FIRST-PRINCIPLES AND ATOMIC-LEVEL SIMULATIONS OF FERROELECTRICS

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Abstract

The combination of two simulation techniques, first-principles methods and atomic-level modeling, are used to investigate finite-temperature properties of ferroelectric perovskites. First, a brief overview is presented on first-principles electronic-structure calculations of ferroelectrics. The direct application of these methods are used to determine ground-state (zero-temperature) properties of ferroelectric materials, such as crystal structure, electronic properties, lattice dynamics, underlying potential surfaces, Born effective charges, etc. Finite-temperature properties are then simulated by an atomic-level approach based on shell-model interatomic potentials fitted to ab-initio results.


1. INTRODUCTION

A considerable progress has been made in the understanding of the fundamental physics of ferroelectrics since the discovery of ferroelectricity in perovskites in 1945. If I have to highlight three notable events in the history of the theory of ferroelectricity, my personal choice would be the following. First, the Landau-Devonshire (LD) theory of ferroelectrics [1] which was important in disclosing what thermodynamic properties are needed in order to account for the experimental facts. This approach is very useful nowadays; several systems, including thin
films, domain structure, etc., are investigated in the framework of the LD theory. Second, the soft-mode theory of Cochran [2] who showed that the displacement required to transform the paraelectric high temperature phase into a lower-symmetry ferroelectric phase corresponds to an eigenvector of a single normal mode. My third choice is directed to a methodology of calculation, which is not only related with ferroelectrics, but with materials science: the first-principles methods.

The first-principles calculations which can really give insight into the microscopic interactions and the origin of the driving forces for a ferroelectric transition have become feasible only recently, as sufficiently fast band structure calculations which put no restriction onto the shape of the potential and charge density. Calculation of this type for perovskite oxides have been made firstly by Weyrich and Siems in 1985 [3]. More extensive studies on the lattice dynamics of BaTiO$_3$ were followed by Cohen and Krakauer [4], and the essential role of the hybridization between electronic states for the origin of ferroelectric behavior was conclusively demonstrated [5]. Since then, ten years of concerted effort began to apply first-principles methods to the problem of ferroelectricity, trying to clarify why ferroelectric materials are extremely sensitive to changes in temperature, strain, composition and defects [6, 7].

We could say that the final goal of first-principles methods is to calculate the properties of a specific material by using, as the only input of the calculations, the information we get from the periodic table of elements. This is easy to say, but of course extremely hard to do, and several approximations should be done. On the other hand, due to the heavy computational load, only systems of up to approximately a hundred ions can be simulated. Moreover, such calculations cannot provide anything but static, zero temperature, properties. There is thus a significant need for a methodology which can provide microscopic information on ferroelectric behavior, and yet is computationally efficient enough to allow finite-temperature properties to be addressed.

In the next section the main ideas of density-functional theory, together with the local density and generalized gradient approximations are introduced in order to present the general framework of the theory. A brief overview on first-principles electronic-structure calculations of ferroelectric perovskites is presented in Section 3. For the simulation of finite-temperature properties, we present in Section 4 an atomic-level approach based on interatomic potentials fitted to ab-initio results. Conclusions are presented in Section 5.
2. DENSITY FUNCTIONAL THEORY

The basic theorems of the density functional formalism were derived by Hohenberg and Kohn [8]. They showed that i) the ground state (GS) properties of a system of electrons in the presence of an external potential $V_{ext}$ can be determined from the electron density $\rho(r)$ alone, ii) The total energy $E$ is a functional of the density, and $E(\rho)$ satisfies the variational principle $E(\rho) \geq E_{GS}$. The density for which the equality holds is the ground state density $\rho_{GS}$.

The usual implementation of this scheme results from the observation of Kohn and Sham [9] that the minimization of $E(\rho)$ is simplified if we write

$$E(\rho) = T_o[\rho] + \int V_{ext}(r)\rho(r)dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} drdr' + E_{xc}(\rho)$$

(1)

where $T_o[\rho]$ is the kinetic energy that a system with density $\rho$ would have in the absence of electro-electron interactions, and $E_{xc}$ defines the exchange-correlation energy. The variational principle

$$\delta E/\delta \rho = 0$$

(2)

leads to a set of Schrödinger equations for a system of noninteracting electrons

$$[-1/2\nabla^2 + V_{eff}(\rho)]\phi_i(r) = \epsilon_i \phi_i(r)$$

(3)

where

$$V_{eff}(\rho) = V_{ext} + \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{xc}}{\delta \rho}$$

(4)

$$\rho(r) = \sum_{i}^{occ} |\phi_i(r)|^2$$

(5)

From the self-consistent solution of a single particle equation we can determine the total energy and electron density of the ground state of a system of electrons and ions, and all quantities derivable from them. For example, i) the equilibrium lattice constant of a solid is the lattice constant that minimizes the total energy, ii) from the computation of the total energy (or forces) as function of the displacements of the ions, the dynamical matrix can be constructed and diagonalized, providing phonon frequencies and eigenvectors, iii) the elastic constants arise from the computation of the total energy as a function of strain, etc.
All terms in the energy expression (1) are straightforward to evaluate, apart from the exchange-correlation energy $E_{xc}$, for which approximations are unavoidable. The most widely used is the local density approximation (LDA)

$$E_{xc}(\rho) = \int \rho(r) \epsilon_{xc}(\rho(r)) dr$$  \hspace{1cm} (6)

where $\epsilon_{xc}$ is the exchange-correlation energy per particle of the homogeneous electron gas at density $\rho$. This approximation is free of adjustable parameters. However, several shortcomings have motivated a number of attempts to go beyond the LDA in the search of a better framework. In this way, the most widely used is the generalized gradient approximation (GGA) for the exchange-correlation functional with explicit dependence on the gradient of charge density

$$E_{xc}(\rho) = \int \rho(r) F(\rho(r), \nabla \rho(r)) dr$$  \hspace{1cm} (7)

These functionals have demonstrated useful improvements over LDA in applications to atoms, molecules and solids.

### 3. FIRST-PRINCIPLES CALCULATIONS OF FERROELECTRIC PEROVSKITES

Some of the results obtained from the application of first-principles methods to ferroelectric perovskites are presented in this section. We will concentrate mainly in structural, dynamical and electronic properties, emphasizing their connections.

#### 3.1 Equilibrium volume: a problem!!!

The main drawback of the LDA when applied to perovskites is the systematic underestimation of the equilibrium volume, and several properties are poorly reproduced at this volume. In fact, in prototypical materials, like $\text{KNbO}_3$ and $\text{BaTiO}_3$, ferroelectricity is strongly suppressed at the LDA equilibrium volume. Unfortunately, the application of GGA to $\text{KNbO}_3$ and $\text{BaTiO}_3$ showed that the equilibrium volumes of the two compounds are overcorrected; although in $\text{KNbO}_3$ GGA yielded an equilibrium volume that is much closer to the experimental volume than the LDA result, in $\text{BaTiO}_3$ the GGA error was almost as large as found within the LDA [10].

Table 1 lists the lattice parameters and bulk moduli [11] as derived from energy-volume curves obtained within the LDA as well as the GGA, together with the experimental values. The equilibrium volumes obtained from the LDA calculations are 4.3\%, 5.0\%, 2.3\% and 2.0\%
Table 1. Lattice parameter $a$ (in a.u.) and Bulk modulus $B$ (in GPa) obtained for LDA and GGA and compared with experimental values. In parantheses: bulk modulus at the experimental equilibrium volume. From Ref. [11].

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNbO₃</td>
<td>a 7.48</td>
<td>7.63</td>
<td>7.59</td>
</tr>
<tr>
<td></td>
<td>B 206(155)</td>
<td>171(186)</td>
<td>138</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>a 7.44</td>
<td>7.61</td>
<td>7.57</td>
</tr>
<tr>
<td></td>
<td>B 195(155)</td>
<td>160(173)</td>
<td>138</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>a 7.30</td>
<td>7.46</td>
<td>7.358</td>
</tr>
<tr>
<td></td>
<td>B 204(176)</td>
<td>167(194)</td>
<td>179</td>
</tr>
<tr>
<td>KTaO₃</td>
<td>a 7.475</td>
<td>7.625</td>
<td>7.526</td>
</tr>
<tr>
<td></td>
<td>B 222(192)</td>
<td>183(213)</td>
<td>220</td>
</tr>
</tbody>
</table>

smaller than experiment for KNbO₃, BaTiO₃, SrTiO₃ and KTaO₃, respectively. This agrees with the generally observed tendency to overbinding in this approximation. The LDA bulk moduli are overestimated when evaluated at these too small volumes. The values calculated at the experimental volumes (see the values in brackets) agree better with the experiments. As is the general trend in the application of GGA functionals to solids, it expands bonds, an effect that sometimes corrects and sometimes overcorrects the LDA prediction. GGA calculations overestimate the equilibrium volumes, namely by 1.6 %, 1.6 %, 4.2 % and 4.0 % for KNbO₃, BaTiO₃, SrTiO₃ and KTaO₃ respectively.

Although a discrepancy of 1% in the lattice constants seems not to be too serious, it is a real problem in ferroelectric perovskites because ferroelectricity is very sensitive to volume.

A new approximation to the exchange-correlation functional called Weighted Density Approximation (WDA) [12] yields an equilibrium volume in close agreement with experiments. However, the general trend is still the application of LDA or GGA with a simple *ad hoc* correction consisting in using the experimental rather than the calculated equilibrium volumes.

3.2 Lattice dynamics

The evaluation of vibrational properties is known to be a hard test on the quality of first-principles calculations. The curvature of the total energy surface over a set of atomic displacements is much more sensitive than the equilibrium geometry. There have been a lot of first-principles studies of vibrational properties in ferroelectric perovskites, using the
Table 2. Frequencies (in cm$^{-1}$) of the $\Gamma_{15}$ modes obtained for LDA and GGA. From Ref. [11].

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNbO$_3$</td>
<td>211i</td>
<td>197i</td>
<td>soft</td>
</tr>
<tr>
<td></td>
<td>166</td>
<td>182</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>466</td>
<td>478</td>
<td>521</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>239i</td>
<td>203i</td>
<td>soft</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>168</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>454</td>
<td>463</td>
<td>482</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>57i</td>
<td>64</td>
<td>soft</td>
</tr>
<tr>
<td></td>
<td>157</td>
<td>166</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>532</td>
<td>551</td>
<td>545</td>
</tr>
<tr>
<td>KTaO$_3$</td>
<td>99</td>
<td>107</td>
<td>soft</td>
</tr>
<tr>
<td></td>
<td>172</td>
<td>189</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>529</td>
<td>550</td>
<td>546</td>
</tr>
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</table>

frozen phonon approximation. For the case of KNbO$_3$, for example, we can mention the early works of Singh et al. [13] and Postnikov et al. [14]. As illustration, Table 2 shows LDA and GGA phonon frequencies of the $\Gamma_{15}$ modes for four selected perovskites at their experimental lattice constants in the cubic phase. It can be seen that the GGA functional hardens the phonon frequencies (as compared to the LDA frequencies) of the four perovskites. This hardening produces a slight reduction of the errors, since the LDA provides phonon frequencies which are underestimated by 10-20% compared with experiments. Nevertheless, the agreement of LDA with experiments is very good, considering the sensitivity of the involved energetics.

As another output of the frozen phonon calculation, we show in Table 3 LDA and GGA eigenvectors of cubic KNbO$_3$ to exemplify the effect produced on the phonon polarizations by the application of the different functionals. Note that the eigenvectors are practically unchanged. The same occurs for the other three perovskites [11]. For the unstable ferroelectric soft mode, the displacement (the eigenvectors over the square roots of the masses) is primarily that of Nb moving opposite that of the oxygen cage. A similar features is obtained for BaTiO$_3$ where the LDA eigenvector is $e_{Ba} = -0.017, e_{Ti} = -0.660, e_{Oz} = 0.644, e_{Oy} = e_{Ox} = 0.273$. In this case, however, the oxygen cage is more distorted.

The frozen phonon technique is very accurate to determine phonon frequencies and eigenvectors for a particular k-point (zone center or zone boundaries). Nowadays, the phonon dispersion curves in the full Brillouin zone of a ferroelectric perovskite can be calculated from first-
Table 3. Frequencies and eigenvectors of the $\Gamma_{15}$ modes in $\text{KNbO}_3$ using LDA and GGA. From Ref. [11].

<table>
<thead>
<tr>
<th></th>
<th>$\omega$(cm$^{-1}$)</th>
<th>Eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K      Nb    O1    O2 and O3</td>
</tr>
<tr>
<td>$\text{KNbO}_3$</td>
<td>210</td>
<td>0.015  -0.58  0.6    0.39</td>
</tr>
<tr>
<td>LDA</td>
<td>166</td>
<td>-0.88   0.36   0.146  0.178</td>
</tr>
<tr>
<td></td>
<td>466</td>
<td>0.027   -0.11  -0.73  0.48</td>
</tr>
<tr>
<td>$\text{KNbO}_3$</td>
<td>196i</td>
<td>0.042   -0.59  0.57    0.40</td>
</tr>
<tr>
<td>GGA</td>
<td>182</td>
<td>-0.88   0.35   0.178  0.18</td>
</tr>
<tr>
<td></td>
<td>478</td>
<td>0.006   -0.08  -0.75  0.47</td>
</tr>
</tbody>
</table>

principles using a linear response approach. Calculations in $\text{KNbO}_3$ [15] and $\text{BaTiO}_3$ [16] revealed the presence of structural instabilities with pronounced two-dimensional character in the Brillouin zone, corresponding to chains of displaced B ions oriented along the [001] directions. A number of different ferroelectrics have now been studied using linear response methods.

3.3 Underlying potential surfaces

Once the eigenvectors at $\Gamma$ have been determined, it is interesting to evaluate the total energy as a function of the displacement pattern of the unstable (ferroelectric) mode. This energy curve will reflect the anharmonicity of this particular mode.

For the case of $\text{BaTiO}_3$, LAPW results for the amplitude of (001), (011) and (111) ferroelectric mode normal coordinates are shown in the left panel of figure 1. Energy lowerings of $\approx 0.9$, 1.6 and 2.0 mRy/cell are obtained for the (001), (011) and (111) ferroelectric mode displacements, respectively; which is consistent with the experimentally observed phase transitions sequence (ie. cubic - tetragonal - orthorhombic - rhombohedral). Concerning the energetics for the (001) displacements, it can be also seen in the right panel of Figure 1 that the effect of the tetragonal strain is to stabilize these displacements with a deeper minimum and a higher energy barrier at the centrosymmetric positions. A similar feature is observed for the orthorhombic strain, while an almost negligible effect of the rhombohedral strain on the total energies is observed.

The energetics of $\text{BaTiO}_3$ was originally reported by Cohen and Kraukauer in 1990 [4]. Latter on, it was shown that the large strain (6%) stabilizes the tetragonal phase with respect to the rhombohedral one in $\text{PbTiO}_3$ [5]. The primary cause of the difference between the structural
behavior of these two materials arises from their electronic structures; in ABO$_3$ perovskites covalency becomes crucial.

As we will see in the next section, underlying first-principles surfaces are also important for the development of classical models, which can be used for the investigation of finite-temperature properties.

### 3.4 Electronic structure

As we have seen in Section 2, in DFT the variational principle leads to a set of Schrödinger equations for a system of noninteracting electrons (Equation 3). From these equations the band structure of the material can be obtained.

Figure 2 shows the band structure of eight cubic ABO$_3$ perovskites between Γ and X.

A common feature for all the perovskites is that the valence band is mainly formed by O(2p) states while the conduction band is formed by B(d) states. Examination of projected the density of states reveals that there is also substantial O(2p) character in the conduction band and B(d) character in the valence band. This is an indication of a quite strong covalent bonding effect. This strong O(2p)-B(d) hybridization, which is enhanced by the ferroelectric distortion, is essential for ferroelectricity.

In each material there is a fairly narrow set of O(2s) bands between -16 and -18 eV, and semicore states associated with the A cation, which have been labeled in Figure 2. Whereas the A cation states do not play a relevant role for Ba, K, Sr, Ca, and Na compounds, they are quite important for the lead compounds. In fact, the primary cause of the
different structural behavior between BaTiO$_3$ and PbTiO$_3$ is the large hybridization between Pb(6$s$) and O(2$p$) states. This Pb-O covalency leads to a large strain that stabilizes the tetragonal phase, whereas the Ba ion is essentially a fully ionic Ba$^{+2}$ favoring the rhombohedral structure [5].

A deep understanding of the electronic structure is then essential in order to dilucidate the structural behavior of perovskites. We can mention, as another example, that differences in the the band structures of KTaO$_3$ and KNbO$_3$ lead to a dramatically different structural behavior [18].

### 3.5 Born effective charges

King-Smith and Vanderbilt showed that the polarization of a crystal can be computed from first-principles using a Berry’s phase approach [19]. In this way the Born effective charges can be determined from ab-initio calculations. An excellent overview on this topic was written by Ghosez et al. [20].

The Born effective charge tensor is conventionally defined as the proportionality coefficients between the components of the dipole moment per unit cell and the components of the $\kappa$ sublattice displacement which
Table 4. Born effective charges of titanates in the cubic structure.

<table>
<thead>
<tr>
<th></th>
<th>$Z_A^*$</th>
<th>$Z_{Ti}^*$</th>
<th>$Z_{O\perp}^*$</th>
<th>$Z_{O\parallel}^*$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>+2</td>
<td>+4</td>
<td>-2</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>+2.70</td>
<td>+7.10</td>
<td>-2.12</td>
<td>-5.56</td>
<td>Ref.[22]</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>+2.54</td>
<td>+7.12</td>
<td>-2.00</td>
<td>-5.66</td>
<td>Ref.[23]</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>+2.58</td>
<td>+7.08</td>
<td>-2.00</td>
<td>-5.65</td>
<td>Ref.[23]</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>+3.90</td>
<td>+7.06</td>
<td>-2.56</td>
<td>-5.83</td>
<td>Ref.[23]</td>
</tr>
</tbody>
</table>

gives rise to such dipole moment:

$$Z_{k,\alpha\beta}^* = \frac{\partial P_\beta}{\partial \delta_{k,\alpha}}$$  \hspace{1cm} (8)

For the cubic structure of ABO$_3$ perovskites, the effective charge tensor is fully characterized by four independent numbers. Experimental data had suggested that the amplitude of the Born effective charges should deviate substantially from the nominal static charges, with two essential features: the oxygen charge tensor is highly anisotropic, and the Ti and O$_\parallel$ (oxygen displaced parallel to the Ti-O bond) effective charges are anomalously large. This is confirmed by first-principles calculations [21, 22, 23], demonstrating the crucial role played by the O(2p)-B(d) hybridization as a dominant mechanism for such anomalous contributions [24]. The Born effective charges for cubic titanates are listed in Table 4. The above mentioned anomalies in $Z_{Ti}^*$ and $Z_{O\parallel}^*$ are present in all the materials. For the Pb compound, however, there are additional anomalies concerning $Z_A^*$ and $Z_{O\perp}^*$ which are related to the more covalent bond of lead with oxygen, as was discussed in the previous section.

3.6 Other properties

Many other properties of the ferroelectric materials are now explored by using first-principles methods. We can mention the computation of piezoelectric constants, surface properties, solid solutions, etc. This field of research remains very active and new challenges to be addressed frequently appear.

4. FINITE-TEMPERATURE PROPERTIES

The Landau-Devonshire approach has proved very successful in providing significant insights into the ferroelectric properties of materials. However, it cannot provide microscopic information. Moreover, it has
a large number of parameters; many of these are straightforward to determine since they are related to the dielectric, piezoelectric and elastic properties. However, others such as the parameters of the gradient terms are difficult to determine. On the other hand, first-principles methods are able to provide detailed microscopic information. These methods, however, have limitations. In particular, due to the heavy computational load, only systems of up to approximately a hundred ions can be simulated.

There is thus a significant need for a methodology which can provide microscopic information on ferroelectric behavior, and yet is computationally efficient enough to allow materials problems to be addressed. For the study of the thermal behaviour of perovskites, a very successful approach has been developed on the grounds of effective Hamiltonians. In this approach, a model Hamiltonian is written as a function of a reduced number of degrees of freedom (a local soft-mode amplitude vector and a local strain tensor), and the Hamiltonian parameters are determined in order to reproduce the spectrum of low-energy excitations of a given material as obtained from first-principles calculations [25]. This approach has been applied with considerable success to several ferroelectric materials, producing results in very good qualitative agreement with experiments. However, some quantitative predictions are not so satisfactory; in particular, the calculated transition temperatures can differ from the experimental values by hundreds of degrees. As ferroelectricity is very sensitive to volume, the reason for such a discrepancy could be the thermal expansivity, which is not included in the effective Hamiltonian model.

An alternative approach, and the one we follow in this work, is based on the atomistic modeling using interatomic potentials, which has a long history in the description of ionic materials. Atomistic simulation methods are well known to play an important role in solid state physics and material sciences. The traditional approach consist in adjusting unknown model parameters to macroscopic crystal properties. The success and scope of the field is evident from the large number of investigations on complex oxides crystals. The fundamental idea is to treat the problem at the atomic level, thereby providing spatially much more detailed information than the LD approach, yet without all the heavy computational load associated with the electronic-structure methods.

In the case of ferroelectric perovskites, for example, Lewis and Catlow [26] developed a shell model fitted for BaTiO$_3$ to reproduce its lattice spacing, elastic properties and dielectric constants. This model has been applied more recently to the study of point defects [27] and surface structure [28]. Regarding lattice dynamical properties, the most
successful approach has been carried out in the framework of the nonlinear oxygen polarizability model [29]. In this shell model an anisotropic core-shell interaction is considered at the O\(^{2-}\) ions, with a fourth-order core-shell interaction along the B-O bond. The potential parameters were obtained by fitting experimental phonon dispersion curves of the cubic phase. The main achievement of this model was the description of the soft mode temperature dependence, which was obtained within the self-consistent phonon approximation. This model was used for the investigation of the dynamical properties of several ferroelectric perovskites [30, 31, 32, 33, 34].

Although the above mentioned shell models reproduce several properties of the cubic phase, they do not describe the structural instabilities and phase transitions sequence of the ferroelectric perovskites. In fact, obtaining accurate interatomic potentials which are able to describe the structural instabilities of ABO\(_3\) perovskites constitutes a challenging problem due to the small energy differences involved in the structural transitions. Nowadays it is possible to perform accurate first-principles calculations on ABO\(_3\) ferroelectric perovskites, and this methodology can be used as a tool to derive more reliable interatomic potentials. The reason to use first-principles methods for modeling perovskites is that they provide: (1) underlying potential surfaces which are useful to model instabilities, (2) phonon dispersion curves at T=0K showing the presence of structural instabilities in the full Brillouin zone, (3) reliable results in cases for which experimental data are not available. We indeed find that an atomic-level approach based on first-principles calculations does provide computationally efficient methodology for the simulation of the ferroelectric properties of a number of perovskite materials [35, 36, 37].

Among the perovskites, BaTiO\(_3\) can be considered as a prototypical ferroelectric, which has been one of the most exhaustively studied materials. At high temperatures, it has the classic perovskite structure. This is cubic centrosymmetric, with the Ba at the corners, Ti at the center, and oxygens at the face centers. However, as the temperature is lowered, it goes through a succession of ferroelectric phases with spontaneous polarizations along the [001], [011] and [111] directions of the cubic cell. These polarizations arise from net displacements of the cations with respect to the oxygen octahedra along the above directions. Each ferroelectric phase involves also a small homogeneous deformation which can be thought of as an elongation of the cubic unit cell along the corresponding polarization direction. Thus the system becomes tetragonal at 393 K, orthorhombic at 278 K, and rhombohedral below 183 K.

In this work we introduce an atomistic model for BaTiO\(_3\) which describes accurately its dynamical properties, energy instabilities and
phase transitions sequence. The model was developed from first principles calculations by mapping the potential energy surface for various configurations of some carefully selected atomic displacements. The potential parameters were obtained by performing a fit of interatomic potentials to this energy surface. The temperature driven structural transitions were then investigated through molecular dynamics simulations.

4.1 Shell model and fitting procedure

The fundamental idea underpinning atomic-level modelling is to treat a material at the level of the individual atoms, with the interatomic interactions defined by classical potentials. This approach has enjoyed considerable success in describing the properties of fluids and solids ranging from metals to semiconductors to ionic materials. In the context of ionic materials, the interactions between the point ions are generally described via the Coulombic interactions between the atoms which provides cohesion, supplemented by empirical, largely repulsive interactions which account for the short-ranged repulsion between the ions. This is the so-called rigid ion model. The shell model is an important improvement on the rigid-ion model. In the shell model, atomic polarizability is accounted for by defining a core and a shell for each ion (representing the ion core with the closed shells of electrons, and the valence electrons, respectively), which interact with each other through a harmonic spring (characterizing the ionic polarizability), and interact with the cores and shells of other ions via Coulombic interactions.

A solid interacting purely by Coulombic interactions is unstable to a catastrophic collapse in which all the ions become arbitrary close. To mimic the physical short-ranged repulsion that prevents such a collapse, an empirical largely repulsive interaction is added. One standard choice for this function is the Buckingham potential, which consists of a purely repulsive, exponential decaying Born-Mayer term between shells supplemented by a van-der-Waals attractive term to account for covalency effects:

$$ V(r) = a e^{-\frac{r}{\rho}} - \frac{c}{r^6} $$

In some parameterizations, the ions are assigned their formal charges. However, in ionic material with a significant amount of covalency, the incomplete transfer of electrons between the cations and anions can be accounted for by assigning partial charges (smaller than the formal charges) to the ions. For example, covalency effects, such as Born effective charges, are at least qualitatively accounted for in the shell model through the ionic polarizabilities, whose magnitudes may be considered to include the effects of hybridization. Covalency effects are included by setting the ion charges to values less than the formal valence, and
by adding a van-der-Waals $1/r^6$ attractive term to the O-O shell-shell repulsion.

In this paper, we build on the success of the nonlinear oxygen polarizability model [29] to describe the lattice dynamics of ferroelectric perovskites to develop a shell-model plus Buckingham potential for the description of ferroelectricity in BaTiO$_3$. Here each ion is modeled as a massive core linked to a massless shell. An anisotropic core-shell interaction is considered at the $O^{-2}$ ions, with a fourth-order core-shell interaction along the O-Ti bond. This emphasizes the large anisotropic polarization effects at the oxygens produced by variations of the O-B distance [33]. Such effects are expected in view of the strong environment-dependent oxygen polarizability and its enhancement through hybridization between oxygen p and transition metal d orbitals. The Ba and Ti ions are considered isotropically polarizable.

The model parameters were obtained by performing a fit to first-principles potential energy surfaces for various configurations of atomic displacements. The first-principles total energy calculations were performed within the DFT, using the highly precise full-potential Linear Augmented Plane Wave (LAPW) method. The two more widely used approximations to DFT, LDA (local density approximation) and GGA (generalized gradient approximation), under- and over-estimates the equilibrium volume of ferroelectric perovskites [10, 11]. As a result, quantities that depend sensitively on the lattice constant, such as ferroelectric instabilities, are seriously affected when they are evaluated at the theoretical equilibrium volume. So, the results are closer to the experimental behaviour if one works at the experimental lattice constants.

In order to better quantify the ferroelectric instabilities of the cubic phase, we determined the ab-initio phonon frequencies and polarizations of the infrared active $\Gamma_{15}$ modes, which include the "ferroelectric soft" mode, by calculating atomic forces for several small displacements ($\sim 0.01 \text{ Å}$) consistent with the symmetry of the mode. From the force as a function of displacement, the dynamical matrix was constructed and diagonalized. Finally, the total energy is evaluated as a function of the ferroelectric soft mode displacement pattern for different directions in the cubic phase. We analyze also the effects of the tetragonal strain by performing the [001] soft mode displacements at a lattice parameter ratio $c/a = 1.01$ with the same primitive cell volume.

A starting set of shell model parameters (17 parameters) were obtained by fitting phonon dispersion curves of cubic BaTiO$_3$. Then the potential energy of the model was evaluated for the same displacement patterns employed in the ab-initio total energy calculations. For each given core configuration the shell coordinates were obtained by solving
the adiabatic condition iteratively by a steepest descent procedure. The results obtained with the initial model parameter set showed serious discrepancies with the ab-initio results, in particular the sequence of energy minima in [001], [011] and [111] directions was not in the same order. Thus we modified the model parameters in order to fit the model energy behavior to the ab-initio results. While doing this, we also took care that the equilibrium lattice constant of the model in the cubic phase reproduces the extrapolation to 0 K of the experimental lattice constant in the cubic phase, which yields $a = 3.995\AA$.

It is important to remark that one can not afford to reproduce "spot-on" the ab-initio total energy surface with such simple interatomic potentials. In addition, the adjustment of the potentials is not a straightforward and easy procedure, because all pair potentials and core-shell coupling constants contribute to the total energy of a given distorted lattice structure. So, the goal was to obtain a model which reproduces, as close as possible, the energetics and instabilities calculated by the LAPW method. Recently, M.Sepliarsky and R.Cohen [38] have developed a program for simultaneous fitting of total energies, effective charges, phonon frequencies and eigenvectors for different structures. In this way, shell-model parameters are determined from first-principles calculations using a simple and straightforward procedure. This methodology, which was already applied to PbTiO$_3$, will help in the development of new interatomic potentials for ferroelectric oxides.

4.2 Results

The energy behavior of the model for different structural distortions are shown in Figure 3. The calculations were performed at the experimental primitive cell volume for 0 K, which corresponds to a cubic lattice constant $a = 4.003\AA$. [39] The results of the model are compared with the LAPW calculations for the amplitude of (001), (011) and (111) ferroelectric mode normal coordinates, which are obtained from the following LDA eigenvector: $e_{Ba} = -0.017, e_{Ti} = -0.660, e_{Oz} = 0.644, e_{Oy} = e_{Ox} = 0.273$. For the sake of simplicity, these are represented in the abscissa axis of the figure through the Ti displacement relative to Ba.

A satisfactory overall agreement is achieved. The model yields clear ferroelectric instabilities with similar energetics and minima locations compared with the LAPW calculation. Energy lowerings of $\approx 1.2, 1.65$ and $1.9$ mRy/cell are obtained for the (001), (011) and (111) ferroelectric mode displacements, respectively; which is consistent with the experimentally observed phase transitions sequence. Concerning the energetics for the (001) displacements, it can be also seen in Figure 3 that the effect
of the tetragonal strain is to stabilize these displacements with a deeper minimum and a higher energy barrier at the centrosymmetric positions. A similar feature is observed for the orthorhombic strain, while an almost negligible effect on the total energies for the rhombohedral strain is observed.

The bulk modulus, as in ab-initio calculations, can be obtained from the evaluation of the total energy as a function of the uniform volume expansion for the cubic phase. The model calculations yield a lattice parameter of 3.99 Å for the static cubic structure. The bulk modulus evaluated at this equilibrium volume is 226 GPa, which agrees fairly well with the LDA value of 195 GPa [11].

Another interesting test of the resulting model concerns its phonon dispersion relations. A first-principles linear response calculation of the phonon dispersion curves of cubic BaTiO$_3$, using the plane-wave pseudopotential approach, revealed the presence of structural instabilities with pronounced two-dimensional character in the Brillouin zone, corresponding to chains of displaced Ti ions oriented along the [001] directions [16]. The same wave vector dependence of the instabilities had been previously found in KNbO$_3$ through a linear response approach based on a LAPW calculation [15].

To check if our model is able to reproduce such kind of instabilities, we compute the phonon dispersion curves of the cubic structure at the same lattice constant used in the previous work [16], i.e. the experimental value $a = 4.00$ Å. The result is shown in Fig. 4. An excellent agreement

![Figure 3. Total energy as a function of the ferroelectric mode displacements along the [001] (left panel), [011] (center panel) and [111] (right panel) directions. Energies for [001] displacements in a tetragonal strained structure are plotted in the left panel. First principles calculations are denoted by squares (circles) for the unstrained (strained) structures. Full lines correspond to the shell model result.](image-url)
Figure 4. Phonon dispersion curves of BaTiO$_3$ calculated with the optimized model for the cubic structure at the experimental lattice constant. Imaginary phonon frequencies are represented as negative values.

with the ab-initio linear response calculation is achieved, particularly for the unstable phonon modes (compare with Figure 4 of Reference [16]). Two transverse optic modes are unstable at the $\Gamma$ point, and they remain unstable along the $\Gamma$-X direction with very little dispersion. One of them stabilizes along the $\Gamma$-M and X-M directions; and both become stable along the $\Gamma$-R and R-M lines. These features, which were also observed in KNbO$_3$, indicate chain-like instabilities in real space. As was already pointed out by Yu and Krakauer[15], the finite thickness of the slab region of instability corresponds to a minimum correlation length of the displacement required to observe an unstable phonon mode. From the phonon dispersion curves showed in Figure 4, the length of the shortest unstable chain can be estimated to $\approx 4a$, which is in agreement with the estimation made in Reference [16].

The Born effective charge tensor can be computed in the framework of our model. Although the model does not explicitly include charge transfer between atoms, it takes into account the contribution of the electronic polarizability effects through the shell coordinates. So, it is possible to evaluate the Born effective charge tensor calculating the total dipole moment per unit cell created by the displacement of a given sublattice of atoms as a sum of two contributions:

$$P_\alpha = Z_\kappa \delta_{\kappa,\alpha} + \sum_{\kappa'} Y_{\kappa} w_{\kappa,\alpha}$$ (9)
Table 5. Born effective charges of BaTiO$_3$ in the cubic structure.

<table>
<thead>
<tr>
<th></th>
<th>$Z^*_{Ba}$</th>
<th>$Z^*_{Ti}$</th>
<th>$Z^*_{O}$</th>
<th>$Z^*_{O}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
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<td>+4</td>
<td>-2</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td>+2.9</td>
<td>+6.7</td>
<td>-2.4</td>
<td>-4.8</td>
<td>Ref.[40]</td>
</tr>
<tr>
<td>First-principles</td>
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<td>+7.16</td>
<td>-2.11</td>
<td>-5.69</td>
<td>Ref.[23]</td>
</tr>
<tr>
<td></td>
<td>+2.70</td>
<td>+7.10</td>
<td>-2.12</td>
<td>-5.56</td>
<td>Ref.[22]</td>
</tr>
<tr>
<td>Shell model (static)</td>
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<td>+3.18</td>
<td>-1.68</td>
<td>-1.68</td>
<td>present</td>
</tr>
<tr>
<td>Shell model (dynamic)</td>
<td>+1.93</td>
<td>+6.45</td>
<td>-2.3</td>
<td>-3.79</td>
<td>present</td>
</tr>
</tbody>
</table>

the first one is the sublattice displacement contribution while the second one is the electronic polarizability contribution.

The calculated Born effective charges for cubic BaTiO$_3$ are listed in Table 6 together with results obtained within different approaches. The two essential features of the Born effective charge tensor of BaTiO$_3$ are satisfactorily simulated.

So far we have showed that our model for BaTiO$_3$ reproduces several zero-temperature properties which are relevant for this material. To investigate if the model will prove successful to describe the temperature driven structural transitions of BaTiO$_3$ we perform constant-pressure molecular dynamics (MD) simulations. The runs were performed employing a Hoover constant-(\overline{σ},T) algorithm with external stress set to zero; all cell lengths and cell angles were allowed to fluctuate. Periodic boundary conditions over 7x7x7 primitive cells were considered; the basic molecular dynamics cell therefore contained 1715 ions (plus 1715 shells which are additional degrees of freedom). The time step was 0.4 fs, which provided enough accuracy for the integration of the shell coordinates. The total time of each simulation, after 2 ps of thermalization, was 20 ps.

In Fig. 5(a) we plot the order parameters (the three components of the mean polarization) as a function of temperature. The cell lattice constants are displayed in Fig. 5(b). At high temperatures, the averaged polarizations $p_x$, $p_y$ and $p_z$ are all very close to zero and the three lattice constants have almost identical values. As the system is cooled down below 190 K, $p_x$ acquires a value clearly different from zero, while $p_y \approx p_z \approx 0$, and the structure presents a considerable tetragonal strain (see Fig. 5(b)). This indicates the transition from the paraelectric cubic to the ferroelectric tetragonal phase. When the temperature is further
reduced, the two lower ferroelectric phases appear: the orthorhombic one below $\sim 120$ K, with clearly finite $p_x \simeq p_y$ and still $p_z \simeq 0$, and finally the rhombohedral phase below $\sim 90$ K, with approximately equal values of the three polarization components.

![Graph showing polarization and lattice parameters as functions of temperature.](image)

Figure 5. Phase diagram of BaTiO$_3$ resulting from the MD simulation. (a) The three components of the average polarization (each one represented with a different symbol) and (b) the corresponding cell parameters (idem) as a function of temperature.

An excellent overall agreement is obtained for the structural parameters, showing that our model reproduces the delicate structural changes involved along the transitions. On the other hand, the theoretically determined transition temperatures tend to be too small compared with experiments. The orthorhombic and tetragonal phases are stabilized over a temperature range of only $\approx 30$ K and $\approx 70$ K, respectively. Similar features are obtained with the effective Hamiltonian approach [25].
remarkable point, however, is that the non-trivial phase transition sequence of \( \text{BaTiO}_3 \) is correctly reproduced.

Since ferroelectricity is very sensitive to volume, the neglect of thermal expansivity in the effective Hamiltonian models could be thought to be responsible for the shifts in the predicted transition temperatures relative to experiment. Our model, however, takes into account the anharmonic interactions among all phonon modes which are responsible for thermal expansion, and, nevertheless, a similar behaviour is obtained for the transition temperatures. In order to verify that the thermal expansion is properly described by our model, we study the behaviour of the pseudocubic lattice parameter \( a = V^{-1/3} \), where \( V \) is the cell volume, as a function of temperature. From these data we obtain the expansion coefficients for the different phases. In order to make a detailed comparison of the thermal expansivity with experimental data [41], we need to rescale the theoretical transition temperatures, since they do not agree with the experimental ones. We therefore linearly rescale the theoretical temperatures so that the end points of the stability range of each phase coincide with the experimental \( T_c \)'s. In addition, in order that the graph preserves the expansion coefficients obtained, i.e. the slope within each phase, we perform the same rescaling of the ordinate values. In Figure 6 we plot \( (a - a_0)/a_0 \) vs.\( T \) for both the theoretical and experimental results, where \( a_0 \) is the value of \( a \) at 0 K. The overall agreement with the experimental values is quite satisfactory.

![Figure 6](image-url)

*Figure 6.* Comparison of experimental and MD results for the temperature dependence of the relative variation for the pseudocubic lattice parameter \( a = V^{-1/3} \). \( V \) is the cell volume and \( a_0 \) is the value of \( a \) at 0 K. The abscissa and ordinate values for the model results have been rescaled (see text).
It is interesting to remark the volume anomalies at the phase transitions resulting from the model simulation, a feature also observed experimentally, which indicate that the transitions are all first-order. In particular the remarkable volume expansion at the Curie transition is in very good agreement with the dilatometric measurements carried out on polycrystalline samples [41].

In spite of thermal expansion effects are properly simulated by our atomistic model, the theoretically determined transition temperatures are too small compared with experiments. This seems to indicate that LDA methods underestimates the ferroelectric instabilities in ferroelectric perovskites. Very recently, Tinte et al. [42] performed a very interesting study analysing the source of errors which could affect the transition temperatures in the effective hamiltonian approach. Their results suggest that there are at least two significant source of errors, the improper treatment of the thermal expansion and the ”LDA error” inherent in the first-principles approach. They also conclude that both type of errors may be of the same magnitude.

5. SUMMARY

First-principles methods are a powerful tool to understand and predict the properties of ferroelectric materials. We have seen that this free-parameter theory is able to determine clearly why ferroelectrics are extremely sensitive to changes in strain and composition, linking the electronic structure of the materials with their structural behavior.

While finite-temperature properties of ferroelectric perovskites can not be investigated from first-principles methods, they can be simulated satisfactorily by using an atomic-level approach based on interatomic potentials fitted to ab-initio calculations. This approach is a very important breakthrough because it demonstrated that enough of the electronic effects associated with ferroelectricity can be mimicked at the atomic level to allow the fundamentals of ferroelectric behavior to be reproduced. Atomic-level simulations have been applied with considerable success to investigate the microscopic dynamics of pure crystals [43] and solid solutions [37], surface [44] and thin films [45] properties, superlattices and interface effects [46], and ferroelectric properties of nanoscopic structures [47].

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References