the solution of (P2) since it corresponds to its relaxation.

(P7)

$$\begin{aligned}
&\text{Minimize} && \mu_B \\
&X_i, Y_i, Z_i, \mu_B \\
\text{subject to} &&& \mu_B \geq L(x_i, y_i, z_i, X_i, Y_i, Z_i) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(X_i, Y_i, Z_i, X_j, Y_j, Z_j) \\
&&& + \sum_{i=2}^N \left(\sum_{j=1}^N \alpha_{ij} \right) \min_{x_i} (X_i^K - X_i)(x_i - X_i) \\
&&& + \sum_{i=3}^N \left(\sum_{j=1}^N \alpha_{ij} \right) \min_{y_i} (Y_i^K - Y_i)(y_i - Y_i) \\
&&& + \sum_{i=4}^N \left(\sum_{j=1}^N \alpha_{ij} \right) \min_{z_i} (Z_i^K - Z_i)(z_i - Z_i), \\
&&& x_i^L \leq x_i \leq x_i^U, \quad i = 2, \dots, N, \\
&&& y_i^L \leq y_i \leq y_i^U, \quad i = 3, \dots, N, \\
&&& z_i^L \leq z_i \leq z_i^U, \quad i = 4, \dots, N, \\
&&& x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0,
\end{aligned}$$

$$\begin{aligned}
 x_i^L &\leq X_i \leq x_i^U, & i = 2, \dots, N, \\
 y_i^L &\leq Y_i \leq y_i^U, & i = 3, \dots, N, \\
 z_i^L &\leq Z_i \leq z_i^U, & i = 4, \dots, N, \\
 X_1 &= Y_1 = Z_1 = Y_2 = Z_2 = Z_3 = 0.
 \end{aligned}$$

Problem (P7) is linear in x_i, y_i, z_i so the minimum point x_i, y_i, z_i will be at an upper or lower bound depending on whether their coefficient is negative or positive, respectively. These variables x_i, y_i, z_i are called *connected variables* and the gradients of the Lagrange function in terms of the connected variables are called *qualifying constraints* which in problem (P7) have the following form:

$$X_i^K - X_i, \quad Y_i^K - Y_i, \quad Z_i^K - Z_i.$$

This suggests that instead of minimizing explicitly in terms of the connected variables x_i, y_i, z_i , it is sufficient to solve (P7) once for each combination of their bounds and select the infimum over the calculated minima in all iterations. We have shown that the solution of (P4) provides an upper bound and the solution of (P7) a lower bound on the actual solution of the problem. This calls for an alternative scheme between (P4) and (P7) to determine the global solution of (P2).

Based on the above analysis, the solution of the initial nonconvex problem (P2) has been transformed to the solution of a series of convex nonlinear relaxed dual problems which can be solved efficiently with existing algorithms [63]. The solution of the primal problem, which corresponds to a single function, provides an upper bound to the global minimum, whereas the relaxed dual problems yield lower bounds. It has been proved [1, 2] that by iterating between the primal problem and the relaxed dual problems ε -convergence to the global minimum is achieved in a finite number of steps.

The main limitation with this approach is that for n connected variables, up to 2^n relaxed dual problems must be solved per iteration. These early observations motivated the development of a number of computational properties. First, if a qualifying constraint always maintains constant sign, then the relaxed dual problems involving the reverse qualifying constraint do not need to be solved [3]. Furthermore, if a qualifying constraint is rigorously equal to zero for some iteration k , then the corresponding connected variable can be set to either its lower or upper bound [3].

In this work, the bounds of the variables are updated because this results in tighter lower bounding of the objective function. More specifically, the bounds of the variables for the current iteration are derived from the bounds of the variables of the relaxed dual problem whose solution is the current point. Based on this, we can define a 2^n -tree with nodes corresponding to relaxed dual problems and levels corresponding to iterations. In the current iteration, only the Lagrange functions of relaxed dual problems which correspond to predecessor nodes for the node of the

current relaxed dual problem are incorporated. It is interesting to note that their number is rather small, typically of the order $\log_2(K)$. The bounds for the current iteration are provided by the relaxed dual problem corresponding to the parent node of the current relaxed dual problems. Note also that no qualifying constraints are needed in the formulation. The application of this property greatly reduces the required number of iterations for convergence as well as improving the CPU time for each relaxed dual problem by including only a small number of previous Lagrange functions and by excluding all qualifying constraints from the current relaxed dual problem.

5. Algorithmic procedure

The basic steps of this procedure are as follows:

Step 1: Initialization

An initial point X_i^0, Y_i^0, Z_i^0 is selected, the iteration K is set to zero, and a convergence tolerance ε is decided. Appropriate box constraints $X_i^L, Y_i^L, Z_i^L, X_i^U, Y_i^U, Z_i^U$ for each variable $x_i, y_i, z_i, X_i, Y_i, Z_i$ are selected. P^{UBD}, R^{LBD} are defined as the minimum solution of the primal problems and the maximum solution of the relaxed dual problems so far, respectively.

Step 2: Primal problem

The primal problem (P5) is solved at X_i^K, Y_i^K, Z_i^K for the variables x_i, y_i, z_i and the Lagrange multipliers $\lambda_{xi}, \lambda_{yi}, \lambda_{zi}$. This corresponds to a single function evaluation. If the solution of the primal is less than P^{UBD} then P^{UBD} is equal to the solution of the primal problem.

Step 3: Selection of previous Lagrange functions and update of bounds

The Lagrange functions from relaxed dual problems in previous iterations ($k = 1, 2, \dots, K-1$) corresponding to predecessor nodes for the current iteration are included to be constraints in the current iteration's relaxed dual problems. The box constraints of the current iteration are the ones of the relaxed dual problem corresponding to the parent node for the current tree level (iteration).

Step 4: Update of α_{ij} parameters

The convexification parameters α_{ij} are updated in every iteration as follows:

$$\alpha_{ij} = \max_{r_{ij}} \begin{cases} -\frac{v'(r_{ij})}{2r_{ij}} & \text{if } r_{\min} \leq r_{ij} \leq r_0, \\ 0 & \text{if } r_0 \leq r_{ij} \leq r_1, \\ -\frac{v''(r_{ij})}{2} & \text{if } r_1 \leq r_{ij} \leq r_{\max}; \end{cases}$$

$$r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}$$

$$x_i^l \leq x_i \leq x_i^u, \quad i = 2, \dots, N,$$

$$y_i^l \leq y_i \leq y_i^u, \quad i = 3, \dots, N,$$

$$z_i^l \leq z_i \leq z_i^u, \quad i = 4, \dots, N,$$

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0.$$

Here $x_i^l, y_i^l, z_i^l, x_i^u, y_i^u, z_i^u$ are the current bounds on x_i, y_i, z_i .

Step 5: Non-interior current point (X_i^K, Y_i^K, Z_i^K)

If any of the X_i^K, Y_i^K, Z_i^K is at its bound (lower/upper) then the appropriate relaxed dual problems are eliminated.

Step 6: Solution of relaxed dual problems

For every combination of bounds $B_{x_i}^K, B_{y_i}^K, B_{z_i}^K$ of the connected variables x_i, y_i, z_i respectively, that has not been found to activate the checks in step 5 the following relaxed dual problem is solved.

(P8)

$$\begin{aligned} & \text{Minimize} && \mu_B \\ & X_i, Y_i, Z_i, \mu_B \\ & \text{subject to} && \mu_B \geq L_k \left(x_i^{B_{x_i}^k}, y_i^{B_{y_i}^k}, z_i^{B_{z_i}^k}, X_i, Y_i, Z_i \right), \quad \forall k = 1, 2, \dots, K-1, \\ & && \mu_B \geq L_k \left(x_i^{B_{x_i}^k}, y_i^{B_{y_i}^k}, z_i^{B_{z_i}^k}, X_i, Y_i, Z_i \right), \\ & && x_i^{K,l} \leq X_i \leq x_i^{K,u}, \quad i = 2, \dots, N, \\ & && y_i^{K,l} \leq Y_i \leq y_i^{K,u}, \quad i = 3, \dots, N, \\ & && z_i^{K,l} \leq Z_i \leq z_i^{K,u}, \quad i = 4, \dots, N, \\ & && X_1 = Y_1 = Z_1 = Y_2 = Z_2 = Z_3 = 0. \end{aligned}$$

Here L_k are the Lagrange functions from the previous iterations, and L_K the current one. $B_{x_i}^K, B_{y_i}^K, B_{z_i}^K$ are the set of values of the connected variables x_i, y_i, z_i in the Lagrange function from the k th iteration and $x_i^{K,l}, y_i^{K,l}, z_i^{K,l}, x_i^{K,u}, y_i^{K,u}, z_i^{K,u}$ are the bounds on X_i, Y_i, Z_i in the current iteration K .

Step 7: Update R^{LBD} , X_i^K , Y_i^K , Z_i^K

After all relaxed dual problems have been solved, a new lower bound R^{LBD} for the global minimum is selected which corresponds to the lowest value of the stored solutions of all relaxed dual problems from all iterations so far. At the same time, the values of X_i , Y_i , Z_i of the minimum stored solution are selected for the next current point. Once selected, the stored solution is deleted from the list. This ensures that no relaxed dual problem will return to the same solution during successive iterations.

Step 8: Check for convergence

If $P^{UBD} - R^{LBD} < 0$, then rigorous convergence has been achieved, and the algorithm stops. If $P^{UBD} - R^{LBD} < \epsilon$, then ϵ -convergence has been achieved and the algorithm terminates. Otherwise, we set $K = K + 1$ and we return to **step 2**.

This global optimization algorithmic procedure has been applied to a number of problems which are presented in the next section.

6. Examples for $N \leq 7$

By using the global optimization procedure presented earlier along with the convexification procedure the global minimum potential energy configurations of small microclusters $2 \leq N \leq 7$ are generated. Two different potential expressions have been employed, the scaled Lennard–Jones potential and the Morse potential due to their simplicity and wide acceptance. The value of the parameter a for the Morse potential has been chosen to be $a = 3.0$. Table 3 summarizes the total minimum potential energies for Lennard–Jones microclusters and table 4 the ones for Morse microclusters.

It is quite interesting that both expressions for the potential yield the same global minimum total potential energy configurations. The global minimum structure

Table 3

Global minimum potential energies $2 \leq N \leq 7$
for Lennard–Jones microclusters.

N	V_{total}^{LJ}
2	-1.000
3	-3.000
4	-6.000
5	-9.104
6	-12.712
7	-16.505

Table 4

Global minimum potential energies $2 \leq N \leq 7$
for Morse microclusters.

N	V_{total}^{Morse}
2	-1.000
3	-3.000
4	-4.000
5	-9.019
6	-12.530
7	-15.893

for $N = 2$ corresponds to two particles "touching" each other. For $N = 3$ three particles form a unit equilateral triangle at the global minimum. For $N = 4$ the four particles are placed at the vertices of a regular tetrahedron. For $N = 5$ a trigonal bipyramid, slightly contracted along the symmetry axis and distended in the symmetry plane corresponds to the global energy structure. For $N = 6$ a regular octahedron with slightly contracted sides yields the global optimum configuration. Finally, for $N = 7$ the regular icosahedron (pentagonal bipyramid) with slightly distended edges and contracted axial distances is the structure involving the global minimum total potential energy.

For larger N , the complexity of the problem limits the use of the general global optimization procedure. In the next section, a "relaxation" of the global optimization procedure is presented which for larger microclusters yields tight lower and upper bounds on the global minimum total potential energy as well as excellent initial points for a possible local optimization approach.

7. A relaxation of the global optimization approach

As it has been mentioned earlier, the bottleneck of the employed global optimization approach is the large number of connected variables of the problem which gives rise to a potentially very high number of relaxed dual problems that have to be solved per iteration. This motivates the employed relaxation of the global optimization approach which stems from the fact that usually the global minimum potential energy configuration of an N -particle cluster is composed by the slightly perturbed global minimum configuration for $N - 1$ particles plus an extra particle. This means that when solving for the global minimum structure of N particles and the global minimum configuration for $N - 1$ particles is known, tight bounds for the coordinate variables of the first $N - 1$ particles can be used around the global minimum positions of an $(N - 1)$ -particle microcluster and only for the N th particle "loose" bounds are required. Based on this, the global minimum potential energy problem in (P1) can be reformulated as:

(P9)

$$\begin{aligned} \text{minimize } V &= \left\{ \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(x_i, y_i, z_i, x_j, y_j, z_j) \right\} \\ \text{subject to } & x_i^* - e \leq x_i \leq x_i^* + e, \quad i = 2, \dots, N - 1, \\ & y_i^* - e \leq y_i \leq y_i^* + e, \quad i = 3, \dots, N - 1, \\ & z_i^* - e \leq z_i \leq z_i^* + e, \quad i = 4, \dots, N - 1, \\ & -E \leq x_N \leq E, \quad -E \leq y_N \leq E, \quad -E \leq z_N \leq E, \\ & x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0. \end{aligned}$$

Here $e = 0.01 - 0.05$ accounts for the perturbation around the nominal point x_i^*, y_i^*, z_i^* which corresponds to the global minimum potential energy configuration of an $N - 1$ microcluster. Also, $E = 2.0 - 4.0$ defines a cube where the N th particle is expected to vary. Since x_i^*, y_i^*, z_i^* corresponds to the global minimum potential energy point of an $N - 1$ microcluster, V in formulation (P9) must be convex in terms of $x_i, y_i, z_i, i = 1, \dots, N - 1$ in a neighborhood of x_i^*, y_i^*, z_i^* . By assuming that e in formulation (P9) is sufficiently small, then in order to transform V to the difference of two convex functions only the term $\sum_{j=1}^N \alpha_{i,j}(x_N^2 + y_N^2 + z_N^2)$ is required. Thus, the Lagrange function resumes the following form:

(P10)

$$\begin{aligned}
 L(x_i, y_i, z_i, X_i, Y_i, Z_i) &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N v(X_i, Y_i, Z_i, X_j, Y_j, Z_j) \\
 &+ \left(\sum_{i=1}^N \alpha_{i,N} \right) (X_N^K - X_N)(x_N - X_N) \\
 &+ \left(\sum_{i=1}^N \alpha_{i,N} \right) (Y_N^K - Y_N)(y_N - Y_N) \\
 &+ \left(\sum_{i=1}^N \alpha_{i,N} \right) (Z_N^K - Z_N)(z_N - Z_N).
 \end{aligned}$$

Note that formulation (P10) involves only three connected variables x_N, y_N, z_N which means that irrespective of how large N is, only up to $2^3 = 8$ relaxed dual problems must be solved per iteration. By combining the Lagrange function in formulation (P10) with the presented global optimization procedure a number of examples $8 \leq N \leq 24$ has been considered for the scaled Lennard-Jones case. Tight lower and upper bounds on the global minimum solutions were first established by selecting the tolerance to be between 0.01-0.05. Then, by switching to a local optimization algorithm the global minimum potential energy structures were found. All these results are summarized in table 5 where E^L, E^U correspond to the lower and upper bounds on the global minimum energy E^* and Iter is the total number of iterations for obtaining the bounds.

A further relaxation of this procedure can be realized by "fixing" the first $N - 1$ particles to the coordinates of the global minimum total potential energy configuration of an $N - 1$ microcluster. This implies that the Lagrange function becomes now a function of only three variables X_N, Y_N, Z_N .

Table 5

Bounds and global minimum potential energies for LJ microclusters.

N	E^L	E^U	e	E	Iter	E^*
8	-20.633	-19.683	0.01	1.0	12	-19.822
9	-28.321	-24.111	0.01	1.0	21	-24.113
10	-29.783	-28.326	0.01	1.5	26	-28.423
11	-34.233	-32.559	0.02	1.5	31	-32.766
12	-39.522	-37.557	0.02	1.5	29	-37.968
13	-44.487	-42.290	0.02	1.5	15	-44.327
14	-49.469	-47.218	0.02	1.5	10	-47.845
15	-52.655	-52.083	0.02	1.5	11	-52.323
16	-57.612	-56.601	0.02	1.5	21	-56.816
17	-62.463	-61.222	0.05	1.5	32	-61.318
18	-67.591	-65.615	0.05	1.5	20	-66.531
19	-73.567	-72.117	0.10	1.5	22	-72.660
20	-78.485	-76.972	0.10	1.5	21	-77.177
21	-83.265	-81.427	0.10	1.5	14	-81.685
22	-87.754	-86.116	0.10	1.5	16	-86.810
23	-92.949	-91.276	0.10	1.5	8	-92.844
24	-98.920	-96.997	0.10	1.5	19	-97.349

(P11)

$$\begin{aligned}
L(X_N, Y_N, Z_N) &= \sum_{i=1}^{N-1} v(X_i^*, Y_i^*, Z_i^*, X_N, Y_N, Z_N) \\
&+ \left(\sum_{i=1}^N \alpha_{i,N} \right) (X_N^K - X_N)(x_N - X_N) \\
&+ \left(\sum_{i=1}^N \alpha_{i,N} \right) (Y_N^K - Y_N)(y_N - Y_N) \\
&+ \left(\sum_{i=1}^N \alpha_{i,N} \right) (Z_N^K - Z_N)(z_N - Z_N) \\
&+ \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} v(X_i^*, Y_i^*, Z_i^*, X_j^*, Y_j^*, Z_j^*).
\end{aligned}$$

Note that the point X_i^*, Y_i^*, Z_i^* corresponds to the global minimum for an $N-1$ microcluster. This new formulation results in substantial reduction on the CPU time per relaxed dual problem due to the reduction of the number of variables. However, because the $N-1$ atoms are "fixed" the obtained lower bounds might no longer be valid for the original problem. Nevertheless, by solving this formulation one can quickly generate points that are quite close to the global minimum one. A local optimization can then easily relax to the global minimum candidate. This calls for a two-stage procedure where the relaxed global optimization procedure generates a configuration which is likely to be close to the global minimum one and then a local optimization algorithm "relaxes" this configuration to the nearest minimum one. By applying this procedure for Morse microclusters $8 \leq N \leq 30$ a number of minima have been obtained which are summarized in table 6 where E^{init} is the initial

Table 6

Minimum potential energies of Morse ($a = 3$) microclusters.

N	E^{init}	E^{found}	E^{best}
8	-21.494	-22.043	-22.043
9	-26.307	-26.778	-26.778
10	-31.149	-31.274	-31.889
11	-36.350	-37.931	-37.931
12	-42.605	-44.098	-44.098
13	-51.653	-51.737	-51.737
14	-56.366	-56.660	-56.755
15	-62.746	-63.162	-63.162
16	-68.863	-69.036	-69.036
17	-75.041	-75.662	-75.662
18	-81.855	-82.579	-82.579
19	-89.087	-90.647	-90.647
20	-96.605	-97.417	-97.417
21	-103.960	-104.337	-104.337
22	-111.741	-112.041	-112.041
23	-120.546	-120.787	-120.787
24	-127.642	-127.885	-127.885
25	-135.272	-136.073	-136.073
26	-144.696	-145.322	-145.322
27	-152.161	-152.514	-152.514
28	-160.294	-160.773	-160.773
29	-169.909	-170.115	-170.115
30	-177.285	-177.579	-177.579

point provided by the relaxed global optimization procedure, E^{found} the obtained solution from the local optimization algorithm, and E^{best} the best reported value in

the literature. It appears that this procedure is successful at generating all best known configurations except for $N = 10$ and $N = 14$ because in these cases more than one particle has to be relocated. In fact, by fixing $N - 2$ particles this time and applying the relaxed global optimization procedure on the last two, the global minimum structures for $N = 10, 14$ as well have been reproduced.

Although these simplifications cannot guarantee convergence to the global minimum it appears that the second relaxation approach behaves very well for microclusters $N \leq 30$. Note that these approaches can be readily extended to larger microclusters by allowing more than one particle to have "loose" coordinate bounds. In this case, if M particles involve "loose" coordinate bounds then up to 2^{3M} relaxed dual problems must be solved per iteration.

8. Summary and conclusions

In this work an overview of the minimum total potential energy of microclusters problem has been presented and a global optimization approach was introduced for finding the global minimum potential energy configuration of small microclusters interacting with central forces. It involved the transformation of the initial nonconvex total potential energy expression to the difference of two convex functions (DC transformation) through a novel eigenvalue analysis and the application of a Primal-Relaxed Dual global optimization approach to the resulting formulation guaranteed to converge to the global optimum in a finite number of iterations. For larger microclusters, two different relaxations of this approach yielded tight lower and upper bounds on the global minimum and initial points very close to the global optimum. It should be emphasized that the developed DC transformation as well as the employed global optimization procedure are not restricted to the specifics of the problem at hand. Instead, they can conceptually be extended for systems of many different particles interacting with complex angle-dependent and/or many-body forces. Work in this direction is currently under way.

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