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Generalized relation between electromechanical responses at fixed voltage and fixed electric field

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We present a general relation between the electromechanical couplings of infinitesimal strain and electric field to arbitrary order, measured at fixed voltage and at fixed electric field. We show that the improper response at fixed field can be written as the strain derivative of the nth order susceptibility tensor, and the proper response at fixed voltage drop can be written as the response at fixed field plus corrections for dilations and 90° rotations induced by strain. Our theory correctly reproduces the proper piezoelectric response and we go beyond with the electrostrictive response. We present first-principles calculations of the improper electrostrictive response at fixed field, and illustrate how the correction is used to obtain the proper response at fixed voltage. This distinction is of high importance given the recent interest in giant electrostrictors exhibiting electromechanical responses as large as the piezoelectric ones.

INTRODUCTION

The calculation of the piezoelectric response from first-principles density functional theory (DFT) simulations is nowadays standard, either using finite differences [1] or density functional perturbation theory (DFPT) [2]. However, care should be taken, as two possible piezoelectric responses can be obtained: the so-called "proper" and "improper" responses [1–4]. The improper response is computed from DFT when calculations are performed at fixed electric field, whereas the proper response is typically measured experimentally, where the voltage and not the electric field is held fixed [1, 5]. The distinction between fixed field and fixed voltage drop becomes necessary when strains are introduced.

This problem is sketched in Fig. 1: we have a dielectric material of thickness d sandwiched between two metal plates, across which a potential drop ΔV is applied. The voltage drop is related to the electric field in the material via

$$\Delta V = \mathcal{E} d \,. \tag{1}$$

If a small strain η appears in the material, changing the thickness to $(1+\eta)d$, Eq. (1) becomes:

$$\Delta V(\eta) = \mathcal{E}(1+\eta)d \,. \tag{2}$$

If the field $\mathcal{E}$ is held fixed, which is typically the case in first-principles calculations, the potential difference has to change by $\eta\Delta V$. Thus when strain is introduced we need to compensate for this effect in order to hold the potential difference fixed. If the potential drop ΔV is fixed, then it is the reduced field $\mathcal{E}' = (1+\eta)\mathcal{E}$ rather than $\mathcal{E}$ which is held fixed in Eq. 2. The voltage drop in each calculation will then be

$$\Delta V = (1+\eta)^{-1}\mathcal{E}' \cdot (1+\eta)d = \mathcal{E}' d \tag{3}$$

which is independent of η.

In addition to the strain dependence of the relationship between $\mathcal{E}$ and ΔV (Eq. 2), changes in the volume induced by strain can lead to different ways of measuring the energy per unit volume. Depending on whether calculations are done at fixed $\mathcal{E}$ or ΔV, and whether the energy per unit volume is measured with respect to the equilibrium reference volume (Ω_0) or the perturbed volume (Ω), there are four possible ways to define an electromechanical response, see Fig. 2: (i) the improper response, measured at fixed $\mathcal{E}$ and equilibrium volume Ω_0, (ii) the proper response, measured at fixed ΔV and strained volume Ω, (iii) an intermediate situation with fixed $\mathcal{E}$ and Ω, and (iv) a second intermediate situation with fixed ΔV and Ω_0 are used. This means that great care should be taken when comparing first-principles calculations of any electromechanical response to experimental measurements.

Although this problem is well-known in the context of

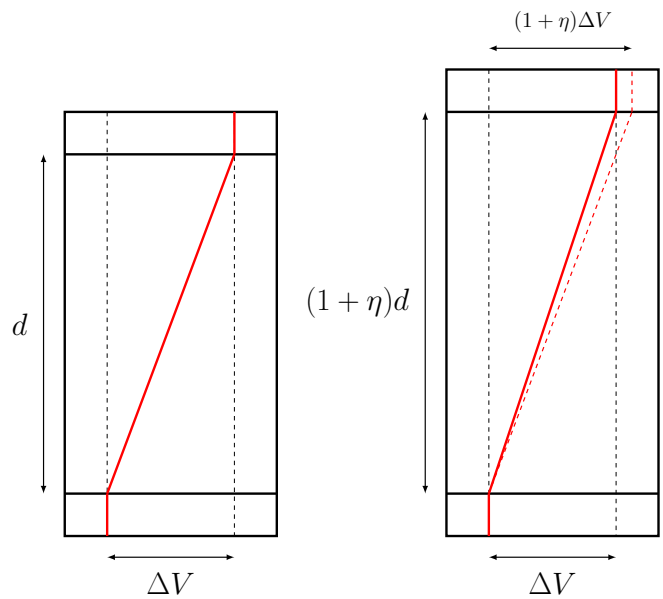

FIG. 1. Sketch of a dielectric material of thickness d sandwiched between two metal plates. A potential difference ΔV is applied, resulting in an electric field of $\mathcal{E} = \frac{\Delta V}{d}$ inside the material. When a strain of η is applied to the material, the field changes to $\mathcal{E} = \frac{\Delta V}{(1+\eta)d}$ if the potential difference is held fixed (experiment), or the potential difference changes to $(1+\eta)\Delta V$ if the field is held fixed (first-principles).

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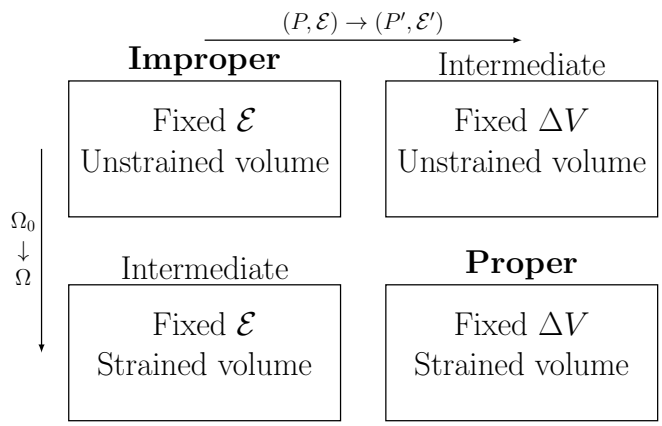

FIG. 2. Illustration of the four possible ways to define electromechanical responses, depending on the quantity held fixed ($\mathcal{E}$ or ΔV) and the units of volume used (Ω_0 or Ω). The improper response is obtained by fixing $\mathcal{E}$ and working in units of unstrained volume, Ω_0, and the improper response is obtained by fixing ΔV and working in units of strained volume, Ω. Two additional 'intermediate' responses which are neither proper nor improper are possible by switching the quantity held fixed or the units of volume.

piezoelectricity, its generalization to other electromechanical responses measured at fixed voltage and fixed electric field has not been reported. This generalization is becoming relevant, with increasing interest in higher-order couplings such as the electro-optic response and electrostriction. Indeed, giant electrostrictors have recently been shown to give rise to electromechanical responses as large as piezoelectric ones [6, 7], or even much larger: up to 2×10^5 pC/N [8]. However, no strict definition nor derivation of the proper versus improper responses have been given for electrostriction. In this paper, we derive an analogous relation for electrostriction and more generally any electromechanical response to an infinitesimal strain.

This paper is organized as follows: first, we review the relation between piezoelectric tensors measured at fixed electric field and fixed potential difference. The same methodology is then applied to obtain a corresponding relation for the electrostrictive tensor, and a general electromechanical coupling between an infinitesimal strain and electric field to arbitrary order. Detailed derivations are available in the Supplementary Material. We then use these relations to correct recent calculations of the electrostrictive response of rocksalt crystals in the literature [9], focusing on MgO, and re-examine the comparison with experimental measurements.

THEORY

For a crystal with mechanical degrees of freedom such as phonon displacements u and macroscopic strain deformations $\tilde{\eta}$, which is subject to an applied electric field $\mathcal{E}$ [10–12], the properties close to the equilibrium state can be described by Toupin's electric enthalpy density [13, 14]:

$$\mathcal{F}_{\Omega_0} = \mathcal{F}_{\text{cell}} - \left(\mathcal{E}\cdot P + \frac{1}{2}\varepsilon_0\mathcal{E}^2\right) , \tag{4}$$

where Ω_0 is the volume of the reference state ($\tilde{\eta}=0$), $\mathcal{F}_{\text{cell}}$ is the zero-field Kohn-Sham energy per unit volume of the system, and P is the total polarization of the system [15, 16]. An homogeneous deformation results in a change in the positions $\mathbf{r}$ in the reference state: $\Delta r_\alpha = \tilde{\eta}_{\alpha\beta} r_\beta$. The symmetric part of $\tilde{\eta}$ is simply the strain tensor, η. In Ref. [2] it was shown that the proper piezoelectric tensor is symmetric under the exchange of the strain indices. Thus, although we consider general deformations $\tilde{\eta}$ in this paper, we use the terms strain and deformation interchangeably.

The various clamped responses ($u=0$) are defined as the derivatives of Eq. (4) about the equilibrium state: $\{\tilde{\eta},\mathcal{E}\}=0$. For example, the piezoelectric tensor e is defined as [2]:

$$e^{(\text{i})}_{\alpha\beta\gamma} \equiv -\left.\frac{\partial^2\mathcal{F}_{\Omega_0}}{\partial\mathcal{E}_\alpha\tilde{\eta}_{\beta\gamma}}\right|_{\{\tilde{\eta},\mathcal{E}\}=0} = \frac{\partial P_\alpha}{\partial\tilde{\eta}_{\beta\gamma}} , \tag{5}$$

where the superscript (i) denotes that this is the improper tensor, measured at fixed electric field. In order to obtain the proper tensor, at a fixed potential difference, two corrections must be made to Eq. (4). First, the electrostatic energy must be scaled by $\frac{\Omega}{\Omega_0}$, where $\Omega = \Omega_0\det(I+\tilde{\eta})$ is the volume after a strain deformation $\tilde{\eta}$. Secondly, in order to hold the potential difference fixed, we make the following change of variables to "reduced coordinates" for the electric field, polarization and displacement field D [17]:

$$\begin{aligned} \mathcal{E}' &= (I+\tilde{\eta})\,\mathcal{E} \\ P' &= \frac{\Omega}{\Omega_0}(I+\tilde{\eta})^{-1}P \\ D' &= \frac{\Omega}{\Omega_0}(I+\tilde{\eta})^{-1}D \end{aligned} , \tag{6}$$

which are equivalent to some of the reduced fields defined in Ref. [5], but here the units of each field are preserved [18]. Thus, the enthalpy Eq. (4) becomes, in reduced coordinates:

$$\mathcal{F}'_\Omega = \mathcal{F}_{\text{cell}} - \mathcal{E}'\cdot P' + \frac{\Omega}{\Omega_0}\frac{1}{2}\varepsilon_0\mathcal{E}'^T g^{-1}\mathcal{E}' . \tag{7}$$

where $g=(I+\tilde{\eta})^T(I+\tilde{\eta})$. By differentiating we can see that $D'_\alpha = -\frac{\partial\mathcal{F}}{\partial\mathcal{E}'_\alpha}$, where we used $D=\varepsilon_0\mathcal{E}+P$, although note that $D'\neq\varepsilon_0\mathcal{E}'+P'$.

The proper piezoelectric tensor, measured at fixed voltage drop, is defined as:

$$e_{\alpha\beta\gamma} \equiv -\left.\frac{\partial^2\mathcal{F}'_\Omega}{\partial\mathcal{E}'_\alpha\partial\tilde{\eta}_{\beta\gamma}}\right|_{\{\tilde{\eta},\mathcal{E}'\}=0} = \frac{\partial P'_\alpha}{\partial\tilde{\eta}_{\beta\gamma}} . \tag{8}$$

The term linear in $\mathcal{E}$ is absent in Eq. (8) as the derivation is carried out about the equilibrium state ($\tilde{\eta},\mathcal{E}\to0$). Summation convention is assumed, using Latin letters for dummy indices

and Greek letters for free indices. Next, we explicitly evaluate the derivative in order to write Eq. (8) in terms of Eq. (5):

$$\begin{aligned} e_{\alpha\beta\gamma} &= \frac{\partial\left[\det(I+\tilde{\eta})\,(I+\tilde{\eta})^{-1}_{\alpha j}P_j\right]}{\partial\tilde{\eta}_{\beta\gamma}} \\ &= \frac{\partial\left[(1+\tilde{\eta}_{ii})\,(\delta_{\alpha j}-\tilde{\eta}_{\alpha j})P_j+\mathcal{O}(\tilde{\eta}^2)\right]}{\partial\tilde{\eta}_{\beta\gamma}} \\ &= \frac{\partial P_\alpha}{\partial\tilde{\eta}_{\beta\gamma}}+P_\alpha\delta_{\beta\gamma}-P_\gamma\delta_{\alpha\beta}+\tilde{\eta}_{ii}\frac{\partial P_\alpha}{\partial\tilde{\eta}_{\beta\gamma}}-\tilde{\eta}_{\alpha j}\frac{\partial P_j}{\partial\tilde{\eta}_{\beta\gamma}} \end{aligned} . \tag{9}$$

Going from the first line to the second line, we used the expansion $(I+\tilde{\eta})^{-1}=I-\tilde{\eta}+\mathcal{O}(\tilde{\eta}^2)$, truncating to linear order, assuming the strain is infinitesimal. For the same reason, we use $\det(I+\tilde{\eta})=1+\mathrm{tr}\,(\tilde{\eta})+\mathcal{O}(\tilde{\eta}^2)$ to simplify the volume term. Note that it is important to do this *before* differentiating, otherwise contributions which are quadratic in strain will be retained. After differentiating, we set $\mathcal{E},\tilde{\eta}\to 0$, because the derivatives are defined about the equilibrium state with zero strain and applied field. The relation between piezoelectric tensors measured at fixed voltage and at fixed field is then:

$$e_{\alpha\beta\gamma}=e^{(\mathrm{i})}_{\alpha\beta\gamma}+P_\alpha\delta_{\beta\gamma}-P_\gamma\delta_{\alpha\beta}\ . \tag{10}$$

As discussed in Ref. 1, the first term is a correction for dilations of the polarization induced by strain. The second term is a correction for rotations of the polarization by 90°, i.e. permutations of the indices. Additionally, a problem unique to the piezoelectric tensor is that Eq. (5) is sensitive to the branch on which the polarization is measured (quantum of polarization), but this is remedied by using Eq. (10), which is branch invariant [1].

Electrostriction

The improper strain electrostrictive tensor m, measured at fixed electric field, is defined as follows:

$$m^{(\mathrm{i})}_{\alpha\beta\gamma\delta}\equiv-\frac{1}{2}\left.\frac{\partial^3\mathcal{F}_{\Omega_0}}{\partial\mathcal{E}_\alpha\partial\mathcal{E}_\beta\partial\tilde{\eta}_{\gamma\delta}}\right|_{\{\tilde{\eta},\mathcal{E}\}=0}=\frac{\partial\varepsilon^{(\mathrm{i})}_{\alpha\beta}}{\partial\tilde{\eta}_{\gamma\delta}}\ , \tag{11}$$

where $\varepsilon^{(\mathrm{i})}_{\alpha\beta}\equiv\frac{\partial D_\alpha}{\partial\mathcal{E}_\beta}$ is the improper permittivity tensor, measured at fixed electric field calculated about the equilibrium state. The proper electrostrictive tensor, measured at fixed voltage, is defined as follows:

$$m_{\alpha\beta\gamma\delta}\equiv-\frac{1}{2}\left.\frac{\partial^3\mathcal{F}'_{\Omega}}{\partial\mathcal{E}'_\alpha\partial\mathcal{E}'_\beta\partial\tilde{\eta}_{\gamma\delta}}\right|_{\{\tilde{\eta},\mathcal{E}'\}=0}=\frac{\partial\varepsilon_{\alpha\beta}}{\partial\tilde{\eta}_{\gamma\delta}}\ , \tag{12}$$

where $\varepsilon_{\alpha\beta}\equiv\frac{\partial D'_\alpha}{\partial\mathcal{E}'_\beta}$ is the proper permittivity tensor, measured at fixed voltage. Immediately we see that Eqs. (11) and (12) are analogous to Eqs. (5) and (8), but with polarization replaced by dielectric permittivity. As before, we must write Eq. (12) in terms of Eq. (11). In order to do this, we must first relate the proper and improper permittivity tensors:

$$\varepsilon_{\alpha\beta}=(1+\tilde{\eta}_{ii})\varepsilon^{(\mathrm{i})}_{\alpha\beta}-\varepsilon^{(\mathrm{i})}_{\alpha i}\tilde{\eta}_{i\beta}-\tilde{\eta}_{\alpha j}\varepsilon^{(\mathrm{i})}_{j\beta}+\mathcal{O}(\tilde{\eta}^2)\ . \tag{13}$$

Note that $\varepsilon_{\alpha\beta}=\varepsilon^{(\mathrm{i})}_{\alpha\beta}$ at $\tilde{\eta}=0$, which is expected. However, it is clear that their derivatives with respect to strain will not be equal at $\tilde{\eta}=0$. Inserting Eq. (13) into Eq. (12):

$$\begin{aligned} m_{\alpha\beta\gamma\delta} &= \frac{\partial\varepsilon_{\alpha\beta}}{\partial\tilde{\eta}_{\gamma\delta}} \\ &= \frac{\partial}{\partial\tilde{\eta}_{\gamma\delta}}\left[(1+\tilde{\eta}_{ii})\varepsilon^{(\mathrm{i})}_{\alpha\beta}-\varepsilon^{(\mathrm{i})}_{\alpha i}\tilde{\eta}_{i\beta}-\tilde{\eta}_{\alpha j}\varepsilon^{(\mathrm{i})}_{j\beta}+\mathcal{O}(\tilde{\eta}^2)\right] . \\ &= \frac{\partial\varepsilon^{(\mathrm{i})}_{\alpha\beta}}{\partial\tilde{\eta}_{\gamma\delta}}+\varepsilon^{(\mathrm{i})}_{\alpha\beta}\delta_{\gamma\delta}-\varepsilon^{(\mathrm{i})}_{\alpha\gamma}\delta_{\beta\delta}-\varepsilon^{(\mathrm{i})}_{\delta\beta}\delta_{\gamma\alpha} \end{aligned} \tag{14}$$

Hence, we obtain an analogous relation between the proper and the improper response to Eq. (10) for the electrostriction:

$$m_{\alpha\beta\gamma\delta}=m^{(\mathrm{i})}_{\alpha\beta\gamma\delta}+\varepsilon_{\alpha\beta}\delta_{\gamma\delta}-\varepsilon_{\alpha\gamma}\delta_{\beta\delta}-\varepsilon_{\delta\beta}\delta_{\gamma\alpha}\ , \tag{15}$$

where we have dropped the (i) superscript on the permittivities because we have set $\tilde{\eta}\to 0$ and hence $\varepsilon^{(\mathrm{i})}=\varepsilon$. The corrections are similar to those appearing in the proper-improper relation for the piezoelectric tensors: the first term is a correction for changes in the permittivity induced by strain. The second term is a correction for permutations of the indices. Note that there are two of these terms, since ε is a rank 2 tensor.

Generalization to all orders of electromechanical coupling

The proper-improper relation can be generalized to electromechanical couplings which are linear in strain and to any order in electric field. The (improper) coupling between linear strain and n^{th} order electric field is described by the following tensor:

$$\begin{aligned} A^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n\tilde{\eta}_1\tilde{\eta}_2} &\equiv -\frac{1}{n!}\left.\frac{\partial^{n+1}\mathcal{F}_{\Omega_0}}{\partial\mathcal{E}_{\mathcal{E}_1}\ldots\partial\mathcal{E}_{\mathcal{E}_n}\partial\tilde{\eta}_{\tilde{\eta}_1\tilde{\eta}_2}}\right|_{\{\tilde{\eta},\mathcal{E}\}=0} \\ &= \frac{\partial\chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n}}{\partial\tilde{\eta}_{\tilde{\eta}_1\tilde{\eta}_2}} \end{aligned} , \tag{16}$$

measured at fixed field, where $n=1$ corresponds to the piezoelectric tensor and $n=2$ corresponds to the electrostrictive tensor. We can see that in general A is the first strain derivative of the nth order susceptibility tensor:

$$\chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n}\equiv\begin{cases} P_{\mathcal{E}_1}, & n=1 \\ \frac{\partial D_{\mathcal{E}_1}}{\partial\mathcal{E}_{\mathcal{E}_2}}, & n=2 \\ \frac{\partial^{n-1}P_{\mathcal{E}_1}}{\partial\mathcal{E}_{\mathcal{E}_2}\ldots\partial\mathcal{E}_{\mathcal{E}_n}}, & n>2 \end{cases} \tag{17}$$

defined to be the polarization and permittivity for $n = 1, 2$, respectively. The proper tensor, measured at fixed voltage, is defined as:

$$A_{\mathcal{E}_1\ldots\mathcal{E}_n\tilde{\eta}_1\tilde{\eta}_2} \equiv -\frac{1}{n!}\left.\frac{\partial^n \mathcal{F}'_\Omega}{\partial\mathcal{E}'_{\mathcal{E}_1}\ldots\partial\mathcal{E}'_{\mathcal{E}_n}\partial\tilde{\eta}_{\tilde{\eta}_1\tilde{\eta}_2}}\right|_{\{\tilde{\eta},\mathcal{E}'\}=0}, \quad (18)$$
$$= \frac{\partial\chi_{\mathcal{E}_1\ldots\mathcal{E}_n}}{\partial\tilde{\eta}_{\tilde{\eta}_1\tilde{\eta}_2}}$$

where

$$\chi_{\mathcal{E}_1\ldots\mathcal{E}_n} \equiv \begin{cases} P'_{\mathcal{E}_1}, & n=1 \\ \frac{\partial D'_{\mathcal{E}_1}}{\partial\mathcal{E}'_{\mathcal{E}_2}}, & n=2 \\ \frac{\partial^{n-1}P'_{\mathcal{E}_1}}{\partial\mathcal{E}'_{\mathcal{E}_2}\ldots\partial\mathcal{E}'_{\mathcal{E}_n}}, & n>2 \end{cases}. \quad (19)$$

Again, the aim is to write Eq. (18) in terms of Eq. (16). In order to do this, we must first obtain the relation between the nth order susceptibility tensors:

$$\chi_{\mathcal{E}_1\ldots\mathcal{E}_n} = \frac{\partial^{n-1}P'_{\mathcal{E}_1}}{\partial\mathcal{E}'_{\mathcal{E}_2}\ldots\partial\mathcal{E}'_{\mathcal{E}_n}}$$
$$= \left[\prod_{i=2}^{n}(I+\tilde{\eta})^{-1}_{k_i\mathcal{E}_i}\right]\frac{\partial^{n-1}P'_{\mathcal{E}_1}}{\partial\mathcal{E}_{k_2}\ldots\partial\mathcal{E}_{k_n}} \quad (20)$$
$$= \left[\prod_{i=1}^{n}(I+\tilde{\eta})^{-1}_{k_i\mathcal{E}_i}\right]\det(I+\tilde{\eta})\chi^{(\mathrm{i})}_{k_1\ldots k_n}$$

Expanding $\det(I+\tilde{\eta})$ and the products of $(I+\tilde{\eta})^{-1}$, and truncating to linear order, we get the following expression:

$$\chi_{\mathcal{E}_1\ldots\mathcal{E}_n} = (1+\tilde{\eta}_{ii})\chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n} - \sum_{i=1}^{n}\chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots k_i\ldots\mathcal{E}_n}\tilde{\eta}_{k_i\mathcal{E}_i}. \quad (21)$$

Eq. (21) is the relation between n^{th} order susceptibility tensors in reduced and unreduced coordinates at finite strain. It is reassuring to see that when $\tilde{\eta}\to 0$ we have $\chi_{\mathcal{E}_1\ldots\mathcal{E}_n} = \chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n}$, as expected. Obtaining the proper-improper relation for A is now straightforward:

$$A_{\mathcal{E}_1\ldots\mathcal{E}_n\tilde{\eta}_1\tilde{\eta}_2} = \frac{\partial}{\partial\tilde{\eta}_{\tilde{\eta}_1\tilde{\eta}_2}}\left((1+\tilde{\eta}_{ii})\chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n} - \sum_{i=1}^{n}\chi^{(\mathrm{i})}_{\mathcal{E}_1\ldots k_i\ldots\mathcal{E}_n}\tilde{\eta}_{k_i\mathcal{E}_i}\right)$$
$$= A^{(\mathrm{i})}_{\mathcal{E}_1\ldots\mathcal{E}_n\tilde{\eta}_1\tilde{\eta}_2} + \delta_{\tilde{\eta}_1\tilde{\eta}_2}\chi_{\mathcal{E}_1\ldots\mathcal{E}_n} - \sum_{i=1}^{n}\chi_{\mathcal{E}_1\ldots\tilde{\eta}_1\ldots\mathcal{E}_n}\delta_{\tilde{\eta}_2\mathcal{E}_i} \quad (22)$$

where $\tilde{\eta}_1$ is in the ith position. There is one term for dilations induced by strain and n terms corresponding to permutations of the n indices of the susceptibility. For $n = 1, 2$, Eqs. (10) and (15) are reproduced, respectively.

First-principles calculations

We illustrate the proper-improper relation for electrostriction using first-principles calculations of the electrostrictive response of MgO, LiCl, LiF and NaCl. Typically, it is the electrostrictive response to stress which is measured experimentally, because it can be measured at fixed voltage [6]. The electrostrictive response to a stress is defined as $M_{\alpha\beta\gamma\delta} = \frac{1}{2}\frac{\partial\varepsilon_{\alpha\beta}}{\partial X_{\gamma\delta}}$, and is related to the electrostrictive response to strain used in the previous section by $M_{\alpha\beta\gamma\delta} = s_{\alpha\beta\mu\nu}m_{\mu\nu\gamma\delta}$, where s is the compliance tensor, the inverse of the elastic tensor. In order to obtain the electrostrictive response to stress at fixed voltage, we first measure the electrostrictive response to strain m, apply the correction Eq. (15), and then contract with the compliance tensor to obtain M.

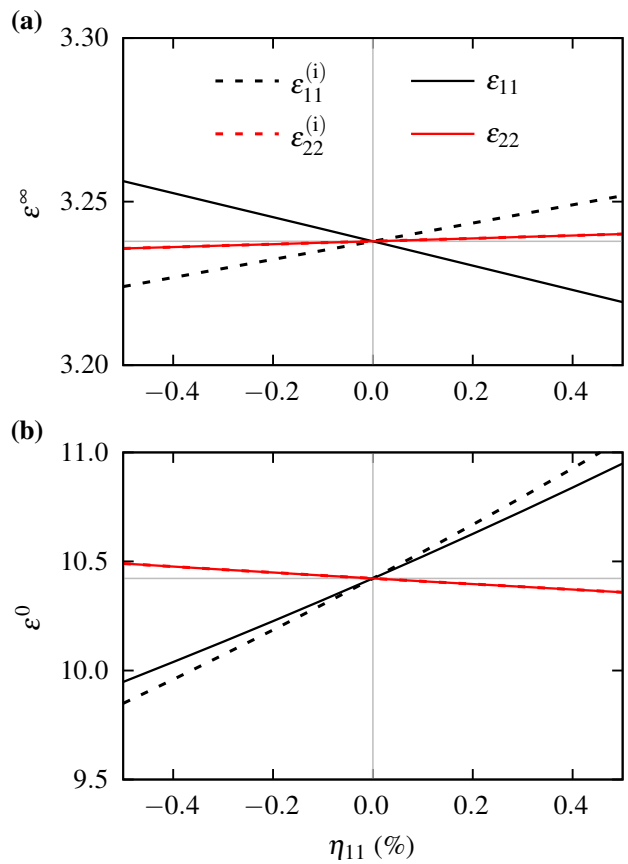

FIG. 3. Improper (relative) dielectric permittivity of MgO as a function of applied strain η_{11} (dashed lines) [9], and the (relative) proper permittivity obtained using Eq. (13) (solid lines), for **(a)**: the electronic permittivity ε^{∞} (clamped ions) and **(b)**: the relaxed-ion permittivity ε^{0}.

Fig. 3 shows the permittivity of MgO versus strain as obtained with the ABINIT code [22, 23], following the methodology of Ref. [9]. Norm conserving pseudopotentials from PseudoDojo were used [24], and the PBEsol functional was used to treat exchange-correlation interactions [25]. A cutoff energy of 50 Ha was used to truncate the plane-wave basis, and a k-point grid of $8\times 8\times 8$ was used to sample the Brillouin zone. The dielectric permittivity was then calculated using DFPT. The electronic or clamped-ion permittivity ε^{∞} was first obtained, and then phonon calculations were performed

Material	M (pm^2/V^2)	Improper fixed $\mathcal{E}$	Intermediate $(\mathcal{E},P)\rightarrow(\mathcal{E}',P')$	Intermediate $\Omega_0\rightarrow\Omega$	Proper fixed ΔV	Experiment
MgO	M_{11}	1829	2460	1514	2144	2020[a]
	M_{12}	-199	-199	-514	-514	-
LiCl	M_{11}	12613	15836	11001	14224	46200[b]
	M_{12}	-1281	-1281	-2892	-2892	-18200[b]
LiF	M_{11}	4640	5941	3989	5290	5230[c]
	M_{12}	-501	-501	-1151	-1151	-1730[c]
NaCl	M_{11}	4572	6516	3600	5544	4030[c]
	M_{12}	-483	-483	-1455	-1455	-1030[c]

TABLE I. Measurements of the improper, proper and intermediate electrostrictive responses $M_{11}\equiv M_{1111}$ and $M_{12}\equiv M_{2211}$ of MgO, LiCl, LiF and NaCl, compared to experimental measurements: a = Ref. [19], b = Ref. [20] and c= Ref. [21].

in order to obtain the relaxed-ion permittivity ε^0.

The dashed lines show the components of the permittivity tensor obtained directly from ABINIT, which are in unreduced units and therefore improper. The components of the proper dielectric tensor, indicated by the solid lines, are obtained using Eq. (13). Note that for ε_{22}, the proper and improper values are identical, which can be verified using Eq. (13). The improper electrostrictive response $m^{(\mathrm{i})}$ is obtained by taking the slope of $\varepsilon^{(\mathrm{i})}$ about $\eta=0$, and the proper response m is obtained by taking the slope of ε about $\eta=0$. The two intermediate values, obtained by either using reduced variables for the electric field or units of strained volume, were calculated using the corrections in Fig. 4 in order to illustrate their individual contributions to the total correction. The electrostrictive response to stress M was then obtained by contracting m with the compliance tensor in each case. In Table I we show a comparison of the electrostrictive responses for the proper, improper and intermediate cases, as well as experimental measurements.

DISCUSSION AND CONCLUSIONS

In this paper, we highlighted the difficulties in comparing electromechanical responses obtained from first-principles calculations to those obtained from experimental measurements. In the context of piezoelectricity, this problem is known as the 'proper-improper' relation, which may not be intuitive as 'proper' and 'improper' are ambiguous terms. We believe it is more physically insightful to reformulate the problem in terms of responses measured at fixed electric field and fixed voltage drop. Similar to the well-known relation for piezoelectricity, we have derived the relations for electrostrictive and general electromechanical responses to infinitesimal strain, measured at fixed field and at fixed voltage drop.

Depending on whether the field or voltage is held fixed, and whether the energy is given per unstrained or strained unit volume, there are four different ways to define an electromechanical response: the so-called 'improper' (fixed field) and 'proper' (fixed voltage) responses, and two intermediate ones. We summarize these possibilities in Fig. 4 to help the reader in identifying each case. In order to correctly compare measurements from first-principles calculations with experimental measurements, it is important to identify which response from Fig. 4 has been measured in each case and, if necessary, make the appropriate correction.

Because the electrostrictive response is proportional to a third derivative of the free energy (Eq. (11)), it can be expressed in several different ways:

$$m_{\alpha\beta\gamma\delta}=\frac{\partial\varepsilon_{\alpha\beta}}{\partial\eta_{\gamma\delta}}=\frac{\partial^2 X_{\gamma\delta}}{\partial\mathcal{E}_\alpha\partial\mathcal{E}_\beta}=\frac{\partial e_{\beta\gamma\delta}}{\partial\mathcal{E}_\alpha}\,. \tag{23}$$

Therefore, the electrostrictive response can be calculated from first-principles using three different approaches:

(i) by calculating the linear evolution of the dielectric permittivity with respect to stress or strain.

(ii) by calculating the quadratic stress induced by an applied electric field.

(iii) by calculating the linear of evolution of the piezoelectric tensor in response to an applied electric field.

Second derivatives of the free energy can be calculated from first-principles calculations using second-order DFPT, and in

$$(P,\mathcal{E}) \rightarrow (P',\mathcal{E}')$$

$\Omega_0 \downarrow \Omega$

Improper

$$\mathcal{F}_{\Omega_0} = \mathcal{F}_{\text{cell}} - \left(\mathcal{E}\cdot P + \frac{1}{2}\epsilon_0\mathcal{E}^2\right)$$
$$e_{\alpha\beta\gamma} = e^{(\text{i})}_{\alpha\beta\gamma}$$
$$m_{\alpha\beta\gamma\delta} = m^{(\text{i})}_{\alpha\beta\gamma\delta}$$

Intermediate

$$\mathcal{F}'_{\Omega_0} = \mathcal{F}_{\text{cell}} - \left(\frac{\Omega_0}{\Omega}\mathcal{E}'\cdot P' + \frac{1}{2}\epsilon_0\mathcal{E}'^T g^{-1}\mathcal{E}'\right)$$
$$e_{\alpha\beta\gamma} = e^{(\text{i})}_{\alpha\beta\gamma} - P_\gamma\delta_{\alpha\beta}$$
$$m_{\alpha\beta\gamma\delta} = m^{(\text{i})}_{\alpha\beta\gamma\delta} - \epsilon_{\alpha\gamma}\delta_{\beta\delta} - \epsilon_{\delta\beta}\delta_{\alpha\gamma}$$

Intermediate

$$\mathcal{F}_{\Omega} = \mathcal{F}_{\text{cell}} - \frac{\Omega}{\Omega_0}\left(\mathcal{E}\cdot P + \frac{1}{2}\epsilon_0\mathcal{E}^2\right)$$
$$e_{\alpha\beta\gamma} = e^{(\text{i})}_{\alpha\beta\gamma} + P_\alpha\delta_{\beta\gamma}$$
$$m_{\alpha\beta\gamma\delta} = m^{(\text{i})}_{\alpha\beta\gamma\delta} + \epsilon_{\alpha\beta}\delta_{\gamma\delta}$$

Proper

$$\mathcal{F}'_{\Omega} = \mathcal{F}_{\text{cell}} - \left(\mathcal{E}'\cdot P' + \frac{\Omega}{\Omega_0}\frac{1}{2}\epsilon_0\mathcal{E}'^T g^{-1}\mathcal{E}'\right)$$
$$e_{\alpha\beta\gamma} = e^{(\text{i})}_{\alpha\beta\gamma} + P_\alpha\delta_{\beta\gamma} - P_\gamma\delta_{\alpha\beta}$$
$$m_{\alpha\beta\gamma\delta} = m^{(\text{i})}_{\alpha\beta\gamma\delta} + \epsilon_{\alpha\beta}\delta_{\gamma\delta} - \epsilon_{\alpha\gamma}\delta_{\beta\delta} - \epsilon_{\delta\beta}\delta_{\alpha\gamma}$$

FIG. 4. Summary of the relations between the free energies, piezoelectric and electrostrictive responses for the four possible scenarios illustrated in Fig. 2.

ABINIT, the proper piezoelectric response is automatically obtained because reduced units $(\mathcal{E}',P')$ are used for the electric field and polarization. However, third-order DFPT for the electrostrictive response is not currently implemented in any widely available DFT code, and therefore in all three of the above methods, at least one of the derivatives must be evaluated using finite difference methods. Thus, a correction must be applied in order to obtain the proper response at fixed voltage.

With method (i), first introduced in Ref. [9] and used in this study, the electrostrictive response is obtained by measuring the derivative of the permittivity with respect to strain. The permittivity can easily be obtained from a single DFPT calculation, avoiding the need to perform a set of finite field calculations for each value of strain. Taking the derivative of the dielectric permittivity output from the code from finite differences will yield the improper response, i.e. Eq. (11) [9]. The proper response can be obtained by taking care to write the permittivity in terms of $\mathcal{E}'$ and P', i.e. using Eq. (13), $m \approx \frac{\varepsilon(\tilde{\eta}_+)-\varepsilon(\tilde{\eta}_-)}{\tilde{\eta}_+-\tilde{\eta}_-}$, or by applying the correction (Eq. (15)) to the improper response. We propose that method (i) is the most straightforward method for calculating the electrostrictive response from first-principles.

With method (ii), the electrostrictive response M is obtained by measuring the quadratic strain response to an applied field, and measuring the curvature about zero field. This has previously been the most widely used method to measure electrostrictive responses from first-principles. However, if finite electric field calculations are performed [9, 26, 27], the improper response will be obtained and a correction will be needed. The proper response can be directly obtained by fixing the reduced electric field $\mathcal{E}'$ or the displacement field [9, 28, 29], both of which are possible in ABINIT, but not in most other widely available DFT codes. Additionally, a geometry relaxation calculation must be performed for each field value in order to find the induced strain, making this method more computationally expensive than method (i).

With method (iii), the electrostrictive response could be obtained by measuring the change in the piezoelectric tensor in response to an applied field [30]. To our knowledge, the electrostrictive response has not yet been calculated from first-principles in this way. However, if the proper piezoelectric response is obtained, and the reduced electric field $\mathcal{E}'$ or displacement field is held fixed, then the proper piezoelectric response should be obtained.

For the electronic permittivity, the sign of the slope changes when correcting from improper to proper. The reason for this is that the electronic permittivity is small and more sensitive to strain than the larger relaxed-ion permittivity (i.e. including phonon contributions), and the correction appears relatively larger.

In each case, the electrostrictive response is larger after correcting to the fixed voltage case. Agreement with experimental measurements is improved for the case of LiF, but not for MgO or NaCl. For the case of LiCl, the reported values in Ref. [21] are an order of magnitude larger than the typical values measured in other experimental studies. Experimental measurements of electrostrictive responses tend to vary significantly, in part due to the various measurement techniques. For example, the M_{11} electrostrictive coefficient of MgO has been reported to be 2020 pm^2/V^2 in Ref. [19] and about four times less (550 pm^2/V^2) in Ref. [30]. For SrF_2, the situation is even more dramatic as experimental reports disagree even on the *sign* of the longitudinal M coefficient: -1160

pm^2/V^2 from Ref. [31] and +260 pm^2/V^2 from Ref. [32]. As a consequence, the agreement with experimental values has to be considered with care. One typical source of error between first-principles calculations and experimental measurements is that first-principles calculations are typically done at zero temperature, whereas experimental measurements are performed at larger temperatures (in this case room temperature [19]). However, the evolution of the electrostrictive coefficients with respect to temperature is normally very small, provided a phase transition does not occur [7].

In spite of this, it is important to emphasise that the fixed field and fixed voltage responses are *physically different quantities*. When comparing first-principles calculations with experimental measurements, it is of primary importance to first ensure that the correct physical quantities are being compared.

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