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Open problem

Unresolved mathematical problems in the representation of potential energy surfaces by many-body potentials

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The proper representation of potential energy surfaces is critical to many theoretical approaches including molecular dynamics and Monte Carlo simulation methods. A large number of points required on the energy surface to adequately represent the surfaces prevents from practical use of large scale quantum-chemical approaches. Thus, potential energy surfaces (PES) have to be represented by simplified expressions. These expressions are derived from existing theoretical or experimental data. There is an open question concerning the reliability of such representations. In general, the assumed form of these expressions should be flexible enough to allow the proper representation of energy of any rearrangement of atoms.

The value of a single point on the energy surface resulting from an N-atom system may be expressed by a general formula comprising contributions of the various subunits [1]. Mathematically, one can cast the potential energy surface as

$$E = \frac{1}{2!}\sum_{\substack{i\\ i\neq j}}^{N}\sum_{j}^{N} u(r_i, r_j) + \frac{1}{3!}\sum_{i}^{N}\sum_{\substack{j\\ i\neq j\neq k}}^{N}\sum_{k}^{N} u(r_i, r_j, r_k) + \dots$$

$$+\frac{1}{n!}\sum_{i}^{N}\sum_{\substack{j\\ i\neq j\neq\dots\neq n}}^{N}\dots\sum_{n}^{N} u(r_i, r_j, \dots, r_n)\,, \tag{1}$$

where $u(r_i, r_j), u(r_i, r_j, r_k), \dots, u(r_i, r_j, \dots, r_n)$ are two-, three- and n-body potentials, respectively. The position of the ith particle is denoted by r_i.

The simplified forms of expression (1) are tested against available exact data. The obvious test points are equilibrium geometries and our discussion will focus on the prediction of these geometries. In the ideal case, the function (1) should predict the energy of any N-atom rearrangement exactly. The description of systems larger than N is possible due to the assumption that higher body interactions contribute to a much smaller degree compared to the terms included in the N-atom function.

The most important term in expansion (1) is the first term involving two-body interactions. However, the most general atom-atom potential (with the only assumption that the $u(r_i, r_j)$ potential has one minimum) leads to the qualitatively wrong prediction of equilibrium geometries. In the case of Li_3, simple two-atom potentials always lead to the equilateral triangle in disagreement with the experimental isosceles triangular geometry or with the expectation from the Jahn-Teller distorsion [2]. In the case of the rombus structure of the four atom system (fig. 1), the total energy expressed by 2-body potentials is as follows:

$$E = u(1,2) + u(2,3) + u(3,4) + u(1,4) + u(1,3) + u(2,4) . \qquad (2)$$

The energy of the system may be changed by folding it along the 1–3 axis. Such a manipulation changes the 2–4 distance only. Since for a flat structure the 2–4 distance is always larger than any other bond distance (e.g. 1–2 bond), the folding of the molecule will always lead to the lowering of energy. Any flat structure described by the atom–atom potentials is more energetical than the non-planar one, often in conflict with high-quality ab initio computations which included both electron correlation effects and geometry optimization, e.g. Li_4 [3], Al_5 [4] and Au_4 [5].

The prediction of topology of more complicated structures requires detailed form of the potential functions. Nevertheless regardless of the form of the atom–atom potentials, some geometries are never reproduced properly. The suggested

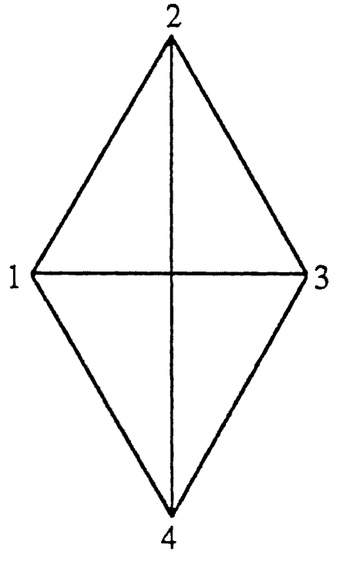

Fig. 1. The structure of hypothetical X_4 molecule.

solution is to include a three-body term [6–9]. The three-body interactions are included in the first two terms of the expression (1). Considerable effort has been put in the generation of such potentials leading in some cases to the well-known London–Eyring–Polayni–Sato (LEPS) functions [11].

Applying a three-body potentials to a four-atom structure (fig. 1) the energy can be expressed as

$$E = u(1,2,3) + u(1,4,3) + u(2,1,4) + u(2,3,4)\,. \tag{3}$$

The three-body potential predicts the correct equilibrium geometry for a trimer such as Li_3. Note that the folding of molecule along the 1–3 axis will lead to minimal energy values for $u(2,1,4)$ and $u(2,3,4)$ potentials. Likewise, the three-body functions which correctly predict the equilibrium geometries of three-body systems, in some cases, fail to predict, even qualitatively, the equilibrium geometries of systems composed of more than 3 atoms. This failure is attributed to the topological properties of the three-body functions which can be remedied by the inclusion of higher-body interactions. Some approaches include four-body potentials through the dihedral angles defined by 4 atoms [10].

Expression (1) converges rather slowly except for rare gas clusters. There is no conclusive evidence to establish that a many-body expression can be terminated when applied to calculations of chemical properties [11]. The incorrect topological structures may be obtained from a restricted approximation to a formal n-body function as exemplified above for a four-body problem.

Based on the above experience with the atom–atom and three- atom potentials, the following general unresolved problems are formulated:

(1) Is the inclusion of 4-body potentials sufficient for qualitative prediction of any rearrangement of atoms?

(2) To what extent perfect N-body potentials can predict the PES for systems composed of more than N atoms. In the worst case, the perfect N-atom potentials would not be able to access some topological structures of the $N + 1$ atom systems.

(3) A related question that has to do with topology is that given a set of N-atom potentials, what types of geometrical topologies can be predicted for systems composed of more than N atoms?

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