Quantum theory of mechanical deformations

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We construct a general metric-tensor framework for treating inhomogenous adiabatic deformations applied to crystalline insulators, by deriving an effective time-dependent Schrödinger equation in the undistorted frame. The response can be decomposed into "static" and "dynamic" terms that correspond, respectively, to the amplitude and the velocity of the distortion. We then focus on the dynamic contributon, which takes the form of a gauge field entering the effective Hamiltonian, in the linear-response limit. We uncover an intimate relation between the dynamic response to the rotational component of the inhomogeneous deformation and the diamagnetic response to a corresponding inhomogeneous magnetic field. We apply this formalism to the theory of flexoelectric response, where we resolve a previous puzzle by showing that the currents generated by the dynamic term, while real, generate no bound charges even at surfaces, and so may be dropped from a practical theory of flexoelectricity.

I. INTRODUCTION

Mechanical deformations are among the most basic perturbations that can be applied to a crystalline solid, and their response is at the origin of many basic materials functionalities, such as elasticity or piezoelectricity. The development of theoretical approaches to calculate and predict these properties from first principles has marked notable milestones for modern electronic-structure theory, paralleling the equally important development of density-functional perturbative approaches to lattice dynamics. In the case of uniform deformations, methods to compute the relevant response coefficients are now well established, and part of the most popular simulation packages that are available to the public. Yet, with the rising interest in flexoelectricity, and more generally in functionalities that depend on the *gradient* of the strain field rather than on the strain itself, the existing computational approaches are of limited applicability, and their generalization to cases where the deformation is inhomogeneous appears far from obvious.

Flexoelectricity, describing the polarization response of a crystalline insulator to a strain gradient, has received considerable attention in the past few years because of its fundamental interest and potential relevance to energy and information technologies. Recent advances in first-principles methods have given a considerable boost to the field. The theoretical understanding of flexoelectric phenomena, however, still presents daunting conceptual and practical challenges, many of which are still unresolved. The purely electronic (clamped-ion) contribution to the flexoelectric response, for example, is riddled with subtleties, and proper methodologies to compute it in the most general case are still missing. (Lattice-mediated effects are comparatively much simpler to understand, both conceptually and computationally – they consists in the dynamical dipoles produced by the internal relaxations of the primitive cell, and bear many analogies to the point-charge model proposed by Tagantsev[1] long ago.)

The main issue resides in that, in order to define the transverse components of the clamped-ion flexoelectric tensor at the bulk level, one needs, in principle, to access the *microscopic* polarization response to a variety of lattice distortions (e.g., long-wavelength acoustic phonons, or displacements of an isolated atom). Indeed, treatments based on the Berry-phase formula are ruled out because a strain gradient breaks translational periodicity; charge-density based theories are not viable either, as they yield only partial information on the flexoelectric tensor components. Calculating the microscopic polarization response implies establishing a time-dependent perturbative framework, where the quantum-mechnical probability current is monitored in the course of a slow distortion of the crystal. Such a procedure, however, falls outside the capabilities of the publically available electronic-structure packages. An implementation of the current-density based theory of flexoelectricity has only very recently been presented in Ref. 2. This implementation required the resolution of some challenging formal issues regarding the current-density response to a macroscopic deformation. A brief account of those issues was given in Ref. 2, but are described more thoroughly and in greater depth in the present manuscript.

The first, obvious, question concerns the physical representation of a microscopic observable, such as the electronic probability current, in a context where the boundary conditions of the Hamiltonian change in the course of the transformation. In a nutshell, even if we limit our attention to the simplest case of a uniform strain (these issues become all the more severe if the deformation is inhomogeneous), the atomic distortion pattern that one needs, in principle, to apply in order to strain the crystal grows linearly with the distance from the origin. (Re-

call that the macroscopic strain is related to the first gradient of the displacement field.) This has two undesirable consequences: (i) the perturbation (and hence all the microscopic response functions associated to it) is nonperiodic and origin-dependent, even if both the initial and the final state enjoy translational periodicity; (ii) the perturbation is never small at the boundaries of a large crystallite, which complicates its treatment within linear-response theory. In Ref. 3 the above problem was elegantly solved by combining the macroscopic deformation with a simultaneous coordinate transformation. This way, one can encode the strain field as a change in the metric of space while the atoms remain at their original locations, thereby removing the need for a nonperiodic and unbound lattice distortion. Also, the transformed coordinate system naturally leads to a sound definition of microscopic response functions, such as polarization, charge density and local electric fields.

The second conceptual issue is even more subtle, and consists in making sure that the fundamental response quantities of interest (e.g. the flexoelectric polarization) are well defined, i.e., that they are independent of the rotations or translations that were applied to the crystal in the course of the deformation. This is required by a proper[4] theory of electromechanical phenomena, which should depend on physically meaningful changes in the relative distances between neighboring material points, and not on their absolute position with respect to some arbitrary coordinate frame. In order to make the problem tractable, in Refs. 3 and 5 we had to make some simplifying assumptions on how the electronic currents, $\mathbf{J}(\mathbf{r})$, respond to a rigid rotation or translation of the crystal lattice, by postulating that

$$\mathbf{J}(\mathbf{r}) = \mathbf{v}(\mathbf{r})\rho(\mathbf{r}),$$

where ρ is the charge density and $\mathbf{v}$ is the velocity of the material point $\mathbf{r}$ imposed by the rototranslation. This is akin to assuming that the electronic cloud behaves as a classical charge distribution that is equal to the true quantum-mechanical one. As we shall see, this is indeed correct in the case of translations, but not in the case of rotations, where there is a further contribution to the current that we neglected in earlier works. It turns out, however, that this additional piece is curl-free, so it is unclear whether it affects the results. Settling this point appears as a clear priority: the theory of flexoelectricity, as it stands, crucially relies on this assumption in order to define[3] and calculate[6] the transverse components of the bulk flexoelectric tensor. A fundamental theoretical framework, where the microscopic polarization currents are derived within a proper quantum-mechanical treatment of deformations, is needed in order to firm up the results obtained so far, and thereby pave the way towards future developments in the field.

Here we attack this problem from its very root, by incorporating coordinate transformations directly into the time-dependent Schrödinger equation. This allows us to perform a formal analysis of the electronic probability current that develops in the course of an arbitrary mechanical deformation, and thereby to identify the relevant physical contribution to the polarization response in the most general case. Interestingly, we find that a non-uniform deformation is generally accompanied by "gauge currents" produced by local rotations of the sample. These currents are divergenceless and correspond to the circulating diamagnetic currents generated by an applied magnetic field ($\mathbf{B}$). This result is explained heuristically by recalling Larmor's theorem, which relates the Lorentz force on a charged particle in a uniform $\mathbf{B}$-field to the Coriolis force on a massive object in a uniformly rotating frame. By performing a long-wavelength analysis in the limit of small deformations, we demonstrate that the bulk flexoelectric tensor has a contribution from these gauge fields that is proportional to the bulk diamagnetic susceptibility of the material. Remarkably, such a contribution is exactly cancelled by an equal and opposite surface term. One is therefore free to remove this term from both sides, leaving a description of the flexoelectric polarization that is consistent with the charge-density-based strategy of Ref. 6.

The present results demonstrate, once more, the intimate connection between surface and bulk contributions to the flexoelectric effect, and the intriguing connections between the latter phenomenon and other, apparently unrelated, areas of research (in this case, orbital magnetism). In addition to providing a firm foundation to the existing theory of flexoelectricity, we also provide an explicit derivation of how a generalized (and time-dependent) coordinate transformation of space is reflected in the most basic quantum-mechanical operators, such as the Hamiltonian or the probability current. This can be of immediate usefulness to a wide range of physical problems, within and beyond[7] the specific context of this work.

Note that describing deformations in terms of coordinate transformations in a quantum mechanical context is a strategy that already has a relatively long history[8–14]; our approach has several points of contact with these works. It also has a broad similarity in spirit to the theory of general relativity[15,16]; indeed, in the latter context, the problem of an electron evolving in a curved spacetime has been studied at length.[17–19] The derivations presented in such works, however, are oriented to the Lorentz-invariant framework, which is not appropriate to the solid-state context. We are, instead, interested in the behavior of the nonrelativistic Schrödinger equation under a time-dependent deformation of space, which is not treated in such theories. A derivation of the low-velocity limit that, in principle, fits our scopes can be found in Ref. 20 and others[21], but the class of transformations that are considered there is restricted to rotations and boosts. Our approach is more general, and recovers the results of Ref. 20 as special cases (see Sections II B 1 and II B 2).

II. GENERAL THEORY

We shall consider a generic time-dependent deformation of the crystal lattice, where all atoms move from their original location, $\mathbf{R}^0_{l\kappa}$, according to a continuous vector function of space and time, $\mathbf{r}(\boldsymbol{\xi}, t)$,

$$\mathbf{R}_{l\kappa}(t) = \mathbf{r}(\mathbf{R}^0_{l\kappa}, t). \tag{1}$$

(Recall that κ and l are sublattice and cell indices, respectively.) The physical effects of the deformation described by $\mathbf{r}(\boldsymbol{\xi}, t)$ are best treated by operating an analogous coordinate transformation that brings every atom back to its original position.[3] This means that the atoms are immobile in the (generally curvilinear) $\boldsymbol{\xi}$-frame, but the frame itself evolves with respect to the Cartesian laboratory frame. All the effects of the mechanical perturbation are, in other words, encoded in the metric of the deformation, rather than in an atomic displacement pattern.

To see how the metric change affects the electronic Hamiltonian, it is useful to introduce a number of auxiliary quantities that will come handy later in the derivation. The first is the so-called deformation gradient,

$$h_{i\alpha} = \frac{\partial r_i}{\partial \xi_\alpha}. \tag{2}$$

The determinant of the deformation gradient, $h = \det(\mathbf{h})$, gives the local volume change with respect to the unperturbed lattice configuration. From the deformation gradient we can construct the metric tensor,

$$g_{\alpha\beta} = \frac{\partial r_i}{\partial \xi_\alpha} \frac{\partial r_i}{\partial \xi_\beta} = h_{i\alpha} h_{i\beta} = (\mathbf{h}^{\mathrm{T}} \mathbf{h})_{\alpha\beta}, \tag{3}$$

which is another central quantity of the formalism; its determinant is $g = \det(\mathbf{g}) = h^2$. (Here and in the following we us an implicit sum notation on indices, with Roman and Greek indices used for Cartesian and curvilinear frames respectively.)

We shall define the wavefunctions in the deformed space in such a way that they comply with the basic orthonormality requirements. This means writing

$$\psi(\mathbf{r}) = h^{-1/2} \tilde{\psi}(\boldsymbol{\xi}). \tag{4}$$

It is easy to show that the wavefunctions ψ are orthonormal in the Cartesian space provided that the "curvilinear" wavefunctions $\tilde{\psi}$ are orthonormal in the $\boldsymbol{\xi}$-space,

$$\int d^3 r \, \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) = \int d^3 r \, h^{-1} \tilde{\psi}_m^*(\boldsymbol{\xi}(\mathbf{r})) \tilde{\psi}_n(\boldsymbol{\xi}(\mathbf{r}))$$

$$= \int d^3 \xi \, \tilde{\psi}_m^*(\boldsymbol{\xi}) \tilde{\psi}_n(\boldsymbol{\xi}). \tag{5}$$

Note that we shall work in a time-dependent context, which is necessary in order to be able to discuss the polarization response. In doing so we assume

$$\psi(\mathbf{r}, t) = h^{-1/2} \tilde{\psi}(\boldsymbol{\xi}, t), \tag{6}$$

i.e., the phase evolution of $\tilde{\psi}$ is locked to that of ψ. The choice of the phase relation between $\tilde{\psi}$ and ψ is mostly a matter of convention, and can be regarded as a "gauge freedom" of the transformed wavefunctions. Indeed, one could postulate $\psi(\mathbf{r}, t) = e^{i\varphi} h^{-1/2} \tilde{\psi}(\boldsymbol{\xi}, t)$, where φ is an arbitrary function of space and time. While the physical conclusions should not depend on φ, the specific form of the time-dependent Schrödinger equation in the comoving frame does. In particular, unfamiliar terms may arise in the Hamiltonian whose physical interpretation needs some caution; we shall briefly discuss an illustrative example in Sec. II B 1

In the following Sections our goal will be to start from a conventional Schrödinger equation, written in Cartesian $\mathbf{r}$-space, and progressively work out the curvilinear version in $\boldsymbol{\xi}$-space, where the electronic wavefunctions are described by $\tilde{\psi}$.

A. Time-dependent Schrödinger equation

The time-dependent Schrödinger equation can be written in the original Cartesian frame as

$$i\frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left[-\frac{\nabla^2}{2} + V(\mathbf{r}, t) \right] \psi(\mathbf{r}, t), \tag{7}$$

where we have set $\hbar = m_e = 1$. Multiplying through by $\sqrt{h}$ and carrying out the coordinate transformations, this becomes (the detailed derivations can be found in the Appendix)

$$i\frac{\partial}{\partial t} \tilde{\psi} = \hat{\tilde{\mathcal{H}}} \tilde{\psi}, \tag{8}$$

where the new effective Hamiltonian operator,

$$\hat{\tilde{\mathcal{H}}} = \frac{1}{2} (\hat{\tilde{p}}_\beta - A_\beta) g^{\beta\gamma} (\hat{\tilde{p}}_\gamma - A_\gamma)$$

$$+ \tilde{V} + V_{\mathrm{geom}} - \frac{1}{2}\phi, \tag{9}$$

contains contributions arising not only from the potential and kinetic terms on the right-hand side of Eq. (7), but also from the time-derivative term on the left. Here $\hat{\tilde{p}}_\beta = -i\partial/\partial \xi_\beta$ indicates the canonical momentum in curvilinear space, $g^{\beta\gamma} = (\mathbf{g}^{-1})_{\beta\gamma}$ is the inverse metric tensor, $\tilde{V}(\boldsymbol{\xi}, t) = V(\mathbf{r}(\boldsymbol{\xi}, t), t)$ is the external potential represented in the curvilinear frame, and we have introduced a number of additional quantities. First, the "geometric" scalar potential V_{geom} originates from the kinetic energy operator, and reads as

$$V_{\mathrm{geom}} = \frac{1}{2} \mathcal{A}_\beta g^{\beta\gamma} \mathcal{A}_\gamma + \frac{1}{2} \partial_\beta (g^{\beta\gamma} \mathcal{A}_\gamma), \tag{10}$$

$$\mathcal{A}_\alpha = \frac{1}{2h} \frac{\partial h}{\partial \xi_\alpha} = \frac{1}{2} \frac{\partial \ln(h)}{\partial \xi_\alpha}. \tag{11}$$

(Note the close relationship of the auxiliary field $\mathcal{A}_\alpha$ to the contracted Christoffel symbol.) Second, we have a

further scalar and vector potential field originating from the time derivative,

$$\phi = \frac{\partial r_i}{\partial t}\frac{\partial r_i}{\partial t}, \tag{12}$$

$$A_\gamma = \frac{\partial r_i}{\partial \xi_\gamma}\frac{\partial r_i}{\partial t}\bigg|_{\boldsymbol{\xi}}. \tag{13}$$

Interestingly, both $\mathbf{A}$ and ϕ have the same form as the metric tensor elements in Eq. (3), except that one or both real-space indices have been replaced here with time. Eq. (9), together with definitions (10), (11), (12) and (13), constitutes one of our central results.

The present theory of deformations bears an intriguing similarity to electromagnetism, as in both cases the electronic Hamiltonian acquires a gauge-dependent vector and scalar potential contribution [see the discussion following Eq. (6)]. We shall see in the following that both $\mathbf{A}$ and ϕ have classical counterparts in the fictitious forces that appear in the noninertial frame defined by the coordinate transformation.

B. Physical interpretation

To see the physical interpretation of the new terms appearing in the Schrödinger equation, it is useful to work out a couple of simple examples.

1. Galilean transformations

Consider a transformation of the type

$$\mathbf{r} = \boldsymbol{\xi} + \mathbf{v}t, \tag{14}$$

where $\mathbf{v}$ is a vector constant with the dimension of a velocity. We have $h_{\alpha\beta} = g_{\alpha\beta} = \delta_{\alpha\beta}$, $\mathcal{A}_\alpha = 0$ and $A_\alpha = v_\alpha$. The result is

$$i\hbar\frac{\partial\tilde{\psi}}{\partial t} = \frac{1}{2m}(\tilde{\mathbf{p}}-m\mathbf{v})\cdot(\tilde{\mathbf{p}}-m\mathbf{v})\tilde{\psi}+\left(V-\frac{1}{2}mv^2\right)\tilde{\psi}, \tag{15}$$

where we have reintroduced the factors of electron mass, m, and $\hbar$ to better illustrate the physical meaning of the various terms. We have also used the fact that the potential in the co-moving frame (i.e., we assume here that the crystal is uniformly moving with respect to the laboratory frame with the same velocity $\mathbf{v}$) is independent of time and equal to the potential of the lattice at rest.

To see that Eq. (15) is reasonable, consider a free particle $\psi(\mathbf{r},t) = e^{i\mathbf{q}_0\cdot\mathbf{r}}e^{-i\omega_0 t}$ with $\hbar\omega_0 = p_0^2/2m$ and $\mathbf{p}_0 = \hbar\mathbf{q}_0$ in the original frame. Classically, the particle has momentum $\mathbf{p}_0 - m\mathbf{v}$ as seen from the moving frame. Eq. (6) gives its transformed wavefunction to be $\tilde{\psi}(\boldsymbol{\xi},t) = e^{i\mathbf{q}_0\cdot\boldsymbol{\xi}}e^{-i(\omega_0-\mathbf{q}_0\cdot\mathbf{v})t}$, which is easily verified to satisfy Eq. (15). The first term of Eq.(15) is just the kinetic energy $(\mathbf{p}_0 - m\mathbf{v})^2/2m$ as seen from the comoving frame; the extra $-mv^2/2$ term is, however, problematic

to the extent that it implies that the energy in the transformed frame cannot be associated with the expectation value of the Hamiltonian operator. (Note that the particle velocity is correct, even if the transformed wavefunctions appears to have the "wrong" phase at first sight.)

The fact that the curvilinear-coordinate Hamiltonian does not reproduce the correct kinetic energy in the co-moving frame may appear at first sight as a serious limitation of the present theory. To ensure that this is not a real issue in the context of this work, some additional words of comments are in order. First, note that the Galilean covariance of the Schrödinger equation is not automatic, but requires a specific assumption about the phase of the transformed wavefunction. We could have certainly used such a prescription in Eq. (6), and this would have restored the standard form of the Schrödinger equation in the uniformly moving frame. However, this would have been of little help in the context of more general displacement fields (e.g. nonuniform in time and/or space); in such cases it is not possible to reabsorb the new gauge potentials with a phase shift. Second, solving these issues is not essential to the scope of this work. As we shall see shortly, we shall either be concerned with the *static* energy of the system, or with the dynamical evolution of the wavefunctions up to first order in the velocity; neither of these is affected by the spurious $\mathcal{O}(v^2)$ term that stems from the "dynamic scalar potential" ϕ. Further delving into these intriguing fundamental issues, while desirable in a general context, would bring us far from our present focus, and therefore we regard this as a stimulating subject for future investigation.

2. Rotating frame

Consider now a transformation of the type

$$\mathbf{r} = \mathbf{R}(t)\boldsymbol{\xi}, \tag{16}$$

where $\mathbf{R}(t)$ is a 3×3 matrix describing a rotation about a given axis $\hat{\boldsymbol{\theta}}$. We have

$$h_{\alpha\beta} = R_{\alpha\beta}, \qquad h = 1, \tag{17}$$

which implies that $g_{ij} = g^{ij} = \delta_{ij}$, and that $\mathcal{A}_j = 0$. On the other hand, we have

$$\mathbf{A} = \boldsymbol{\omega} \times \boldsymbol{\xi}, \tag{18}$$

where $\boldsymbol{\omega}$ is the pseudovector whose direction coincides with $\hat{\boldsymbol{\theta}}$, and whose modulus indicates the angular velocity. This can be easily seen by writing an arbitrary rotation matrix in exponential form,

$$\mathbf{R}(t) = e^{\theta(t)\mathbf{L}^{\hat{\boldsymbol{\theta}}}}, \qquad L^{\hat{\boldsymbol{\theta}}}_{\alpha\beta} = -\epsilon^{\alpha\beta\gamma}\hat{\theta}_\gamma, \tag{19}$$

and by observing that $\mathbf{A} = \mathbf{R}^{\mathrm{T}}\dot{\mathbf{R}}(t)\boldsymbol{\xi}$. We have

$$i\hbar\frac{\partial\tilde{\psi}}{\partial t} = \left[\frac{1}{2m}(\tilde{\mathbf{p}} - m\boldsymbol{\omega}\times\boldsymbol{\xi})^2 + V(\boldsymbol{\xi}) - \frac{1}{2}m(\boldsymbol{\omega}\times\boldsymbol{\xi})^2\right]\tilde{\psi}. \tag{20}$$

The Hamiltonian of the system in the rotating frame of reference is, therefore, identical to that of the system at rest except for two additional terms: a gauge field and a quadratic potential term. The latter is unbound from below – it diverges like $-\rho^2$, where ρ is the distance from the rotation axis. These two terms have direct classical interpretations as the fictitious forces (respectively, Coriolis and centrifugal) that appear in the noninertial rotating frame of reference. It is interesting to observe that the Coriolis force enters the Hamiltonian in the exact same way as a uniform magnetic field, with the only difference that the former acts on the particle mass, while the latter on its charge. A magnetic field, in particular, can be described by a gauge field of the type

$$-\frac{q}{2c}\mathbf{B}\times\boldsymbol{\xi}.$$

The above derivations show that we can obtain the same physical consequences (at first order in the perturbation amplitude) if, instead of applying a magnetic field, we rotate the system with an angular velocity equal to

$$\boldsymbol{\omega}=\frac{q}{2mc}\mathbf{B}. \tag{21}$$

This is, of course, the Larmor frequency. Thus, in the special case of a rigid rotation, our theory correctly recovers Larmor's theorem in its known quantum-mechanical form.[22]

C. Current density

The above derivations provide a general picture of how the electronic Hamiltonian is modified by an arbitrary time-dependent deformation. Since our main motivation stems from flexoelectricity and, more generally, from the description of electromechanical phenomena, in this subsection we shall give special attention to the electronic current density. This is necessary in order to extract useful information on the electric polarization that develops in an insulator following a mechanical deformation.

First of all, we postulate a formula for the current density that is associated with the Hamiltonian of Eq. (9),

$$\tilde{J}_\beta(\boldsymbol{\xi},t)=-\frac{1}{2}g^{\beta\gamma}\left(-i\tilde{\psi}^*\partial_\gamma\tilde{\psi}+i\tilde{\psi}\partial_\gamma\tilde{\psi}^*-2A_\gamma|\tilde{\psi}|^2\right). \tag{22}$$

Note that $\tilde{J}_\beta(\boldsymbol{\xi},t)$ describes the current density *in the curvilinear frame*; this means that the "convective" contribution, due to the displacement of the coordinate frame itself with respect to the laboratory, is not included. For instance, in the limit of a rigid rototranslation, the laboratory current $\mathbf{J}$ is given by $\mathbf{J}=\mathbf{R}\cdot\tilde{\mathbf{J}}+\mathbf{v}\rho$, where $\mathbf{R}$ is a rotation matrix, $\mathbf{v}=\dot{\mathbf{r}}$ is the velocity and ρ the charge density.

Now, we shall proceed to demonstrate that this formula is indeed correct. By "correct" we mean that the probability current satisfies two criteria, namely (i) the

continuity equation, and (ii) the known transformation laws of the classical four-current in the nonrelativistic limit.

1. Continuity equation

We need to show that

$$\left.\frac{\partial}{\partial t}\tilde{\rho}\right|_{\boldsymbol{\xi}}=-\boldsymbol{\nabla}_{\boldsymbol{\xi}}\cdot\tilde{\mathbf{J}}, \tag{23}$$

where $\tilde{\rho}=-|\tilde{\psi}|^2$ is the electronic charge density in the curvilinear frame. The proof proceeds along the same lines as in the textbook case of a standard electronic Hamiltonian in the presence of a vector potential field. In particular, one needs first to multiply both hand sides of Eq. (9) by $\tilde{\psi}^*(\boldsymbol{\xi},t)$, and then focus on the real part of the equation by summing each term with its complex conjugate. One is left with the time derivative of $\tilde{\rho}(\boldsymbol{\xi},t)$ on the left-hand side; after a few manipulations, it is not difficult to show that the right-hand side corresponds to $-\boldsymbol{\nabla}_{\boldsymbol{\xi}}\cdot\tilde{\mathbf{J}}$. The only difference with respect to the textbook derivation consists in the presence of the inverse metric tensor, both in the kinetic energy operator of Eq. (9) and in Eq. (22); however, this does not entail any special complication in the algebra.

As a note of warning, one should keep in mind that the proof of Eq. (23) is valid only under the key assumption that the external potential applied to the electrons is *local*. Thus, the form of the current density as written in Eq. (22) is inadequate in cases where nonlocal pseudopotentials are adopted in the calculation.[2] This issue, however, is not specific to the present theory of deformations (it complicates the definition of the current density already at the level of the standard Cartesian-space Schrödinger equation), and discussing it in detail would lead us far from the scope of this work.

2. Transformation laws

We next check whether the definition of the current density that we postulated in Eq. (22) is compatible with the known Galilean transformation laws of the four-current, which is defined as $J^\mu=(\rho,J_1,J_2,J_3)$. In particular, J^μ transforms as a contravariant vector density,

$$\bar{J}^\mu=\frac{\partial\bar{x}^\mu}{\partial x^\nu}J^\nu\det{}^{-1}\left[\frac{\partial\bar{x}^\rho}{\partial x^\sigma}\right], \tag{24}$$

where $x^\mu=(t,x_1,x_2,x_3)$ is the coordinate four-vector and the barred (unbarred) symbols refer to the deformed (original) frame. In our special case of a nonrelativistic mechanical deformation, we have $\bar{t}=t$, and the time is independent of the space coordinates. By letting the barred and unbarred space coordinates span the Cartesian $\mathbf{r}$-space and the curvilinear $\boldsymbol{\xi}$-space, respectively, we

obtain

$$\rho = h^{-1}\tilde{\rho}, \tag{25}$$

$$J_l = h^{-1}\left(\tilde{\rho}\frac{\partial r_l}{\partial t} + h_{l\beta}\tilde{J}_\beta\right). \tag{26}$$

The transformation law for the charge density is satisfied by construction; we need to prove that the same is true for the current density.

To that end, we write

$$\tilde{J}_\beta = -\frac{1}{2}h_{\beta l}^{-1}h_{\gamma l}^{-1}\left(-i\tilde{\psi}^*\partial_\gamma\tilde{\psi} + i\tilde{\psi}\partial_\gamma\tilde{\psi}^* - 2h_{m\gamma}\frac{\partial r_m}{\partial t}|\tilde{\psi}|^2\right), \tag{27}$$

where we have expanded the symbols $g^{\beta\gamma}$ and B_γ. By observing that $h_{\gamma m}^{-1}\partial_\gamma = \partial/\partial r_m$, this can be conveniently rewritten as

$$\tilde{J}_\beta = -\frac{1}{2}h_{\beta l}^{-1}\left(-i\tilde{\psi}^*\frac{\partial\tilde{\psi}}{\partial r_l} + i\tilde{\psi}\frac{\partial\tilde{\psi}^*}{\partial r_l} - 2\frac{\partial r_l}{\partial t}|\tilde{\psi}|^2\right)$$
$$= hh_{\beta l}^{-1}\left(J_l - \frac{\partial r_l}{\partial t}\rho\right), \tag{28}$$

where

$$J_l = -\frac{1}{2}\left(-i\psi^*\frac{\partial\psi}{\partial r_l} + i\psi\frac{\partial\psi^*}{\partial r_l}\right) \tag{29}$$

is the probability current in the Cartesian frame. This is fully consistent with Eq. (26), thus completing the proof.

III. BULK ELECTROMECHANICAL RESPONSE IN THE LINEAR REGIME

In order to make contact with the linear-response approaches used to describe phenomena such as piezoelectricity and flexoelectricity, we shall consider, in the following, a continuous deformation that starts from the unperturbed state at $t = 0$, and occurs slowly enough that it can be considered small during a finite interval of time following $t = 0$. In such a regime, we can write the elastic deformation as

$$\mathbf{r} = \boldsymbol{\xi} + \mathbf{u}(\boldsymbol{\xi}, t), \tag{30}$$

where both the displacement field, $\mathbf{u}$, and its time derivative (velocity) are small. (This means that, in the linear limit, all terms that are proportional to u^2, $u\dot{u}$, etc. can be safely dropped.) We shall also suppose that the deformation is smooth on the scale of the interatomic spacings. This implies that only the lowest-order gradients of the displacement field, $\mathbf{u}(\boldsymbol{\xi}, t)$, are physically relevant. Finally, as a reminder, note that we shall only deal with "clamped-ion" deformation fields, i.e., we suppose that every atom in the lattice is displaced by hand according to Eq. (1), and neglect any further relaxation of the individual atomic sublattices. (Atomic relaxations are, of course, of central importance for a quantitatively correct description of the electromechanical response. However, lattice-mediated effects are conceptually simpler to

understand, and have been extensively studied in earlier publications. Here we shall only focus on the purely electronic response.)

A. Reciprocal-space analysis

Without loss of generality, we can represent $\mathbf{u}(\boldsymbol{\xi}, t)$ in Fourier space as a superposition of monochromatic perturbations,

$$\mathbf{u}(\boldsymbol{\xi}, t) = \sum_{\mathbf{q}\omega}\mathbf{u}(\mathbf{q}, \omega)e^{i\mathbf{q}\cdot\boldsymbol{\xi}-i\omega t}. \tag{31}$$

In such a representation, the above conditions on adiabaticity and smoothness can be formalized by requiring that $\mathbf{u}(\mathbf{q}, \omega)$ appreciably differs from zero only for small values of $q = |\mathbf{q}|$ and ω. In order to derive the electromechanical properties, we shall be concerned with the electrical current-density as given by Eq. (22), which can be conveniently represented in Fourier space as well,

$$\tilde{\mathbf{J}}(\boldsymbol{\xi}, t) = \sum_{\mathbf{q}\omega}\tilde{\mathbf{J}}(\mathbf{q}, \omega)e^{i\mathbf{q}\cdot\boldsymbol{\xi}-i\omega t}. \tag{32}$$

(For a monochromatic perturbation at a given $\mathbf{q}$ the microscopic polarization response, $\mathbf{J}(\boldsymbol{\xi}, t)$, generally contains all Fourier components of the type $\mathbf{G} + \mathbf{q}$, where $\mathbf{G}$ is a vector of the reciprocal-space Bravais lattice. Here we shall focus on macroscopic effects only, which are encoded in the $\mathbf{G} = \mathbf{0}$ component.) Then one can write the relevant coupling coefficients as the linear relationship between $\mathbf{u}$ and $\mathbf{J}$,

$$\tilde{\mathbf{J}}(\mathbf{q}, \omega) = \boldsymbol{\chi}^{(\mathbf{J})}(\mathbf{q}, \omega)\cdot\mathbf{u}(\mathbf{q}, \omega), \tag{33}$$

where $\boldsymbol{\chi}^{(\mathbf{J})}(\mathbf{q}, \omega)$ is a 3×3 tensor.

To see how the physical information contained in $\boldsymbol{\chi}^{(\mathbf{J})}(\mathbf{q}, \omega)$ relates to the electromechanical (polarization response to a deformation) properties of the crystal, it is useful to recall the relationship $\mathbf{J} = -i\omega\mathbf{P}$, where the polarization $\mathbf{P}$ has been Fourier-transformed as in Eq. (32). Then, one can immediately write, for the polarization response in the curvilinear space,

$$\tilde{\mathbf{P}}(\mathbf{q}, \omega) = \boldsymbol{\chi}^{(\mathbf{P})}(\mathbf{q}, \omega)\cdot\mathbf{u}(\mathbf{q}, \omega), \tag{34}$$

where we have introduced the electromechanical response function

$$\boldsymbol{\chi}^{(\mathbf{P})} = \frac{i}{\omega}\boldsymbol{\chi}^{(\mathbf{J})}. \tag{35}$$

Finally, one obtains the static clamped-ion electromechanical response as the adiabatic $\omega \to 0$ limit of the above,

$$\boldsymbol{\chi}^{(\mathbf{P})}(\mathbf{q}) = \boldsymbol{\chi}^{(\mathbf{P})}(\mathbf{q}, \omega = 0) = i\frac{\partial\boldsymbol{\chi}^{(\mathbf{J})}(\mathbf{q}, \omega)}{\partial\omega}\bigg|_{\omega=0}. \tag{36}$$

This procedure reflects the fundamental physical nature of the electrical polarization, which is understood as the

time integral of the transient current density that flows through the sample in the course of an adiabatic transformation of the crystal.

Note that $\boldsymbol{\chi}^{(\mathbf{P})}(\mathbf{q})$ has a direct relationship to the polarization response tensors that were considered in earlier works, e.g.,

$$\chi_{\alpha\beta}^{(\mathbf{P})}(\mathbf{q}) = \sum_\kappa \overline{P}_{\alpha,\kappa\beta}^{\mathbf{q}}, \tag{37}$$

where $\overline{P}_{\alpha,\kappa\beta}^{\mathbf{q}}$ describes the contribution of a modulated displacement (along β) of the atomic sublattice κ to the macroscopic polarization along α [see Eq. (13) of Ref. 23]. (The nuclear point charges are included in $\overline{P}_{\alpha,\kappa\beta}^{\mathbf{q}}$, following the original definition,[5,23] while they are absent from $\chi_{\alpha\beta}^{(\mathbf{P})}$ by construction – in the curvilinear space, the atoms do not move from their original location, and hence do not produce any current therein.)

B. Perturbation theory

To calculate $\boldsymbol{\chi}^{(\mathbf{J})}$ in a quantum-mechanical context, we shall first derive (in real space) the current density response to a monochromatic perturbation of the type $\mathbf{u}(\mathbf{r}, t) = \boldsymbol{\lambda} e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}$, and subsequently select its lowest Fourier component, as required by the present macroscopic context. Even if the following derivations will be carried out in curvilinear space, as there is no longer a potential risk of confusion we shall indicate the real-space coordinate as $\mathbf{r}$ and omit the "~" symbol henceforth.

Consider the unperturbed single-particle density operator,

$$\hat{\mathcal{P}}^{(0)} = \sum_n |\psi_n^{(0)}\rangle f_n^{(0)} \langle\psi_n^{(0)}|, \tag{38}$$

where $\psi_n^{(0)}(\mathbf{r})$ are eigenstates of the unperturbed Hamiltonian ,

$$\hat{\mathcal{H}}^{(0)}|\psi_n^{(0)}\rangle = \epsilon_n^{(0)}|\psi_n^{(0)}\rangle. \tag{39}$$

($f_n^{(0)}$ indicates the occupation of the state, which is either 0 or 1 for an insulating crystal in its electronic ground state.) In presence of the perturbation, the dynamical evolution of the density matrix is described by the single-particle Liouville equation

$$i\hbar \frac{\partial\hat{\mathcal{P}}}{\partial t} = [\hat{\mathcal{H}}(t), \hat{\mathcal{P}}], \tag{40}$$

where $\hat{\mathcal{H}}(t)$ is the curvilinear-frame Hamiltonian of Eq. (9). (Earlier derivations of the first-order adiabatic current based on the single-particle density matrix can be found in Refs. 24 and 25.) Then, we can rewrite the current density of Eq. (22) as

$$J_\alpha(\mathbf{r}, t) = g^{\alpha\beta} \operatorname{Tr}(\hat{\mathcal{J}}_\beta \hat{\mathcal{P}}), \tag{41}$$

where $g^{\alpha\beta}$, as usual, refers to the inverse metric tensor (implicit summation over β is assumed), the sum runs over the valence wavefunctions, and we have introduced the "curvilinear" current-density operator $\hat{\mathcal{J}}_\alpha$,

$$\hat{\mathcal{J}}_\beta(\mathbf{r}, t) = -\frac{\hat{p}_\beta|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{p}_\beta}{2} + |\mathbf{r}\rangle A_\alpha(\mathbf{r}, t)\langle\mathbf{r}|. \tag{42}$$

The minus sign appears, as in Eq. (22), because in our units the charge of the electron is -1. Note that $\hat{\mathcal{J}}_\alpha$ explicitly depends on space and time via the effective gauge potential $\mathbf{A}(\mathbf{r}, t)$ of Eq. (13). Time dependence is also implicitly present in $\hat{\mathcal{P}}$ via Eq. (40).

In the linear regime, we can expand both operators, $\mathcal{J}$ and $\mathcal{P}$, in powers of the displacement amplitude, $\boldsymbol{\lambda}$,

$$\hat{\mathcal{J}}_\alpha = \hat{\mathcal{J}}_\alpha^{(0)} + \lambda_\beta \hat{\mathcal{J}}_\alpha^{(\lambda_\beta)} + \cdots, \tag{43}$$

$$\hat{\mathcal{P}} = \hat{\mathcal{P}}^{(0)} + \lambda_\beta \hat{\mathcal{P}}^{(\lambda_\beta)} + \cdots, \tag{44}$$

where the dots stand for higher-order terms that have been dropped. By incorporating the above expansions into Eq. (41) we readily obtain

$$\frac{\partial J_\alpha(\mathbf{r}, t)}{\partial\lambda_\beta} = \operatorname{Tr}\left(\hat{\mathcal{J}}_\alpha^{(\lambda_\beta)}\hat{\mathcal{P}}^{(0)}\right) + \operatorname{Tr}\left(\hat{\mathcal{J}}_\alpha^{(0)}\hat{\mathcal{P}}^{(\lambda_\beta)}\right). \tag{45}$$

[Note that the inverse metric tensor of Eq. (41) also depends on λ_β, which in principle would generate an extra term; however, one can easily see that the first-order expansion of $g^{\alpha\beta}$ does not contribute to the current density in a time-reversal symmetric crystal – there are no circulating currents in the ground state. Thus, in the present context $g^{\alpha\beta}$ can be safely replaced with a Kronecker delta.]

The expansion of the current-density operator of Eq. (42) is relatively straightforward after observing that, in the linear limit, Eq. (13) gives $\mathbf{A} = \dot{\mathbf{u}} = -i\omega\boldsymbol{\lambda}e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}$; we obtain

$$\hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{r}) = -\frac{\hat{p}_\alpha|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\hat{p}_\alpha}{2}, \tag{46}$$

$$\hat{\mathcal{J}}_\alpha^{(\lambda_\beta)}(\mathbf{r}, t) = -i\omega\delta_{\alpha\beta} |\mathbf{r}\rangle e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}\langle\mathbf{r}|. \tag{47}$$

At order zero, we correctly recover the standard textbook expression for the current-density operator in a Cartesian space, which does not depend explicitly on time, while at first order we have a real-space projection operator times some complex prefactors. The only remaining task is now to derive an explicit formula for the first-order density matrix, $\hat{\mathcal{P}}^{(\lambda_\beta)}$, which we shall do in the following paragraphs.

By linearizing the Liouville equation, Eq. (40), and by assuming that the time dependence of the response is the same as that of the perturbing field, we easily arrive at

$$\langle\psi_m|\hat{\mathcal{P}}^{(\lambda_\beta)}|\psi_n\rangle = \frac{\langle\psi_m|\hat{\mathcal{H}}^{(\lambda_\beta)}|\psi_n\rangle(f_n - f_m)}{\epsilon_n - \epsilon_m + \omega}, \tag{48}$$

where we have dropped the superscript "(0)" on the wavefunctions, eigenvalues and occupancies to simplify

the notation, and $\hat{\mathcal{H}}^{(\lambda_\beta)}$ relates to the expansion of the Hamiltonian operator in powers of $\boldsymbol{\lambda}$,

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} + \lambda_\beta \hat{\mathcal{H}}^{(\lambda_\beta)} + \cdots. \tag{49}$$

(An explicit expression of $\hat{\mathcal{H}}^{(\lambda_\beta)}$ is derived in the Appendix.) We thus arrive at a closed expression for the current density of Eq. (45),

$$\frac{\partial J_\alpha(\mathbf{r}, t)}{\partial \lambda_\beta} = i\omega \delta_{\alpha\beta} e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t} \rho^{(0)}(\mathbf{r}) + \tag{50}$$

$$\sum_{mn} \frac{\langle \psi_n | \hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{r}) | \psi_m \rangle \langle \psi_m | \hat{\mathcal{H}}^{(\lambda_\beta)} | \psi_n \rangle (f_n - f_m)}{\epsilon_n - \epsilon_m + \omega},$$

where $\rho^{(0)}(\mathbf{r}) = -\sum_n |\psi_n(\mathbf{r})|^2$ is the ground-state electronic charge density.

We shall now filter out the macroscopic component of the response at wavevector $\mathbf{q}$ and eliminate the trivial phase factor of $e^{-i\omega t}$. After performing both operations, we obtain the desired current-response function as a Fourier transform

$$\chi_{\alpha\beta}^{(\mathbf{J})}(\mathbf{q}, \omega) = \frac{e^{i\omega t}}{\Omega} \int_{\text{cell}} d^3 r\, e^{-i\mathbf{q}\cdot\mathbf{r}} \frac{\partial J_\alpha(\mathbf{r}, t)}{\partial \lambda_\beta}. \tag{51}$$

By combining Eq. (51) with Eq. (50), we arrive at

$$\chi_{\alpha\beta}^{(\mathbf{J})}(\mathbf{q}, \omega) = -i\omega \frac{N}{\Omega} \delta_{\alpha\beta} + e^{i\omega t} \times \tag{52}$$

$$\sum_{mn} \frac{\langle \psi_n | \hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q}) | \psi_m \rangle \langle \psi_m | \hat{\mathcal{H}}^{(\lambda_\beta)} | \psi_n \rangle (f_n - f_m)}{\epsilon_n - \epsilon_m + \omega},$$

where we have introduced the reciprocal-space representation of the unperturbed current-density operator

$$\hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q}) = -\frac{1}{\Omega} \int d^3 r \frac{e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{p}_\alpha + \hat{p}_\alpha e^{-i\mathbf{q}\cdot\mathbf{r}}}{2}$$

$$= -\frac{1}{\Omega} \int d^3 r \left(\hat{p}_\alpha + \frac{q_\alpha}{2} \right) e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{53}$$

and N is the number of valence electrons in the primitive cell.

As a last step, it is useful to bring Eq. (52) into a simpler form by observing that the occupation factor $(f_n - f_m)$ only selects cross-gap matrix elements. Thus, we can introduce the first-order wavefunction response to the perturbation at the frequency ω as a sum over conduction states (c) only,

$$|\psi_v^{(\lambda_\beta)}(\mathbf{q}, \omega)\rangle = e^{i\omega t} \sum_c |\psi_c\rangle \frac{\langle \psi_c | \hat{\mathcal{H}}^{(\lambda_\beta)}(\mathbf{q}, \omega) | \psi_v \rangle}{\epsilon_v - \epsilon_c + \omega}, \quad (54)$$

where we have made the $(\mathbf{q}, \omega)$-dependence of the first-order Hamiltonian explicit, and rewrite Eq. (52) as a summation over valence states (v),

$$\chi_{\alpha\beta}^{(\mathbf{J})}(\mathbf{q}, \omega) = -i\omega \frac{N}{\Omega} \delta_{\alpha\beta} +$$

$$\sum_v \left\{ \langle \psi_v | \hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q}) | \psi_v^{(\lambda_\beta)}(\mathbf{q}, \omega)\rangle + \right. \tag{55}$$

$$\left. \langle \psi_v^{(\lambda_\beta)}(-\mathbf{q}, -\omega)| \left[\hat{\mathcal{J}}_\alpha^{(0)}(-\mathbf{q}) \right]^\dagger |\psi_v\rangle \right\}.$$

To arrive from Eq. (52) to Eq. (55) we have used the following general property of any first-order Hamiltonian that is associated with a monochromatic perturbation,

$$\left[\hat{\mathcal{H}}^{(1)}(\mathbf{q}, \omega) \right]^\dagger = \hat{\mathcal{H}}^{(1)}(-\mathbf{q}, -\omega) \tag{56}$$

which follows from the continued Hermiticity of $\hat{\mathcal{H}}(\mathbf{r}, t)$ in the presence of the perturbation. Note that the current operator is related to the first-order Hamiltonian in presence of an electromagnetic vector potential field, $\mathbf{A}$,

$$\hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q}) = -\left[\hat{\mathcal{H}}^{(A_\alpha)}(\mathbf{q}) \right]^\dagger. \tag{57}$$

This means that Eq. (56) holds for the current operator as well, thus completing the proof of Eq. (55).

In summary, the heavy algebra of this section has provided us with an important result for the current response function, $\chi_{\alpha\beta}^{(\mathbf{J})}$. To clarify what we have achieved so far, it is useful to rewrite Eq. (55) as

$$\chi_{\alpha\beta}^{(\mathbf{J})}(\mathbf{q}, \omega) = -i\omega \frac{N}{\Omega} \delta_{\alpha\beta} + F_{\alpha\beta}(\mathbf{q}, \omega) + F_{\alpha\beta}^*(-\mathbf{q}, -\omega), \tag{58}$$

where the auxiliary functions $F_{\alpha\beta}$ can be expressed as sums over occupied-state indices only,

$$F_{\alpha\beta}(\mathbf{q}, \omega) = \sum_v \langle \psi_v | \hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q}) | \psi_v^{(\lambda_\beta)}(\mathbf{q}, \omega)\rangle. \tag{59}$$

At first sight, our progress towards a numerically tractable theory might appear only cosmetic, since an infinite sum over unoccupied states is still present in the definition of the first-order wavefunctions in Eq. (54). This is, in principle, undesirable from the point of view of an implementation. However, expressions like Eq. (54) can easily be replaced, in the context of density-functional perturbation theory, by computationally more palatable Sternheimer equations.

C. Frequency expansion

We shall now extract the static polarization response function, $\chi_{\alpha\beta}^{(\mathbf{P})}(\mathbf{q})$, by taking the zero-frequency limit of the current response according to Eq. (36). Substituting Eq. (58) and taking note of the fact that $F_{\alpha\beta}(\mathbf{q}, \omega) = F_{\alpha\beta}^*(-\mathbf{q}, -\omega)$, which follows from the assumption of time-reversal symmetry, we obtain

$$\chi_{\alpha\beta}^{(\mathbf{P})}(\mathbf{q}) = \frac{N}{\Omega} \delta_{\alpha\beta} + 2i \frac{\partial F_{\alpha\beta}(\mathbf{q}, \omega)}{\partial \omega}\bigg|_{\omega=0}. \tag{60}$$

Our next task, then, is to work out the frequency expansion of the auxiliary function $F_{\alpha\beta}(\mathbf{q}, \omega)$, which in turn depends on ω via the first-order wavefunctions of Eq. (54). We shall, first of all, separate the "static" (frequency-independent) and "dynamic" contributions to the first-order Hamiltonian,

$$e^{i\omega t} \hat{\mathcal{H}}^{(\lambda_\beta)}(\mathbf{q}, \omega) = \hat{\mathcal{H}}^{(\lambda_\beta)}(\mathbf{q}) - i\omega \hat{\mathcal{H}}^{(\dot{\lambda}_\beta)}(\mathbf{q}), \tag{61}$$

where we have set $\omega = 0$ in the first term, and collected the remainder in the second term. (Note that there are no other terms, e.g., dependent on ω^2, as we are working within the linear approximation in the displacement field amplitude.) By combining Eq. (61) and Eq. (54) we obtain then, for the wavefunction response,

$$|\psi_v^{(\lambda_\beta)}(\mathbf{q},\omega)\rangle = |\psi_v^{(\lambda_\beta)}(\mathbf{q},\omega=0)\rangle - i\omega|\delta\psi_v^{(\lambda_\beta)}(\mathbf{q})\rangle$$
$$-i\omega|\psi_v^{(\dot\lambda_\beta)}(\mathbf{q})\rangle + \cdots, \quad (62)$$

where the second and third terms originate, respectively, from the frequency expansion of the energy denominator in Eq. (54),

$$|\delta\psi_v^{(\lambda_\beta)}(\mathbf{q})\rangle = -i\sum_c |\psi_c\rangle \frac{\langle\psi_c|\hat{\mathcal{H}}^{(\lambda_\beta)}(\mathbf{q})|\psi_v\rangle}{(\epsilon_v - \epsilon_c)^2}. \quad (63)$$

and of the first-order Hamiltonian, Eq. (61),

$$|\psi_v^{(\dot\lambda_\beta)}(\mathbf{q})\rangle = \sum_c |\psi_c\rangle \frac{\langle\psi_c|\hat{\mathcal{H}}^{(\dot\lambda_\beta)}(\mathbf{q})|\psi_v\rangle}{\epsilon_v - \epsilon_c}. \quad (64)$$

Note that Eq. (64) is very similar in form to Eq. (63), except for the power of two in the denominator and the factor of $-i$ appearing in the latter. In fact, one can show that $|\delta\psi_v^{(\lambda_\beta)}(\mathbf{q})\rangle$ is directly related to the *adiabatic* wavefunction response, at first order in the velocity, to the "static" perturbation $\hat{\mathcal{H}}^{(\lambda_\beta)}(\mathbf{q})$, when such a perturbation is slowly switched on as a function of time. To see this, one can go back to the Liouville equation, Eq. (40), and perform an expansion in the velocity of the perturbation, rather than its amplitude. First we write

$$i\hbar\dot\lambda\frac{\partial\hat{\mathcal{P}}(\lambda)}{\partial\lambda} = [\hat{\mathcal{H}}(\lambda),\hat{\mathcal{P}}(\lambda)], \quad (65)$$

and use a trial solution of the type

$$\hat{\mathcal{P}}(\lambda) \simeq \hat{\mathcal{P}}^{(0)}(\lambda) + \dot\lambda\hat{\mathcal{P}}^{(1)}(\lambda). \quad (66)$$

Next, by expanding in powers of $\dot\lambda$ we have, at order zero, the usual adiabatic limit of the quantum system following its instantaneous ground state,

$$[\hat{\mathcal{H}}(\lambda),\hat{\mathcal{P}}^{(0)}(\lambda)] = 0. \quad (67)$$

Finally, at first order in $\dot\lambda$, we obtain

$$i\partial_\lambda\hat{\mathcal{P}}^{(0)}(\lambda) = [\hat{\mathcal{H}}(\lambda),\hat{\mathcal{P}}^{(1)}(\lambda)], \quad (68)$$

which after projecting over a basis of instantaneous eigenstates of $\hat{\mathcal{H}}(\lambda)$ leads to

$$\langle\psi_m|\hat{\mathcal{P}}^{(1)}|\psi_n\rangle = -i\frac{\langle\psi_m|\partial_\lambda\hat{\mathcal{P}}^{(0)}|\psi_n\rangle}{\epsilon_n - \epsilon_m}. \quad (69)$$

(We have omitted the obvious parametric dependence on λ of all quantities in the above equation.) This result illustrates the physical meaning of the additional energy denominator and the factor of $-i$ in Eq. (63).

Returning to our main argument, we are ready to carry out the expansion of $F_{\alpha\beta}(\mathbf{q},\omega)$. Plugging Eq. (62) into Eq. (59), we obtain

$$F_{\alpha\beta}(\mathbf{q},\omega) = f_{\alpha\beta}(\mathbf{q}) - i\omega\left[\bar{g}_{\alpha\beta}(\mathbf{q}) + \Delta g_{\alpha\beta}(\mathbf{q})\right] + \cdots, \quad (70)$$

where the three contributions derive from the three terms on the right-hand side of Eq. (62) respectively. That is, $f_{\alpha\beta}(\mathbf{q}) = F_{\alpha\beta}(\mathbf{q},0)$ and

$$\bar{g}_{\alpha\beta}(\mathbf{q}) = \sum_v \langle\psi_v|\hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q})|\delta\psi_v^{(\lambda_\beta)}(\mathbf{q})\rangle, \quad (71)$$

$$\Delta g_{\alpha\beta}(\mathbf{q}) = \sum_v \langle\psi_v|\hat{\mathcal{J}}_\alpha^{(0)}(\mathbf{q})|\psi_v^{(\dot\lambda_\beta)}(\mathbf{q})\rangle. \quad (72)$$

We shall refer to the above responses as as *static* and *dynamic* respectively. It is important to note, in this context, that the words "static" and "dynamic" do not refer to the physical nature of these terms: Indeed, both contribute to the bulk polarization field that results from a *static* strain gradient; also, both pieces contribute to the (transient) macroscopic current that flows at the bulk level when the deformation is applied *dynamically*. Instead, this nomenclature is motivated by the mathematical origin of these contributions, which stem respectively from the first-order variation of the Hamiltonian operator, and from the effect of the coordinate transformation on the time derivative (see Appendix A).

After plugging Eq. (70) into Eq. (60), we finally obtain the polarization response function as

$$\chi_{\alpha\beta}^{(\mathbf{P})}(\mathbf{q}) = \bar{\chi}_{\alpha\beta}(\mathbf{q}) + \Delta\chi_{\alpha\beta}(\mathbf{q}). \quad (73)$$

Here $\bar{\chi}_{\alpha\beta}$ is the static part encoding the contribution of the static first-order Hamiltonian via $|\delta\psi_v^{(u_\beta)}(\mathbf{q})\rangle$,

$$\bar{\chi}_{\alpha\beta}(\mathbf{q}) = 2\bar{g}_{\alpha\beta}(\mathbf{q}), \quad (74)$$

while the remainder in Eq. (73) is the dynamic part,

$$\Delta\chi_{\alpha\beta}(\mathbf{q}) = 2\Delta g_{\alpha\beta}(\mathbf{q}) + \frac{N}{\Omega}\delta_{\alpha\beta}, \quad (75)$$

which arises due to the effective vector-potential field that appears in the time-dependent Schrödinger equation, Eq. (9), as a result of the coordinate transformation. Indeed, as we shall see shortly, the perturbing operator $\hat{\mathcal{H}}^{(\dot\lambda_\beta)}(\mathbf{q})$ of Eqs. (61) and (64) corresponds to *minus* the first-order Hamiltonian in a vector potential field,

$$\hat{\mathcal{H}}^{(\dot\lambda_\beta)}(\mathbf{q}) = -\hat{\mathcal{H}}^{(A_\beta)}(\mathbf{q}). \quad (76)$$

(The minus sign comes from the negative electron charge, which implies that the velocity operator is $\hat{v}_\beta = \hat{p}_\beta + A_\beta$ in the electromagnetic case.) For this reason, we shall refer to this contribution as either "gauge-field", "vector-potential" or "dynamic" henceforth.

The dynamic contribution $\Delta\chi_{\alpha\beta}(\mathbf{q})$ is unusual in the context of the existing literature, and deserves further

attention. The clear priority at this point is to understand whether it produces any contribution to the macroscopic electromechanical tensors, and whether such contribution can be related somehow to some well-defined (and possibly measurable) property of the material. We shall primarily focus on this task in the remainder of the manuscript.

D. Long-wave expansion

After dealing with the linear expansion in the deformation amplitude and frequency (above subsections), there is one last step that we need to take care of in order to arrive at the macroscopic electromechanical tensors – the long-wave expansion of $\chi^{(\mathbf{P})}(\mathbf{q})$ in powers of the wavevector $\mathbf{q}$. This readily yields the clamped-ion piezoelectric ($\mathbf{e}$) and flexoelectric ($\boldsymbol{\mu}$) tensors at first and second order in $\mathbf{q}$ respectively,

$$\chi^{(\mathbf{P})}_{\alpha\beta}(\mathbf{q}) = iq_\gamma e_{\alpha,\beta\gamma} - q_\gamma q_\delta \mu_{\alpha\beta,\gamma\delta} + \cdots. \quad (77)$$

We shall separately discuss the expansion of $\bar{\chi}$ and $\Delta\chi$ in the following, highlighting their respective contribution to the aforementioned tensors.

Before doing so, we need to remove the incommensurate phases from the operators and wavefunctions, as they are problematic in the context of a parametric $\mathbf{q}$-expansion; the standard approach to deal with this issue is to introduce a crystal momentum representation. For the ground-state orbitals we have

$$|\psi_{n\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}|\phi_{n\mathbf{k}}\rangle, \quad (78)$$

where $\phi_{n\mathbf{k}}$ are cell-periodic functions. Then, all the sums over occupied states of the previous sections need to be replaced by a sum over valence bands plus a Brillouin-zone average,

$$\sum_v \rightarrow \sum_n \int [d^3k], \quad (79)$$

where we have introduced the short-hand notation $[d^3k] = \Omega/(2\pi)^3 d^3k$. Note that the first-order wavefunctions contain a shift in momentum space by $\mathbf{q}$, which reflects the monochromatic nature of the perturbation,

$$|\psi^{(1)}_{n\mathbf{k}}(\mathbf{q})\rangle = e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}|\phi^{(1)}_{n\mathbf{k},\mathbf{q}}\rangle, \quad (80)$$

Finally, the cell-periodic operators are constructed in order to conveniently reabsorb the above phase factors,

$$\hat{\mathcal{H}}^{(1)}_{\mathbf{k},\mathbf{q}} = e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}\,\hat{\mathcal{H}}^{(1)}(\mathbf{q})\,e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (81)$$

Note that, consistent with Eq. (57), we shall define

$$\hat{\mathcal{J}}^{(0)}_{\alpha\mathbf{k},\mathbf{q}} = -\left(\hat{\mathcal{H}}^{(A_\alpha)}_{\mathbf{k},\mathbf{q}}\right)^\dagger = e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\mathcal{J}}^{(0)}_\alpha(\mathbf{q})e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}. \quad (82)$$

Equation (56) becomes

$$(\hat{\mathcal{O}}_{\mathbf{k},\mathbf{q}})^\dagger = \hat{\mathcal{O}}_{\mathbf{k}+\mathbf{q},-\mathbf{q}} \quad (83)$$

where $\hat{\mathcal{O}}$ stands for either $\hat{\mathcal{J}}^{(0)}_\alpha$ or a generic first-order Hamiltonian $\hat{\mathcal{H}}^{(1)}$.

1. Static contribution

Regarding the static part $\bar{\chi}$, we defer the detailed derivation of the operator $\hat{\mathcal{H}}^{(\lambda_\beta)}_{\mathbf{k},\mathbf{q}}$ to Appendix B. Here we shall limit ourselves to using some key properties of its small-$\mathbf{q}$ expansion,

$$\hat{\mathcal{H}}^{(\lambda_\beta)}_{\mathbf{k},\mathbf{q}} = iq_\gamma \hat{\mathcal{H}}^{(\beta\gamma)}_{\mathbf{k}} - q_\gamma q_\delta \hat{\mathcal{H}}^{(\beta,\gamma\delta)}_{\mathbf{k}} + \cdots, \quad (84)$$

which we summarize as follows:

- $\hat{\mathcal{H}}^{(\lambda_\beta)}_{\mathbf{k},\mathbf{q}}$ vanishes at $\mathbf{q} = 0$. This has to do with the fact that the $\mathbf{q} \rightarrow 0$ limit of a monochromatic displacement wave is a rigid translation, and a rigid translation has no effect whatsoever on the static physical properties of the crystal.

- The first-order term $\hat{\mathcal{H}}^{(\beta\gamma)}_{\mathbf{k}}$ is symmetric with respect to $\beta\gamma$ exchange, and corresponds to the *uniform strain* perturbation of Ref. 9.

- Both properties propagate to the first-order static and adiabatic wavefunctions, which can be expanded as

$$|\phi^{(\lambda_\beta)}_{n\mathbf{k}}(\mathbf{q})\rangle = iq_\gamma|\phi^{(\beta\gamma)}_{n\mathbf{k}}\rangle + \cdots, \quad (85)$$

$$|\delta\phi^{(\lambda_\beta)}_{n\mathbf{k}}(\mathbf{q})\rangle = iq_\gamma|\delta\phi^{(\beta\gamma)}_{n\mathbf{k}}\rangle + \cdots. \quad (86)$$

The functions $|\phi^{(\beta\gamma)}_{n\mathbf{k}}\rangle$, in particular, correspond to the strain response functions $|\psi^{(\eta_{\beta\gamma})}_{n\mathbf{k}}\rangle$ of Ref. 9.

The above considerations readily yield, by combining Eqs. (71), (74), (77) and (86), an explicit formula for the contribution of $\bar{\chi}$ to the piezoelectric tensor,

$$\bar{e}_{\alpha,\beta\gamma} = 2 \int [d^3k] \sum_v \langle\phi_{v\mathbf{k}}|\hat{\mathcal{J}}^{(0)}_{\mathbf{k}\alpha}|\delta\phi^{(\beta\gamma)}_{v\mathbf{k}}\rangle, \quad (87)$$

where $\hat{\mathcal{J}}^{(0)}_{\mathbf{k}\alpha} = -\partial\hat{\mathcal{H}}^{(0)}_{\mathbf{k}}/\partial k_\alpha$ is the macroscopic current operator. This is easily shown to match Eq. (16) of Ref. 9 by rearranging the energy denominators,

$$\sum_v \langle\phi_{v\mathbf{k}}|\hat{\mathcal{J}}^{(0)}_{\mathbf{k}\alpha}|\delta\phi^{(\beta\gamma)}_{v\mathbf{k}}\rangle$$
$$= -i\sum_{vc} \frac{\langle\phi_{v\mathbf{k}}|\hat{\mathcal{J}}^{(0)}_{\mathbf{k}\alpha}|\phi_{c\mathbf{k}}\rangle\langle\phi_{c\mathbf{k}}|\hat{\mathcal{H}}^{(\beta\gamma)}_{\mathbf{k}}|\phi_{v\mathbf{k}}\rangle}{(\epsilon_{v\mathbf{k}} - \epsilon_{c\mathbf{k}})^2}$$
$$= -\sum_v \langle i\tilde{\partial}_\alpha\phi_{v\mathbf{k}}|\phi^{(\beta\gamma)}_{v\mathbf{k}}\rangle, \quad (88)$$

where we have introduced the standard definition of the auxiliary "d/dk" wavefunctions,

$$|i\tilde{\partial}_\alpha\phi_{v\mathbf{k}}\rangle = i\sum_c |\phi_{c\mathbf{k}}\rangle\frac{\langle\phi_{c\mathbf{k}}|\partial\hat{\mathcal{H}}^{(0)}_{\mathbf{k}}/\partial k_\alpha|\phi_{v\mathbf{k}}\rangle}{\epsilon_{v\mathbf{k}} - \epsilon_{c\mathbf{k}}}. \quad (89)$$

Thus, the present theory yields the widely accepted formula for the clamped-ion piezoelectric response as a long-wave expansion of the static contribution to the electromechanical response.

By pushing the **q**-expansion to second order [recall Eq. (77)], one can readily access the static[26] contribution to the clamped-ion flexoelectric tensor, $\bar{\boldsymbol{\mu}}$. While the resulting formulas can be derived analytically, they are significantly more complex (e.g., both the contribution of the uniform strain and strain gradient response functions need, in principle, to be taken into account), and their physical interpretation is not as obvious as in the piezoelectric case. From the point of view of the code implementation it might be convenient to calculate, instead, the electromechanical response at finite **q**, and later take the long-wave expansion of Eq. (77) numerically; we took such an approach in Ref. 2.

2. Dynamic contribution

We now elaborate on the dynamic term and derive its contributions to the piezoelectric and flexoelectric tensor. First of all, we need an explicit expression for the operators that are implicitly involved in Eq. (75). By combining Eq. (76) with Eq. (82) we readily obtain

$$\hat{\mathcal{J}}_{\alpha\mathbf{k},\mathbf{q}} = \hat{\mathcal{H}}_{\mathbf{k},\mathbf{q}}^{(\dot{\lambda}_\alpha)} = -\left(\hat{p}_{\mathbf{k}\alpha} + \frac{q_\alpha}{2}\right), \tag{90}$$

~~Then,~~ We can then write a closed expression for the intermediate function $\Delta g_{\alpha\beta}(\mathbf{q})$,

$$\Delta g_{\alpha\beta}(\mathbf{q}) = -\int [d^3k] \sum_{nc} \frac{\langle u_{n\mathbf{k}}|\,(\hat{p}_{\mathbf{k}\alpha} + q_\alpha/2)\,|u_{c\mathbf{k}+\mathbf{q}}\rangle\langle u_{c\mathbf{k}+\mathbf{q}}|\,(\hat{p}_{\mathbf{k}\beta} + q_\beta/2)\,|u_{n\mathbf{k}}\rangle}{\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}}}, \tag{91}$$

which is clearly Hermitian in the Cartesian indices. (n and c run, as usual, over valence and conduction states, respectively). Note that $\Delta\chi_{\alpha\beta}(\mathbf{q})$ of Eq. (75) can then be recognized as the usual electromagnetic response function (**J**-response to a spatially modulated **A**-field) in the zero-frequency limit. This is one of the central results of this work.

Its relevance to the calculation of the macroscopic electromechanical tensors can be appreciated by looking at the lowest terms in its small-q expansion. At zero-th order in q we have

$$\Delta\chi_{\alpha\beta}(\mathbf{q} = 0) = 2\Delta g_{\alpha\beta}(\mathbf{q} = 0) + \frac{N}{\Omega}\delta_{\alpha\beta}, \tag{92}$$

By invoking the f-sum rule, one can show that the result vanishes, consistent with expectations: As we said, the zero-th order in q corresponds to a rigid translation, which should not produce any macroscopic electronic current *in the reference frame that moves with the crystal*. Similarly, this can be regarded as a manifestation of the gauge invariance of electromagnetism in the context of macroscopic electromechanical response properties.

The first order in q also vanishes, again as a consequence of gauge invariance. Physically, one can show that the **q**-derivative of $\Delta\chi_{\alpha\beta}(\mathbf{q})$ describes the **J**-response to a static **B**-field, or equivalently the **M**-response (**M** is the orbital magnetization) to a static **A**-field; both are forbidden in insulators, and only allowed in certain categories of metals in a transport regime.[27] This unambiguously proves that the contribution of the gauge fields, via the dynamical term $\Delta\chi_{\alpha\beta}$, to the macroscopic piezoelectric tensor identically vanishes, and can be regarded as providing a formal proof (*a posteriori*) that the metric tensor approach of Hamann *et al.*[9] rests on firm theoretical grounds.

3. Relationship to orbital magnetism

The interesting physics, in our present context, occurs at second order in q. By using Eq. (77) and substituting Eqs. (73) and (75), we can write the gauge-field contribution to the bulk flexoelectric tensor as

$$\Delta\mu_{mn,kl} = -\frac{1}{2}\frac{\partial^2\Delta\chi_{mn}(\mathbf{q})}{\partial q_k \partial q_l}\Big|_{\mathbf{q}=0} = -\frac{\partial^2\Delta g_{mn}(\mathbf{q})}{\partial q_k \partial q_l}\Big|_{\mathbf{q}=0}. \tag{93}$$

To see that this expansion term is directly related to orbital magnetism (earlier derivations were reported by Vignale (PRL 1991) and Mauri and Louie[28]), define the magnetic susceptibility tensor as

$$M_\alpha = \chi_{\alpha\beta}^{\text{mag}}B_\beta, \tag{94}$$

(**M** and **B** are the magnetization and the magnetic field, respectively), which for a monochromatic **A**-field implies ($\mathbf{J} = -\boldsymbol{\nabla}\times\mathbf{M}$, and $\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A}$) that the magnetically induced current density is

$$J_m = \epsilon^{ml\alpha}q_l\chi_{\alpha\beta}^{\text{mag}}\epsilon^{\beta kn}q_k A_n. \tag{95}$$

Now observe that, in our context, the vector potential is the time derivative of the displacement field, and that the polarization is the time derivative of the current. By taking the time integral on both sides of Eq. (95), and by recalling Eq. (34) we have, then

$$\Delta\chi_{mn}(\mathbf{q}) \sim \epsilon^{ml\alpha}q_l\chi_{\alpha\beta}^{\text{mag}}\epsilon^{\beta kn}q_k. \tag{96}$$

Now, we can derive both sides twice with respect to **q**, which leads to

$$\Delta\mu_{mn,kl} = \frac{1}{2}\sum_{\alpha\beta}(\epsilon^{\alpha mk}\epsilon^{\beta nl} + \epsilon^{\alpha ml}\epsilon^{\beta nk})\chi_{\alpha\beta}^{\text{mag}}. \tag{97}$$

In the special case of a solid with cubic symmetry, where $\chi_{\alpha\beta}^{\text{mag}} = \chi^{\text{mag}}\delta_{\alpha\beta}$, the above expression can be simplified

by using

$$\sum_\alpha \epsilon^{\alpha mk}\epsilon^{\alpha nl} = \delta_{mn}\delta_{kl} - \delta_{ml}\delta_{nk},$$

which leads to

$$\Delta\mu_{mn,kl} = \frac{\chi^{\mathrm{mag}}}{2}(2\delta_{mn}\delta_{kl} - \delta_{ml}\delta_{nk} - \delta_{mk}\delta_{nl}). \quad (98)$$

Thus, in a cubic solid only two independent combinations of indices yield a nonzero value,

$$\Delta\mu_{11,22} = \chi^{\mathrm{mag}}, \qquad \Delta\mu_{12,12} = -\frac{\chi^{\mathrm{mag}}}{2}. \quad (99)$$

The fact that the flexoelectric response involves a contribution that is exactly proportional to the diamagnetic susceptibility may appear surprising at first sight, as this result combines two material properties that are, at first sight, completely unrelated. Yet, by recalling the equivalence between rotations and magnetism discussed in Section II B 2, the above result, which is one of the key messages of this work, becomes reasonable: Certain components of the strain-gradient tensor involve gradients of the local rotation. A uniform rotation, in turn, produces an orbital magnetization, $\mathbf{M}$; then, a rotation *gradient* that is applied adiabatically to the crystal produces a macroscopic current (recall the relationship from electromagnetism $\mathbf{J} = -\nabla \times \mathbf{M}$) that, integrated over time, yields a macroscopic polarization.

To summarize this long Section, we have achieved a decomposition of the electronic flexoelectric tensor into two physically distinct terms,

$$\boldsymbol{\mu} = \bar{\boldsymbol{\mu}} + \Delta\boldsymbol{\mu}. \quad (100)$$

At this point, we are left with the obvious questions of whether the two contributions $\bar{\boldsymbol{\mu}}$ and $\Delta\boldsymbol{\mu}$ are separately measurable and, if yes, of how they should be treated in the perspective of comparing the results to the experiments. To provide a reliable answer, however, one needs to account for the surface contributions along side the bulk ones, as we know that the two form an undissociable entity in the context of the flexoelectric response. We shall discuss this topic in the following section.

IV. MICROSCOPIC POLARIZATION RESPONSE AND SURFACE CONTRIBUTIONS

To quantify the surface contributions to the flexoelectric response of a finite object, we need to adapt the theory developed in the previous Section to the calculation of the *microscopic* polarization response to a deformation. (The physical properties of the surface substantially differ from those of the bulk, thus requiring a spatially resolved description.) In particular, we shall be concerned with the response functions $\bar{\chi}^{\mathbf{q}}_{\alpha\beta}(\mathbf{G})$ and $\Delta\chi^{\mathbf{q}}_{\alpha\beta}(\mathbf{G})$, which

we define by generalizing their macroscopic counterparts, Eq. (74) and Eq. (75), as follows,

$$\bar{\chi}^{\mathbf{q}}_{\alpha\beta}(\mathbf{G}) = 2\int [d^3k]\sum_v \langle \phi_{v\mathbf{k}}|\hat{\mathcal{J}}_{\alpha\mathbf{k},\mathbf{G}+\mathbf{q}}|\delta\phi^{(\lambda_\beta)}_{v\mathbf{k}}(\mathbf{q})\rangle,$$

$$\Delta\chi^{\mathbf{q}}_{\alpha\beta}(\mathbf{G}) = 2\int [d^3k]\sum_v \langle \phi_{v\mathbf{k}}|\hat{\mathcal{J}}_{\alpha\mathbf{k},\mathbf{G}+\mathbf{q}}|\phi^{(\dot\lambda_\beta)}_{v\mathbf{k}}(\mathbf{q})\rangle$$
$$+\delta_{\alpha\beta}n^{(0)}_{\mathrm{el}}(\mathbf{G}). \quad (101)$$

The only difference with respect to the previous formulas is that the polarization response is now calculated at $\mathbf{G} + \mathbf{q}$, where $\mathbf{G}$ is a vector of the reciprocal-space Bravais lattice. [Note that the average electron density, $n_{\mathrm{el}}(\mathbf{G} = 0)$, corresponds to N/Ω, consistent with the macroscopic formula, Eq. (75).] Of course, the above expressions include the macroscopic response defined earlier as a special case,

$$\chi^{\mathbf{q}}_{\alpha\beta}(\mathbf{G} = 0) = \chi_{\alpha\beta}(\mathbf{q}), \quad (102)$$

where χ stands for either $\bar{\chi}$ or $\Delta\chi$.

A. The role of the gauge fields

To make a more direct connection with the existing treatments of the surface problem, we shall assume a slab geometry henceforth, with the surface normal oriented along x, and periodic boundary conditions in the yz plane. As in earlier works, we shall adopt open-circuit electrical boundary conditions along x, as appropriate for a slab with free surfaces, and focus our attention on the total *open-circuit voltage* that is linearly induced by a strain-gradient deformation. To determine such "flexovoltage"[6] response we need the induced electrostatic potential and this, in turn, is uniquely given (modulo an irrelevant global constant) by the charge-density response of the system to the perturbation. This observation makes the analysis of a finite object conceptually simpler than that of a bulk crystal – the explicit inclusion of the boundaries allows us to study the charge rather than the polarization, which is much easier to define and calculate.

The charge response functions that are associated with the static and dynamic terms can be written as minus the divergence of the polarization response, which in reciprocal space can be written as (ρ stands for $\bar{\rho}$ or $\Delta\rho$, and χ for either $\bar{\chi}$ or $\Delta\chi$)

$$\rho^{\mathbf{q}}_\beta(\mathbf{G}) = -i\sum_\alpha (G_\alpha + q_\alpha)\chi^{\mathbf{q}}_{\alpha\beta}(\mathbf{G}), \quad (103)$$

Crucially, the dynamic gauge-field contribution to the charge-density response vanishes identically,

$$\Delta\rho^{\mathbf{q}}_\beta(\mathbf{G}) = 0. \quad (104)$$

This result may appear surprising at first sight, but it is really a simple consequence of time-reversal symmetry:

In absence of spin-orbit coupling, a vector potential field applied to the orbital degrees of freedom produces, in the linear regime, a divergenceless circulating current, which does not alter the ground-state electron density. Still, the situation is paradoxical in light of the results of the previous Section: How can we reconcile the irrelevance of the gauge fields for the electromechanical response of a slab, clearly stated by Eq. (104), with their nonvanishing contribution to the bulk flexoelectric tensor, as expressed by Eq. (97)? The answer, as we anticipated at the end of the previous Section, resides in the presence of surface contributions to the overall flexo-response of a slab that are equal in magnitude and opposite in sign to $\Delta\boldsymbol{\mu}$, leading to an exact cancellation of their combined effect.

To prove that such a cancellation indeed occurs, it suffices to review Section II B 2, where the equivalence between a uniform rotation of the sample and an effective orbital magnetic field is established; we shall see that this result can quantitatively explain both the bulk and surface contributions of the gauge fields to the flexoelectric response. It is convenient, to that end, to introduce a quantity $\mathbf{T}(\mathbf{r})$ corresponding to the time integral of the orbital magnetization,

$$\mathbf{T}(\mathbf{r}) = \int_0^t \mathbf{M}(\mathbf{r}, t) dt, \qquad (105)$$

and since $\mathbf{J} = \boldsymbol{\nabla} \times \mathbf{M} = d\mathbf{P}/dt$, it follows that

$$\mathbf{P}(\mathbf{r}) = -\boldsymbol{\nabla} \times \mathbf{T}(\mathbf{r}). \qquad (106)$$

Loosely speaking, $\mathbf{T}$ can be thought of as a kind of electric toroidization. In the linear-response regime, the dynamic gauge-field term in the Hamiltonian produces a $\mathbf{T}$-field whose amplitude is proportional to the local rotation of the sample (we neglect the spatial dispersion of the orbital diamagnetic response, which is irrelevant in the context of the present discussion) with respect to the unperturbed configuration [recall Eq. (21)],

$$\mathbf{T}(\mathbf{r}) = -2\chi^{\mathrm{mag}}\boldsymbol{\theta}(\mathbf{r}). \qquad (107)$$

Now consider a displacement field of the type

$$u_y(\mathbf{r}) = \frac{\eta}{2}x^2, \qquad (108)$$

corresponding to a uniform shear strain gradient applied to the slab, as illustrated in Fig. 1. The rotation angle is given by $\theta_z = \eta x/2$, and its curl is readily given by $\boldsymbol{\nabla} \times \boldsymbol{\theta} = -\hat{\mathbf{y}}/2$; Eqs. (105-106) then yield a contribution to the bulk flexoelectric response equal to $\Delta P_y = \eta\chi^{\mathrm{mag}}$, consistent with Eq. (99).

To gain a more intuitive insight into this result, one can regard the strain-gradient deformation of the slab as a piecewise shear [Fig. 1(a)], which we suppose to be uniform within individual segments. (The realistic physical picture is then recovered upon reducing the segment length to zero.) The rotation of each segment is associated with a circulating surface polarization (black arrows), and as the rotation amplitude linearly increases
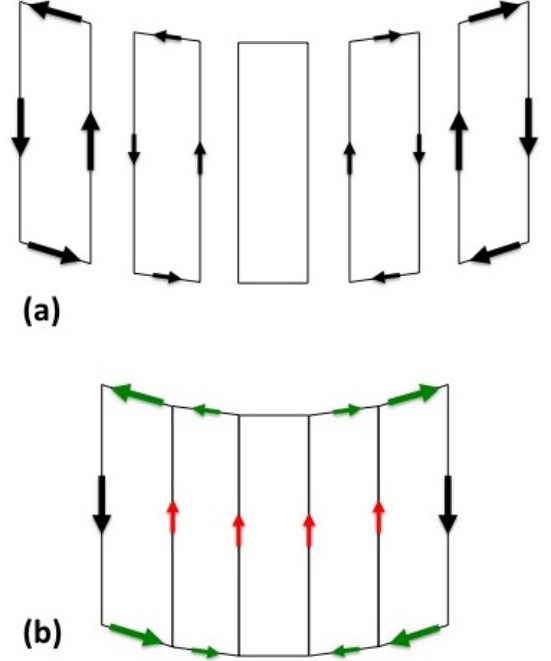

FIG. 1. Dynamical vector-potential contributions to the polarization of a slab subjected to a shear strain gradient. (a) Decomposition into circulating currents withing segments; (b) Decomposition between bulk and surface contributions.

along x, the contribution of the facets that lie next to each other (i.e. within the interior of the slab) does not cancel out; on the contrary, they result in a uniform $\mathbf{P}$ [red arrows in Fig. 1(b)]. In principle, a bulk polarization would result in a net surface charge; however, the cartoon of Fig. 1(a) clearly illustrates why here this is not the case. Indeed, in addition to the aforementioned bulk effect, there is also a polarization that develops at the outer surfaces of the segments [green arrows in Fig. 1(b)]. Such a surface polarization is oriented in-plane, and linearly increases along the same direction x. This polarization field yields (recall $\rho = -\boldsymbol{\nabla} \cdot \mathbf{P}$) a uniform, net surface charge that exactly cancels the contribution of the bulk, thereby settling the paradox that we described at the beginning of this Section.

Summarizing the above, there are two equally valid ways to understand the gauge-field contribution to the polarization field induced by a deformation, which are illustrated by the two panels in Fig. 1. We can think of it either [panel (a)] as the sum of local circulating currents that arise because individual segments of the slab undergo a local rotation with respect to the original configuration; or [panel (b)], as in earlier treatments of the flexoelectric problem, as a sum of bulk and surface contributions. In either case, the overall sum yields a vanishing charge density, and is therefore irrelevant in the context of an electrical measurement. The conclusion is that we can discard the "dynamical" contributions to

the flexoelectric effect altogether, and build a predictive theory of the electromechanical response based on the static contribution only.

B. Connection to the existing theory of flexoelectricity

Our next task is to clarify how all of the above relates to the calculations of flexoelectricity that have recently been reported.[6,29,30] These previous works based their analysis on the microscopic response functions $P_{\alpha,\kappa\beta}^{\mathbf{q}}(\mathbf{r})$, which are defined as the α component of the polarization response, calculated in the laboratory frame, to a monochromatic displacement of the sublattice κ along the Cartesian direction β. To summarize this approach, it is useful to begin by considering the sum of the above sublattice displacements, which corresponds to the polarization response to an acoustic phonon in the laboratory frame. Following Ref. 3 we shall define

$$P_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}) = \sum_{\kappa} P_{\alpha,\kappa\beta}^{\mathbf{q}}(\mathbf{r}). \tag{109}$$

By taking into account the transformation properties of the current density between the laboratory and the curvilinear frame in the linear regime of small deformations, one can then write the following relationship,

$$P_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}) = \delta_{\alpha\beta}\rho^{(0)}(\mathbf{r}) + \chi_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}), \tag{110}$$

where the last term on the rhs is defined as the Fourier transform of the microscopic response function $\chi_{\alpha\beta}^{\mathbf{q}} = \bar{\chi}_{\alpha\beta}^{\mathbf{q}} + \Delta\chi_{\alpha\beta}^{\mathbf{q}}$,

$$\chi_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} \chi_{\alpha\beta}^{\mathbf{q}}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{111}$$

and $\rho^{(0)}(\mathbf{r})$ is the ground-state charge density, inclusive of the nuclear point charges.

To access the macroscopic electromechanical properties of the system, a long-wave decomposition is performed,[3]

$$P_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}) = P_{\alpha\beta}^{(0)}(\mathbf{r}) - iq_{\gamma}P_{\alpha\beta}^{(1,\gamma)}(\mathbf{r}) - \frac{q_{\gamma}q_{\delta}}{2}P_{\alpha\beta}^{(2,\gamma\delta)}(\mathbf{r}) + \cdots, \tag{112}$$

where the cell averages of the expansion terms yield the electronic parts of the macroscopic piezoelectric and flexoelectric tensors,

$$-\frac{1}{\Omega}\int_{\text{cell}} d^3r P_{\alpha\beta}^{(1,\gamma)}(\mathbf{r}) = e_{\alpha,\beta\gamma}, \tag{113}$$

$$\frac{1}{2\Omega}\int_{\text{cell}} d^3r P_{\alpha\beta}^{(2,\gamma\delta)}(\mathbf{r}) = \mu_{\alpha\beta,\gamma\delta}, \tag{114}$$

consistent with the $\mathbf{q}$-expansion of the macroscopic $\chi_{\alpha\beta}(\mathbf{q})$ tensors defined in the previous Sections. In fact, after observing that at $\mathbf{q} = 0$ the microscopic polarization response function $\chi_{\alpha\beta}^{\mathbf{q}}(\mathbf{r})$ vanishes identically, one

can use Eq. (110) to directly relate the $\mathbf{q}$-expansion of the laboratory $\mathbf{P}$-response to that of the curvilinear $\mathbf{P}$-response even at the microscopic level ,e.g. by writing

$$\chi_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}) = iq_{\gamma}\chi_{\alpha\beta}^{(1,\gamma)}(\mathbf{r}) - q_{\gamma}q_{\delta}\chi_{\alpha\beta}^{(2,\gamma\delta)}(\mathbf{r}) + \cdots, \tag{115}$$

and equating terms at each order in $\mathbf{q}$.

At this point, one would be tempted to proceed as in Ref. 3, and identify the first- and second-order expansion terms as the microscopic polarization response to a uniform strain and to a strain gradient, respectively. (This step was a crucial prerequisite to the calculation of the transverse components of the bulk flexoelectric tensor that was performed in Ref. 3.) This implies tentatively writing the induced polarization as

$$\mathbf{P}(\mathbf{r}) = \varepsilon_{\beta\gamma}(\mathbf{r})\mathbf{P}_{\beta\gamma}^{\mathrm{U}}(\mathbf{r}) + \frac{\partial\varepsilon_{\beta\gamma}(\mathbf{r})}{\partial r_{\delta}}\mathbf{P}_{\beta\gamma,\delta}^{\mathrm{G}}(\mathbf{r}) + \cdots, \tag{116}$$

where $\varepsilon_{\beta\gamma}(\mathbf{r})$ is a spatially nonuniform symmetric strain field, and $\mathbf{P}^{\mathrm{U}}$ and $\mathbf{P}^{\mathrm{G}}$ describe the linear polarization response to a uniform (U) strain and to its gradient (G), respectively. In Refs. 3 and 6 it was assumed that such response functions simply correspond to the $\mathbf{q}$-expansion terms of $P_{\alpha\beta}^{\mathbf{q}}(\mathbf{r})$. In light of the results of this work, however, an expression such as Eq. (116) is physically problematic, as it implicitly assumes that the polarization response to a rigid translation or a rotation of the crystal vanishes. While we know this to be true for translations, rigid rotations do contribute to $\mathbf{P}(\mathbf{r})$ via the dynamic gauge-field terms discussed in the previous section. As a consequence, we cannot identify $P_{\alpha,\beta\gamma}^{\mathrm{U}}(\mathbf{r})$ with either $\chi_{\alpha\beta}^{(1,\gamma)}(\mathbf{r})$ or, equivalently, with $-P_{\alpha\beta}^{(1,\gamma)}(\mathbf{r})$: $P_{\alpha,\beta\gamma}^{\mathrm{U}}$ is symmetric with respect to $\beta\gamma$ by construction, while the other two functions implicitly contain an antisymmetric contribution that is mediated by the gauge-field rotation response.

As we anticipated in the previous Section, an elegant solution to this problem consists in dropping the dynamic gauge-field response altogether, and writing the theory in terms of the static response function $\bar{\chi}$ only. The latter enjoys a $\mathbf{q}$-expansion analogous to that of the total χ,

$$\bar{\chi}_{\alpha\beta}^{\mathbf{q}}(\mathbf{r}) = iq_{\gamma}\bar{\chi}_{\alpha\beta}^{(1,\gamma)}(\mathbf{r}) - q_{\gamma}q_{\delta}\bar{\chi}_{\alpha\beta}^{(2,\gamma\delta)}(\mathbf{r}) + \cdots, \tag{117}$$

with the key advantage that the first-order term is now symmetric under $\beta\gamma$ exchange. This formally justifies the use of Eq. (116), together with the definitions

$$P_{\alpha,\beta\gamma}^{\mathrm{U}}(\mathbf{r}) = \bar{\chi}_{\alpha\beta}^{(1,\gamma)}(\mathbf{r}), \tag{118}$$

$$P_{\alpha\delta,\beta\gamma}^{\mathrm{G}}(\mathbf{r}) = \bar{\chi}_{\alpha\beta}^{(2,\gamma\delta)}(\mathbf{r}) + \bar{\chi}_{\alpha\gamma}^{(2,\beta\delta)}(\mathbf{r}) - \bar{\chi}_{\alpha\delta}^{(2,\beta\gamma)}(\mathbf{r}), \tag{119}$$

where we have operated the standard permutation of indices on the rhs of Eq. (119) in order to move from a "type-I" (second gradient of the displacement field) to a "type-II" (first gradient of the symmetrized strain tensor) representation of the strain-gradient tensor.[5,23] This way, we can connect the present analytical results with
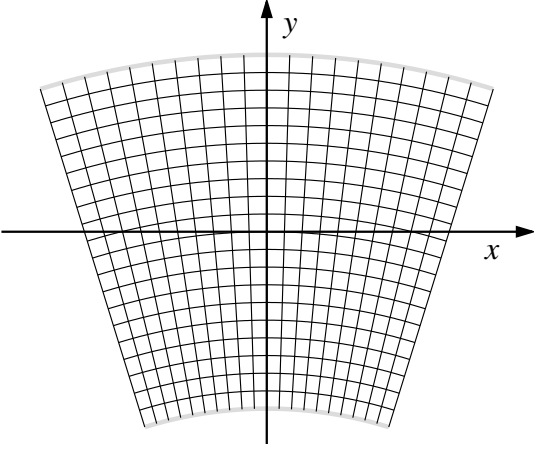
FIG. 2. Schematic illustration of the flexural deformation of a slab. Thick arrows indicate the Cartesian axes, thick gray curves indicate the slab surfaces.

the existing theory of the flexoelectric response. Most importantly, this allows us to formally reconcile the existing calculations of the bulk flexoelectric tensor, which were based on an analysis of the charge-density response in a supercell geometry,[6] with the more fundamental current-response theory that we have developed in this work.

C. Calculation of the transverse components

To illustrate the above arguments, it is useful to explicitly work out the example of a symmetric slab, finite in the y direction, subjected to a transverse (i.e., flexural) strain gradient deformation via the displacement field

$$u_x = \eta x y, \qquad (120)$$
$$u_y = -\frac{\eta}{2} x^2 \qquad (121)$$

(see Fig. 2). The symmetric strain tensor has only one non-zero entry,

$$\varepsilon_{xx} = \frac{\partial u_x}{\partial x} = \eta y, \qquad (122)$$

indicating a linear increase of the transverse component along the normal to the slab surface, i.e., a constant strain-gradient field of the type

$$\varepsilon_{xx,y} = \frac{\partial \varepsilon_{xx}}{\partial y} = \eta. \qquad (123)$$

By using Eq. (116), we can readily write the resulting polarization field (within the linear approximation and discarding higher-order gradient effects) as

$$\frac{\partial \mathbf{P}(\mathbf{r})}{\partial \eta} = y \mathbf{P}^{\mathrm{U}}_{xx}(\mathbf{r}) + \mathbf{P}^{\mathrm{G}}_{xx,y}(\mathbf{r}). \qquad (124)$$

To move further it is convenient to operate, as customary, a macroscopic averaging procedure on the $\mathbf{P}^{\mathrm{U}}$ and

$\mathbf{P}^{\mathrm{G}}$ functions in order to filter out the irrelevant oscillations on the scale of the interatomic spacings. This way, the in-plane spatial resolution is completely suppressed, leaving response functions that depend on y only. Note that, by symmetry, the induced polarization can only have nonzero y components,

$$\frac{\partial P_y(y)}{\partial \eta} = y P^{\mathrm{U}}_{y,xx}(y) + P^{\mathrm{G}}_{yy,xx}(y), \qquad (125)$$

and that since the bulk is nonpiezoelectric the first function on the rhs, $P^{\mathrm{U}}_{y,xx}(y)$, can only be nonzero near the surface. These observations allow one to conclude that the induced *surface charge*, σ is uniquely determined by the second term on the rhs of Eq. (125); in the limit of a thick slab, we can then write

$$\frac{\partial \sigma}{\partial \eta} = \frac{\bar{\mu}_{\mathrm{T}}}{\epsilon_\infty}, \qquad (126)$$

where

$$\bar{\mu}_{\mathrm{T}} = 2\bar{\mu}_{12,12} - \bar{\mu}_{11,22} \qquad (127)$$

is the transverse component of the "barred" (no gauge fields) bulk flexoelectric tensor in type-II form, and ϵ_∞ is the bulk relative permittivity at the clamped-ion level.

We stress that the above arguments, linking $\bar{\mu}_{\mathrm{T}}$ to the surface charge σ, and hence to the macroscopic electric field that develops in the interior of the slab upon bending, $E_y = -\sigma/\epsilon_0$ (ϵ_0 is the vacuum permittivity), hold under the hypothesis that the effect of rotations is excluded from Eq. (116), which can only be justified if the gauge-field contribution is excluded from *both* bulk and surface contributions to the overall flexoelectric response. This means that the explicit calculation of the bulk flexoelectric tensor of SrTiO$_3$ that was carried out in in Ref. 6 really concerned $\bar{\boldsymbol{\mu}}$, and not the total tensor $\boldsymbol{\mu} = \bar{\boldsymbol{\mu}} + \Delta\boldsymbol{\mu}$. We believe that the former quantity, $\bar{\boldsymbol{\mu}}$, given its more direct relationship to the charge-density response of the system, is physically more meaningful than $\boldsymbol{\mu}$, and should be preferred to the latter when reporting the results of first-principles calculations.

D. A simple example

Consider a simple cubic lattice made of spherical, closed-shell atoms, with a cell parameter that is sufficiently large as to avoid any direct interaction between neighboring sites. Such a crystal is, of course, unrealistic as there is no force whatsoever keeping the atoms in place. Nevertheless, it is a useful toy model to discuss some fundamental aspects of the flexoelectric response, without the complications that characterize a real material. This model was introduced in Ref. 3 to illustrate some subtleties related to surface contributions; here we shall use it to illustrate the two alternative definitions of the bulk flexoelectric tensor, either excluding ($\bar{\boldsymbol{\mu}}$) or including ($\boldsymbol{\mu}$) the dynamic gauge-field response.

The basic quantities that define the model are: (i) the spherical charge distribution $\rho_{\mathrm{at}}(r)$ of each isolated atom, and (ii) the lattice parameter a_0. Then the charge density can be readily written as

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \rho_{\mathrm{at}}(|\mathbf{r} - \mathbf{R}|), \qquad (128)$$

where the sum runs over the Bravais lattice defined by a_0. To calculate the flexoelectric tensor via the current-density response we need the microscopic polarization field that is induced by the displacement of an isolated atom. As the atoms are spherical, there are no long-range electrostatic forces involved, and since they are noninteracting, one can readily use the transformation laws of the probability current to write

$$\mathcal{P}_{\alpha,\beta}(\mathbf{r}) = \rho_{\mathrm{at}}(r)\delta_{\alpha\beta} \qquad (129)$$

where we have dropped the sublattice index κ since we are dealing with a single atom per unit cell. This equation reflects the fact that the probability current associated with an isolated spherical atom located at the origin and moving with uniform velocity $\mathbf{v}$ is simply given by $\mathbf{v}$ times the atomic charge density,

$$\mathbf{J}(\mathbf{r}) = \mathbf{v}\rho_{\mathrm{at}}(r). \qquad (130)$$

Now, recall the definition of the flexoelectric tensor given by Eq. (114). We have, for the three independent components,

$$\mu_{\mathrm{L}} = \mu_{\mathrm{S}} = \frac{Q}{2\Omega}, \qquad \mu_{\mathrm{T}} = -\frac{Q}{2\Omega}, \qquad (131)$$

where Q is the quadrupolar moment of the static atomic charge,

$$Q = \int d^3 r \, \rho_{\mathrm{at}}(r) x^2, \qquad (132)$$

and the longitudinal (L), transverse (T) and shear (S) components are given by

$$\mu_{\mathrm{L}} = \mu_{11,11}, \qquad \mu_{\mathrm{S}} = \mu_{11,22},$$

$$\mu_{\mathrm{T}} = 2\mu_{12,12} - \mu_{11,22}. \qquad (133)$$

To calculate the "revised" version of the flexoelectric tensor we need to calculate the gauge-field contribution, which is in turn given by the macroscopic diamagnetic susceptibility via Eq. (99),

$$\Delta\mu_{\mathrm{L}} = 0, \qquad \Delta\mu_{\mathrm{S}} = \chi^{\mathrm{mag}},$$

$$\Delta\mu_{\mathrm{T}} = -2\chi^{\mathrm{mag}}. \qquad (134)$$

Given the noninteracting nature of the spherical atoms, we can apply Langevin theory to calculate χ^{mag},

$$\chi^{\mathrm{mag}} = \frac{Q}{2\Omega}, \qquad (135)$$

which immediately yields

$$\mu'_{\mathrm{L}} = \mu'_{\mathrm{T}} = \frac{Q}{2\Omega}, \qquad \mu'_{\mathrm{S}} = 0. \qquad (136)$$

Eq. (136) matches the conclusions of earlier works, where the flexoelectric tensor components were inferred from the behavior of the macroscopic electrostatic potential under a deformation. (The interested reader can find a detailed derivation in the Supplementary Note 1 of Ref. 3, or in Ref. 23.)

By comparing the two "versions" of the flexoelectric tensor, it is clear that the quantitative differences can be substantial, even in the trivially simple case of the toy model described in this section. Further work is needed to assess the impact of these effects on the calculation of flexoelectricity in realistic materials. In any case, the discussion presented should serve as a warning against potential misunderstandings when interpreting the results of calculations of flexoelectric responses.

V. DISCUSSION

It is important to stress that Eq. (116), together with the definitions of Eqs. (118) and (119), does not describe the total polarization response, but only a part of it. This part is enough for an exact description of electromechanical effects, as we have seen in the case of flexoelectricity. One can wonder, however, whether there is any physical significance that can be associated with the part that we have discarded from our analysis, i.e., the gauge-field contribution. In this Section we shall briefly discuss this topic.

The connection of rotations and orbital magnetization has been noted earlier in other contexts; for example, it plays an important role in the theory of molecular g-factors. Ceresoli and Tosatti[31] (CT) have shown how such quantities can be understood (and calculated from first principles) as the Berry phases that the wavefunctions accumulate in the course of a rotation of the molecule around its center of mass. It is interesting to analyse their approach in some detail, in order to show its strong relationship to the topics of the present work.

CT base their formalism on the electronic ground state of an isolated molecule, whose rotation state about the z axis is measured by an angle, θ. The instantaneous ground state of the molecule is defined by the lowest N eigenstates of the Hamiltonian, which depend parametrically on θ,

$$\hat{\mathcal{H}}(\theta)|\psi_n(\theta)\rangle = \epsilon_n|\psi_n(\theta)\rangle. \qquad (137)$$

(ϵ_n does not depend on θ, as the energy of the system is invariant upon rotations.) Then, by discretizing the $[0, 2\pi]$ interval into M equally spaced points θ_i, one can write the Berry phase corresponding to a complete cycle as

$$\gamma \simeq -\mathrm{Im} \log \prod_{i=1,M} \det \mathbf{S}(\theta_i, \theta_{i+1}), \qquad (138)$$

where S are $N \times N$ matrices,

$$S_{mn}(\theta_i, \theta_j) = \langle \psi_m(\theta_i) | \psi_n(\theta_j) \rangle, \qquad (139)$$

and we have enforced periodic boundary conditions on the wavefunction gauge,

$$|\psi_n(\theta_{M+1})\rangle = |\psi_n(\theta_1)\rangle. \qquad (140)$$

Note that γ is a well-defined physical observable in spite of the arbitrariness of the wavefunction phases,[32] and vanishes identically in the absence of an applied magnetic field. The strategy taken by CT was to assume that a small uniform $\mathbf{B}$-field, oriented along the rotation axis, was applied in the calculation of the instantaneous ground states that define γ. In particular, one can introduce the Berry curvature that is associated with the two-dimensional parameter space (B, θ),

$$\Omega_{B\theta} = -2 \, \text{Im} \sum_n \langle \psi_n^{(B)} | \psi_n^{(\theta)} \rangle, \qquad (141)$$

where the superscripts indicate the first-order wavefunctions with respect to either B or θ. These, in turn, can be written as sums over conduction states,

$$|\psi_n^{(\lambda)}\rangle = \sum_c |\psi_c\rangle \frac{\langle \psi_c | \partial \hat{\mathcal{H}} / \partial \lambda | \psi_n \rangle}{\epsilon_n - \epsilon_c}, \qquad (142)$$

where $\partial \hat{\mathcal{H}} / \partial \lambda$ is, as usual, the variation of the Hamiltonian at linear order in the perturbation parameter. It is easy then to show[32] that, at linear order in B, γ is the flux of $\Omega_{B\theta}$ through the rectangle spanned by B and 2π,

$$\gamma = 2\pi B \Omega_{B\theta}. \qquad (143)$$

In order to recast the above result into the formalism developed in this work, we shall choose an electromagnetic gauge for the vector potential such that

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \qquad (144)$$

where $\mathbf{B} = (0, 0, B)$ and the coordinate origin coincides with the rotation axis of the molecule. (γ, of course, does not depend on the electromagnetic gauge; the above choice has been made in order to facilitate the analytic derivations that follow.) Then, the first-order Hamiltonian with respect to the external $\mathbf{B}$ is

$$\hat{\mathcal{H}}^{(B)} = \frac{1}{2} \hat{z} \cdot \int \mathbf{r} \times \hat{\mathcal{J}}(\mathbf{r}) d^3 r, \qquad (145)$$

where $\mathcal{J}(\mathbf{r})$ is the current-density operator in the Cartesian frame, and $\hat{z}$ is a unit vector oriented along z.

One can then write

$$\langle \psi_n^{(B)} | \psi_n^{(\theta)} \rangle = -\frac{i}{2} \hat{z} \cdot \int d^3 r \, \mathbf{r} \times \langle \psi_n | \hat{\mathcal{J}}(\mathbf{r}) | \delta \psi_n^{(\theta)} \rangle, \quad (146)$$

where $|\delta \psi_n^{(\theta)}\rangle$ is the adiabatic counterpart of the first-order wavefunction $|\psi_n^{(\theta)}\rangle$. We can recognize, in the integral, the microscopic current-density field that is induced by a uniform rotation of the molecule,

$$\frac{\partial \mathbf{J}(\mathbf{r})}{\partial \dot{\theta}} = 2 \, \text{Re} \sum_n \langle \psi_n | \hat{\mathcal{J}}(\mathbf{r}) | \delta \psi_n^{(\theta)} \rangle. \qquad (147)$$

Then γ can be readily rewritten, in the linear regime, as

$$\gamma = \pi B \hat{z} \cdot \int \mathbf{r} \times \frac{\partial \mathbf{J}(\mathbf{r})}{\partial \dot{\theta}} d^3 r, \qquad (148)$$

i.e. it is proportional to the z-component of the electronic magnetic moment, $\mathbf{m}$, that is associated with the rotation,

$$\gamma = \pi B \frac{\partial m_z}{\partial \dot{\theta}}. \qquad (149)$$

This also implies that

$$\Omega_{B\theta} = \frac{1}{2} \frac{\partial m_z}{\partial \dot{\theta}}. \qquad (150)$$

To summarize, γ tells us the electronic contribution to the magnetic moment associated with the rotation of the molecule, which could be combined with the trivial contribution from the nuclear motion to compute the g-factor of the molecule as a whole. Interestingly, though, the same γ is also closely related the the magnetic susceptibilty of the static molecule. In particular, an earlier work[33] demonstrated that the quantity we call γ corresponds to the *paramagnetic* part of the susceptibility of the molecule. The theory developed here nicely fits with this result.

To see this, note that in the theory of molecular magnetic susceptibility, the "diamagnetic" contribution is defined such that it is given by the second moment of the ground-state electronic density, and the "paramagnetic part" is defined as the remainder. As we have discussed in Sec. II B 2, a uniform rotation at a frequency ω produces, in the rotating frame that is rigid with the molecule, the same effects (at linear order) as a uniform B-field, i.e., the sum of the diamagnetic and paramagnetic pieces just discussed. To get the total moment in the laboratory frame, as reflected in γ, we have to add to this a trivial piece coming from the rigid rotation of the ground-state electronic cloud, which is just minus the diamagnetic contribution to the susceptibility. Thus, it follows that γ corresponds precisely to the paramagnetic part of the magnetic susceptibility of the molecule.

Of course, the case of a molecule is relatively simple to deal with. Being an isolated object, it does not present serious technical issues no matter how the calculation is carried out (either by using the Ceresoli and Tosatti approach, or the linear response to B as discussed in the above paragraphs). It would be interesting, however, to explore these ideas in the case of extended solids, where

orbital magnetic effects associated with zone-center optical phonons have received some attention in the past. In an infinite crystal, a finite magnetic field (which CT used for calculating γ via the Berry phase approach) is far less obvious to apply, and our linear-response strategy may prove handy. We shall leave this interesting topic for future investigations.

VI. CONCLUSIONS AND OUTLOOK

In summary, we have established a full-fledged quantum theory of inhomogeneous mechanical deformations, by working within a linear-response density-functional framework. An intimate and unsuspected connection to orbital magnetism has emerged, where the latter naturally enters as a consequence of a dynamically applied deformation of the crystal. This effect produces a contribution to the bulk flexoelectric coefficient that corresponds to the orbital magnetic susceptibility of the material.

An obvious question that may be asked is whether this unusual interplay of elasticity and magnetism can lead to interesting new physics, beyond the topics that we discussed in this work, in terms of experimentally measurable effects. We believe that the best candidates may be magnetic materials in a proximity of a phase transition to a ferromagnetic state, where the susceptibility peaks to huge values. However, ferromagnetism only occurs in presence of spins, and whether deformations affect the spin degree of freedom in the same way we have shown for the orbital ones, still remains to be seen. Interest in this mechanism has been growing in the past few years, with the proposal that surface acoustic waves may be used to manipulate the magnetic state of nanoparticles.[34] Thus, we regard this as a stimulating avenue for future research.

In the context of flexoelectricity, we expect that this work will provide substantial simplifications to the practical calculation of the bulk flexoelectric tensor. Indeed, the static part of the first-order Hamiltonian can be regarded as a monochromatic "metric" perturbation, which, after an appropriate long-wave expansion, should directly yield the desired physical constants. The method is straightforward to incorporate in a standard linear-response code by following the prescriptions of Appendix B. Further details on the implementation and testing will be provided in a forthcoming communication.

Appendix A: Derivation of the curvilinear-frame Schrödinger equation

In this Appendix we shall back up the results of Sec. II A with a more detailed derivation.

1. Potential term

The potential $V(\mathbf{r}, t)$ generally contains contributions from the external potential of the nuclei, plus self-consistent Hartree and exchange and correlation terms. As in this manuscript we have assumed an all-electron framework, the external potential is that of the nuclear point charges. Thus, $V(\mathbf{r}, t)$ reduces to an electrostatic (Hartree) term plus the exchange and correlation potential,

$$V(\mathbf{r}, t) = V_{\mathrm{H}}(\mathbf{r}, t) + V_{\mathrm{XC}}(\mathbf{r}, t), \tag{A1}$$

where V_{H} is the solution of the following Poisson's equation,

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi[n_{\mathrm{el}}(\mathbf{r}) - \rho_{\mathrm{ion}}(\mathbf{r})]. \tag{A2}$$

Here ρ_{ion} is a sum of delta functions representing the nuclei, $n_{\mathrm{el}}(\mathbf{r}) = |\psi(\mathbf{r})|^2$ the electronic *particle* density, and V_{XC} is the functional derivative of the exchange and correlation energy with respect to the electron density,

$$V_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}}{\delta n_{\mathrm{el}}(\mathbf{r})}. \tag{A3}$$

The transformation to a curvilinear coordinate system is relatively easy for both the electrostatic and exchange and correlation terms. First, we introduce the electron density in the curvilinear frame,

$$\tilde{n}_{\mathrm{el}}(\boldsymbol{\xi}, t) = |\tilde{\psi}(\boldsymbol{\xi}, t)|^2 = h^{-1}(\boldsymbol{\xi}, t)\, n_{\mathrm{el}}(\mathbf{r}(\boldsymbol{\xi}, t), t), \tag{A4}$$

where we have used the shortcut $h = \det(\mathbf{h})$. Then, the Poisson's equation in the curvilinear frame becomes

$$\partial_\alpha(h g^{\alpha\beta} \partial_\beta V_{\mathrm{H}}) = -4\pi(\tilde{n}_{\mathrm{el}} - \tilde{\rho}_{\mathrm{ion}}), \tag{A5}$$

where $\partial_\alpha = \partial/\partial\xi_\alpha$ is the gradient operator in $\boldsymbol{\xi}$-space, $\tilde{\rho}_{\mathrm{ion}} = h^{-1}\rho_{\mathrm{ion}}$, and

$$g^{\alpha\beta} = (\mathbf{g}^{-1})_{\alpha\beta} \tag{A6}$$

is the inverse of the metric tensor. This means that, from the point of view of the electrostatics, the curvilinear frame is essentially equivalent to a Cartesian frame, with one exception: the vacuum permittivity, ϵ_0, must be replaced with a (generally anisotropic) dielectric tensor, $\boldsymbol{\epsilon}$, that in turn depends on the metric of the deformation

as $\boldsymbol{\epsilon} = \epsilon_0 \sqrt{g}\,\mathbf{g}^{-1}$ where $g = \det \mathbf{g} = h^2$. The exchange and correlation energy, at the level of the local density approximation, can be written as

$$E_{\mathrm{XC}} = \int d^3r \, n_{\mathrm{el}}(\mathbf{r})\epsilon_{\mathrm{XC}}(n_{\mathrm{el}}(\mathbf{r}))$$
$$= \int d^3\xi \, \tilde{n}_{\mathrm{el}}(\boldsymbol{\xi})\epsilon_{\mathrm{XC}}(h^{-1}(\boldsymbol{\xi})\,\tilde{n}_{\mathrm{el}}(\boldsymbol{\xi})), \qquad (A7)$$

which leads to a straightforward expression for the potential.

2. Kinetic term

To derive the kinetic contribution to $\hat{\tilde{H}}$, one can start from the Laplace-Beltrami operator and apply it to the curvilinear representation of the wavefunction,

$$\nabla^2\psi(\mathbf{r},t) = \frac{1}{h}\partial_\alpha\left[hg^{\alpha\beta}\partial_\beta\left(\frac{1}{\sqrt{h}}\tilde{\psi}(\boldsymbol{\xi},t)\right)\right]. \qquad (A8)$$

After some tedious (but otherwise straightforward) algebra, one obtains

$$-\frac{1}{2}\nabla^2\psi(\mathbf{r},t) = \frac{1}{2\sqrt{h}}(\hat{\tilde{p}}_\beta - i\mathcal{A}_\beta)g^{\beta\gamma}(\hat{\tilde{p}}_\gamma + i\mathcal{A}_\gamma)\tilde{\psi}(\boldsymbol{\xi},t), \qquad (A9)$$

where $\hat{\tilde{p}}_\alpha = -i\partial_\alpha$ is the canonical momentum operator in $\boldsymbol{\xi}$-space, and $\mathcal{A}_\alpha$ is the auxiliary vector field defined in Eq. (11). This result almost exactly matches the expression derived by Gygi[8], except for a sign discrepancy in the contribution of the "vector potential" $\mathcal{A}_\beta$ [see Eq. (7) therein]. One can then rewrite the kinetic contribution to $\hat{\tilde{H}}$ as

$$\frac{1}{2}(\hat{\tilde{p}}_\beta - i\mathcal{A}_\beta)g^{\beta\gamma}(\hat{\tilde{p}}_\gamma + i\mathcal{A}_\gamma) = \frac{1}{2}\hat{\tilde{p}}_\beta g^{\beta\gamma}\hat{\tilde{p}}_\gamma + V_{\mathrm{geom}}(\boldsymbol{\xi}),$$

where $V_{\mathrm{geom}}(\boldsymbol{\xi})$ corresponds to Eq. (10). Thus, the auxiliary field $\boldsymbol{\mathcal{A}}$ does not really act as a vector, but rather as a scalar potential. Note that the $\boldsymbol{\mathcal{A}}$-field essentially coincides (apart from a factor of $1/2$ with the contracted Christoffel symbol $\Gamma^\mu_{\mu\nu}$; thus, the operator $\hat{p}_\gamma + i\mathcal{A}_\gamma$ can be thought as a sort of covariant derivative[8] acting on the electronic wavefunctions.

3. Time derivative

Our starting point is

$$i\frac{\partial}{\partial t}\psi(\mathbf{r},t) = i\frac{\partial}{\partial t}\left[\sqrt{|\mathbf{h}^{-1}(\mathbf{r},t)|}\tilde{\psi}\left(\boldsymbol{\xi}(\mathbf{r},t),t\right)\right], \qquad (A10)$$

where $\boldsymbol{\xi}(\mathbf{r},t)$ is the *inverse* coordinate transformation from $\mathbf{r}$-space to $\boldsymbol{\xi}$-space, and

$$h^{-1}_{\beta\gamma} = \frac{\partial\xi_\beta(\mathbf{r},t)}{\partial r_\gamma}. \qquad (A11)$$

Now observe that

$$\boldsymbol{\xi}(\mathbf{r}(\boldsymbol{\xi},t),t) = \boldsymbol{\xi}, \qquad (A12)$$

which implies that

$$\left.\frac{\partial\xi_\beta}{\partial t}\right|_{\mathbf{r}} = -\frac{\partial\xi_\beta}{\partial r_\gamma}\left.\frac{\partial r_\gamma}{\partial t}\right|_{\boldsymbol{\xi}}. \qquad (A13)$$

(Note that the time derivative on the left-hand side has to be taken at fixed $\mathbf{r}$, while the time derivative on the right-hand side is at fixed ξ – this is usually obvious, we made it explicit here to avoid possible sources of confusion.)

We shall derive things piece by piece. First, the derivative of the wavefunction,

$$\left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\mathbf{r}} = \left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\boldsymbol{\xi}} + \frac{\partial\tilde{\psi}}{\partial\xi_\beta}\left.\frac{\partial\xi_\beta}{\partial t}\right|_{\mathbf{r}}, \qquad (A14)$$

by using Eq. (A13) becomes

$$\left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\mathbf{r}} = \left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\boldsymbol{\xi}} - \frac{\partial\tilde{\psi}}{\partial\xi_\beta}\frac{\partial\xi_\beta}{\partial r_\gamma}\left.\frac{\partial r_\gamma}{\partial t}\right|_{\boldsymbol{\xi}}. \qquad (A15)$$

We can now insert an identity operator,

$$\left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\mathbf{r}} = \left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\boldsymbol{\xi}} - \frac{\partial\tilde{\psi}}{\partial\xi_\beta}\frac{\partial\xi_\beta}{\partial r_\gamma}\frac{\partial\xi_\delta}{\partial r_\gamma}\frac{\partial r_\lambda}{\partial\xi_\delta}\left.\frac{\partial r_\lambda}{\partial t}\right|_{\boldsymbol{\xi}}, \qquad (A16)$$

and finally rewrite the above as

$$\left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\mathbf{r}} = \left.\frac{\partial\tilde{\psi}}{\partial t}\right|_{\boldsymbol{\xi}} - A_\beta g^{-1}_{\beta\gamma}\frac{\partial\tilde{\psi}}{\partial\xi_\gamma}. \qquad (A17)$$

where A_β is the effective vector potential of Eq. (13). Second, the time derivative of the volume prefactor reads as

$$\frac{\partial}{\partial t}\frac{1}{\sqrt{h}}\bigg|_{\mathbf{r}} = -\frac{1}{2h\sqrt{h}}\frac{\partial h}{\partial t}\bigg|_{\mathbf{r}} = -\frac{1}{2h\sqrt{h}}\left(\frac{\partial h}{\partial t}\bigg|_{\boldsymbol{\xi}} + \frac{\partial h}{\partial\xi_\beta}\frac{\partial\xi_\beta}{\partial t}\bigg|_{\mathbf{r}}\right). \qquad (A18)$$

By using again Eq. (A13), this leads to

$$\frac{\partial}{\partial t}\frac{1}{\sqrt{h}}\bigg|_{\mathbf{r}} = -\frac{1}{2h\sqrt{h}}\left(\frac{\partial h}{\partial t}\bigg|_{\boldsymbol{\xi}} - \frac{\partial h}{\partial\xi_\beta}\frac{\partial\xi_\beta}{\partial r_\lambda}\frac{\partial r_\lambda}{\partial t}\right). \qquad (A19)$$

Now, recall Jacobi's rule for the derivative of a determinant,

$$\frac{\partial h(\lambda)}{\partial\lambda} = h\,h^{-1}_{ij}\frac{\partial h_{ji}}{\partial\lambda}, \qquad (A20)$$

where λ is an arbitrary parameter on which the elements of $\mathbf{h}$ depend. This allows us to write

$$\frac{\partial}{\partial t}\frac{1}{\sqrt{h}}\bigg|_{\mathbf{r}} = -\frac{1}{2\sqrt{h}}\left(\frac{\partial\xi_i}{\partial r_\lambda}\frac{\partial^2 r_\lambda}{\partial\xi_i\partial t} - \frac{\partial\xi_i}{\partial r_j}\frac{\partial^2 r_j}{\partial\xi_i\partial\xi_\beta}\frac{\partial\xi_\beta}{\partial r_\lambda}\frac{\partial r_\lambda}{\partial t}\right). \qquad (A21)$$

At this point, observe that for a matrix $\mathbf{A}$ that depends parametrically on λ, we have

$$\frac{\partial\mathbf{A}^{-1}(\lambda)}{\partial\lambda} = -\mathbf{A}^{-1}\frac{\partial\mathbf{A}(\lambda)}{\partial\lambda}\mathbf{A}^{-1} \qquad (A22)$$

We use this relationship to observe that

$$-\frac{\partial \xi_i}{\partial r_j}\frac{\partial^2 r_j}{\partial \xi_i \partial \xi_\beta}\frac{\partial \xi_\beta}{\partial r_\lambda} = \frac{\partial}{\partial \xi_i}\left(\frac{\partial \xi_i}{\partial r_\lambda}\right). \qquad (A23)$$

This allows us to write the derivative of the volume factor in a compact form,

$$\frac{\partial}{\partial t}\frac{1}{\sqrt{h}}\bigg|_{\mathbf{r}} = -\frac{1}{2\sqrt{h}}\frac{\partial}{\partial \xi_i}\left(\frac{\partial \xi_i}{\partial r_\lambda}\frac{\partial r_\lambda}{\partial t}\right). \qquad (A24)$$

By using the quantities that we introduced earlier, we can equivalently write

$$\frac{\partial}{\partial t}\frac{1}{\sqrt{h}}\bigg|_{\mathbf{r}} = -\frac{1}{2\sqrt{h}}\frac{\partial}{\partial \xi_\beta}\left(g_{\beta\gamma}^{-1}A_\gamma\right). \qquad (A25)$$

After few straightforward steps of algebra, one finally arrives at

$$i\frac{\partial \psi}{\partial t}\bigg|_{\mathbf{r}} = \frac{i}{\sqrt{h}}\frac{\partial \tilde{\psi}}{\partial t}\bigg|_{\boldsymbol{\xi}} + \frac{1}{2\sqrt{h}}\left(A_\beta g_{\beta\gamma}^{-1}\hat{\tilde{p}}_\gamma + \hat{\tilde{p}}_\beta g_{\beta\gamma}^{-1}A_\gamma\right)\tilde{\psi}. \qquad (A26)$$

Then, by observing that the effective scalar potential of Eq. (12) can also be written as

$$\phi = A_\beta g_{\beta\gamma}^{-1}A_\gamma, \qquad (A27)$$

one can combine Eq. (A26) with the kinetic terms that we have derived in the previous subsection, leading to Eq. (9).

Appendix B: Static perturbation in the linear regime

In this Appendix we shall provide an explicit expression for the "static" perturbation of Sec. III D 1, in the specific case of a monochromatic perturbation at wavevector $\mathbf{q}$. We shall also show that it reduces to Hamann's metric perturbation at first order in $\mathbf{q}$.

The first-order Hamiltonian can be decomposed as follows,

$$\hat{\mathcal{H}}_{\mathbf{k},\mathbf{q}}^{(\lambda_\beta)} = \hat{\mathcal{T}}_{\mathbf{k},\mathbf{q}}^{(\lambda_\beta)} + \hat{V}_{\text{geom},\mathbf{q}}^{(\lambda_\beta)} + \hat{V}_{\text{H},\mathbf{q}}^{(\lambda_\beta)} + \hat{V}_{\text{XC},\mathbf{q}}^{(\lambda_\beta)}, \qquad (B1)$$

where the four terms on the rhs are related, respectively, to the kinetic ($\hat{\mathcal{T}}$) operator, and the geometric, Hartree and exchange-correlation potentials. In the following, we shall discard all the dynamical terms that emerge from the time derivative. Note that all the operators in Eq. (B1) are cell-periodic, i.e., the static curvilinear-space Hamiltonian can be written, in the linear regime, as

$$\hat{\tilde{\mathcal{H}}}(\boldsymbol{\lambda}) = \hat{\mathcal{H}}^{(0)} + \lambda_\beta e^{i\mathbf{q}\cdot\mathbf{r}}\hat{\mathcal{H}}_{\mathbf{k},\mathbf{q}}^{(\lambda_\beta)} + \cdots. \qquad (B2)$$

Note the use of $\mathbf{r}$ instead of $\boldsymbol{\xi}$ to indicate the coordinates in curvilinear space; we shall follow this convention henceforth (and omit the tilde on the curvilinear operators). For a generic perturbation $\mathcal{O}$, we shall also use the following notation convention to distinguish the full operator from its cell-periodic part,

$$\hat{\mathcal{O}}_{\mathbf{k}}^{(\lambda_\beta)}(\mathbf{q}) = e^{i\mathbf{q}\cdot\mathbf{r}}\hat{\mathcal{O}}_{\mathbf{k},\mathbf{q}}^{(\lambda_\beta)}. \qquad (B3)$$

1. Kinetic term

The curvilinear kinetic operator can be expanded, in powers of the deformation amplitude, as

$$\hat{\mathcal{T}}_{\mathbf{k}} = \frac{\hat{p}_{\mathbf{k}}^2}{2} - \hat{p}_{\mathbf{k}\beta}\,\varepsilon_{\beta\gamma}(\mathbf{r})\,\hat{p}_{\mathbf{k}\gamma} + \cdots, \qquad (B4)$$

where $\varepsilon_{\beta\gamma}(\mathbf{r})$ is the symmetric strain tensor associated with a generic inhomogeneous deformation. In the specific case of a monochromatic displacement wave, the strain reads as

$$\varepsilon_{\beta\gamma}(\mathbf{r}) = \frac{i}{2}\left(\lambda_\beta q_\gamma + \lambda_\gamma q_\beta\right)e^{i\mathbf{q}\cdot\mathbf{r}}. \qquad (B5)$$

This immediately leads to

$$\hat{\mathcal{T}}_{\mathbf{k},\mathbf{q}}^{(\lambda_\beta)} = -\frac{i}{2}\left[(\hat{p}_{\mathbf{k}\beta} + q_\beta)\,\mathbf{q}\cdot\hat{\mathbf{p}}_{\mathbf{k}} + (\hat{\mathbf{p}}_{\mathbf{k}} + \mathbf{q})\cdot\mathbf{q}\,\hat{p}_{\mathbf{k}\beta}\right]. \qquad (B6)$$

At first order in $\mathbf{q}$, we have

$$\frac{\partial \hat{\mathcal{T}}_{\mathbf{k},\mathbf{q}}^{(\lambda_\beta)}}{\partial q_\gamma}\bigg|_{\mathbf{q}=0} = -i\,\hat{p}_{\mathbf{k}\beta}\hat{p}_{\mathbf{k}\gamma} = i\hat{\mathcal{T}}_{\mathbf{k}}^{(\beta\gamma)}, \qquad (B7)$$

where we have indicated with a superscript $(\beta\gamma)$ the response to a uniform strain, $\varepsilon_{\beta\gamma}$, within Hamann's formalism.

2. Geometric potential

By retaining only terms that are linear in the deformation amplitude, we have

$$V_{\text{geom}} = \frac{1}{2}\partial_\alpha \mathcal{A}_\alpha, \qquad \mathcal{A}_\alpha = -\frac{1}{2}\boldsymbol{\lambda}\cdot\mathbf{q}\,q_\alpha e^{i\boldsymbol{\xi}\cdot\mathbf{q}}. \qquad (B8)$$

Then, one immediately obtains

$$V_{\text{geom}}^{(\beta,\mathbf{q})} = -\frac{i}{4}q_\beta\,q^2. \qquad (B9)$$

This structureless potential is irrelevant for either the uniform strain or the strain-gradient response, as it is of third order in $\mathbf{q}$.

3. Electrostatic potential

Recall Poisson's equation in curvilinear space,

$$\partial_\alpha(hg^{\alpha\gamma}\partial_\gamma V_{\text{H}}) = -4\pi(n_{\text{el}} - \rho_{\text{ion}}). \qquad (B10)$$

In the linear limit one has

$$hg_{\alpha\gamma}^{-1} = \delta_{\alpha\gamma} + i(\boldsymbol{\lambda}\cdot\mathbf{q}\delta_{\alpha\gamma} - \lambda_\alpha q_\gamma - \lambda_\gamma q_\alpha)e^{i\mathbf{r}\cdot\mathbf{q}}, (B11)$$

$$V_{\text{H}} = V_{\text{H}}^{(0)} + \lambda_\beta e^{i\mathbf{q}\cdot\mathbf{r}}V_{\text{H},\mathbf{q}}^{(\lambda_\beta)}, \qquad (B12)$$

$$n_{\text{el}} = n_{\text{el}}^{(0)} + \lambda_\beta e^{i\mathbf{q}\cdot\mathbf{r}}n_{\text{el},\mathbf{q}}^{(\lambda_\beta)}. \qquad (B13)$$

(Note that the ionic point charges do not move within the curvilinear frame; thus, their density, ρ_{ion}, is unsensitive to the deformation.) By collecting the terms that are linear in λ_β, and by following analogous derivation steps as in Ref. 3, we have

$$|\boldsymbol{\nabla} + i\mathbf{q}|^2 V_{\text{H},\mathbf{q}}^{(\lambda_\beta)} = -4\pi \left(n_{\text{el},\mathbf{q}}^{(\lambda_\beta)} + n_{\text{met},\mathbf{q}}^{(\lambda_\beta)} \right), \qquad \text{(B14)}$$

where the "metric density" $n_{\text{met},\mathbf{q}}^{(\lambda_\beta)}$ is given in terms of the ground-state Hartree potential,

$$n_{\text{met},\mathbf{q}}^{(\lambda_\beta)} = \frac{i}{4\pi}(\partial_\alpha + iq_\alpha)[\delta_{\alpha\gamma}q_\beta - \delta_{\alpha\beta}q_\gamma - \delta_{\beta\gamma}q_\alpha]\partial_\gamma V_{\text{H}}^{(0)}. \tag{B15}$$

At order zero in $\mathbf{q}$, all the scalar fields involved in Eq. (B14) manifestly vanish. (The kinetic and geometric perturbations discussed in the previous subsections both vanish, yielding a null first-order density; $n_{\text{met},\mathbf{q}}^{(\lambda_\beta)}$ vanish as well, as it has a leading dependence on $\mathbf{q}$; the first-order potential then vanishes as well as a consequence of Eq. (B14).) At first order in $\mathbf{q}$, one has

$$\nabla^2 V_{\text{H},\zeta}^{(\lambda_\beta)} = -4\pi \left(n_{\text{el},\zeta}^{(\lambda_\beta)} + n_{\text{met},\zeta}^{(\lambda_\beta)} \right), \tag{B16}$$

where we have indicated the derivatives with respect to q_ζ calculated at $\mathbf{q} = 0$ with a ζ subscript, and

$$n_{\text{met},\zeta}^{(\lambda_\beta)} = \frac{i}{4\pi} \left(\nabla^2 \delta_{\zeta\beta} - 2\partial_\zeta\partial_\beta \right) V_{\text{H}}^{(0)}. \tag{B17}$$

Finally, by expressing the cell-periodic scalar fields in Fourier space, we obtain

$$V_{\text{H},\gamma}^{(\lambda_\beta)} = \frac{4\pi}{G^2} \left[n_{\text{el},\gamma}^{(\lambda_\beta)} - in^{(0)} \left(\delta_{\beta\gamma} - 2\frac{G_\beta G_\gamma}{G^2} \right) \right], \tag{B18}$$

where $n^{(0)} = n_{\text{el}}^{(0)} - \rho_{\text{ion}}$ is the ground-state electronic density minus the ionic point-charges (i.e., it corresponds to the opposite of the total charge density of the crystal). After observing that $n_{\text{el},\gamma}^{(\lambda_\beta)} = in_{\text{el}}^{(\beta\gamma)}$, one can easily verify that the above formula coincides (modulo a factor of i) with Hamann's Eq. (57).

4. XC potential

Starting from Eq. (A7), one can write the exchange-correlation potential as

$$V_{\text{XC}}(\boldsymbol{\xi}) = \frac{\delta E_{\text{XC}}}{\delta n(\boldsymbol{\xi})} = \epsilon_{\text{XC}}(h^{-1}n) + h^{-1}n\epsilon'_{\text{XC}}(h^{-1}n). \tag{B19}$$

(The prime symbol indicates a first derivative with respect to the particle density.) After a few algebra steps, one arrives at an expression for the perturbed potential,

$$V_{\text{XC},\mathbf{q}}^{(\lambda_\beta)}(\mathbf{r}) = K_{\text{XC}}(\mathbf{r}) \left[n_{\text{el},\mathbf{q}}^{(\lambda_\beta)}(\mathbf{r}) - iq_\beta n_{\text{el}}^{(0)}(\mathbf{r}) \right], \tag{B20}$$

where

$$K_{\text{XC}} = 2\epsilon'_{\text{XC}}(n^{(0)}) + n^{(0)}\epsilon''_{\text{XC}}(n^{(0)}) \tag{B21}$$

is the exchange-correlation kernel, and the contribution that depends on $n^{(0)}$ originates from the derivative of the inverse determinant,

$$h^{-1} = 1 - i\boldsymbol{\lambda} \cdot \mathbf{q}e^{i\boldsymbol{\xi} \cdot \mathbf{q}}. \tag{B22}$$

Again, the first-order potential vanishes at $\mathbf{q} = 0$ and coincides with Hamann's metric formulation of the uniform strain perturbation at first order in $\mathbf{q}$.

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[26] We stress that the "static" and "dynamic" attributes that we use in this work in the context of the purely electronic response have nothing to do with the mass dependence of the lattice-mediated contribution, which was discussed in earlier works.[5]

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