Structure prediction based on \textit{ab initio} simulated annealing

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Abstract. The prediction of possible crystal structures, with the type of atoms as the only input, has become a fast growing field of research. The general approach consists of the global exploration of the energy landscape of the chemical system, with typical methods being simulated annealing or genetic algorithms. In the case of simulated annealing, combinations of model potentials and \textit{ab initio} calculations for the energy evaluation are state of the art. Only very recently, the possibility of simulated annealing based on \textit{ab initio} calculations at all stages of the calculations has become feasible. This article summarizes the recent developments in this area.

1. Introduction

The knowledge of the crystal structure of a solid compound is one of the basic questions in solid state theory\cite{1, 2, 3, 4, 5}. In theoretical descriptions, the usual approach is to use the experimentally determined structure for the calculations of physical properties. In the past few years, however, an effort has been made to develop methods to predict structures of solids without the knowledge of any experimental information about the structure. The question of finding structures is not necessarily restricted to the determination of the global minimum, but also local minima are of interest: they correspond to stable or metastable configurations of the chemical system.

The most common methods used for the structure prediction of solids are simulated annealing\cite{6, 7, 8} or the related threshold algorithm\cite{9, 10}, genetic algorithms\cite{11, 12, 13, 14}, basin hopping\cite{15, 16}, or the recently introduced metadynamics\cite{17}.

Structure prediction usually involves a huge amount of CPU time, and therefore efficient ways to keep the calculations tractable have to be found. Thus, the procedures were initially split in two steps: first, a global search on the potential surface was performed. The energy was evaluated with empirical potentials, e.g. Coulomb and Lennard-Jones potentials. After the global search, e.g. using simulated annealing, possible structure candidates were locally optimized on the \textit{ab initio} level, e.g. with Hartree-Fock or density functional theory. Since all the calculations were performed without imposing any symmetry, algorithms to identify the symmetry and space group were applied to the structures found. The systems considered were ionic systems, e.g.\cite{18, 19, 20}, systems exhibiting polar covalent bonds such as zeolites\cite{21, 22, 14} or molecular crystals\cite{23, 24, 25}.
2. The method

The method described in the present work is the simulated annealing approach, where \textit{ab initio} calculations are used at all the stages of the calculations, i.e. especially also during the global search. The simulated annealing approach will be summarized in the following:

I. The simulated annealing run

1) A number of atoms is chosen.

2) These atoms are placed randomly in a relatively large unit cell; e.g. the volume is of the order of 5 times larger than an estimated cell size (using e.g. radii for the neutral atoms).

3) The energy of the configuration is computed.

4) A new configuration is created by applying certain moves to the last configuration. Typical moves are:
   - moving an individual atom (the majority of the moves)
   - exchanging atoms
   - changing the lattice constant with fixed cartesian atom positions (cartesian coordinates, i.e. atom positions in Å inside the cell, are fixed, and a slice is removed from or added to the cell)
   - changing the lattice constant with fixed fractional atom positions (atom positions in fractions of the cell parameters are fixed while the cell parameters are changed)

5) The energy of the new configuration is computed.

6) The new configuration is accepted according to the probability \( \text{exp}(-\Delta E/kT) \) (strictly speaking, the minimum of \( \text{exp}(-\Delta E/kT) \) and 1) where \( \Delta E \) is the energy difference between the two configurations. \( T \) is a fictitious temperature, and thus a control parameter of the global optimization. This is just the Metropolis [26, 27] algorithm. After this, the algorithm continues again at step 4, until a certain criterion is fulfilled, e.g. a maximum number of steps (which may well be of the order of \( 10^4 \ldots 10^6 \)). During the run, the temperature is gradually lowered.

II. The quench run

This simulated annealing procedure is followed by a quench, which is a special variant of simulated annealing: the temperature is chosen as exactly zero, and thus only downhill moves are accepted and the energy is monotonously decreasing. Note that the length of the initial simulated annealing run should be sufficiently large to have reached a basin containing a crystalline modification, because otherwise the quench will usually lead to an amorphous structure.

III. The local optimization

Close to the actual minimum, the local optimization is performed with a standard \textit{ab initio} code; in this work the CRYSTAL [28, 29, 30] code and analytical gradients [31, 32, 33, 34] together with an optimizer [35] were used. Usually, both Hartree-Fock and density functional theory are employed, as it is useful to compare the various methods.

IV. Analyzing the symmetry
The global search is performed in the most general way (space group $P\overline{1}$), i.e. without imposing any symmetry. The minimum configurations are analyzed with algorithms to find symmetries [36] and to determine the space group [37]. These algorithms are implemented in the software KPLOT[38]. In addition, duplicate structures can be eliminated from the set of minima found with an algorithm to compare cells [39]. Step IV can already be done before step III, in order to exploit the symmetry and thus speed up the local optimization. In any case, the symmetry analysis must be repeated after the local optimization, as the local optimization may change the symmetry of the structure.

3. Simulated annealing on the $ab\ initio$ energy landscape

There are various reasons why it would be desirable to employ $ab\ initio$ energies already during the simulated annealing run:

- $ab\ initio$ energies are expected to be more accurate as they mainly depend on the functional, but are otherwise free of empirical parameters.
- $ab\ initio$ energy calculations should be more generally applicable than empirical energy functions, i.e. not only for ionic systems where often good classical potentials exist but also for covalent or metallic systems. In particular, $ab\ initio$ energies are required if the type of bonds that will be formed is not known in advance.
- It would be very interesting to compare $ab\ initio$ energy landscapes with energy landscapes derived from calculations with empirical potentials.

The downside is that $ab\ initio$ calculations are much more time consuming than calculations based on empirical potentials. For example, a single $ab\ initio$ calculation for LiF with default parameters, but without symmetry, takes of the order of 10 minutes on a single CPU. A simulated annealing run with 100000 steps would thus last roughly two years. If $\sim 100$ runs were required, then the total CPU time would easily reach hundreds of years. It is therefore crucial to speed up the $ab\ initio$ calculations. This can be achieved in the following way:

- The number of integrals to be computed can be reduced by selecting less strict tolerances. For example, the threshold [28] to neglect overlap between two Gaussians is $10^{-6}$ as the default, and can be reduced to $10^{-4}$ without too much loss of accuracy.
- The basis set may be reduced, e.g. one may consider omitting polarization functions. Having less diffuse exponents also helps to enhance the numerical stability and to speed up the calculations.
- Other computational parameters may be chosen to be less rigorous, e.g. less $\vec{k}$-points or less strict thresholds for the convergence of the self-consistent field cycles.
- In addition, concerning the simulated annealing parameters, the length of the simulated annealing and subsequent quench run may be optimized. Similarly, the type of moves can be optimized, e.g. the reduction from a very large to a reasonable cell volume can be accelerated by enhancing the probability of moves which shorten the lattice constant.

An additional complication is that it is necessary to converge the $ab\ initio$ calculations at a random geometry, which is not trivial: the Hartree-Fock or Kohn-Sham equations have to be converged for a geometry which is often far away from the experimental geometry. To deal with this issue in the context of the global search, an infinite energy may be assigned to non-converged geometries, but this should not happen too often, in order to keep the simulated annealing procedure progressing in a reasonable way. One of the findings of the hitherto
performed computations was that Hartree-Fock calculations facilitate convergence at even the most unusual geometries, due to the large band gap, whereas calculations with the local density approximation may have severe convergence problems.

4. Examples

LiF bulk was chosen as a first example. The reasons were the low number of electrons, the expected ionic configurations as local minima, which facilitates convergence, and finally, the fact that earlier calculations on the level of empirical potentials exist [18]. In fact, it turned out that the results of these earlier calculations were confirmed: when sampling the energy surface, the important minima on the level of *ab initio* calculations and calculations with empirical potentials were the same. The structures found are shown in figure 1. They are in an energy range of 0.5 eV (for four formula units), at the Hartree-Fock level. An additional step would be to compute phonon frequencies to ensure the stability, which is presently implemented for \( \vec{k} = \vec{0} \) in the CRystal code.

Figure 1. The structures found for LiF: the rock salt, \( B_k \), wurtzite, sphalerite (zincblende) and NiAs structure, and some more unusual structures. Figures from [40], for more details see also there. Reproduced by permission of the PCCP Owner Societies.

The full details are given in [40], together with the computational parameters employed. These parameters were calibrated and the CPU requirements downsized in such a way that a
single run took about one week on a single CPU. However, one should note that even this system is not trivial and the calculations require some careful adjustments.

An important next step is to investigate a system like BN, which was actually one of the first systems studied with the CRYS TAL code[41]. In BN, covalent bonds are present which are more difficult to describe with empirical potentials compared to an ionic system such as LiF. The initial calculations confirm that the procedure works also for this system; but again, a careful adjustment of parameters is required. Besides the wurtzite, zincblende and the $B_k$ (hexagonal BN) structure type, more unusual structures were found, such as visualized in figure 2.

![Figure 2. Some of the more unusual structures found for BN, with the space groups 160, 187, 136.](image)

5. Conclusion

In this article, structure prediction based on ab initio calculations at all stages of the calculations (global energy landscape exploration and local optimization) was described. This task is not trivial due to the necessity to reduce the CPU time by huge factors, compared to standard ab-initio calculations, and due to the fact that numerical stability and convergence at random geometries is required. In calculations for the system LiF, it was shown that the important minima on the level of ab initio calculations and calculations with empirical potentials were the same which is an important confirmation of the method. Initial calculations for the system BN indicate that the method also works for covalent systems.

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