From flexoelectricity to absolute deformation potentials: The case of SrTiO$_3$

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(Dated: October 12, 2015)

Based on recent developments in the first-principles theory of flexoelectricity, we generalize the concept of absolute deformation potential to arbitrary nonpiezoelectric insulators and deformation fields. To demonstrate our formalism, we calculate the response of the band edges of SrTiO$_3$ to both dynamic (sound waves) and static (bending) mechanical loads, respectively at the bulk level and in a slab geometry. Our results have important implications for the understanding of strain-gradient-related phenomena in crystalline insulators, formally unifying the description of band-structure and electrostatic effects.

PACS numbers: 71.15.-m, 77.65.-j, 63.20.dk

I. INTRODUCTION

The so-called deformation potentials, introduced in 1950 by Bardeen and Shockley\textsuperscript{1,2} describe the shifts in the single-particle electronic energy levels that are induced by a strain field. Originally aimed at estimating the intrinsic contributions to carrier mobility in semiconductors, this concept is nowadays important for a wide range of phenomena of fundamental and technological interest. For example, deformation potentials were invoked to explain band offset formation at strained semiconductor heterojunctions\textsuperscript{3}, carrier confinement in optoelectronic devices\textsuperscript{4} and the impact of dopants and impurities on the lattice parameter of insulators.\textsuperscript{4,5,6} In all the above contexts, one needs to know how the energy of a given electronic state is modulated by an inhomogeneous strain field, which can be produced by an acoustic phonon, by a compositional gradient or by an applied external load. This physical property goes now by the name of absolute deformation potential (ADP), where the qualification “absolute” was introduced\textsuperscript{6} to emphasize the focus on the single energy levels, rather than their relative differences.

For theoretical analysis and computational purposes, ADPs are typically split into two separate contributions, a macroscopic electrostatic (ME) term and a band-structure (BS) term. The latter consists in the strain derivative of the Bloch eigenvalues, where the (arbitrary) energy reference is fixed to the average electrostatic potential (or to the Fermi level in a metal). This is manifestly a bulk property, as it can be readily obtained by performing periodic calculations that involve the primitive unit cell of the crystal only. The former, which is by far the most challenging to calculate, consists in the strain derivative of the electrostatic reference itself. (This term is due to long-range electrostatic interactions, and therefore it is only present in insulators.) As such reference is generally ill-defined in an infinite crystal\textsuperscript{7} one needs to explicitly consider an inhomogeneous strain field, where the cell parameters gradually evolve between two different configurations A and B. The integral of the electric field along the AB path yields then the sought-after voltage lineup. The nonanalyticity of electrostatic interactions implies that the lineup depends not only on the end points, A and B, but also on the specific path connecting them. Yet, once the direction of such a path is known (assuming it is rectilinear), this term can also be expressed as a bulk property\textsuperscript{8} and explicit first-principles calculations have been reported for a number of materials.\textsuperscript{3,5,6,9}

In all the aforementioned works, the focus has been mainly restricted to a particular class of deformations (longitudinal acoustic phonons) and dielectrics (nonpolar semiconductors like Si or Ge). These essentially reflect the established range of validity of the current ADP theory.\textsuperscript{5} There are increasingly good reasons, however, to seek a more general approach to the problem in order to overcome the above limitations. Regarding the materials issue, there has been recently increasing interest in semiconducting oxides: ZnO, SrTiO$_3$, etc. with highly confined 2D electron gases. Acoustic phonon scattering has been identified as one of the main factors limiting mobility, e.g., at the LaAlO$_3$/SrTiO$_3$ interface, either in the superconducting state\textsuperscript{10} or in thermoelectric applications\textsuperscript{11}. In other cases, ADPs were invoked to explain the carrier confinement mechanism itself\textsuperscript{12}. Polar materials (in this work we shall indicate as “polar” all crystals where the Born charge tensor does not vanish) presently fall outside the scopes of ADP theory\textsuperscript{5} and this poses a clear problem for the interpretation of the above phenomena. Regarding the “geometric” issue, there has been recently a strong interest in the electronic properties of bent nanostructures, and in particular in determining how curvature affects the effective potential felt by quantum particles.\textsuperscript{13} Accurate knowledge of the bending-related ADPs is necessary to obtain a quantitative solution to this problem\textsuperscript{12}, but bending is a type of deformation that cannot be described as a longitudinal acoustic phonon; this seriously limits the applicability of first-principles methods in this context.

Here we show that the theory of flexoelectricity, which has undergone an impressive development in the past few years, is now mature enough to provide a rigorous answer to both questions. Flexoelectricity (FxE) describes
the electrical polarization that is linearly induced by a strain gradient, and is therefore ideally suited to tackle the macroscopic electrostatic contribution to the ADPs in the most general case. (Indeed, the longitudinal components of the macroscopic FxE tensor reduce\textsuperscript{13} to the ME term of Ref. 8 in a nonpolar crystal.) In particular, we argue that (i) the atomic relaxations (internal strains) that occur in a strain-gradient field are bulk properties of the material (just like the purely electronic effects that were considered in earlier works\textsuperscript{8,9}), thereby extending the ADP theory to polar insulators; and (ii) the transverse components of the FxE tensor naturally yield the desired information on the bending-induced electrostatic effects, which allows us to formally extend the ADP theory to arbitrary deformation fields. As a practical demonstration, we provide a full calculation of the ADPs in cubic SrTiO$_3$, considering both the dynamic regime of sound waves and the static one of a bent slab.

Apart from the immediate relevance to the physics of SrTiO$_3$, these results highlight a crucial aspect of flexoelectricity that is absent in other types of electromechanical couplings: As each energy level experiences a different tilt, in a macroscopic strain gradient the very notion of \emph{macroscopic} electric field is inherently ambiguous, and depends on the physical nature (electron, hole, classical “test” charge, etc.) of the charged particle that is used to define it. An elegant solution to this conceptual puzzle consists in identifying the flexovoltage coefficients with the ADPs, and thereby rationalizing the aforementioned ambiguity via the band-energy dependence of the deformation potential. This points to a formal unification of ADP and flexoelectricity theories, with important implications for both the interpretation of the experiments and the theoretical modeling of strain-gradient related phenomena.

II. THEORY

Consider a macroscopic deformation where a given component of the symmetric stress tensor, $\varepsilon_{\beta\gamma}$, undergoes a linear increase along the direction $\mathbf{q}$. The absolute deformation potential of the $n$-th band at the point $\mathbf{k}$ in the Brillouin zone can be written as

$$D_{\beta\gamma}^{\beta\gamma}(\mathbf{q}) = \frac{dE_n(\mathbf{q})}{d\varepsilon_{\beta\gamma}} - \frac{e}{\epsilon_0\epsilon_\mathbf{q}} \mu_{\alpha\beta\gamma\lambda}^{||} \hat{\mathbf{q}}_\alpha \hat{\mathbf{q}}_\lambda.$$

Here $E_n(\mathbf{q})$ is the energy eigenvalue referred to the mean potential energy,

$$\mu_{\alpha\beta\gamma\lambda}^{||} = \frac{dP_\alpha}{d\varepsilon_{\beta\gamma\lambda}},$$

is the type-II flexoelectric tensor (referring to the derivative of the polarization with respect to the strain gradient component $\varepsilon_{\beta\gamma\lambda}$, where the latter is the gradient of $\varepsilon_{\beta\gamma}$ along the Cartesian direction $r_\lambda$, $\epsilon_\mathbf{q} = \mathbf{q} \cdot \mathbf{\epsilon} \cdot \mathbf{q}$ is the relative permittivity along $\mathbf{q}$, and $\epsilon_0$ is the vacuum permittivity. The first term on the rhs of Eq. (1) is the band-structure term, and is independent of the direction $\mathbf{q}$; following earlier works\textsuperscript{8,9} we shall focus on the valence ($v$) and conduction ($c$) band edges, and indicate the corresponding BS terms as $\Delta D_{\beta\gamma}^{v,c}$. The second term in Eq. (1) is \emph{minus} the electric field that is generated by the strain gradient $\varepsilon_{\beta\gamma\lambda} \hat{\mathbf{q}}_\lambda$ when open-circuit boundary conditions are imposed along $\mathbf{q}$; this corresponds precisely to the macroscopic electrostatic term in the ADP. (Note the $-e$ factor, reflecting the negative electronic charge.)

To see that the present theory recovers earlier treatment\textsuperscript{8} as special cases, consider the macroscopic displacement pattern associated with an acoustic phonon of wavevector $\mathbf{q}$,

$$u_{\beta\kappa}^{l} = U_{\beta} e^{i\mathbf{q} \cdot \mathbf{r}},$$

where $l$ is a cell index, $\kappa$ is a sublattice index, and $U_{\beta}$ is a real-space vector indicating the displacement amplitude and direction. For a longitudinal phonon, the symmetric strain is

$$\varepsilon_{\beta\gamma}(\mathbf{r}) = i q U_{\beta} \hat{\mathbf{q}}_{\beta} \hat{\mathbf{q}}_{\gamma},$$

where $q = |\mathbf{q}|$ and $U = |U|$. We readily obtain, for the ME part,

$$D_{\text{(macro)}}^{\beta\gamma}(\mathbf{q}) = -\frac{e}{\epsilon_0\epsilon_\mathbf{q}} \mu_{\alpha\beta\gamma\lambda}^{||} \hat{\mathbf{q}}_{\alpha} \hat{\mathbf{q}}_{\beta} \hat{\mathbf{q}}_{\gamma} \hat{\mathbf{q}}_{\lambda}.$$  

It is then straightforward to show\textsuperscript{3} that, in the case of a nonpolar insulator, $D_{\text{(macro)}}^{\beta\gamma}(\mathbf{q})$ reduces to the expression of Ref. 8, written in terms of the dynamical quadrupole and octupole tensors. In a material with cubic symmetry this can be written, in turn, as

$$D_{\text{macro}}^{\beta\gamma}(\mathbf{q}) = A_{\text{macro}} + f(\mathbf{q})B,$$

where the anisotropy function $f(\mathbf{q}) = 3(1 - \sum_{\alpha} \hat{q}_\alpha^2)/2$ varies between 0 and 1 depending on the direction. Then, the final result is

$$D_{v,c}(\mathbf{q}) = A_{v,c} + f(\mathbf{q})B,$$

where $A_{v,c} = A_{\text{macro}} + \Delta D_{v,c}$.

Having shown the consistency of Eq. (1) with earlier works, we can now move on to clarifying in what respects such expression generalizes the scopes of the ADP theory to a broader range of phenomena. In a nutshell, by using Eq. (1) to define the ADPs, one can in principle tackle all materials (including polar crystals) and deformation fields (including bending) for which the flexoelectric tensor is well defined. To appreciate the practical implications of this statement, it is useful to discuss in some detail the example of a polar (but nonpiezoelectric\textsuperscript{13}) insulator. In Ref. 8, the authors argued that ADPs cannot be written as bulk material properties in this case, as the displacement of a plane of atoms induces a net dipole density, and hence an arbitrary shift in the electrostatic lineup. The theory of flexoelectricity, however, shows that such displacements are \emph{not} arbitrary, but can
be themselves written as bulk material properties, via a higher-order internal-strain tensor (indicated as N or L in Ref. 14). This allows one to write, in full generality, the lattice-mediated (LM) contribution to the ADPs, which for a LA phonon in a cubic insulator has the same form as Eq. (6). (The frozen-ion and relaxed-ion ADPs retain the same functional form, only with different values of the coefficients $A_{\text{macro}}$ and $B$.)

It is worth making, in this context, an additional comment on the physical nature of the LM contribution. Such contribution depends, as we said, on the flexoelectric internal-strain tensor components, and this is an inherently dynamic quantity, i.e. it depends explicitly on the atomic masses [14] this characteristic obviously propagates to the relaxed-ion ADPs. This is not a concern when studying, e.g., the impact of acoustic vibrations (a dynamic effect) on carrier mobility, but questions, at first sight, the applicability of the present theory to genuinely static cases, such as a bent slab under an external mechanical load. Note, however, that the condition of static equilibrium imposes a precise linear relationship between the strain-gradient components that are present in a given region of the sample interior. (For example, in a bent plate the “primary” transverse deformation is always accompanied by a “secondary” longitudinal strain gradient that is oriented along the surface normal [15,16].) Once these elastic relaxation effects are appropriately incorporated, the mass-dependent terms that are present in the internal-strain tensor L exactly cancel out [16]. This clears up the above worries regarding lattice-mediated effects: the ADPs described by Eq. (1) are indeed static quantities in the slab-bending case, while they are dynamic in the context of LA phonons, consistent with the physical nature of the phenomenon under study.

### III. RESULTS

#### A. Longitudinal acoustic phonons

In the following, we shall illustrate the above arguments by explicitly calculating the relaxed-ion ADPs in SrTiO$_3$. Our calculations are performed within the local-density approximation [14] to density-functional theory. We use the same pseudopotentials and computational parameters as in Ref. [15] from which we also take the numerical values of the relevant bulk flexoelectric tensor components. These data are then processed to yield the macroscopic electrostatic contributions to the ADPs. The band-structure terms, $\Delta D_{\nu,c}^{\beta}$, are calculated by finite differences, considering an isotropic volume expansion (or compression) of the cubic SrTiO$_3$ cell. This corresponds to neglecting the splittings induced by anisotropic deformations, consistent with earlier works [15]. The reported values correspond to the valence-band top at the $\Gamma$ point of the Brillouin zone, and to the conduction-band bottom at $\Gamma$.

We shall start by discussing our results for the “acoustic” ADPs, which are described by Eq. (6). Our calculated numerical values for $A_{\text{macro}}$, $A_c$, $A_v$, and $B$, both at the frozen-ion and relaxed-ion levels, are reported in Table I. The case of a [100]-oriented LA phonon is also schematically illustrated in Fig. 1.

First, note the large difference in absolute value between $A_{\text{macro}}$ and $A_{v,c}$, which points to a substantial cancellation between the (positive) macroscopic and (negative) band-structure terms. A closer look at the numerical data indicates that such cancellation occurs at the purely electronic (frozen-ion) level. To rationalize this outcome (which is a common feature of ADP calculation [15]), recall that the frozen-ion value of the longitudinal flexoelectric coefficients (and hence of $A_{\text{macro}}$) are related [14] to the octupolar moments of the electronic charge that each atom “drags” along during the deformation. Such moments are typically dominated by a spherical term, which originates from the inner orbitals that rigidly follow each nucleus along its distortion path. These orbitals, in turn, are chemically inert, meaning that their displacement contribute to $A_{\text{macro}}$ but not to

|          | $A_{\text{macro}}$ | $A_c$ | $A_v$ | $B$  |
|----------|-------------------|-------|-------|------|
| Frozen-ion | 16.15             | -0.33 | 1.40  | 1.29 |
| Total    | 18.68             | 2.20  | 3.93  | 0.98 |

### TABLE I: Deformation potentials referring to longitudinal phonons along an arbitrary direction. Values are in eV.

FIG. 1: Illustrative sketch of the deformation potentials in a [100]-oriented sound wave in SrTiO$_3$. Conduction (CBM) and valence (VBM) band edges are shown, as well as the mean electron potential energy, $\phi(x) = -eV(x)$. ($V$ stands for the electrostatic potential.) The snapshot of the deformation is shown as black circles displacing from their equilibrium position (gray circles). An unrealistically large local strain of ±20% (at the extremes of the sinusoidal wave) is used for illustration purposes.

\[ \phi(x) = -eV(x) \]
the band energies. (In a ideally ionic solid, e.g. like the noninteracting rigid-ion model of Ref. [16], the cancellation would be complete, and yield vanishing values for $A_{v,c}$.)

Next, it is interesting to note the relatively large and positive contribution from lattice-mediated effects. (Once relaxation effects are accounted for, both bands undergo an upward shift upon uniaxial tension, see Fig. 1.) This observation can be readily explained by recalling the dynamical nature of the lattice-mediated flexoelectric effect in sound waves. Indeed, a strain gradient dynamically induces (in addition to the mass-independent contributions from the interatomic force constants) a force on each ionic sublattice that is directly proportional to its nuclear mass. Since the cations (Sr, Ti) are much heavier than the anions (O), this produces a systematic bias on the sign of the flexoelectric coefficients, consistent with the results of Table I. To verify such a hypothesis, we have performed a computational experiment, where we have recalculated the lattice-mediated contribution to $A_{\text{macro}}, A_{\text{LM}}$, while setting all nuclear masses to a uniform value. As a result, $A_{\text{LM}}$ changed from $2.53 \text{ eV}$ to $-1.88 \text{ eV}$, confirming our arguments. (A closely related analysis was also performed in Ref. [18] with qualitatively similar conclusions, see Table IV therein.)

Finally, note the relatively small anisotropy, which is only marginally affected by lattice-mediated effects, and the comparably larger value of $A_{v}$ respect to $A_{c}$. The latter observation indicates that the gap of SrTiO$_3$ shrinks upon volume expansion, consistent with the dominant ionic character of the bonding. (Our calculated gap deformation potential is $A_{\text{gap}} = -1.73 \text{ eV}$.)

Our frozen-ion results can be directly compared with those that were recently reported by Janotti et al.[23] There appears to be a significant discrepancy ($A_{v} = -1.5 \text{ eV}$, $A_{c} = -4.0 \text{ eV}$, $A_{\text{gap}} = -2.5 \text{ eV}$ in Ref. [5]), whose precise origin is unclear at present. One possible source of disagreement may stem from the different exchange and correlation functional that was used therein (HSE).[15] This, however, would imply a worrisome dependence of the ADPs on the specific details of the computational model; further investigations will be necessary in order to clarify this important point.

### B. Static bending of a (100)-oriented plate

Our flexoelectricity-based theory of ADPs can readily answer another important physical question[12] that was so far unaddressed at the first-principles level. This concerns the modifications to the electronic structure of a slab that are induced by a bending deformation. The validity of the ADP concept in this specific case rests on the demonstration, provided in Ref. [16], that the open-circuit internal field of a slab subjected to bending is a bulk material property. As we mentioned earlier, it is most appropriate here to assume mechanical equilibrium (under the action of an external load), and therefore consider static ADPs. These can be expressed as effective linear combination of the transverse and longitudinal strain gradients, consistent with the mechanical equilibrium conditions. Values are in eV.

![FIG. 2: Sketch of the relevant energy levels in a bent SrTiO$_3$ slab. Thin solid black lines indicate the flat conduction and valence band edges in the unperturbed system. Thin dashed black lines indicate the slab surfaces. Colored thin lines indicate the vacuum level. Upon bending, the band edges tilt and the vacuum levels shift (thick lines). An unrealistically large strain gradient, corresponding to $t = e_{yy,x}$ = 1 is assumed for illustrative purposes. The inset illustrates the type (not the amplitude) of the deformation applied to the slab.](image)

TABLE II: Deformation potentials associated with static bending of a SrTiO$_3$ slab (plate-bending limit). The surface is assumed to be oriented along the [100] cubic direction. The (*) symbol indicates that “frozen-ion” here is referred to a linear combination of transverse and longitudinal strain gradients, consistent with the mechanical equilibrium conditions. Values are in eV.

|                | $\varphi_{\text{macro}}$ | $\varphi_{c}$ | $\varphi_{v}$ |
|----------------|--------------------------|---------------|---------------|
| Frozen-ion(*)  | 10.37                    | -1.31         | -0.08         |
| Total          | 10.81                    | -0.87         | 0.36          |

Values are in eV.

$D_{v,c}^{\text{eff}} = D_{\text{macro}}^{\text{eff}} + \Delta D_{v,c}^{\text{eff}}$.  

$D_{\text{macro}}^{\text{eff}} = -e\varphi_{\text{eff}}$ corresponds to minus the effective flexovoltage coefficient[13] $\varphi_{\text{eff}}$, scaled by the electron charge. The band-structure term, on the other hand, consists in the usual isotropic volume shift with a prefactor$[13] 1 - \nu$, that accounts for Poisson’s ratio effects,

$D_{\text{HSE}}^{\text{eff}} = (1 - \nu) \frac{dE_{v,c}}{d\ln(\Omega)}$.  

($\nu = c_{12}/c_{11}$, where $c_{ij}$ is the bulk elastic tensor in Voigt notation.)
As a testcase, we considered a (100)-oriented slab of SrTiO$_3$ in the plate-bending regime, analogous to Ref. [15]. (A more extensive analysis, involving slabs of different orientations and a comparison of the beam-bending versus plate-bending limits, is reported in Section III C.) In Table I, we show our results for $D^\text{eff}_{\text{macro}}$ and $D^\text{eff}_{\text{c}}$. Again, we calculated both quantities at the frozen-ion level first (note that here “frozen-ion” implies neglect of the internal strains, but inclusion of the aforementioned Poisson’s ratio effects), and later incorporating full atomic relaxation. As in the phonon case discussed earlier, there is a large cancellation between the macroscopic and the band-structure terms at the frozen-ion level. Due to this cancellation, the relative impact of the lattice-mediated contribution, small on the scale of the large macroscopic term, becomes significant in the context of the ADPs (the latter are about an order of magnitude smaller than $D^\text{eff}_{\text{macro}}$); for example, the valence-band parameter $D^\text{eff}_{\text{v}}$ changes sign after relaxation. Compared to the phonon ADPs of Table I, the relaxed-ion valence is significantly smaller in magnitude; also, the conduction-band and valence-band ADP have opposite signs. This corroborates our interpretation that the large and positive values of the phonon ADPs are mainly due to dynamical effects, which are absent in the present slab-bending case.

The above results are schematically illustrated in Fig. 1, where we also have incorporated the results of Ref. [15] regarding the surface contributions to the open-circuit flexovoltage.

C. Back to flexoelectricity

The energy level diagram of Fig. 1 may appear, at first sight, confusing: in the slab interior we have represented band-structure effects (which are the realm of ADP theory), while in the vacuum regions we have plotted the electromechanical response coefficients of Ref. [15] (which were derived in the context of flexoelectricity). Such a juxtaposition was made on purpose – as we shall explain shortly, there is an even more intimate link between flexoelectricity and ADPs than the earlier sections of this work suggest.

To see this, consider the total open-circuit voltage induced by bending, $\varphi^\text{total}$, which in Fig. 2 corresponds to (minus) the net shift between the (constant) vacuum potentials located at either side of the bent slab. (This is the physical quantity that flexoelectric experiments typically focus on.) In Ref. [15] such a quantity was obtained by summing up the relevant bulk flexovoltage coefficient (corresponding to $\varphi^\text{bulk}$ i.e. the tilt of the macroscopic electrostatic potential in the slab interior) and the surface dipolar contribution, $\varphi^\text{surf}$,

$$\varphi^\text{total} = \varphi^\text{bulk} + \varphi^\text{surf}.$$  

(10)

Fig. 2 shows that the same quantity can be, equivalently, obtained by summing up the bulk ADP (either the valence-band $D^\text{eff}_{\text{v,c}}$ or the conduction-band $D^\text{eff}_{\text{c}}$), and the appropriate surface deformation potential $D^\text{surf}_{\text{v,c}}$, and

$$-e\varphi^\text{total} = D^\text{eff}_{\text{v,c}} + D^\text{surf}_{\text{v,c}}.$$  

(11)

(The latter is the strain derivative of the offset between the conduction or valence band edges and the vacuum level; such offsets are commonly known in the literature by the name of electron affinity and ionization potential, respectively.) In our slab models of SrTiO$_3$, we find $D^\text{SrO} = 1.92$ eV, and $D^\text{TiO}_2 = -1.73$ eV, where the superscript refers to the two types of surface terminations considered in Ref. [15] (The corresponding values for the conduction band surface deformation potentials can be trivially determined by using the data of Table I)

The fact that, by summing up either the bulk and surface flexovoltage coefficients or the corresponding valence-band ADPs, we have obtained the same number (the total flexovoltage response of the slab) is not fortuitous. Flexovoltage coefficients really are ADPs in disguise (they can be thought as “electrostatic potential ADPs”) and, similarly, ADPs can be perfectly well regarded as flexovoltage coefficients. The former statement is an obvious consequence of Eq. (1); by setting the band-structure term to zero, and by recalling the relationship between flexovoltage and flexoelectric coefficients, [13] one trivially obtains $\varphi^\text{bulk} = -D^\text{eff}_{\text{macro}}/e$. Accepting the latter statement, on the other hand, may seem awkward at first sight, as it implies that the bulk flexoelectric tensor is not uniquely defined. (ADPs depend on the specific band feature that is being considered.) This is, however, perfectly consistent with the fundamental theory of flexoelectricity, where such a nonuniqueness emerges as a natural consequence of the formalism [23].

To appreciate the physical origin of this arbitrariness, one does not necessarily need to go through pages of complicated algebra. In fact, it suffices to take a closer look at Fig. 2 and Table I to get a reasonably clear idea of what’s going on: The valence band, conduction band and mean electrostatic potential all undergo a different tilt. This means that a conduction electron, a valence hole and a classical “test” charge will not feel the same electrical force. Otherwise stated, in a uniform strain gradient the very definition of “macroscopic electric field”, $E$, depends on the physical nature of the charged particle that is used to probe it. As the $E$-field in the interior of a bent slab is, in the above sense, ambiguous, the notion of “short-circuit boundary conditions” (a necessary ingredient for defining the bulk flexoelectric tensor) is equally ambiguous therein – it depends on the (arbitrary) energy reference that we choose when imposing the $E = 0$ (i.e. flat-band) condition [23].

Now, while it is true that selecting one or the other reference potential to define the internal electric field of the slab does not affect the overall result (the total open-circuit voltage), this choice does modify the way the effect is split into surface and bulk contributions. In practice, such a freedom can be exploited to achieve a more meaningful physical description of the two individual pieces.
flexoelectric response (under bending) of SrTiO$_3$ consistent with the experimental setup of Refs. 21 and 23.}

The opposite of the values in the table can be regarded as bulk flexovoltage coefficients (in V). In both the (110)- and (100)-oriented cases, the bending axis is assumed to be along [001], consistent with the experimental setup of Refs. 21 and 22. [SrTiO$_3$ is isotropic in the (111) plane, which means that the choice of the bending axis is irrelevant in this latter case.]

In the present case of the SrTiO$_3$ slab, for example, it appears tempting to identify the relevant flexovoltage coefficients with the valence-band (VB) ADPs,

\[
\varphi_{\text{bulk-VB}} = -\frac{D_v^{\text{eff}}}{e}, \quad \varphi_{\text{surf-VB}} = -\frac{D_v^{\text{surf}}}{e},
\]

rather than with the gradient of the bare electrostatic potential as it was done earlier. This way, we obtain a partition between bulk and surface effects where both contributions are small in magnitude (i.e. of the same order as the total open-circuit flexovoltage of the slab), thereby facilitating the identification of the physical mechanisms that play a dominant role in either context. (Recall that the “electrostatic” flexovoltages are typically characterized by a large cancellation between bulk and surface contributions, which complicates the physical interpretation of the two individual terms.)

### D. Bending anisotropy of SrTiO$_3$ slabs

To illustrate the above ideas, it is an insightful exercise to compute the bulk ADPs under static slab bending by considering different surface orientations and mechanical boundary conditions. (The two extremes in the latter context are represented by the plate-bending and beam-bending limits.) This is especially interesting in light of the experimental results of Ref. [21] which concern the flexoelectric response (under bending) of SrTiO$_3$ slabs with different orientations. Zubko et al. [21] argued, based on their analysis, that the measured coefficients can be interpreted reasonably well by assuming a purely bulk flexoelectric response, i.e. by neglecting possible surface effects. It would then be desirable to compare the reported values with the existing theoretical estimates of the bulk flexoelectric coefficients. Interestingly, reliable \textit{ab initio} calculations of these quantities have been recently performed, but the reported values show a marked discrepancy with the experimental data: The first-principles results for the bulk flexovoltage coefficients are of the order of $-10$ V, and are systematically negative, while the measurements cluster around $1 - 2$ V, with a positive or negative sign depending on sample orientation. To account for such a discrepancy, the contribution of surfaces is typically invoked. The concepts developed in this work, however, suggest that an alternative interpretation is possible: The disagreement may be largely due to an unfortunate choice of the energy reference when calculating the bulk contribution, and only to a lesser extent to the aforementioned surface effects.

Following up on this speculation, we report in Table III a complete overview of the (bulk) conduction-band and valence-band ADPs in a SrTiO$_3$ slab subjected to static bending. (The three surface orientations and the choices of the bending axes are consistent with the experimental setup of Ref. [21] for completeness we report the results for both the plate-bending and beam-bending regimes.) Clearly, the calculated ADPs are much closer to the experimentally measured flexoelectric data of Zubko \emph{et al.} than the bulk coefficients that were quoted in Refs. [15,18] which corroborates our point. (The values of Table III are of the order of 1 V; both negative and positive values are present.) Note that the difference between the plate-bending and beam-bending results is minor, which suggests that assuming one or the other regime might be of relatively little importance for a qualitatively correct interpretation of the experiments. Note also the relatively small orientation dependence, which amounts to about 1 V; this supports the idea, recently proposed in Ref. [23] that an unusually large anisotropy (as measured by Navaez \emph{et al.} in BaTiO$_3$ samples) is a clear signature of other effects (i.e. not bulk-like in origin) being at play.

### IV. CONCLUSIONS AND OUTLOOK

We have proposed a unified perspective on the theory of absolute deformation potentials and flexoelectricity. To illustrate our ideas, we have used cubic SrTiO$_3$ (either in bulk or slab form) as a testcase. The concepts developed here have important implications, both for the interpretation of the experimental measurements and for the macroscopic modeling of electromechanical phenomena. In the latter context, our work highlights the arbitrariness of the bulk flexoelectric tensor, and the need for a consistent treatment of bulk and surface effects in order to achieve a sound physical picture. On a positive note, our work opens the way to the first-principles (and first-principles-based) study of an essentially unlimited range of phenomena related to inhomogeneous deformation fields, complementing long-range electrostatics with band-structure effects.
Acknowledgments

This work was supported by MINECO-Spain (Grant No. FIS2013-48668-C2-2-P), and Generalitat de Catalunya (2014 SGR301). We thankfully acknowledge the computer resources, technical expertise and assistance provided by the Supercomputing Center of Galicia (CESGA).

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24 Of course, one can always think of depositing metal electrodes onto the slab surfaces – this way, the short-circuit condition is no longer arbitrary. Still, the precise way that a “zero external potential” translates into a “vanishing internal field” depends on the properties (i.e. on the interface deformation potential) of the film-electrode interface. In some sense, the interface/surface “selects” a given energy reference out of the infinite possibilities that exist at the bulk level, thereby lifting the aforementioned arbitrariness.