First-principles model potentials for lattice-dynamical studies: general methodology and example of application to ferroic perovskite oxides

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Abstract
We present a scheme to construct model potentials, with parameters computed from first principles, for large-scale lattice-dynamical simulations of materials. We mimic the traditional solid-state approach to the investigation of vibrational spectra, i.e., we start from a suitably chosen reference configuration of the compound and describe its energy as a function of arbitrary atomic distortions by means of a Taylor series. Such a form of the potential-energy surface is general, trivial to formulate for any material, and physically transparent. Further, such models involve clear-cut approximations, their precision can be improved in a systematic fashion, and their simplicity allows for convenient and practical strategies to compute/fit the potential parameters. We illustrate our scheme with two challenging cases in which the model potential is strongly anharmonic, namely, the ferroic perovskite oxides PbTiO3 and SrTiO3. Studying these compounds allows us to better describe the connection between the so-called effective-Hamiltonian method and ours (which may be seen as an extension of the former), and to show the physical insight and predictive power provided by our approach—e.g., we present new results regarding the factors controlling phase-transition temperatures, novel phase transitions under elastic constraints, an improved treatment of thermal expansion, etc.

(Some figures may appear in colour only in the online journal)

1. Introduction

The development of methods for statistical simulations with first-principles accuracy remains one of the major challenges for the community working on computational condensed-matter physics and materials science. In spite of recent advances, state-of-the-art first-principles methods are still unable to reach the length and time scales that are relevant for the study of many properties of interest at realistic operating conditions. Ranging from temperature-driven phase transitions to thermally-activated processes of all sorts, there are countless phenomena whose first-principles treatment has a prohibitive computational cost, even if one resorts to the most numerically-efficient schemes such as density-functional theory (DFT) [1]. Hence, there is a need to develop approximate methods that allow for fast calculations while retaining the first-principles accuracy and, if possible, predictive power. Much of the on-going activity on multi-scale simulations is the direct consequence of this situation.
Whenever one is concerned with the lattice-dynamical properties of materials, it may be possible to avoid explicit treatment of the electrons in the simulations. Such is typically the case when we are interested in structural and mechanical properties, dielectric and piezoelectric responses (which are dominated by the lattice part of the effect, as opposed to the electronic one, in the materials that are most attractive for applications), or lattice thermal transport, to name a few important examples. Many methods have been developed to address this subset of problems, which are the focus of the present work.

In the context of lattice-dynamical studies, there are essentially two families of effective potentials that allow for large-scale simulations. The most widely used methods have been developed in the physics and chemistry communities. Such models—which include Lennard-Jones potentials [2], shell models [3], bond-valence models [4–6], and even Tersoff potentials [7] and reactive force fields [8], to name a few—tend to rely on a physically-analytic force fields. Unfortunately, that restriction is often a very small set of problems. One relevant example is the work above-mentioned deficiencies, but which have been applied to very successful approaches that overcome most of the can become quite complex. costly from a computational point of view, as the potentials (extrapolate) new behaviors). Additionally, they are relatively good for interpolating between the first-principles data points transferability and a limited predictive power (i.e., they are not physically-motivated usually implies that they have poor fundamental understanding, the fact that such models are a clear physical interpretation. On top of the loss in fundamental understanding, the fact that such models are not physically-motivated usually implies that they have poor transferability and a limited predictive power (i.e., they are good for interpolating between the first-principles data points used to fit the model, but often fail when used to predict (extrapolate) new behaviors). Additionally, they are relatively costly from a computational point of view, as the potentials can become quite complex.

Another approach is represented by the methods that rely on artificial neural networks [9], importing techniques developed by the artificial-intelligence community. In this case, one uses very versatile models that can reproduce first-principles data with arbitrary precision, at the expense of creating complicated potentials that do not allow for a clear physical interpretation. On top of the loss in fundamental understanding, the fact that such models are not physically-motivated usually implies that they have poor transferability and a limited predictive power (i.e., they are good for interpolating between the first-principles data points used to fit the model, but often fail when used to predict (extrapolate) new behaviors). Additionally, they are relatively costly from a computational point of view, as the potentials can become quite complex.

Interestingly, some workers have developed alternative, very successful approaches that overcome most of the above-mentioned deficiencies, but which have been applied to a very small set of problems. One relevant example is the work of Rabe, Vanderbilt, and others on ferroelectric perovskite oxides. Already in the 1990s these authors constructed first-principles model potentials, which are usually called effective Hamiltonians, to investigate the ferroelectric phase transitions of perovskites like BaTiO$_3$ [10, 11] and PbTiO$_3$ [12]. (These works built upon the ideas introduced in [13] to investigate the structural phase transition in GeTe from first principles.) The effective-Hamiltonian approach involves a drastic simplification of the material, which is coarse-grained to retain only those degrees of freedom associated with the ferroelectric properties (i.e., local dipoles and cell strains). The potential-energy surface (PES) corresponding to these relevant variables is written as a Taylor series around a suitably chosen reference structure (i.e., the prototype cubic perovskite structure). Such a scheme is physically-motivated, computationally very efficient, and its precision can be improved, to some extent, in a well-defined way. Further, the application of the original approach to increasingly complex oxides (e.g., compounds with non-polar transitions like SrTiO$_3$ [14, 15], chemically-disordered materials like PbZr$_{1-x}$Ti$_x$O$_3$ [16, 17], and magnetoelectric multiferroics like BiFeO$_3$ [18, 19]) has shown its generality, the good transferability of the interatomic couplings among dissimilar chemical environments, and the reliability and predictive power of the models. Unfortunately, as far as we know, such an approach has not been adopted in other research fields, remaining much confined within a small community working on ferroic perovskite oxides.

In our opinion, to understand why the effective-Hamiltonian method has failed to gain widespread popularity, one has to consider the coarse-graining step involved in the construction of the potential. When these models were first developed, there were plenty of reasons to adopt such a simplification. On the one hand, by restricting to a subset of the configuration space, it is possible to construct simpler potentials and run faster simulations. On the other hand, by the time first-principles methods started to be applied to these problems, there was already a whole body of literature devoted to similar, semi-empirical models used in theoretical studies of phase transitions driven by soft modes [20–22]. Indeed, the effective Hamiltonians of [10, 12] can be viewed as the natural evolution of the models that already existed in the literature, as for example the so-called discrete $\phi^4$ model [23]. In some sense, the main innovation in those pioneering works was to develop a systematic and well-defined scheme to compute the parameters of such Hamiltonians from first principles. To do that, the key step was to establish a connection between the variables of the traditional effective models (i.e., the so-called local modes representing the localized atomic distortions whose collective occurrence leads to the structural transition, and which involve the formation of local electric dipoles in the case of ferroelectrics) and the displacements of the actual atoms in the crystal. Such a connection can be made in a variety of ways, ranging from the more elementary [11] (e.g., by defining the local modes from direct inspection of the strongest structural instabilities of the high-symmetry phase, which can be determined from first principles as discussed below) to the more sophisticated [24, 25] (e.g., by identifying the local modes with lattice Wannier functions computed from knowledge of the full phonon dispersion bands of the high-symmetry phase as obtained from first principles). Once the local modes are defined in terms of actual atomic displacements, the first-principles calculation of the Hamiltonian parameters follows in a rather straightforward way.

However, in general there are no clear reasons to introduce such a coarse graining. Suppose, for example, that we want to investigate a stable phase of a material, and need a model that captures the first-principles energetics with very high precision. In such a case, in the absence of structural instabilities of our reference configuration, it may be unclear how to choose a subset of relevant degrees of freedom. Further, we may typically find that most of the modes, even
the relatively high-energy ones, play an important role in
determining the properties of such a phase at a quantitative
level; hence, the restriction to a configuration subspace,
and the reduced accuracy it entails, may not be acceptable.
Even in cases where the focus is on the investigation of
structural phase transitions, and assuming that we would be
satisfied by a sound qualitative description of such a drastic
effect, the coarse-graining step may turn out to be both
unhelpful and difficult to implement. Consider, for example,
the modern perovskite oxide super-lattices that present a
wealth of appealing physical effects, some of which are
attributed to novel interatomic couplings occurring at the
interfaces between different layers. In such situations, suitably
exemplified by the short-period PbTiO$_3$/SrTiO$_3$ super-lattices
studied by some of us [26], identifying a small set of relevant
degrees of freedom may be very difficult; indeed, a large
number of local modes may need to be considered, which
would result in complicated effective models. Other cases
where similar difficulties are likely to appear are crystals
in which the relative stability of different phases depends
strongly on secondary structural order parameters (as in
the case of BiFeO$_3$ [27]), situations in which strong strain
gradients and non-trivial structural relaxations occur (as in
the vicinity of ferroelectric domain walls [28]), etc. In our
opinion, the local-mode approximation is not well suited for
the study of such problems.

In view of this, we decided to develop an approach that
retains many of the good features of the effective-Hamiltonian
method developed within the ferroelectrics community and
avoids its most serious limitations. In short, we decided
to create models that describe the energetics of a material
by Taylor expanding the PES around a suitably chosen
reference structure as a function of all the atomic degrees
of freedom. Working with a simple polynomial model has many
important advantages: (i) it is general and can be trivially
formulated for any material; (ii) the involved parameters
have an obvious and convenient physical interpretation, as
we essentially follow the approach adopted in solid-state
textbooks to discuss lattice-dynamical and elastic properties;
(iii) many of the potential parameters can be obtained directly
from perturbative first-principles calculations; and (iv) the
precision of the potential can be improved in a systematic
and well-defined way. Here, we describe the details of
such a scheme and illustrate it with applications to two
challenging cases: the ferroics PbTiO$_3$ and SrTiO$_3$, both of
which present soft-mode-driven structural phase transitions
whose description requires the use of strongly anharmonic
potentials. We are thus introducing a method that we think
should be very useful and of general applicability.

Since this method relies on a textbook expression for
the energy, the originality of this work is not in the generic
formulation of the theory. (In fact, we have recently learned
that similar ideas have been applied, to relatively simple
cases, in the context of thermal transport studies [29].) Rather,
here we discuss the fundamental and technical difficulties
that appear when one tries to implement such a scheme
in the general case, introducing practical approximations
and formal/technical solutions that allow us to tackle even
materials with non-trivial lattice-dynamical properties. Our
presentation is deliberately detailed, as we aim at providing
a self-contained reference that discusses all the important
aspects and is accessible to readers with limited experience
in model-potential and lattice-dynamics problems.

The paper is organized as follows. In section 2 we
describe the general methodology, using perovskite oxides as
an illustrative sample case. We also introduce the approach
we adopted to compute the potential parameters from first
principles. In section 3 we describe the models constructed for
the perovskite oxides PbTiO$_3$ and SrTiO$_3$. We also solve
the models by means of Monte Carlo simulations, showing that
they reproduce the experimentally observed phase transitions.
Finally, in section 4 we summarize and conclude the paper.

2. Model construction

In the following we present our general scheme for
constructing effective model potentials for lattice-dynamical
studies. The proposed methodology is general and can
be applied to any material, including cases of reduced
dimensionality (e.g., surfaces, slabs, wires, molecules),
disordered systems, etc. Nevertheless, for the sake of clarity,
here we will refer to the case of an infinite periodic crystal,
and take the family of perovskite oxides as a representative
element of application.

2.1. Reference structure and model variables

The construction of our models begins with the choice of
a reference structure (RS) that will typically be a minimum
or a saddle point of the PES. Thus, for example, if we
were interested in the properties of a particular (meta)stable
phase of a material, the RS would correspond to the solution
obtained for such a phase by performing a first-principles
structural relaxation nominally at $T = 0$ K. If we were
interested in the more challenging case of a material
undergoing structural phase transitions driven by the softening
(i.e., destabilization) of some vibrational modes or cell strains,
it would be convenient to take the high-symmetry phase of the
material as our RS. More specifically, in that case we would
determine the RS by performing a constrained relaxation
(i.e., one in which the high symmetry of the undistorted
phase is imposed) using first-principles calculations at $T =
0$ K; the result will typically be a saddle point of the
PES, and will have an associated Hessian matrix (i.e., a
matrix of second derivatives of the energy) with negative
eigenvalues corresponding to the structural instabilities. Our
chosen examples of application—i.e., the ferroics PbTiO$_3$ and
SrTiO$_3$—belong to this second category.

For the sake of concreteness, let us assume that we
are treating a three-dimensional infinite crystal composed of
periodically-repeated cells. Then, our RS is fully specified by
the lattice vectors $R_l$, where $l$ labels cells, and the positions
$r_\kappa$ of the atoms $\kappa$ inside the cell. We will describe all accessible
crystal configurations as distortions of the RS. The most
general atomic state will be given by the position vectors

$$r_{l\kappa} = \sum_\rho (\delta_{\alpha l} + n_{\alpha l})(R_{l\beta} + r_{\kappa\beta}) + u_{l\kappa},$$

(1)
where $\alpha$ and $\beta$ denote Cartesian directions. The distortions are thus captured by the homogeneous strain $\eta$ and the individual atomic displacements $u_\kappa$. It is important to note that the homogeneous strain affects both the $R_i$ and $\tau_i$ vectors defining the RS, and that we describe the deviation from the strained RS by means of the absolute displacements $u_\kappa$. Hence, the $u_\kappa$ vectors are given in Cartesian coordinates and have units of length.

The homogeneous strain $\eta_{ab}$ in equation (1) contains both symmetric and anti-symmetric parts. Typically, it will be convenient to exclude the anti-symmetric part (i.e., rigid rotations of the whole material) from the description. We will thus restrict ourselves to the symmetric components $(\eta_{a'b'} + \eta_{b'a'})/2$, for which we will use the well-known Voigt notation $\eta_{\kappa}$, with $\kappa = 1, \ldots, 6$ [30].

To alleviate the notation in the formulas below, it is convenient to introduce the following bijective mapping:

$$lk \leftrightarrow i,$$

so that any $lk$ pair can be expressed by a single index $i$, and vice versa. Hence, we can use $u_i$ instead of $u_\kappa$, and even write $R_i$ or $\tau_i$, without any ambiguity.

Figure 1 shows the cubic phase of an ABO$_3$ perovskite oxide, which is the RS of the applications discussed below. The cell shown is repeated along the three spatial directions and, while the displacements $u_i$ may change from cell to cell, the homogeneous strain $\eta$ is the same throughout the material.

In figure 2 we illustrate how an arbitrary distortion is captured by the variables defined in equation (1). Panel (a) shows an unstrained configuration ($\eta = 0$) with atoms fluctuating around their RS positions. Panel (b) shows a homogeneously strained state with the atoms maintaining their relative positions ($u_i = 0$). Finally, panels (c) and (d) show configurations in which, while the homogeneous strain is zero, we do have local strains resulting in expansion along the vertical direction of some cells of the material (panel (c)) or a shear-like deformation (panel (d)). Such inhomogeneous strains are naturally described by the $u_i$ variables in our model.

Before we continue, it is worth mentioning the advantages and limitations of constructing model potentials based on a reference structure. As will be obvious below, this approach makes it trivial to formulate the potential for arbitrary materials and with arbitrary precision. Hence, it allows for a general and clear-cut methodology that offers the possibility of improving the models systematically; these are obviously very important assets that are not so frequently found in model-potential schemes. At the same time, our approach is specifically suited for the description of relatively small distortions of the RS. In other words, we expect our effective models to describe the energy of configurations that resemble the RS in some fundamental way; for example, the bond topology should be roughly preserved, and we would not advise the use of the present method to describe situations in which chemical bonds break or form.

Finally, let us stress that our scheme is applicable to any material, not only to the infinite three-dimensional crystals that we focus on for the sake of the presentation. Indeed, materials of arbitrary dimensionality, or disordered compounds, can be tackled by making the appropriate adjustments. For example, to study a molecule we would work with atomic positions defined by $r_{\kappa\alpha} = r_{\kappa\alpha} + u_{\kappa\alpha}$, to work with materials that are periodic only along one or two directions we would just need to consider an appropriate homogeneous strain tensor, to deal with chemically-disordered materials we would construct potentials that depend on the chemical environment of the atoms, etc. While some situations may be more challenging than others, our methodology can in principle be applied in all cases.

2.2. Definition of the effective potential

Based on the variables defined above, we write the energy changes around the RS, $\Delta E_{\text{eff}} = E_{\text{eff}} - E_{\text{RS}}$, as

$$\Delta E_{\text{eff}}(\{u_i\}, \eta) = E_p(\{u_i\}) + E_s(\eta) + E_{\text{an}}(\{u_i\}, \eta).$$

(3)

where

$$E_p(\{u_i\}) = E_{\text{har}}(\{u_i\}) + E_{\text{anh}}(\{u_i\}).$$

(4)

Here, we use the subscript ‘eff’ to distinguish between the energy that our effective potential gives for configuration ($\{u_i\}$, $\eta$) and the exact energy $E(\{u_i\}, \eta)$ that we would obtain from a first-principles simulation of the same atomic state. The above terms are the energy of the RS ($E_{\text{RS}}$); the energy change when the RS is distorted by atomic displacements $\{u_i\}$ ($E_p$, where the ‘p’ subscript stands for ‘phonon’), which we split into harmonic ($E_{\text{har}}$) and anharmonic ($E_{\text{anh}}$) contributions; the energy change when we strain the RS ($E_s$, where the ‘s’ subscript stands for ‘strain’); and the additional energy variations occurring when homogeneous strains and atomic distortions appear simultaneously ($E_{\text{an}}$, where ‘sp’ stands for ‘strain–phonon’). Let us discuss each of these terms.
2.2.1. $E_{\text{har}}([u_i])$ and $E_{\text{anh}}([u_i])$. Traditionally, the energy change caused by atomic distortions $[u_i]$ is written as a Taylor series around the RS in the following way:

$$E_p([u_i]) = \frac{1}{2} \sum_{i \alpha j \beta} K^{(2)}_{i \alpha j \beta} u_{i \alpha} u_{j \beta} + \cdots,$$

where the first line shows the harmonic terms included in $E_{\text{har}}([u_i])$ and the second line gathers all the higher-order terms contained in $E_{\text{anh}}([u_i])$. The tensor $K^{(n)}$ is formed by the $n$th derivatives of the energy, with

$$K^{(n)}_{i \alpha j \beta \gamma \cdots} = \frac{\partial^n E_{\text{eff}}}{\partial u_{i \alpha} \partial u_{j \beta} \cdots}_{\text{RS}}.$$  \hspace{1cm} (6)

Note that we assume that the RS is a stationary point of the PES (i.e., a minimum or a saddle), so that $K^{(1)} = 0$.

It is important to realize that the coefficients $K^{(n)}$ in equation (5) are not independent. At each order in the Taylor series, they are related by the point and lattice-translational symmetries of the RS structure. Additionally, and more fundamentally, they have to comply with translational invariance in free space, which results in the so-called acoustic sum rules (ASRs). In essence, the ASRs guarantee that a rigid translation of the material—i.e., one given by atomic displacement patterns; note that the distortions in the unstrained areas are rigid translations, which do not contribute to the energy because of the ASR satisfied by $E_p([u_i])$ (see the text).

This set of conditions for the harmonic terms is rather manageable, and allows for simple procedures to enforce the ASR in practice. For example, a common strategy is to derive the self-energy parameters from the interactions between different atoms, by taking

$$K^{(2)}_{i \alpha j \beta} = - \sum_{j \neq i} K^{(2)}_{j \beta i \alpha},$$

and simultaneously imposing the symmetric character of the force-constant matrix ($K^{(2)}_{i \alpha j \beta} = K^{(2)}_{j \beta i \alpha}$). Note that such a correction is necessary whenever we spatially truncate the interatomic couplings, as such an approximation will generally break the ASR. Also, it is customary to use this type of correction when dealing with a force-constant matrix whose coefficients may suffer from some numerical noise or inaccuracy. As we will discuss in section 2.3, today there are well-established and widely available first-principles methods to compute a force-constant matrix that is ASR-compliant. Hence, we use the above form (i.e., the one in equation (5)) for the harmonic term $E_{\text{har}}$ in our models.

However, as one can imagine from equation (7), enforcing the ASR becomes much more intricate for $n > 2$. In particular, it would complicate enormously the procedure to compute the parameters in $E_{\text{anh}}$ discussed in section 2.3. Fortunately, in that case we can resort to an alternative representation in which the ASR is automatically satisfied at all orders.

Indeed, the energy $E_p([u_i])$ can be equivalently expanded as a function of displacement differences in the following way:

$$E_p([u_i]) = \frac{1}{2} \sum_{ij kh \alpha} \tilde{K}^{(2)}_{ijkh \alpha \beta} (u_{i \alpha} - u_{j \alpha})(u_{k \beta} - u_{h \beta})$$

$$+ \frac{1}{2} \sum_{ijkh \alpha \beta \gamma} \tilde{K}^{(3)}_{ijkh \alpha \beta \gamma} (u_{i \alpha} - u_{j \alpha})(u_{k \beta} - u_{h \beta})(u_{l \gamma} - u_{m \gamma}) + \cdots.$$  \hspace{1cm} (10)

From this expression, it is obvious that $E_p$ does not change for a rigid displacement of the material, as every single term cancels out in that case; it is also easy to prove that a
rigid displacement does not induce any forces on the atoms. Hence, the model parameters $\vec{K}^{(n)}$ do not need to satisfy any ASR to guarantee translational invariance, which facilitates enormously the task of fitting their values to best reproduce first-principles results.\(^4\)

The relation between equations (5) and (10) is a subtle one and deserves a few comments. (i) It is important to realize that these two expressions for $E_{sp}$ are not connected by a simple transformation of the basis in which we express the atomic distortions of the material. Indeed, the atomic displacements $\{u_i\}$ do define the independent variables of our problem. In contrast, the set of differences $\{(u_{ia} - u_{ia})\}$ has many more, linearly-dependent members; hence, the displacement differences are not an acceptable basis. (ii) It is possible to go from equation (5) to equation (10) by application of the ASR at each order of the expansion. More precisely, at a given order $n$, one can use the corresponding ASRs to write some of the $K_{ij}^{(n)}$ parameters as a function of the rest, e.g. by performing substitutions such as the one given in equation (9) for $n = 2$. The result of such a procedure is an expression in terms of differences, such as the one in equation (10). However, there is no unique way to perform such a transformation and, thus, the form of the resulting energy function is somewhat arbitrary. Indeed, there are many ways in which we can use the ASRs to rewrite equation (5) (e.g., for n = 2, equation (9) is just one possibility among many others), and we see no clear reasons to prefer any specific strategy. (iii) In equation (10), it may look like we have many-body terms already at very low orders of the expansion. For example, the harmonic terms can involve up to four different atoms. Such couplings are the consequence of the ASR-related connections between the energy derivatives $K^{(0)}$, which result in terms that look like many-body ones when we write the energy as a function of displacement differences. (iv) It is possible to understand better the inner structure of the difference terms of equation (10). Thus, for example, for $n = 2$ it can be seen that all four-body terms can be written as combinations of two- and three-body terms, but three-body terms are in general not reducible to two-body terms. These considerations are of little importance for our present purposes, though, and we will not pursue them further. (v) Finally, let us note that the $\vec{K}^{(n)}$ parameters in equation (10) can be viewed as some sort of generalized spring constants; this interpretation is especially apparent for the pairwise terms involving products of the form $(u_{ia} - u_{ia})^2$.\(^5\)

\[E_s(\eta) = \frac{N}{2} \sum_{ab} C_{ab}^{(2)} \eta_a \eta_b + \frac{N}{6} \sum_{abc} C_{abc}^{(3)} \eta_a \eta_b \eta_c + \cdots, \quad (11)\]

\[C_{ab}^{(m)}_{\text{ab...}} = \frac{1}{N} \frac{\partial^m E_{\text{eff}}}{\partial \eta_a \partial \eta_b \cdots} \bigg|_{\text{RS}}, \quad (12)\]

and $N$ is the number of cells in the crystal. There is no linear term in equation (11) because we assume that the RS is a stationary point of the PES. The harmonic parameters in this series are the usual elastic constants; more precisely, they are the so-called frozen-ion or undressed elastic constants, as they quantify the elastic response of the material with the ions clamped at the relative positions that they have in the RS. For the strain–phonon interaction energy $E_{sp}(\{u_i\}, \eta)$, we can write

\[E_{sp}(\{u_i\}, \eta) = \frac{1}{2} \sum_a \sum_{ia} \Lambda_{ai}^{(1.1)} \eta_a u_{ia} + \frac{1}{6} \sum_a \sum_{aij} \Lambda_{aij}^{(1.2)} \eta_a u_{ia} u_{i\alpha} + \cdots. \quad (13)\]

The lowest-order coupling term $\Lambda^{(1.1)}$ corresponds (except for non-essential prefactors) to the so-called force–response internal strain tensor, and describes the forces that act on the atoms as a consequence of homogeneous strains. Hence, this kind of coupling contributes to determine the full, relaxed-ion or dressed, elastic response of the material, in the way that is described e.g. in [31].

The $\Lambda^{(m,n)}$ parameters in equation (13) have to comply with a set of ASRs that are analogous to the ones discussed above for the $K^{(n)}$ coefficients. As in the case of $E_p$, we can use an alternative expression for $E_{sp}$, namely

\[E_{sp}(\{u_i\}, \eta) = \frac{1}{2} \sum_a \sum_{ia} \tilde{\Lambda}_{ai}^{(1.1)} \eta_a (u_{ia} - u_{ia}) + \frac{1}{6} \sum_a \sum_{aij} \tilde{\Lambda}_{aij}^{(1.2)} \eta_a (u_{ia} - u_{ia}) (u_{i\alpha} - u_{i\alpha}) + \cdots. \quad (14)\]

with $\tilde{\Lambda}^{(m,n)}$ parameters that are free from ASR-related restrictions. Our choosing between the former or the latter expressions for $E_{sp}$ will be a matter of practical convenience; more precisely, we will use the regular representation (equation (13)) whenever we compute the parameters directly from first principles, and the alternative one (equation (14)) in cases in which we need to fit the parameters to reproduce specific first-principles results. This will be discussed in detail in section 2.3.

2.2.2. $E_s(\eta)$ and $E_{sp}(\{u_i\}, \eta)$. For the elastic energy $E_s(\eta)$, we use a simple Taylor series

\[E_s(\eta) = \frac{N}{2} \sum_{ab} C_{ab}^{(2)} \eta_a \eta_b + \frac{N}{6} \sum_{abc} C_{abc}^{(3)} \eta_a \eta_b \eta_c + \cdots, \quad (11)\]

4 In our models, the $K^{(2)}$ parameters are obtained by using equation (9) to impose the ASR. As a byproduct, this step usually corrects for other inaccuracies in the DFT results. In contrast, there is no need to impose the ASR on the anharmonic couplings $K^{(0)}$ with $n > 2$, and we treat them directly in the uncorrected first-principles results. Hence, one needs to be especially vigilant as regards the convergence of the DFT calculations employed to compute the anharmonic terms in our models.

2.2.3. Symmetry considerations. We will often deal with reference structures that present certain lattice-translational and/or point symmetries. Such symmetries imply a reduction in the number of independent parameters of the model, and we can take advantage of them to simplify its construction. In the following we describe the general ideas and procedures that
where $S$ is the 3x3 matrix representation of a point symmetry and $t$ is a three-dimensional vector, both expressed in our Cartesian reference frame. By applying such an operation to an arbitrary vector $x$, we obtain the transformed vector $x' = (S|t)x$ given by

$$x'_{\alpha} = \sum_{\beta} S_{\alpha\beta} x_{\beta} + t_{\alpha}.$$  

For $S|t$ to be a symmetry of the RS, it is necessary and sufficient to have

$$(S|t)(R_i + \tau_i) = R_i' + \tau_i',$$

where, for any atom $i$, there is an atom $i'$ of the same atomic species that satisfies this relation. In other words, equation (16) states that the RS is invariant upon the application of $(S|t)$.

The distortions of the RS transform as

$$u'_{\alpha i} = \sum_{\beta} S_{\alpha\beta} u_{\beta i},$$

where $i$ and $i'$ are related by equation (16), and we also have

$$\eta'_{\alpha\beta} = \sum_{\gamma\delta} S_{\alpha\gamma} \eta_{\gamma\beta}(S^{-1})_{\delta\beta} = \sum_{\gamma\delta} S_{\alpha\gamma} S_{\beta\delta} \eta_{\gamma\delta},$$

where the strains are expressed in the Cartesian basis. Finally, the symmetry condition for the energy reads

$$\Delta E_{\text{eff}}([u']_{i}, \eta') = \Delta E_{\text{eff}}([u]_{i}, \eta).$$

Figure 3. Example of symmetry-adapted terms (SATs) involving displacements of neighboring B and O atoms. We show the SATs represented by the $(B_1-O_3)\times(B_1-O_3)$ (left) and $(B_1-O_1)\times(B_1-O_1)$ (right) coupling terms (the representative terms are colored in the figure). For the atomic displacements we use the compact notation described in the text. An arrow along the $x$ direction, and located at the center of the line connecting atoms $i$ and $j$, represents the $(u_{i\alpha} - u_{j\alpha})$ displacement difference. Whenever a displacement difference appears squared, we draw a double arrow, which indicates invariance under mirror-plane reflections. Without loss of generality, we assume that the B atom is located at the $l = 0$ cell of the lattice (i.e., $R_i = R_0 = (0, 0, 0)$); superscripts at the oxygen sites denote the cell to which they correspond.

Of course, similar relations hold for all the individual terms in the energy and at all orders of the Taylor series (e.g., we have $E_{\text{anh}}([u']_{i1}) = E_{\text{anh}}([u]_{i1})$).

Let us describe how these general symmetry relations allow us to simplify our model potential. Given a particular product of $u_{\alpha\beta}$ displacements and $\eta_{\alpha \beta}$ strains in the Taylor series, we can use the operations of the space group to generate the collection of symmetry-related products, which will involve transformed $u'_{\alpha\beta}$ and $\eta'_{\alpha\beta}$ distortions. Figure 3 illustrates this process pictorially. For example, in the left panel we start with the product $(u_{0Bx} - u_{0O3x})^2(u_{0By} - u_{0O3y})^2$ that couples atoms B and O3 in the unit cell at the origin of our coordinate system (i.e., without loss of generality, we choose $R_i = R_0 = (0, 0, 0)$). Then, by application of the symmetry operations of the cubic space group of the ideal perovskite structure, we can generate a collection of related products; for example, a 90° rotation about the $y$ axis transforms the original product into $(u_{0Bx} - u_{0O3x})^2(u_{0By} - u_{0O3y})^2$, etc. Figure 3 sketches the products thus generated and involving the B atom in the $l = 0$ cell; lattice-translational symmetry leads to analogous couplings centered at all other B atoms in the crystal.

Naturally, symmetry-related products can be grouped together in the Taylor series, as their contribution to the energy is quantified by a common coupling coefficient. We refer to such a group as a symmetry-adapted term (SAT). An SAT is fully defined by a representative coupling term ($(u_{0Bs} - u_{0O3s})^2(u_{0By} - u_{0O3y})^2$ for the case mentioned above as an example) and the corresponding coupling constant ($K_{15}$ for the above example, using the simplified notation of table 1).

Note also that, in some cases, by applying all the space group operations to a representative coupling we may generate an SAT that exactly cancels out. Hence, working with SATs provides us with an automatic way to identify couplings that are forbidden by symmetry, which may result in drastic
Table 1. Representatives of the symmetry-adapted terms (SATs) that couple first-nearest-neighbors in the ABO₃ cubic structure. The atom labels correspond to those in figure 3. The atomic displacements are given in a compact notation, so that Bₓᵧ denotes the displacements mᵢₓᵧ of the central B atom, etc. (Note that all these representative couplings can be chosen so that the two atoms involved are in the same crystal cell.) We number the couplings to follow: implementing the automatic generation of the notation for the coupling coefficients; for example, the SATs involved are in the same crystal cell. We number the couplings to refer to them easily in the text. This also allows for a compact notation for the coupling coefficients; for example, the SATs sketched in figure 3 correspond to the coefficients Kᵢᵧ and Kᵢᵢ (right).

| Order | A–O terms | Fourth-order A–O terms |
|-------|------------|-------------------------|
| 1     | (Aₓ–O₁ᵧ)³ | (Aₓ–O₂ᵧ)⁴              |
| 2     | (Aₓ–O₃ᵧ)² (Aₓ–O₁ᵧ) | (Aₓ–O₂ᵧ)⁴              |
| 3     | (Aₓ–O₂ᵧ)² (Aₓ–O₁ᵧ) | (Aₓ–O₂ᵧ)⁴              |
| 4     | (Aₓ–O₁ᵧ)³ | (Aₓ–O₂ᵧ)⁴              |
| 5     | (Aₓ–O₁ᵧ)² (Aₓ–O₁ᵧ) | (Aₓ–O₂ᵧ)⁴              |
| 6     | (Aₓ–O₁ᵧ)³ (Aₓ–O₁ᵧ) | (Aₓ–O₂ᵧ)⁴              |
| 7     | (Aₓ–O₁ᵧ)² (Aₓ–O₁ᵧ) (Aₓ–O₁ᵧ) | (Aₓ–O₂ᵧ)⁴ |

| Order | B–O terms | Fourth-order B–O terms |
|-------|------------|-------------------------|
| 10    | (Bₓ–O₁ᵧ)³ | (Bₓ–O₂ᵧ)⁴              |
| 11    | (Bₓ–O₁ᵧ)² (Bₓ–O₁ᵧ) | (Bₓ–O₂ᵧ)⁴              |
| 12    | (Bₓ–O₁ᵧ)³ | (Bₓ–O₂ᵧ)⁴              |
| 13    | (Bₓ–O₁ᵧ)² (Bₓ–O₁ᵧ)² | (Bₓ–O₂ᵧ)⁴              |
| 14    | (Bₓ–O₁ᵧ)³ (Bₓ–O₁ᵧ)² | (Bₓ–O₂ᵧ)⁴              |
| 15    | (Bₓ–O₁ᵧ)² (Bₓ–O₁ᵧ)³ | (Bₓ–O₂ᵧ)⁴ |

Table 2. The same as in table 1, but involving couplings between strains (linear) and atomic displacements of nearest-neighbor atoms (quadratic). Strains are given in the Cartesian notation nᵢᵧ to facilitate the interpretation of the terms.

| A–O terms | B–O terms |
|-----------|-----------|
| 1 | (Aₓ–O₂ᵧ)² nᵧy |
| 2 | (Aₓ–O₂ᵧ)² nᵧz |
| 3 | (Aₓ–O₃ᵧ)² nᵧz |
| 4 | (Aₓ–O₂ᵧ)² nₓz |
| 5 | (Aₓ–O₁ₜ)² nᵧy |
| 6 | (Aₓ–O₁مصالح)² nᵧz |
| 7 | (Aₓ–O₁ᵧ)² nₓz |
| 8 | (Aₓ–O₂ᵧ)² (Aₓ–O₂ᵧ) nᵧy |
| 9 | (Aₓ–O₂ᵧ)² (Aₓ–O₂ᵧ) nₓz |
| 10 | (Aₓ–O₃ᵧ)² (Aₓ–O₃ᵧ) nₓz |
| 11 | (Aₓ–O₃ᵧ)² (Aₓ–O₃ᵧ) nᵧy |
| 12 | (Aₓ–O₃ᵧ)² (Aₓ–O₃ᵧ) nₓz |

2.2.4. Long-range interactions in insulators. The potentials described above can in principle involve interatomic interactions of arbitrary spatial range. However, in practice we will truncate the spatial extent of such interactions, which will constitute one of the approximations in our models. Generally speaking, such a truncation can be expected to work well in metals, where the free charges provide an efficient means of screening. In contrast, the truncation is not justified when we deal with semiconductors or insulators, where long-range (strictly speaking, infinite-range) Coulomb interactions must necessarily be considered. Fortunately, such couplings have a well-known analytic form in the limit of long distances, and they can be conveniently treated in a way that is essentially exact.

To understand the role of ion–ion Coulomb interactions in insulators, let us consider two separate effects. (In the following we will implicitly consider the case of short-circuit boundary conditions, which corresponds to the ideal situation for an infinite bulk material. The treatment of different electrostatic boundary conditions is discussed, e.g., in [32].) First, these interactions give rise to the so-called Madelung field that contributes to determine the cohesive energy of the material. In our model potentials, such a Madelung field is captured in the energy of the RS. Hence, by taking Eᵦs directly as a result of the first-principles calculations, we avoid the need to model the Madelung energy, as well as the other effects (e.g., short-range interactions associated with chemical bonding) that control the basic cohesive energy. Second, the Coulombic interaction between ions also influences the energy changes associated with the distortions of the RS. To leading order in the Taylor series, such an effect is essentially captured by the electrostatic interaction between the dipoles that appear when ions move from their RS positions. Such atomic dipoles are usually written, within a linear approximation, as

\[ dᵢᵢ = \sum_ρ Zᵢρα uᵢβ, \]
In the case of insulating ABO$_3$ rearrangement that occurs in response to the atomic distortion, as well as the additional effects arising from the electronic rearrangement that occurs in response to the atomic distortion. In the case of insulating ABO$_3$ perovskites like PbTiO$_3$ and SrTiO$_3$, the electronic effects are very large and result in Born charges that even double the value corresponding to the rigid-ion limit [33]. Such huge dynamical charges reflect Born effective-charge tensor $Z^e_i$, for example, we have distortions where $Z^e_i$ for atom $i$. Note that the Born charge $Z^e_i$ quantifies the dipole caused by the displacement of the ionic charge associated with ion $i$ at its RS position, as well as the additional effects arising from the electronic rearrangement that occurs in response to the atomic distortion. In the case of insulating ABO$_3$ perovskites like PbTiO$_3$ and SrTiO$_3$, the electronic effects are very large and result in Born charges that even double the value corresponding to the rigid-ion limit [33]. Such huge dynamical charges reflect changes in the oxygen–cation bonding that play a crucial role in the ferroelectric and response properties of these materials [34, 35].

Hence, when working with insulators, it will be convenient to split the energy terms involving atomic distortions $u_i$ into short-range (\textquoteleft{}sr\textquoteleft{}) and long-range (\textquoteleft{}lr\textquoteleft{}) parts. Thus, for example, we have

$$K^{(n)} = K^{(n),\text{sr}} + K^{(n),\text{lr}}$$

for the couplings in $E_p$, where it is important to note that the decomposition can be made at all orders in the Taylor series. Analogously, the strain–phonon terms in $E_{ap}$ can be split as

$$\Lambda^{(m,n)} = \Lambda^{(m,n),\text{sr}} + \Lambda^{(m,n),\text{lr}}.$$  

Of course, analogous splittings can be considered for the parameters that appear in our displacement-difference representation of equations (10) and (14).

Here, we will only discuss the lowest-order dipole–dipole interactions, which are captured by the harmonic coupling $K^{(2)}$ and have been described in detail in the literature. Note that harmonic couplings involving other terms in the multipole expansion of the electrostatic energy also exist; as is usual in first-principles treatments, we will neglect their contribution to the long-range part of the energy, and effectively capture their possible effects in the short-range part.

Following Gonze and Lee [36], we write the long-range couplings as

$$K^{(2),\text{lr}} = \sum_{\gamma\delta} Z^{\gamma}_{\alpha ij} Z^{\delta}_{\beta j} \left( \frac{\epsilon_\infty^{-1}}{3D^3} \Delta r_{\alpha\beta} \right) \text{det} \epsilon_\infty^{-1/2},$$

where

$$\Delta r_{\alpha\beta} = \sum_{\beta} (\epsilon_\infty^{-1})_{\alpha\beta} \Delta r_{\beta} \tag{24}$$

and

$$D = \sqrt{\Delta r \cdot \Delta r}. \tag{25}$$

with

$$\Delta r = R_j + \tau_j - R_i - \tau_i. \tag{26}$$

This is the usual expression for the Coulombic interaction between two dipoles, generalized for a medium that presents an arbitrary dielectric tensor $\epsilon_\infty$ quantifying the purely electronic (frozen-ion) response of the material. As discussed by Gonze and Lee [36], equation (23) captures the non-analytical behavior of the phonon bands for homogeneous ($q = 0$) distortions, and the related electrostatic effects (e.g., the so-called longitudinal-optical–transverse-optical splitting of the phonon frequencies). It is also trivial to show that the ASR for the $K^{(2),\text{lr}}$ coefficients translates into the condition

$$\sum_i Z^{\gamma}_{\alpha i} = N \sum_k Z^{\gamma}_{\alpha k} = 0 \quad \forall \alpha, \beta. \tag{27}$$

which guarantees that no net dipole is created by a rigid displacement of all the atoms in the crystal. Note that the $Z^e_i$ tensors are cell-independent, which allows us to use the notation $Z^e_i$. Finally, let us mention that in an actual atomistic simulation, which usually involves a periodically-repeated simulation box or supercell, such infinitely-ranged couplings can be accurately computed by performing an Ewald summation, as described, e.g., in [11].

In this work we only considered the Coulombic dipole–dipole term associated with $K^{(2)}$. Indeed, as discussed below, higher-order long-ranged couplings in $E_p$, and further interactions involving strain in $E_{sp}$, were either neglected or treated in an effective way. These approximations, which follow the spirit of the usual effective-Hamiltonian approach to perovskite oxides, will be discussed in sections 2.3.3 and 3.

2.2.5. Miscellaneous remarks. Approximations involved: typically, to construct an effective potential for a material, one starts by considering the simplest possible model that makes physical sense, and then extends it only as much as needed to get a sufficiently accurate description of the first-principles data of interest (i.e., a good description of what is usually called the training set of first-principles results). Given the conceptual simplicity of our proposed potentials, it is straightforward to identify three qualitatively different ways in which they can be systematically extended. Indeed, our models can be improved as regards (i) the order of the polynomial expansion, (ii) the spatial range of the interatomic couplings considered, and (iii) the complexity of the coupling terms, i.e., the maximum number of atoms (bodies) involved in the couplings. These three truncations constitute the approximations of our models.

Relation with effective-Hamiltonian work: for the most part, the connections between our method and the above-mentioned effective-Hamiltonian approach are rather obvious. Yet, there are a couple of subtle points that deserve a comment.

Firstly, the effective Hamiltonians often include local variables that account for the inhomogeneous strains that may occur in the material; further, the energy landscape for such local strains is typically derived from the elastic constants associated with the homogeneous ones, following the approximation proposed by Keating [37]. In our models, inhomogeneous strains are naturally captured by the appropriate atomic distortions $u_l$, as illustrated in figures 2(c) and (d). The energy changes associated with such local strains are given by $E_p$, and there is no need to derive them from the elastic constants for homogeneous cell deformations. Of course, one should note that the force constants $K^{(2)}$ and the elastic constants $C^{(2)}$ are connected by well-known relations, and the latter can be computed from
knowledge of the former [38]. As explained in section 2.3, we include in our models the exact first-principles results for both \( K^{(2)} \) and \( C^{(2)} \), so that the relations between such coefficients are fulfilled by construction. Additionally, our models also capture correctly the energy changes associated with strong strain gradients. This is a definite improvement over the usual effective-Hamiltonian approach, especially when taking into account the growing interest in flexoelectric effects resulting from large strain gradients near ferroelectric domain walls [28], etc.

Secondly, the action of an external electric field \( \mathbf{E} \) can be trivially incorporated in an effective-Hamiltonian simulation by including the leading coupling term between the field and the local dipoles that are the basic variables of the model [39]. Equivalently, within our approach (and as long as we are dealing with insulators), we can use the effective-charge tensors \( Z_i^\text{lr} \) to compute the local dipole \( d_i \) resulting from atomic displacements (equation (20)), and write the corresponding energy as

\[
E_{\text{eff}}(\{u_i\}, \eta; \mathbf{E}) = E_{\text{eff}}(\{u_i\}, \eta) - \sum_i d_i \mathbf{E} \cdot \mathbf{a}_i \eta.
\]

Finally, let us note that the action of an external stress \( \sigma \) can be treated in an analogous way [39], by introducing

\[
E_{\text{eff}}(\{u_i\}, \eta; \sigma) = E_{\text{eff}}(\{u_i\}, \eta) - N \sum_a \eta_a \sigma_a.
\]

Here the sign convention is chosen so that a negative stress implies a compression of the material.

Implementation in a simulation code: let us briefly mention some details of our implementation of a statistical simulation (in particular, a Monte Carlo (MC) scheme) based on our model potentials.

First, let us note that the long-range part of the force-constant matrix, \( K^{(2)}(r,\mathbf{r}) \), depends on the specific size and shape of the periodically-repeated simulation box used for the MC runs. Hence, for a given supercell, we compute these parameters before the MC simulation starts, by performing the corresponding Ewald sums that take into account interactions between periodically-repeated dipole images. Then, we add up the long-range and short-range parts of \( K^{(2)} \) to obtain a total harmonic interaction term that effectively couples all atoms in the simulation box. This is what we use for the energy evaluations in the simulation.

Once we have a supercell-dependent potential, the underlying lattice-translational symmetry allows us to store only the interactions between the atoms in one elemental unit cell and all other atoms in the supercell. Hence, the storage requirements grow linearly with the number of unit cells in the supercell.

In our MC simulations, we attempt to change the strains only after completing one sweep through all the atoms in the simulation supercell. It is therefore convenient to recalculate the parameters controlling the energetics of the atomic displacements, such as for example

\[
K^{(2)}_{\alpha\beta\gamma} = K^{(2)}_{\alpha\beta\gamma} + \sum_\lambda \Lambda^{(1,2)}_{\alpha\beta\lambda\gamma} \eta_\lambda + \mathcal{O}(\eta^3),
\]

after the strains are updated. These strain-dependent parameters are then used for energy evaluations during the sweep over atomic displacements.

The SATs for the calculation of the anharmonic part of our models are automatically generated based on the symmetry of the RS. We store them in symbolic form, so that they can be used for the calculation of both the energy and (via a simple manipulation of the polynomial) the forces on the atoms.

2.3. Parameter calculation

Once we have defined a potential, many schemes can be applied to calculate its parameters. Here, we describe the strategy that we followed in this first application of our effective models, which takes advantage of the direct availability of first-principles results for many of the terms in the potential. Some approximations that we used for the treatment of long-range interactions, which are somewhat specific to the case of insulators undergoing structural phase transitions, are also described.

2.3.1. Parameters computed directly from first principles.

The low-order couplings of our model potentials quantify the response of the RS of the material to small perturbations, may they be atomic distortions, cell strains, or a combination of both. In particular, the leading harmonic terms \( K^{(2)}, C^{(2)} \), and \( \Lambda^{(1,1)} \) can be obtained directly from density-functional perturbation theory (DFPT) calculations such as those described in [36, 40, 31]. DFPT schemes are efficiently implemented in widely available first-principles codes, such as the ABINIT package [41] used in this work. Alternatively, one could obtain the same information by performing systematic finite-difference calculations considering both atomic displacements and strains. Such an approach, which is somewhat more elementary but equally valid, is available in all major first-principles packages. Hence, we can conclude that computing exactly the harmonic parameters of models like ours is a trivial task nowadays.

Let us stress that the ability to incorporate an exact description of the harmonic energy of the material by construction is a great asset of our models. Indeed, in most materials the thermodynamic properties are essentially captured at the harmonic level, with small corrections coming from anharmonic effects; hence, a good description of the harmonic lattice-dynamical properties is critical. Further, even in cases with soft-mode-driven phase transitions, it is the harmonic part of the energy that essentially determines the nature of the leading structural instabilities. Hence, also in such situations, a faithful harmonic description seems mandatory to have an accurate model. Figure 4 shows representative results for our model of PbTiO

\[
\text{as the A}\_\text{BINIT}
\]

\[
\text{(DOS)}
\]

\[
\text{plots shown come from differences in the way BZ}
\]

\[
\text{integrations are performed in ABINIT and in our codes. The}
\]

\[
\text{most important structural instabilities, marked in figure 4}
\]

\[
\text{and sketched in figure 5, are also reproduced exactly.}
\]
calculations of distorted configurations in which some atomic displacements are frozen in—one could access the parameters in $E_{\text{anh}}$.

As described below, we tried such an approach when constructing our models for PbTiO$_3$ and SrTiO$_3$, specifically as regards the strain–phonon couplings. Based on our experience, we believe that such a systematic scheme may render accurate potentials in relatively simple cases, i.e., whenever the RS does not present structural instabilities. On the other hand, in the challenging situations here considered, this strategy may be impractical if a very precise description of some PES features is targeted. Indeed, we found that the PES of materials like PbTiO$_3$ or SrTiO$_3$ is strongly anharmonic; more precisely, if we aimed at an accurate description of the whole PES connecting the RS with the lower-energy phases, we would need to consider a Taylor series extending up to a rather high order. In such cases it seems more convenient to adopt an effective approach, aiming at reproducing the PES only around the RS and the most relevant low-energy structures. This permits a lower-order expansion that quantitatively captures the main effects and retains much of the physical transparency of the simpler (effective-Hamiltonian and phenomenological) models traditionally used to investigate phase transitions, which include only as many terms as strictly needed for a qualitatively correct description.

2.3.2. Parameters fitted to first-principles results. To compute the higher-order couplings of our effective potentials—i.e., $K^{(n)}$ with $n > 2$ and $\Lambda^{(m,n)}$ with $m + n > 2$—it is convenient to implement a fitting procedure aimed at obtaining a model that reproduces a training set of first-principles results. Here, we describe the strategy we adopted in our work with PbTiO$_3$ and SrTiO$_3$, where the training set was composed of low-energy structures that are more stable than the RS, and the key properties that we request our models to capture are energy differences and equilibrium atomic configurations. Nevertheless, the ideas presented are rather general and can be easily adapted to other situations.

In essence, our parameter-optimization calculations were based on three goal functions defined in the following way. Let the superindex $s$ number the structures $(|u_i^s|, \eta^s)$ in our training set. First, to get our model to reproduce the first-principles energies $|E^s|$, we considered the goal function

$$ \mathcal{G}_{E}(\mathcal{P}) = \sum_s \left[ E_{\text{eff}}(\mathcal{P})(|u_i^s|, \eta^s) - |E^s| \right]^2, \quad (32) $$

where $\mathcal{P}$ represents all the free adjustable coefficients in the model and the parametric dependence of $E_{\text{eff}}$ on $\mathcal{P}$ is indicated. Second, all the structures in our training sets were stationary points of the PES (minima or saddles). Hence, we imposed the zero-gradient condition for such structures by minimizing the goal function

$$ \mathcal{G}_{\nabla E}(\mathcal{P}) = \sum_s \left[ \nabla E_{\text{eff}}(\mathcal{P})(|u_i^s|, \eta^s) \right]^2, \quad (33) $$

As regards the anharmonic terms, one could try a similar direct calculation of each one of the parameters. For example, to compute the strain–phonon couplings $\Lambda^{(1,2)}$, one could run DFPT calculations for the RS subject to a small strain $\delta \eta$. The resulting force-constant matrix would be described in our model by

$$ K_{\delta ij}^{(2)} = K_{\delta ij}^{(2)} + \sum_a \Lambda_{\alpha a i j}^{(1,2)} \delta \eta_a, \quad (31) $$

which would allow us to calculate the targeted couplings. Following a similar scheme—e.g., by running DFPT

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Figure 4. Left: dispersion bands of cubic PbTiO$_3$, as calculated from first principles (lines) and obtained from our effective model (circles). The bands correspond to the eigenvalues $\lambda_q$ of the Fourier-transformed force-constant matrices $K_q^{(2)}$, which we call stiffness coefficients. The leading structural instabilities are labeled; they involve ferroelectric (FE) and antiferrodistortive (AFD) motions such as those sketched in figure 5. The color code indicates the dominant atomic character of the $K_q^{(2)}$ eigenvectors. Right: density-of-states (DOS) plots constructed from the $K_q^{(2)}$ eigenvalues, as obtained from first-principles simulations using a very fine $q$ point mesh, and from our effective potential by solving the eigenmode problem for an $8 \times 8 \times 8$ supercell and making use of a simple interpolation between the computed eigenvalues.

Figure 5. Sketch of the atomic displacements corresponding to the most important structural instabilities in ABO$_3$ perovskite oxides. (a) Ferroelectric (FE) instability. The subscript in FE labels the polar direction. (b) Antiferrodistortive (AFD) instability with neighboring $O_k$ octahedra along the $z$ direction rotating in-phase (distortion associated with the $\overline{M}q$-point of the cubic Brillouin zone). (c) The same as in (b), but with octahedral rotations modulated in antiphase along $z$ (R-point distortion). The subscript and superscript in the notation for the AFD modes label, respectively, the direction of the rotation axis and the in-phase or antiphase modulation of the rotations along that axis.
improved description of the lattice-dynamical properties of key low-energy structures, we also used a goal function that contains information about the corresponding Hessian matrices. More precisely, we used

\[ \mathcal{G}F_{\text{hess}}(\mathcal{P}) = \sum_i \sum_{q \in \mathcal{Q}_i} D^i(\mathcal{P})[q], \]

(34)

where \( \{q\}_i \) is a set of \( q \)-points of the first Brillouin zone of structure \( s \) (we restricted ourselves to zone-center and zone-boundary \( q \)-points). The function \( D^i(\mathcal{P})[q] \) quantifies the difference between the Hessian for structure \( s \) obtained from the model \( (K_{\text{eff},q}) \) and its first-principles counterpart \( (K_q) \); we define it as

\[ D^i(\mathcal{P})[q] = \sum_j \left\| K_{\text{eff},q}^j \hat{v}_j^q - \lambda_q^j \hat{v}_q^j \right\|^2, \]

(35)

where \( \hat{v}_q^j \) and \( \lambda_q^j \) stand, respectively, for the eigenvectors and eigenvalues of the first-principles Hessian \( K_q \). This strategy to compare the Hessian matrices allowed us to achieve meaningful parameters in a reliable and robust way; in contrast, we found that simpler schemes, based on a direct comparison of eigenvalues or eigenvectors, lead to difficult optimization problems that present many spurious local minima of the goal function.

The above functions can be combined to run optimizations targeting simultaneously different properties. However, it is not clear a priori how to weight the different goal functions in order to construct a single \( \mathcal{G}F \) that renders a well-posed optimization problem. Hence, we adopted the following alternative approach, which we used to generate most of the results presented in section 3. We start the parameter optimization by minimizing one of the goal functions, \( \mathcal{G}F_1 \). Then a second goal function \( \mathcal{G}F_2 \) is minimized, with the parameters subject to the constraint that the result for \( \mathcal{G}F_1 \) must be preserved within a certain tolerance. In this way, successive optimizations can be performed, with constraints involving all previously-optimized goal functions, until we impose all the necessary conditions. Naturally, the tolerances for the constraints can be chosen so that the most critical properties are reproduced better. Typically, in our work with PbTiO\(_3\) and SrTiO\(_3\) we started by minimizing \( \mathcal{G}F_{E_s} \), as we prioritize that our models reproduce correctly the first-principles energies of the structures in the training set. Then, the most usual sequence of optimizations involved \( \mathcal{G}F_{E_s \text{hess}} \) evaluated at the \( \Gamma \) (i.e., \( q = 0 \)) point of the lowest-energy structure(s), and finally \( \mathcal{G}F_{\text{hess}} \) evaluated at selected zone-boundary \( q \)-points of the lowest-energy structure(s).

The optimization of \( \mathcal{G}F_{\text{hess}} \) was never prioritized in the applications considered in this work; in fact, we found that, when working with relatively simple (low-order) models such as the ones considered here, it is not realistic to aim at a very precise description of the first-principles Hessians of structures that deviate significantly from the RS. Nevertheless, we found that it was often possible to adjust the low-lying eigenmodes at a reduced number of \( q \)-points. Also, generally speaking, we found that considering \( \mathcal{G}F_{\text{hess}} \) was a good strategy to obtain energy-bounded potentials, as such an optimization step helps to impose the stability of the ground state structure.

2.3.3. Further comments on the long-range interactions. As mentioned above, the atomic interactions in insulators can be conveniently decomposed into short- and long-range parts. Further, at the harmonic level we have a simple analytical expression for the dipole–dipole coupling (equation (23)) that depends on the RS geometry, the dynamical charges \( Z_i^s \), and the dielectric tensor \( \varepsilon_{\infty} \). Conveniently, these tensors, as well as the decomposition of \( K^{(2)} \) into \( K^{(2),sr} \) and \( K^{(2),lr} \), are produced automatically by most DFPT implementations; in particular, they are readily provided by ABINIT\(^6\). Alternatively, all the relevant parameters controlling the dipole–dipole interactions can be obtained by considering the response to finite electric fields\([42]\).

As regards the anharmonic terms, we could continue to distinguish between short- and long-range couplings. In essence, the anharmonic long-range couplings in \( E_p \) would capture the changes in the effective charges or dielectric constants that may be caused by the atomic displacements and which affect the magnitude of the Coulombic dipole–dipole interactions. As regards the strain–phonon couplings in \( E_{sp} \), an additional effect comes from the change in the cell shape and dimensions.

Our model potentials provide a framework to capture such effects by considering appropriate high-order terms. Unfortunately, considering such couplings would result in computationally-heavy atomistic simulations. Indeed, as discussed in section 2.2.5, for a practical implementation of the harmonic long-range interactions it is convenient to precalculate, for the RS geometry and our specific choice of simulation supercell, the dipole–dipole couplings by performing the appropriate Ewald sums. Once the interaction coefficients \( K^{(2),lr} \) are known, the corresponding energy can be readily obtained during the course of the simulation; yet, because such a term couples all the atoms in the supercell, its calculation is by far the most time-consuming part of the energy evaluation. In principle, one may proceed similarly with the higher-order long-ranged terms. For example, consider

\[ \Lambda^{(1,2)} = \Lambda^{(1,2),sr} + \Lambda^{(1,2),lr}, \]

(36)

which is the leading strain–phonon coupling for materials like PbTiO\(_3\) and SrTiO\(_3\). In this case, we can model \( \Lambda^{(1,2),lr} \) by considering the dependence of \( K^{(2),lr} \) (equation (23)) on a strain \( q \) to linear order. (To do this, one could proceed by introducing the strain dependence of the effective charges, dielectric tensor, and interatomic distances in equation (23), and then Taylor expand with respect to \( q \).) The corresponding coefficients could be precomputed for the RS geometry and particular simulation supercell, which would permit an easy

\(^6\) The typical DFPT scheme computes the total interatomic force constants. Then, in essence, it is assumed that the long-range part \( K^{(2),lr} \) is given by the dipole–dipole term in equation (23), and the short-range part is obtained as \( K^{(2),sr} = K^{(2)} - K^{(2),lr} \).
(but still computationally costly) evaluation of such an energy contribution during the course of the simulation.

In our work with PbTiO$_3$ and SrTiO$_3$, wanting to obtain models that allow for fast simulations, we did not treat explicitly the anharmonic corrections to the long-range dipole–dipole interactions. Yet, we captured the effects on the properties of interest (e.g., the energy, equilibrium structure, and Hessian of low-lying phases) in the short-range anharmonic couplings. Whenever the anharmonic couplings are determined by the fitting procedure outlined in section 2.3.2, this can be carried out in the most natural way. We simply assume that $\tilde{K}^{(n)}_{\alpha\beta}$, and $K^{(n,m)}_{\alpha\beta}$, and fit the anharmonic terms $K^{(n)}_{\alpha\beta}$ and $\Lambda^{(n,m)}_{\alpha\beta}$ to reproduce first-principles information about the structures in our training set, thus capturing effectively the consequences of possible anharmonicities in the long-range couplings.

Additionally, we also computed the strain–phonon couplings directly, without performing any fit, by proceeding in the following way. We considered the full interatomic constants for the RS and strained configurations, and assumed that the following approximate version of equation (31),

$$K^{(2)}_{\alpha\beta\gamma\delta} = K^{(2)}_{\alpha\beta\gamma\delta} + K^{(2)}_{\alpha\beta\gamma\delta} \approx K^{(2)}_{\alpha\beta\gamma\delta} + K^{(2)}_{\alpha\beta\gamma\delta} + \sum_n \Lambda^{(1,2)}_{\alpha\beta\gamma\delta} \delta n_{\alpha}, \quad (37)$$

holds within a certain spatial range (i.e., for a maximum separation of atoms $i$ and $j$). Then, we demanded that the short-range part of $\Lambda^{(1,2)}_{\alpha\beta\gamma\delta}$ capture strain-induced changes in both $K^{(2)}_{\alpha\beta\gamma\delta}$ and $K^{(2)}_{\alpha\beta\gamma\delta}$. It must be noted that, because of the spatial truncation, the $\Lambda^{(1,2)}_{\alpha\beta\gamma\delta}$ thus calculated will in general break translational invariance. To remedy this, we added to $\Lambda^{(1,2)}_{\alpha\beta\gamma\delta}$ a correction $\Delta \Lambda^{(1,2)}_{\alpha\beta\gamma\delta}$ that was determined by demanding that our model reproduce exactly the Hessian of the strained configurations at the $\Gamma$ point. In this way, by imposing a correct description of the acoustic modes, we restore the ASR. Further, this procedure also guarantees that the effect of strain on the $\Gamma$ distortions, which is critical for the investigation of ferroic perovskites like ours, is captured by our models. As shown in section 3.2, this approximation leads to a very precise description of the strain effects on the force-constant bands in the case of PbTiO$_3$.

3. Examples of application

Now we describe the model potentials for the ferroic perovskites PbTiO$_3$ (PTO) and SrTiO$_3$ (STO) that we constructed following the above scheme. These materials are representative of the large family of compounds undergoing structural phase transitions driven by soft phonon modes. The lattice-dynamical properties of such systems are strongly anharmonic, and the description of their transitions requires the use of high-order potentials. Further, in the case of these perovskite oxides the relevant energy scale for the soft mode instabilities is relatively small, of about 50 meV per formula unit (f.u.) or less. Hence, achieving a good description of such compounds constitutes a challenge for first-principles theory and, naturally, for our model-potential approach.

Additionally, PTO and STO present peculiarities that make them especially interesting in the present context. At the temperature $T_C = 760$ K, PTO undergoes a transition between the high-$T$ paraelectric structure (i.e., the ideal cubic perovskite prototype, with space group $Pm\bar{3}m$, that we take as our RS) and its low-$T$ ferroelectric (FE) phase (with tetragonal space group $P4mm$) [22, 43]. The structural distortion that appears at low temperatures has a polar character, and it essentially involves a displacement of the Ti and Pb cation sublattices against the O$_6$-octahedron network, as sketched in figure 5(a). Note that this corresponds to the condensation of a soft mode at the zone center (at the $\Gamma$ point) of the BZ of the RS. This transition has a significant first-order character that previous theoretical work has linked with the accompanying deformation of the cell [12]; further, first-principles theory predicts that cell strains are critical to determine the symmetry of the ground state of PTO [44]. Hence, to model this compound we have to deal with both the FE instability responsible for the transformation at $T_C$ and the strain–phonon couplings that have a strong impact in the occurring equilibrium phases and the features of the FE transition.

SrTiO$_3$ too undergoes a single phase transition, as it transforms at 105 K from the high-$T$ cubic perovskite phase to a low-$T$ structure of tetragonal ($I4/mcm$) symmetry [22]. The structural distortion occurring in the low-$T$ phase involves concerted rotations of the $O_6$ octahedra about the tetragonal axis, with the peculiarity that $O_6$ groups that are first neighbors along $z$ rotate in antiphase. Such a pattern is denoted $a'0d'c'$ in the well-known notation introduced by Glazer [45], and corresponds to a so-called antiferrodistortive (AFD) mode associated with the $R$ point of the BZ of the RS ($q_R = \pi/a_0(1, 1, 1)$, where $a_0$ is the lattice constant of the RS cubic unit cell); the corresponding atomic displacements are sketched in figure 5(c). Additionally, STO is close to presenting an FE instability; in fact, this compound is experimentally believed to be a quantum-paraelectric, i.e., a material whose ferroelectricity is suppressed by zero-point fluctuations [46, 47, 15]. Further, previous first-principles work has shown that the FE and AFD soft modes compete in STO [14], complicating even more the description of the behavior of the material at low temperatures. Hence, STO offered us the possibility of testing our approach in cases in which several structural instabilities are relevant and their interaction must be considered in detail.

We first describe our work with PTO, which turned out to present all the challenging features that we had anticipated (i.e., the very critical strain–phonon couplings) and additional ones that we were not expecting (i.e., a very significant competition between FE and AFD modes). Hence, we discuss the case of PTO in detail, giving illustrative examples of how our models can be extended when it is necessary to do so. In contrast, it was relatively easy to obtain a sound model for STO. Hence, in that case we will present a very minimal approach to the construction of an effective potential. In both cases, we will describe the $T$-driven transitions obtained when solving our models by means of Monte Carlo simulations (in which, as is usual, we treated atoms as classical objects).
showing that they capture correctly the basic experimental behaviors. We will also comment on the probable origin of the quantitative discrepancies observed between our model predictions and experiment. Note that here we will not elaborate much on the physics emerging from our models, as such a discussion falls beyond of the scope of this paper.

3.1. First-principles and Monte Carlo methods

All first-principles calculations were carried out with the ABINIT package [41], and employed the local-density approximation (LDA) to density-functional theory [48, 49]. The ionic cores were treated by using extended norm-conserving Teter pseudopotentials [50], and the following electrons were considered explicitly in the calculations: Pb's 5d, 6s2, and 6p2; Sr's 4s2, 4p6, and 5s2; Ti's 3s2, 3p6, 3d2, and 4s2; and O's 2s2 and 2p6. Electronic wavefunctions were represented in a plane-wave basis truncated at 1500 eV. We used an 8 × 8 × 8 k-point grid to compute integrals in the Brillouin zone of the five-atom perovskite cell, and equivalent meshes for other cells. In structural relaxations, atomic positions were optimized until the residual forces on atoms were below 10−4 eV Å−1. The interatomic force constants, elastic constants, Born charges, and dielectric tensor were calculated by using the DFPT implementation in ABINIT. The $K_q$ matrices, from which the real-space interatomic constants are obtained, were computed for a $2 \times 2 \times 2$ q-point mesh; in agreement with previous studies [51], this was found to be sufficient to get accurate results. The resulting cut-off radius for the short-range interactions is therefore about 6.8 Å for all of the presented models.

Let us note that, in the case of PbTiO$_3$, our LDA calculations for the tetragonal phase render a c/a ratio of 1.029 (see table 4), while the values previously reported in the literature are typically between 1.04 and 1.07 [52–54]. Our calculations were very carefully converged, and we tend to believe that this discrepancy comes from the different pseudopotentials employed. Interestingly, when we correct for LDA’s well-known overbinding problem at the level of our model potential (see below), the predicted c/a reaches a value of about 1.07, in good agreement with experiment. At any rate, these issues with LDA accuracy are somewhat particular to ferroelectrics like PbTiO$_3$ and not central to the present work; hence, we will not discuss them further.

Thermal averages of the quantities of interest were calculated by a standard Metropolis Monte Carlo method [55]. The Markov chain was constructed by sequentially considering movements of (i.e., by sweeping through) all atoms in the simulation box. After each sweep, a single attempt to modify each of the strain components was made. Both the attempted displacements and strain modifications were drawn from appropriate uniform distributions, whose widths were varied by a simple linear controller with the goal of attaining an acceptance rate of 50% on average. In most cases, we used an 8 × 8 × 8 periodically-repeated simulation supercell, and thermalized the material by running 20 000 MC sweeps starting from the RS (i.e., $u_i = \eta = 0$). The averages for the relevant structural distortions were then calculated from 20 000 to 40 000 additional sweeps, and we checked convergence by inspection of the corresponding histograms. At temperatures in the vicinity of the phase transitions, this procedure did not lead to converged results because of either slow thermalization or finite-size effects. In such cases, we found it necessary to run the calculations of up to 80 000 sweeps in $10 \times 10 \times 10$ simulation supercells. For presentation purposes, all of the computed average distortions were rotated so that the axes for the FE polarization and AFD rotations lay along the [001] (respectively [111]) Cartesian direction for tetragonal (respectively rhombohedral) phases.

3.2. PbTiO$_3$

3.2.1. Harmonic terms $E_{\text{har}}(\{u_i\})$ and $E_s(\eta)$. The first step in the construction of our model potential is the computation of the harmonic energy terms, $E_{\text{har}}$ and $E_s$, for which we use the DFPT scheme [36, 31] implemented in ABINIT [41]. As mentioned above, the third harmonic term—i.e., the strain–phonon coupling $\Lambda^i|_0$ in $E_{\text{sp}}$—is identically zero in PTO and STO due to the cubic symmetry of the RS.

Representative results are given in figure 4, which shows the bands corresponding to the stiffness coefficients or force constants of the cubic RS. Notably, we find that some distortions have a negative stiffness, indicating that they are structural instabilities of the RS. The leading instabilities correspond to those previously reported [51] and are pictorially represented in figure 5: the FE soft mode at the $\Gamma$ point (panel (a)), the in-phase AFD mode at the $M$ point ($q_{M} = \pi/a_0(1, 1, 0)$, where $a_0$ is the lattice constant of the RS cubic unit cell; panel (b)), and the antiphase AFD mode at the $K$ point (panel (c)). As shown in figure 4, the energetics of all such instabilities are captured exactly, at the harmonic level, by our model.

As a result of our DFPT calculations, we obtained an $E_{\text{har}}$ term that includes all short-range interactions within a spatial range slightly below 7 Å. (For example, this includes couplings between Ti pairs that are third nearest neighbors.) Additionally, $E_{\text{har}}$ includes the already-mentioned analytic form of the long-range dipole–dipole couplings, which involves five symmetry-independent parameters; more precisely, we have four Born effective charges (which reduce to three independent ones if the ASR in equation (27) is considered) and one dielectric constant that fully defines the diagonal and isotropic tensor. As regards the harmonic elastic constants in $E_s$, the model incorporates the three symmetry-independent terms that define the full elastic tensor for a crystal with cubic $m\overline{3}m$ point symmetry.

3.2.2. Fitting $E_{\text{anh}}(\{u_i\})$. Next we tackled the construction of the anharmonic terms of the potential. We first considered the case in which the cell is fixed to be that of the RS, i.e., we assumed $\eta = 0$ and focused on $E_{\text{anh}}$. As described above, we computed $E_{\text{anh}}$ by fitting its parameters to a set of relevant first-principles data. Naturally, we populated our training set with information about the low-energy structures that can be accessed by condensing the different instabilities of the RS. More specifically, our list of low-symmetry phases
Table 3. Structural parameters of the considered low-symmetry PbTiO₃ structures (see the text) calculated for a cubic cell with lattice constant \( a = 3.880 \, \text{Å} \). First-principles LDA results are presented along with those obtained from the model discussed in the text. We show the \( \Gamma \)-point displacements corresponding to the polar distortion, \( u_i^{PBC} \), given in Ångstrom; we chose them so that there is no rigid shift of the whole structure (i.e., \( u_{PBC} = u_{TIC} = 2u_{O1}; u_{O3} = 0 \)). For \( P4mm \), all the displacements are along the \( z \) direction and we have \( u_{O1z}^f = u_{O2z}^f \). For \( R3m \) and \( R3c \), we have \( u_i^{R} = u_i^{L} \) for the Pb and Ti atoms, as well as \( u_{O3z}^f = u_{O1z}^f = u_{O2z}^f \) and \( u_{O1z}^f = u_{O3z}^f = u_{O2z}^f = u_{O3y}^f = u_{O3y}^f \). The amplitude of the AFD modes is quantified by the corresponding \( O_{\alpha} \) rotation angle given in degrees (in the rhombohedral cases, we have equal-magnitude rotations about the three Cartesian axes; we give the rotation angle for one axis). Energies are given in meV/L.u., taking the result for the RS as the zero of energy.

| Structure | Method     | \( u_{PBC} \)  | \( u_{TIC} \)  | \( u_{O1z} \)  | \( u_{O3z} \)  | \( O_{\alpha} \) rot. | Energy |
|-----------|------------|----------------|----------------|----------------|----------------|------------------------|--------|
| \( FE_c \) (\( P4mm \)) | LDA         | 0.179          | 0.072          | −0.104         | −0.043         | −0.132                  | 24.8   |
|           | Model       | 0.180          | 0.073          | −0.105         | −0.043         | −0.132                  | 24.8   |
| \( FE_{3yc} \) (\( R3m \)) | LDA         | 0.104          | 0.048          | −0.063         | −0.027         | −0.028                  | 28.3   |
|           | Model       | 0.105          | 0.049          | −0.063         | −0.028         | −0.028                  | 28.3   |
| AFD\(_c\) (\( I4/mcm \)) | LDA         | —              | —              | —              | —              | —                      | 5.4    |
|           | Model       | —              | —              | —              | —              | —                      | 5.4    |
| AFD\(_c\) (\( R3c \)) | LDA         | —              | —              | —              | —              | —                      | 3.4    |
|           | Model       | —              | —              | —              | —              | —                      | 3.4    |
| AFD\(_c\) (\( P4/mmm \)) | LDA         | —              | —              | —              | —              | —                      | 4.3    |
|           | Model       | —              | —              | —              | —              | —                      | 4.3    |
| \( FE_{3yc} + AFD\(_c\) \) (\( R3c \)) | LDA         | 0.096          | 0.047          | −0.058         | −0.026         | 2.8                    | 29.5   |
|           | Model       | 0.098          | 0.047          | −0.060         | −0.026         | 2.1                    | 29.5   |

Table 4. Results for the tetragonal ground state structure of PTO with relaxed cell parameters. Lattice vectors and atomic displacements are given in Ångstroms. The atomic displacements are as described in the caption to table 3. We show the first-principles results (first row) followed by the results obtained from models with different descriptions of the strain–phonon coupling terms (see the text). Energies are given in meV/L.u., and we take \( E_{RS} \) as the zero of energy.

| Method     | \( a \)  | \( c \)  | \( c/a \) | \( u_{PBC} \) | \( u_{TIC} \) | \( u_{O1z} \) | \( u_{O3z} \) | Energy          |
|------------|---------|---------|----------|---------------|---------------|--------------|--------------|----------------|
| LDA        | 3.864   | 3.974   | 1.029    | 0.230         | 0.106         | −0.133       | −0.071       | −37.7          |
| model \( L^0 \) | 3.908   | 3.987   | 1.020    | 0.200         | 0.103         | −0.122       | −0.060       | −34.5          |
| model \( L^1 \) | 3.863   | 3.968   | 1.027    | 0.220         | 0.099         | −0.128       | −0.063       | −39.9          |
| model \( L^II \) | 3.861   | 3.978   | 1.030    | 0.227         | 0.102         | −0.132       | −0.066       | −43.1          |
| model \( L^III \) | 3.856   | 3.968   | 1.029    | 0.221         | 0.098         | −0.128       | −0.062       | −39.9          |

In order to fit \( E_{\text{anh}} \), we worked with the displacement-difference representation and \( \mathbf{K}^{(n)} \) parameters (with \( n > 2 \)) of equation \( (10) \). We restricted ourselves to models that include only pairwise interactions and extend up to fourth-order in the Taylor series. These approximations define the minimal model needed to capture structural phase transitions like the ones we want to describe, and are analogous to the ones adopted in most of the previous theoretical works that we are aware of. (Among the few exceptions, high-order terms for the local polar modes were considered in \( [12, 56] \)). In our case, we maintained such approximations in order to keep our models relatively simple and computationally efficient, as well as to test the actual ability of such an elementary potential to reproduce the first-principles data in a quantitative way.

As regards the spatial extent of the anharmonic couplings, most of the previous works on phenomenological models and effective Hamiltonians adopt what is sometimes called the \( \text{on-site-anharmonicity} \) approximation, which implies that the non-harmonic couplings are taken to be strictly confined in space and contribute only to the self-energy of the atoms or local modes \( [21, 22, 10–12] \). Interestingly, our first-principles results give us a direct way to test whether such an approximation is justified. Figure 6 shows the difference

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7 In effective-Hamiltonian works, the relevant configuration space is usually defined by the eigenvectors of the RS soft modes. Hence, the ground state structure is described in an approximate way, and the accuracy may be poor if there are significant anharmonic interactions between the RS unstable modes and other distortions, as is the case for PTO. Our approach is free from such approximations.
between the harmonic interatomic couplings computed for the RS (which are given by \(K^{(2)}\) directly) and those corresponding to the several distorted states of PTO that maintain the cubic cell (which are described by \(K^{(2)}\) plus a distortion-dependent correction involving \(\tilde{K}^{(n)}\) with \(n > 2\)). From these results, it is apparent that the distortion-induced changes decay very rapidly with the interatomic distance, indicating that the anharmonic corrections have a limited spatial range; similar calculations for other distorted configurations confirmed this conclusion. Hence, our model for PTO included only anharmonic \(\tilde{K}^{(n)}\) couplings between neighboring atom pairs (i.e., each Pb atom is coupled with its 12 neighboring oxygens, and each Ti atom with the six oxygens in the surrounding \(O_6\) group), which results in couplings extending up to about 3 Å. Note that this approximation is essentially equivalent to the on-site-anharmonicity assumption of the effective-Hamiltonian method, but adapted to our displacement-difference representation. Together with the other truncations mentioned above (pairwise interactions, fourth-order Taylor series), this local-anharmonicity approximation results in the 15 SATs listed in table 1.

Using the model and training set described above, we fitted the 15 anharmonic parameters of table 1 by successive optimization of the \(GF_E\), \(GF_{\nabla E}\), and \(GF_{\text{hess}}\) goal functions, following the procedure outlined in section 2.3.2. In \(GF_{\text{hess}}\) we considered the Hessian matrices of distorted configurations, including modes corresponding to the \(\Gamma\) and, in some cases, \(R\) points of the BZ of the RS. For each \(q\)-point, we considered only the six lowest-lying optical eigenmodes (i.e., we did not fit to the full spectrum). As evidenced by table 3 and figure 7, the model thus constructed describes with good accuracy our first-principles results for the equilibrium structures and energies of the relevant \(\eta = 0\) configurations. Additionally, figure 8 shows the results that our model gives for the force-constant bands of two distorted structures; as expected, the low-lying Hessian eigenmodes are reasonably well reproduced, and the inaccuracies grow as we move up in energy.

To test our model for a fixed-cell version of PTO, we ran MC simulations and computed the evolution of the equilibrium structure as a function of temperature. Figure 9 shows our basic results, which reveal a sequence of two phase transitions. At \(T \approx 200\) K the material develops a spontaneous polarization, which manifests itself in a non-zero value of...
the dipole moments averaged over all cells in the simulation box. Such a transition drives the system from its high-\(T\) cubic (\(Pm\bar{3}m\)) phase to a rhombohedral (\(R3m\)) one; the spontaneous polarization is parallel to the rhombohedral axis, which lies along the [1,1,1] Cartesian direction. Such an \(R3m\) structure is usually thought to be the ground state of PTO subject to the \(\eta = 0\) condition [44, 12]. However, our MC simulations rendered a second transition, at \(T \approx 100\) K, in which an AFD mode freezes in. More precisely, at low temperatures we observe the occurrence of a distortion involving antiphase \(Pm\bar{3}m\) groups about all three Cartesian axes, which we denoted by \(\text{AFD}_{17}\) in the description above. The spontaneous polarization remains essentially unaltered under the condensation of this AFD mode, and the new phase presents the \(R3c\) rhombohedral space group. Remarkably, this structure was not part of the initial training set that we used to fit the parameters in \(E_{\text{anh}}\); indeed, we discovered it by running MC simulations with our initial model potentials for PTO, which led us to better characterize it from first principles and eventually include it in the training set. This clearly illustrates the usefulness of our model-potential approach to discover new phenomena. Note that the force-constant bands of figure 8(c) already indicate that the \(R3m\) structure cannot be the ground state of our fixed-cell version of PTO; they present a negative stiffness for one \(R\)-point mode, which corresponds exactly to the low-\(T\) AFD instability observed in the MC runs.

3.2.3. Strain–phonon term \(E_{\text{sp}}(\{u_i\}, \eta)\). We began by considering in \(E_{\text{sp}}(\{u_i\}, \eta)\) some of the lowest-order terms that are not zero by symmetry, i.e., those corresponding to the coefficients \(\Lambda^{(1,2)}\) or, equivalently, \(\hat{\Lambda}^{(1,2)}\). This constitutes the minimal approximation that captures the strain–phonon couplings leading to physically relevant phenomena in ferroelectric perovskites (e.g., piezoelectricity and the elastic effects associated with the structural transitions), and is analogous to the one adopted in the effective-Hamiltonian literature [10–12].

As regards the spatial extent of the \(\Lambda^{(1,2)}\) interatomic couplings, the effective-Hamiltonian works have traditionally adopted an on-site approximation that is analogous to the one used for the anharmonic terms in \(E_{\text{anh}}\) [10–12]; consequently, only one-body interactions are typically considered. Further, strain effects on the long-range dipole–dipole interactions have never been treated in the literature, to the best of our knowledge.

In our case, we went beyond such approximations by computing \(\Lambda^{(1,2)}\) via the approach described by equations (31) and (37), using strains of \(\pm2\%\) for the finite-difference calculations. (The spatial extent of the \(\Lambda^{(1,2)}\) interactions thus computed is essentially identical to that of the \(\mathbf{K}^{(2)}\) terms.) The model constructed in this way, which we call \(L^0\), captures very accurately the strain dependence of the long-range interactions between dipoles, which was described in section 2.3.3. Moreover, this \(L^0\) model also renders the correct low-\(T\) structure for the real (unconstrained) PTO. Indeed, the experimental ground state of bulk PTO at ambient pressure is tetragonal (\(P4mm\) space group), as opposed to the rhombohedral (\(R3c\)) solution that we predict when imposing the \(\eta = 0\) condition. Remarkably, the strain–phonon couplings calculated with our finite-difference scheme capture such an effect, even though they were not explicitly fitted to do so. On the other hand, the predictions provided by this model do not reach the quantitative accuracy of the results.

Figure 9. Temperature-dependent polarization and AFD\(^\nu\) order parameters of PTO as obtained from MC simulations of our model under the \(\eta = 0\) condition.

Figure 10. Force-constant bands corresponding to PTO structures with \(u_i = 0\) and subject to a uniaxial strain of 2\% (stretching along \(z\)), as obtained from three models that include different strain–displacement couplings (see the text). Black solid lines are the model results, and red dashed lines depict the bands obtained from first principles. Note the non-analytic behavior of the spectrum when approaching \(\Gamma\) from the \([q_x, 0, 0]\) or \([0, 0, q_y]\) directions. (a) Model \(L^0\), (b) model \(L^1\) and (c) model \(L^{10}\).
obtained in the fixed-cell case. More precisely, table 4 shows significant differences between the first-principles results (labeled ‘LDA’) and the predictions of the $L_0$ model for the structure of the tetragonal ground state, especially as regards the aspect ratio ($c/a$) of the unit cell and the participation of the Pb atoms in the ferroelectric distortion.

As we wanted to increase the accuracy of the model, we decided to improve the description of the strain–phonon couplings by adding the SAT represented by $(\text{Pb}_x\text{O}_2\text{O}_2)_2\eta_1$, where we use the compact notation introduced above (see figure 3 and table 2). Note that the resulting model, which we label $L_1$, combines $\Lambda$-like terms, whose values are fixed to those of the $L_0$ potential, with one $\Lambda$-like free adjustable parameter. Such a parameter was fitted to better reproduce the ground state structure; as shown in table 4, this led to a significant improvement over the $L_0$ result. Further improvement of the $c/a$ value can be achieved by additionally introducing the higher-order SAT represented by $(\text{Pb}_x\text{O}_2\text{O}_2)_2\eta_2$ (model $L_2$), at the expense of worsening the agreement for other structural parameters and energies.

Let us mention another model-construction experiment that we made. Noting the importance of the strain–phonon couplings in PTO, one may wonder which are the interaction terms responsible for the main effects. By inspecting the $\Lambda^{(1,2)}$ parameters computed directly from first principles, it is easy to identify the two most prominent ones, which involve Pb–O and Ti–O nearest-neighboring pairs. More specifically, the key couplings are captured by the $\Lambda$-like parameters number 2 and number 13 from table 2. Hence, we considered a model that includes only these two strain–phonon couplings ($L_{III}$); interestingly, as shown in table 4, such a simple potential is able to render good results for the structure and energy of PTO’s ground state.

The quality of these models can be further evaluated by checking how well they reproduce the first-principles results for the force-constant bands of strained configurations. As already mentioned, figure 10 shows an essentially perfect agreement for model $L_0$, which is largely preserved in models $L_1$ and $L_{II}$ (the latter is not shown). Naturally, the agreement is worse for the minimal model $L_{III}$. Figure 11 also shows the results that model $L_1$ gives for the force-constant bands of PTO’s tetragonal ground state, as compared with the first-principles calculations. As in the fixed-cell cases of figure 8, it is apparent that the considered model is not sufficient to render a precise description of all the bands. Yet, the qualitative agreement is satisfactory.

3.2.4. Temperature-dependent behavior. We studied the $T$-dependent behavior of our PTO models by running MC simulations in which both the atomic displacements and strains were allowed to thermally fluctuate. Figure 12 shows the basic results for our $L_0$ model when simulated in two different situations: (i) under the condition of zero external pressure and (ii) by imposing an external hydrostatic pressure of $-13.9$ GPa, which counteracts the underestimation of the LDA result for the cubic lattice constant. (Taking as a reference the cubic lattice constant obtained by extrapolating to 0 K the experimental results in [43], this underestimation can be approximated to be about 2.2%.) Note that this kind of correction is customarily made in LDA-based effective-Hamiltonian works [10–12], and we adopt it here for the sake of an easier comparison with the literature.

As can be appreciated from figure 12, our simulated PTO undergoes a phase transition from the high-$T$ cubic phase to a low-$T$ tetragonal structure in which one polarization...
The same as figure 12, but for the refined PTO model potentials discussed in the text. In all cases an external pressure of $-13.9$ GPa is applied. In (a) the dashed lines show the result for $L_0$.

Component ($z$ in our default Cartesian setting) becomes different from zero. The transition is accompanied by a deformation of the cell, which acquires a $c/a > 1$ aspect ratio. The computed Curie temperature is about 225 K when no external pressure is applied, and increases to about 450 K when we correct for the LDA overbinding. This is the expected behavior, as it is known that the strength of the FE instabilities in these perovskite oxides is very sensitive to volume changes (which is the reason why they have very good piezoelectric properties).

Figure 13 shows the results obtained for all the model potentials listed in table 4 simulated under the same hydrostatic pressure of $-13.9$ GPa. Remarkably, in spite of their similarly good description of the ground state energy and structure, we observe very large differences in the predicted $T_C$s. It is interesting to note that, contrary to what we would have expected [57, 58], the obtained $T_C$s do not correlate well with the energy difference between the ground state and the RS, nor with the magnitude of the FE distortion. Thus, for example, the lowest $T_C$ (about 440 K) corresponds to the $L_{III}$ model. (The same trends were observed in the MC runs with no applied pressure.) It is thus clear from these results that the computed $T_C$s are strongly dependent on details of the PES that are not reflected in the energy and structure of the ground state, a conclusion that can be extended to other physical properties that we may obtain from our MC simulations.

Hence, the results in figure 13 evidence the critical importance of developing models that include all the atomic degrees of freedom, and allow for a systematic improvement of the PES description, if we want to obtain accurate first-principles results for the thermodynamic properties of materials like PTO.

Let us conclude by giving an additional and striking example of the importance of hidden atomistic effects in determining the macroscopic properties of this material. Our best model for PTO is probably the one labeled $L^I$, which renders an FE transition at $T_C \approx 510$ K. Interestingly, Waghmare and Rabe (WR) constructed an effective Hamiltonian for PTO, considering only polar local modes and strains as the model variables, that results in a significantly higher $T_C$ of about 660 K [12]. At first sight such a discrepancy may seem surprising, and we made an effort to understand its origin in some detail. First, we checked that our model reproduces the energetics of the FE instabilities given by the WR Hamiltonian rather closely, despite the differences in the first-principles calculations (e.g., in the pseudopotentials) employed to compute the parameters. Further, we ran simulations with modified versions of our model to test subtle features of the WR energy parametrization (e.g., the inclusion of high-order terms for the polar local modes), and concluded that they cannot account for the discrepancy in the computed $T_C$.

We thus turned our attention to the qualitatively distinct features of our model. Most notably, we describe not only the FE instabilities and strains, but also the unstable AFD distortions sketched in figure 5. It is known that, in most perovskite oxides, the interaction between FE and AFD modes is a competitive one, so that they tend to suppress each other [14]. Hence, to evaluate the effect of such a competition in our simulated PTO, we ran simulations in which the $O_6$ rotational modes were not allowed. We imposed this constraint by restricting the motion of the oxygen atoms as shown in the sketch of figure 14. Let us stress that such a
constraint does not affect the energetics associated with the development of the spontaneous polarization, the FE ground state being exactly retained. Figure 14 shows the results for our $L^2$ model. In the case without AFDs we got $T_C \approx 825$ K, which lies about 300 K above the result obtained from the unconstrained simulation. (The FE–AFD competition was which lies about 300 K above the result obtained from the)

The FE–AFD interactions will be discussed at length in a future publication. We show this result here just as a striking example of the physical effects that we are likely to miss if we restrict ourselves to effective models that, in spite of example of the physical effects that we are likely to miss if we restrict ourselves to effective models that, in spite of these FE–AFD interactions may turn out to be too simple.

3.3. SrTiO$_3$

3.3.1. Harmonic terms $E_{anh}(\{u_i\})$ and $E_1(\eta)$. We extracted all the non-zero harmonic coupling terms from DFPT calculations [36, 31] carried out with ABINIT [41]. Representative results for the force-constant bands of the cubic RS are shown in figure 15. Note that in this case we only have AFD-related instabilities; indeed, our LDA calculations render low-energy, but perfectly stable, FE modes for the cubic phase of STO.

The short-range interatomic interactions that we obtained for STO have the same spatial extent as those computed for PTO and described above. As regards the electronic dielectric tensor, Born effective charges, and harmonic elastic constants, our results for STO are also analogous to the ones for PTO described above, as the number of symmetry-independent terms is the same for both materials.

3.3.2. Fitting $E_{anh}(\{u_i\})$. We fitted the terms in $E_{anh}(\{u_i\})$ by working with a training set of relevant low-symmetry phases that maintain the cubic STO cell (i.e., with $\eta = 0$). More precisely, we considered the following AFD-distorted structures: AFD$_x^I$ (I4/mcm space group), AFD$_z^I$ (I4/mcm), AFD$_x^I$ (Imma) with rotations of equal amplitude about $x$ and $z$ and AFD$_x^{\tilde{x}c}$ (R3c). As in the case of PTO, we determined such low-symmetry structures ab initio by distorting the RS according to a specific unstable eigenvector and relaxing the resulting structure while preserving the targeted symmetry. The energies and distortion amplitudes computed for these structures are given in table 5.

Additionally, in our set we also included two structures generated by distorting the cubic phase according to the lowest-energy FE eigendisplacement obtained from our DFPT calculations (which strongly resembles the typical FE unstable mode depicted in figure 5(a)). More precisely, we considered two distortions involving polarizations along the [001] and [111] Cartesian directions, respectively. We included such structures in the training set to capture the anharmonicity of the low-lying FE modes, which should play a role in determining the non-linear dielectric response properties of interest in STO.

As in the case of PTO, we worked with a relatively simple model restricted to pairwise anharmonic interactions extending up to the fourth-order of the Taylor series. Further, we restricted ourselves to interactions between first-nearest-neighboring atoms, an approximation that is justified by the rapid spatial decay of the anharmonic corrections that we observed for STO as well. As we have mentioned already, these truncations result in the 15 SATs listed in table 1.

Additionally, in the case of STO we tried to identify the minimal set of SATs that capture the energetics of

| Structure          | Method | Energy (meV/f.u.) | $O_6$ rot. (Å) |
|--------------------|--------|-------------------|----------------|
| AFD$_x^I$ (I4/mcm) | LDA    | -18.9             | 6.7            |
|                   | Model  | -18.8             | 6.6            |
| AFD$_x^I$ (Imma)  | LDA    | -19.4             | 4.9            |
|                   | Model  | -20.0             | 4.9            |
| AFD$_x^{\tilde{x}c}$ (R3c) | LDA | -18.8             | 3.9            |
|                   | Model  | -19.7             | 3.9            |
| AFD$_x^I$ (P4/mmb) | LDA    | -3.7              | 4.5            |
|                   | Model  | -3.2              | 4.3            |
| AFD$_x^I$ (I4/mcm)$^*$ | LDA | -23.0             | 7.5            |
|                   | Model  | -23.0             | 7.4            |

$\approx$ 825 K, $\eta = 0$.

Figure 15. The same as figure 4, but for SrTiO$_3$. TABLE 5. Structural parameters of STO’s low-energy phases (see the text) as obtained from first-principles LDA calculations and from the presented model. A cubic cell with $a = 3.845$ Å was used in all cases, except for the one marked with an asterisk; in that case, a full structural relaxation was performed and the resulting pseudocubic lattice constants are given. The amplitude of the AFD modes is quantified by the corresponding $O_6$ rotation angle given in degrees, with the result for the RS as well as the zero of energy. Note that the AFD$_x^I$ structure displays additional small distortions; for example, there are anti-polar displacements of the Sr atoms, the off-centering being about 0.008 Å and about 0.002 Å for the LDA and model calculations, respectively.
the corresponding parameters by optimizing \( GF \) with numbers 4, 12, 13, and 15 in table 1. We computed constructed a model including only the fourth-order terms cannot be distinguished.

All the states shown preserve the cubic cell of the RS \((\eta = 0)\). The \( \Lambda^1 \) and \( \Lambda^2 \) curves are essentially on top of each other and cannot be distinguished.

The agreement with the first-principles data is very good, and we checked that no significant improvement is obtained by including other SATs listed in table 1.

To construct the present model of STO, we did not take the additional step of minimizing a goal function \( GF_{\text{hess}} \) with information about the Hessian matrices of the low-energy structures. It is therefore interesting to check whether the mode stiffnesses calculated using our effective potential reproduce well the first-principles data. Representative results are depicted in figure 17(a), where we show DOS plots constructed from the force-constant eigenvalues for the \( \Lambda^1 \) structure, which is the predicted ground state of the material for \( \eta = 0 \) (see table 5). As can be seen, our model properly describes the structure as being a stable one (i.e., we find no modes with negative stiffness); it also reproduces well the general shape of the spectrum, but fails to capture its details. In fact, the DOS predicted by our model for the \( \Lambda^1 \) structure is very similar to the one for the cubic phase shown in figure 15; this is a rather natural result, given that we considered a minimal \( \Lambda_{\text{anis}} \) term whose parameters were fitted to reproduce only energies and structures.

3.3.3. Strain–phonon term \( E_{\text{sp}}(\{u\}, \eta) \). As in the case of PTO, we considered only the lowest-order terms that are allowed by symmetry and capture the most important strain–phonon effects, which are given by the coefficients \( \Lambda^{(1,2)} \). We computed them directly by employing the finite-difference approach summarized by equations (31) and (37), using strains of \( \pm 2\% \) for the finite-difference calculations. The resulting model describes the correct ground state of STO, which is characterized by an \( \Lambda^1 \) distortion (14/mcm space group). Note that, for \( \eta = 0 \), our first-principles calculations indicate that the ground state is associated with an \( \Lambda^2 \) distortion. Hence, as in PTO’s case, the strain–phonon couplings play a key role in determining the symmetry of the lowest-energy structure; also like in the case of PTO, such an effect is captured by the \( \Lambda^{(1,2)} \) parameters computed directly via our finite-differences scheme, even though they were not explicitly fitted to do so.

This model gives an excellent quantitative description of STO’s ground state (see table 5), and reproduces reasonably well the corresponding Hessian matrix (see figure 17(b)). Hence, we took this potential as our effective model for STO, without any further refinement.

3.3.4. Temperature-dependent behavior. Figure 18 shows the basic results from the MC simulations performed with our model potential for STO. As in the case of PTO, we ran simulations (i) under zero applied pressure and (ii) under an expansive hydrostatic pressure of \(-9.2\) GPa, which approximately corrects for the LDA overbinding. (To compute the correction, we used as reference a cubic lattice constant of 3.90 Å, obtained by extrapolating to 0 K the experimental results for the cubic phase of STO in [59].) In both cases we get a phase transition from the high-\( T \) cubic phase to a low-\( T \) tetragonal structure (14/mcm) with \( \Lambda^2 \) character. The transition temperature is about 300 K when no pressure is applied, and decreases to about 160 K upon application of \(-9.2\) GPa. This is the expected behavior, as the applied pressure is known to (i) reduce the strength of the AFD instabilities and (ii) enhance the FE–AFD competition by softening the FE distortions. These effects have been studied in previous theoretical works on STO and related perovskites [14, 60]; we have captured them implicitly (i.e., without any ad hoc fitting) when constructing our model.

3.4. Discussion

Let us conclude this section by commenting on how well our models reproduce experiment. In the limit of 0 K, our \( L^1 \) model for PTO renders a spontaneous polarization of
about 0.99 C m$^{-2}$ and $c/a \approx 1.07$, to be compared with the values of 0.85 C m$^{-2}$ and 1.07, respectively, obtained by extrapolating to low temperatures the experimental results in [43]. In the case of STO, at low temperatures we get $c/a \approx 1.007$ and an AFD$^\alpha$ rotation angle of about 5.8$^\circ$, to be compared, respectively, with experimental values of 1.001 and 2.0$^\circ$ measured at 1.5 K [61]. Note that, in this regard, our models perform as well as an LDA theory with the above-mentioned correction for the overbinding. The agreement is good in the case of PTO, but for STO we clearly exaggerate the magnitude of the tetragonal distortion, in line with first-principles results in the literature [62].

To evaluate the performance of our effective potentials, it is more interesting to consider the temperature-dependent behavior. In particular, let us focus on one of the most basic properties of these ferroic materials, namely, the temperature of their structural transition.

The effective-Hamiltonian approach to FE perovskites has been very successful in reproducing non-trivial behaviors of many complex materials qualitatively; examples include the phase diagram of chemically-disordered solid solutions [16, 17], the occurrence of multiferroic orders [18, 19], strain- [63], finite-size- [64–66], and electrostatics- [65, 66] driven effects, and quantum-phase transitions [15, 67]. However, whenever the model parameters have been obtained directly from first principles, and despite the use of pressure corrections such as the one considered here, the quantitative agreement for the predicted transition temperature has been poor. Thus, for example, the cubic-to-tetragonal transition of BaTiO$_3$ was predicted to occur at a temperature ranging from 297 K [10, 11] to 335 K [56], while the experimental result is 400 K. In the case of KNbO$_3$ [68], the simulations render a cubic-to-tetragonal transition at 370 K, while the experimental $T_C$ is about 700 K. In this context, the result of Waghmare and Rabe [12] for PTO—i.e., a $T_C$ of 660 K that compares reasonably well with the observed value of 760 K—might be considered as an example of good agreement between theory and experiment.

The difficulties of the effective-Hamiltonian method in obtaining correct transition temperatures were analyzed in [69], where it was suggested that the discrepancy is to be partly attributed to an incorrect description of thermal expansion, a problem that is a direct consequence of the coarse-graining step involved in the construction of the model. Indeed, the effective Hamiltonians tend to give an essentially null thermal expansion at high temperatures (see, e.g., figure 10 in [12]), which is clearly against the experimental evidence.

Our models take into account all the degrees of freedom in the material, and we can thus hope to improve on this aspect. As can be seen in figure 12, for PTO we get a thermal expansion coefficient at high temperatures between $8.3 \times 10^{-6}$ K$^{-1}$ (from simulations with no applied pressure) and $9.1 \times 10^{-6}$ K$^{-1}$ (obtained when pressure is applied to correct for the LDA overbinding), to be compared with the experimental result of $12.6 \times 10^{-6}$ K$^{-1}$ [43]. Similarly, figure 18 shows a thermal expansion between $7.2 \times 10^{-6}$ and $8.3 \times 10^{-6}$ K$^{-1}$ for STO at high temperatures, to be compared with the value of $8.8 \times 10^{-6}$ K$^{-1}$ obtained from experiments [59]. Hence, our models clearly improve the effective-Hamiltonian description of this effect; yet, the discrepancy between the computed and measured transition temperatures remains present.

In the case of PTO, we have found solid evidence that $T_C$ depends very significantly on details of the PES that are most often ignored in theoretical works. In particular, our results strongly suggest that a realistic model for PTO must necessarily include both FE and AFD degrees of freedom, as their competition is far from being negligible. Accordingly, we should probably consider as partly fortuitous the relatively accurate result obtained for $T_C$ in [12], where a model without AFDs was employed.

Our results lead to the following important conclusion: we cannot expect to obtain accurate values for PTO’s $T_C$ from models that only reproduce the basic first-principles results (i.e., energy and structure) for the low-symmetry phases of the material. Further, in order to improve the agreement with experiment, we should probably extend our model to better reproduce the lattice-dynamical properties of the key low-energy structures and other details of the PES. Our results in figure 13 suggest that improvements of that sort, even though they may look like second-order corrections to the relevant PES, can actually affect the computed $T_C$ by as much as 100 K.

On the other hand, such a strong sensitivity to the details of the potential has important implications regarding...
the accuracy required from the first-principles methods used to compute the model parameters. Together with the incorrect treatment of thermal expansion, the authors of [69] mentioned DFT inaccuracy as the second reason to explain the fact that the Curie temperatures obtained from effective-Hamiltonian simulations are typically too low as compared with the experimental ones. Their conjecture was that the FE instabilities obtained from first principles were too weak, meaning that DFT was probably underestimating the \(|E_{gs} - E_{RS}|\) energy difference between the RS and the FE ground state. Our results show that, while important, this is by no means the only characteristic of the PES that has a large impact on the computed \(Tc\). Hence, to get accurate results, we need a first-principles theory that not only describes correctly the energetics of the FE instability, but also captures accurately more subtle PES features such as the anharmonic couplings between different structural distortions, including those that do not participate directly in the transitions. These are very demanding requirements for our simulation techniques; thus, it is unclear whether we currently have first-principles methods that can predict an accurate \(Tc\) for materials like PTO.

Most of the above considerations probably apply to STO as well. Yet, as the transition occurs at a relatively low temperature in this case, an additional factor must be taken into account. As demonstrated in a variety of theoretical works [15, 67, 70], in order to get a precise calculation of the structural transition temperatures of ABO\(_3\) perovskites, it is important to consider the zero-point fluctuations of the atoms. Indeed, Zhong and Vanderbilt simulated STO at both the classical and quantum-mechanical levels, using an effective Hamiltonian constructed from first principles, and found that quantum fluctuations shift down the cubic-to-tetragonal transition by about 20 K [15]. (Quantum effects will typically promote disorder, and thus result in reduced transition temperatures.) Hence, in the case of STO, we can assume that part of the discrepancy between our computed transition temperature (\(\sim 160\) K) and the experimental one (105 K) comes from the fact that we treated atoms as classical objects in our MC simulations. Finally, let us note that our result for the transition temperature seems consistent with the value of about 130 K reported in [15] for the classical case.

4. Summary and conclusions

We have described a method for the construction of first-principles model potentials that permit large-scale simulations of lattice-dynamical phenomena. Our scheme mimics the traditional approach to lattice dynamics in solid-state textbooks, i.e., we start from a suitably chosen reference structure (RS) and express the energy of the material as a Taylor series for the structural distortions of such an RS. There are many advantages in adopting such a simple approach; most notably, the potentials can be trivially formulated for any compound, and their ability to reproduce the first-principles data can be improved in a systematic and well-defined way. Further, most of the potential parameters correspond to the usual (elastic, force-constant, etc) tensors discussed in condensed-matter theory, which allows for a transparent physical interpretation. It is also important to note that expanding around an RS implies some limitations; most notably, our models are designed to describe phenomena involving relatively small distortions of the RS, and drastic changes in atomic coordination (e.g., formation or breaking of chemical bonds) fall in principle out of their scope.

We have described the details of such an approach, and proposed a practical strategy to compute the model parameters from first principles. Our method is especially convenient in that regard too, as we have shown that many of the key model parameters (e.g., all the couplings at the harmonic level) can be readily obtained from density-functional-perturbation-theory calculations that are widely available today.

We have illustrated our method with applications to two especially challenging cases, namely, the ferroic oxides PbTiO\(_3\) and SrTiO\(_3\). These materials undergo structural phase transitions driven by soft phonon modes, which implies that the potential-energy surface (PES) that our models have to capture is strongly anharmonic. We have discussed in detail the case of PTO, where the large structural deformations involved in the ferroelectric phase transition make it especially challenging to construct a quantitatively accurate model. Moreover, we have solved our PTO potential by means of Monte Carlo simulations and discovered a variety of unexpected effects, ranging from novel structural phases when the strain deformations are constrained to a surprisingly strong dependence of the computed Curie temperature on the details of the PES. The case of STO turned out to be much easier to tackle and led to quantitatively more accurate predictions, probably because the structural distortions involved in its ferroic transformation are smaller. The connections of our method with the so-called first-principles effective Hamiltonian approach to the study of temperature-driven effects in ferroic perovskite oxides—which was introduced about 20 years ago, and of which our scheme can be considered a natural extension and generalization—have been discussed in some detail.

We believe that these effective potentials can be used to great advantage in the investigation of the thermodynamic properties of (meta)stable material phases, which are largely dominated by harmonic effects that our models describe with first-principles accuracy. While we have not considered any such case in this work, we think that the demonstrated ability of the present models to deal with strongly anharmonic effects suggests that their application to (the much simpler) quasi-harmonic cases will be a very successful one. Indeed, recent results based on a similar scheme [29] are very promising in this regard. Hence, we hope that the current methodology can become a standard tool for large-scale simulations of the lattice-dynamical properties of materials at realistic operating conditions of temperature, pressure, etc.

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