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Method and advantages of genetic algorithms in parameterization of interatomic potentials: Metal oxides



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ABSTRACT

The method and the advantages of an evolutionary computing based approach using a steady state genetic algorithm (GA) for the parameterization of interatomic potentials for metal oxides within the shell model framework are developed and described. We show that the GA based methodology for the parameterization of interatomic force field functions is capable of (a) simultaneous optimization of the multiple phases or properties of a material in a single run, (b) facilitates the incremental re-optimization of the whole system as more data is made available for either additional phases or material properties not included in previous runs, and (c) successful global optimization in the presence of multiple local minima in the parameter space. As an example, we apply the method towards simultaneous optimization of four distinct crystalline phases of Barium Titanate (BaTiO_3 or BTO) using an ab initio density functional theory (DFT) based reference dataset. We find that the optimized force field function is capable of the prediction of the two phases not used in the optimization procedure, and that many derived physical properties such as the equilibrium lattice constants, unit cell volume, elastic properties, coefficient of thermal expansion, and average electronic polarization are in good agreement with the experimental results available from the literature.

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1. Introduction

The temperature and pressure dependent atomistic molecular dynamics (MD) simulations of material systems lie at the core of many advances in the discovery and optimization of novel materials in a wide variety of applications areas. The accuracy of the material properties resulting from MD simulations, however, is always directly correlated to the quality of the interatomic interaction potentials or force field functions underlying the dynamics. The potential function is comprised of a functional form and an accompanying set of numerical coefficients or parameters fitted to optimize the physical properties of the simulated materials. The functional form is generally an ansatz chosen so as to reproduce known symmetries, crystal structure, and basic physical or chemical properties of the material. An initial dataset comprising of the crystal structures including the lattices constants, bond lengths and angles, and systematic changes in the energies of the

system as these values are changed (in other words elastic constants) are obtained either through higher accuracy ab initio quantum mechanical simulations or through experimental measurements. Given such a reference dataset and a chosen ansatz for the functional form, the potential parameters are generally obtained by finding a set that gives the best fit to a defined set of properties or material features [1]. Optimizing the parameters for a given set of the properties is often a combination of local curve fitting to the selected material's characteristic trends followed by closed-loop MD or static structural simulations in which known macro-scale material quantities are targeted by iterative manual adjustment of the chosen parameter sets [2].

The above process by definition is sequential in nature and needs to be wholly repeated whenever a reference dataset is augmented with new materials' structural or properties data. As a result, in the earlier days, for well known semiconductors like silicon more than 30 interatomic potentials or force field functions were developed [3] but mainly the Stillinger–Weber or Tersoff potentials for silicon or their derivatives have been used extensively over the last two decades [4–6]. Similarly, for reactive hydrocarbons the original Brenner potential [7] was developed in the early 90s and has been used extensively over the last two decades [8], but only minor changes or improvements have been added since then [9].

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The conventional local gradient based curve fitting methods, such as steepest descent and conjugate gradient, used in the traditional optimization loop: (i) are inherently local in nature and strongly dependent on the initial configurations for the fitting, (ii) have a tendency to get trapped in or find mainly the nearest local minima in a many dimensional fitting parameter space, (iii) cannot include incremental additions to the reference dataset or the physical properties without sacrificing completely the previous optimization and starting all over again, and (iv) are limited overall by how much data or how many physical properties can be accommodated for a given set of parameters in the optimization procedure. In certain cases when these methods are used, the limitations of a resulting parameterization are a product of the functional form of the potential itself, but many times these limitations result from the sequential nature and local dependency of the optimization loop used by local gradient based techniques. For example, in many cases, the commonly used functional forms have been reported with one set of parameterization for the bulk properties and another set of the parameterization for the cluster or surface properties of the same material.

Concurrently, in recent years there has also been a focus on the generation and sharing of more and more materials structure and properties data through focused programs such as the Materials Genome Initiative (MGI) [10] and the recent OpenKIM project [11], the latter of which seeks to implement a standard infrastructure for introducing novel potential functions which can make the implementation and testing of new force fields more expedient. These type of focused initiatives, along with the broader capacity of high-performance computing resources available to the materials academic and industrial community, are dramatically increasing the range and depth of material characterization data. Such data includes not only the quantum mechanical *ab initio* density functional theory based simulations of a wide variety of materials structures and properties, but also the synthesis and atomic scale characterization of the structure and properties of the same materials in experiments. It is natural, therefore, that alternate optimization or fitting procedures be investigated for not only the direct search and discovery of new materials and properties from these large databases, but also for the development of the down-the-stream simulation techniques such as MD or Monte Carlo (MC) methods which are explicitly geared towards exploiting the large amount of available data in the literature and online databases. An interesting example of said alternate optimization schemes is that of the neural network (NN) potential, which is actively being explored for the modeling of a variety of materials [12–14]. In the NN setting, the functional form of the potential function is replaced with a network of interconnected nodes categorized as input, hidden and output nodes [15]. The inputs of the NN are coordinates, or generalized coordinates [15], of the system and the output is the system's total energy. The connection between any two nodes of the network is associated with a specific weight, which is the parameter that is adjusted when fitting the NN to a reference potential energy landscape [16]. This innovative approach to modeling interatomic interactions as well as the technique discussed here, are derived from machine learning principles [17,18], which although applied to other fields of research for quite some time, have only recently begun to make significant contributions to MD techniques.

In this work, we investigate an evolutionary computing (EC) based genetic algorithm (GA) method for the optimization of interatomic potentials for molecular dynamics of materials systems. The optimization occurs for a cost function that measures the fitness of the force field parameter set. The optimization or fitness within the GA context is a measure of the agreement between the target values of a reference database, irrespective of the number of structures and properties in the database, and the

values produced from a given initial or fitted parameter set. Roughly speaking, the challenges faced by optimization approaches is that, for even a limited range of parameter variations, the fitness function may live on a very rugged landscape often with many closely-spaced local minima.

The general GA method is derived from biological genetic theory and Darwinian evolutionary principles [19–21]. In the GA method, a randomly generated set of parameters, which constitute the so-called population pool, are adjusted through recombination and mutation operators [22] to improve the parameter sets according to a metric, also known as the fitness. A reference dataset of the atomic configurations and their energies obtained from quantum simulations are stored and the GA subsequently refers to the reference dataset continuously during the fitting procedure. A randomly generated population of parameter sets is initially created, and the GA then begins the stochastic process of recombining and mutating the population pool to iteratively generate better and better evolved parameter sets over subsequent generations which are in agreement with the entire reference dataset.

GA-based evolutionary techniques have been used for a wide range of applications, including the optimization of gas transmission lines in petroleum piping [23], satellite scaffolding design [20], pattern recognition and image analysis [24], microcircuit design [25], and drug design [26] for pharmaceutical applications. In more recent work, Oh et al. [27,28] predicted and optimized the configuration of nanoalloys consisting of Pt-Ag, Pt-Au and Pt-Cu, by using a GA engine to drive an embedded atom model (EAM) energy evaluation to determine the lowest total energy configurations of each bimetallic combination. Within the context of the development and optimization of force field functions, Wang and Kollman [21] were one of the first to use a GA method to create a parameterization for an interatomic potential consisting of bonded and non-bonded force field components for non-reactive bio-molecular systems. The implementation presented here is derived directly from Globus et al. [29,30], where GA was employed to reproduce the Stillinger–Weber potential parameters for silicon [4] as an initial test case.

In this work we develop and extend the method to the optimization of parameters for interatomic potentials for metal oxides, which are known to exist in multiple phases at different temperatures. As an example, we apply the GA method to the parameterization of Barium Titanate (BaTiO_3 or BTO), for which a reference dataset is first created using a DFT method, and then we explicitly show that it is possible to (i) optimize the multiple phases of BTO in a simultaneous single run, (ii) include incrementally more and more data in the reference dataset during the optimization loop, and (iii) include both the near-equilibrium and far-from-equilibrium configurations in the optimization. All four known phases of BTO, rhombohedral, orthorhombic, tetragonal and cubic, are simultaneously fitted within a single GA parameterization run, and the results are found to be in good agreement with the entire DFT reference dataset, as well as with the available experimental measurements of the basic mechanical and thermal properties of BTO reported in the literature.

In Section 2, we describe the details of the GA method as used for the parameterization of interatomic force field functions with an example application for the optimization of the shell model potential [31] for BTO described in Section 3. In Section 4, the main results of the GA fitting to multiple phases of BTO in a single simultaneous run are reported, and the validation of the evolved parameterization in comparison with experimentally reported values of the basic structural, mechanical, and thermal properties of BTO are described. Finally in Section 5, we summarize the main advantages and suitability of the GA method in fitting parameters of force field functions as larger and larger reference datasets for different materials are developed and made available online.

2. The genetic algorithm (GA) method for parameterization of force field functions

The description of the technique is derived loosely from biological genetic concepts in which it has been established that chromosomes and their respective sequence of genes form the foundation on which heredity leads to environmental adaption through the genotype-to-phenotype cycle. In the GA model a set of genes forms a chromosome and a set of chromosomes forms a population. The concepts of genes, chromosomes and population are illustrated in Fig. 1. Each gene corresponds to one parameter in the force field function. There are as many genes in a chromosome as there are needed to form a complete set of force field parameters. Thus, a single parameter set corresponds to one complete chromosome but a population may have an arbitrary number of chromosomes. The technique starts by randomly creating a population of a selected size by generating each chromosome with randomly generated genes.

The algorithm randomly generates each gene between predefined regime limits specific to that gene. The gene is generated by either sampling from a purely uniform distribution, or from a distribution which is biased toward either end of the gene's parameter limits using a logarithmic distribution [32]. A random coin flip decides from which distribution the gene will be selected. Describing a distinct chromosome, we have

$$\mu_i \in \mathcal{K}, \mu_i = \{\eta_1, \eta_2, \dots, \eta_n\} \quad (1)$$

where κ is the total population, η are the distinct genes within the chromosome, n is the total number of genes, and i is the index of the chromosome in the total population pool. The gene generation operator is defined as

$$\hat{G}(\eta_j, p) = \begin{cases} \eta_j = \text{RandomLogarithmic}(\eta_{\min}, \eta_{\max}) & \text{if } p \leq \frac{1}{2} \\ \eta_j = \text{RandomUniform}(\eta_{\min}, \eta_{\max}) & \text{otherwise} \end{cases} \quad (2)$$

where p is a uniform random number in $[0,1]$ generated at each gene initiation. $\text{RandomLogarithmic}(\eta_{\min}, \eta_{\max})$ is the probability function defined by the density

$$P(\eta) = \frac{1}{X_{\min \text{ or } \max} \ln(\eta_{\max}) - \ln(\eta_{\min})} \quad (3)$$

with $X_{\min \text{ or } \max}$

$$X_{\min \text{ or } \max} = \begin{cases} \eta_{\max} - \eta & \text{or (a random choice)} \\ \eta - \eta_{\min} \end{cases} \quad (4)$$

indicating that the gene is randomly biased toward the maximum or minimum of the gene's parameter limit.

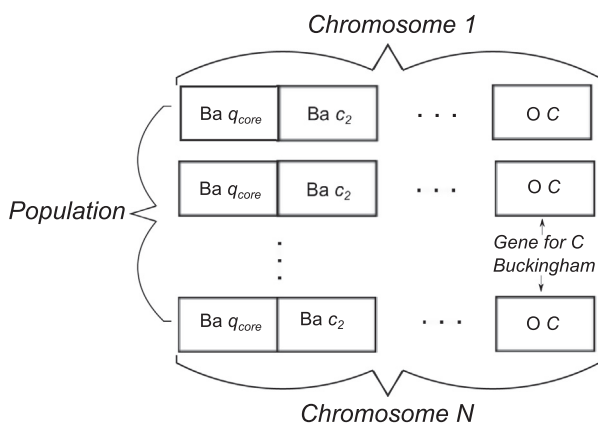


Fig. 1. Gene, chromosome, and population representations in the GA.

The GA generates a predefined number of population members and this population size is maintained throughout the evolutionary cycle. Thus this variant of evolutionary strategy is characterized as steady state [29]. To move the population pool towards increasing fitness, a tournament selection operator is used to randomly select two parents from the population pool,

$$\hat{T}(\kappa) \rightarrow \{\mu_{\text{mom}}, \mu_{\text{dad}}\}. \quad (5)$$

Based on this operator, a *child* or offspring is created from its two parents via the recombination operator. In the current implementation, a random selection is made between the parents' gene values, such that

$$\mu_{\text{child}} = \hat{R}(\mu_{\text{mom}}, \mu_{\text{dad}}) \quad (6)$$

where gene j of μ_{child} is generated using

$$\text{RandomUniform}((\eta_{\text{mom}})_j, (\eta_{\text{dad}})_j) \quad \forall j \in \{1, \dots, n\} \quad (7)$$

(the interval $[(\eta_{\text{mom}})_j, (\eta_{\text{dad}})_j]$ is used, assuming $(\eta_{\text{mom}})_j \leq (\eta_{\text{dad}})_j$) and thus a novel gene set results. Subsequent to the recombination operator, this new offspring chromosome can be submitted to a mutation operator, which alters the value of a distinct gene based on a predefined mutation frequency p_m . For each gene in the chromosome, the mutation operator is

$$\hat{M}(\eta_i, p, p_m)_{\text{child}} = \begin{cases} \eta_j = \text{RandomNormal}(\eta_{\text{MF}}, \sigma) & \text{if } p \leq p_m \\ \text{Do not alter} & \text{otherwise} \end{cases} \quad (8)$$

where RandomNormal is a random normal variable with mean η_{MF} and standard deviation σ . The value of η_{MF} is taken from the most fit of either of the two parents.

The next step in the cycle is to use an anti-tournament selection operator, in which the least fit of two parents is compared to the offspring. If the offspring is of greater fitness than the weaker parent, this parent is removed from the general population and replaced with the child. In this Darwinian-derived selection process, the population pool is continuously driven toward a more fit genotype. Once a child making cycle is completed, the process is initiated once again and continues until a certain predefined number of generations is produced. An outline of the method as a whole is given in Algorithm 1.

Algorithm 1. Steady state with tournament/anti-tournament selection.

```

{Initiate the population}
for i = 1:N do
  {Loop over the genes in a chromosomes}
  for j = 1:n do
    {Random generation of genes}
    if p ≤ 1/2 then
      ηj = RandomLogarithmic (ηmin, ηmax)
    else
      ηj = RandomUniform (ηmin, ηmax)
    end if
  end for
  Determine resulting chromosome's fitness.
end for
{Finished creation of initial population pool κ}
{Begin recombination/mutation operators for children}
while Generation ≤ Max Generations do
  for i = 1:Nchildren do
    {Use tournament to select parents from the population pool}

```

(continued on next page)

```

 $\hat{T}(\kappa) \rightarrow \{\mu_\alpha, \mu_\beta\}$ 
for  $j = 1:n$  do
  {Perform a recombination operation to produce child genes}
   $\mu_{child} = \hat{R}(\mu_{mom}, \mu_{dad})$ 
  if  $p \leq p_m$  then
    {Perform a mutation operation on the child's gene if under a predefined mutation frequency}
     $\hat{M}(\eta_j, p, p_m)_{child} = \text{RandomNormal}(\eta_{MF}, \sigma)$ 
  end if
end for
  Determine resulting child chromosome's fitness.
  Perform an anti-tournament operator to determine the least fit member of the three chromosomes and update the population pool.
end for
  Determine statistics of resulting population pool.
end while

```

Legend:
 η : gene/parameter value

 μ : chromosome/parameter set

 κ : population pool/total set of parameterizations

There are five critical evolutionary parameters that play a prominent role in the evolutionary process which are the size of the population, the number of children-per-generation to be produced, the mutation frequency, the standard deviation of the Gaussian distribution for the mutation operations, and the number of independent GA evolutions that are run based on the exact same parameters. Given the stochastic nature of the GA process and the high-dimensional solution space of the problem, a series of initial trial-and-error evolutions were conducted that provided a range of combinations of these parameters which proved to be the most productive. The results presented in this work are based on the evolutionary parameters listed in Table 1.

The selection of the cost, i.e., fitness, function is often specific to the type of parameterization being evolved. The cost function selected in the present implementation is derived from the root-mean square (RMS) difference between the energy evaluations using the GA-derived parameter set and energy evaluations using DFT. Thus, we have

$$\widehat{CF}(\mu, \text{basis set}) = \sqrt{\frac{\sum_{i=1}^{N_{\text{configs}}} (E_{\text{DFT}}(\text{basis set}_i) - E_{\text{GA}}(\mu, \text{basis set}_i))^2}{N_{\text{configs}}}} \quad (9)$$

where the subscript GA indicates an energy evaluation using the shell model potential with a GA-derived parameterization and N_{configs} is the total number of displacement configurations involved

in the fitting. As a result, the GA strives to minimize the cost function of each parameter set and thus those population members with lower cost function values are of greater fitness.

3. Application to a shell model potential for metal oxides: BTO

As an example, we apply the GA method to the parameterization of an interatomic potential for metal oxides. Metal oxides are found in a diverse range of applications that include piezoelectrics transducers and actuators [33,34], ion carriers for batteries [35], catalysts for fuel-cells [36], and elements for gas sensing [37], and yet currently there are not as established and tested interatomic potentials for metal oxides as exist for the semiconductor or metal class of materials. This is possibly because the simulations of metal oxides need to account for explicit charges (positive on the metal side and negative on the oxygen side) in the structures and during the dynamics. Therefore both non-bonding long range Coulomb and bonding short range interactions need to be properly incorporated in the potential.

To demonstrate the method and the advantages of using GA for optimizing a force field function over the traditional local gradient based methods, we have chosen to optimize the parameters of the shell model potential, which is suitable for non-reactive modeling of metal oxides in general and BTO in particular. Currently, numerous parameter sets exist in the literature for BTO type metal oxides developed over the past years. Tinte et al. [38] present a parameterization of the shell model potential using the phase transition properties in terms of lattice lengths and average electronic polarization to produce different crystal phases with increasing temperature. Sepiarsky et al. [33] have extended the potential to simultaneously model BTO as well as Barium Strontium Titanate (BST). Both of these studies review distinct facets of material behavior, but noteworthy is that they offer different short-range parameters for the Buckingham potential and consequently strive to model different BTO properties.

Within the context of using the GA method for optimizing a BTO type metal-oxide, in the following we briefly describe (i) the ansatz or the functional form for the shell model potential for modeling metal oxides, (ii) the structures and multiple phases of BTO which are needed as the underlying crystal structures for the input reference database, and (iii) the ab initio quantum mechanical DFT simulations for the structural (energy vs structure for different phases) and mechanical (changes in the energy vs structure) properties of BTO, which populate the reference dataset for the results shown in Section 4 of this work.

3.1. Shell model potential for metal oxides

The shell model potential was initially proposed by Dick and Overhauser [31] in order to capture the polarizability of dielectric materials within the context of a simplified potential field. Since its introduction and the advent of computational methods and systems, the shell model potential has been applied to an ever increasing range of dielectric materials [33,39,40].

The general premise of the shell model is to represent each ion in the system as a two-component entity: a positively-charged core and a negatively-charged shell which are coupled together through a spring-like potential. Long-range Coulomb, or electrostatics, effects are present between all the cores and shells of the system, except the core and shell of a given ion. Short-range Buckingham repulsion forces exist between the shells of neighboring ions up to a prescribed cut-off. In our model, Buckingham forces are present only between the shell of an oxygen and the shell of another ion. In addition, the core and shell of each ion are coupled by a spring-like potential consisting of harmonic and anharmonic components. The primary role of the coupling term

Table 1
Parameters of the evolutionary cycle.

Evolutionary Parameter	Value
Population Size	400
Child-per-Generation	160
Mutation Frequency	75%
STD of Mutator	2
Number of concurrent trajectories	8–16

is to affix each shell to its corresponding core, thus allowing the shell model potential to capture dipole-induced effects so as to predict the general polarizability of the dielectric. These interactions are summarized in Fig. 2.

The general functional form of the potential is

$$\begin{aligned}
 U(\mathbf{r}, \mathbf{w}) &= U_{\text{PME}}(\mathbf{q}, \mathbf{r}) + U_{\text{BCKH}}(\mathbf{r}) + U_{\text{CPL}}(\mathbf{r}) \\
 &= \frac{1}{2} \sum_n \sum_{i,j,i \neq j} \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}|} + \sum_{\substack{i,j,i \neq j \\ |\mathbf{r}_{ij}| \leq r_c}} \left(A \exp\left(-\frac{|\mathbf{r}_{ij}|}{\rho}\right) - \frac{C}{|\mathbf{r}_{ij}|^6} \right) \\
 &\quad + \sum_i \left(\frac{c_2 w_i^2}{2} + \frac{c_4 w_i^4}{24} \right). \quad (10)
 \end{aligned}$$

The first summation term is the electrostatic contribution, the second is the short-range Buckingham potential, and the final term is the coupling term between the shell and core of a given ion. To avoid cumbersome notations, we do not precisely specify the particle pairs involved in each interaction. Instead all interactions that need to be considered are described in Fig. 2. We denote

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$$

the displacement vector between two particles, and

$$\mathbf{w}_i = |\mathbf{r}_{\text{core of ion } i} - \mathbf{r}_{\text{shell of ion } i}|$$

where \mathbf{r}_{core} and $\mathbf{r}_{\text{shell}}$ are the coordinates of the core and shell of the same ion. Details of each contribution are described below.

For an ionic material, long range electrostatic forces are a vital contribution to the energy landscape of the dielectric system. A highly accurate and computationally efficient technique by which to treat electrostatic effects is the Particle Mesh Ewald (PME) method. The formulation of PME as applied here is based on Refs. [41–43]. The implementation of $U_{\text{BCKH}}(\mathbf{r})$, the short-range Buckingham potential, is directly derived from its functional form as given in Eq. (10) and was applied up to an imposed cut-off.

As noted previously, the coupling term $U_{\text{CPL}}(\mathbf{r})$ in itself is a constraining force which allows the shell model to capture polarization within the dielectric's bulk crystalline structure by introducing a restoring force on the shell of a given ion. In effect, unlike the electrostatic or Buckingham short-range interactions, it is not directly correlated to the configurational energy of the basis geometry and thus the coupling constants are primarily adjusted to capture the correct polarizability of the dielectric. It is noted that in its initial form in [31], the coupling term consisted of only the harmonic constant c_2 . However, in later iterations of the model, the anharmonic term c_4 was added to account for the effects of hybridization of the ionic structure [33].

For the current cost function as given in Eq. (9), our primary focus in this initial work is in accurately capturing the configura-

tional energy landscape of the BTO basis in each of its four phases. Therefore, as a first approximation, we do not directly address the polarizability of the dielectric and the fitting of the harmonic and anharmonic terms of the coupling potential. The shell positions are then held fixed in relation to their respective cores, so that coupling potential remains consistent and constant through all four phases. In general, it is possible to modulate the Born effective charges [38] for the polarizability values under an applied field within the DFT framework [44], and use those in fitting the coupling terms as well using the GA approach.

The total parametric space of the shell model is now clearly identified with six distinct charges for the core and shell of each ion species, the same number of harmonic/anharmonic constants to define the coupling terms, and nine distinct coefficients for the Buckingham potential's oxygen-centric short range interactions. An overall summary of the interaction parameters is given in Table 2.

In effect, there are a total of 20 independent parameters, since the BTO basis has a neutral net charge, i.e., by prescribing five of the six system charges, the sixth charge directly results.

3.2. Crystal structures and structural displacements of BTO

Our objective is to prepare a reference dataset including the lattice constants for original crystal structures and the displacements around their equilibrium configurations to represent the elastic properties of BTO in all four phases. We start by selecting the reference equilibrium configurations for each of the crystal phases and then proceed to permute the positions of each atom or pairs of atoms in turn where the DFT energy is determined for each new configuration. The original configuration and the lattice constants for the cubic phase are shown in Fig. 3(a).

All possible displacements of pairs of atoms along x, y, and z directions are considered. For any pair of atoms, this leads to 9 possible combinations of displacements. Each atom in a pair is moved in increments of 0.05 Å up to a maximum of 0.25 Å from the equilibrium positions as determined in [45]. The different displacement orientations are listed in Table 3. An example of Type 3 displacement in Table 3 is shown in Fig. 3(b).

In the phases with orthogonal primitive vectors, (i.e., orthorhombic, tetragonal and cubic phases), the orientation of the basis vectors **a**, **b**, and **c** correspond to the Cartesian axis and are dealt as above. The rhombohedral phase has non-orthogonal primitive vectors and requires the use of reduced coordinates to define its displacements consistently. Using a similar convention as defined in [46], the rhombohedral displacements are carried out along the appropriately defined primitive vectors, resulting in a maximum magnitude of displacement from the equilibrium position of ± 0.2 Å per ion displaced.

It is noted that in this work, a comprehensive set of displaced basis configurations along the primary axes has been included in the reference database so as to ensure a complete resolution of the elastic properties of the material. In general, however, this may prove to be superfluous. A smaller dataset for near-equilibrium and far-from-equilibrium displacements with

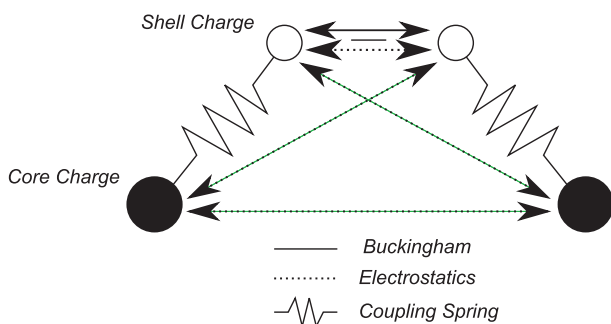


Fig. 2. Distinct interactions within the shell model potential.

Table 2

Parameterization of the shell model potential as applied to BTO.

Potential	Parameters	Entity 1	Entity 2	Total # parameters
Electrostatics	$q_{\text{core}}, q_{\text{shell}}$	Core/Shell	Core/Shell	6
Buckingham	A, ρ, C	Shell	Shell	9
Coupling	c_2, c_4	Core	Shell	6
Total				21

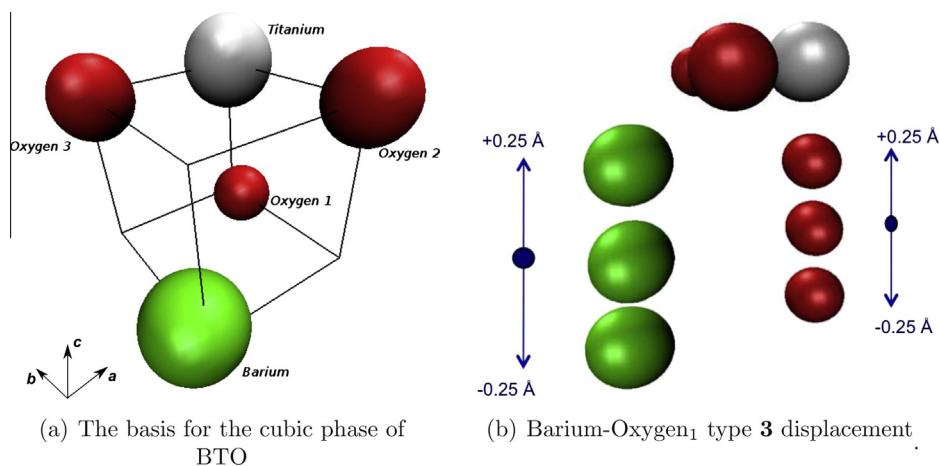


Fig. 3. Cubic basis and sample atomic displacement. Atom displacements begin at -0.25 Å from their cohesive configuration and are incremented in 0.05 Å steps.

Table 3
Types of displacements of the BTO basis.

Displacement key	Type of displacement
1	Ion 1 in the a direction/ion 2 in the a direction
2	Ion 1 in the b direction/ion 2 in the b direction
3	Ion 1 in the c direction/ion 2 in the c direction
4	Ion 1 in the a direction/ion 2 in the b direction
5	Ion 1 in the a direction/ion 2 in the c direction
6	Ion 1 in the b direction/ion 2 in the c direction
7	Ion 1 in the b direction/ion 2 in the a direction
8	Ion 1 in the c direction/ion 2 in the a direction
9	Ion 1 in the c direction/ion 2 in the b direction

systematic, Boltzmann, and randomly distributed configurations could in fact prove to be sufficient for the reference dataset, and so many time consuming DFT structures and their respective energies may not be needed. This will be tested in further development of the methodology in the future.

To run the GA loop for the optimization, for a given set of the input parameters, the shell model energies are calculated for all the configurations listed above, whereas, the reference energies dataset comes from the ab initio quantum DFT simulations described later. For the GA to efficiently calculate the shell model energies, a basis-replication scheme has been implemented within the optimization code. In this adaption, derived from conventional periodic boundary conditions [1], images of the original basis are replicated in the surrounding space using the primitive translation vectors of the given phase. The interaction energies of the reference cell are summed up with energies of the images as well. A series of studies were used to determine the convergence in terms of the short range Buckingham cut-off, the PME cut-off, and the required number of replica images. Based on these studies, the short range cut-off was set at 10 Å and a long range cut-off was set at 16 Å. Further details of the image replication scheme are given in Solomon [32].

Because of the symmetries in the crystal, many of the displacements actually produce configurations that are identical up to rotations and reflections. As a result, of the 90 total sets of displacements for the cubic phase, only 18 curves are needed to reproduce the required energy landscapes. The tetragonal phase has less intrinsic symmetries and therefore 48 distinct curves were required. Smaller subsets of net displacements were used for the two lower temperature phases, with the orthorhombic and rhombohedral phases referencing to 40 and 10 distinct displacement curves respectively. A summary of the reference displacement curves is given in Table 4.

3.3. DFT Energies of the crystal structures and structural displacements

The DFT calculations were performed using ABINIT [44] in conjunction with ultra-soft pseudopotentials as prescribed by Vanderbilt [47]. The differences in the symmetry of each phase require distinct kinetic energy cut-offs of the plane wave expansion as well as the distinct gridding of the reciprocal space. The key parameters of each series of DFT calculations were derived from a set of convergence studies. For cubic and tetragonal phases, energy cut-offs of 35 and 50 Ha respectively were used, with high density Monkhorst–Pack gridding for the reciprocal space [48]. The orthorhombic phase has twice the number of ions in its basis at ten ions and as a result far less planes of symmetry in its geometry, thus requiring a higher energy cut-off of 70 Ha and a $6 \times 6 \times 6$ uniform reciprocal space grid. The rhombohedral phase with its non-orthogonal basis vectors required a high energy cut-off as well at 80 Ha, with a $8 \times 8 \times 8$ uniform reciprocal space grid.

The equilibrium configurations from which the coupled-ion displacements are referenced were obtained from temperature dependent Neutron diffraction data presented by Kwei et al. [45] used in conjunction with the reduced coordinate data given by Uludogan and Cagin [49]. For the cubic phase, a relaxation of the ion structure was performed using a Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization cycle, rendering negligible change in the basis geometry. For the remaining phases, no minimization was attempted and the empirical lattice geometry provided by Kwei was used directly since the focal interest of the GA is the relative energy of displacements around the established equilibrium configurations. Table 5 presents the lattice geometry in the equilibrium configuration used for each of the four phases, and a sample of DFT energies corresponding to the cubic crystal phase and the displacements around the equilibrium configuration are shown in Fig. 4.

Table 4
Reference database of displacement curves.^a

Phase	# Ions in basis	# Displacement curves	# Distinct basis configurations
Cubic	5	18	181
Tetragonal	5	48	481
Orthorhombic	10	40	401
Rhombohedral	5	10	101
Total Configurations			1164

^a These configurations comprise a full set of atomic pair displacements for the tetragonal and cubic phase up to rotations and reflections.

4. Results of the GA optimization of BTO interatomic potential

The GA methodology described above is applied to the tunable dielectric BTO, which is known to have four known stable phases or crystal structures in a rather small temperature range of a few hundred degree Kelvin. In the following, we describe the results of GA parameterization runs of the BTO potential using first an incomplete reference dataset comprising of DFT energies for the configurations of only two of the four crystal phases, followed by a second GA optimization in a single run with a complete reference dataset including DFT energies for all four of the crystal phases. The measure of accuracy of the first GA run with incomplete reference dataset consisting of only two phases, cubic and tetragonal, is assessed by computing and comparing the structures and energies of the other two phases, rhombohedral and orthorhombic, which were not included in the incomplete reference dataset with their respective DFT calculated values. The accuracy of the second GA run with the complete dataset with all four crystal phases is assessed by MD simulations of the basic elastic and thermal properties and comparing with the experimental and DFT results available in the literature. Additionally in this section we also show that, depending on the starting initial conditions, a conjugate gradient method for the same fit for a cubic phase has a tendency to get stuck in nearby local minima of the starting configuration, whereas the GA method can accommodate a wide range of both near-equilibrium and far-from-equilibrium starting initial conditions or configurations in the fitting procedure.

4.1. GA Parameterization using two BTO phases: incomplete reference dataset

Using the data from a set of cubic and tetragonal DFT curves listed in Table 4 (a total of 662 configurations), a series of four iterative GA

Table 5
Lattice geometry of the equilibrium configurations.

Phase	Primitive Vectors	Basis angle
Cubic	$\mathbf{a} = [4.0 \ 0 \ 0]$, $\mathbf{b} = [0 \ 4.0 \ 0]$, $\mathbf{c} = [0 \ 0 \ 4.0]$	\perp
Tetragonal	$\mathbf{a} = [3.99095 \ 0 \ 0]$, $\mathbf{b} = [0 \ 3.99095 \ 0]$, $\mathbf{c} = [0 \ 0 \ 4.0352]$	\perp
Orthorhombic	$\mathbf{a} = [3.9841 \ 0 \ 0]$, $\mathbf{b} = [0 \ 5.6741 \ 0]$, $\mathbf{c} = [0 \ 0 \ 5.6916]$	\perp
Rhombohedral	$\mathbf{a} = [3.26473 \ 0 \ 2.31843]$, $\mathbf{b} = [-1.63237 \ -2.82734 \ 2.31843]$, $\mathbf{c} = [-1.63237 \ 2.82734 \ 2.31843]$	89.836°

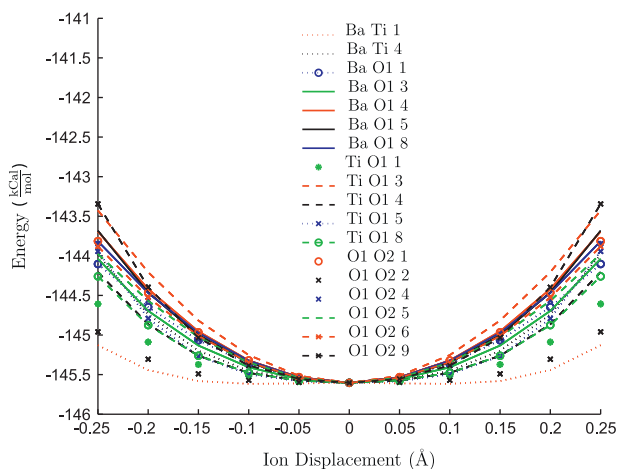


Fig. 4. Subset of DFT displacement curves for the cubic phase.

evolution cycles were generated based on the higher temperature phases. In general, in the GA optimization procedure, the initial starting parameters in the first chromosomes are chosen randomly within a range defined by physics-based considerations for a given model (the shell model in our case). However, for our test case of BTO, a shell model potential with a parameter set (fitted through conventional techniques) has already been reported in the literature by Sepiarsky et al. [33]. This potential was used as a loose guide to define the initial ranges within which the parameters of the starting chromosomes were chosen. Each individual parameter's initial regime was iteratively adjusted so that with all other parameters fixed, the parameter was able to explore a resulting energy range of ± 100 kCal/mol. For a completely new case, similar criteria for a range of variations for the initial energies could be used to set-up the initial ranges for choosing the parameters.

Once an initial evolution of 400 generations was created for 16 independent GA runs, the trajectories of each of the distinct parameters of the fittest member of the 16 different populations were studied. The GA allows for the definition of limits for each evolvable parameter. Those parameters which drifted to the edges or limits of their pre-defined range, (the η_{min} and η_{max} discussed in Section 2), were allowed to explore the expanded range by shifting the limits during the subsequent evolution cycles. It is noted that no parameter's search range was ever contracted. A comparison of the thus GA-fitted shell model energies with the input DFT energies in the reference dataset for the cubic and tetragonal phases, fitted simultaneously in a single GA optimization run over four cycles is shown in Fig. 5. In the current context, an evolution cycle consists of the 400 generations between expansion of the parameter exploration limits.

Overall improvement in the resulting parameterization is evident as the distribution of shell model and DFT energy data points start to cluster tightly around the $slope = 1$ line representing a perfect fit for all data points in the considered energy range. Unless otherwise noted, the RMS of each GA cycle is given on a per-ion basis so as to directly compare the quality of the fidelity across the different phases, specifically given that the orthorhombic basis consists of twice the number of atoms or ions. It is noted that as the GA optimization proceeds, the initial good fit is achieved at the low or lowest energy configurations even in the 1st GA cycle, which could be similar to local gradient based fitting methods focused entirely around the near-equilibrium configurations. We note that the RMS spread of the fitted and the input data-points for explicitly far-from-equilibrium (higher energy) configurations also start to decrease sharply in subsequent GA cycles 2, 3, and 4 of the same GA run. The procedure is stopped when the RMS of the spread of all the data-points for all the near-equilibrium and far-from-equilibrium configurations is within some prescribed RMS value.

Another key differentiation with the traditional local gradient based methods is that in the GA fitting procedure, the entire DFT based reference dataset is used in the fitting procedure and not any derived physical properties such as the elastic constants, which by definition are also limited to including only small deviated or displaced configurations from the equilibrium values. This brings out two key advantages of the GA fitting procedure over the typical local gradient based methods: (i) since the GA includes the entire raw data of the DFT structures and their respective energies in a single run it will be straightforward to incrementally include additional data, such as DFT structures and energies of additional phases, surfaces, and clusters as it becomes available, and repeat the GA run over a much shorter period of time than that required for ad hoc fitting procedures to improve or extend the fitted potential, and (ii) since both the near-equilibrium (low energy) and far-from-equilibrium (high energy) configurations or structures are explicitly included, the GA will be better suited to fit potentials with explicitly very high temperature and high reactivity data and properties in the

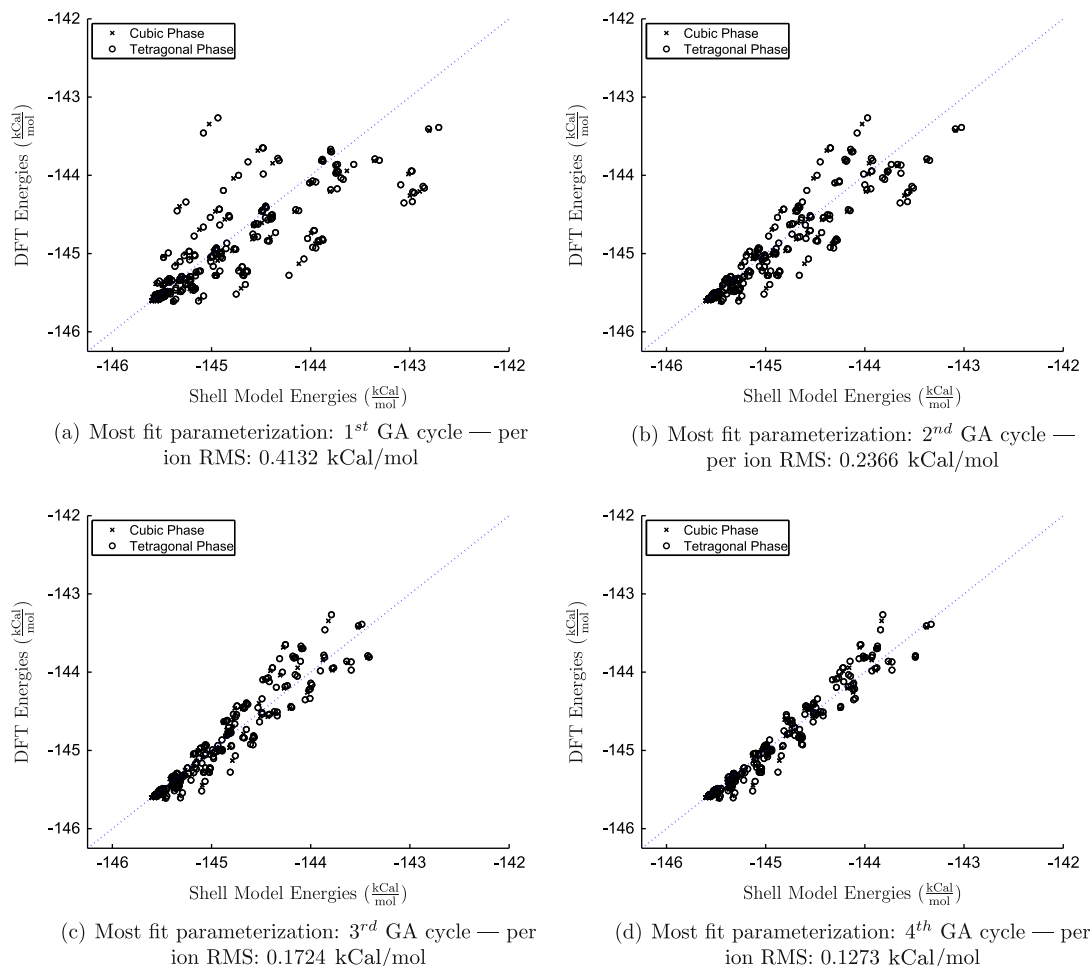


Fig. 5. DFT to GA shell model energy comparisons based on parameterizations derived from the GA evolutionary cycle. The dashed line here represents $y = x$; i.e., exact agreement. Plots illustrate the GA optimization cycle starting from the initial literature-derived parameterization space of the 1st GA cycle to an entirely GA redefined parameterization space which produces the most-fit parameter set of 4th GA cycle.

dataset, which are generally not explicitly included in the fitting procedures for the interatomic potentials thus far.

As an example, in Fig. 6 we compare the energies obtained from the Sepliarsky et al. [33] parameterization for all the structures included in our dataset and our GA-fitted energies, for the same structures from the parameterization after the 4th GA cycle, directly to the corresponding DFT energies. For the near-equilibrium or lowest energy structures there is a good overlap between our GA-fitted values and the Sepliarsky's values with the corresponding DFT simulated structures and energies. However, as we include the far-from-equilibrium or higher energy data-points and compare the slopes of linear fits in the two cases, the slope of GA-fitted energies is 1.05 for nearly a one-to-one correspondence, whereas for the Sepliarsky's values not only does the slope of the linear fit to the data of 0.29 have a larger deviation from the ideal value of 1 but the RMS spread of energies around the linear fit is also much larger (~ 2.1 kCal/mol). This was expected as the traditional local gradient based methods generally focus on using only the near-equilibrium structures and energies in the fitting procedure. The evolved parameterization of the 4th GA cycle which produced the energy evaluations in Fig. 6 is given in Table 6.

Lastly in this section we assess the robustness of the above GA optimized potential fitted with only the tetragonal and cubic phases of BTO in the incomplete reference dataset. This is done by predicting the near-equilibrium (low energy) and far-from-equilibrium (high energy) configurations of the other two orthorhombic and rhombohedral phases of BTO not included in the

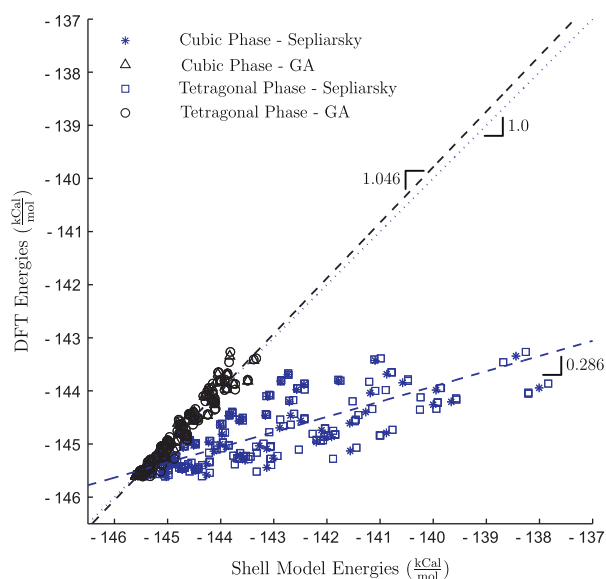


Fig. 6. Comparison of 4th GA cycle parameterization to that of Sepliarsky et al. [33]. Plots that have linear fits, such as the one presented here, have the symbol \lrcorner to indicate a trend line. The plot emphasizes the role of GA optimization in producing a parameterization with greater fidelity to the ab initio calculations than that of current parameterizations presented in the literature.

reference dataset. The GA-fitted energies for orthorhombic and rhombohedral phases using the incomplete reference dataset are directly compared to their DFT values simulated for the complete reference dataset to be used in the next section. The comparison is shown in Fig. 7. Interestingly, the comparison shows that the structures corresponding to rhombohedral phase are captured accurately in the entire energy range with an RMS between the predicted and DFT values of 0.1599 kCal/mol. The predicted values of orthorhombic phase show a larger deviation for higher energy structures but low energy structures are in good agreement.

These results show the utility and robustness of the method given that the potential for having to contend with a Pareto set scenario is greatly reduced. Pareto set analysis, [19,20], applies to evolution strategies with multiple cost functions in which no one solution dominates all others. The concept of Pareto front is central in problems where the cost functions are somehow in conflict with one another and therefore the optimal solution involves in general a trade-off amongst the competing objectives. The above results indicate that the simultaneous optimization for the two (cubic and tetragonal) phases is in relative congruence with an optimization for the remaining two (orthorhombic and rhombohedral) phases of the perovskite, which is an interesting result in itself and indicate that optimization for one phase does not occur at the detriment of another. This may not be the case in fitting other structures such as clusters, surfaces, and reactivity. In that case, with GA it is possible to also specify the relative importance of one desired set of properties over the others. In the later Section 4.3, we will describe a simultaneous optimization with all four phases in the complete reference dataset.

4.2. Comparison of GA optimization with a local gradient based method

One of the main limitations of the local gradient based methods, as used for the fitting of the complex interatomic potentials thus far, has been to fit one set of the properties such as bulk structure

or crystal phase at a time. For an overall optimization for a system with multiple objectives, such as multiple crystal phases or properties, a serial procedure is often used because one phase or property is fitted at a time and one needs to manually go back and forth to iteratively fit the parameters in different sets to get overall averaged parameters for more than one crystal phase or property. That is why it has generally taken years to incrementally improve a previously optimized potential to incorporate additional data for new phases or properties. In the case of BTO, we seek a single parameter set capable of accurately representing the lattice constants and mechanical properties across the four known phases.

Because of the above limitation on the typical use of local gradient based methods to fit only one system or crystal phase at a time, in this section, we compare the GA approach with the conjugate gradient (CG) technique applied only to the well known high temperature cubic phase of BTO. The Brent method [50] was used in conjunction with the robust bracketing method to determine the step size in the line search direction. For validation, the method was initially applied to a number of single displacement curves, and for all curves tested, CG parameterizations with an RMS of ~ 0.03 kCal/mol were obtained. In applying the procedure to the full set of cubic phase curves, different parameter sets from a GA evolution of the cubic phase were selected as the starting points. Fig. 8 shows 16 distinct GA trajectories. The CG minimization was initiated from three distinct parameter sets along these trajectories. The results of three subsequent CG minimization trajectories from these three initial starting points are reported in Table 7. In all cases, the CG initiates a minimization trajectory, but with varying degrees of success resulting in little to no improvement in the fidelity of the parameterization to the DFT energies.

4.3. GA parameterization using all four BTO phases and simulations of material properties

This next set of results is derived from the GA evolution based on displacement data from all four phases of BTO. In this section,

Table 6

Parameterization of the shell model potential after 4th GA Cycle. For direct comparison to other parameterization given in the literature [2,38,33], units are given for length, charge and energy in terms of Å, e and eV.

Species	q_{core}	q_{shell}	C_2^a	C_4^a	A	ρ	C
Ba	5.63546	−3.66155	230.5152	107.6093	1721.4643	0.3347	43.8520
Ti	3.62644	−2.44219	304.8866	483.5996	2362.5255	0.2566	69.0100
O	1.27176	−2.32448	29.4573	3952.6778	4179.7247	0.2768	107.8916

^a Un-evolved parameter.

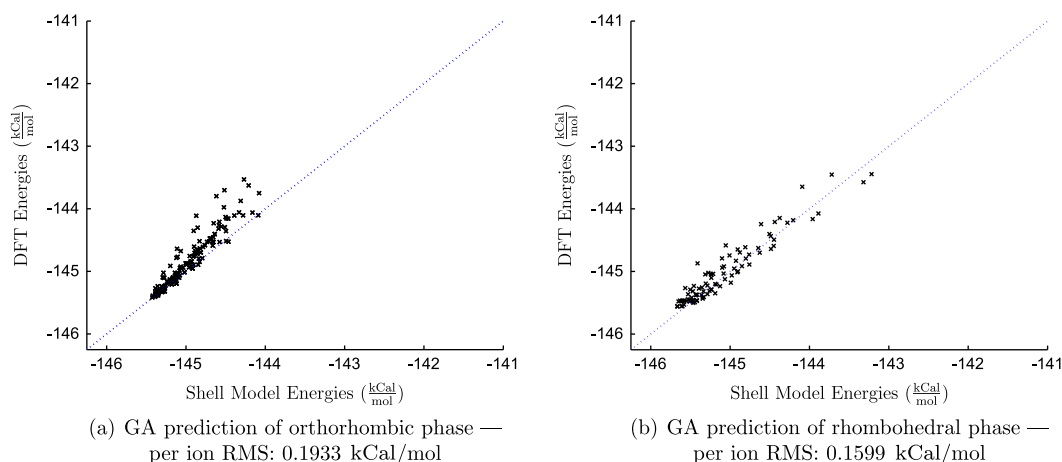


Fig. 7. GA predictive parameterization of the orthorhombic and rhombohedral phases as compared to the reference DFT data set.

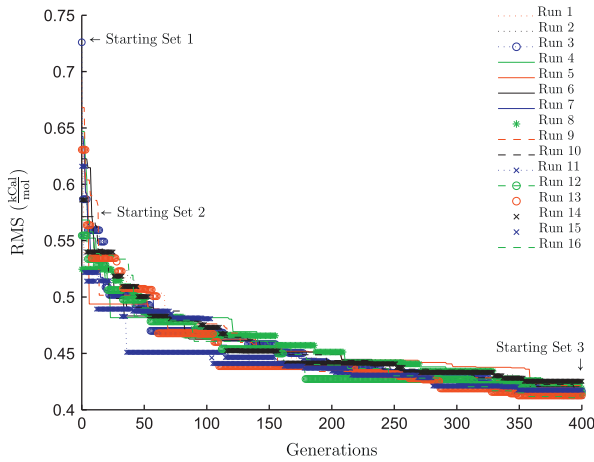


Fig. 8. Three distinct starting points for the CG minimization routine.

Table 7
GA minimization results, (RMS in kCal/mol).

Starting set	Initial value	End value	Reduction in RMS
Set 1	0.7260	0.7190	~0.007
Set 2	0.5711	0.5605	~0.0106
Set 3	0.4106164	0.4106126	~3.8 × 10 ⁻⁶

we first describe the GA optimization of the BTO potential with all four phases, followed by the simulation of the basic structural, mechanical, and thermal properties of BTO for comparison with experimental and simulation results reported in the literature.

4.3.1. GA parameterization with all four phases of BTO

In this context, a subset of the total DFT database was selected for the fitting procedure so as to reduce the computational cost of the evolutionary cycle. Since different numbers of curves were used to represent each of the distinct phases, a weighted-sum fitness cost function was selected so that all phases would have an equivalent impact on the evolved parameterization. The general form of the weighted cost function is

$$\widehat{CF}_{\text{Weighted}}(\mu, \text{basis set}) = \sum_{j=1}^{N_{\text{phases}}} \text{Weight}_{(j)} \times \sqrt{\frac{\sum_{i=1}^{N_{\text{Configs}}(j)} (E_{\text{DFT}}(\text{basis set}_i) - E_{\text{GA}}(\mu, \text{basis set}_i))^2}{N_{\text{Configs}}(j)}} \quad (11)$$

The subset of DFT basis configurations used in the current evolution is given in Table 8. Reviewing the results of 16 distinct GA trajectories, it is found that a net weighted RMS of ~0.788 was achieved, as shown in Fig. 9. Plotting energies of all four GA-fitted phases in comparison with their respective DFT energies in Fig. 10, we show a linear fit to the data (with slope ~0.979) for both the near-equilibrium and far-from-equilibrium configurations in the entire energy range. This shows a very good one-to-one agreement between the GA-fitted energies with their corresponding DFT energies for all the structures in the entire energy range. The GA evolved parameters corresponding to the fit of all four phases in the reference DFT dataset are given in Table 9.

4.3.2. Simulations of basic structural, mechanical, and thermal properties of BTO

An assessment of the quality of the GA parameterization can be done by the simulations of the basic structural, mechanical, and

Table 8
Subset of displacement curves for full spectrum evolutions.

Phase	# Ions in basis	# Displacement curves	# Distinct basis configurations
Cubic	5	18	181
Tetragonal	5	18	181
Orthorhombic	10	9	91
Rhombohedral	5	9	91
		Total configurations	544

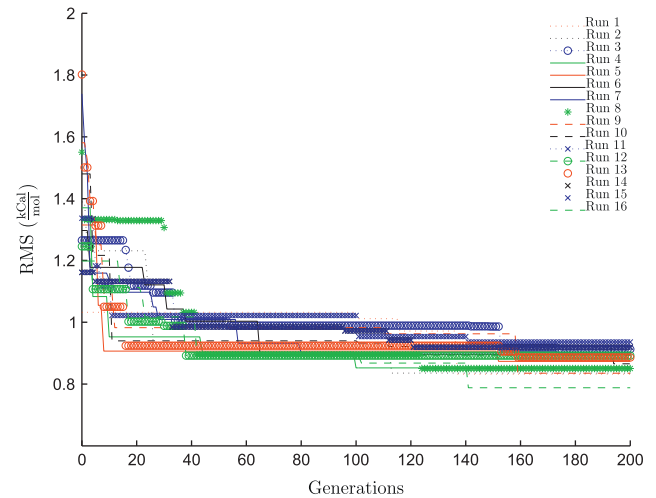


Fig. 9. GA evolution trajectories based on all four BTO phases.

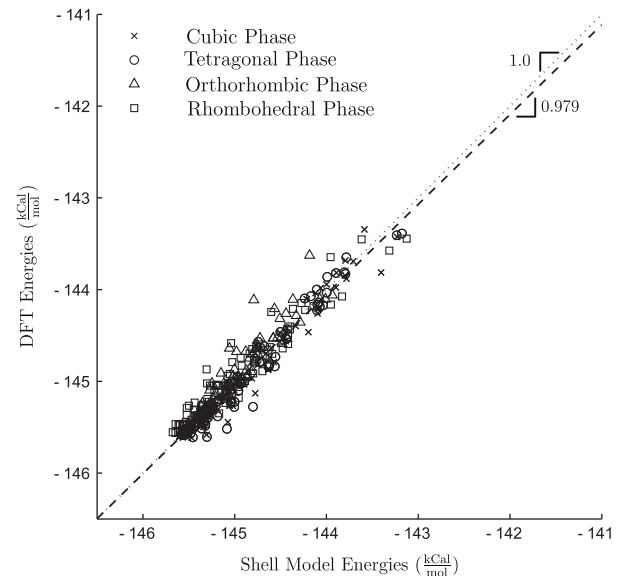


Fig. 10. DFT to GA evolved shell model energy comparison with linear fit to total phase spectrum; slope of linear fit ~0.979.

thermal properties of BTO using the optimized parameters given in Table 9, and comparing the results with experimental or DFT simulated results reported elsewhere in the literature. We do that using both the static structural and dynamic MD simulation methods.

Using the equilibrium geometries given in Table 5, a series of iterative adjustments to the unit cell were performed in each phase to arrive at the equilibrium lattice lengths and bulk modulus. At each unit cell adjustment, the energy of the specific configuration

Table 9

Parameterization of the shell model potential as applied to BTO. Units are given for length, charge and energy in terms of Å, e and eV.

Spices	q_{core}	q_{shell}	c_2^a	c_4^a	A	ρ	C
Ba	5.59664	−3.14348	233.2602	254.3762	2489.3499	0.3281	41.4167
Ti	3.41576	−2.35313	291.2780	366.8786	2093.7480	0.2581	61.4168
O	1.10895	−2.28088	19.1422	3839.1070	2469.9863	0.2658	5.6318
Net Weighted RMS: 0.7879							

^a Un-evolved parameter.

was evaluated using the shell model potential with the GA optimized parameters presented in Table 9. For the cubic and rhombohedral phases, the unit cell volume was adjusted by uniform expansion and contraction. However, in the tetragonal and orthorhombic phases, where lattice lengths are dissimilar, two sets of separate calculations were performed in each phase. First, to find the equilibrium lattice length each axis was adjusted independently. Second, for the bulk modulus calculation the axes were adjusted uniformly as in the cubic and rhombohedral phases. Fitting a fourth-order polynomial to the energy, and scaling by atomic volume, the bulk modulus was directly calculated by

$$B = V \frac{\partial^2 \Phi}{\partial^2 V} \quad (12)$$

where Φ is the equation of the polynomial. Performing this series of calculations, the cohesive volumes, equilibrium lattice and bulk modulus were calculated for each phase of the material, and compared with experimental or other simulated values reported in the literature. These values are presented in Table 10. As can be seen from the tabulated results, the GA parameterized potential accurately captures the physical properties in all four phases. The equilibrium lattice lengths and thus the stable unit cell volumes are in good agreement with the values reported in the literature. Similarly, the bulk modulus is also well represented throughout the phases and there is notable close agreement with cubic phase experimental values [51].

As a next step of the validation of the GA evolved parameterization in Table 9, we use the optimized shell model parameters in MD simulations at 400 K at which the BTO has been shown to

exhibit the cubic phase in experiments [45]. So far, with a focus on developing and showing the advantages of the GA method, we have applied the GA procedure only to the short range Buckingham and long range Coulomb potentials with spring constants effectively set to zero since shell positions are fixed to the respective core positions. In temperature dependent dynamic simulations, the spring constants for the core-shell coupling, however, cannot be zero and need to be selected. Very small or soft spring constants may not apply enough restoring forces, whereas very large or stiff spring constants may lead to a neglect of the polarization effects observed in lower temperature phases for BTO.

The initial spring constants used here were thus selected from a mean of the range reported in the literature and adjusted iteratively in a series of NVT and NPT simulations for the cubic phase at 400 K such that the crystal structure during the dynamics remained stable and general polarization was close to zero. The selected spring constants are listed in Table 11.

The following reported MD simulations were performed using the package DL POLY [54] on a $10 \times 10 \times 10$ unit cell simulation domain with spring constants listed in Table 11 and Buckingham and electrostatic constants given in Table 9. In addition to thermalization and lattice equilibration studies, the BTO block was loaded under 0.5–1.5% uni-axial strain along each primary axis to determine the elements of the stiffness tensor. For example, the diagonal components of the stiffness tensor as a function of strain at 400 K are shown in Fig. 11. As a result of this series of simulations, the equilibrium lattice lengths, equilibrium volume, general polarization, uni-axial components of the stiffness tensor, the bulk

Table 10

Static energetic phase characterizations.

Source	Unit cell vol (Å ³)	Equil. lattice (Å)	B (GPa)
<i>Cubic phase</i>			
GA evolved ^a	63.426	3.988	124.17
Experimental [51]	–	–	135
Experimental [52]	64.00	4.00	162
DFT [49]	65.85	4.0382	160.84
DFT [53]	64.28	4.0058	167.64
MD [38]	64.77	4.016	226
<i>Tetragonal Phase</i>			
GA evolved ^a	63.121	$a = 3.9750, c = 3.9948$	116.97
Experimental [45]	64.271	$a = 3.99095, c = 4.0352$	–
DFT [49]	67.50	$a = 4.00480, c = 4.2087$	82.94
DFT [53]	65.95	$a = 3.9759, c = 4.1722$	98.60
MD [38]	64.75	$a = 4.002, c = 4.043$	–
<i>Orthorhombic phase</i>			
GA evolved ^a	126.108	$a = 3.9682, b = 5.6287, c = 5.6461$	110.54
Experimental [45]	128.66	$a = 3.9984, b = 5.6741, c = 5.6916$	–
DFT [49]	67.81 ^b	$a = 3.9914, b = 5.7830, c = 5.8223$	87.39
DFT [53]	66.02 ^b	–	97.54
MD [38]	64.63 ^b	$a = 3.995, b = c = 4.022^b$	–
<i>Rhombohedral phase</i>			
GA evolved ^a	63.248	$a = 3.9842, \alpha = 89.836^b$	116.57
Experimental [45]	64.201	$a = 4.0042, \alpha = 89.836$	–
DFT [49]	67.76	$a = 4.073, \alpha = 89.74$	94.62
DFT [53]	65.99	$a = 4.042, \alpha = 89.77$	103.5
MD [38]	64.577	$a = 4.012, \alpha = 89.81$	–

^a Current work.^b This value is based on the pseudomonoclinic cell discussed in [45].

Table 11
Spring coupling term set.

Element	c_2	c_4
Ba	900	0
Ti	1170	3600
O	500	4200

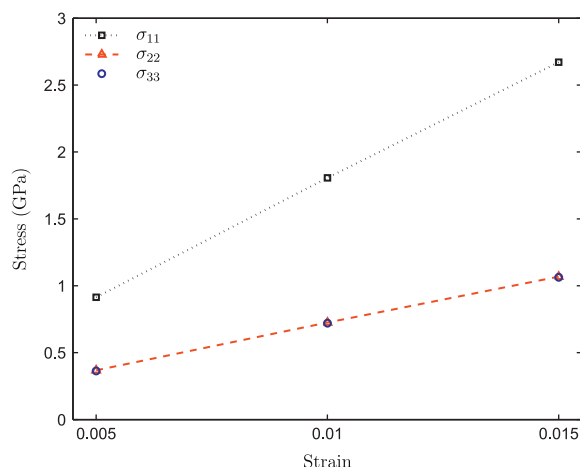


Fig. 11. Stress–strain relationships under the ϵ_{11} strain condition at 400 K.

modulus and coefficient of thermal expansion (CTE) were calculated at 400 K, and are summarized in Table 12. Experimentally determined values, where available, are also given for comparison.

As can be seen from the values in Table 12, the GA evolved parameterization captures the cubic phase with a high degree of fidelity while the various material properties are simulated. It is interesting to note that both the equilibrium volume and bulk modulus compare very well with experimental results, especially noting that the Pruzan et al. [51] value is of a more recent experimental work than that of Hellwege and Hellwege [52]. In addition, the CTE is in good agreement with Bland results [55], indicating good correlation with experimental changes in the lattice constants as the temperature is varied around 400 K. Finally, we also note that a set of input files has been prepared for the direct application of the parameterization on BTO in the $N\sigma T$ ensemble for the MD package DL_POLY [54], and can be acquired by contacting Solomon.

5. Summary on the advantages of the GA method

In summary, we have set-up the background and framework for a GA method that can be used to systematically obtain and optimize parameters for interatomic force field functions for MD simulations by fitting to an energy landscape or reference database. As an example, we have developed and applied the GA method to the fitting of a potential for BTO, a member of an important class of metal oxides, which have been known to have applications in a wide variety of areas such as tunable and low- k dielectrics, energy storage, fuel-cells, and automotive catalysts. The resulting GA optimized parameterization of the BTO potential has been able to (i) reproduce the relaxed structures and energies in good agreement with their corresponding DFT values for both the near-equilibrium and far-from-equilibrium configurations, (ii) capture the basic structural, mechanical, and thermal properties of the BTO up to 400 K, and (iii) predict the two crystalline phases of the BTO, (orthorhombic and rhombohedral) which were not included in an incomplete reference DFT dataset simulation as a test case.

Using BTO as a testbed, the GA technique is shown to be able to contend with both the stiffness of the potential framework as well as the rugged topology of the system's energy landscape. In future work, where other materials of a more exotic nature are investigated, the methods key strengths of (i) global optimizations where multiple local minima may be present and (ii) the ability to add incremental DFT and experimental data for a diverse set of properties to the reference set with little to no modifications in the optimization procedure will prove valuable assets. For a given functional form, in the GA optimization procedure, the quality of the finally fitted force field function is limited only by the quality of the data in the reference dataset, which can be improved incrementally by both advanced experimental and simulation approaches.

In addition, the success of the GA method also stems from the single-objective framework in which the sole cost function, while being of relatively low computational cost, is able to reflect the quality of the parameterization in a wide range of physical configurations. From the perspective of the GA, the reference dataset is nothing more than a list of configurations and their respective energies. In actuality, these energies and configurations may represent a diverse landscape with respect to temperature, stress–strain, surfaces, clusters, and reactivity conditions, but the GA optimization procedure remains the same. By coupling the GA approach to wider and more robust databases in the future, it may be possible to not only evaluate and improve parameterizations of existing functional forms used in MD simulations, but to also search for new functional forms which are needed but are not available today.

Table 12
Material characterization at 400 K.

Quantity	Current work	Reference value	
a	3.991 Å	4.00 Å	[52] – Experiment
Equil. volume	63.560 Å ³	64.00 Å ³	[52] – Experiment
P_x	−0.410	~−2	
P_y	−0.247 micro C/cm ²	~−1.75 micro C/cm ^{2a}	[38] – MD
P_z	−0.761	~−1.75	
C11	182.769 GPa	–	–
C22	183.170	–	
C33	182.172	–	
C12 (C21)	73.325	–	
C13 (C31)	72.813	–	
C23 (C32)	73.068	–	
B	109.614 GPa	135, 162 GPa	[51,52] – Experiment
CTE	9.879×10^{-6} per °C	11.3×10^{-6} per °C	[55] – Experiment

^a Values are approximated from plot on page 9687 of [38] at 220 K, for which the reported parameterization exhibits the cubic phase.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.commatsci.2013.08.054>.

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