

Electric displacement as the fundamental variable in electronic-structure calculations

Massimiliano Stengel^{1*}, Nicola A. Spaldin¹ and David Vanderbilt²

Finite-field calculations in periodic insulators are technically and conceptually challenging, owing to fundamental problems in defining polarization in extended solids. Although significant progress has been made recently with the establishment of techniques to fix the electric field $\mathbf{E}$ or the macroscopic polarization $\mathbf{P}$ in first-principles calculations, both methods lack the ease of use and conceptual clarity of standard zero-field calculations. Here we develop a new formalism, in which the electric displacement $\mathbf{D}$, rather than $\mathbf{E}$ or $\mathbf{P}$, is the fundamental electrical variable. Fixing $\mathbf{D}$ has the intuitive interpretation of imposing open-circuit electrical boundary conditions, which is particularly useful in studying ferroelectric systems. Furthermore, the analogy to open-circuit capacitors suggests an appealing reformulation in terms of free charges and potentials, which dramatically simplifies the treatment of stresses and strains. Using PbTiO_3 as an example, we show that our technique enables full control over the electrical variables within the density functional formalism.

The development of the modern theory of polarization¹ has fuelled exciting progress in the theory of the ferroelectric state. Many properties that could previously be inferred only at a very qualitative level can now be computed with quantum mechanical accuracy within first-principles density functional theory. Early *ab initio* studies focused on bulk ferroelectric crystals, elucidating the delicate balance between covalency and electrostatics that gives rise to ferroelectricity. Over time, these methods were extended to treat the effects of external parameters such as strains or electric fields^{2,3}. Of particular note is the recent introduction of a method for performing calculations at fixed macroscopic polarization $\mathbf{P}^4$. The ability to compute crystal properties from first principles as a function of $\mathbf{P}$ provides an intuitive link to Landau–Devonshire and related semiempirical theories in which $\mathbf{P}$ serves as order parameter.

Despite its obvious appeal, however, the constrained- $\mathbf{P}$ method has found limited practical application so far for several reasons. First, fixing $\mathbf{P}$ does not correspond to experimentally realizable electrical boundary conditions (Fig. 1). Second, in an inhomogeneous heterostructure, the local polarization can vary from one layer to another, and its average is therefore best regarded as a derived, not a fundamental, quantity. Finally, the procedure used to constrain $\mathbf{P}$ in the electronic minimization is relatively involved, hampering its applicability to large systems, where computational efficiency is crucial. In the following we show that considering $\mathbf{D}$ as the fundamental electrical variable overcomes these physical limitations, and that constraining $\mathbf{D}$ rather than $\mathbf{P}$ leads to a simpler implementation.

Formalism

We consider a periodic insulating crystal defined by three primitive translation vectors $\mathbf{a}_j$, with Ω the unit cell volume, and we introduce the new functional

$$U(\mathbf{D}, \nu) = E_{\text{KS}}(\nu) + \frac{\Omega}{8\pi} [\mathbf{D} - 4\pi\mathbf{P}(\nu)]^2 \quad (1)$$

$U(\mathbf{D}, \nu)$ depends directly on an external vector parameter $\mathbf{D}$, and indirectly on the internal (ionic and electronic) coordinates

ν through the Kohn–Sham energy E_{KS} and the Berry-phase polarization $\mathbf{P}$ (ref. 1). (For the moment we fix the lattice vectors; strains will be discussed shortly.) The minimum of U at fixed $\mathbf{D}$ is given by

$$\left. \frac{\partial U}{\partial \nu} \right|_{\mathbf{D}} = \frac{\partial E_{\text{KS}}}{\partial \nu} - \Omega (\mathbf{D} - 4\pi\mathbf{P}) \cdot \frac{\partial \mathbf{P}}{\partial \nu} = 0$$

Comparing with the fixed- $\mathbf{E}$ approach of refs 2,3 in which the electric enthalpy F is given by

$$F(\mathbf{E}, \nu) = E_{\text{KS}}(\nu) - \Omega \mathbf{E} \cdot \mathbf{P}(\nu) \quad (2)$$

we see that

$$\left. \frac{\partial F}{\partial \nu} \right|_{\mathbf{E}} = \left. \frac{\partial U}{\partial \nu} \right|_{\mathbf{D}} \quad (3)$$

provided that we set $\mathbf{E} = \mathbf{D} - 4\pi\mathbf{P}$. We thus discover that $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ is the macroscopic electric displacement field. The functional in equation (1) takes the form $U = E_{\text{KS}} + (\Omega/8\pi) \mathbf{E}^2$, which is the correct expression for the internal energy of a periodic crystal when a uniform external field is present (details are given in Supplementary Information, Section S2.4). Equation (1) thus provides a framework for finding the minimum of the internal energy $U(\mathbf{D})$ with respect to all internal degrees of freedom at specified electric displacement $\mathbf{D}$. This is the essence of our constrained- $\mathbf{D}$ method.

As a consequence of equation (3), the method is algorithmically very similar to a standard finite- $\mathbf{E}$ -field calculation^{2,3}. In particular, the Hellmann–Feynman forces are computed in the same way. The only difference is that the field is updated according to $\mathbf{E} = \mathbf{D} - 4\pi\mathbf{P}$ on every iteration of the self-consistency (or ionic-relaxation) cycle. This implies that the implementation and use of the constrained- $\mathbf{D}$ method in an existing finite- $\mathbf{E}$ -field code is immediate; in our case it required the modification of only two lines of code.

The effect of constraining $\mathbf{D}$, rather than $\mathbf{E}$, essentially corresponds to the imposition of longitudinal, rather than

¹Materials Department, University of California, Santa Barbara, California 93106-5050, USA, ²Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA. *e-mail: stengel@mrl.ucsb.edu.

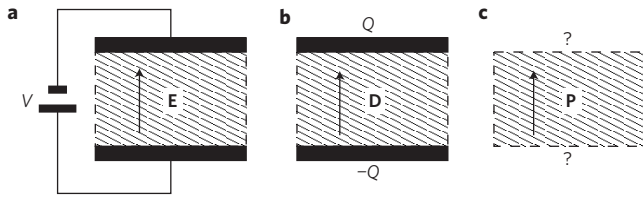


Figure 1 | Electrical boundary conditions within different methods.

a, The fixed-**E** method corresponds to adopting closed-circuit boundary conditions with a constant applied bias V . **b**, Constraining **D** corresponds to a capacitor in open-circuit conditions with a fixed value of the free charge Q on the plates. **c**, Constraining **P** does not correspond to a clear experimental set-up.

transverse, electrical boundary conditions. For example, as we shall see below, the phonon frequencies obtained from the force-constant matrix computed at fixed **D** are the longitudinal optical ones, whereas the usual approach yields instead the transverse optical frequencies. Furthermore, the longitudinal electrical boundary conditions are appropriate to the physical realization of an open-circuit capacitor with fixed free charge on the plates, whereas the usual approach applies to a closed-circuit one with a fixed voltage across the plates (Fig. 1).

Stress tensor

This analogy with an open-circuit capacitor suggests an intuitive strategy for deriving the stress tensor, a quantity that plays a central role in piezoelectric materials. In particular, the electrode of an isolated open-circuit capacitor cannot exchange free charge with the environment. This suggests that the flux of the vector field **D** through the three independent facets of the primitive unit cell should remain constant under an applied strain. These fluxes are $\mathbf{a}_i \times \mathbf{a}_j \cdot \mathbf{D} = \Omega \mathbf{b}_i \cdot \mathbf{D}$, where the $\mathbf{b}_i$ are duals ($\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$) differing by a factor of 2π from the conventional reciprocal lattice vectors. We then rewrite the functionals in terms of the ‘internal’ or ‘reduced’ variables $d_i = (\Omega/4\pi) \mathbf{b}_i \cdot \mathbf{D}$. It is also useful to define the reduced polarization $p_i = \Omega \mathbf{b}_i \cdot \mathbf{P}$ and the ‘dual’ reduced electric field $\bar{\varepsilon}_i = \mathbf{a}_i \cdot \mathbf{E}$. Additional details are provided in Supplementary Information, Section S4.

By Gauss’s law, $d_i = -Q_i$, where the Q_i are the free charges per surface unit cell located on the cell face normal to $\mathbf{b}_i$. With these definitions, the internal energy can be rewritten as

$$U(\{d\}) = E_{\text{KS}} + \frac{2\pi}{\Omega} \sum_{ij} (d_i - p_i) g_{ij} (d_j - p_j)$$

where we have introduced the metric tensor $g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$. We then define the fixed- $\{d\}$ stress tensor as

$$\sigma_{\mu\nu} = \frac{1}{\Omega} \left(\frac{dU}{d\eta_{\mu\nu}} \right)_{\{d\}} \quad (4)$$

where $\eta_{\mu\nu}$ is the strain tensor. By a Hellmann–Feynman argument (see Supplementary Information, Section S4.3) the total derivative in equation (4) can be replaced by a partial derivative. Using $dg_{ij}/d\eta_{\mu\nu} = 2a_{i\mu}a_{j\nu}$, we find

$$\sigma_{\mu\nu} = \sigma_{\mu\nu}^{\text{KS}} + \sigma_{\mu\nu}^{\text{Max}} + \sigma_{\mu\nu}^{\text{aug}}$$

where $\sigma_{\mu\nu}^{\text{KS}}$ is the standard zero-field expression,

$$\sigma_{\mu\nu}^{\text{Max}} = \frac{2E_\mu E_\nu - \delta_{\mu\nu} E^2}{8\pi}$$

is the Maxwell stress tensor (which originates from the derivative acting on g_{ij} and Ω^{-1}) and

$$\sigma_{\mu\nu}^{\text{aug}} = -\frac{1}{\Omega} \sum_i \bar{\varepsilon}_i \frac{\partial p_i}{\partial \eta_{\mu\nu}}$$

is the ‘augmented’ part. If the internal variables v are chosen as reduced atomic coordinates and plane-wave coefficients in a norm-conserving pseudopotential context, neither the ionic nor the Berry-phase component of p_i has any explicit dependence on strain, and $\sigma_{\mu\nu}^{\text{aug}}$ vanishes. The name thus refers to the fact that $\sigma_{\mu\nu}^{\text{aug}}$ is non-zero only in ultrasoft-pseudopotential⁵ and projector augmented-wave⁶ contexts.

We note that, as a consequence of fixing the reduced variables d_i rather than the Cartesian **D**, the proper treatment of piezoelectric effects^{7,8} is automatically enforced. This formal simplification allows for an enhanced flexibility in the simultaneous treatment of electric fields and strains. For example, it is possible to introduce a rigorous constant-pressure enthalpy by simply defining

$$U^\pi(d) = \min_\eta [U(d, \eta) - \pi\Omega] \quad (5)$$

where π is the external pressure and Ω is the cell volume. We will demonstrate the use of this strategy in the application to PbTiO₃.

Legendre transformation

The transformation from variables **D** to variables **E** can be regarded as part of a Legendre transformation. We spell out this connection here, working instead with reduced variables (d_1, d_2, d_3) and $(\bar{\varepsilon}_1, \bar{\varepsilon}_2, \bar{\varepsilon}_3)$. First, we note that

$$\frac{dU}{dd_i} = \frac{\partial U}{\partial d_i} = \bar{\varepsilon}_i \quad (6)$$

Recall that $\bar{\varepsilon}_i = \mathbf{a}_i \cdot \mathbf{E}$, so $-\bar{\varepsilon}_i$ is just the potential step V_i encountered while moving along lattice vector $\mathbf{a}_i$, whereas Q_i is just the free charge on cell face i . Thus, when the system undergoes a small change at fixed $(\bar{\varepsilon}_1, \bar{\varepsilon}_2, \bar{\varepsilon}_3)$, the work done by the battery is $-\sum_i V_i dQ_i = -\sum_i \bar{\varepsilon}_i dd_i$. We therefore define

$$\tilde{F}(\bar{\varepsilon}_1, \bar{\varepsilon}_2, \bar{\varepsilon}_3) = \min_{d_1, d_2, d_3} [U(d_1, d_2, d_3) - \sum_i \bar{\varepsilon}_i d_i]$$

where the potentials $\bar{\varepsilon}_i$ have become the new independent variables and d_i are now implicit in the minimum condition. The energy functionals $U(\{d_i\})$ and $\tilde{F}(\{\bar{\varepsilon}_i\})$ thus form a Legendre-transformation pair.

All the gradients with respect to the internal and strain degrees of freedom are preserved by the Legendre transformation and need not be rederived for $\tilde{F}$. The physical electrical boundary conditions, however, have changed back to the closed-circuit case. It is therefore natural to expect the functional $\tilde{F}$ to be closely related to the fixed-**E** enthalpy F of equation (2). Indeed, it is straightforward to show that

$$\tilde{F} = U - \frac{\Omega}{4\pi} \mathbf{E} \cdot \mathbf{D} = F - \frac{\Omega}{8\pi} |\mathbf{E}|^2$$

At fixed strain and $\bar{\varepsilon}_i$, the $\Omega E^2/8\pi$ term is constant, and thus does not contribute to the gradients with respect to the internal variables, consistent with equation (3). However, the stress derived from F differs from that derived from $\tilde{F}$ by the Maxwell term $\sigma_{\mu\nu}^{\text{Max}}$, which is absent from F (details of the derivation are provided in Supplementary Information, Section S4.3). Although the Maxwell stress is typically tiny (for example, 10^8 V m^{-1} produces a pressure of 44.3 kPa, whereas for the same applied field our calculated piezoelectric stress amounts to 0.54 GPa in PbTiO₃), for reasons of formal consistency we encourage the use of $\tilde{F}$ in place of F in future works.

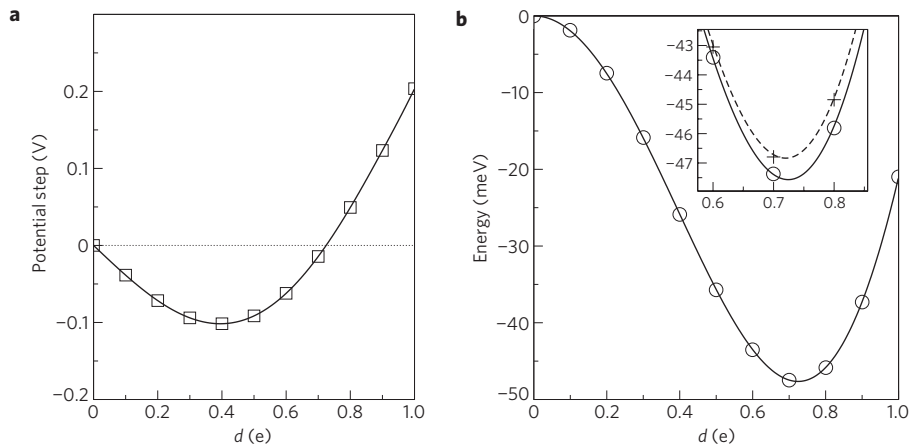


Figure 2 | Potential step and internal energy as a function of d . **a**, Symbols, calculated using constrained- $\mathbf{D}$ method, reduced electric field $\bar{\varepsilon}$; solid curves, numerical cubic spline fit to the symbols. **b**, Symbols, calculated using constrained- $\mathbf{D}$ method, internal energy U ; solid curves, numerical integral of the spline fit in **a**. Inset: enlargement near the minimum, also showing the magnitude of the error made if Pulay stresses are ignored (dashed curve).

Partial Legendre transformations

It is also possible to define hybrid thermodynamic functionals through partial Legendre transformations that act on only one or two of the three electrical degrees of freedom. Of most interest is the case of two fixed V and one fixed Q , that is, functions of variables $(\bar{\varepsilon}_1, \bar{\varepsilon}_2, d_3)$. The special direction is denoted by unit vector $\hat{\mathbf{q}}$, which is along direction $\mathbf{b}_3$. When $\bar{\varepsilon}_1 = \bar{\varepsilon}_2 = 0$, this applies to two common experimental situations: the case of an insulating film sandwiched in the $\hat{\mathbf{q}}$ direction between parallel electrodes in open-circuit boundary conditions, and the case of a long-wavelength longitudinal optical phonon of wavevector $\mathbf{q}$ where the $\mathbf{q} \rightarrow 0$ limit is taken along direction $\hat{\mathbf{q}}$.

This latter case of longitudinal optical phonons exemplifies the physical interpretation of our method and its usefulness. Although the gradients of U and its partially Legendre-transformed partner are identical, the force-constant matrices, which are second derivatives, are not. Indeed, the force-constant matrices are found to differ by

$$\Delta K_{I\alpha, J\beta} = \frac{4\pi}{\Omega} \frac{(\mathbf{Z}_{I\alpha} \cdot \hat{\mathbf{q}})_\alpha (\mathbf{Z}_{J\beta} \cdot \hat{\mathbf{q}})_\beta}{\hat{\mathbf{q}} \cdot \epsilon_\infty \cdot \hat{\mathbf{q}}}$$

where $I\alpha$ labels atom I and its displacement direction α , $\mathbf{Z}_{I\alpha}$ is the corresponding dynamical charge and ϵ_∞ is the purely electronic dielectric tensor. This is readily identified as the non-analytic contribution to the longitudinal optical–transverse optical splitting of a phonon of small wavevector $\mathbf{q}$ in the theory of lattice dynamics⁹. This demonstrates that the lattice-dynamical properties of a given insulating crystal within our fixed- D method are fully consistent with what should be expected from a change in the electrical boundary conditions from transverse to longitudinal.

Dielectric tensor and linear response

This scheme lends itself naturally to the perturbative linear-response analysis of the second derivatives of the internal energy as described in ref. 8, with two important differences. First, in our scheme the derivatives at constant $\mathbf{D}$ become the elementary tensors, whereas the derivatives at constant $\mathbf{E}$ are ‘second-level’ quantities; this is an advantage, because using $\mathbf{D}$ as independent variable is very convenient in ferroelectric systems. Second, the use of the reduced field variables d_i and $\bar{\varepsilon}_i$ in place of the macroscopic vector fields $\mathbf{P}$ and $\mathbf{E}$ makes the discussion of strains under an applied field much more rigorous and intuitive.

As an example of the relationship between constrained- $\bar{\varepsilon}$ and constrained- d tensors it is useful to introduce the inverse

capacitance, $\gamma = C^{-1}$, in matrix form as

$$\gamma_{ij} = \frac{d^2 U}{dd_i dd_j}$$

Incidentally, although this expression is fully general and well-defined in the nonlinear regime, for the special case of a linear medium we can write

$$U = U_0 + \frac{1}{2} \sum_{ij} \gamma_{ij} Q_i Q_j$$

which generalizes the textbook formula $U = Q^2/2C$ to the case of three mutually coupled capacitors. It can be shown that the same information can be obtained within the constrained- $\bar{\varepsilon}$ approach by means of the relationship

$$(\gamma^{-1})_{ij} = \frac{d^2 \bar{F}}{d\bar{\varepsilon}_i d\bar{\varepsilon}_j}$$

The matrix γ_{ij} can be thought of a ‘reduced’ representation of the macroscopic dielectric tensor,

$$(\epsilon^{-1})_{\alpha\beta} = \frac{\Omega}{4\pi} \sum_{ij} \gamma_{ij} b_{i,\alpha} b_{j,\beta}$$

or equivalently

$$\epsilon_{\alpha\beta} = \frac{4\pi}{\Omega} \sum_{ij} (\gamma^{-1})_{ij} a_{i,\alpha} a_{j,\beta}$$

We will consider, in addition to the total static capacitance above, the closely related frozen-strain γ_{ij}^n and frozen-ion γ_{ij}^∞ tensors.

The remainder of the response functions discussed in ref. 8 can be similarly defined in terms of the second derivatives of $U(\{d\}, u, \eta)$.

Applications

In the following we illustrate our method by computing the electrical equation of state of a prototypical ferroelectric material, PbTiO_3 . Starting from the relaxed cubic structure in zero field, we calculate the equilibrium state for 10 evenly spaced values of the reduced displacement d , ranging from $d = 0.1e$ to $1.0e$ (where $-e$ is the electron charge), and relaxing all the structural variables at each d value.

First we check the internal consistency of the formalism by verifying that our calculated potential drop $\bar{\varepsilon}$ coincides with the numerical derivative of U with respect to d as expected

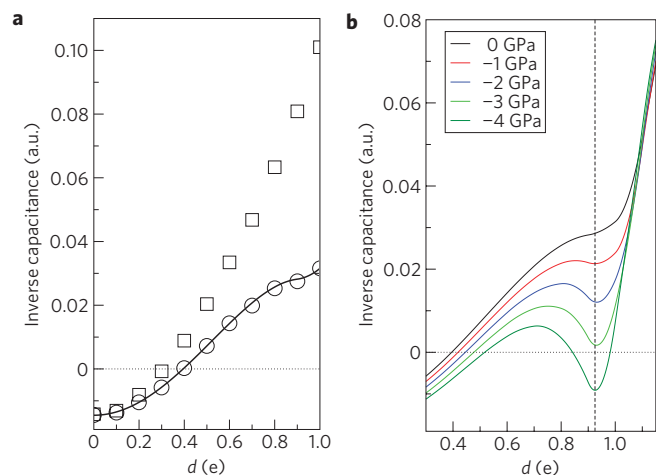


Figure 3 | Dielectric properties. **a**, Calculated inverse capacitance in the free-stress (γ , circles) and fixed strain (γ^η , squares) limits. The points were obtained by extracting the symmetric 6×6 elementary response tensors by finite differences (steps of ± 0.001 were taken for each parameter) for each value of d ; the continuous curve is the result of numerical differentiation of the splined potential. **b**, Evolution of γ for increasingly larger negative pressures.

from equation (6). The comparison is shown in Fig. 2, where the discrepancies, of order 10^{-6} Ha, are not even visible. The minimum in Fig. 2b (which coincides with the zero-crossing in (a)) at $d = 0.725 e$ corresponds to a spontaneous polarization of $P_s = 0.78 \text{ C m}^{-2}$ and a tetragonal ratio $c/a = 1.045$.

We note that this comparison is sensitive to the Pulay stress, even in the present case where our conservative choice of the plane-wave cutoff makes this error as small as $\pi_p = 82 \text{ MPa}$. Ignoring such error corresponds to applying a spurious hydrostatic pressure of $-\pi_p$, which leads to a discrepancy between the integrated potential (dashed curve in the inset of Fig. 2) and the calculated internal energy values. The agreement can be restored by plotting, instead of U (circles), the correct functional, equation (5), for constant-pressure conditions (plus symbols).

Having verified the accuracy and consistency of our method, we now demonstrate its utility by analysing the second derivative of the internal energy (or equivalently the first derivative of the potential) as a function of d , which corresponds to the inverse capacitance γ . The symbols in Fig. 3a show the linear-response values of both γ^η and γ , which are identical in the non-piezoelectric cubic limit. The numerical derivative of the splined potential of Fig. 2a accurately matches γ , again confirming the high numerical quality of our calculations. Figure 3a shows that the inverse capacitance is negative for $0 < d < 0.395$ (the zero-crossing point corresponds to the inflection point of the $U(d)$ curve of Fig. 2b, and to the minimum of $\bar{\epsilon}(d)$ of Fig. 2a). This is indicative of the fact that cubic PbTiO_3 is characterized by a ferroelectric instability, which means that the $U(d)$ curve has a negative curvature around the saddle point $d = 0$. We suggest, therefore, that the constrained- $\mathbf{D}$ inverse capacitance at $d = 0$, although not accessible experimentally (because it corresponds to an unstable configuration of the crystal), is a useful indicator of the strength of the ferroelectric instability. As such, it can play an important role in determining the critical thickness for ferroelectricity in thin perovskite films; in particular, a material with lower γ should be ferroelectric down to smaller thicknesses, provided that the depolarizing effects due to the ferroelectric/electrode interface are equally important¹⁰. Note that in our terminology one ferroelectric can be both stronger and less polar than another if it has a more negative γ but a smaller spontaneous polarization $|P_s|$.

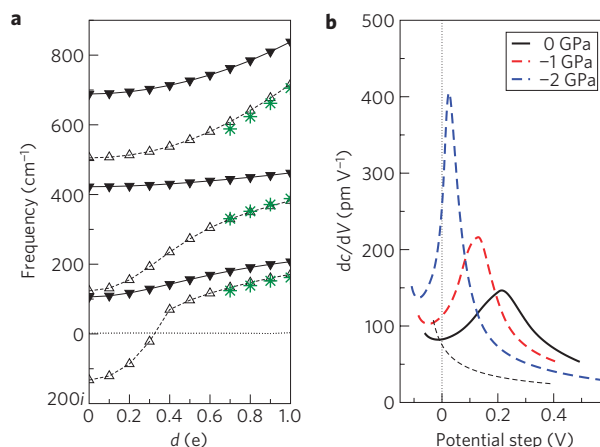


Figure 4 | Lattice-dynamical and piezoelectric properties. **a**, Longitudinal (filled symbols, continuous curves) and transverse (open symbols, dashed curves) optical modes of I_{15} symmetry as a function of d at zero pressure. Selected transverse optical frequencies for $\pi = -4 \text{ GPa}$ are shown as green star symbols. **b**, Calculated piezoelectric coefficient as a function of external pressure π and bias V (thick curves). Results of the Landau-Devonshire model of refs 14 and 11 are shown as a thin dashed curve for comparison.

Piezoelectricity

Interestingly, the free-stress $\gamma(D)$ curve in Fig. 3a shows a peculiar plateau for $0.8 < d < 1.0$, indicative of a ‘softening’ of the response of the crystal to the applied electric field. This behaviour is surprising, as an electric field of increasing strength would rather be expected to drive a perovskite crystal further into the anharmonic regime, with a consequent progressive hardening of the overall dielectric response¹¹. To analyse this effect, we start by observing that the evolution of the fixed-strain γ^η dielectric response as a function of d is essentially featureless. This indicates that optical phonons alone cannot be responsible for the effect, and volume (and/or cell-shape) relaxations are crucially involved. To investigate this, we repeated our calculations within a negative hydrostatic pressure by using the mixed fixed- D , fixed- π enthalpy defined in equation (5). The results for the free-stress $\gamma(D)$, plotted in Fig. 3b, show a dramatic influence of the external pressure on the dielectric response of the system. In particular, the plateau in $\gamma(D)$ becomes an increasingly deeper local minimum, which crosses the $\gamma = 0$ axis for π between -3 and -4 GPa ; the local minimum is approximately centred at $d = 0.925$ for all values of π .

A negative γ indicates a structural instability, and structural instabilities in ferroelectric systems are usually understood in terms of ‘soft’ phonon modes. To see whether this picture applies here, we plotted in Fig. 4a the zone-centre polar-mode frequencies as a function of d . At zero pressure, the curves show no notable irregularity, consistent with the smooth evolution of the fixed-strain response γ^η . Remarkably, the external pressure has a negligible influence on such frequencies, which remain practically unchanged for the strained crystal at the same value of d , confirming our hypothesis that the effect is essentially of piezoelectric nature.

Pursuing this idea, we combined the values of the potential drop $V(d)$ with the equilibrium values of out-of-plane lattice parameter, and calculated the free-stress piezoelectric coefficient by numerical differentiation as

$$h = -\frac{dc}{dV}$$

The results, plotted in Fig. 4b, show for zero pressure a clear peak at $V \sim 0.2 \text{ V}$, corresponding to a value of the internal field of

about 450 MV m^{-1} . We identify this peak with the plateau in the inverse capacitance curve of Fig. 3a. For increasingly large negative pressures, the piezoelectric peak becomes sharper and shifts to smaller values of the potential; for $\pi < -3 \text{ GPa}$ (not shown) the piezoelectric coefficient diverges, corresponding to the crossover to the unstable region in Fig. 3b.

These results shed light on the recent experimental measurements of ref. 12, where a remarkable anomaly in the piezoelectric response of lead zirconate titanate films in high fields ($E = 200\text{--}300 \text{ MV m}^{-1}$) was detected. Such an anomaly was rationalized in terms of a transition to a supertetragonal state, which previous first-principles calculations¹³ predicted to be stable in PbTiO_3 under an applied negative hydrostatic pressure. However, the question remained whether the electric field might actually produce such a transition within the experimental range of applied fields. Our results demonstrate that the piezoelectric coupling is indeed capable of driving such a transition, at least under isotropic free-stress boundary conditions. (In future work, we plan to extend these investigations by considering epitaxial strain clamping effects.) We note that our calculated value of the piezoelectric coefficient of PbTiO_3 at zero field and pressure ($h = 82.5 \text{ pm V}^{-1}$) is in excellent agreement with previous Landau–Devonshire theories^{11,14}, but the evolution of h for non-zero values of the applied potential substantially differs (see Fig. 4b). For small values of the electric field, in particular, our *ab initio* results indicate that h remains roughly constant. Then h increases significantly at higher fields, up to a value $E \sim 450 \text{ MV m}^{-1}$, where it starts decreasing again. A monotonic decrease was predicted instead by the model of ref. 11. This result, therefore, has important implications for the tunability of the piezoresponse of lead titanate crystals.

Summary and outlook

We have in mind several immediate applications for our method. First and foremost, fixing D in ferroelectric capacitors by using the methods of ref. 15 will allow for a detailed analysis of the microscopic mechanisms determining the depolarizing field, in both the linear and anharmonic regimes, an issue that is central to the development of efficient ferroelectric devices. Second, imposing constant- D electrical boundary conditions has the virtue of making the force-constant matrix of layered heterostructures short ranged in real space. This enables us to accurately model the polarization and response of complex superlattices, capacitors and interfaces in terms of the electrical properties of the elementary building blocks; a demonstration of this strategy was recently reported in ref. 16. Third, complex couplings between different order parameters can now be treated with unprecedented flexibility, opening new avenues in the theoretical study of magnetoelectric multiferroics and improper ferroelectrics.

Methods

Our calculations are performed within the local-density approximation¹⁷ (LDA) of density-functional theory using norm-conserving¹⁸ pseudopotentials and a plane-wave cutoff of 150 Ryd. Angular-momentum channels up to $l = 2$ are included in all pseudopotentials. The reference states (the numbers in brackets indicate the core radius in bohr) of the isolated neutral atom used for the generation of the pseudopotentials are $2s$ (1.4), $2p$ (1.4) and $3d$ (1.4) for O, $6s$ (2.4), $6p$ (2.4) and $5d$ (2.0) for Pb and $3s$ (1.2), $3p$ (1.3) and $3d$ (1.3) for Ti. The local angular-momentum channel is $l = 2$ for O, $l = 0$ for Pb and Ti. The tetragonal PbTiO_3 unit cell contains one formula unit, and a $6 \times 6 \times 6$ Monkhorst–Pack¹⁹ grid is used to sample the Brillouin zone. The finite electric field is applied through

a Wannier-based real-space technique¹⁵, which converges quickly as a function of k -point mesh resolution²⁰; indeed, tests made with finer meshes showed no differences within numerical accuracy. We obtain an equilibrium lattice constant of $a = 3.879 \text{ \AA}$ for cubic paraelectric PbTiO_3 , in line with values previously reported in the literature. Owing to the tetragonal symmetry, the state of the system is fully determined by six parameters: the electric displacement d , the cell parameters a and c , and three internal coordinates describing relative displacements along z . We set a stringent accuracy threshold of 10^{-5} Ha/bohr for atomic forces and $10^{-7} \text{ Ha/bohr}^3$ for stresses.

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Additional information

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