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Symmetry building Monte Carlo-based crystal structure prediction

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ABSTRACT

Methods are presented that allow for the automatic increase and preservation of symmetry during global optimization of crystal structures. This systematic building of symmetry allows for its incorporation into structure prediction simulations even when the space group information is not known *a priori*. It is shown that simulations that build and maintain symmetry converge much more rapidly to ground state crystal structures than when symmetry is ignored, allowing for the treatment of unit cells much larger than would otherwise be possible, especially when beginning from the P1 space group.

1. Introduction

There is a distinct relation between the physical properties of a material and its atomic structure. For example, graphitic carbon is an electrical conductor that is very soft whereas diamond, despite having the same composition, is an insulator that is extremely hard [1,2]. With the possibility of such wildly different properties even within a given chemical composition, accurate crystal structures are vital to the study of materials. While there exist large databases of known crystal structures [3–5], many compounds have either incomplete entries or are missing entirely. In an effort to solve these unknown structures, many successful global optimization methods have been developed [6–17]. However, in an unconstrained search, the number of degrees of freedom that must be optimized increases as three times the number of atoms that are included, making the unconstrained prediction of structures with large unit cells difficult or practically impossible.

Of roughly 130,000 structures that are currently in the Inorganic Crystal Structure Database (ICSD) [3], only slightly more than 5000 belong to the P1 space group. The other 96% of structures are of higher symmetry, which puts constraints on the cell shape, atomic coordinates, or both. Leveraging crystal symmetry is therefore a potentially powerful and widely applicable method that can be used to significantly reduce the number of degrees of freedom that must be treated. A number of structure prediction methods have been developed that use symmetry to improve the efficiency of the optimization [14,12,16,13,17]. However, in general, they require that the space group symmetry be known *a priori*.

Here, we outline a strategy that leverages symmetry to reduce the complexity of the optimization while starting from structures that are in the P1 space group. The main points underlying our approach can be divided into two categories, which are described in more detail throughout this paper: first, is symmetry building where in a structure is refined under symmetry operations that are nearly, but not exactly satisfied so that the symmetry is *increased* on-the-fly during a simulation; second, the preservation of these symmetries when generating new structures to reduce the number of free variables and increase the efficiency of the search. As an illustration of our approach, we show the ways in which these steps can be incorporated into Monte Carlo-based crystal structure prediction. However, we emphasize that the application of these methods is not restricted to Monte Carlo simulations, but that they can be generalized to other global optimization methods as well. We show that simulations that build and leverage symmetry using these methods converge much more rapidly than those in which symmetry is ignored entirely, allowing for the treatment of larger unit cells than would otherwise be possible.

2. Methods

2.1. Structure refinement

The first step in the symmetry-building routine is structure refinement, which represents the key step of the method since it allows structures to move from low symmetry space groups to ones with higher symmetry in a meaningful way. The process of increasing symmetry is accomplished by searching for symmetry

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operations using a wide tolerance, which is defined such that two atomic positions are taken to be equal under an operation if the distance between them is less than this value (0.5 Å is used in all simulations). The larger this tolerance is made, the more likely it is that symmetry operations will be found in a structure. Refinement is the process of adjusting the basis vectors and atomic positions so that they exactly satisfy the symmetries that were discovered, the details of which are described in the following paragraphs.

Addressing first the refinement of the unit cell parameters, restraints on the basis vectors imposed by a set of symmetry operations are easily described by their effect on the metric matrix [18]:

$$\mathbf{G} = \begin{pmatrix} \mathbf{a}\cdot\mathbf{a} & \mathbf{a}\cdot\mathbf{b} & \mathbf{a}\cdot\mathbf{c} \\ \mathbf{a}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{c} \\ \mathbf{a}\cdot\mathbf{c} & \mathbf{b}\cdot\mathbf{c} & \mathbf{c}\cdot\mathbf{c} \end{pmatrix} \tag{1}$$

where **a**, **b**, and **c** are the unit cell basis vectors. A symmetry operation $\mathbf{W}_i$ consists of a rotation, $\mathbf{R}_i$, and a translation $\mathbf{t}_i$ so that the coordinates of an atom j transform as $\mathbf{x}'_j = \mathbf{R}_i\mathbf{x}_j + \mathbf{t}_i$. Under every rotational part of the symmetry operations, the metric matrix must remain unchanged, which can be expressed as

$$\mathbf{R}_i^{\mathrm{T}}\mathbf{G}\mathbf{R}_i - \mathbf{G} = 0. \tag{2}$$

Eq. (2) defines nine equations, each a linear function of one of the nine elements of **G**. Since Eq. (2) must be satisfied for every one of the N_{sym} symmetry operations that are found, there are in total $9N_{\mathrm{sym}}$ simultaneous equations that constrain the metric matrix. Following the procedure described in Ref. [18], we take advantage of the fact that **G** is symmetric to reduce the constraints to $6N_{\mathrm{sym}}$ equations, each a function of one of the unique elements of **G**. The system of equations can be written in the matrix–vector form as

$$\mathbf{C}\begin{pmatrix} \mathbf{a}\cdot\mathbf{a} \\ \mathbf{b}\cdot\mathbf{b} \\ \mathbf{c}\cdot\mathbf{c} \\ \mathbf{a}\cdot\mathbf{b} \\ \mathbf{a}\cdot\mathbf{c} \\ \mathbf{b}\cdot\mathbf{c} \end{pmatrix} = \mathbf{0} \tag{3}$$

where **C** is a $6N_{\mathrm{sym}} \times 6$ matrix. The column vector in Eq. (3) is initialized with the metric matrix values of the structure that has yet to be refined. **C** is then row-reduced and the refined values of $\mathbf{a}\cdot\mathbf{a}$, $\mathbf{b}\cdot\mathbf{b}$, etc. are obtained from back-substitution, after which it is straightforward to solve for the refined lengths of **a**, **b**, and **c** and the angles between them.

The second step of refinement is the modification of positions of the atoms in the unit cell. For each of the symmetrically unique atoms the structure, its special position operator is constructed according to [19]

$$\mathbf{S}_j = \frac{1}{N_j^{\mathrm{sym}}}\sum_i^{N_j^{\mathrm{sym}}} \mathbf{W}_i \tag{4}$$

where N_j^{sym} is the number of site symmetry operations for atom j; that is, those operations that satisfy $\mathbf{x}_j = \mathbf{R}_i\mathbf{x}_j + \mathbf{t}_i$. Applying the special position operator for the atom to its unrefined coordinates moves the atom onto its high symmetry site. In other words, the application of the special position operator has the same effect as applying all site symmetry operations to the atom and averaging over the resulting positions. All symmetry operations of the crystal are then applied to this refined coordinate in order to generate the orbit of symmetrically equivalent atoms.

After refinement of the basis vectors and atomic coordinates, the structure will exactly satisfy the symmetry operations that were only approximate to some wide tolerance. As an example of its effect, a disordered NaCl structure is shown in Fig. 1(a),

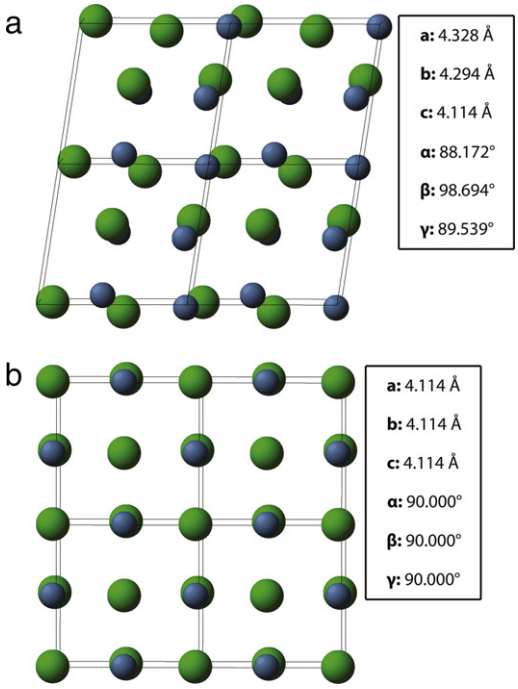

Fig. 1. Example of the refinement operator acting to increase the symmetry of a structure. The structure in (a) was generated by taking the conventional cell of the rock salt structure and adding a random vector of length 0.4 Å to each of the atomic positions and lattice vectors. The structure in (b) was generated from (a) using the refinement operator with symmetries obtained using a tolerance of 0.8 Å.

which was obtained from the perfect NaCl crystal structure by adding vectors of length 0.4 Å with random orientations to each of the atomic positions and basis vectors. Fig. 1(b) shows the same structure, but following application of the refinement operator. In this case, the refinement recovers the full symmetry of the original, unperturbed NaCl structure.

2.2. Preservation of symmetry

The increased symmetry that results from refinement reduces the number of free variables in the simulation, making the optimization more efficient as long as the symmetries are maintained during subsequent changes to the structure. In the following, the ways in which the symmetry is preserved under changes made to the unit cell vectors and internal atomic coordinates are discussed, where the latter occurs via simple displacements as well as swaps of atoms.

Using the same methods that were implemented in structure refinement, it is straightforward to make changes to the unit cell vectors that maintain symmetry. In practice, this is accomplished by adding random vectors to each of the basis vectors, making the cell triclinic regardless of its starting symmetry. The metric matrix (Eq. (1)) is formed for this modified cell and then refined so that it satisfies any constraints imposed by the current set of symmetries. The new cell is taken as the one resulting from this symmetrized metric matrix.

Symmetry-preserving atomic displacements are made using the special position operators of the atoms (Eq. (4)). It can be shown that the rotational part of the special position operator is a projection matrix; that it satisfies $\mathbf{P}_j \cdot \mathbf{P}_j = \mathbf{P}_j$, where

$$\mathbf{P}_j = \frac{1}{N_j^{\mathrm{sym}}}\sum_i^{N_j^{\mathrm{sym}}} \mathbf{R}_i \tag{5}$$