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CALYPSO structure prediction method and its wide application

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ABSTRACT

Atomistic structure prediction from "scratch" is one of the central issues in physical, chemical, materials and planetary science, and it will inevitably play a critical role in accelerating materials discovery. Along this thrust, CALYPSO structure prediction method by taking advantage of structure smart learning in a swarm was recently developed in Prof. Yanming Ma's group, and it has been demonstrated through a wide range of applications to be highly efficient on searching ground state or metastable structures of materials with only the given knowledge of chemical composition. The purpose of this paper is to provide an overview of the basic theory and main features of the CALYPSO method, as well as its versatile applications (limited only to a few works done in Ma's group) on design of a broad range of materials including those of isolated clusters/nanoparticles, two-dimensional reconstructed surfaces, and three-dimensional bulks (at ambient or high pressure conditions) with a variety of functional properties. It is to say that CALYPSO has become a major structure prediction technique in the field, with which the door for a functionality-driven design of materials is now opened up.

1. Introduction

There is a growing need for efficient methods to predict materials' atomic structures. In recent years, first principles methods have been widely used in materials science. Such approaches apply quantum mechanics and statistical mechanics to the structural information of a material to simulate with acceptable accuracy many of its macroscopic physical properties [1]. However, a lack of suitable structural information can lead the predicted properties to diverge permanently away from those experimentally measured. Therefore, structure prediction methods that could inform which atomic configuration of a material usually exists experimentally are greatly needed to accelerate the discovery of useful new materials.

Structure prediction involves exploring the potential energy surface (PES), which gives the energy of a structure as a function of its atomic coordination. The PES can be regarded as a multi-dimensional system consisting of many hills and valleys connected by saddle points. A local minimum (i.e., the lowest point in a valley) gives a stable structure. The global minimum of the PES represents the ground-state structure. An experimentally synthesizable material should have the ground state structure if which is kinetically accessible; therefore, the global minimum is the target of structure prediction. It is not difficult to predict the ground-state structure for a small system of several atoms, as all the local minima on the PES are generally obtainable by local structure optimizations starting from a number of guessed structures [2]. In this case, the global minimum can be determined in one shot; however, the challenge of structure prediction increases significantly with increasing complexity of the PES. For large systems with tens or hundreds of atoms, the ground-state structure might hide among very many stable structures. Consequently, finding the ground-state structure would require global optimization methods to greatly improve the efficiency and success rate of structure prediction.

In the past decade, much effort has been devoted to structure prediction. Several advanced methods have been developed [3–16] and these methods have led to many exciting discoveries that have been examined in several reviews (e.g., Refs. [17–21] and references therein). We have recently developed an efficient CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) method [22–27] on structure prediction from "scratch". Here we focus on CALYPSO methodology and its application to structural design on some typical material systems.

2. CALYPSO methodology for structure prediction

CALYPSO is a global optimization algorithm for crystal structure prediction. Its efficiency derives from the successful integration of

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several major techniques that are critical for PES exploration. These are: (i) structural evolution through a swarm-intelligence algorithm for driving the search to deep valleys on the PES; (ii) structural characterization techniques to avoid duplicated searching of equivalent regions of the PES; (iii) symmetry constraints during structure generation and local optimization to reduce the searching space; and (iv) local structural optimization to find local minima on the PES.

2.1. Swarm-intelligence algorithm

Our CALYPSO method adopts a "self-improving" strategy to locate the global minimum of the PES via particle swarm optimization (PSO) [28]. The PSO algorithm is a typical swarm-intelligence scheme [29] inspired by natural biological systems (e.g., ants, bees, or birds), and has been applied to a variety of fields in engineering and chemical science [30]. The application of PSO algorithm in structure prediction started only recently [31]. Within the CALYPSO method, structures are evolved in the energy landscape through velocity according to formula (1). The new velocity of each structure (v^{t+1}) is calculated by Eq. (2) using the properties of itself and of the global population. The calculation includes the structure's previous location (x^t) before optimization, previous velocity (v^t), and current location ($pbest^t$) with an achieved best fit (i.e., the lowest enthalpy) of the individual structure. The population global location ($gbest^t$) with the best fit for the entire population is also considered.

$$x^{t+1} = x^t + v^{t+1} \tag{1}$$

$$v^{t+1} = \omega v^t + c_1 r_1 (pbest^t - x^t) + c_2 r_2 (gbest^t - x^t) \tag{2}$$

where w denotes the inertia weight, which is dynamically varied and decreases linearly from 0.9 to 0.4 during the iteration; c_1 and c_2 are the self-confidence factor and swarm confidence factor, respectively; and r_1 and r_2 are random numbers distributed in the range [0, 1]. The random parameters r_1 and r_2 ensure good coverage of the searching space, and avoid entrapment in local minima. The strong ability of PSO to overcome large barriers in energy landscapes derives from the use of swarm intelligence.

Two versions of the PSO method (one local and one global) have been implemented in CALYPSO [22–27]. The global PSO, outlined in Fig. 1(a), has only one global best structure acting as the attractor for the entire structure population, and all particles seek new positions only in the regions close to the uniquely overall best position. This method converges quickly for small systems (i.e., those with fewer than 30 atoms in the simulation cell), but it may be less effective for larger systems containing more than 30 atoms per simulation cell, because the PES becomes much more complex. The local PSO is outlined in Fig. 1(b). Each particle (i.e., a candidate structure) selects a set of other particles as its neighbors, and its velocity is adjusted according to both its position and the best position achieved so far in the community formed by its neighborhood. Thus, at each iteration the particle will move toward its own best position and the best position of its local neighborhood, rather than the overall best position in the swarm. By maintaining multiple attractors that lead to the formation of different structural motifs, the local PSO allows an unbiased and efficient exploration of large space on the PES, thus effectively avoiding premature convergence during structure searches.

2.2. Fingerprinting structures via a bond characterization matrix

Structure evolution is hindered by similar nearby structures in the same valley of the PES. It is challenging to remove similar structures to enhance the structural diversity and also to avoid wasting computational efforts during structure evolution. Assessing similarities among structures requires fingerprinting them based on their complete geometric information (i.e., bond lengths and angles). Our developed structural characterization technique, the bond characterization matrix (BCM), is based on bond lengths and angles, and is implemented in our CALYPSO method. BCM is realized by constructing a set of modified bond-orientational order metrics [32] for structure quantification, where spherical harmonic and exponential functions are used to characterize the bond angles and lengths, respectively. Specifically, for a given structure, a bond vector $\vec{r}_{ij}$ between atoms i and j is defined if the interatomic distance is less than a given cutoff distance. This vector is associated with the spherical harmonics $Y_{lm}(\theta_{ij}, \phi_{ij})$, where θ_{ij} and ϕ_{ij} are the polar angles, and where the weighted average over all bonds formed by, for instance, the A and B atoms can be derived as follows:

$$\overline{Q}_{lm}^{\delta_{AB}} = \frac{1}{N_{\delta_{AB}}} \sum_{i \in A, j \in B} e^{-\alpha(r_{ij} - b_{AB})} Y_{lm}(\theta_{ij}, \phi_{ij}), \tag{3}$$

where δ_{AB} and $N_{\delta_{AB}}$ denote the type and the number of bonds, respectively. Only even-l spherical harmonics are used in Eq. (3) to guarantee invariant bond information with respect to the direction of the bonds. To avoid dependence on the choice of reference frame, it is important to consider the rotationally invariant combinations [32],

$$Q_l^{\delta_{AB}} = \sqrt{\frac{4\pi}{2l+1}} \sum_{m=-l}^{l} \left| \overline{Q}_{lm}^{\delta_{AB}} \right|^2, \tag{4}$$

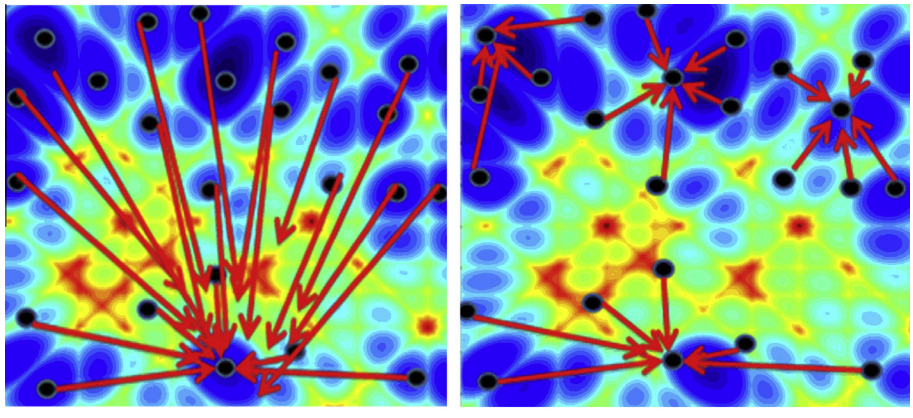

Fig. 1. The schematic diagram of global (a) and local (b) PSO.