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A new optimization method for shell model interatomic potential parameters of perovskite ferroelectrics

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ABSTRACT

An effective interatomic potential is crucial to molecular dynamics simulation and hence an efficient method for optimizing potential parameters is necessary. A new method to find the key parameters in shell model potential of perovskite ferroelectrics based on sensitivity analysis is presented. Whereafter, the genetic algorithm is applied to optimize the key parameters, and the insignificant parameters are kept constant in optimization. This approach can substantially reduce the dimension and computer time of optimization. Simulation results using the optimized potential parameters show that the crystalline structures and physical properties of perovskite ferroelectrics agree well with the experimental data.

1. Introduction

Perovskite ferroelectrics are very important for a wide range of technological applications in optoelectronics, waveguides, laser frequency doubling devices, high capacity computer memory cells, etc. [1–4]. With the development of the computer technology and algorithm, simulation method has been widely used to study the structures and properties of the perovskite-type ferroelectrics. Molecular dynamics (MD) simulation is an important computer simulation technique. Tinte et al. [5] and Sepliarsky et al. [6] applied the shell model potential for MD to examine the crystal structure, polarization and phase transition sequence for barium titanate and qualitative agreement with experimental results was achieved. Wunderlicha et al. [7] used the rigid-ion model for MD to calculate the misfit dislocations at the $BaTiO_3$–$SrTiO_3$ interface. Thomas et al.developed a pair potential for simulating radiation damage in complex oxides and studying the defects [8] and threshold displacement energies in $SrTiO_3$ [9].

Interatomic potentials are the key to determine the reliability of MD simulations [10]. The accuracy and reliability of the simulation depend critically on the quality of the interatomic potentials employed. Because there are a number of shell model potential parameters for perovskite ferroelectrics, it is a challenging task to optimize these parameters efficiently. In this study, a more effective optimization method is proposed. The sensitivity analysis is first applied to find the key parameters that are the most influential in determining the structures and physical properties among all the potential parameters. A genetic algorithm is then used to optimize the key parameters, while the other secondary parameters are kept constant. The dimension of the optimization is substantially reduced. The crystalline structures and physical properties of ABO_3-type perovskite ferroelectrics are calculated based on the optimized parameters and the results are in good agreement with experimental measurements.

2. The sensitivity analysis of shell model potential parameters

The interatomic potential function in this paper takes the shell model for ionic materials. In the shell model, each atom is described as two charged and coupled particles: a massive core and a massless shell, which are linked by a spring as illustrated in Fig. 1. The shell model has been widely used in atomistic simulations of oxides, because it is a simple method to phenomenologically describe the deformation of the electronic structure of an ion [11,12].

There are three kinds of potential functions: long-ranged, short-ranged and harmonic potentials, which are given by

$$V_{LR}^{ij} = \frac{q_i q_j}{4\pi\varepsilon_0}\frac{1}{r_{ij}} \quad (1)$$

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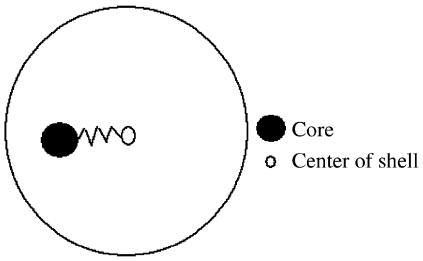

Fig. 1. Schematic of the shell model composed of a positively charged core and a massless shell with a spherical charge distribution.

$$V_{SR}^{ij} = A_{ij} \cdot \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \tag{2}$$

$$V_{Harmonic}^{ij}(r_{ij}) = \frac{1}{2} k r_{ij}^2 \tag{3}$$

The long-ranged electrostatic interactions among all cores and shells except between the core and shell of the same atom and only short-ranged interactions between shells are taken into account.

The simulations in this work were performed using the general utility lattice program (GULP) [13]. With the potential parameters given in Ref. [6], the crystal structure of ABO_3 perovskite ferroelectrics was accurately reproduced, but some physical properties, such as elastic constants (C_{11}, C_{12} and C_{44}), present apparent difference compared with measurements, which indicates that the potential parameters in Ref. [6] may be is not the global optimal, and a further optimization of these parameters is possible.

Because the charges of ions must be conserved, the charge of Ba is not considered as an independent parameter. Furthermore, only the short-range interaction parameter C between O–O is taken into account, so there are 17 independent potential parameters of $BaTiO_3$ in all.

The optimization is a challenging task if the dimension of the independent variables increases. For example, if the dimension is very high, the amount of the iterative calculation in Newtom–Raphson method will be very large and have no guarantee of global optimum. Even using intelligent optimization algorithms, such as genetic algorithm, the time of intelligent search will also increase as the dimension increases. In order to reduce the dimension of the problem, the sensitivity analysis is applied firstly to identify the most sensitive parameters. Before optimizing, the sensitivity coefficients of all the parameters on the optimization object function are calculated, and the sequences of these parameters' sensitivity are obtained. The parameters with higher sensitivity will be taken as key variables, while the other ones with much lower sensitivity will be ignored in the optimization and be kept constant as given in Ref. [6].

The complex system's mathematic model can be expressed in a vector form as follows:

$$\begin{aligned} Y &= g(X) \\ X &= (X_1, X_2, \ldots, X_n) \\ Y &= (Y_1, Y_2, \ldots, Y_m) \end{aligned} \tag{4}$$

In the actual process of analyses, the dimensions n and m of the vectors X and Y can be very large, and the function g can be quite complicated (e.g., the numerical solution of a system). For example, GULP program is a complex model, which takes the potential parameters as input variables, and crystal structures, elastic constants, bulk modulus, etc. as output variables. The value of output Y has uncertainty because of the uncertainty in the X input. The sensitivity analysis is to evaluate the contribution of the input parameters to the output uncertainty. The sensitivity analysis may be categorized according to the outcome of the related sensitivity measures: qualitative or quantitative methods, local or global methods and methods that are dependent or independent on the model characteristic. Saltelli et al. [14] proposed a number of methods for sensitivity analysis, including scatterplot method, sample-based method, variance-based sensitivity analysis (VBSA) method, etc. In this paper, the variance-based sensitivity analysis (VBSA) method is applied, which is a global, quantitative and model-independent method.

The fundamental of the variance-based sensitivity analysis is that the uncertainty of the output can be expressed by the variance of the output. In the variance-based sensitivity analysis, the model can be represented as a function of

$$Y = f(X_1, X_2, \ldots, X_n) \tag{5}$$

where $X = (X_1, X_2, \ldots, X_n)$ is a vector of inputs and Y is the output. The first-order sensitivity index S_i of input factor X_i is defined as follows:

$$S_i = \frac{\sigma_{E(Y/X_i)}^2}{\sigma_Y^2} \tag{6}$$

where σ_Y^2 is the variance of the output Y and $\sigma_{E(Y/X_i)}^2$ is the variance of the conditional expectation value $E(Y/X_i)$. The first-order sensitivity index is a quantitive sensitivity measure for linear models.

For non-linear models the interactions among the input factors must be taken into account, so that the total effect sensitivity index is necessary. The total effect sensitivity index is expressed as follows:

$$S_{Ti} = 1 - \frac{\sigma_{E(Y/X_{\tilde{i}})}^2}{\sigma_Y^2} \tag{7}$$

where $\sigma_{E(Y/X_{\tilde{i}})}^2$ is the variance of the conditional expectation value $E(Y/X_1, X_2, \ldots, X_{i-1}, X_{i+1}, \ldots, X_n)$.

In this paper, the object function of optimization is as follow:

$$F = \sum_i w_i \cdot |f_{icalc} - f_{iobs}| / f_{iobs} \tag{8}$$

where f_{icalc} is the lattice constant or other physical properties calculated by GULP, f_{iobs} is the corresponding experimental measurement value and $|f_{icalc} - f_{iobs}|/f_{iobs}$ indicates the relative error between the calculated and experimental values. w_i is a weight factor and the choice of weight factor for each observable values depends on several factors such as the relative magnitude of the quantities and the reliability of the measurement data. Because the crystalline structures are generally more reliable than the elastic constant, the lattice constant weight factor is 0.8 and the physical properties' weight factor, such as elastic constant (C_{11}, C_{12} and C_{44}) and bulk modulus, is only 0.05.

Before the optimization, the sensitivity indices of all the potential parameters in shell model from Eqs. (1)–(3) on the object function F are calculated. Each potential parameter has uniform distribution in the range $[a, b]$, where $a(b)$ is minus (plus) 20% of the respective central value from Ref. [6]. The sensitivity indices for $BaTiO_3$ potential parameters are shown in Table 1, which gives the first and total sensitivity coefficients as well as their ranks.

Comparing the total sensitivity indices from Table 1, we can conclude that the charge parameters and the short-range interaction parameters ρ between Ba–O, Ti–O and O–O are the significant parameters, which contribute the most to the output variability; whereas the sensitivity indices of other parameters are low, especially, the spring constants k_2 and k_4. Therefore, these