Effective-Hamiltonian modeling of external pressures in ferroelectric perovskites

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The phase-transition sequence of a ferroelectric perovskite such as $BaTiO_3$ can be simulated by computing the statistical mechanics of a first-principles derived effective Hamiltonian [Zhong, Vanderbilt and Rabe, Phys. Rev. Lett. 73, 1861 (1994)]. Within this method, the effect of an external pressure (in general, of any external field) can be studied by considering the appropriate "enthalpy" instead of the effective Hamiltonian itself. The legitimacy of this approach relies on two critical assumptions that, to the best of our knowledge, have not been adequately discussed in the literature to date: (i) that the zero-pressure relevant degrees of freedom are still the only relevant degrees of freedom at finite pressures, and (ii) that the truncation of the Taylor expansion of the energy considered in the effective Hamiltonian remains a good approximation at finite pressures. Here we address these issues in detail and present illustrative first-principles results for $BaTiO_3$. We also discuss how to construct effective Hamiltonians in cases in which these assumptions do not hold.

I. INTRODUCTION

A few years ago it was shown that it is possible to reproduce the phase transition sequence of a ferroelectric such as $BaTiO_3$ by simulating the statistical mechanical properties of an effective Hamiltonian built on the basis of first-principles calculations [1]. Since then, this approach has been used to study the phase diagrams and electromechanical responses of other perovskite crystals ($SrTiO_3$ [2], $PbTiO_3$ [3], and $KNbO_3$ [4]), and even of *disordered* perovskite solid solutions ($Pb(Zr_{1-x}Ti_x)O_3$ (PZT) [5] and $Pb(Sc_{0.5}Nb_{0.5})O_3$ [6]). These calculations have typically resulted in a very good qualitative agreement with experiment and clear physical pictures of the phenomena studied. Presently, even though the method usually gives poor results for the actual values of the transition temperatures and other quantities, it is regarded as having the predictive power necessary to tackle materials-design problems [7, 8].

An effective Hamiltonian can be viewed as a Taylor expansion of the energy of the system, in terms of a set of relevant degrees of freedom, around a high-symmetry reference structure. For ferroelectric perovskites, the relevant variables are typically the strains and, most importantly, the local polar distortions that sum up to produce the spontaneous polarization. The high-symmetry reference structure is chosen to be the non-polar, cubic perovskite phase, whose equilibrium volume is computed *ab initio*.

Very conveniently, within this approach it is straightforward to consider the effect of external fields on the system. One just has to add a term to the Hamiltonian that transforms the energy into the appropriate enthalpy. For instance, an external hydrostatic pressure p would enter the model in a term pV, where V is the volume of the simulated system. Examples of such applications are the calculation of the T-p phase diagram of $BaTiO_3$ [9] and, very recently, the study of electric-field driven transition paths in PZT [10].

This approach to modeling external fields stems directly from statistical mechanics, and it is exact *provided the considered Hamiltonian is the complete Hamiltonian of the system.* Using effective *incomplete* Hamiltonians actually involves a number of implicit approximations in the description of the effect of an external field. To the best of our knowledge, these implicit approximations have neither been adequately discussed, nor has their importance been carefully tested, in the literature to date.

In this paper we address these questions in detail. For concreteness, we consider the case of an external pressure, but our formal argument applies to any external field. We illustrate the discussion with calculations of the effect of pressure on $BaTiO_3$, which should be representative of ferroelectric perovskites and is specially interesting because of the discrepancy between the theoretical [9] and experimental [11] results for its T-p phase diagram.

The paper is organized as follows. In Section II we discuss the pressure dependence of the relevant degrees of freedom that define the effective Hamiltonian. In Section III we show how the truncation in the effective-Hamiltonian energy expansion actually implies an approximation in what we call the "pressure dependence" of the parameters of the model. In Section IV we tackle the issue of the anharmonic couplings between the chosen relevant degrees of freedom and the rest of variables in the system. Finally, we summarize and present our conclusions in Section V.

II. RELEVANT DEGREES OF FREEDOM AS A FUNCTION OF PRESSURE

The fundamental variables entering effective Hamiltonians for ferroelectric perovskites are the localized, polar displacement patterns associated with the spontaneous polarization. In order to define these local polar modes *ab initio*, one examines the calculated phonon [12] dispersion curves of the high-symmetry cubic phase; the soft phonons (i.e., those with very small or negative force constant) are obviously those to be included in the model. (Note that the spontaneous polarization will correspond to an unstable zone-center phonon.) The local modes, or lattice Wannier functions, are then obtained from the corresponding eigenvectors [13].

Taking the calculated equilibrium, high-symmetry phase as a reference implies that the relevant variables we determine are actually the relevant variables *at zero pressure*. Including the effect of pressure by simply adding an extra pV term to the Hamiltonian thus relies on the fundamental assumption that the relevant variables at zero pressure will remain the relevant variables at finite pressure. There are two situations in which this assumption could fail, namely the applied pressure could give raise to additional soft modes and/or the zero-pressure relevant configuration space could change significantly. In the former case, the obvious solution is to include the new soft modes in the model. In the latter, one would have to redetermine the relevant polar degrees of freedom, now under applied pressure, and recalculate the effective Hamiltonian accordingly.

We have performed first-principles calculations to study these issues in $BaTiO_3$ [14]. In this material, the modes that most likely may become soft under compression are those at the M and R zone-boundary points that involve rotations of the oxygen octahedra. We have calculated the evolution of the eigenvalues of such modes as a function of the lattice parameter, ranging from $a = 7.46$ a.u. (the calculated equilibrium lattice parameter of the cubic phase) to $a = 7.36$ a.u. (which is well beyond the value at which the ferroelectric instability disappears; see next section). We find no softening with increasing pressure; on the contrary, the modes become slightly harder. (For instance, the eigenvalues of the modes at R, which are softer than those at M, are 0.0200 a.u. and 0.0220 a.u. for $a = 7.46$ a.u. and $a = 7.36$ a.u. respectively.) On the other hand, the evolution with pressure of the relevant variables related to the ferroelectric instability can be monitored by observing the change of the zone-center soft mode. We find that the overlap between the unstable eigenmode at $a = 7.46$ a.u. and the corresponding, nearly-unstable eigenmode at $a = 7.36$ a.u. is above 98%. In summary, for $BaTiO_3$ the relevant variables defined at the zero-pressure equilibrium lattice constant remain a very good approximation all through the interesting pressure range.

III. "PRESSURE DEPENDENCE" OF THE HAMILTONIAN PARAMETERS

Let us assume that the zero-pressure relevant degrees of freedom continue to be the relevant ones in the pressure range of interest. In the following we argue that, even in this case, the effect of pressure is not fully captured by the addition of the pV term.

For simplicity, we consider a one dimensional ferroelectric, and describe it in terms of the macroscopic variables P (polarization) and η (strain). For small P and η, the energy of the system can be written as a low-order Taylor expansion around the high-symmetry paraelectric phase ($P = \eta = 0$),

$$E(P,\eta) = E_0 - C_{2,0}P^2 + C_{4,0}P^4 + C_{0,2}\eta^2 - C_{2,1}P^2\eta, \tag{1}$$

where all the expansion coefficients (in obvious notation) are chosen to be positive. (The maximum orders included in the expansion of Eq. (1) are those normally adopted in the effective Hamiltonians proposed to date in the literature [1, 4, 5, 6].) Let us include the effect of an external pressure p by adding the term $pV_0(1+\eta)$, with V_0 the equilibrium volume of the paraelectric phase. It is now convenient to consider the change of variables

$$\eta \rightarrow \tilde{\eta} - \frac{V_0}{2C_{0,2}}p \equiv \tilde{\eta} + \eta_p \tag{2}$$

where $V_0(1+\eta_p)$ is the equilibrium volume of the paraelectric phase under applied pressure. The enthalpy then becomes

$$\begin{aligned} E(P,\eta;p) &= E_0(p) - \left[C_{2,0} - \frac{V_0 C_{2,1}}{2C_{0,2}}p\right]P^2 \\ &\quad + C_{4,0}P^4 + C_{0,2}\tilde{\eta}^2 - C_{2,1}P^2\tilde{\eta}, \end{aligned} \tag{3}$$

where $E_0(p)$ is the pressure-dependent energy of the nonpolar phase. If we now denote the bracketed prefactor of the P^2 term as $\tilde{C}_{2,0}$, and also introduce $\tilde{E}_0$, we can rewrite the enthalpy as

$$\tilde{E}(P,\tilde{\eta}) = \tilde{E}_0 - \tilde{C}_{2,0}P^2 + C_{4,0}P^4 + C_{0,2}\tilde{\eta}^2 - C_{2,1}P^2\tilde{\eta}, \tag{4}$$

which is formally identical to Eq. (1). Thus, we have proven that, within our model, the system under applied pressure is in all respects equivalent to the original, pressure-free system described by Eq. (1), but with some modified parameters (indicated by tildes) that can be regarded as being "pressure dependent". (In the following, references to the "pressure dependence" of the parameters of the Hamiltonian should be understood in this sense.)

Having reformulated the problem in this way, an obvious question arises. If E_0 and $C_{2,0}$ are modified by pressure, why is it that the remaining parameters in Eq. (1) are not? The answer is that pressure should indeed affect the rest of the parameters in Eq. (1), but this effect is not captured by our model because we are using a truncated Taylor expansion of the energy. Imagine, for instance, that Eq. (1) contained the higher-order term $C_{4,1}P^4\eta$. The variable change in Eq. (2) would then generate new

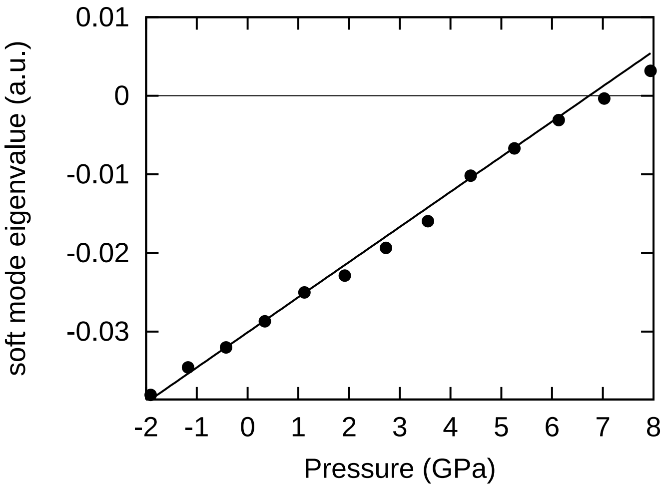

FIG. 1: Calculated eigenvalue of the ferroelectric soft mode of $BaTiO_3$ as a function of pressure (dots), as compared with the behavior predicted (see text) from the zero-pressure effective Hamiltonian (solid line). (See [14] for the technical details of the *ab initio* calculations.) From the explicit calculation we obtain a ferroelectric transition point at $p_c = 7.0$ GPa ($V_c/V_0 = 0.966$), while the effective-Hamiltonian approach places the transition at $p_c = 6.7$ GPa ($V_c/V_0 = 0.964$, as given by the equation of state built into the effective Hamiltonian itself). In both cases, the calculated equilibrium volume of the cubic phase is $V_0 = 414$ a.u.

terms $C_{4,1}P^4\tilde{\eta} + C_{4,1}\eta_p P^4$, thus modifying $C_{4,0}$ to become $\widetilde{C}_{4,0} = C_{4,0} + C_{4,1}\eta_p$.

The previous argument can readily be applied to the microscopic effective Hamiltonians of interest [17]. We have thus shown that a truncation of the energy expansion, which may be perfectly well justified for the calculation of zero-pressure properties, actually implies an approximation in the pressure dependence of the parameters of the model. Obviously, we can improve on this approximation by including higher-order terms in the effective Hamiltonian. However, our experience tells us that it is usually difficult to calculate high-order terms accurately, and the very issue of where to truncate the expansion may become a problem. There is, fortunately, an alternative approach suggested by the derivation above. One can instead take the equilibrium, high-symmetry phase at pressure p as the reference structure from which one calculates the Taylor expansion of the energy. Such an expansion, which could likely be kept low-order, would be analogous to Eq. (4) but with all the parameters containing their full pressure dependence by construction.

In order to make these ideas explicit, we have calculated the pressure dependence of the parameters in the effective Hamiltonian of $BaTiO_3$ [14]. The soft-mode eigenvalue, which is exactly the equivalent of $-2\widetilde{C}_{2,0}$ in Eq. (4), is computed as a function of the unit-cell volume, and the corresponding pressure is determined from the equation of state of the cubic phase. The results are shown in Fig. 1. We find that the linear law resulting from the pV term (see the bracketed term in Eq. (3)) turns out to agree surprisingly well with the values explicitly calculated at different pressures. We also computed the pressure dependence of the parameters that are analogous to $C_{4,0}$, $C_{0,2}$ and $C_{2,1}$ in Eq. (1). In all cases the values calculated as a function of pressure lay within approximately 10% of the zero-pressure value. Very importantly, this applies to the parameter that determines the relative stability of the different ferroelectric phases of $BaTiO_3$ (γ' in Ref. [16]). Therefore, we find that the ground state of the system is rhombohedral throughout the pressure range in which the ferroelectric instability exists, in agreement with the first-principles effective-Hamiltonian results of Zhong *et al.* [9].

IV. THE COUPLING BETWEEN RELEVANT AND IRRELEVANT VARIABLES

The experimental work of Ref. [11] suggests that, along isotherms at very low temperature, $BaTiO_3$ undergoes a transition sequence with increasing pressure that progresses from the zero-pressure ferroelectric rhombohedral phase to ferroelectric orthorhombic, then ferroelectric tetragonal, and finally paraelectric cubic phases. As we have seen in the previous sections, we have found no indication of such a behavior in our first-principles results. This disagreement is not necessarily a serious one, since the authors of Ref. [11] attributed their observed transition sequence to quantum fluctuations (zero-point atomic motion), an effect that is not taken into account in our calculations. In any case, it led us to explore yet another possible effect of pressure that could, in principle, account for such a discrepancy.

The effective-Hamiltonian approach relies on the assumption that the coupling between the chosen relevant variables and the rest of the degrees of freedom in the system is not important. Since the relevant modes are defined in terms of phonons that diagonalize the harmonic part of the total Hamiltonian of the system, such a coupling is anharmonic, which partly justifies our neglecting it. However, we know that in $BaTiO_3$, as we approach the critical pressure at which the ferroelectric instability disappears, the energy differences among the various low-symmetry phases go to zero. Small anharmonic effects could then be essential to the determination of the ground state of the system. Note that, if this were the case, the usual effective-Hamiltonian approach, in which the relevant variables are identified by looking at the *harmonic* phonon dispersion curves, should be modified.

We can study this issue very easily in $BaTiO_3$ by fully relaxing the structure of the system in different constrained symmetries, while keeping the volume fixed [18]. The symmetries we consider are of course the tetragonal, orthorhombic, and rhombohedral ones corresponding to

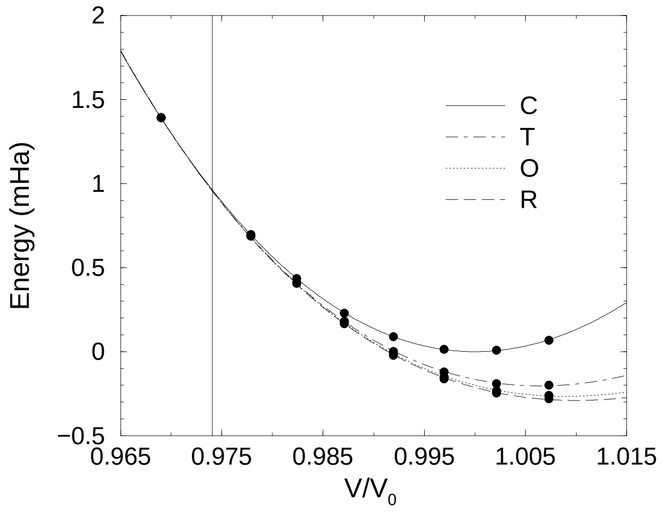

FIG. 2: Energies of the different phases of $BaTiO_3$ (cubic, tetragonal, orthorhombic, and rhombohedral) as a function of the volume of the unit cell. The energies are computed by relaxing the atomic positions and cell shape under the constraints of preserving the corresponding symmetry and keeping the cell volume fixed. (See [18] for the technical details.) We have marked with a vertical line the ferroelectric transition point between the non-polar cubic and polar rhombohedral phases, located at $V_c/V_0 = 0.974$ ($p_c = 5.6$ GPa) where $V_0 = 417$ a.u. is the calculated equilibrium volume of the cubic phase. The discrepancy between these numbers and those in the caption of Fig. 1 is not surprising if we take into account that they have been computed using two different codes (and two different kinds of pseudopotential schemes).

the ferroelectric phases of the material, and we explore the interesting range of volumes. Figure 2 shows the energy of the relaxed structures as a function of volume. For $V/V_0 < 0.980$ the energies of the different phases differ by less than 0.01 mHa. Such small differences are beyond the accuracy of our computational technique and, therefore, we are not able to study the critical region in detail. Nevertheless, we can determine the critical volume quite reliably as the point at which $C_{2,0}$ passes through zero; we obtain $V_c/V_0 = 0.974$, indicated with a vertical line in Fig. 2. On the other hand, we find that, down to $V/V_0 \sim 0.977$, there is no common tangent among the curves in Fig. 2 that would correspond to a first-order phase transition between two ferroelectric phases at $p < p_c$. It thus seems reasonable to conclude that the calculated ground state is rhombohedral up to p_c, the point at which it undergoes a second-order transition to the paraelectric cubic phase. This result is in complete agreement with the predictions of the effective-Hamiltonian approach.

The importance of the above-mentioned anharmonic couplings in determining the ground state of the system can be quantified, for a given volume, by expanding the displacement vector corresponding to the relaxed atomic positions as a linear combination of the zone-center modes calculated at that same volume. We find that, throughout the interesting range, the ferroelectric soft mode accounts for approximately 99% of the total atomic relaxation. This result further justifies neglecting the anharmonic couplings among relevant and irrelevant variables in the case of $BaTiO_3$.

V. SUMMARY AND CONCLUSIONS

In the usual approach to simulating external pressures within the effective-Hamiltonian scheme, one starts from the calculated zero-pressure effective Hamiltonian and adds to it a pV term to obtain the appropriate enthalpy. Such a procedure implies a number of approximations that we have discussed in detail in this paper. Our discussion is actually general, and applies to any external field.

On the one hand, we have seen that there are approximations related with the determination of the relevant degrees of freedom to be included in the model. In principle, one should determine the relevant variables as a function of pressure. One should also check that the relevant variables do not have significant anharmonic couplings with the rest of the degrees of freedom of the system throughout the interesting pressure range.

On the other hand, we have discussed a rather subtle implicit approximation that has to do with the truncation of the energy expansion in the effective Hamiltonian. We have shown that such a truncation, which may be justified for the purpose of zero-pressure calculations, actually implies an approximation in what we have called the "pressure dependence" of the parameters of the model. As a solution to this problem we propose the calculation of effective Hamiltonians "under pressure," meaning that for a given pressure we would take as our reference structure the calculated, equilibrium high-symmetry phase at that pressure.

We have studied in detail all these issues for $BaTiO_3$. We have shown that all the previous approximations are actually highly accurate for this material, which we believe should be representative of ferroelectric perovskites. The usual approach to simulating external pressures thus seems to be fairly reliable.

Regarding the T-p phase diagram of $BaTiO_3$, our results indicate that at a *classical* level (i.e., without considering the zero-point motion of the ions) the only possible polar phase at 0 K is the rhombohedral one. On the other hand, as Fig. 2 shows, the differences in energy among the ferroelectric phases become very small as the volume decreases towards V_c. It thus seems possible that, at low temperatures, the quantum fluctuations of the ions may be able to change the relative stability of the ferroelectric phases and lead to a phase diagram similar to the one reported by Ishidate *et al.* (see Fig. 1 in Ref. [11]). This very interesting question will be addressed elsewhere [21].

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