

**First-principles theory and calculation of flexoelectricity**

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We develop a general and unified first-principles theory of piezoelectric and flexoelectric tensor, formulated in such a way that the tensor elements can be computed directly in the context of density-functional calculations, including electronic and lattice contributions. We introduce practical supercell-based methods for calculating the flexoelectric coefficients from first principles, and demonstrate them by computing the coefficients for a variety of cubic insulating materials including C, Si, MgO, NaCl, CsCl, BaZrO<sub>3</sub>, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and SrTiO<sub>3</sub>.

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**I. INTRODUCTION**

Flexoelectricity (FxE) describes the linear coupling between electric polarization and a strain gradient, and is always symmetry allowed because a strain gradient automatically breaks the inversion symmetry. This is unlike the case of piezoelectricity (coupling of polarization to strain), which arises only in noncentrosymmetric materials. FxE was theoretically proposed about 50 years ago,<sup>1</sup> and was discovered experimentally four years later by Scott<sup>2</sup> and Bursian *et al.*<sup>3</sup> The FxE effect received very little attention for decades because of its relatively weak effects. Recently, it has attracted increasing attention, however, largely stimulated by the work of Ma and Cross<sup>4-10</sup> in which they found that the flexoelectric coefficient (FEC) could have an order of magnitude of  $\mu\text{C}/\text{m}$ , three orders larger than previous theoretical estimations.<sup>1</sup>

A second reason for the revival of interest in FxE is that strain gradients are typically much larger at the nanoscale than at macroscopic scales. For example, a 1% strain that relaxes in 1 nm in a nanowire or nanodot has a strain gradient  $10^3$  higher than for a similar geometry in which a 1% strain relaxes to zero at the micron scale. Thus, FxE can have a significant effect on the properties of nanostructures. For example, a decrease in dielectric constant<sup>11,12</sup> and an increase in critical thickness<sup>13</sup> in thin films was attributed to flexoelectric effects, and the transition temperature and distribution of polarization can also be significantly influenced.<sup>14</sup> A giant enhancement of piezoelectric response<sup>15</sup> and energy harvesting ability<sup>16</sup> was predicted in thin beams. FxE was also shown to affect the properties of superlattices<sup>17</sup> and domain walls.<sup>18-20</sup> For example, domain configurations and polarization hysteresis curves were shown to be strongly affected by FxE because of giant strain gradients present in epitaxial films.<sup>21</sup> A FxE-induced rotation of polarization in certain domain walls in PbTiO<sub>3</sub> was found,<sup>22</sup> and purely mechanical writing of domains in thin BaTiO<sub>3</sub> films was demonstrated.<sup>23</sup> Some piezoelectric devices based on the FxE effect have been proposed and their effective piezoelectric response has been measured in Cross's group.<sup>24-26</sup> Recently, it was found that a strain gradient can generate a "flexoelectric diode effect"<sup>27</sup> based on a very different principle from that of conventional diodes, such as  $p-n$  junctions or Schottky barriers at metal-semiconductor interfaces, which depend on the asymmetry of the system. The continuum theory considering the FxE effect was also developed recently for the nanodielectrics<sup>28</sup> and heterogeneous membranes.<sup>29,30</sup>

In order to understand the FxE response and to apply the FxE effect in the design of functional devices, it is necessary to measure the FECs for different materials. Clearly, it is desirable to look for materials with large FECs, for direct applications of the FxE effect. For other nanoscale devices, on the other hand, it may actually be desirable to identify materials where FxE is weak, so that unwanted side effects of strain gradients are avoided.

Originally, FECs were estimated to be on the order of nC/m and to scale linearly with static dielectric constant.<sup>1</sup> Forty years later, Ma and Cross found that the FECs, as measured by beam bending experiments (see Sec. IV C), could be three orders of magnitude larger than this in some high- $K$  materials.<sup>4-10</sup> This work set off a wave of related work by other groups using a wide variety of approaches. Using the same technique as Ma and Cross, Zubko *et al.*<sup>31,32</sup> measured the FECs for single-crystal SrTiO<sub>3</sub> along different crystallographic orientations in an attempt to obtain the full FEC tensor. They report FECs for SrTiO<sub>3</sub> that are on the order of nC/m, much smaller than in previous experimental work. They also found that it is impossible to obtain the full FEC tensor through bending measurements alone, and that it is even difficult to determine the sign of the effect. Another technique to measure FECs is to apply uniaxial compression to a sample prepared in a truncated-pyramid geometry, thus inducing a strain gradient in the pyramid.<sup>10</sup> This also measures some kind of effective FEC, but does not easily allow for extracting individual longitudinal components, due to the complicated inhomogeneous strain gradient distribution. However, based on this idea but using an inverse FxE effect, Fu *et al.*<sup>25</sup> measured the FEC for Ba<sub>0.67</sub>Sr<sub>0.33</sub>TiO<sub>3</sub> and obtained the same results as those from the direct FxE effect. Hana *et al.* also used the inverse FxE effect to measure the FEC for ceramic PMN-PT (a solid solution of lead magnesium niobate and lead titanate).<sup>33,34</sup> By using a nanoindentation method, Gharbi *et al.*<sup>35</sup> obtained the same order of FEC for BaTiO<sub>3</sub> as in the work of Ma and Cross.<sup>9</sup> Finally, Zhou *et al.*<sup>36</sup> proposed a method to measure the flexocoupling coefficient by applying a homogeneous electric field. They found that the hysteresis loop shifts due to FxE effect, and that it can be restored by applying a homogeneous electric field. The size of the required electric field was shown to be related to the flexocoupling coefficient, and thus could be used to measure the FEC. This method avoids the need to apply a dynamic mechanical load and may increase the accuracy of measurement.

On the theoretical side, efforts to understand the FxE effect and to extract FECs from theory began with the pioneering work of Kogan, who first estimated FECs for simple dielectrics to be on the order of nC/m and to scale linearly with static dielectric constant.<sup>1</sup> Twenty years later, Tagantsev developed a model for FxE that was based on classical point-charge models.<sup>37,38</sup> The FxE response was divided into four contributions denoted as “static bulk,” “dynamic bulk,” “surface FxE,” and “surface piezoelectricity.” The first-principles electronic response was not accounted for in this theory, which focused more on the lattice effects. The calculation of static bulk FxE was later implemented by Maranganti *et al.*,<sup>39</sup> and FECs for several different materials were obtained. The FxE response of two-dimensional systems was also investigated by Kalinin *et al.*<sup>40</sup> and Naumov *et al.*<sup>41</sup>

The first attempt at a first-principles calculation of FECs for bulk materials was carried out for BaTiO<sub>3</sub> and SrTiO<sub>3</sub> by Hong *et al.*,<sup>42</sup> who performed calculations on supercells in which a longitudinal strain variation of cosine form was imposed. This gives access to the longitudinal FEC  $\mu_{1111}$ , and implicitly corresponds to fixed-*D* (electric displacement field) electric boundary conditions. In this work, the positions of the Ba or Sr atoms were fixed and other atoms were allowed to relax. Their calculations include both electronic and lattice contributions to the FECs, and their results show that FECs all take on negative values. This method is limited to the longitudinal contribution to the FEC tensor at fixed-*D* boundary conditions.

Inspired by Martin’s classical piezoelectric theory,<sup>43</sup> Resta<sup>44</sup> developed a first-principles theory of FxE, but it was limited to the longitudinal electronic contribution to the FEC response of elemental materials, and was not implemented in practice. Shortly afterwards, Hong and Vanderbilt<sup>45</sup> extended this theory to general insulators and implemented it to calculate FECs for a variety of materials, from elementary insulators to perovskites. This theory was still limited to the electronic response, and only the longitudinal  $\mu_{1111}$  components were computed in practice. The calculations were at fixed-*D* boundary conditions, and several practical and convenient methods for achieving this were proposed. The results indicated that the electronic FECs are all negative in sign and that they do not vary very much between different materials classes. This work also raised several important issues, such as the dependence of the results on choice of pseudopotential, the presence of surface contributions related to the strain derivative of the surface work function, and the need to introduce a current-density formulation, instead of a charge-density one, to treat the transverse components of the FEC tensor.

More recently, Ponomareva *et al.*<sup>46</sup> have developed an approximate effective Hamiltonian technique to study FxE in (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> thin films in the paraelectric state at finite temperature. Parameters in the model are fit to first-principles calculations on a small supercell in which an artificial periodic strain gradient has been introduced. The authors computed both the flexocoupling coefficients (FCCs, see Sec. II H) and FECs for (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> films for different thicknesses above the ferroelectric transition temperatures. Unlike some of the previous theories, they found all of the FEC tensor components to be positive. They provided evidence that the dependence of the FEC tensor on thickness and temperature basically tracked with the dielectric susceptibility, suggesting a

strategy in which FCCs are computed as a “ground-state bulk property” and the FECs scale with susceptibility. However, since FEC calculations tend to be very sensitive to the size of the supercell,<sup>42</sup> their small supercell size may introduce a significant approximation. They also did not attempt to calculate the electronic contribution separately, and the role of fixed- $\mathcal{E}$  versus fixed-*D* electric boundary conditions was not discussed.

In this paper, we present a complete first-principles theory of flexoelectricity, based on a long-wave analysis of induced dipoles, quadrupoles, and octupoles in the spirit of the work of Martin<sup>43</sup> and Resta,<sup>44</sup> together with an implementation via supercell calculations and a presentation of computed values for a series of materials. We find that the flexoelectric response can be divided into “longitudinal” and “transverse” components, and that the treatment of the latter requires that one go beyond a charge-response treatment to a current-response one. The formalism for this is presented in detail in Appendix A, but its implementation is left for future work. Therefore, we present the longitudinal FEC tensor coefficients in their full generality for our materials of interest, and in addition we present some preliminary information about the transverse components.

During the preparation of this paper, we learned that Stengel has also developed a first-principles theory of flexoelectricity<sup>47</sup> that bears many similarities to the work presented here, although the point of view is different in several respects. Reference 47 does not describe an actual implementation of the method in the first-principles context or present any numerical results. Nevertheless, the two theories seem to be in agreement on fundamental points, and we hope that they will strengthen one another.

In the remainder of this Introduction, we emphasize five points that should be kept in mind when comparing calculated and/or measured values of FECs. Before proceeding, we refer the reader to several useful review articles that have appeared recently covering both experimental and theoretical aspects of the study of flexoelectricity.<sup>10,38,48–50</sup>

First, as indicated above, there are two contributions to the FECs: a purely electronic (or “frozen-ion”) contribution associated with a naive set of atomic displacements that are simply quadratic functions of their unperturbed positions, and a lattice (or “relaxed-ion”) contribution arising from additional internal atomic displacements induced by the strain gradient. Some of the previous theoretical work focused on the electronic part,<sup>44,45</sup> while others focused on the lattice part,<sup>37–39</sup> and still others considered both implicitly but did not separate them.<sup>42,46</sup> In this work, we have developed a first-principles theory which includes these two contributions explicitly, and we have proposed a method to calculate them efficiently.

Second, the question of what, precisely, is meant by “relaxed-ion” is subtle for FxE and is discussed in Sec. II F and Appendix B. We find that the calculation of the lattice contribution to the FECs depends on a choice of “force pattern” applied to the atoms in the unit cell in order to preserve the strain gradient, even after the induced internal displacements have taken place. It is possible to make different choices for this force pattern. A mass-weighted choice appears to be implicit in some previous work, and is also appropriate to the analysis of dynamical long-wavelength phonons. However, other choices

are possible, e.g., restricting the forces to the  $A$  atoms of  $ABO_3$  perovskites.<sup>42</sup> We caution that it is not meaningful to compare FECs computed using different force patterns. However, for an inhomogeneously strained system in static equilibrium, the stress gradient  $\nabla \cdot \sigma$  must vanish, where  $\sigma$  is the local stress tensor. In such a case, the total FxE response is not dependent on the choice of force pattern since there is no ambiguity about the meaning of relaxed atomic positions in this case. This independence is confirmed by our numerical calculations.

Third, it is important to obtain all symmetry-independent elements of the FEC tensor in order to understand the FxE response in the case of an arbitrary strain distribution and to aid in the design of functional FxE devices. However, it is challenging to obtain the full FEC tensor for general materials, which have 54 independent components.<sup>51</sup> Even for cubic materials, which have only three independent components, there is still no straightforward way to measure the full FEC tensor. Most first-principles calculations have been limited to reporting the longitudinal component in cubic materials,<sup>42,45</sup> although lattice (but not electronic) transverse components have also been reported in some works.<sup>39</sup> Here, we develop a first-principles theory for the full FEC tensor. However, our current implementation is still limited to longitudinal components and to certain combinations of transverse components. A formalism addressing the full set of transverse components is presented in Appendix A, but the implementation of such an approach is left to future work. Moreover, we limit our formal considerations here to the case of isotropic dielectric materials since the convergence of some moment expansions in Sec. II A does not otherwise appear to be guaranteed.

Fourth, the reader should be aware that there are many different definitions of FECs in the literature. For example, the FECs can be defined in terms of unsymmetrized strain, which tends to be more convenient for the derivation of the formalism, or in terms of symmetrized strain, which is more convenient in connecting to experimental measurements. A third object is the flexocoupling coefficient (FCC), which appears directly in a Landau free-energy expansion. Aside from the confusion caused by the physical distinction between these objects, there is also the practical problem that different symbols and different subscript orderings are used for the same quantity in different papers, making it very confusing when referring to the FECs appearing in different contributions to the literature. To help clarify this issue, we define the various kinds of FECs (based on unsymmetrized versus symmetrized strain) and the FCC, deriving the transformations that can be used to convert between them.

Fifth, there is a well-known issue for FxE, namely, the roughly three-orders-of-magnitude discrepancy between most theoretical estimates and experimental measurements of the FECs. Our work suggests that this gap can largely be closed by paying close attention to the difference between FECs computed at fixed  $\mathcal{E}$  versus at fixed  $D$ . This is important mainly for materials such as  $BaTiO_3$  that have a large and strongly temperature-dependent static dielectric constant  $\epsilon^0$ . The basic idea is to look for quantities that scale only weakly with temperature, calculate these from first principles, and then use the experimentally known temperature dependence of  $\epsilon^0$  to predict the FxE response at elevated temperature. Indeed, previous theory and calculations predict that the FECs should

scale linearly with dielectric constant,<sup>1,37,46</sup> and experiments have also verified this.<sup>31</sup> Previous work has identified the FCC as an object with weak temperature dependence that can be used in this way; as derived from Landau–Ginzburg–Devonshire (LGD) theory,<sup>49,50</sup> the FCC is roughly the ratio between the FEC and  $\epsilon^0$ . Indeed, Ponomareva *et al.*<sup>46</sup> argue that the FCC is “ground-state bulk property” that is independent of the temperature and size of system. In this work, we point out that the FECs computed at fixed- $D$  boundary conditions are also suitable for this purpose. They are, in fact, closely related to the FCCs, as we shall see in Sec. II H, but they are more easily and directly computed from first principles. Furthermore, we show formally in Sec. II G that the ratio of the fixed- $\mathcal{E}$  to the fixed- $D$  FEC is just equal to  $\epsilon^0$ . Therefore, the strategy adopted here is to compute the fixed- $D$  FECs at zero temperature and to use the known temperature dependence of  $\epsilon^0$  to make room-temperature predictions. Using this method, we find that the FECs computed from our theory are much closer to the experimental values, falling short by perhaps one order of magnitude instead of three.

The paper is organized as follows. In Sec. II, we derive the charge-response formalism for the first-principles theory of piezoelectricity and FxE, including electronic and lattice contributions, based on the density of local dipoles, quadrupoles, and octupoles induced by a long-wave deformation. Careful attention is paid to the lattice contributions, the choice of fixed- $D$  and fixed- $\mathcal{E}$  electric boundary conditions, and the form of the flexocoupling tensor and FxE tensor in the case of cubic symmetry. In Sec. III, we propose a supercell approach for calculating the FEC tensor for cubic materials based on the charge-response formalism. Using two supercells, one extended along a Cartesian direction and one rotated  $45^\circ$ , we obtain all of the longitudinal components of the response. In Sec. IV, we report the longitudinal FECs for different cubic materials at fixed  $D$  from our first-principles calculations. The room-temperature FECs at fixed  $\mathcal{E}$  are also obtained by using experimental static dielectric constants. The full FEC tensor is also reported after introducing some assumptions. We then compare our computed FECs with available experiment and theoretical results. In Sec. V, we give a summary and conclusions. Finally, in the Appendixes, we provide details about three issues: the current-response formalism for full FEC tensors (including longitudinal and transverse ones), the definition and construction of the pseudoinverse of force-constant matrix, and the treatment of O atoms in the cubic perovskite structures.

## II. FORMALISM

In 1972, Martin<sup>43</sup> introduced a theory of piezoelectricity based on the density of local dipoles and quadrupoles induced by a long-wave deformation (frozen acoustic phonon). In recent years, Martin’s theory of piezoelectricity has essentially been superseded by linear-response and Berry-phase methods in the computational electronic structure community. These approaches only require consideration of a single unit cell, and are therefore much more direct and efficient. However, they are derived from Bloch’s theorem, so that while they do apply to the case of a uniformly strained crystal, they do not apply in the presence of a strain gradient.

To treat the problem of FxE, therefore, we follow Resta<sup>44</sup> in returning to the long-wave method pioneered by Martin.<sup>43</sup> For flexoelectricity, this requires an analysis not only of induced dipoles and quadrupoles, but also of induced octupoles. While parts of our derivations are built upon previous work,<sup>37,38,43–45,50</sup> we attempt here to present a comprehensive and self-contained derivation.

### A. General theory of charge-density response

We define

$$f_{I\tau}(\mathbf{r} - \mathbf{R}_{lI}) = \frac{\partial \rho(\mathbf{r})}{\partial u_{lI\tau}} \quad (1)$$

to be the change of charge density induced by the displacement of atom  $I$  in cell  $l$ , initially at  $\mathbf{R}_{lI}$ , by a distance  $u_{lI\tau}$  along direction  $\tau$ , keeping all other atoms fixed. We also define the moments of the induced charge redistribution via

$$Q_{l\alpha\tau}^{(1)} = \int d\mathbf{r} r_\alpha f_{I\tau}(\mathbf{r}), \quad (2)$$

$$Q_{l\alpha\tau\beta}^{(2)} = \int d\mathbf{r} r_\alpha f_{I\tau}(\mathbf{r}) r_\beta, \quad (3)$$

$$Q_{l\alpha\tau\beta\gamma}^{(3)} = \int d\mathbf{r} r_\alpha f_{I\tau}(\mathbf{r}) r_\beta r_\gamma. \quad (4)$$

Note that  $Q^{(2)}$  and  $Q^{(3)}$  are symmetric under interchange of  $\alpha\beta$  or  $\alpha\beta\gamma$ , respectively.

It is worth briefly discussing the electric boundary conditions here. For the displacement of a single atom, we do not have to specify fixed- $\mathcal{E}$  or  $-D$  boundary conditions; we just choose boundary conditions such that the macroscopic potential and  $\mathcal{E}$  field vanish as  $r^{-2}$  and  $r^{-3}$ , respectively. Since the induced charge density is screened,  $Q^{(1)}$  corresponds to the Callen dynamical charge, not the Born one. If instead of moving one atom we were to move an entire sublattice, the Callen and Born charges would correspond to the application of fixed- $D$  and fixed- $\mathcal{E}$  boundary conditions, respectively. In this sense, we can regard the moment tensors  $Q^{(1)}$ ,  $Q^{(2)}$ , and  $Q^{(3)}$  as being fixed- $D$  quantities.

The convergence properties of Eqs. (2)–(4) also deserve some discussion. At large distances, the induced charge  $f_{I\tau}(\mathbf{r})$  is mainly induced by the dipole field  $\mathcal{E} \propto r^{-3}$ , raising questions about the convergence of the integrals in Eqs. (2)–(4) at large  $r$ . Fortunately,  $f_{I\tau}(\mathbf{r})$  also oscillates and averages to zero on the unit-cell scale at large  $r$ , helping to tame any such divergences, at least for the case of isotropic dielectrics (i.e., cubic materials). This is less clear when the dielectric tensor is anisotropic, so we accept Eqs. (2)–(4) as being well defined for isotropic dielectrics and focus on this case in the rest of this paper.

We now introduce the *unsymmetrized* strain and strain gradient tensors, defined as

$$\eta_{\alpha\beta} = \frac{\partial u_\alpha}{\partial r_\beta}, \quad (5)$$

$$v_{\alpha\beta\gamma} = \frac{\partial \eta_{\alpha\beta}}{\partial r_\gamma} = \frac{\partial^2 u_\alpha}{\partial r_\beta \partial r_\gamma} \quad (6)$$

(here we think of  $\mathbf{r}$  as a spatial coordinate in the continuum elasticity sense). Note that  $\eta_{\alpha\beta}$  is *not* generally symmetric

( $\eta_{\alpha\beta} \neq \eta_{\beta\alpha}$ ), while  $v_{\alpha\beta\gamma}$  is only symmetric in its last two indices ( $v_{\alpha\beta\gamma} = v_{\alpha\gamma\beta}$ ).

We now consider a long-wavelength displacement wave (“frozen acoustic phonon”) of wave vector  $\mathbf{k}$  in the crystal, so that the strain and strain gradient are given by

$$\mathbf{u}^{(0)}(\mathbf{r}) = \mathbf{u}_0 e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (7)$$

the displacement  $\mathbf{u}$ , strain  $\boldsymbol{\eta}$ , and strain gradient  $\mathbf{v}$  are

$$u_\alpha(\mathbf{r}) = u_{0\alpha} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (8)$$

$$\eta_{\alpha\beta}(\mathbf{r}) = i u_{0\alpha} k_\beta e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (9)$$

$$v_{\alpha\beta\gamma}(\mathbf{r}) = -u_{0\alpha} k_\beta k_\gamma e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (10)$$

To a first approximation, the atom displacements will follow the nominal pattern of Eq. (7), but the presence of the strain and strain gradient may induce additional “internal” displacements such that the total displacement of atom  $I$  in cell  $l$  is<sup>43</sup>

$$\mathbf{u}_{lI} = (\mathbf{u}^{(0)} + \mathbf{u}_I^{(1)} + \mathbf{u}_I^{(2)}) e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}. \quad (11)$$

Here,  $\mathbf{u}^{(0)}$  is the “acoustic” displacement of the cell as a whole (independent of atom index  $I$ ),  $\mathbf{u}_I^{(1)}$  is the additional displacement induced by strain  $\boldsymbol{\eta}$ , and  $\mathbf{u}_I^{(2)}$  is the additional displacement induced by strain gradient  $\mathbf{v}$ . That is,

$$\mathbf{u}_{I\tau}^{(1)} = \Gamma_{I\tau\beta\gamma} \eta_{\beta\gamma}, \quad (12)$$

$$\mathbf{u}_{I\tau}^{(2)} = N_{I\tau\beta\gamma\delta} v_{\beta\gamma\delta}, \quad (13)$$

where  $\Gamma_{I\tau\beta\gamma}$  is the internal-strain tensor describing the additional atomic displacements induced by a strain, and  $N_{I\tau\beta\gamma\delta}$  is the corresponding tensor describing the response to a strain gradient. Note that we adopt an implicit sum notation for Greek indices representing Cartesian components of polarization, field, or wave vector, such as  $\beta\gamma\delta$  above, although we will always write sums over the atomic displacement direction  $\tau$  explicitly.

We shall see in Sec. IIF how  $\Gamma_{I\tau\beta\gamma}$  and  $N_{I\tau\beta\gamma\delta}$  can be related, via the force-constant matrix, to force-response tensors  $\Lambda_{I\tau\beta\gamma}$  and  $T_{I\tau\beta\gamma\delta}$  describing the force  $F_{I\tau}$  induced, respectively, by a strain or strain gradient. This is straightforward for  $\Lambda$ , but we shall see there that an ambiguity arises for  $N$ . Deferring this issue for now, we substitute Eqs. (9) and (10) into (12) and (13) to find

$$\mathbf{u}_{I\tau}^{(0)} = u_{0\tau} e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}, \quad (14)$$

$$\mathbf{u}_{I\tau}^{(1)} = i \Gamma_{I\tau\beta\gamma} u_{0\beta} k_\gamma e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}, \quad (15)$$

$$\mathbf{u}_{I\tau}^{(2)} = -N_{I\tau\beta\gamma\delta} u_{0\beta} k_\gamma k_\delta e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}. \quad (16)$$

Defining

$$W_{I\tau\beta}(\mathbf{k}) = \delta_{\tau\beta} + i \Gamma_{I\tau\beta\gamma} k_\gamma - N_{I\tau\beta\gamma\delta} k_\gamma k_\delta, \quad (17)$$

Eq. (11) can be written as

$$u_{lI\tau} = W_{I\tau\beta} u_{0\beta} e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}. \quad (18)$$

Then, we can write the induced charge density at  $\mathbf{r}$  as

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{lI\tau} f_{I\tau}(\mathbf{r} - \mathbf{R}_{lI}) u_{lI\tau} \\ &= \sum_{lI\tau} f_{I\tau}(\mathbf{r} - \mathbf{R}_{lI}) W_{I\tau\beta} u_{0\beta} e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}, \end{aligned} \quad (19)$$



and compute its Fourier transform as

$$\begin{aligned}\rho(\mathbf{k}) &= V^{-1} \int d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \\ &= V_c^{-1} \sum_{I\tau} W_{I\tau\beta}(\mathbf{k}) \left( \frac{1}{N} \sum_l \int d\mathbf{r} f_{I\tau}(\mathbf{r} - \mathbf{R}_{lI}) e^{-i\mathbf{k}\cdot(\mathbf{r} - \mathbf{R}_{lI})} \right) u_{0\beta} \\ &= V_c^{-1} \sum_{I\tau} W_{I\tau\beta}(\mathbf{k}) \left( \int d\mathbf{r}' f_{I\tau}(\mathbf{r}') e^{-i\mathbf{k}\cdot\mathbf{r}'} \right) u_{0\beta}.\end{aligned}\quad (20)$$

(In going from the second to the third line above, we change the integration variable to  $\mathbf{r}' = \mathbf{r} - \mathbf{R}_{lI}$ , notice that the result is independent of  $l$ , and cancel  $\sum_l$  against  $N$ , where  $N$  is the number of cells of volume  $V_c$  in the total system of volume  $V$ .<sup>52</sup>) Thus, we have

$$\rho(\mathbf{k}) = V_c^{-1} \sum_{I\tau} W_{I\tau\beta}(\mathbf{k}) f_{I\tau}(\mathbf{k}) u_{0\beta}, \quad (21)$$

where the Fourier transform of  $f_{I\tau}(\mathbf{r})$  is

$$\begin{aligned}f_{I\tau}(\mathbf{k}) &= \int d\mathbf{r} f_{I\tau}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \\ &= \int d\mathbf{r} f_{I\tau}(\mathbf{r}) \left( 1 - ik_\mu r_\mu - \frac{1}{2} k_\mu k_\nu r_\mu r_\nu + \frac{1}{6} i k_\mu k_\nu k_\sigma r_\mu r_\nu r_\sigma + \dots \right).\end{aligned}\quad (22)$$

Keeping terms up to third order in  $\mathbf{k}$ , we get

$$f_{I\tau}(\mathbf{k}) = -i k_\mu Q_{I\mu\tau}^{(1)} - \frac{1}{2} k_\mu k_\nu Q_{I\mu\tau\nu}^{(2)} + \frac{1}{6} i k_\mu k_\nu k_\sigma Q_{I\mu\tau\nu\sigma}^{(3)}, \quad (23)$$

where the neutrality of the induced charge  $f_{I\tau}(\mathbf{r})$  has been used to eliminate the zero-order term.

Plugging Eqs. (17) and (23) into Eq. (21), we obtain an overall expansion of  $\rho(\mathbf{k})$  in powers of wave vector  $\mathbf{k}$ . The linear-in- $k$  term vanishes by the acoustic sum rule in the form  $\sum_I Q_{I\tau\mu}^{(1)} = 0$ , so we get

$$\begin{aligned}\rho(\mathbf{k}) &= V_c^{-1} \sum_I \left[ \sum_\tau Q_{I\mu\tau}^{(1)} \Gamma_{I\tau\beta\gamma} k_\mu k_\gamma - \frac{1}{2} Q_{I\mu\beta\nu}^{(2)} k_\mu k_\nu \right] u_{0\beta} \\ &+ V_c^{-1} \sum_I \left[ i \sum_\tau Q_{I\mu\tau}^{(1)} N_{I\tau\beta\gamma\delta} k_\mu k_\gamma k_\delta - \frac{1}{2} i \sum_\tau Q_{I\mu\tau\nu}^{(2)} \Gamma_{I\tau\beta\gamma} k_\mu k_\nu k_\gamma + \frac{1}{6} i Q_{I\mu\beta\nu\sigma}^{(3)} k_\mu k_\nu k_\sigma \right] u_{0\beta} + \dots.\end{aligned}\quad (24)$$

We now want to relate this to the polarization  $\mathbf{P}$ , in terms of which we can define the (unsymmetrized) piezoelectric and flexoelectric tensors as

$$e_{\alpha\beta\gamma} = \frac{\partial P_\alpha}{\partial \eta_{\beta\gamma}} \quad (25)$$

and

$$\mu_{\alpha\beta\gamma\delta} = \frac{\partial P_\alpha}{\partial v_{\beta\gamma\delta}} \quad (26)$$

so that

$$P_\alpha = e_{\alpha\beta\gamma} \eta_{\beta\gamma} + \mu_{\alpha\beta\gamma\delta} v_{\beta\gamma\delta} + \dots \quad (27)$$

Note that  $v_{\beta\gamma\delta}$  is symmetric in its last two indices  $\gamma\delta$ , so that  $\mu_{\alpha\beta\gamma\delta}$  is not uniquely specified by Eq. (27); to make it so, we adopt the convention that  $\mu_{\alpha\beta\gamma\delta}$  is symmetric in  $\gamma\delta$  as well. For the wave in question we find, using Eqs. (9) and (10),

$$P_\alpha(\mathbf{k}) = e_{\alpha\beta\gamma} i u_{0\beta} k_\gamma + \mu_{\alpha\beta\gamma\delta} (-u_{0\beta}) k_\gamma k_\delta + \dots \quad (28)$$

Using Poisson's equation in the form  $\rho(\mathbf{k}) = -ik_\alpha P_\alpha(\mathbf{k})$ , we obtain

$$\rho(\mathbf{k}) = e_{\alpha\beta\gamma} k_\alpha k_\gamma u_{0\beta} + i \mu_{\alpha\beta\gamma\delta} k_\alpha k_\gamma k_\delta u_{0\beta} + \dots \quad (29)$$

Now, the strategy is to compare Eqs. (24) and (29) term by term in powers of  $\mathbf{k}$ . Since the equation must be true for all  $\mathbf{u}_0$  vectors for a given  $\mathbf{k}$ , equating the second-order-in- $\mathbf{k}$  terms gives

$$e_{\alpha\beta\gamma} k_\alpha k_\gamma = V_c^{-1} \sum_I \left[ \sum_\tau Q_{I\mu\tau}^{(1)} \Gamma_{I\tau\beta\gamma} k_\mu k_\gamma - \frac{1}{2} Q_{I\mu\beta\nu}^{(2)} k_\mu k_\nu \right], \quad (30)$$

and similarly at the next order

$$\begin{aligned}\mu_{\alpha\beta\gamma\delta} k_\alpha k_\gamma k_\delta &= V_c^{-1} \sum_I \left[ \sum_\tau Q_{I\mu\tau}^{(1)} N_{I\tau\beta\gamma\delta} k_\mu k_\gamma k_\delta \right. \\ &\left. - \frac{1}{2} \sum_\tau Q_{I\mu\tau\nu}^{(2)} \Gamma_{I\tau\beta\gamma} k_\mu k_\nu k_\gamma + \frac{1}{6} Q_{I\mu\beta\nu\sigma}^{(3)} k_\mu k_\nu k_\sigma \right].\end{aligned}\quad (31)$$

These equations describe the piezoelectric and flexoelectric responses, respectively.

### B. Piezoelectric response

We begin with the piezoelectric case. From Eq. (30) it follows that

$$e_{\alpha\beta\gamma} = V_c^{-1} \sum_{I\tau} Q_{I\alpha\tau}^{(1)} \Gamma_{I\tau\beta\gamma} - \frac{1}{2} V_c^{-1} \sum_I Q_{I\alpha\beta\gamma}^{(2)} + A_{\alpha\beta\gamma}, \quad (32)$$

where  $A_{\alpha\beta\gamma}$  is antisymmetric in the first and third indices but otherwise arbitrary. The first two terms represent the lattice and electronic responses, respectively. The third vanishes under the symmetric sum over  $\alpha\gamma$  on the left side of Eq. (30), and serves as a reminder that the forms given in the first two terms may not be fully determined. There is little danger of this regarding the first term, which has a transparent interpretation in terms of dipoles associated with strain-induced internal displacements of the atomic coordinates. Thus, we can write

$$e_{\alpha\beta\gamma} = e_{\alpha\beta\gamma}^{\text{ld}} + e_{\alpha\beta\gamma}^{\text{el}}, \quad (33)$$

where the lattice contribution

$$e_{\alpha\beta\gamma}^{\text{ld}} = V_c^{-1} \sum_{I\tau} Q_{I\alpha\tau}^{(1)} \Gamma_{I\tau\beta\gamma} \quad (34)$$

is denoted “ld” for “lattice dipole.” The absence of a correction term in Eq. (34) is demonstrated in Appendix A. In the electronic term  $e_{\alpha\beta\gamma}^{\text{el}}$ , however, a correction having the form of  $A_{\alpha\beta\gamma}$  can not be discounted; relabeling  $A$  as  $e^{\text{el,T}}$ , we obtain

$$e_{\alpha\beta\gamma}^{\text{el}} = -\frac{1}{2} V_c^{-1} \sum_I Q_{I,\alpha\beta\gamma}^{(2)} + e_{\alpha\beta\gamma}^{\text{el,T}}. \quad (35)$$

An explicit expression for  $e_{\alpha\beta\gamma}^{\text{el,T}}$  is given in Appendix A.

We denote the first (symmetric in  $\alpha\gamma$ ) and second (antisymmetric in  $\alpha\gamma$ ) terms of Eq. (35) as the “longitudinal” (L) and “transverse” (T) parts, respectively. To clarify this terminology, note that a given deformation of the medium will generate a polarization field  $\mathbf{P}(\mathbf{r})$  whose longitudinal and transverse parts are defined as the curl-free and divergence-free portions, respectively, so that any piezoelectrically induced charge density  $\rho = -\nabla \cdot \mathbf{P}$  comes only from the longitudinal part. But, a simple calculation shows that

$$\partial_\alpha P_\alpha(\mathbf{r}) = \partial_\alpha (e_{\alpha\beta\gamma} \eta_{\beta\gamma}) = e_{\alpha\beta\gamma} \nu_{\beta\alpha\gamma} = e_{\alpha\beta\gamma}^S \nu_{\beta\alpha\gamma}, \quad (36)$$

where the symmetry of  $\nu_{\beta\alpha\gamma}$  under  $\alpha\gamma$  is used in the last step. This shows that the “symmetric” and “antisymmetric” parts of  $e_{\alpha\beta\gamma}$  are indeed just the longitudinal and transverse contributions, respectively.

Recall that this is the piezoelectric response to the unsymmetrized strain tensor of Eq. (5), and so contains responses to the rotation of the medium as well as to a symmetric strain. Defining the symmetric and antisymmetric parts as

$$\epsilon_{\alpha\beta} = (\eta_{\alpha\beta} + \eta_{\beta\alpha})/2, \quad (37)$$

$$\omega_{\alpha\beta} = (\eta_{\alpha\beta} - \eta_{\beta\alpha})/2, \quad (38)$$

and considering the general case  $e_{\alpha\beta\gamma} = e_{\alpha\beta\gamma}^S + e_{\alpha\beta\gamma}^A$  (with  $e^S$  and  $e^A$ , respectively, symmetric and antisymmetric under

indices  $\alpha\gamma$ ), one finds that

$$P_\alpha = e_{\alpha\beta\gamma}^S \epsilon_{\beta\gamma} + e_{\alpha\beta\gamma}^A \omega_{\beta\gamma}. \quad (39)$$

Here, the antisymmetric part corresponds to the change of polarization resulting from rotation of the crystal, and thus contributes to the “improper” piezoelectric response.<sup>53</sup> However, the improper response also includes symmetric contributions (e.g., from volume-nonconserving symmetric strains), so the “proper” piezoelectric tensor can not simply be equated with  $e_{\alpha\beta\gamma}^S$ . After a careful analysis that made use of sum rules associated with uniform translations and rotations of the lattice, Martin<sup>43</sup> was able to show that the proper piezoelectric response is given by Eqs. (33) and (34) with Eq. (35) replaced by

$$e_{\alpha\beta\gamma}^{\text{el,prop}} = -\frac{1}{2} V_c^{-1} \sum_I [Q_{I\alpha\beta\gamma}^{(2)} - Q_{I\gamma\alpha\beta}^{(2)} + Q_{I\beta\gamma\alpha}^{(2)}]. \quad (40)$$

Thus, while it is far from obvious, it turns out that the proper piezoelectric tensor depends only on the symmetric parts of the response. This is consistent with simple counting arguments: the tensor describing the polarization response to a symmetric strain has 18 independent elements, as does  $Q_{I\alpha\beta\gamma}^{(2)}$ .

Interestingly, the distinction between proper and improper responses does not arise for flexoelectricity, which is defined in terms of the polarization at a point in the material at which  $\eta_{\alpha\beta}$  is zero (although the strain gradient is not). Also, while the symmetrized strain tensor contains less information than the unsymmetrized  $\eta_{\alpha\beta}$  (six elements versus nine), this is not true of strain gradients. Instead, the symmetrized and unsymmetrized strain gradients contain the same information (18 unique elements) and are related by<sup>54</sup>

$$\nu_{\beta\gamma\delta} = \frac{\partial^2 u_\beta}{\partial r_\gamma \partial r_\delta} = \frac{\partial \epsilon_{\beta\gamma}}{\partial r_\delta} + \frac{\partial \epsilon_{\beta\delta}}{\partial r_\gamma} - \frac{\partial \epsilon_{\gamma\delta}}{\partial r_\beta}. \quad (41)$$

In this one respect, the treatment of the flexoelectric response is actually simpler than for the piezoelectric one.

### C. Flexoelectric response

We turn now to the flexoelectric response. The general solution of Eq. (31) is

$$\begin{aligned} \mu_{\alpha\beta\gamma\delta} = & V_c^{-1} \sum_{I\tau} Q_{I\alpha\tau}^{(1)} N_{I\tau\beta\gamma\delta} \\ & - \frac{1}{4} V_c^{-1} \sum_{I\tau} (Q_{I\alpha\tau\delta}^{(2)} \Gamma_{I\tau\beta\gamma} + Q_{I\alpha\tau\gamma}^{(2)} \Gamma_{I\tau\beta\delta}) \\ & + \frac{1}{6} V_c^{-1} \sum_I Q_{I\alpha\beta\gamma\delta}^{(3)} + B_{\alpha\beta\gamma\delta}, \end{aligned} \quad (42)$$

where the  $Q^{(2)}$  term has been symmetrized to obey the requirement that  $\mu_{\alpha\beta\gamma\delta}$  be symmetric in  $\gamma\delta$ , and  $B_{\alpha\beta\gamma\delta}$  is an extra “antisymmetric” piece. For our purposes, we define the “symmetric part” of  $X_{\alpha\beta\gamma\delta}$  (that is symmetric in its last two indices) to be

$$X_{\alpha\beta\gamma\delta}^S = \frac{1}{3} (X_{\alpha\beta\gamma\delta} + X_{\gamma\beta\delta\alpha} + X_{\delta\beta\alpha\gamma}) \quad (43)$$

and the antisymmetric part to be  $X^A = X - X^S$ . So, we are allowed to add an extra antisymmetric term  $B = B^A$  to Eq. (42) because it will vanish under the sum over  $\alpha\gamma\delta$  in Eq. (31).

Clearly, Eq. (42) contains three terms, two of which involve lattice responses. We write

$$\mu_{\alpha\beta\gamma\delta} = \mu_{\alpha\beta\gamma\delta}^{\text{ld}} + \mu_{\alpha\beta\gamma\delta}^{\text{dq}} + \mu_{\alpha\beta\gamma\delta}^{\text{el}}, \quad (44)$$

where the terms on the right side are the lattice dipole, lattice quadrupole, and electronic terms, respectively. Writing these explicitly,

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld}} = V_c^{-1} \sum_{I\tau} Q_{I\alpha\tau}^{(1)} N_{I\tau\beta\gamma\delta}, \quad (45)$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{dq}} = -\frac{1}{4} V_c^{-1} \sum_{I\tau} (Q_{I\alpha\tau\delta}^{(2)} \Gamma_{I\tau\beta\gamma} + Q_{I\alpha\tau\gamma}^{(2)} \Gamma_{I\tau\beta\delta}) + \mu_{\alpha\beta\gamma\delta}^{\text{dq,J}}, \quad (46)$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{el}} = \frac{1}{6} V_c^{-1} \sum_I Q_{I\alpha\beta\gamma\delta}^{(3)} + \mu_{\alpha\beta\gamma\delta}^{\text{el,J}}, \quad (47)$$

where the last terms in Eqs. (46) and (47) are extra antisymmetric contributions and  $\mu^{\text{dq,J}} + \mu^{\text{el,J}}$  corresponds to the  $B$  term in Eq. (42). The label ‘‘J’’ indicates that these terms arise from the current-response formulation given in Appendix A; explicit expressions for these corrections, and a demonstration that no correction is needed for  $\mu^{\text{ld}}$ , are given there.

Let us emphasize again the physics of these corrections. First, we can straightforwardly extend the discussion at the end of the last section to the case of flexoelectricity. In place of Eq. (36) we find

$$\begin{aligned} \partial_\alpha P_\alpha(\mathbf{r}) &= \partial_\alpha (\mu_{\alpha\beta\gamma\delta} v_{\beta\gamma\delta}) \\ &= \mu_{\alpha\beta\gamma\delta} h_{\beta\alpha\gamma\delta} \\ &= \mu_{\alpha\beta\gamma\delta}^{\text{S}} h_{\beta\alpha\gamma\delta}, \end{aligned} \quad (48)$$

where

$$h_{\beta\alpha\gamma\delta} = \frac{\partial \eta_{\beta\gamma\delta}}{\partial r_\alpha} = \frac{\partial^3 u_\beta}{\partial r_\alpha \partial r_\gamma \partial r_\delta} \quad (49)$$

is fully symmetric in the last three indices  $\alpha\gamma\delta$ . It again follows that ‘‘symmetric’’ and ‘‘antisymmetric’’ correspond to ‘‘longitudinal’’ (L) and ‘‘transverse’’ (T), respectively.

Now, the essential problem is that the charge density appearing in Eq. (19), used as the starting point of the derivation given above, is only sensitive to the longitudinal response since it only depends on the divergence of  $\mathbf{P}(\mathbf{r})$ . Thus, the expression given for the FEC tensor in Eq. (42), excluding the final antisymmetric  $B_{\alpha\beta\gamma\delta}$  term, must contain *all* of the longitudinal response, but may contain only part of, or may omit altogether, the transverse response. A simple calculation shows that the  $Q^{(1)} N$  and  $Q^{(2)} \Gamma$  terms in Eqs. (45) and (46) do contain transverse parts, while the  $Q^{(3)}$  term in Eq. (47) does not. The last terms in Eqs. (46) and (47) are contributions to the transverse parts  $\mu^{\text{dq,T}}$  and  $\mu^{\text{el,T}}$  of the lattice-quadrupole and electronic responses.

While the transverse parts  $\mu^{\text{dq,T}}$  and  $\mu^{\text{el,T}}$  make no contribution to the induced internal charge density  $\rho(\mathbf{r})$ , this does not mean that the transverse terms have no physical consequence. Polarization-related bound charges also arise at surfaces and interfaces of the sample, and these can depend on the transverse as well as the longitudinal part of the flexoelectric response, as occurs for example for beam-bending geometries as discussed in Sec. IV C. Thus, a full theory of flexoelectricity should

contain both contributions, as derived in Appendix A. In the remainder of this paper, however, we concentrate on computing the longitudinal contributions alone.

Finally, we note that the need for transverse corrections is also evident from counting arguments. For example, looking at the electronic contribution of Eq. (47), we can see that  $\mu_{\alpha\beta\gamma\delta}^{\text{el}}$  has 54 independent tensor elements ( $3 \times 3 \times 6$  since it is symmetric under  $\gamma\delta$ ) while  $Q_{I\alpha\beta\gamma\delta}^{(3)}$  has only 30 ( $3 \times 10$  since it is symmetric under  $\alpha\gamma\delta$ ). Thus, the  $Q$  moment tensors do not contain enough information to fully specify the flexoelectric response. On the other hand, the symmetric (i.e., longitudinal) part of  $\mu^{\text{el}}$  has only 30 independent elements and can thus be captured by  $Q_{I\alpha\beta\gamma\delta}^{(3)}$ .

#### D. Crystals with cubic symmetry

For crystals with full cubic point symmetry, the piezoelectric tensor vanishes by symmetry and the flexoelectric tensor  $\mu_{\alpha\beta\gamma\delta}$  has only three independent elements,<sup>51</sup> namely,  $\mu_{1111}$ ,  $\mu_{1221}$ , and  $\mu_{1122}$ . Others related by interchange or cycling of Cartesian indices are equal (e.g.,  $\mu_{1221} = \mu_{3113}$ ) and those with any Cartesian index appearing an odd number of times (e.g.,  $\mu_{1223}$ ) vanish.

Using these relations and Eq. (49) we can explicitly write  $-\rho(\mathbf{r}) = A \mu_{1111} + B \mu_{1122} + C \mu_{1221}$  with  $A = h_{1111} + h_{2222} + h_{3333}$ ,  $B = h_{1122} + h_{2211} + h_{1133} + h_{3311} + h_{2233} + h_{3322}$ , and  $C = 2B$ . The internal bound charge resulting from the flexoelectric response to the deformation is then proportional to  $A \mu_{1111} + B (\mu_{1122} + 2\mu_{1221})$ . This motivates us to define a new set of three coefficients as

$$\mu_{\text{L1}} = \mu_{1111}, \quad (50)$$

$$\mu_{\text{L2}} = \mu_{1122} + 2\mu_{1221}, \quad (51)$$

$$\mu_{\text{T}} = \mu_{1122} - \mu_{1221}. \quad (52)$$

Here L1 and L2 indicate longitudinal terms which contribute to the internal bound charges in proportion to combinations  $A$  and  $B$ , respectively, while T indicates a transverse term. Thus, we see that a general cubic material is characterized by two longitudinal and one transverse flexoelectric coefficient. For a material such as glass that has isotropic symmetry, one finds that  $\mu_{1111} = \mu_{1122} + 2\mu_{1221}$ , i.e.,  $\mu_{\text{L1}} = \mu_{\text{L2}}$ , in which case there is only one longitudinal coefficient. Thus, we can think of  $\Delta = \mu_{\text{L2}} - \mu_{\text{L1}}$  as a measure of the anisotropy of the cubic medium, which shows up only in the longitudinal response.

In general, the flexoelectric response of a cubic crystal can have contributions from all three terms in Eq. (44). However, as we shall see in Sec. II F1, the lattice-quadrupole term of Eq. (46) vanishes in simple cubic materials including those found in rocksalt, cesium chloride, and perovskite crystal structures. This term can be nonzero in more complex cubic materials, such as spinels and pyrochlores; the technical requirement is the presence of zone-center Raman-active phonon modes, or equivalently, the existence of free Wyckoff parameters. This will be discussed further in Sec. II F1.

#### E. Definitions in terms of symmetrized strains

There are many different definitions of FECs in the literature. Up until now, we have been working with the

unsymmetrized strain tensor  $\eta_{\alpha\beta} = \partial u_\alpha / \partial r_\beta$  and its gradient  $v_{\alpha\beta\gamma} = \partial \eta_{\alpha\beta} / \partial r_\gamma$  defined in Eqs. (5) and (6); this form is convenient for formal derivations and for practical calculations, and corresponds to the  $\mu$  in Refs. 39, 45, and 55, and the  $f$  in Ref. 38. On the other hand, the FEC related to *symmetrized* strain is convenient for experimental measurements; see, e.g.,  $g$  in Ref. 54,  $f$  in Refs. 21–23, 31, 42, and 56,  $\mu$  in Refs. 4–10, 25, 26, 35, 44, 46, 57, and 58, and  $F$  in Ref. 51, and  $\gamma$  in Ref. 59. Researchers sometimes use different definitions without emphasizing their relations. Complicating matters further is the fact that different conventions are frequently used in the literature for the order of the four subscript indexes of the FEC tensor, both for unsymmetrized and symmetrized strain cases, which can cause confusion especially for the transverse components. In this section, therefore, we clarify the relations between the unsymmetrized and symmetrized formulations following the analysis in Zubko’s thesis.<sup>54</sup> Throughout our paper, we use the notations  $\mu$  and  $g$  for the FECs defined in terms of unsymmetrized and symmetrized strains, respectively.

We define the gradient of the symmetrized strain as

$$v_{\beta\gamma\delta}^s = \frac{\partial \epsilon_{\beta\gamma}}{\partial r_\delta} = \frac{1}{2}(v_{\beta\gamma\delta} + v_{\gamma\beta\delta}). \quad (53)$$

Note that  $v_{\beta\gamma\delta}^s$  is symmetric in the first two indices  $\beta\gamma$ , while instead  $v_{\beta\gamma\delta}$  is symmetric in the last two indices  $\gamma\delta$ . The inverse relation to the above equation is

$$v_{\beta\gamma\delta} = \frac{\partial^2 u_\beta}{\partial r_\gamma \partial r_\delta} = v_{\beta\gamma\delta}^s + v_{\beta\delta\gamma}^s - v_{\gamma\delta\beta}^s, \quad (54)$$

which appeared earlier as Eq. (41). In the context of symmetrized strains, we then define the flexoelectric coefficient  $\tilde{g}_{\alpha\beta\gamma\delta}$  to obey (note the order of indices)

$$P_\alpha = \tilde{g}_{\alpha\delta\beta\gamma} v_{\beta\gamma\delta}^s. \quad (55)$$

Comparing this with

$$P_\alpha = \mu_{\alpha\beta\gamma\delta} v_{\beta\gamma\delta}, \quad (56)$$

it follows that

$$\tilde{g}_{\alpha\delta\beta\gamma} = \mu_{\alpha\beta\gamma\delta} + \mu_{\alpha\beta\delta\gamma} - \mu_{\alpha\delta\beta\gamma}. \quad (57)$$

Recall that we defined  $\mu_{\alpha\beta\gamma\delta}$  to be symmetric in  $\gamma\delta$  by convention. Then,  $\tilde{g}_{\alpha\delta\beta\gamma}$  as given by Eq. (57) is *not* generally symmetric in its own last indices  $\beta\gamma$ .<sup>54</sup> Alternatively, we may define

$$\begin{aligned} g_{\alpha\delta\beta\gamma} &= \frac{1}{2}(\tilde{g}_{\alpha\delta\beta\gamma} + \tilde{g}_{\alpha\delta\gamma\beta}) \\ &= \mu_{\alpha\beta\gamma\delta} + \mu_{\alpha\gamma\beta\delta} - \mu_{\alpha\delta\beta\gamma}. \end{aligned} \quad (58)$$

This is symmetric in  $\beta\gamma$ , making it a more natural definition in the symmetrized-strain context, where also  $v_{\beta\gamma\delta}^s$  is symmetric in  $\beta\gamma$ . In this case, however, the  $\tilde{\mu}_{\alpha\beta\gamma\delta}$  that is related to  $g_{\alpha\delta\beta\gamma}$  by the analog of Eq. (57) is no longer symmetric in its own last indices  $\gamma\delta$ . By convention,  $\mu$  and  $g$  are usually used in the unsymmetrized-strain and symmetrized-strain contexts, respectively, so Eq. (58) should be used to do the conversion instead of Eq. (57).<sup>60</sup>

For a cubic system, we have

$$g_{1111} = \mu_{1111}, \quad (59)$$

$$g_{1122} = 2\mu_{1221} - \mu_{1122}, \quad (60)$$

$$g_{1221} = \mu_{1122}, \quad (61)$$

and the flexoelectric coefficients defined in Eqs. (50)–(52) can be written as

$$\mu_{L1} = g_{1111}, \quad (62)$$

$$\mu_{L2} = g_{1122} + 2g_{1221}, \quad (63)$$

$$\mu_T = -\frac{1}{2}(g_{1122} - g_{1221}). \quad (64)$$

## F. Lattice contributions

We return now to the lattice (or “relaxed-ion”) contributions to the flexoelectric response, given by Eqs. (45) and (46), neglecting now the current-response contribution to the latter. In Sec. II A, we defined

$$\Gamma_{I\tau\beta\gamma} = \frac{\partial u_{I\tau}^{(1)}}{\partial \eta_{\beta\gamma}}, \quad (65)$$

$$N_{I\tau\beta\gamma\delta} = \frac{\partial u_{I\tau}^{(2)}}{\partial v_{\beta\gamma\delta}}, \quad (66)$$

which are the “internal-strain” tensors describing the *displacements* of the atoms in response to a strain or strain gradient, respectively. Correspondingly, we define

$$\Lambda_{I\tau\beta\gamma} = \frac{\partial F_{I\tau}}{\partial \eta_{\beta\gamma}}, \quad (67)$$

$$T_{I\tau\beta\gamma\delta} = \frac{\partial F_{I\tau}}{\partial v_{\beta\gamma\delta}}, \quad (68)$$

representing the *forces* appearing on the atoms due to a homogeneous strain or strain gradient.

For the strain-induced case, we assume that the atoms adjust to their equilibrium positions as the strain is applied. The force balance equations then take the form  $0 = dF_{I\tau}/d\eta_{\beta\gamma}$ , or

$$\begin{aligned} 0 &= \frac{\partial F_{I\tau}}{\partial \eta_{\beta\gamma}} + \sum_{J\tau'} \frac{\partial F_{I\tau}}{\partial u_{J\tau'}^{(1)}} \frac{\partial u_{J\tau'}^{(1)}}{\partial \eta_{\beta\gamma}} \\ &= \Lambda_{I\tau\beta\gamma} - \sum_{J\tau'} K_{I\tau, J\tau'} \Gamma_{J\tau'\beta\gamma}, \end{aligned} \quad (69)$$

where

$$K_{I\tau, J\tau'} = -\frac{\partial F_{J\tau'}}{\partial u_{I\tau}} \quad (70)$$

is the zone-center force-constant matrix. It follows that

$$\Gamma_{I\tau\beta\gamma} = \sum_{J\tau'} (K^{-1})_{I\tau, J\tau'} \Lambda_{J\tau'\beta\gamma}, \quad (71)$$

where  $(K^{-1})$  is the pseudoinverse of  $K$  (see Sec. II F2). When inserted in Eq. (34), this gives the standard result for the lattice piezoelectric response

$$e_{\alpha\beta\gamma}^{\text{ld}} = V_c^{-1} \sum_{I\tau, J\tau'} Q_{I\alpha\tau}^{(1)} (K^{-1})_{I\tau, J\tau'} \Lambda_{J\tau'\beta\gamma}, \quad (72)$$



and a similar substitution can be made in Eq. (46) for the lattice-quadrupole flexoelectric response to get

$$\mu_{\alpha\beta\gamma\delta}^{\text{1q}} = -\frac{V_c^{-1}}{4} \sum_{I\tau, J\tau'} Q_{I\alpha\tau\delta}^{(2)} (K^{-1})_{I\tau, J\tau'} \Lambda_{J\tau'\beta\gamma} + \dots, \quad (73)$$

where the “...” refers to the term with  $(\gamma, \delta)$  interchanged.

For the lattice-dipole flexoelectric response of Eq. (45), we would similarly like to write the force-balance equations

$$\begin{aligned} 0 &= \frac{\partial F_{I\tau}}{\partial v_{\beta\gamma\delta}} + \sum_{J\tau'} \frac{\partial F_{I\tau}}{\partial u_{J\tau'}^{(2)}} \frac{\partial u_{J\tau'}^{(2)}}{\partial v_{\beta\gamma\delta}} \\ &= T_{I\tau\beta\gamma} - \sum_{J\tau'} K_{I\tau, J\tau'} N_{J\tau'\beta\gamma}, \end{aligned} \quad (74)$$

which would lead to

$$N_{I\tau\beta\gamma\delta} = \sum_{J\tau'} (K^{-1})_{I\tau, J\tau'} T_{J\tau'\beta\gamma\delta}, \quad (75)$$

so that Eq. (45) becomes

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld}} = V_c^{-1} \sum_{I\tau, J\tau'} Q_{I\alpha\tau}^{(1)} (K^{-1})_{I\tau, J\tau'} T_{J\tau'\beta\gamma\delta}. \quad (76)$$

This is how we calculate lattice flexoelectric response in this work; we first compute  $Q^{(1)}$ ,  $K$ , and  $T$  from our first-principles calculations, and then combine them via Eq. (76).

Strictly speaking, however, Eq. (74) has no solution, for the simple reason that a true force balance is not possible: relaxing the atoms to their equilibrium positions would erase the strain gradient. Formally, the problem is that when summed over the atom index  $I$ , the first term of Eq. (74) is generally nonzero, while the second vanishes by the acoustic sum rule. Physically, the problem is that a strain gradient is always accompanied by a stress gradient, which in general gives rise to a force density. Thus, external forces, not accounted for in Eq. (74), need to be applied to the atoms in each unit cell in order to oppose this force density. As will be discussed in Sec. II F2, we can still use Eq. (75) as long as  $K^{-1}$  is replaced by an appropriately chosen pseudoinverse. There is some freedom in the choice of this pseudoinverse, but physical results for static deformations, such as the beam-bending configurations discussed in Sec. IV C, will ultimately be independent of this choice.

Finally, following Tagantsev,<sup>37</sup> we note that the zone-center force-constant matrix  $K_{I\tau, J\tau'}$  and the force-response tensors  $\Lambda_{I\tau\beta\gamma}$  and  $T_{I\tau\beta\gamma\delta}$  can themselves be written in a manner somewhat parallel to (2)–(4), but this time as moments of the full force-constant matrix

$$\Phi_{\tau\tau'}^{IJ} = -\frac{\partial F_{0I\tau}}{\partial u_{IJ\tau'}}. \quad (77)$$

Using

$$\Lambda_{I\tau\beta\gamma} = \frac{\partial F_{0I\tau}}{\partial \eta_{\beta\gamma}} = \sum_{IJ\tau'} \frac{\partial F_{0I\tau}}{\partial u_{IJ\tau'}^{(0)}} \frac{\partial u_{IJ\tau'}^{(0)}}{\partial \eta_{\beta\gamma}}, \quad (78)$$

$$T_{I\tau\beta\gamma\delta} = \frac{\partial F_{0I\tau}}{\partial v_{\beta\gamma\delta}} = \sum_{IJ\tau'} \frac{\partial F_{0I\tau}}{\partial u_{IJ\tau'}^{(0)}} \frac{\partial u_{IJ\tau'}^{(0)}}{\partial v_{\beta\gamma\delta}}, \quad (79)$$

it follows that

$$K_{I\tau, J\tau'} = \sum_l \Phi_{\tau\tau'}^{IJl}, \quad (80)$$

$$\Lambda_{I\tau\beta\gamma} = -\sum_{IJ} \Phi_{\tau\beta}^{IJ} \Delta R_{\gamma}^{IJ}, \quad (81)$$

$$T_{I\tau\beta\gamma\delta} = -\frac{1}{2} \sum_{IJ} \Phi_{\tau\beta}^{IJ} \Delta R_{\gamma}^{IJ} \Delta R_{\delta}^{IJ}, \quad (82)$$

where  $\Delta R_{\beta}^{IJ} = (\mathbf{R}_{IJ} - \mathbf{R}_{0I})_{\beta}$ . As a reminder,  $l'$  are unit-cell labels while  $IJ$  and  $\tau\tau'$  are atom and displacement-direction labels, respectively. Regarding the convergence of these sums at large  $\Delta R$ , considerations similar to those discussed below Eqs. (2)–(4) apply. The practical calculation of the elements of the  $T$  tensor will be described in Sec. III A, where Eq. (82) takes the form of Eq. (116) after being adapted to the supercell context.

### 1. Transformation to mode variables

In simple binary crystals such as NaCl or CsCl, the above formulas can be used directly. For more complicated crystals such as perovskites, however, it is useful to carry out a transformation to symmetry-mode variables. Here, we briefly sketch the transformation to an arbitrary set of mode variables, and then discuss in particular the case of symmetry modes chosen according to the irreducible representations (irreps) of the zone-center force-constant matrix.

Let  $\xi_j$  ( $j = 1, \dots, 3N$ ) be a set of mode variables that are related to the  $3N$  atomic displacements according to

$$\xi_j = \sum_{I\tau} A_{j, I\tau} u_{I\tau}, \quad (83)$$

with  $A_{j, I\tau}$  expressing the linear transformation from one basis to the other. The inverse relation is

$$u_{I\tau} = \sum_j (A^{-1})_{I\tau, j} \xi_j. \quad (84)$$

Then, using a tilde to indicate quantities expressed in the mode representation, the various quantities of interest transform as

$$\tilde{Q}_{j\alpha}^{(1)} = \sum_{I\tau} (A^{-1})_{I\tau, j} Q_{I\alpha\tau}^{(1)}, \quad (85)$$

$$\tilde{Q}_{j\alpha\beta}^{(2)} = \sum_{I\tau} (A^{-1})_{I\tau, j} Q_{I\alpha\tau\beta}^{(2)}, \quad (86)$$

$$\tilde{K}_{ij} = \sum_{IJ\tau\tau'} (A^{-1})_{I\tau, i} (A^{-1})_{J\tau', j} K_{I\tau, J\tau'}, \quad (87)$$

$$\tilde{\Lambda}_{j\beta\gamma} = \sum_{I\tau} (A^{-1})_{I\tau, j} \Lambda_{I\tau\beta\gamma}, \quad (88)$$

$$\tilde{T}_{j\beta\gamma\delta} = \sum_{I\tau} (A^{-1})_{I\tau, j} T_{I\tau\beta\gamma\delta}. \quad (89)$$

Then, Eqs. (34), (45), and (46) become

$$e_{\alpha\beta\gamma}^{\text{ld}} = V_c^{-1} \sum_j \tilde{Q}_{j\alpha}^{(1)} \tilde{\Gamma}_{j\beta\gamma}, \quad (90)$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld}} = V_c^{-1} \sum_j \tilde{Q}_{j\alpha}^{(1)} \tilde{N}_{j\beta\gamma\delta}, \quad (91)$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{dq}} = -\frac{1}{4} V_c^{-1} \sum_j (\tilde{Q}_{j\alpha\delta}^{(2)} \tilde{\Gamma}_{j\beta\gamma} + \tilde{Q}_{j\alpha\gamma}^{(2)} \tilde{\Gamma}_{j\beta\delta}), \quad (92)$$

where Eqs. (71) and (75) have been replaced by

$$\tilde{\Gamma}_{i\beta\gamma} = \sum_j (\tilde{K}^{-1})_{ij} \tilde{\Lambda}_{j\beta\gamma}, \quad (93)$$

$$\tilde{N}_{i\beta\gamma\delta} = \sum_j (\tilde{K}^{-1})_{ij} \tilde{T}_{j\beta\gamma\delta}. \quad (94)$$

Note that the  $\mu^{\text{ld}}$  term of Eq. (46) has been omitted in Eq. (92) above, but can easily be restored by converting  $J_{I,\alpha\beta\gamma}^{(1,T)}$  of Eq. (A25) into the mode representation in a manner analogous to Eq. (86).

This formulation becomes especially advantageous if the mode variables are chosen to be symmetry adapted. Let us relabel the modes as  $j \rightarrow \{s\sigma a\}$ , where  $s$  is the irrep label,  $\sigma$  labels the copy of the irrep if there is more than one, and  $a = 1 \dots m_s$  ( $m_s$  is the dimension of irrep  $s$ ) labels the basis vectors. Then, the zone-center force-constant matrix  $K$  is diagonal in  $s$  and  $a$ ,

$$\tilde{K}_{s\sigma a, s'\sigma' a'} = \delta_{ss'} \delta_{aa'} \tilde{k}_{s\sigma\sigma'}^s, \quad (95)$$

and its pseudoinverse can be written similarly but using  $\tilde{k}_s^{-1}$  which is the  $m_s \times m_s$  pseudoinverse of  $\tilde{k}^s$ . In this notation, we have

$$e_{\alpha\beta\gamma}^{\text{ld}} = V_c^{-1} \sum_{s\sigma\sigma' a} \tilde{Q}_{s\sigma a, \alpha}^{(1)} \tilde{k}_{s, \sigma\sigma'}^{-1} \tilde{\Lambda}_{s\sigma' a, \beta\gamma}, \quad (96)$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld}} = V_c^{-1} \sum_{s\sigma\sigma' a} \tilde{Q}_{s\sigma a, \alpha}^{(1)} \tilde{k}_{s, \sigma\sigma'}^{-1} \tilde{T}_{s\sigma' a, \beta\gamma\delta}, \quad (97)$$

$$\begin{aligned} \mu_{\alpha\beta\gamma\delta}^{\text{dq}} = & -\frac{1}{4} V_c^{-1} \sum_{s\sigma\sigma' a} (\tilde{Q}_{s\sigma a, \alpha\delta}^{(2)} \tilde{k}_{s, \sigma\sigma'}^{-1} \tilde{\Lambda}_{s\sigma' a, \beta\gamma} \\ & + \tilde{Q}_{s\sigma a, \alpha\gamma}^{(2)} \tilde{k}_{s, \sigma\sigma'}^{-1} \tilde{\Lambda}_{s\sigma' a, \beta\delta}). \end{aligned} \quad (98)$$

It is clear that  $\tilde{Q}^{(1)}$ , which describes the electric dipole appearing in response to a mode displacement, behaves like a Cartesian vector, and so will only be nonzero for vector irreps. Thus, the sums over  $s$  in Eqs. (96) and (97) can be restricted to irreps of vector character, and  $\tilde{\Lambda}$  and  $\tilde{T}$  need only be evaluated for these, i.e., for infrared-active modes. For cubic materials, there is just one such irrep, namely,  $T_1^-$  (also known as  $\Gamma_{15}^-$ ). It is well known for piezoelectricity that only infrared-active modes contribute, but the above makes it clear that the same is true for the lattice-dipole flexoelectric response.

As for the lattice-quadrupole contribution in Eq. (98),  $\tilde{Q}^{(2)}$  describes the electric-quadrupole response, which has the character of a symmetric second-rank tensor and thus only couples to quadrupolar or fully symmetric irreps. These are precisely the ones displaying Raman activity, so we can restrict our attention just to Raman-active modes when computing  $\mu^{\text{ld}}$ .

In this paper, we consider three types of cubic crystals. First, for C and Si in the diamond structure, the dynamical charges

vanish so that  $e^{\text{ld}}$  and  $\mu^{\text{ld}}$  vanish. Of course,  $e^{\text{el}}$  also vanishes as the crystal is not piezoelectric. However,  $\mu^{\text{ld}}$  does not vanish because the zone-center optic mode has  $T_2^+$  ( $\Gamma_{25}^+$ ) symmetry and is Raman active. The symmetry is such that  $\Gamma_{1\alpha\beta\gamma} = -\Gamma_{2\alpha\beta\gamma} = \gamma \varepsilon_{\alpha\beta\gamma}$ ,  $Q_{1\alpha\beta\gamma}^{(2)} = -Q_{2\alpha\beta\gamma}^{(2)} = q \varepsilon_{\alpha\beta\gamma}$  (where  $\varepsilon$  is the fully antisymmetric tensor and “1” and “2” label the two atoms in the primitive cell). It is a short exercise to show that  $\mu_{L1} = \mu_{L2} = 0$  and  $\mu_T = -3\gamma q/2V_c$ . In these materials, therefore,  $\mu_{L1}$  and  $\mu_{L2}$  have only electronic contributions, while  $\mu_T$  has both electronic and lattice-quadrupole contributions.

Second, we consider binary materials in the rocksalt or cesium chloride structure. The zone-center modes consist of two copies of the  $T_1^-$  ( $\Gamma_{15}^-$ ) irrep, which is not Raman active. In this case,  $\mu_{L1}$ ,  $\mu_{L2}$ , and  $\mu_T$  all have contributions from electronic and lattice-dipole terms only.

Third, we consider perovskite  $ABO_3$  compounds. Here, the zone-center modes comprise four copies of the IR-active  $T_1^-$  ( $\Gamma_{15}^-$ ) irrep, plus one  $T_2^-$  ( $\Gamma_{25}^-$ ) irrep that is neither IR nor Raman active. The situation is therefore similar to the binary-compound case, with  $\mu_{L1}$ ,  $\mu_{L2}$ , and  $\mu_T$  having electronic and lattice-dipole contributions only. Two of the  $T_1^-$  irreps correspond simply to displacements of the  $A$  or  $B$  atom, while the other two correspond to particular linear combinations of oxygen displacements. The symmetry-mode treatment of the oxygen displacements in the perovskite structure is detailed in Appendix C.

Note that more complex cubic crystals, such as spinels and pyrochlores, may have both IR-active and Raman-active zone-center modes. In particular, any cubic crystal having one or more free Wyckoff coordinates has Raman-active  $A_1^+$  ( $\Gamma_1^+$ ) modes. For such materials,  $\mu_{L1}$ ,  $\mu_{L2}$ , and  $\mu_T$  may all have contributions from all three terms in the flexoelectric response.

## 2. Pseudoinverse of force-constant matrix and force-pattern dependence

Recall that the force-response tensors  $\Gamma$  and  $T$  of Eqs. (67) and (68) need to be converted into displacement-response tensors  $\Lambda$  and  $N$  of Eqs. (65) and (66) via the application of a pseudoinverse as in Eqs. (71) and (75), respectively. For the piezoelectric response, this is straightforward because  $\Lambda$  obeys the acoustic sum rule, i.e.,  $\sum_I \Lambda_{I\tau\beta\gamma} = 0$ . This reflects the fact that a uniform strain induces no net force on an entire unit cell. Unfortunately, this is not true in general for  $T$ , which describes the force response to a uniform strain *gradient*. In general, such a strain gradient is accompanied by a stress gradient, i.e., a force density proportional to  $\nabla \cdot \sigma$ . This means that  $\sum_I T_{I\tau\beta\gamma\delta} \neq 0$  in general, and the definition and application of the pseudoinverse in Eq. (75) is more subtle.

For the present purposes, we can regard the force  $T_{I\tau\beta\gamma\delta}$  induced by a strain gradient  $v_{\beta\gamma\delta}$  as an “external” force  $f_{I\tau}^{\text{ext}}$ , and we have in general that  $b_\tau \equiv \sum_I f_{I\tau}^{\text{ext}} \neq 0$ . We would like to find a set of displacements  $u_{I\tau}$  obeying

$$f_{I\tau}^{\text{ext}} - \sum_{J\tau'} K_{I\tau, J\tau'} u_{J\tau'} = 0. \quad (99)$$

We know this is not possible, however, since  $K$  obeys the Acoustic Sum Rule (ASR)  $\sum_I K_{I\tau, J\tau'} = 0$ , so applying  $\sum_I$  on the left-hand side yields  $b_\tau$ . Therefore, the best we can

hope to do is to find a solution to

$$f_{I\tau}^{\text{ext}} - \sum_{J\tau'} K_{I\tau, J\tau'} u_{J\tau'} = b_\tau w_I \quad (100)$$

instead, where the  $w_I$  are a set of weights obeying  $\sum_I w_I = 1$ . These weights describe the residual force pattern that is left after the displacements  $u_{I\tau}$  are applied, and we have freedom to choose these as we wish. For example, setting  $w_I = 0$  except for  $w_1 = 1$  would establish that we seek a displacement pattern that makes the force vanish on all atoms in the cell except atom 1. A more natural choice is the ‘‘evenly weighted’’ one given by  $w_I = 1/N$  for all  $I$ , which asks for displacements that leave an equal residual force on every atom. A third possibility is the mass-weighted choice  $w_I = M_I/M_{\text{tot}}$  where  $M_{\text{tot}} = \sum_I M_i$  is the total mass per cell. This choice does affect the computation of the individual FEC tensor components because the dynamical charges  $Q^{(1)}$  appearing in Eq. (76) depend on atom  $I$ , thus yielding a different response to different displacements. In Sec. IV, we normally present our results for the second and third of the choices discussed above (evenly weighted or mass weighted), which appear to be the most natural ones.

In Appendix B, we explain how to define and compute a pseudoinverse  $J_{I\tau, J\tau'}^{[w]}$  to  $K_{I\tau, J\tau'}$  having the desired property that

$$u_{I\tau} = \sum_{J\tau'} J_{I\tau, J\tau'}^{[w]} f_{J\tau'}^{\text{ext}} \quad (101)$$

solves Eq. (100). The superscript  $[w]$  appears on the pseudoinverse to emphasize that it is not unique, but depends on the choice of force pattern embodied in the weights  $w_I$ . We then use this pseudoinverse  $J^{[w]}$  in place of  $(K^{-1})$  in Eq. (75) or (76).

The freedom in the choice of the force-pattern weights  $w_I$  seems disconcerting at first sight, but we emphasize that any *physical* prediction of our theory is either independent of this choice, or else determines it in an obvious way. For example, consider a *static* deformation  $\mathbf{u}(\mathbf{r})$  such as that occurring in the beam-bending configuration discussed in Sec. IV C. In this case, a combination of different strain gradient components  $v_{\beta\gamma\delta}$  is present, and while the net force per unit cell arising from just one of these components may be nonzero, it must be canceled by those associated with the other components. Thus, individual FECs such as  $g_{1111}$  and  $g_{1122}$  in Eq. (125) may be force-pattern dependent, but the effective coupling  $g^{\text{eff}}$  will not be.

Alternatively, consider the case of a crystal that is in static equilibrium under the force of gravity, as for a sample sitting on a tabletop. A uniform strain gradient  $v_{333}$  is present because the force of gravity provides a downward external force  $f^{\text{ext}}$  along the vertical direction, compressing the bottom of the sample more than the top. The polarization induced by this strain gradient is admittedly small, but so is the strain gradient itself, and the ratio between these defines a FEC. Clearly, this FEC should be computed using the mass-weighted choice of force pattern since gravity applies forces in proportion to masses. The mass-weighted choice is also appropriate to the study of the dynamics of long-wavelength acoustic phonons since the force needed to accelerate an atom during its acoustic oscillation is again proportional to its mass.

### G. FEC under different electric boundary conditions

Up to now, we have not been careful to distinguish quantities defined at fixed electric field  $\mathcal{E}$  from those defined at fixed electric displacement field  $D$ . Most of our calculations are performed under fixed- $D$  boundary conditions, but experimental results are typically reported in terms of fixed- $\mathcal{E}$  coefficients. In this section, we give the relationships between the two kinds of quantities, which will be denoted with superscripts ‘‘ $D$ ’’ and ‘‘ $\mathcal{E}$ ’’ to specify the type of electric boundary conditions under which they are defined.

The relationship between the fixed- $\mathcal{E}$  and fixed- $D$  FECs follows from

$$\begin{aligned} \mu_{\alpha\beta\gamma\delta}^D &= \left. \frac{dP_\alpha}{dv_{\beta\gamma\delta}} \right|_{D=0} \\ &= \left. \frac{\partial P_\alpha}{\partial v_{\beta\gamma\delta}} \right|_{\mathcal{E}=0} + \left. \frac{\partial P_\alpha}{\partial \mathcal{E}_\lambda} \frac{\partial \mathcal{E}_\lambda}{\partial v_{\beta\gamma\delta}} \right|_{D=0} \\ &= \mu_{\alpha\beta\gamma\delta}^\mathcal{E} - 4\pi \chi_{\alpha\lambda} \left. \frac{\partial P_\lambda}{\partial v_{\beta\gamma\delta}} \right|_{D=0} \\ &= \mu_{\alpha\beta\gamma\delta}^\mathcal{E} - 4\pi \chi_{\alpha\lambda} \mu_{\lambda\beta\gamma\delta}^D. \end{aligned} \quad (102)$$

In the third line above, we introduce the (full lattice plus electronic) dielectric susceptibility  $\chi_{\alpha\lambda} = \partial P_\alpha / \partial \mathcal{E}_\lambda$  and use  $D = \mathcal{E} + 4\pi P$ . Moving the  $4\pi \chi \mu^D$  term to the left-hand side, this becomes

$$\epsilon_{\alpha\lambda}^0 \mu_{\lambda\beta\gamma\delta}^D = \mu_{\alpha\beta\gamma\delta}^\mathcal{E}, \quad (103)$$

where  $\epsilon_{\alpha\lambda}^0 = \delta_{\alpha\lambda} + 4\pi \chi_{\alpha\lambda}$  is the static dielectric constant.

In the above derivation we assumed that the atoms could relax in response to the applied strain gradient, arriving at Eq. (103). The entire argument can be repeated for the frozen-ion FECs, in which case  $\chi$  and  $\epsilon^0$  are replaced by  $\chi^{\text{el}}$  and  $\epsilon^\infty$ , respectively, leading to

$$\epsilon_{\alpha\lambda}^\infty \mu_{\lambda\beta\gamma\delta}^{\text{el}, D} = \mu_{\alpha\beta\gamma\delta}^{\text{el}, \mathcal{E}}. \quad (104)$$

Introducing the Born effective charge tensor  $Z_{I\alpha\tau}^\mathcal{E} = V_c (\partial P_\alpha / \partial u_{I\tau})|_\mathcal{E}$  and the Callen effective charge tensor  $Z_{I\alpha\tau}^D = V_c (\partial P_\alpha / \partial u_{I\tau})|_D = (\epsilon_{\alpha\beta}^{-1})_{\alpha\beta} Z_{I\beta\tau}^\mathcal{E}$ , defined at fixed  $\mathcal{E}$  and  $D$ , respectively, we can relate the zone-center force-constant matrices via

$$K_{I\alpha, J\beta}^D = K_{I\alpha, J\beta}^\mathcal{E} + \frac{4\pi}{V_c} Z_{I\alpha\lambda}^\mathcal{E} Z_{J\beta\lambda}^D. \quad (105)$$

Similarly, the force-response internal strain gradient tensors are related by

$$T_{I\alpha\beta\gamma\delta}^D = T_{I\alpha\beta\gamma\delta}^\mathcal{E} - 4\pi Z_{I\alpha\lambda}^\mathcal{E} \mu_{\lambda\beta\gamma\delta}^{\text{el}, D}. \quad (106)$$

In the case of an isotropic dielectric tensor  $\epsilon_{\alpha\beta}^\infty = \epsilon_\infty \delta_{\alpha\beta}$ , as occurs in cubic crystals, we can make contact with Eq. (2) by identifying  $Q_{I\alpha\tau}^{(1)} = Z_{I\alpha\tau}^D = \epsilon_\infty^{-1} Z_{I\alpha\tau}^\mathcal{E}$ . In the most general case, however, it is unclear whether  $Q_{I\alpha\tau}^{(1)}$  and the higher moments defined in Eqs. (2)–(4) will transform as true tensors, and the connection to the Callen charge would have to be reconsidered.

### H. Flexocoupling tensor

Like for the FECs, there are many different notations for the FCCs (flexocoupling coefficients) in the literature, e.g.,

$2(\gamma + \eta)$  in Refs. 11–14,  $h$  in Ref. 39, and even  $f$  in Ref. 61 related to unsymmetrized strain. Here, we follow Refs. 46, 49, and 50 in defining the FCC  $f_{\alpha\delta\beta\gamma}$  as the coefficient in the flexoelectric contribution

$$-\frac{1}{2}f_{\alpha\delta\beta\gamma}\left(P_\alpha\frac{\partial\epsilon_{\beta\gamma}}{\partial r_\delta}-\epsilon_{\beta\gamma}\frac{\partial P_\alpha}{\partial r_\delta}\right) \quad (107)$$

to the thermodynamic potential density. Minimizing this energy functional leads to

$$g_{\alpha\delta\beta\gamma}^\mathcal{E} = \chi_{\alpha\lambda} f_{\lambda\delta\beta\gamma}. \quad (108)$$

Equations (58) and (103) imply that

$$g_{\alpha\delta\beta\gamma}^\mathcal{E} = \epsilon_{\alpha\lambda}^0 g_{\lambda\delta\beta\gamma}^D. \quad (109)$$

We can also relate  $f_{\alpha\delta\beta\gamma}$  to the FEC under fixed- $D$  boundary condition via

$$f_{\alpha\delta\beta\gamma}^D = \frac{1}{4\pi}(\delta_{\alpha\lambda} - \epsilon_{\alpha\lambda}^{0-1}) f_{\lambda\delta\beta\gamma}. \quad (110)$$

For high- $K$  materials it is reasonable to make the approximation that  $f_{\alpha\delta\beta\gamma} \simeq 4\pi g_{\alpha\delta\beta\gamma}^D$ . (Note that while Gaussian units have been used in the derivations here, the results for FECs and FCCs in Sec. IV are converted to SI units for easier comparison with experimental and previous theoretical results.) In some previous works, the FCCs have been obtained either by deriving them from incomplete experimental results<sup>49,50</sup> or indirectly from first-principles calculations on small supercells.<sup>46</sup> Once the FCCs have been obtained, they can be used to obtain reasonable estimates for the room-temperature FECs  $g_{\alpha\delta\beta\gamma}^\mathcal{E}$  via Eqs. (109) and (110).

Finally, we note in passing that the (macroscopic electrostatic) absolute deformation potentials  $D^{\text{(macro)}}$  of Refs. 62 and 63 can be related to the FEC  $g$  and the FCC  $f$  via

$$D_{\alpha\delta\beta\gamma}^{\text{(macro)}} = 4\pi e g_{\alpha\delta\beta\gamma} \quad (111)$$

and

$$D_{\alpha\delta\beta\gamma}^{\text{(macro)}} = e(\delta_{\alpha\lambda} - \epsilon_{\alpha\lambda}^{0-1}) f_{\lambda\delta\beta\gamma}, \quad (112)$$

where  $e$  is the electron charge.

### III. FIRST-PRINCIPLES CALCULATIONS

Although we have laid out the formalism for the theory of flexoelectricity above, expressing the FEC tensor in terms of more elementary objects, it is still a challenge to calculate this tensor from first principles.

In our previous work,<sup>45</sup> we described how to calculate the longitudinal frozen-ion component  $\mu_{L1}^{\text{el},D} = \mu_{1111}^{\text{el},D}$  under fixed- $D$  boundary conditions<sup>64</sup> from first principles. Here, we first review supercell calculations and discuss how to extend them to obtain the  $T$ -tensor elements needed for the lattice flexoelectric response. We also show how to carry out similar supercell calculations, but in a rotated frame, to obtain the corresponding  $\mu_{L2}$  components. We then provide the details of the first-principles calculations, and briefly present some computed information about the atomic cores and about the ground-state properties of the crystals that will be needed later.

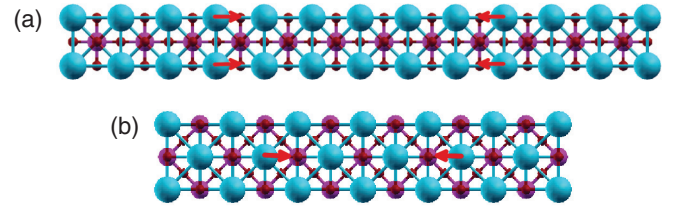


FIG. 1. (Color online) Original (a) and  $45^\circ$ -rotated (b) supercells used for calculations on  $ABO_3$  perovskites. Arrows (red) denote the displacement of  $A$  atoms consistent with fixed- $D$  boundary conditions. Large ball is  $A$  atom, medium is  $B$  atom, and small is  $O$  atom.

#### A. Supercell calculations in original Cartesian frame

Figure 1(a) illustrates the supercell that we introduced in Ref. 45 in order to compute  $\mu_{1111}^{\text{el}}$ . For each type of atom, we move two planes of these atoms, located approximately  $\frac{1}{4}$  and  $\frac{3}{4}$  along the supercell long dimension, by equal and opposite amounts, as illustrated in the figure. We do this in order that the electric field between these displaced planes should vanish; since the polarization also vanishes there, this corresponds to fixed- $D$  boundary conditions. As a result, we obtain a very rapid spatial convergence (locality) of the induced charge distribution  $f_{i\tau}(\mathbf{r})$  of Eq. (1), and of the induced forces reflected in the force-constant elements  $\Phi_{\tau\tau'}^{IJ}$  of Eq. (77), as illustrated in Fig. 2. (For details of these calculations, see Sec. III C.) Displacing only a single plane of atoms with  $\mathcal{E} = 0$  boundary conditions on the entire supercell would set up a

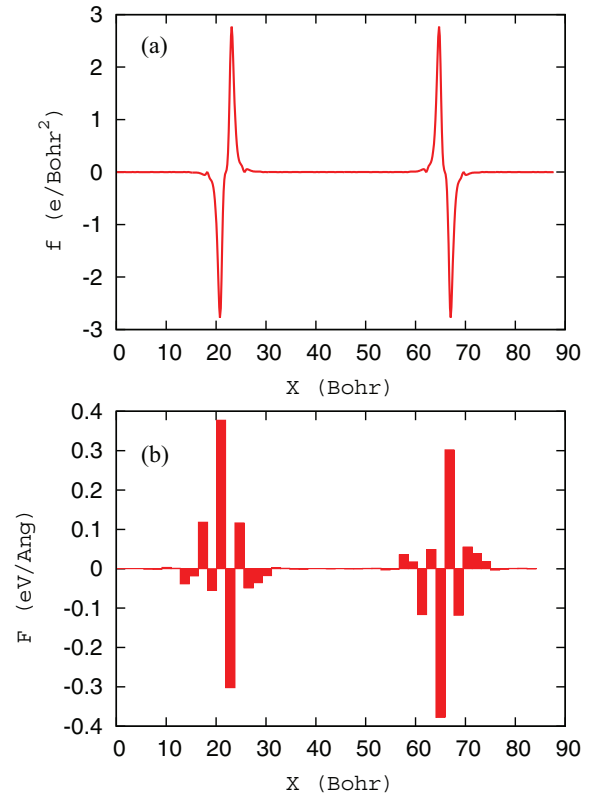


FIG. 2. (Color online) Change of charge-density distribution (a) and force distribution (b) in  $\text{SrTiO}_3$  supercell (original frame) at fixed  $D$ .



macroscopic local  $\mathcal{E}$  field even far from the displaced plane leading to oscillations in  $f_{I\tau}(\mathbf{r})$  and the corresponding forces, making it difficult or impossible to calculate the needed spatial moments of  $f_{I\tau}(\mathbf{r})$  and of the induced forces.

From finite differences of the computed charge densities with small positive and negative displacements, repeated for each type of atom  $I$ , we calculate  $Q_{I11}^{(1)}$  and  $Q_{I1111}^{(3)}$  via Eqs. (2) and (4), respectively. We emphasize again that these are fixed- $D$  quantities by definition, and so are given correctly by the configuration of Fig. 1.

At the same time, we compute the forces on all the atoms in the supercell as illustrated in Fig. 2(b), and use these to construct the force-constant elements needed for computing  $T_{I1111}^D$  from Eq. (82). In practice, this works as follows. Let  $i$  denote the atom in the supercell for which we want to compute  $T_{I1111}$ , and let  $j$  run over other atoms in the supercell. Imagine that there is a uniform strain gradient causing displacements

$$u_{jx} = \frac{1}{2} v_{xxx} (\Delta x_{ij})^2 \quad (113)$$

in the vicinity of atom  $i$ , where  $\Delta x_{ij} = x_j - x_i$ . The total force on atom  $i$  would then be

$$f_{ix} = \sum_j F_{ix}^{(jx)} u_{jx}, \quad (114)$$

where  $F_{i\alpha}^{(j\beta)}$  is the force induced on atom  $i$  in direction  $\alpha$  by a displacement of atom  $j$  in direction  $\beta$ . Using the definition that  $T_{i,xxxx} = f_{ix}/v_{xxx}$  and substituting Eq. (113) into (114), we get

$$T_{i,xxxx}^D = \frac{1}{2} \sum_j F_{ix}^{(jx)} (\Delta x_{ij})^2. \quad (115)$$

Note, however, that  $F_{i\alpha}^{(j\beta)}$  is just minus the zone-center force-constant matrix of the supercell, which is symmetric under interchange of indices, so the above can be rewritten as

$$T_{i,xxxx}^D = \frac{1}{2} \sum_j F_{jx}^{(ix)} (\Delta x_{ij})^2. \quad (116)$$

Equation (116) is the formula that we use to calculate  $T_{I1111}^D$  in practice. That is, rather than displace other atoms and compute the force on atom  $i$ , we displace atom  $i$  and compute the forces on other atoms, then calculate the the second moment of these forces from Eq. (116). The sum is truncated when the distance  $|\Delta x_{ij}|$  approaches half the distance to the next plane of displaced atoms (i.e.,  $\sim \frac{1}{4}$  of the supercell long dimension). For large enough supercells, this is already in the region in which the  $F_{jx}^{(ix)}$  have essentially vanished [i.e., see Fig. 2(b)], so that the sum is well converged. Note that Eq. (116) is essentially the same as Eq. (82), but adapted to practical supercell calculations.

We also carry out calculations in which the plane of atoms is displaced in the transverse  $y$  direction, i.e., vertically in Fig. 1, and compute the  $y$  forces on the other atoms in the cell. This is not useful for computing moments of the  $Q$  tensors, but it allows us to compute the  $T_{I2211}^{\mathcal{E}}$  (later presented as  $T_{I1122}^{\mathcal{E}}$ ) which are eventually needed to compute  $\mu_{\text{T}}^{\text{ld}}$ , in a manner entirely analogous to the  $T_{I1111}^D$  calculation. Note, however, that the calculation is carried out at fixed (vanishing)  $\mathcal{E}_y$  in this

case, so the resulting quantity is to be interpreted as a fixed- $\mathcal{E}$  one, as indicated by the superscript on  $T_{I2211}^{\mathcal{E}}$ .

For the case of oxygen atoms in the perovskite structure,  $T_{I1111}^D$  and  $T_{I2211}^{\mathcal{E}}$  are computed as above for  $I = \text{O1}, \text{O2},$  and  $\text{O3}$ , and then converted into the symmetry-mode representation ( $\xi = 3, 4$ ) as described in Appendix C.

## B. Supercell calculations in rotated frame

The calculations described above are sufficient to compute the  $Q_{I1111}$  and  $T_{I1111}^D$  tensor components needed to compute the electronic and lattice parts of  $\mu_{\text{L}1}$  of Eq. (50), but not  $\mu_{\text{L}2}$  of Eq. (51). In order to calculate the latter, we introduce the rotated frame shown in Fig. 1(b) and calculate the longitudinal FEC in this rotated frame.

We label the FEC in the original frame as  $\mu_{\alpha\beta\gamma\delta}$  and in the rotated frame as  $\mu'_{\alpha\beta\gamma\delta}$ . These are related by applying the rotation matrix

$$R(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (117)$$

with  $\theta = 45^\circ$  four times,

$$\mu'_{\alpha'\beta'\gamma'\delta'} = \sum_{\alpha\beta\gamma\delta} R_{\alpha'\alpha} R_{\beta'\beta} R_{\gamma'\gamma} R_{\delta'\delta} \mu_{\alpha\beta\gamma\delta}, \quad (118)$$

giving

$$\mu'_{1111} = \frac{1}{2}(\mu_{1111} + \mu_{1122}) + \mu_{1221}, \quad (119)$$

$$\mu'_{1122} = \frac{1}{2}(\mu_{1111} + \mu_{1122}) - \mu_{1221}, \quad (120)$$

$$\mu'_{1221} = \frac{1}{2}(\mu_{1111} - \mu_{1122}). \quad (121)$$

Referring to Eqs. (50)–(52), note that  $\mu'_{1111} - \mu_{1111} = (\mu_{\text{L}2} - \mu_{\text{L}1})/2$ , confirming that  $\Delta = \mu_{\text{L}2} - \mu_{\text{L}1}$  is a measure of anisotropy as was discussed there. From Eq. (119), it follows that

$$\mu_{\text{L}2} = 2\mu'_{1111} - \mu_{1111}. \quad (122)$$

It is therefore straightforward to obtain the missing FEC component  $\mu_{\text{L}2}$  once  $\mu'_{1111}$  has been calculated.

To obtain  $\mu_{1111}^{\text{el}}$ , we compute  $Q_{I1111}^{\prime(3)} = Q_{I,x'x'x'x'}^{(3)}$  for each atom  $I$  in the rotated supercell just as we did for  $Q_{I1111}^{(3)} = Q_{I,xxxx}^{(3)}$  in the original cell. However, as explained in Appendix C, for the oxygen atoms in perovskites we have to compute  $Q_{\text{O}1,x'y'x'x'}^{(3)}$  as well. Since  $Q_{\text{O}1,x'y'x'x'}^{(3)} = -Q_{\text{O}2,x'y'x'x'}^{(3)}$ , a convenient way to do this is to move atoms O1 and O2 by equal and opposite amounts along  $y'$ , thus preserving the  $\mathcal{E}_y = D_y = 0$  boundary conditions as was done for other displacements. For the lattice part, we similarly need the  $T^D$  tensors in the rotated frame. The  $T_{x'x'x'x'}^D$  matrix elements are computed similarly as for the original supercell, except that for oxygens in perovskites we also need  $T_{\text{O}1,y'x'x'x'}^D$  (see Appendix C). Again, this requires a displacement of O1 along  $y'$  (or better, equal and opposite displacements of O1 and O2 along  $y'$ ), with the  $x'$  second moments of the  $x'$  forces on the other atoms obtained in the same way as for  $x'$  displacements.

### C. Details of the calculations

The calculations have been performed within density-functional theory. We used the local-density approximation<sup>65</sup> for C, Si, MgO, NaCl, CsCl, and SrTiO<sub>3</sub>, and the generalized gradient approximation<sup>66</sup> for BaZrO<sub>3</sub>, BaTiO<sub>3</sub> and PbTiO<sub>3</sub>. We used the SIESTA (Ref. 67) package for the calculations. Norm-conserving pseudopotentials were used, with semicore shells included for Ti (*3s3p3d*), Ba (*5s5p*), Zr (*4p4d*), Pb (*5d*), Sr (*4s4p*), and Cs (*5s5p*). In all cases, the *k*-space mesh was chosen to correspond to a 12-Å cutoff<sup>68</sup> while the real-space integrals were carried out on an *r*-space mesh corresponding to a 450-Ry cutoff.<sup>67</sup> Supercells were built from 12 unit cells for CsCl and perovskites in the original frame and 6 cells in the 45°-rotated frame (see Fig. 1). For C, Si, MgO, and NaCl, we used 8 conventional cells in original frame and 4 cells in the 45°-rotated frame. Atomic displacements of 0.04 Å were used in our calculations. In order to reduce the anharmonic effect, two calculations were performed, one with negative displacement and the other one with positive displacement.

For the cubic perovskite structure *ABO*<sub>3</sub>, atoms *A* and *B* have the cubic symmetry, but the individual O atom has tetragonal symmetry, not the cubic symmetry. In our calculation, we chose to use “mode coordinate” for perovskites in which two oxygen modes have the cubic symmetry. Please refer to Appendix C for the details.

### D. Ground-state properties of materials

In order to calculate the FEC, we need to obtain some basic properties of our materials of interest, including the lattice constant (*a*), optical dielectric constant ( $\epsilon^\infty$ ), static dielectric constant ( $\epsilon^0$ ), and Born effective charges. These are summarized in Table I.

The optical dielectric constants are obtained as  $\epsilon^\infty = Z^\mathcal{E}/Q^{(1)}$ , where  $Q^{(1)}$  is the Callen charge as given in Table III. (For C and Si,  $\epsilon^\infty = \epsilon^0$  and we do not compute  $\epsilon^\infty$  explicitly.) The Born effective charges  $Z^\mathcal{E}$  are obtained by finite differences, e.g., by displacing each atom slightly and calculating the induced Berry-phase polarization.<sup>69</sup>

The theoretical static dielectric constant is obtained via  $\epsilon^0 = \mu^\mathcal{E}/\mu^D$  following Eq. (103). We also checked that these results are exactly the same as obtained by the usual method based on the effective-charge and force-constant tensors (see, e.g., Ref. 70). However, we do not attempt to compute  $\epsilon^0$  for BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and SrTiO<sub>3</sub> because our calculations are for the reference cubic paraelectric structure, which is either unstable (BaTiO<sub>3</sub> and PbTiO<sub>3</sub>) or nearly unstable (SrTiO<sub>3</sub>) to the formation of a ferroelectric ground state. For this reason, a direct calculation of  $\epsilon^0$  would give negative or extremely large formal values, leading to nonphysical results for  $\mu^\mathcal{E}$  and other quantities in subsequent calculations. Instead, we have chosen to adopt room-temperature experimental values for  $\epsilon^0$  for these materials, as given in Table I, and we use these to predict meaningful values of  $\mu^\mathcal{E}$  at room temperature. Our rationale for this approach was explained in more detail at the end of Sec. I.

### E. Rigid-core corrections for pseudopotentials

Our previous work<sup>45</sup> showed that the frozen-ion FEC  $\mu^{\text{el}}$  is dependent on the choice of pseudopotential. To see why,

TABLE I. Lattice constant *a* [of conventional cell (Ref. 52)], optical dielectric constant  $\epsilon^\infty$ , theoretical (zero-temperature) and experimental (room-temperature) static dielectric constant  $\epsilon^0$ , and Born effective charge  $Z^\mathcal{E}$  for materials considered in this study.

	<i>a</i> (bohrs)	$\epsilon^\infty$	$\epsilon^0$ (theor.)	$\epsilon^0$ (expt.) <sup>a</sup>	$Z^\mathcal{E}$ (e)
C	6.69			5.5	C 0
Si	10.22			11.9	Si 0
MgO	7.82	3.0	7.8	9.8	Mg 1.89 O -1.89
NaCl	10.66	2.4	6.1	5.6	Na 1.07 Cl -1.07
CsCl	7.45	3.2	6.4	7.2	Cs 1.36 Cl -1.36
BZO	7.92	5.0	57.1	15	Ba 2.84 Zr 6.26 O <sub>1</sub> -5.04 O <sub>3</sub> -2.03
BTO	7.52	6.8		2300	Ba 2.78 Ti 7.50 O <sub>1</sub> -6.04 O <sub>3</sub> -2.12
PTO	7.43	8.8		134	Pb 3.93 Ti 7.21 O <sub>1</sub> -6.03 O <sub>3</sub> -2.55
STO	7.31	6.3		310	Sr 2.52 Ti 7.47 O <sub>1</sub> -5.89 O <sub>3</sub> -2.05

<sup>a</sup>Room-temperature experimental values: MgO and NaCl (Ref. 71); CsCl (Ref. 72); BZO (Ref. 73); BTO (Ref. 9); PTO (Ref. 74); STO (Ref. 75).

consider a model in which each cation or anion is represented by a spherically symmetric charge  $\rho_i(r)$  that displaces rigidly as a unit. A brief calculation shows that

$$Q_i^{(3)} = \int d^3r x^3 [-\partial_x \rho_i(\mathbf{r})] = 4\pi \int dr r^4 \rho_i(r). \quad (123)$$

It can be seen that  $Q^{(3)}$  and hence  $\mu^{\text{el}}$  should depend on the treatment of the core density and the pseudopotential construction. The difference between  $Q^{(3,\text{AE})}$  (all-electron) and  $Q^{(3,\text{PS})}$  (pseudopotential) can be corrected by introducing a “rigid-core correction” (RCC)

$$Q_i^{(3,\text{RCC})} = 4\pi \int dr r^4 [\rho_i^{\text{AE}}(r) - \rho_i^{\text{PS}}(r)] \quad (124)$$

for each atom type *i* by using the densities from free-atom AE and PS calculations, and then adding these  $Q^{(3,\text{RCC})}$  corrections to the  $Q^{(3,\text{PS})}$  values calculated in our supercells.

In order to obtain accurate FECs, we calculate this RCC for all elements appearing in our selected materials, as shown in Table II. It can be seen that the RCC tends to be large for large-radius atoms such as Cs, Ba, and Pb, even though their semicore shells are included in the valence in the pseudopotential construction. From these values it is clearly essential to include the RCC for elements with large radius if one wants to compute the FxE response accurately.

TABLE II. Rigid-core corrections (RCCs), in e bohrs<sup>2</sup>. Pseudopotentials O1 and O2 are used for MgO and perovskites, respectively.

	RCC		RCC		RCC
C	-0.19	Si	-2.93	Cs	-14.58
O1	-0.06	Cl	-1.67	Ba	-13.34
O2	-0.09	Ti	-0.84	Pb	-15.46
Na	-6.64	Sr	-5.41		
Mg	-4.85	Zr	-7.72		

#### IV. RESULTS

In this section, we first present the basic charge-moment tensors  $Q$  and force-response tensors  $T$  as they are extracted from our supercell calculations. We then combine these to obtain the longitudinal FECs at fixed  $D$ , as well as the longitudinal flexocoupling coefficients, for all of the materials considered. Up to this point, the results do not depend on current-response terms  $\mu^{\text{iq},J}$  and  $\mu^{\text{el},J}$  in Eqs. (46) and (47), but to go further we then make the uncontrolled assumption that these two quantities vanish in order to get a rough idea of the behavior of the full FEC tensors at fixed  $D$  and  $\mathcal{E}$ .

##### A. Calculated charge-moment and force-response tensors

As described in Secs. III A and III B, we carry out calculations on supercells extended along  $x$  with small  $x$  displacements to obtain  $Q^{(1)}$ ,  $Q_{L1}^{(3)}$ , and  $T_{L1}^D$  (all at fixed  $D$ ). We also calculate  $T_{1122}^{\mathcal{E}}$  by applying small- $y$  displacements (at fixed- $\mathcal{E}$  boundary conditions) instead. Then, we carry out similar calculations on 45°-rotated supercells to obtain  $Q_{L2}^{(3)}$  and  $T_{L2}$  as well. The treatment of the oxygen displacements in perovskites requires special care as described in Sec. III B and Appendix C.

The results are presented in Table III. The RCCs from Table II have been included in the calculation of the  $Q^{(3)}$  moments. From Table III, it can be seen that a modified acoustic sum rule has to be used for the mode variables in  $ABO_3$  perovskites, namely,  $Q_A^{(1)} + Q_B^{(1)} + Q_{\xi_3}^{(1)} + \sqrt{2}Q_{\xi_4}^{(1)} = 0$ . Almost all  $Q^{(3)}$  values are seen to be negative, which can be understood heuristically from the rigid-ion model of Eq. (123), in which the positive nuclear charge at  $r = 0$  makes no contribution so that the electronic charge gives an unbalanced negative contribution to  $Q^{(3)}$ . The only exceptions are for the  $\xi_4$  modes in the perovskites, where the oxygen motion along  $y'$  is involved so that the sign is less intuitive. In the  $ABO_3$  perovskites, the  $A$  atom makes a significant contribution to all  $Q$  and  $T$  tensors. Also note that oxygen mode  $\xi_4$  contributes only very weakly to  $T_{L1}^D$ , while  $\xi_3$  contributes strongly.

##### B. Longitudinal contribution to flexoelectric response

The longitudinal FEC constants  $\mu_{L1}^D$  and  $\mu_{L2}^D$ , and their electronic and lattice contributions, are presented in Table IV, following the definitions in Eqs. (50) and (51). The electronic (frozen-ion) response is obtained from Eq. (47) (recall that  $\mu^{\text{el},J}$  does not contribute to the longitudinal response), and is seen to be negative in all cases, as expected from the sign of the  $Q^{(3)}$  contributions. The lattice-quadrupole contribution  $\mu^{\text{iq}}$  of Eq. (46) vanishes for all of our compounds except for

TABLE III.  $Q^D$  and  $T$  tensors computed from first-principles calculations. Units: e for  $Q^{(1)}$ ; e bohrs<sup>2</sup> for  $Q^{(3)}$ ; eV for  $T$ . The RCCs from Table II are included in the  $Q^{(3)}$  moments.

		$Q^{(1)}$	$Q_{L1}^{(3)}$	$Q_{L2}^{(3)}$	$T_{L1}^D$	$T_{L2}^D$	$T_{1122}^{\mathcal{E}}$
C	C	0	-13.2	-25.4	0	0	0
Si	Si	0	-30.9	-54.9	0	0	0
MgO	Mg	0.63	-13.7	-23.3	37.5	65.4	16.3
	O	-0.63	-12.8	-15.8	41.5	30.4	20.1
NaCl	Na	0.45	-10.1	-24.2	10.5	11.8	30.8
	Cl	-0.45	-27.6	-30.6	14.0	5.4	-3.0
CsCl	Cs	0.43	-64.1	-72.3	11.6	10.3	16.3
	Cl	-0.43	-30.2	-40.1	8.1	11.6	20.1
BZO	Ba	0.57	-75.5	-63.3	18.8	42.2	11.1
	Zr	1.25	-30.5	-63.5	63.9	37.6	5.3
	$\xi_3$	-1.01	-34.7	-132.0	73.4	35.6	6.2
	$\xi_4$	-0.57	-11.7	67.9	1.8	10.3	7.5
BTO	Ba	0.40	-79.2	-65.7	24.1	52.9	13.1
	Ti	1.11	-14.9	-46.0	46.0	40.2	7.6
	$\xi_3$	-0.89	-29.2	-109.4	45.2	36.4	14.4
	$\xi_4$	-0.44	-8.4	52.4	9.2	17.9	15.6
PTO	Pb	0.44	-73.7	-66.7	16.1	38.0	6.1
	Ti	0.83	-23.8	-49.5	44.0	38.6	3.5
	$\xi_3$	-0.69	-24.5	-135.8	52.0	25.6	13.4
	$\xi_4$	-0.41	-12.9	69.6	4.9	20.3	12.0
STO	Sr	0.39	-57.5	-43.5	17.0	35.7	8.4
	Ti	1.20	-16.2	-45.0	52.3	38.9	3.0
	$\xi_3$	-0.92	-28.6	-44.0	68.7	13.1	15.7
	$\xi_4$	-0.47	-9.5	7.7	3.6	18.2	12.0

C and Si, where it only makes a contribution to the transverse component  $\mu_T$ , as discussed in the next section. Regarding the lattice-dipole contributions  $\mu^{\text{ld}}$ , which vanish for C and Si, these are computed from Eq. (76) using the information in Table III together with the computed zone-center force-constant matrices and their pseudoinverses.

As emphasized in Sec. II F2, the lattice contributions to the FECs depend on the force pattern applied on each atom in the unit cell. Here, we chose two different force patterns, either evenly weighted on all atoms, or else weighted according to the atomic mass. From Table IV we can see that the total fixed- $D$  FECs are comparable for all of our selected materials. The lattice contribution, and therefore the total FEC, is force-pattern dependent. However, the anisotropy ( $\Delta = \mu_{L2} - \mu_{L1}$ ) (Ref. 18) shows hardly any force-pattern dependence, and the anisotropy is much larger in the perovskites than in the elemental and binary materials. It can be seen that C, Si, MgO, NaCl have a nearly isotropic behavior. From this table, we can also see that at fixed  $D$  the lattice contribution is much smaller than the electronic contribution. For the even force pattern, the lattice contributions are positive, which reduces the total FEC. However, under the mass-weighted force pattern, the lattice contributions are negative, enhancing the total FEC. Therefore, the FECs under the mass-weighted force pattern are larger (more negative) than those under the evenly weighted force pattern.

We next present the results for the flexocoupling coefficients (FCCs) defined in Sec. II H, which can be regarded as fundamental materials properties because they are not strongly temperature dependent.<sup>46</sup> The FCCs can easily be obtained

TABLE IV. Longitudinal components of FEC tensor at fixed  $D$ .  $\mu_{L1} = \mu_{1111}$ ,  $\mu_{L2} = \mu_{1122} + 2\mu_{1221}$ , and anisotropy  $\Delta = \mu_{L2} - \mu_{L1}$ . Units: pC/m.

	$\mu_{L1}^{el}$		Even force					Mass-weighted force				
	$\mu_{L1}^{el}$	$\mu_{L2}^{el}$	$\mu_{L1}^{ld}$	$\mu_{L2}^{ld}$	$\mu_{L1}$	$\mu_{L2}$	$\Delta$	$\mu_{L1}^{ld}$	$\mu_{L2}^{ld}$	$\mu_{L1}$	$\mu_{L2}$	$\Delta$
C	-175.4	-163.5	0	0	-175.4	-163.5	11.9	0	0	-175.4	-163.5	11.9
Si	-106.0	-90.8	0	0	-106.0	-90.8	15.2	0	0	-106.0	-90.8	15.2
MgO	-111.7	-164.8	-5.7	50.5	-117.4	-114.4	3.0	-29.2	22.0	-140.8	-142.8	-2.0
NaCl	-62.8	-91.2	-9.0	16.3	-71.8	-74.9	-3.1	4.2	25.6	-58.6	-65.6	-7.0
CsCl	-115.2	-137.4	5.8	-2.2	-109.4	-139.6	-30.2	-13.2	-23.3	-128.4	-160.6	-32.2
BZO	-154.8	-194.1	29.3	34.7	-125.5	-159.3	-33.8	-35.2	-18.1	-190.0	-212.2	-22.2
BTO	-155.8	-199.7	10.5	9.8	-145.3	-189.9	-44.6	-5.4	-9.4	-161.2	-209.1	-47.9
PTO	-165.7	-224.1	16.5	23.1	-149.2	-201.0	-51.8	-31.4	-29.6	-197.1	-253.7	-56.6
STO	-143.9	-160.9	24.8	22.3	-119.1	-138.6	-19.5	-12.1	-11.6	-156.1	-172.4	-16.3

from our fixed- $D$  FECs via Eq. (110). To evaluate this equation, we use the theoretical dielectric constants  $\epsilon^0$  in Table I for MgO, NaCl, CsCl, and BZO, while using the experimental  $\epsilon^0$  values for other materials.

The FCCs for our various materials under the two different force patterns are presented in Table V. It can be seen that  $|f_{L1}| \equiv |f_{1111}|$  is in the range of [10 V, 20 V], which is slightly larger than the value [1 V, 10 V] in a previous theoretical estimate.<sup>50</sup> The FCC is slightly larger under the mass-weighted force pattern than under the evenly weighted one, and  $f_{L2}$  is also larger than  $f_{L1}$ . Interestingly, the FCCs are all of roughly comparable size for all of the materials, reinforcing the picture that they constitute fundamental materials properties that are hardly affected by the large static dielectric constants present in some materials. The anisotropy of the FCCs is also nearly force-pattern independent, just like for the FECs. From Eq. (112) we calculate  $D_{L1}^{(macro)} = 11.0$  eV, close to the result (12.0 eV) in Ref. 62.

Zubko *et al.*<sup>49</sup> summarized the available FEC data in their recent review paper and converted them to FCCs by using  $f \simeq 4\pi g/\epsilon^0$ . They found that the FCCs change substantially (including in sign) in different materials. The discrepancy relative to our results may result in part because their analysis rests on experimental data for the effective beam-bending FECs and they also include surface effects.

Ponomareva *et al.*<sup>46</sup> calculated the FCCs for  $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$  from first principles by introducing

 TABLE V. Longitudinal flexocoupling coefficients.  $f_{L1} = f_{1111}$ ,  $f_{L2} = f_{1122} + 2f_{1221}$ , and anisotropy  $\Delta = f_{L2} - f_{L1}$ . Units: V.

	Even force			Mass-weighted force		
	$f_{L1}$	$f_{L2}$	$\Delta$	$f_{L1}$	$f_{L2}$	$\Delta$
C	-19.8	-18.5	1.3	-19.8	-18.5	1.3
Si	-12.0	-10.3	1.7	-12.0	-10.3	1.7
MgO	-15.2	-14.8	0.4	-18.2	-18.5	-0.3
NaCl	-9.7	-10.1	-0.4	-7.9	-8.9	-1.0
CsCl	-14.6	-18.7	-4.1	-17.2	-21.5	-4.3
BZO	-14.4	-18.3	-3.9	-21.8	-24.4	-2.6
BTO	-16.4	-21.5	-5.1	-18.2	-23.6	-5.4
PTO	-17.0	-22.9	-5.9	-22.4	-28.9	-6.5
STO	-13.5	-15.7	-2.2	-17.7	-19.5	-1.8

periodic strain gradients in small supercells. Their results show that the FCC is indeed a fundamental quantity that is only weakly dependent on the temperature and thickness for  $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$  films. However,  $f_{1111}$  is about 5 V for  $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ , smaller than our value presented in Table V, and with opposite sign. One possible reason could be that their supercells were too small; other previous work has shown that the FEC is very sensitive to the size of supercell when inducing a periodic strain gradient via first-principles calculations.<sup>42</sup> The FCC obtained in the small supercell in their work, taking into account only the interactions between the local dipoles and strain gradient, may not reflect the full contribution to the FCC.<sup>50</sup>

We now turn to our results for the FECs at fixed  $\mathcal{E}$ . According to Eqs. (103) and (104), the total FEC  $\mu^\mathcal{E}$  and the electronic (frozen-ion) FEC  $\mu^{el,\mathcal{E}}$  and are given by multiplying  $\mu^D$  or  $\mu^{el,D}$  by the static  $\epsilon^0$  or optical  $\epsilon^\infty$ , respectively. Because we are interested in comparing with room-temperature experiments, we used room-temperature static dielectric constants  $\epsilon^0$  for all the materials as given in Table I. Our results are given in Table VI, where  $\mu^{ld}$  is obtained through  $\mu^{ld} = \mu - \mu^{el}$ . From this table we can see that the lattice contributions are larger than the electronic ones under fixed- $\mathcal{E}$  boundary conditions, especially for the high-dielectric-constant materials. It is also evident that the anisotropic flexoelectric response for nonperovskite materials is small, indicating that the FxE tensor of these materials is close to that of an isotropic material having only two independent FEC components.<sup>51</sup> However, note that the experimental  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  materials are tetragonal ferroelectrics at room temperature, and the room-temperature  $\epsilon^0$  values used in the conversion to  $\mu^\mathcal{E}$  for these materials were obtained from this tetragonal structure. Therefore, the results presented for  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  in Table VI are not fully consistent and should be interpreted with caution. We also assume for all materials that the optical dielectric constants and fixed- $D$  FECs are temperature independent, but we expect this to be a rather good approximation.

From Table IV it can be seen that the FECs at fixed  $D$  for the different perovskites are very similar, while instead the fixed- $\mathcal{E}$  FECs reported in Table VI show dramatic variations. This is because  $\mu^\mathcal{E}$  is linearly scaled to the static dielectric constant, as in Eq. (103), and these perovskites have very different dielectric constants as shown in Table I.  $\text{BaTiO}_3$  has



TABLE VI. Longitudinal FEC components at fixed  $\mathcal{E}$  at room temperature.  $\mu_{L1} = \mu_{1111}$ ,  $\mu_{L2} = \mu_{1122} + 2\mu_{1221}$ , and anisotropy  $\Delta = \mu_{L2} - \mu_{L1}$ . Units: nC/m. Note that the choice of units is three orders or magnitude larger than in Table IV.

	$\mu_{L1}^{\text{el}}$		Even force					Mass-weighted force				
	$\mu_{L1}^{\text{el}}$	$\mu_{L2}^{\text{el}}$	$\mu_{L1}^{\text{ld}}$	$\mu_{L2}^{\text{ld}}$	$\mu_{L1}$	$\mu_{L2}$	$\Delta$	$\mu_{L1}^{\text{ld}}$	$\mu_{L2}^{\text{ld}}$	$\mu_{L1}$	$\mu_{L2}$	$\Delta$
C	-1.0	-0.9	0	0	-1.0	-0.9	0.1	0	0	-1.0	-0.9	0.1
Si	-1.3	-1.1	0	0	-1.3	-1.1	0.2	0	0	-1.3	-1.1	0.2
MgO	-0.3	-0.5	-0.8	-0.6	-1.1	-1.1	0.0	-1.1	-0.9	-1.4	-1.4	0.0
NaCl	-0.1	-0.2	-0.3	-0.2	-0.4	-0.4	0.0	-0.2	-0.2	-0.3	-0.4	-0.1
CsCl	-0.4	-0.4	-0.4	-0.5	-0.6	-1.0	-0.4	-0.5	-0.8	-0.9	-1.2	-0.3
BZO	-0.8	-1.0	-1.1	-1.4	-1.9	-2.4	-0.5	-2.0	-2.2	-2.8	-3.2	-0.4
BTO	-1.1	-1.4	-333.2	-435.4	-334.3	-436.8	-102.5	-369.7	-479.6	-370.8	-481.0	-110.2
PTO	-1.5	-2.0	-18.5	-24.9	-20.0	-26.9	-6.9	-24.9	-32.0	-26.4	-34.0	-7.6
STO	-0.9	-1.0	-36.0	-42.0	-36.9	-43.0	-6.1	-47.5	-52.5	-48.4	-53.5	-5.1

the largest FEC due to its large dielectric constant, which also explains the large FEC observed in the work of Ma and Cross;<sup>4-9</sup> all of the materials they measured displayed large dielectric constants (typically several thousands). However, they also observed that the FEC does not exactly scale linearly with the dielectric constants in some materials, which may indicate that  $\mu^D$  also has some weak temperature dependence. Their measurements may also be affected by surface effects not considered here.

Our flexoelectricity theory is valid for materials with any symmetry, but our current first-principles calculations are limited to cubic materials. However, our previous work has shown that ferroelectric tetragonal BaTiO<sub>3</sub> has a similar  $\mu_{1111}$  value (along the [001] direction) as for cubic BaTiO<sub>3</sub>,<sup>42</sup> and ferroelectric tetragonal PbTiO<sub>3</sub> has a similar  $\mu_{1111}^{\text{el}}$  (along [001]) as for cubic PbTiO<sub>3</sub>.<sup>45</sup> These results hint that  $\mu_{1111}$  may have similar values in tetragonal and cubic phases of a given perovskite material.

### C. Transverse and full Cartesian flexoelectric response

In order to make closer contact with experiment, in this section our goal is to present results for the fixed- $\mathcal{E}$  FECs in the Cartesian frame. If  $\mu_{L1}$ ,  $\mu_{L2}$ , and  $\mu_T$  are known, it is straightforward to invert Eqs. (50)–(52) to obtain  $\mu_{1111}$ ,  $\mu_{1122}$ , and  $\mu_{1221}$ . However, as discussed in Sec II C and more fully in Appendix A, we can only obtain the longitudinal contributions  $\mu_{L1}$  and  $\mu_{L2}$  from our first-principles calculations based on the charge-response formulation; additional terms from the current-response formulation would be needed to obtain  $\mu_T$ . Since  $\mu_{1111} = \mu_{L1}$ , there is no ambiguity about its value, but  $\mu_{1122}$  and  $\mu_{1221}$  can not be obtained individually without access to  $\mu_T$ .

Another way to see the problem is that we can imagine obtaining  $\mu_{1122}^{\text{ld}}$  or  $\mu_{1221}^{\text{ld}}$  at fixed  $D$  directly from Eq. (76). However, this requires a knowledge of  $T_{1122}^D$ , which is not one of the raw ingredients available to us in Table III. Instead, we have  $T_{1122}^{\mathcal{E}}$ , but converting this to  $T_{1122}^D$  would require the use of Eq. (106); this in turn requires  $\mu_{1122}^{\text{el,D}}$ , which is not available without the current-response calculation.

So, the problem is that we do not have the lattice quadrupole contribution  $\mu^{\text{la},J}$  to  $\mu^{\text{la},T}$  in Eqs. (46) and (A25), nor do we have the electronic contribution  $\mu^{\text{el},J} = \mu^{\text{el},T}$  in Eqs. (47) and

(A26). The lattice quadrupole contribution  $\mu^{\text{la}}$  vanishes by symmetry for all of our compounds except for C and Si, where it makes a contribution only to the transverse component  $\mu_T$ . We have computed these contributions, neglecting any current-response contribution  $\mu^{\text{la},J}$ , following the discussion in Sec. II F1. We find  $\gamma = 0.14$  (0.72) bohrs,  $q = -0.10$  (0.12) e bohrs, and  $\mu^{\text{la},T} = -0.84$  pC/m (1.5 pC/m) for C (Si), respectively. These values are much smaller than the other values in Table IV, and we speculate that the current-response contributions are probably small too. We do not consider the lattice quadrupole contributions any further here.

For the materials other than C and Si, the only missing ingredient is the electronic contribution  $\mu^{\text{el},T}$  to the transverse response, which comes entirely from the current-response contribution  $\mu^{\text{el},J}$  in Eq. (A26). We have essentially no information about this contribution. On the other hand, we can still calculate the full lattice-dipole contribution  $\mu^{\text{ld}}$  since there is no current-response correction for this term. To do so, we move one layer of atoms along the  $y$  direction under fixed- $\mathcal{E}_y$  boundary conditions and obtain  $T_{1122}^{\mathcal{E}}$  and thus  $\mu_{1122}^{\text{ld},\mathcal{E}}$  and  $\mu_{1221}^{\text{ld},\mathcal{E}}$ .<sup>76</sup> For high- $K$  materials in which the lattice contribution dominates the FEC, calculating  $\mu^{\text{ld}}$  is a good approximation for the total FEC response. However, for the low- $K$  materials in which the electronic contribution  $\mu^{\text{el}}$  is comparable to the lattice contribution, we need to obtain  $\mu_{1122}^{\text{el}}$  and  $\mu_{1221}^{\text{el}}$  for the full FEC tensor. Here, we introduce the assumption that  $\mu_{1122}^{\text{el}} = \mu_{1221}^{\text{el}}$ , i.e.,  $\mu^{\text{el},T} = \mu^{\text{el},J} = 0$ , to obtain a rough first approximation to the full FEC tensor. A proper calculation would require the inclusion of the current-response terms of Appendix A, which are not currently implemented in this work.

The results for the full fixed- $\mathcal{E}$  FEC tensor at room temperature, making use of this assumption, are presented in Table VII. We present the results in terms of the FEC components defined in terms of both *unsymmetrized* strains ( $\mu$ ) and *symmetrized* strains ( $g$ ). We also give values for the effective beam-bending FEC defined as<sup>31,32</sup>

$$g^{\text{eff}} = -tg_{1111} + (1-t)g_{1122}, \quad (125)$$

where  $t = C_{1122}/(C_{1111} + C_{1122})$  is Poisson's ratio with  $C$  being the elastic stiffness tensor. Experimental values of  $g^{\text{eff}}$  were reported in Table VII for our materials of interest. Letting  $x$  and  $z$  be the thickness and length directions, respectively, Eq. (125) follows from the expression for the

TABLE VII. Cartesian FECs at fixed  $\mathcal{E}$  using the assumption  $\mu_{1122}^{\text{el}} = \mu_{1221}^{\text{el}}$ . Room-temperature  $\epsilon^0$  values are used for perovskites (see Table I). First column is experimental Poisson's ratio  $t$  (dimensionless); others are FECs in nC/m. FECs  $\mu$  and  $g$  are defined in terms of unsymmetrized and symmetrized strains, respectively, and are related by Eqs. (59)–(61).

	Poisson's ratio $t$	Even force					Mass-weighted force				
		$\mu_{1111}$	$\mu_{1122}$	$\mu_{1221}$	$g_{1122}$	$g^{\text{eff}}$	$\mu_{1111}$	$\mu_{1122}$	$\mu_{1221}$	$g_{1122}$	$g^{\text{eff}}$
		$g_{1111}$	$g_{1221}$				$g_{1111}$	$g_{1221}$			
C	0.1 <sup>a</sup>	-1.0	-0.3	-0.3	-0.3	-0.2	-1.0	-0.3	-0.3	-0.3	-0.2
Si	0.22 <sup>a</sup>	-1.3	-0.4	-0.4	-0.4	0.0	-1.3	-0.4	-0.4	-0.4	0.0
MgO	0.18 <sup>a</sup>	-1.1	-0.3	-0.4	-0.6	-0.3	-1.4	-0.4	-0.5	-0.7	-0.3
NaCl	0.25 <sup>a</sup>	-0.2	0.0	-0.2	-0.4	-0.2	-0.2	0.0	-0.2	-0.4	-0.3
CsCl	0.27 <sup>a</sup>	-0.8	-0.2	-0.4	-0.6	-0.2	-0.9	-0.5	-0.3	-0.2	0.0
BZO	0.24 <sup>a</sup>	-1.9	0.0	-1.2	-2.3	-1.3	-2.8	-0.2	-1.5	-2.7	-1.4
BTO	0.27 <sup>a</sup>	-334.3	13.8	-225.3	-464.3	-248.7	-370.8	-2.5	-239.2	-475.9	-247.3
PTO	0.31 <sup>a</sup>	-20.0	0.1	-13.5	-27.2	-12.4	-26.4	-2.0	-16.0	-30.0	-12.3
STO	0.24 <sup>a</sup>	-36.9	-1.4	-20.8	-40.2	-21.6	-48.4	-5.0	-24.2	-43.5	-21.4

<sup>a</sup>Experimental values: C (Ref. 77); Si (Ref. 78); MgO (Ref. 79); NaCl (Ref. 80); CsCl (Ref. 81); BZO (Ref. 82); BTO (Ref. 83); PTO (Ref. 84); STO (Ref. 85).

displacement field in the case of pure beam bending, given by<sup>86</sup>  $u_x = -[z^2 + t(x^2 - y^2)]/2R$ ,  $u_y = -txy/R$ , and  $u_z = xz/R$ , where  $R$  is the radius of curvature of the neutral surface of the beam. Thus, the symmetrized strain gradient is  $v_{xxx}^s = v_{yyx}^s = -t v_{zzx}^s$ , leading to Eq. (125).

As we discussed in Sec. II F, the lattice contribution to the FECs has a dependence on the choice of force pattern because of the force density that arises due to the nonzero divergence of the stress in a general strain gradient configuration. However, in the beam-bending experiment, the beam is in local static equilibrium at every interior point, so there is no such force density; the contributions coming from individual elements of the strain gradient tensor cancel each other. Therefore, the effective beam-bending FEC  $g^{\text{eff}}$  should not depend on the choice of force pattern in our calculation. This can be confirmed by referring to Table VII, where  $g^{\text{eff}}$  obtained from different force patterns are indeed the same to within the numerical precision of the calculations. This confirms that although the individual FEC components are force-pattern dependent coming from the first-principles calculations, using them for problems of static equilibrium should not cause any problem. Conversely, it follows that it may be problematic to measure the full set of FEC components experimentally from static-equilibrium experiments since only special linear combinations of strain gradient components, for which the force density vanishes, are accessible in this way.

Since quantities related to elastic properties are usually defined in the literature for symmetrized strain, we focus on the FECs  $g_{\alpha\beta\gamma\delta}$  related to symmetrized strain for the remainder of this section. From Table VII, we can see that the values of  $g_{1111}$  and  $g_{1122}$  are comparable, but the value of  $g_{1221}$  is much smaller than the other two components, indicating that the gradient of the shear strain  $\epsilon_{21,2}$  makes only a very weak contribution to the flexoelectric response (under the assumption  $\mu^{\text{el}} = 0$ ), in agreement with the results of Ponomareva *et al.*<sup>46</sup>

According to Eq. (125), in order to obtain a large bending flexoelectric response, a large  $g_{1122}$  and a small  $g_{1111}$  are preferred, as well as a small Poisson's ratio. Even if the individual FEC components are all negative, the effective beam-bending FEC can still be positive, depending on the

ratio of  $g_{1111}$  to  $g_{1122}$ . Specifically,  $g^{\text{eff}}$  has a positive value if  $g_{1111}/g_{1122} > (1 - t)/t$  (assuming  $g_{1111}$  and  $g_{1122}$  are negative).

#### D. Comparison with experiment and previous theoretical results

As mentioned in the Introduction, large discrepancies between experimental and theoretical results for the FECs have been reported. For example, for high- $K$  materials, the experimental effective FECs are usually reported to be on the order of  $\mu\text{C/m}$  (Refs. 4–9) with a positive sign, while the theoretical results are typically on the order of nC/m with negative sign.<sup>39,42</sup> One possible reason is that the theoretical results are calculated at 0 K while the experimental results are measured at room temperature (or above the Curie temperature), and very strong dependence of the static dielectric constant can contribute to this large discrepancy. Regarding the sign problem, the effective beam-bending coefficient is given by Eq. (125), and as discussed in the previous section, the negative individual components can give a positive effective beam-bending FEC even if  $g_{1111}$  and  $g_{1122}$  are negative.<sup>87</sup>

As we showed in the previous section, the individual FEC components are dependent on the force pattern adopted for the first-principles calculations. Therefore, we should not expect that individual FEC tensor components, such as  $\mu_{1111}$ , can be compared directly between theory and experiment.

In order to obtain the full FEC tensor, we need to have information about  $\mu_{\text{T}}$ . In Sec. IV C, we assumed that  $\mu^{\text{el,T}} = 0$  in order to obtain a rough estimate of the the full FEC tensor as presented in Table VII. However, it can be seen that the effective beam-bending FEC computed in that way does not agree with available experiment results. For example,  $g^{\text{eff}}$  has been reported to be 6.1 nC/m for SrTiO<sub>3</sub> single crystals<sup>31,32</sup> and 9  $\mu\text{C/m}$  for BaTiO<sub>3</sub> ceramics<sup>9</sup> at room temperature, while we obtain -22 nC/m and -0.246  $\mu\text{C/m}$  for SrTiO<sub>3</sub> and BaTiO<sub>3</sub>, respectively. There are several possible reasons for this discrepancy. First, it may well be that our assumption that  $\mu^{\text{el,T}} = 0$ , introduced to obtain the full FEC tensor in Table VII, is strongly inadequate.<sup>87</sup> Second, the experiment

results include surface effects that have not been included here. To do so would require computing the surface contributions as discussed in Ref. 45, which is beyond the scope of this paper.

Hong *et al.*<sup>42</sup> also calculated the longitudinal FECs for SrTiO<sub>3</sub> and BaTiO<sub>3</sub> at fixed  $D$ , including electronic and lattice contributions, by imposing a strain wave of cosine form for the  $A$  atoms in the supercell and relaxing all other atoms. This corresponds to a choice of force pattern in which all of the force is on the  $A$  atoms. Their results are  $\mu_{1111}^D = -0.37 \pm 0.03$  nC/m for BaTiO<sub>3</sub> and  $\mu_{1111}^D = -1.38 \pm 0.65$  nC/m for SrTiO<sub>3</sub>. It can be seen that our results agree with their BaTiO<sub>3</sub> result in order of magnitude and sign, with the remaining discrepancy coming mostly from the difference in force patterns.

## V. CONCLUSION

A general and unified first-principles theory of piezoelectric and flexoelectric tensors has been developed and presented here. The longitudinal contributions to the flexoelectric tensor can be computed from the dipoles associated with strain-gradient-induced displacements (lattice dipole), quadrupoles associated with strain-induced displacements (lattice quadrupole), and octupoles associated with an ideal strain gradient (electronic). The full tensor also requires the transverse part, which has contributions that can only be obtained from the adiabatic currents that flow in response to the flexoelectric displacements.

While the full formalism is presented in Appendix A, we have implemented only the charge-response formalism in this work, following the equations presented in the main text and working in the framework of first-principles density-functional calculations. We have paid careful attention to the distinction between FECs computed at fixed  $\mathcal{E}$  versus fixed  $D$  and presented the relationships connecting them. We have argued that the FECs at fixed  $D$  provide a characteristic “ground-state bulk property” that can be used to predict finite-temperature fixed- $\mathcal{E}$  properties by scaling to the dielectric constant. We also show how the FCCs can be computed from our approach and used in a similar way as for the fixed- $D$  FECs.

A practical supercell-based method is proposed to calculate the FECs from first principles and is demonstrated by computing the coefficients of several cubic insulating materials, namely, C, Si, MgO, NaCl, CsCl, BaZrO<sub>3</sub>, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and SrTiO<sub>3</sub>. It is found that the FECs at fixed  $D$  are on the order of  $-0.1$  nC/m for all these materials, and their FCCs are in the range of  $-10$  to  $-20$  V, indicating that when large FECs are found in experiment, it is likely to arise from a large dielectric constant, or possibly from surface effects not treated explicitly here. Therefore, searching for large dielectric-constant materials is a good way to obtain materials with a large FxE response. The FECs computed from our first-principles theory at fixed  $\mathcal{E}$  still do not agree well with available experiment results, even after considering the relations between different electric boundary conditions. However, this discrepancy is two orders of magnitude less severe than some previous discrepancies between theory and experiment for the FECs (i.e., for BaTiO<sub>3</sub>). When surface effects are treated properly, it is hoped that this discrepancy will become even smaller.

Our calculations show that the lattice contribution to the FECs depends on the force pattern applied in the unit cell to maintain the strain gradient. Therefore, the total FECs are also dependent on the force pattern, and it is not meaningful to compare with FECs computed using a different force pattern. However, for a system in static equilibrium (zero stress gradient), the force-pattern dependence should cancel out, and we have confirmed that this is indeed the case from our numerical calculations.

The full FEC tensor is critical for an understanding of the FxE response in cases of complicated strain distributions, as well as for the design of functional FxE devices. In general, it is impossible to obtain all the elements of this tensor using only the charge-response formulation, even for cubic materials which have only three independent components. Therefore, it is clearly of interest to develop a full implementation based on the current-response tensors as described in Appendix A. The implementation of such a method, and the calculation of the remaining terms in the FxE response, remains as an important avenue for future work.

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## APPENDIX A: CURRENT-RESPONSE FORMALISM AND TRANSVERSE TENSOR COMPONENTS

In Sec. II A, we carried out a derivation that expresses the flexoelectric tensor in terms of changes in the charge density induced by the atomic displacements associated with the strain gradient. However, this procedure only determines a part of the flexoelectric response, which we denote as the “longitudinal” part since it corresponds to the longitudinal part of the current-density field that arises as the deformation of the material is adiabatically turned on. In this appendix, we derive the full expression in terms of the current-density response, thus clarifying the status of the expressions given in Sec. II A.

As we discussed in our previous work,<sup>42</sup> the choice of the induced current density instead of the induced charge density provides a more complete description of the response. We define

$$\mathcal{P}_{l,\alpha\beta}(\mathbf{r} - \mathbf{R}_{lI}) = \frac{\partial \mathcal{J}_\alpha(\mathbf{r})}{\partial \dot{u}_{lI,\beta}} \quad (\text{A1})$$

to be the current density  $\mathcal{J}_\alpha(\mathbf{r})$  in Cartesian direction  $\alpha$  resulting from the adiabatic motion of atom  $I$  in cell  $l$  at some small velocity  $\dot{u}_{lI,\beta}$  along the  $\beta$  direction, keeping all other atoms fixed. We can simply think of this as the local polarization field  $\Delta\mathbf{P}(\mathbf{r})$  induced by the displacement of the atom. Such a quantity is not generally well defined for a *finite* adiabatic deformation; while its cell average is fixed by the change in Berry-phase polarization and its longitudinal (curl-free) part is fixed by the change in ground-state charge density, its transverse (i.e., divergence-free) part is not guaranteed to be independent of path. However, for an *infinitesimal*

displacement, as arises here in the linear response to a small strain gradient, there is no such ambiguity.

We then define the moments of the induced current densities in analogy with Eqs. (2)–(4) as

$$J_{I,\alpha\beta}^{(0)} = \int d\mathbf{r} \mathcal{P}_{I,\alpha\beta}(\mathbf{r}), \quad (\text{A2})$$

$$J_{I,\alpha\beta\gamma}^{(1)} = \int d\mathbf{r} \mathcal{P}_{I,\alpha\beta}(\mathbf{r}) r_\gamma, \quad (\text{A3})$$

$$J_{I,\alpha\beta\gamma\delta}^{(2)} = \int d\mathbf{r} \mathcal{P}_{I,\alpha\beta}(\mathbf{r}) r_\gamma r_\delta. \quad (\text{A4})$$

Note that  $J_{I,\alpha\beta\gamma\delta}^{(2)}$  is symmetric in indices  $\gamma\delta$ , but otherwise these tensors are general. The charge-response tensors of Eqs. (2)–(4) are related to the current-response tensors via

$$Q_{I,\alpha\beta}^{(1)} = J_{I,\alpha\beta}^{(0)}, \quad (\text{A5})$$

$$Q_{I,\alpha\beta\gamma}^{(2)} = J_{I,\alpha\beta\gamma}^{(1)} + J_{I,\gamma\beta\alpha}^{(1)}, \quad (\text{A6})$$

$$Q_{I,\alpha\beta\gamma\delta}^{(3)} = J_{I,\alpha\beta\gamma\delta}^{(2)} + J_{I,\gamma\beta\alpha\delta}^{(2)} + J_{I,\delta\beta\alpha\gamma}^{(2)}. \quad (\text{A7})$$

These equations follow after integration by parts using the Poisson continuity condition

$$f_{I,\beta}(\mathbf{r}) = -\partial_\alpha \mathcal{P}_{I,\alpha\beta}(\mathbf{r}). \quad (\text{A8})$$

For example, inserting Eq. (A8) in Eq. (3) gives

$$\begin{aligned} Q_{I,\alpha\beta\gamma}^{(2)} &= -\int d\mathbf{r} r_\alpha r_\gamma \partial_\mu \mathcal{P}_{I,\mu\beta}(\mathbf{r}) \\ &= \int d\mathbf{r} \mathcal{P}_{I,\mu\beta}(\mathbf{r}) \partial_\mu (r_\alpha r_\gamma), \end{aligned} \quad (\text{A9})$$

which leads to Eq. (A6) using Eq. (A3) after noting that  $\partial_\mu (r_\alpha r_\gamma) = \delta_{\mu\alpha} r_\gamma + \delta_{\mu\gamma} r_\alpha$ .

Equations (A5)–(A7) make it clear that the charge-response and current-response tensors are closely related. In fact,  $Q^{(1)}$  and  $J^{(0)}$  are identical. For the higher-order tensors, however, the charge-response tensors contain less information. Essentially, they only contain information about the longitudinal part of the induced current response and lack the additional information contained in the transverse part. A simple way to see this is just to count elements: recalling the symmetries of the various tensors under interchanges of indices, we note that  $Q_{I,\alpha\beta\gamma}^{(2)}$  has  $3 \times 6 = 18$  independent elements while  $J_{I,\alpha\beta\gamma}^{(1)}$  has  $3 \times 3 \times 3 = 27$ , and  $Q_{I,\alpha\beta\gamma\delta}^{(3)}$  has  $3 \times 10 = 30$  elements while  $J_{I,\alpha\beta\gamma\delta}^{(2)}$  has  $3 \times 3 \times 6 = 54$ . This makes it clear that some information is missing from the charge-response tensors.

To make this more precise, we define the longitudinal parts of the  $J$  tensors to be

$$J_{I,\alpha\beta\gamma}^{(1,L)} = \frac{1}{2}(J_{I,\alpha\beta\gamma}^{(1)} + J_{I,\gamma\beta\alpha}^{(1)}) \quad (\text{A10})$$

and

$$J_{I,\alpha\beta\gamma\delta}^{(2,L)} = \frac{1}{3}(J_{I,\alpha\beta\gamma\delta}^{(2)} + J_{I,\gamma\beta\alpha\delta}^{(2)} + J_{I,\delta\beta\alpha\gamma}^{(2)}), \quad (\text{A11})$$

and the transverse parts to be the remainders

$$J_{I,\alpha\beta\gamma}^{(1,T)} = J_{I,\alpha\beta\gamma}^{(1)} - J_{I,\alpha\beta\gamma}^{(1,L)}, \quad (\text{A12})$$

$$J_{I,\alpha\beta\gamma\delta}^{(2,T)} = J_{I,\alpha\beta\gamma\delta}^{(2)} - J_{I,\alpha\beta\gamma\delta}^{(2,L)}. \quad (\text{A13})$$

The longitudinal current-response tensors describe the moments of the curl-free part of  $\mathbf{P}_{I,\alpha}$  and can be written, using

Eqs. (A6) and (A7), as

$$J_{I,\alpha\beta}^{(0)} = Q_{I,\alpha\beta}^{(1)}, \quad (\text{A14})$$

$$J_{I,\alpha\beta\gamma}^{(1,L)} = \frac{1}{2} Q_{I,\alpha\beta\gamma}^{(2)}, \quad (\text{A15})$$

$$J_{I,\alpha\beta\gamma\delta}^{(2,L)} = \frac{1}{3} Q_{I,\alpha\beta\gamma\delta}^{(3)}, \quad (\text{A16})$$

thus reproducing the information in the charge-response tensors. On the other hand, the transverse current-response tensors  $J^{(1,T)}$  and  $J^{(2,T)}$  contain new information that is not otherwise available.

The entire derivation of Sec. II A can now be repeated using the current-response formalism. Equation (19) is replaced by

$$P_\alpha(\mathbf{r}) = \sum_{I\tau} \mathcal{P}_{I,\alpha\tau}(\mathbf{r} - \mathbf{R}_{II}) u_{I\tau}, \quad (\text{A17})$$

and its Fourier transform is

$$P_\alpha(\mathbf{k}) = V_c^{-1} \sum_{I\tau} W_{I\tau\beta}(\mathbf{k}) \mathcal{P}_{I,\alpha\tau}(\mathbf{k}) u_{0\beta}, \quad (\text{A18})$$

where  $\mathcal{P}_{I,\alpha\tau}(\mathbf{k})$  is the Fourier transform of  $\mathcal{P}_{I,\alpha\tau}(\mathbf{r})$ . Equation (24) is then replaced by

$$\begin{aligned} P_\alpha(\mathbf{k}) &= V_c^{-1} \sum_I \left[ i \sum_\tau J_{I\alpha\tau}^{(0)} \Gamma_{I\tau\beta\gamma} k_\gamma - i J_{I\alpha\beta\nu}^{(1)} k_\nu \right] u_{0\beta} \\ &+ V_c^{-1} \sum_I \left[ - \sum_\tau J_{I\alpha\tau}^{(0)} N_{I\tau\beta\gamma\delta} k_\gamma k_\delta \right. \\ &+ \sum_\tau J_{I\alpha\tau\nu}^{(1)} \Gamma_{I\tau\beta\gamma} k_\nu k_\gamma - \frac{1}{2} J_{I\alpha\beta\nu\mu}^{(2)} k_\nu k_\mu \left. \right] u_{0\beta} \\ &+ \dots \end{aligned} \quad (\text{A19})$$

Comparing this with Eq. (28) we conclude that

$$e_{\alpha\beta\gamma} = V_c^{-1} \sum_{I\tau} J_{I\alpha\tau}^{(0)} \Gamma_{I\tau\beta\gamma} - V_c^{-1} \sum_I J_{I\alpha\beta\gamma}^{(1)}. \quad (\text{A20})$$

Using Eqs. (A14) and (A15) we find that the lattice-dipole part  $e^{\text{ld}}$  is still given by Eq. (34) while the electronic part  $e^{\text{el}}$  becomes

$$e_{\alpha\beta\gamma}^{\text{el}} = V_c^{-1} \sum_I \left( -\frac{1}{2} Q_{I,\alpha\beta\gamma}^{(2)} - J_{I\alpha\beta\gamma}^{(1,T)} \right). \quad (\text{A21})$$

Thus, the free contribution  $e_{\alpha\beta\gamma}^{\text{el}}$  in Eq. (35) has now been determined and can be seen to represent precisely the transverse components that were omitted in the charge-response derivation.

In a similar way, we can now obtain the full flexoelectric tensor. Remembering that  $\mu_{\alpha\beta\gamma\delta}$  is forced by definition to be symmetric in the last two indices, we find that the contributions to the flexoelectric tensor, Eq. (44), are now



given by

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld}} = V_c^{-1} \sum_{I\tau} J_{I\alpha\tau}^{(0)} N_{I\tau\beta\gamma\delta}, \quad (\text{A22})$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld}} = -\frac{1}{2} V_c^{-1} \sum_{I\tau} (J_{I,\alpha\beta\gamma}^{(1)} \Gamma_{I\tau\beta\delta} + J_{I,\alpha\beta\delta}^{(1)} \Gamma_{I\tau\beta\gamma}), \quad (\text{A23})$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{el}} = \frac{1}{2} V_c^{-1} \sum_I J_{I,\alpha\beta\gamma\delta}^{(2)}. \quad (\text{A24})$$

Once again, Eqs. (46) and (47) are recovered, but now we can identify the missing transverse pieces as

$$\mu_{\alpha\beta\gamma\delta}^{\text{ld,J}} = -\frac{1}{2} V_c^{-1} \sum_{I\tau} (J_{I,\alpha\beta\gamma}^{(1,T)} \Gamma_{I\tau\beta\delta} + J_{I,\alpha\beta\delta}^{(1,T)} \Gamma_{I\tau\beta\gamma}), \quad (\text{A25})$$

$$\mu_{\alpha\beta\gamma\delta}^{\text{el,J}} = \frac{1}{2} V_c^{-1} \sum_I J_{I,\alpha\beta\gamma\delta}^{(2,T)}. \quad (\text{A26})$$

This completes the full derivation of the flexoelectric response tensor using the current-response formalism.

Methods for computing the transverse parts of the current-response tensors  $J^{(1,T)}$  and  $J^{(2,T)}$  have not been developed as part of this work. No extra contributions are needed for the lattice-dipole contribution, and the lattice-quadrupole terms vanish for all of the cubic materials considered in this work except for C and Si. For the electronic contribution, however, we are only able to report on the longitudinal contributions  $\mu^{\text{el,L1}}$  and  $\mu^{\text{el,L2}}$ , leaving the calculation of  $\mu^{\text{el,T}}$  for future work.

## APPENDIX B: PSEUDOINVERSE OF FORCE-CONSTANT MATRIX

We begin by restating the problem posed in Sec. II F2, simplifying the notation by dropping the Cartesian indices. This is clearly sufficient for the binary cubic materials considered here since the force-constant matrix is block diagonal in the Cartesian representation, and the procedure outlined applies to each  $N \times N$  block ( $N$  is the number of atoms per cell). (For the perovskites, the transformation to symmetry-mode variables outlined in Appendix C is performed first. For more complex crystals, the force-constant matrix would be block diagonalized by IR-active irrep before the procedure would be applied, with  $N$  replaced by the number of copies of the irrep.)

With this simplification, the problem is as follows. We are given a force-constant matrix  $K = K^T$  obeying the acoustic sum rule  $\sum_j K_{ij} t_j = 0$ , where  $t_j$  is a vector all of whose elements are 1, and a set of weights  $w_i$  specifying a ‘‘force pattern.’’ We wish to construct a pseudoinverse  $J^{[w]}$  having the property that Eq. (100) is obeyed, i.e.,

$$f_i^{\text{ext}} - \sum_{jk} K_{ik} J_{kj}^{[w]} f_j^{\text{ext}} = \left( \sum_j t_j f_j^{\text{ext}} \right) w_i \quad (\text{B1})$$

for any external force vector  $f^{\text{ext}}$ . To simplify the notation we use a bra-ket notation for vectors with implied matrix-matrix and matrix-vector products, so that this is equivalent to

$$K J^{[w]} = I - |w\rangle\langle t| \quad (\text{B2})$$

with  $\langle w|t\rangle = 1$ .

The construction proceeds as follows. Construct an  $N \times N$  matrix  $E$  whose first column is  $|w\rangle$  and whose remaining

columns are all orthogonal to  $|t\rangle$ , being sure to keep the columns linearly independent. Also define  $D = (E^T)^{-1}$ , i.e., the matrix whose columns are the duals to those of  $E$  (that is,  $D^T E = I$ ). This means that the first column of  $D$  is just  $|t\rangle$ . We can think of  $D$  and  $E$  as giving the transformations back and forth between the original atomic displacements and a set of mode variables of which the first is the uniform translation.

Next let  $D_r$  and  $E_r$  be the  $N \times (N-1)$  rectangular matrices constructed by dropping the first column of  $D$  and  $E$ , respectively. Letting  $|o\rangle$  be the vector  $(1, 0, \dots)$ , this can be written as  $D_r = D - |t\rangle\langle o|$  and  $E_r = E - |w\rangle\langle o|$ , and it follows that

$$E_r D_r^T = I - |w\rangle\langle t| \quad (\text{B3})$$

after using that  $D|o\rangle = |t\rangle$  and  $E|o\rangle = |w\rangle$ . Since  $K$  obeys the acoustic sum rule, the first row and column of  $D^T K D$  are zero, and  $K$  is fully represented by the ‘‘reduced’’ matrix

$$K_r = D_r^T K D_r \Leftrightarrow K = E_r K_r E_r^T. \quad (\text{B4})$$

Then, our solution is to set

$$J^{[w]} = D_r (K_r^{-1}) D_r^T, \quad (\text{B5})$$

which is well defined because the reduced matrix  $K_r$  is nonsingular. Substituting into Eq. (B2) we get

$$\begin{aligned} K J^{[w]} &= (E_r K_r E_r^T) (D_r K_r^{-1} D_r^T) \\ &= E_r K_r K_r^{-1} D_r^T \\ &= E_r D_r^T = I - |w\rangle\langle t|, \end{aligned} \quad (\text{B6})$$

where Eq. (B3) was used on the last line. This satisfies Eq. (B2), showing that  $J^{[w]}$  is indeed the needed pseudoinverse.

## APPENDIX C: OXYGEN IN THE PEROVSKITES

As discussed in the main text, the site symmetry of individual O atoms in cubic perovskites is not cubic, and some of the space-group operations interchange O atoms. To handle this case, it is convenient to introduce ‘‘mode coordinates.’’

We define O1, O2, and O3 as the oxygen atoms displaced by  $a/2$  from the central Ti along  $\hat{x}$ ,  $\hat{y}$ , and  $\hat{z}$ , respectively. Taking SrTiO<sub>3</sub> as our example system, we start by considering zone-center phonons and carrying out a linear transformation between the 15 sublattice displacement variables  $u_{I\tau}$  describing the displacement of sublattice  $I = \{\text{Sr}, \text{Ti}, \text{O1}, \text{O2}, \text{O3}\}$  in Cartesian direction  $\tau = \{x, y, z\}$ , and symmetrized mode variables  $\xi_{\sigma\tau}$  that we choose to define as

$$\begin{aligned} \xi_{1x} &= u_{\text{Sr}x}, & \xi_{1y} &= u_{\text{Sr}y}, & \xi_{1z} &= u_{\text{Sr}z}, \\ \xi_{2x} &= u_{\text{Ti}x}, & \xi_{2y} &= u_{\text{Ti}y}, & \xi_{2z} &= u_{\text{Ti}z}, \\ \xi_{3x} &= u_{\text{O1}x}, & \xi_{3y} &= u_{\text{O2}y}, & \xi_{3z} &= u_{\text{O3}z}, \end{aligned} \quad (\text{C1})$$

$$\xi_{\{4,5\}x} = (u_{\text{O3}x} \pm u_{\text{O2}x})/\sqrt{2},$$

$$\xi_{\{4,5\}y} = (u_{\text{O1}y} \pm u_{\text{O3}y})/\sqrt{2},$$

$$\xi_{\{4,5\}z} = (u_{\text{O2}z} \pm u_{\text{O1}z})/\sqrt{2},$$

where  $\{4,5\}$  means that the plus and minus apply to cases 4 and 5, respectively. Here  $\sigma$  is a label running over  $\sigma = 1, 2, 3, 4$  for the four copies of the IR-active  $\Gamma_{15}$  irrep, while  $\sigma = 5$  corresponds to the IR-silent  $\Gamma_{25}$  irrep. We can summarize this

as

$$\xi_{\sigma\tau} = \sum_{I\tau'} A_{\sigma\tau, I\tau'} u_{I\tau'}, \quad (\text{C2})$$

where the elements of  $A_{\sigma\tau, I\tau'}$  are given in Eq. (C1).

We have chosen an orthogonal transformation  $A^{-1} = A^T$  so that forces transform in the same way,

$$\tilde{f}_{\sigma\tau} = \sum_{I\tau'} A_{\sigma\tau, I\tau'} f_{I\tau'}. \quad (\text{C3})$$

The  $T$  tensor elements of Eq. (68) will also transform in the same way,

$$\tilde{T}_{\sigma\tau, \beta\gamma\delta} = \sum_{I\tau'} A_{\sigma\tau, I\tau'} T_{I\tau', \beta\gamma\delta}, \quad (\text{C4})$$

which is essentially Eq. (89) using  $A^{-1} = A^T$ .

### 1. Original frame

Our main interest here is the calculation of these  $T$ -tensor elements. We start with the original supercell extended along  $x$  as in Fig. 1(a) and detailed in Figs. 3(a) and 3(b), and consider the forces in response to a longitudinal strain gradient  $v_{xxx}$ . In this case, all forces are along  $x$  by symmetry, and from Eq. (C3) with  $A$  given by Eq. (C1) it follows that

$$\begin{aligned} \tilde{f}_{3x} &= f_{01x}, & \tilde{f}_{4x} &= (f_{03x} + f_{02x})/\sqrt{2}, \\ \tilde{f}_{5x} &= (f_{03x} - f_{02x})/\sqrt{2}. \end{aligned} \quad (\text{C5})$$

For this case we find  $f_{02x} = f_{03x}$ , so  $\tilde{f}_{5x}$  vanishes and  $\tilde{f}_{4x}$  simplifies. Applying this to the  $T$ -tensor elements, we find

$$\begin{aligned} \tilde{T}_{1,xxxx} &= T_{\text{Sr},xxxx}, & \tilde{T}_{2,xxxx} &= T_{\text{Ti},xxxx}, \\ \tilde{T}_{3,xxxx} &= T_{\text{O1},xxxx}, & \tilde{T}_{4,xxxx} &= \sqrt{2} T_{\text{O2},xxxx}, \\ \tilde{T}_{5,xxxx} &= 0. \end{aligned} \quad (\text{C6})$$

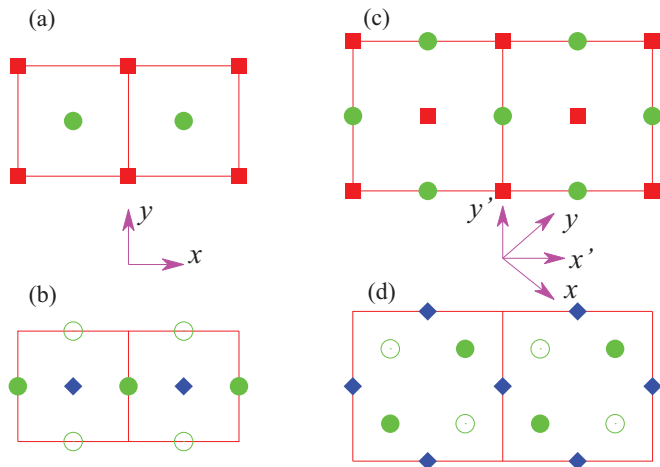


FIG. 3. (Color online)  $\text{ABO}_3$  perovskite atomic geometry in (a), (b) original Cartesian frame, and (c), (d)  $45^\circ$ -rotated frame, as appropriate to the two supercells of Fig. 1, respectively. (a), (c) slice at  $z = 0$ ; filled squares (red) are  $A$  and filled circles (green) are  $\text{O}_3$  atoms. (b), (d) slice at  $z = c/2$ ; filled diamonds (blue) are  $B$ , filled circles (green) are  $\text{O}_1$ , and open circles (green) are  $\text{O}_2$  atoms.

These correspond to  $T_{I1111}$  elements in the notation of the main part of the paper. Similar results hold for the  $Q^{(1)}$  and  $Q^{(3)}$  tensors:

$$\tilde{Q}_{3,xx}^{(1)} = Q_{\text{O1},xx}^{(1)}, \quad \tilde{Q}_{4,xx}^{(1)} = \sqrt{2} Q_{\text{O2},xx}^{(1)}, \quad (\text{C7})$$

$$\tilde{Q}_{3,xxxx}^{(3)} = Q_{\text{O1},xxxx}^{(3)}, \quad \tilde{Q}_{4,xxxx}^{(3)} = \sqrt{2} Q_{\text{O2},xxxx}^{(3)}. \quad (\text{C8})$$

If instead we consider the presence of a transverse strain gradient  $v_{yxx}$ , we find that  $f_{01y} \neq f_{02y} \neq f_{03y}$  are nonzero. Again using the transformation rules of Eq. (C1), we find

$$\begin{aligned} \tilde{T}_{1,yyxx} &= T_{\text{Sr},yyxx}, & \tilde{T}_{2,yyxx} &= T_{\text{Ti},yyxx}, \\ \tilde{T}_{3,yyxx} &= T_{\text{O2},yyxx}, \\ \tilde{T}_{4,yyxx} &= (T_{\text{O1},yyxx} + T_{\text{O3},yyxx})/\sqrt{2}, \\ \tilde{T}_{5,yyxx} &= (T_{\text{O1},yyxx} - T_{\text{O3},yyxx})/\sqrt{2}. \end{aligned} \quad (\text{C9})$$

Using symmetry, these correspond to the  $T_{I1122}$  elements in the notation of the main part of the paper.

### 2. $45^\circ$ -rotated frame

Referring now to Figs. 3(c) and 3(d), we consider the  $45^\circ$ -rotated geometry as in Fig. 1(b). Then, to relate the forces, we have to carry out  $45^\circ$  rotations on Cartesian indices twice, once before and once after the transformation to mode variables. This is trivial for the Sr and Ti atoms, giving  $\tilde{f}_{1x'} = f_{\text{Sr}x'}$ , etc., but for the oxygens it is more complex. We find, for example,

$$\begin{aligned} \tilde{f}_{3x'} &= (\tilde{f}_{3x} + \tilde{f}_{3y})/\sqrt{2} \\ &= (f_{01x} + f_{02y})/\sqrt{2} \\ &= (f_{01x'} - f_{01y'} + f_{02x'} + f_{02y'})/2. \end{aligned} \quad (\text{C10})$$

Using similar algebra, we find the full set of transformations to be given by

$$\begin{pmatrix} \tilde{f}_{3x'} \\ \tilde{f}_{3y'} \\ \tilde{f}_{4x'} \\ \tilde{f}_{4y'} \\ \tilde{f}_{5x'} \\ \tilde{f}_{5y'} \end{pmatrix} = \begin{pmatrix} h & \bar{h} & h & h & 0 & 0 \\ \bar{h} & h & h & h & 0 & 0 \\ t & t & t & \bar{t} & s & 0 \\ t & t & \bar{t} & t & 0 & s \\ t & t & \bar{t} & t & 0 & \bar{s} \\ t & t & t & \bar{t} & \bar{s} & 0 \end{pmatrix} \begin{pmatrix} f_{01x'} \\ f_{01y'} \\ f_{02x'} \\ f_{02y'} \\ f_{03x'} \\ f_{03y'} \end{pmatrix}, \quad (\text{C11})$$

where  $h = 1/2$ ,  $s = \sqrt{2}$ ,  $t = 1/2\sqrt{2}$ , and a bar indicates a minus sign.

We restrict our attention now to longitudinal strain gradients of the form  $v_{x'x'x'}$ . For the oxygens we find  $f_{01x'} = f_{02x'}$ ,  $f_{01y'} = -f_{02y'}$ , and  $f_{03x'}$  are nonzero. Then, using Eq. (C11) we find

$$\begin{aligned} \tilde{f}_{3x'} &= f_{01x'} - f_{01y'}, \\ \tilde{f}_{4x'} &= (f_{01x'} + f_{01y'} + f_{03x'})/\sqrt{2}, \\ \tilde{f}_{5y'} &= (f_{01x'} + f_{01y'} - f_{03x'})/\sqrt{2}, \end{aligned} \quad (\text{C12})$$

while  $\tilde{f}_{3y'} = \tilde{f}_{4y'} = \tilde{f}_{5x'} = 0$ . It follows that

$$\begin{aligned}\tilde{T}_{1,x'x'x'x'} &= T_{\text{Sr},x'x'x'x'}, & \tilde{T}_{2,x'x'x'x'} &= T_{\text{Ti},x'x'x'x'}, \\ \tilde{T}_{3,x'x'x'x'} &= T_{\text{O}1,x'x'x'x'} - T_{\text{O}1,y'y'x'x'}, \\ \tilde{T}_{4,x'x'x'x'} &= (T_{\text{O}1,x'x'x'x'} + T_{\text{O}1,y'y'x'x'} + T_{\text{O}3,x'x'x'x'})/\sqrt{2}, \\ \tilde{T}_{5,y'y'x'x'} &= (T_{\text{O}1,x'x'x'x'} + T_{\text{O}1,y'y'x'x'} - T_{\text{O}3,x'x'x'x'})/\sqrt{2}.\end{aligned}\tag{C13}$$

Similarly, for the  $\tilde{Q}^{(3)}$  tensors in the rotated frame we find

$$\begin{aligned}\tilde{Q}_{3,xxxx}^{(3)} &= Q_{\text{O}1,x'x'x'x'}^{(3)} - Q_{\text{O}1,x'y'x'x'}^{(3)}, \\ \tilde{Q}_{4,xxxx}^{(3)} &= (Q_{\text{O}1,x'x'x'x'}^{(3)} + Q_{\text{O}1,x'y'x'x'}^{(3)} + Q_{\text{O}3,x'x'x'x'}^{(3)})/\sqrt{2},\end{aligned}\tag{C14}$$

where we used that  $Q_{\text{O}1,x'x'x'x'}^{(3)} = Q_{\text{O}2,x'x'x'x'}^{(3)}$  and  $Q_{\text{O}1,x'y'x'x'}^{(3)} = -Q_{\text{O}2,x'y'x'x'}^{(3)}$  from symmetry.

### 3. Discussion

Note that  $\tilde{T}_{\sigma\alpha\beta\gamma\delta}$  has the same symmetry for  $\sigma \in \{1,2,3,4\}$ . That is, we have arranged things so that the  $\sigma = 3$  and 4 cases behave just like  $\sigma = 1$  (Sr) or  $\sigma = 2$  (Ti), so that any formulas used for Si and Ti contributions can easily be extended to the oxygen modes of  $\Gamma_{15}$  symmetry. Note that strain gradients also induce forces of  $\Gamma_{25}$  symmetry, corresponding to  $\sigma = 5$ , which in turn cause first-order  $\Gamma_{25}$  displacements. However, because these modes are not IR active, they do not contribute to the flexoelectric response.

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