Deformation-potential theorem in metals and in dielectrics

R. Resta*

Scuola Internazionale Superiore di Studi Avanzati (SISSA), via Beirut 4, I-34014 Trieste, Italy†
and Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA),
PHB-Ecublens, CH-1015 Lausanne, Switzerland

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Using linear response within the density-functional theory, I provide an expression of the matrix elements for electron scattering by long-wavelength phonons, both optic and acoustic. In the latter case, I prove that the matrix elements are exactly related to the strain-induced shifts of the electronic levels by the identity known as the deformation-potential theorem, and which had been demonstrated so far only for metals within the rigid- or deformable-ion models. The case of dielectrics shows additional complications due to the long-range nature of the Coulomb interaction; a generalized form of the theorem is proved in this case, where the macroscopic effects are embedded in a bulk fourth-rank tensor. The relationship to recent results on the "absolute" deformation potentials for homogeneous strain is discussed.

I. INTRODUCTION

The interaction between electrons and lattice vibrations is one of the fundamental interaction processes in solids. In 1950, Bardeen and Shockley introduced the concept of a deformation potential to describe the interaction between electrons and acoustic phonons:[1] their main conjecture—known as the "deformation-potential theorem"—relates the matrix elements of the electron-phonon interaction to the shifts of the electronic levels in crystals as functions of macroscopic strain. There have been over the years several papers about the deformation-potential theorem. In 1984, Khan and Allen[2] provided a rigorous and general proof, which, however, holds only within the rigid-ion model;[3] later, Kartheuser and Rodriguez[4] extended the proof to the deformable-ion model.[5] The simplicity of the result of Refs. 2 and 4 suggests, however, that its validity should not be limited to such oversimplified models. Once a theoretical framework is consistently established for one-electron levels in solids, the deformation-potential theorem should be proved as an *exact* result, that does not rely on any approximation: this is in fact the main issue of the present work.

The density-functional-theory (DFT) framework[6] is adopted here in order to define both the electron-phonon matrix elements and the deformation potentials. The lattice distortions induce modifications of the electronic charge of the crystal, which crucially affect the electron-lattice interaction: here this feature is dealt with exactly, within self-consistent linear-response theory, thus avoiding any shape approximations such as within the rigid- or deformable-ion models. The problem shows different aspects in metals and in dielectrics, because of qualitatively different screening properties of the Coulomb interaction, the case of metals being the simplest.

Starting with the metallic case, I provide a general expression for the electron-phonon matrix elements—valid for any Bloch state and for any long-wavelength phonon—which is formally exact in the DFT framework. The matrix elements for acoustic-phonon scattering are then related to the deformation potentials for homogeneous strain by the same identify as found—under a rather restrictive hypothesis—in Refs. 2 and 4.

As for dielectrics, additional problems arise from the long-range nature of the Coulomb interaction. First of all, some phonons may be accompanied by a macroscopic electric field: these are the longitudinal-optic phonons in polar materials and some acoustic phonons in piezoelectric material. In both such cases, the macroscopic field provides the dominant electron-scattering mechanism, and the usual macroscopic theory is *exact* (to leading order in the phonon wave vector):[7] these cases will not be further addressed in the present work. In all of the other cases, a theory of electron-phonon scattering is necessarily microscopic, but long-range Coulomb effects are responsible for nontrivial contributions.

Even in the simplest dielectrics, i.e., in nonpiezoelectric and nonpolar materials, the electron-acoustic-phonon scattering is affected by long-range features. Although this fact has been known for many years,[8,9] only recently has it been fully realized[10,11] that the deformation potentials for homogeneous strain have some fundamental difficulties, too, which can be traced back as well to the long-range nature of electron-ion interaction in dielectrics: this is the problem of the so-called "absolute" deformation potentials (ADP's) for which an important existence theorem has been recently proved.[12]

In this work I give an exact expression for the electron-phonon matrix elements in dielectrics, valid for any Bloch state and for any long-wavelength phonon, provided it does not induce a macroscopic field. These matrix elements have in general an explicit macroscopic (i.e., long-range) contribution; in the acoustic case, they cannot be related to an ordinary deformation potential. However, I show that the concept of a deformation potential can be generalized by introducing a basic fourth-rank tensor, which is a bulk material constant accounting

for all of the macroscopic effects; a generalized deformation-potential theorem is then proved for dielectrics. In the particular case of a nonpiezoelectric and nonpolar material, the present generalized deformation potentials coincide with the ADP's defined for homogeneous strain in Ref. 12. Finally, I analyze the symmetry selection rules allowing nonvanishing macroscopic contributions to electron-phonon scattering.

II. ELECTRON-PHONON MATRIX ELEMENTS

Let us consider a solid with a frozen-in monochromatic phonon of small momentum $\mathbf{q}$, defined by the ionic displacements

$$u_{ls,\alpha} = u_{s,\alpha}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_{ls}} , \tag{1}$$

where l is a lattice index, s indicates different atoms in the unit cell, and α is a Cartesian index. Such perturbation induces a variation in the electronic Hamiltonian, whose matrix elements between unperturbed band states govern the electron-phonon interaction. In this work I consistently adopt a DFT viewpoint, i.e., the one-electron Hamiltonian and eigenstates are those defined by the Kohn-Sham (KS) theory.[6] The variation in the electronic Hamiltonian coincides therefore with δV_{KS}, the self-consistent KS potential induced by the phonon. Up to linear order in the ionic displacements, we may write quite generally

$$\delta V_{\mathrm{KS}}(\mathbf{r}) = \sum_{ls} u_{ls,\alpha} v_{s,\alpha}(\mathbf{r} - \mathbf{R}_{ls}) , \tag{2}$$

where the potentials $v_{s,\alpha}(\mathbf{r} - \mathbf{R}_{ls})$, which are the basic ingredients of the present work, are defined as the linear variation of the KS potential per unit displacement in the α direction of the atom at $\mathbf{R}_{ls}$, keeping all the other atoms fixed; sum over repeated Cartesian indices is implicitly understood throughout. Expansions similar to Eq. (2) have been previously used in various circumstances.[13-15]

The electron-phonon matrix elements are by definition[1] the elements of δV_{KS} between the neighboring (in $\mathbf{k}$ space) Bloch states $\psi_{v,\mathbf{k}+\mathbf{q}}$, and $\psi_{v,\mathbf{k}}$, belonging to the same band:

$$\langle \mathbf{k}+\mathbf{q}|\delta V_{\mathrm{KS}}|\mathbf{k}\rangle = \sum_{ls} u_{ls,\alpha}\langle \mathbf{k}+\mathbf{q}|v_{s,\alpha}(\mathbf{r} - \mathbf{R}_{ls})|\mathbf{k}\rangle , \tag{3}$$

where the band index v has been omitted for the sake of simplicity.

The above Eqs. (1)–(3)—as well as some of the following ones—are similar in form to those of the rigid-ion approximation,[2,3] the important difference being that the present approach is formally *exact* within self-consistent DFT: all of the screening effects are included. I also point out that the $v_{s,\alpha}(\mathbf{r})$ are the Cartesian components of vector fields which are in general *not* curl-free,[14] and cannot therefore be expressed as gradients of scalar fields, as it is instead the case within the rigid-ion or deformable-ion models.[2,4]

Using Eq. (1) the electron-phonon matrix element are

expressed as an integral over lattice-periodical functions:

$$\langle \mathbf{k}+\mathbf{q}|\delta V_{\mathrm{KS}}|\mathbf{k}\rangle = \frac{1}{\Omega}\int_{\mathrm{cell}} d\mathbf{r}\, \varphi^*_{\mathbf{k}+\mathbf{q}}(\mathbf{r})\varphi_{\mathbf{k}}(\mathbf{r})$$
$$\times \sum_{ls} u_{s,\alpha}(\mathbf{q})$$
$$\times e^{-i\mathbf{q}(\mathbf{r}-\mathbf{R}_{ls})}v_{s,\alpha}(\mathbf{r} - \mathbf{R}_{ls}) , \tag{4}$$

where the φ's are the periodic parts of the Bloch KS orbitals, and Ω is the cell volume. Equation (4) is now recast as a Fourier series, whose terms depend parametrically on $\mathbf{q}$:

$$\langle \mathbf{k}+\mathbf{q}|\delta V_{\mathrm{KS}}|\mathbf{k}\rangle = \frac{1}{\Omega}\sum_{\mathbf{G},s} e^{-i\mathbf{G}\cdot\mathbf{R}_s}u_{s,\alpha}(\mathbf{q})\tilde{v}_{s,\alpha}(\mathbf{q}+\mathbf{G})$$
$$\times \int_{\mathrm{cell}} d\mathbf{r}\, \varphi^*_{\mathbf{k}+\mathbf{q}}(\mathbf{r})\varphi_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{G}\cdot\mathbf{r}} ; \tag{5}$$

our next task is to evaluate Eq. (5) to the leading nonvanishing order in $\mathbf{q}$. As for the amplitudes $u_{s,\alpha}(\mathbf{q})$, I perform the usual decomposition:[2,13]

$$u_{s,\alpha}(\mathbf{q}) = u_\alpha(\mathbf{q}) + \delta_{s,\alpha}(\mathbf{q}) , \tag{6}$$

where the first term is the displacement of the cell as a whole and the second term is a relative displacement. These are also called "acoustic" and "optic" components, respectively, because in the long-wavelength limit $u_\alpha(\mathbf{q})$ vanishes for optic modes and $\delta_{s,\alpha}(\mathbf{q})$ vanishes for acoustic branches.

III. METALS

Under the hypothesis that the v's are *short range* (as in metals), their Fourier transforms are *analytic:* we will remain with this hypothesis throughout this section in evaluating the low-q expansion of Eq. (5).

I start with the case of optic phonons, where the leading term is $\mathbf{q}$ independent: its expression, in terms of the zone-center displacements $\delta_{s,\alpha}$, is simply obtained from the matrix element of the *periodic* potential induced by the phonon:

$$\langle \mathbf{k}+\mathbf{q}|\delta V^{(\mathrm{opt})}_{\mathrm{KS}}|\mathbf{k}\rangle$$
$$\simeq \langle \mathbf{k}|\delta V^{(\mathrm{opt})}_{\mathrm{KS}}|\mathbf{k}\rangle$$
$$= \sum_{\mathbf{G}}\left\langle \mathbf{k}\left|e^{i\mathbf{G}\cdot\mathbf{r}}\sum_s e^{-i\mathbf{G}\cdot\mathbf{R}_s}\delta_{s,\alpha}\tilde{v}_{s,\alpha}(\mathbf{G})\right|\mathbf{k}\right\rangle . \tag{7}$$

I now switch to zone-center acoustic phonons: the $u_\alpha(\mathbf{q})$ amplitude is then related to the macroscopic strain, whose (unsymmetrized) tensor is

$$\varepsilon_{\alpha\beta} = iu_\alpha(\mathbf{q})q_\beta , \tag{8}$$

and which is linear in **q**. The second term in Eq. (6) for a zone-center acoustic phonon can be expressed via the internal-strain tensor Γ as[13]

$$\delta_{s,\alpha}(\mathbf{q}) \simeq \Gamma_{s,\alpha\beta\gamma}\varepsilon_{\beta\gamma} \ . \tag{9}$$

The leading-order term in the electron-acoustic-phonon matrix element is linear in **q**. Starting from Eq. (5), its low-q expansion is performed along the same lines as for the rigid-ion approximation;[2] using Eq. (8) the linear term takes the following form:

$$\langle \mathbf{k}+\mathbf{q}|\delta V_{\mathrm{KS}}^{(\mathrm{ac})}|\mathbf{k}\rangle \simeq \varepsilon_{\alpha\beta}\left[(\langle \mathbf{k}|p_{\alpha}|\mathbf{k}\rangle\langle \mathbf{k}|p_{\beta}|\mathbf{k}\rangle - \langle \mathbf{k}|p_{\alpha}p_{\beta}|\mathbf{k}\rangle)/m_e \right.$$
$$\left. + \sum_{\mathbf{G}}\left\langle \mathbf{k}\left|e^{i\mathbf{G}\cdot\mathbf{r}}\sum_{s}e^{-i\mathbf{G}\cdot\mathbf{R}_s}\left[\Gamma_{s,\gamma\alpha\beta}\tilde{v}_{s,\gamma}(\mathbf{G}) - i\frac{\partial}{\partial G_{\beta}}\tilde{v}_{s,\alpha}(\mathbf{G})\right]\right|\mathbf{k}\right\rangle \right] \ , \tag{10}$$

where the tensor in square brackets plays the role of an effective deformation potential for electron-acoustic-phonon scattering. The internal-strain contribution to Eq. (10) is identical to the electron-optic-phonon matrix element of Eq. (7), where the amplitude of optic mode is governed by the Γ tensor.

IV. DIELECTRICS

New features arise in a dielectric material, owing to the long-range nature of the electron-ion interaction. First of all, one has to specify the boundary conditions used in defining the potentials $v_{s,\alpha}(\mathbf{r})$, or equivalently in defining the charge variations $f_{s,\alpha}(\mathbf{r})$ linearly induced by unitary ionic displacements, which generate such potentials. These quantities have been introduced by Martin in the context of piezoelectricity,[13] and subsequently used for lattice dynamics.[14,15] Following Martin, I impose the electrical condition that the displacements are performed at zero macroscopic field: under such hypothesis, the $f_{s,\alpha}(\mathbf{r})$ are short range and their Fourier transforms are analytic.

It follows that the $v_{s,\alpha}(\mathbf{q}+\mathbf{G})$ are analytic at $\mathbf{G}\neq0$; as for the $\mathbf{G}=0$ component, we notice that the leading multipoles in the induced charge densities $f_{s,\alpha}(\mathbf{r})$ are either dipoles (in polar lattices), quadrupoles (in diamond lattice[8,9]), or octupoles (in Bravais lattices). The small-q expansion of the potentials has therefore the following *nonanalytic* form:

$$\tilde{v}_{s,\alpha}(\mathbf{q}) \simeq \frac{4\pi e}{q^2}\left[-iQ_{s,\alpha\beta}^{(1)}q_{\beta} - \tfrac{1}{2}Q_{s,\alpha\beta\gamma}^{(2)}q_{\beta}q_{\gamma} \right.$$
$$\left. + \frac{i}{6}Q_{s,\alpha\beta\gamma\delta}^{(3)}q_{\beta}q_{\gamma}q_{\delta} \right] \ , \tag{11}$$

where the 2^j-polar tensors $Q^{(j)}$ are well-defined linear-response properties of the bulk; they have rank $j+1$ and will be assumed symmetric only in their last j indices. The dipoles are nothing else than the Born effective charge tensors; because of charge neutrality, they obey the acoustic-sum rule[16]

$$\sum_{s}Q_{s,\alpha\beta}^{(1)}=0 \ . \tag{12}$$

The expansion of Eq. (11) includes nonelectrostatic contributions—such as due to exchange-correlation effects—which are expected to be analytic: this means, e.g., that the quadrupole $Q^{(2)}$ is in general *not* traceless, and its trace provides indeed, after Eq. (11), the leading (zero-order in q) short-range contribution to $v_{s,\alpha}(\mathbf{q})$.

Strictly speaking, the electrical condition cannot be formulated as a boundary condition independent of geometry; this fact, however, does not cause any harm,[13] provided our basic ingredients $v_{s,\alpha}(\mathbf{q}+\mathbf{G})$ are used *only* for phonons which do not induce a macroscopic field in the long-wavelength limit. Whenever a macroscopic field is present, the $v_{s,\alpha}(\mathbf{q}+\mathbf{G})$ are nonanalytic even at $\mathbf{G}\neq0$: this nontrivial fact—although awkward—is a well-established feature of dielectric screening in periodic insulating media,[16] and can be explained in terms of local-field effects.[17,18]

Therefore the present microscopic theory does *not* apply either to LO phonons in polar materials, or to piezoelectric acoustic phonons; this is not a severe limitation indeed, since in these cases electron-phonon scattering is dominated by the macroscopic field,[7] and the phenomenological macroscopic theory is exact to leading order. For all of the other cases, I develop a microscopic theory starting again from Eq. (5), and using Eq. (11) in its $\mathbf{G}=0$ term; the long-wavelength limit is evaluated keeping q in the actual direction, of the phonon wave vector. To this aim, I write $\mathbf{q}=q\hat{\mathbf{q}}$ and I perform a low-q expansion at fixed $\hat{\mathbf{q}}$; Eq. (11) is then conveniently rewritten as

$$\tilde{v}_{s,\alpha}(q\hat{\mathbf{q}}) \simeq 4\pi e\left[-\frac{i}{q}Q_{s,\alpha\beta}^{(1)}\hat{q}_{\beta} - \tfrac{1}{2}Q_{s,\alpha\beta\gamma}^{(2)}\hat{q}_{\beta}\hat{q}_{\gamma} \right.$$
$$\left. + \frac{i}{6}qQ_{s,\alpha\beta\gamma\delta}^{(3)}\hat{q}_{\beta}\hat{q}_{\gamma}\hat{q}_{\delta} \right] \ . \tag{13}$$

Starting again with the case of zone-center optic phonons, I explicitly separate the $\mathbf{G}=0$ term, where Eq. (13) is used in performing the long-wavelength limit. The result is

$$\langle \mathbf{k}+\mathbf{q}|\delta V_{KS}^{(opt)}|\mathbf{k}\rangle \simeq -\frac{2\pi e}{\Omega}\sum_s Q_{s,\alpha\beta\gamma}^{(2)}\delta_{s,\alpha}\hat{q}_\beta\hat{q}_\gamma + \sum_\mathbf{G}{}'\left\langle\mathbf{k}\left|e^{i\mathbf{G}\cdot\mathbf{r}}\sum_s e^{-i\mathbf{G}\cdot\mathbf{R}_s}\delta_{s,\alpha}\tilde{v}_{s,\alpha}(\mathbf{G})\right|\mathbf{k}\right\rangle , \tag{14}$$

with the usual meaning of the primed sum; the two terms in Eq. (14) will be referred to as macroscopic and microscopic, respectively. The dipoles $Q^{(1)}$ from Eq. (13) would apparently contribute a $1/q$ term, which in fact vanishes because of the zero-field condition. For a cubic binary material this is easily understood[17] either because the displacements are orthogonal to $\mathbf{q}$ (in the TO case), or because of the acoustic-sum rule, Eq. (12) (in the LO case for nonpolar materials, like diamond). The macroscopic term in Eq. (14) is identical to the result given in Ref. 9 for nonpolar semiconductors.

Both the terms in Eq. (14) are of zero order in $\mathbf{q}$, but the macroscopic one displays explicit dependence upon the direction of the phonon wave vector. The microscopic term, instead, is independent of such direction: It does not show new features with respect to the short-range case, Eq. (7), and can be easily evaluated via, e.g., a self-consistent frozen-phonon calculation at the zone center.

Switching now to the acoustic case, I express the macroscopic term as

$$\frac{1}{\Omega}\sum_s u_{s,\alpha}(\mathbf{q})v_{s,\alpha}(\mathbf{q}) \simeq \frac{4\pi e}{\Omega}\sum_s (u_\alpha+iq\Gamma_{s,\alpha\beta\gamma}u_\beta\hat{q}_\gamma)\left[-\frac{i}{q}Q_{s,\alpha\beta}^{(1)}\hat{q}_\beta - \frac{1}{2}Q_{s,\alpha\beta\gamma}^{(2)}\hat{q}_\beta\hat{q}_\gamma + \frac{i}{6}qQ_{s,\alpha\beta\gamma\delta}^{(3)}\hat{q}_\beta\hat{q}_\gamma\hat{q}_\delta\right]$$

$$\simeq C_{-1}(\hat{q})q^{-1}+C_0(\hat{q})+C_1(\hat{q})q , \tag{15}$$

where Eqs. (8) and (9) have been used in the long-wavelength limit. The C_{-1} coefficients vanish because of the acoustic sum rule, Eq. (12); the following term is

$$C_0(\hat{q})=\frac{4\pi e}{\Omega}\left[\sum_s \Gamma_{s,\delta\alpha\beta}Q_{s,\delta\gamma}^{(1)} - \tfrac{1}{2}\sum_s Q_{s,\alpha\beta\gamma}^{(2)}\right]u_\alpha\hat{q}_\beta\hat{q}_\gamma , \tag{16}$$

where the quantity in large parentheses is easily related to the microscopic expression for the piezoelectric tensor.[13] For nonpiezoelectric materials (or more generally for nonpiezoelectric phonons) C_0 vanishes; we thus remain in Eq. (15) with the term linear in q, which I cast as

$$\frac{1}{\Omega}\sum_s u_{s,\alpha}(\mathbf{q})v_{s,\alpha}(\mathbf{q}) \simeq \varepsilon_{\alpha\beta}\mathcal{D}_{\alpha\beta\gamma\delta}\hat{q}_\gamma\hat{q}_\delta , \tag{17}$$

and where the fourth-rank tensor $\mathcal{D}$ is

$$\mathcal{D}_{\alpha\beta\gamma\delta}=\frac{4\pi e}{\Omega}\left[-\tfrac{1}{2}\sum_s \Gamma_{s,\eta\alpha\beta}Q_{\eta\gamma\delta}^{(2)} + \tfrac{1}{6}\sum_s Q_{s,\alpha\beta\gamma\delta}^{(3)}\right] . \tag{18}$$

This tensor is a well-defined bulk material property, which accounts for all of the macroscopic effects in the acoustic-phonon scattering; it was originally introduced in Ref. 12 in order to deal with ADP's.[19] All of the other terms in Eq. (10) are not affected by long-range features: I thus arrive at the final form for the electron-acoustic-phonon matrix element:

$$\langle \mathbf{k}+\mathbf{q}|\delta V_{KS}^{(ac)}|\mathbf{k}\rangle \simeq \varepsilon_{\alpha\beta}\left[(\langle\mathbf{k}|p_\alpha|\mathbf{k}\rangle\langle\mathbf{k}|p_\beta|\mathbf{k}\rangle - \langle\mathbf{k}|p_\alpha p_\beta|\mathbf{k}\rangle)/m_e + \mathcal{D}_{\alpha\beta\gamma\delta}\hat{q}_\gamma\hat{q}_\delta\right.$$

$$\left. + \sum_\mathbf{G}{}'\left\langle\mathbf{k}\left|e^{i\mathbf{G}\cdot\mathbf{r}}\sum_s e^{-i\mathbf{G}\cdot\mathbf{R}_s}\left[\Gamma_{s,\gamma\alpha\beta}\tilde{v}_{s,\gamma}(\mathbf{G}) - i\frac{\partial}{\partial G_\beta}\tilde{v}_{s,\alpha}(\mathbf{G})\right]\right|\mathbf{k}\right\rangle\right] . \tag{19}$$

The above formulation applies either to LA or TA phonons; in both cases the effective deformation potential for acoustic-phonon scattering has a macroscopic term which depends explicitly upon the direction of the phonon wave vector, via the $\mathcal{D}$ tensor in Eq. (19). Here again we notice that the internal-strain contribution to Eq. (19) is identical to the electron-optic-phonon matrix element of Eq. (14), both in its macroscopic and microscopic terms.

The macroscopic contribution to electron-phonon scattering in nonpolar semiconductors has been previously studied by Lawaetz;[9] his result shows a different $\hat{q}$ dependence than in Eq. (19). The reasons can be traced back to an incorrect long-wavelength limit, which is *not* performed (see Appendix B in Ref. 9) at fixed $\hat{q}$, as is the case here.

V. DEFORMATION POTENTIALS

I analyze here the useful concept,[1] known as the deformation-potential theorem, that the electron-acoustic-phonon matrix element is directly related to the shift in energy of the relevant electronic level with an externally imposed strain of the same symmetry as the

acoustic phonon: I study therefore the case of homogeneous strain for the macroscopic system.

In the previous section I have pointed out delicate features in performing the long-wavelength limit: in the case of homogeneous macroscopic strain, related features show up in performing the thermodynamic limit to the infinite system. In order to perform such a limit, let us start with a large, but *finite* system within periodic boundary conditions: The Bloch states are therefore labeled with the *discrete* $\mathbf{k}_i$ quantum numbers. The derivative of the band energy with respect to macroscopic strain, for a given i, is by definition the deformation potential:

$$D_{\alpha\beta}(\mathbf{k}_i) = \partial E(\mathbf{k}_i)/\partial\varepsilon_{\alpha\beta} = \langle \mathbf{k}_i | (\partial V_{KS}/\partial\varepsilon_{\alpha\beta}) | \mathbf{k}_i \rangle \ , \quad (20)$$

where the second equality stems from first-order perturbation theory. I use now the basic decomposition, Eq. (2), where the displacements corresponding to a homogeneous deformation are[13]

$$u_{ls,\alpha} = R_{ls,\beta}\varepsilon_{\alpha\beta} + \Gamma_{s,\alpha\beta\gamma}\varepsilon_{\beta\gamma} \ , \quad (21)$$

and the second term accounts for internal strain. We thus get

$$D_{\alpha\beta}(\mathbf{k}_i) = \left\langle \mathbf{k}_i \left| \sum_{ls} [R_{ls,\beta}v_{s,\alpha}(\mathbf{r}-\mathbf{R}_{ls}) \right.\right.$$
$$\left.\left. + \Gamma_{s,\gamma\alpha\beta}v_{s,\gamma}(\mathbf{r}-\mathbf{R}_{ls})] \right| \mathbf{k}_i \right\rangle \ , \quad (22)$$

where the first term in square brackets is an ill-defined operator when acting upon Bloch functions. However, this problem is overcome via some standard manipulations,[1] starting from the identity $R_{ls,\beta} = x_\beta - (\mathbf{r}-\mathbf{R}_{ls})_\beta$, and using the "scaling" trick:[20]

$$\left\langle \mathbf{k}_i \left| x_\beta \sum_{ls} v_{s,\alpha}(\mathbf{r}-\mathbf{R}_{ls}) \right| \mathbf{k}_i \right\rangle = -\langle \mathbf{k}_i | p_\alpha p_\beta | \mathbf{k}_i \rangle/m_e \ . \quad (23)$$

The deformation potential is therefore cast as the matrix element of a lattice-periodical operator, and the Bloch quantum number can be safely taken as continuous:

$$D_{\alpha\beta}(\mathbf{k}) = \left\langle \mathbf{k} \left| \left[-p_\alpha p_\beta/m_e \right.\right.\right.$$
$$+ \sum_{ls} [\Gamma_{s,\gamma\alpha\beta}v_{s,\gamma}(\mathbf{r}-\mathbf{R}_{ls})$$
$$\left.\left.\left. - (\mathbf{r}-\mathbf{R}_{ls})_\beta v_{s,\alpha}(\mathbf{r}-\mathbf{R}_{ls})] \right] \right| \mathbf{k} \right\rangle \ . \quad (24)$$

In the *metallic* case, i.e., for short-range interactions, Eq. (24) is easily transformed into a Fourier series; comparison with Eq. (10) yields

$$\langle \mathbf{k}+\mathbf{q} | \delta V_{KS}^{(ac)} | \mathbf{k} \rangle$$
$$\simeq \varepsilon_{\alpha\beta}[D_{\alpha\beta}(\mathbf{k}) + \langle \mathbf{k}|p_\alpha|\mathbf{k}\rangle\langle \mathbf{k}|p_\beta|\mathbf{k}\rangle/m_e] \ . \quad (25)$$

This is in fact the deformation-potential theorem, demonstrated in the rigid-ion model[3] by Khan and Allen,[2] extended to the deformable-ion model[5] by Kartheuser and

Rodriguez,[4] and which I have proved here to be *exact* in the DFT framework for any metallic system.

The next step amounts to investigating the thermodynamic limit of Eq. (24) for dielectrics, where—owing to the long-range nature of Coulomb interaction—the lattice sum is conditionally convergent. When transforming Eq. (24) into a Fourier series, the (state-independent) $\mathbf{G}=0$ term is ill defined: this is in fact known as the ADP problem in insulators and semiconductors, for which some theoretical advances have been recently achieved.[11,12] The difficulty can be traced back to the well-known fact that the average of the electrostatic potential is ill defined in an infinite solid, and no absolute scale exists for the one-electron band energies.[21]

We have recently demonstrated an important existence theorem[12] about ADP's, which holds for a specific class of materials *and* for a specific class of strain tensors. As for the material properties, two conditions are necessary and sufficient in order for the ADP's to be well defined: (i) all the individual Born effective charge tensors $Q_{s,\alpha\beta}^{(1)}$ individually vanish; (ii) the sum over s of the quadrupoles $Q_{s,\alpha\beta\gamma}^{(2)}$ vanishes. These two conditions are equivalent to requiring that the material is nonpolar and nonpiezoelectric.[22] In such materials, the existence of the ADP's has been demonstrated in Ref. 12 for *uniaxial* macroscopic strain (along an arbitrary axis $\hat{n}$), where the tensor has the form $\varepsilon_{\alpha\beta} = \varepsilon\hat{n}_\alpha\hat{n}_\beta$: We notice that this is exactly the kind of strain induced by a long-wavelength LA phonon, whose $\mathbf{q}$ vector is along $\hat{n}$. For this class of strain tensors, the ADP $dE(\mathbf{k})/d\varepsilon$ is a well-defined bulk property whose expression can be cast as

$$dE(\mathbf{k})/d\varepsilon = D_{\alpha\beta}^{(bs)}(\mathbf{k})\hat{n}_\alpha\hat{n}_\beta + \mathcal{D}_{\alpha\beta\gamma\delta}\hat{n}_\alpha\hat{n}_\beta\hat{n}_\gamma\hat{n}_\delta \ . \quad (26)$$

Here the band-structure (or short-range) deformation potential for the $\mathbf{k}$ state $D_{\alpha\beta}^{(bs)}(\mathbf{k})$ is a genuine ($\hat{n}$-independent) bulk second-rank tensor, which can be easily evaluated from a standard self-consistent calculation performed for the periodic solid at the strained geometry. The macroscopic effects are instead state-independent and are accounted for by the second term in Eq. (26), where the same fourth-rank tensor $\mathcal{D}$ as in Eq. (18) occurs.[19]

Comparison of Eq. (26) with Eq. (19) immediately yields the generalization of Eq. (25) to insulators:

$$\langle \mathbf{k}+\mathbf{q} | \delta V_{KS}^{(ac)} | \mathbf{k} \rangle \simeq \varepsilon_{\alpha\beta}[D_{\alpha\beta}^{(bs)}(\mathbf{k}) + \mathcal{D}_{\alpha\beta\gamma\delta}\hat{q}_\gamma\hat{q}_\delta$$
$$+ \langle \mathbf{k}|p_\alpha|\mathbf{k}\rangle\langle \mathbf{k}|p_\beta|\mathbf{k}\rangle/m_e] \ . \quad (27)$$

The proof given so far only covers the LA case, but Eq. (27) is nonetheless correct for TA phonons as well. In fact—as was already outlined in Ref. 12—a more general condition on the macroscopic strain in order for the ADP's to exist is the condition of "epitaxial geometry," meaning with this term that the strained system is periodic in all the planes perpendicular to a given direction $\hat{n}$, with the same two-dimensional periodicity as the unstrained system.

The epitaxial geometry is the key point allowing the conditionally convergent lattice sums in Eq. (24) to have

a well-defined thermodynamic limit: incidentally, similar reasons allow the band offsets between two semi-infinite solids to be well defined, although the absolute position of each of the two band structures is not.[21] Analyzing now long-wavelength acoustic phonons, the strains induced by the LA and the TA modes are both epitaxial: in the latter case, the *unsymmetrized* strain of Eq. (8) has to be used in Eq. (27), which nevertheless remains valid.

I now investigate the case where the conditions (i) and (ii) given above break down: In such materials the ADP's for homogeneous strain do not exist,[12] but the electron-acoustic-phonon matrix elements are still well defined, and given by Eq. (27), provided only that the phonon itself is *nonpiezoelectric*.[22] Therefore the fourth-rank tensor $\mathcal{D}$, originally introduced to cope with the ADP's—for nonpolar and nonpiezoelectric[22] materials only—can be used indeed in any material for nonpiezoelectric-electron-phonon scattering. With this caveat in mind, Eq. (27) is the generalized deformation-potential theorem in dielectrics.

VI. SELECTION RULES

I have shown that the matrix elements for the electron-phonon scattering in dielectrics have in general a nontrivial dependence on the direction of the phonon wave vector. This feature occurs—both for optic and acoustic phonons—through a macroscopic term, which is independent of the band state $|\mathbf{k}\rangle$. I investigate here the selection rules for this macroscopic term only.

I start with the optical case, Eq. (14), where only the quadrupoles $Q_{s,\alpha\beta\gamma}^{(2)}$ govern the macroscopic term. If the site s is a center of inversion, then all the even multipoles in Eq. (11) vanish: therefore the macroscopic effect cannot contribute to optic-phonon scattering in centrosymmetric material. The highest-symmetry crystal structure allowing a nonvanishing macroscopic effect is diamond, where the quadrupole depends on a single parameter. Suppose now that we are interested only into the *average* of the matrix elements over the directions of the scattered phonon: then we get, from Eq. (14),

$$\langle \mathbf{k}+\mathbf{q} | \delta V_{KS}^{(opt)} | \mathbf{k} \rangle_{ave} \simeq -\frac{2\pi e}{3\Omega} \sum_s Q_{s,\alpha\beta\beta}^{(2)} \delta_{s,\alpha} + \sum_{\mathbf{G}}' \left\langle \mathbf{k} \left| e^{i\mathbf{G}\cdot\mathbf{r}} \sum_s e^{-i\mathbf{G}\cdot\mathbf{R}_s} \delta_{s,\alpha} \tilde{v}_{s,\alpha}(\mathbf{G}) \right| \mathbf{k} \right\rangle .$$ (28)

If the sites s have tetrahedral symmetry (such as within diamond or zinc-blende structures), then the quadrupole traces appearing in Eq. (28) are symmetry vanishing. Therefore only materials of symmetry lower than cubic may show a nonvanishing macroscopic contribution to the *spherically averaged* optic-phonon scattering cross section.

I switch now to the acoustic case, where the macroscopic effects are given by the fourth-rank tensor $\mathcal{D}$ in Eq. (18). For a centrosymmetric crystal, only the octupoles $Q_{s,\alpha\beta\gamma\delta}^{(3)}$ contribute: these, however, are in general nonzero in any lattice. For a site of cubic symmetry, the octupole depends on two independent parameters,[23] and can be decomposed into a spherical term, plus a strictly cubic correction: Only the latter is responsible for the actual $\hat{\mathbf{q}}$ dependence of the macroscopic term in the electron-

acoustic-phonon matrix elements. The term in the potential due to the spherical octupole is analytic, after Eqs. (11) and (13), and is therefore short-range, quite similar in nature to the $\mathbf{G}=0$ term occurring for metals in Eq. (10). If the site s is not a center of inversion (such as within diamond or zinc-blende structures), then both the quadrupolar and octupolar terms in Eq. (18) contribute on equal footing to the $\hat{\mathbf{q}}$ dependence of the macroscopic term in the electron-acoustic-phonon matrix elements.

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*Electronic address: RESTA@ITSSISSA.

†Permanent address.

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