








# First-principles theory of nonlinear long-range electron-phonon interaction


Matthew Houtput <sup>1,2</sup>, Luigi Ranalli <sup>2</sup>, Carla Verdi <sup>3</sup>, Serghei Klimin <sup>1</sup>, Stefano Ragni <sup>2</sup>,  
Cesare Franchini <sup>2,4</sup> and Jacques Tempere <sup>1</sup>

<sup>1</sup>*Theory of Quantum Systems and Complex Systems, Universiteit Antwerpen, B-2000 Antwerpen, Belgium*

<sup>2</sup>*Faculty of Physics, Computational Materials Physics, University of Vienna, Kolingasse 14-16, Vienna A-1090, Austria*

<sup>3</sup>*School of Mathematics and Physics, University of Queensland, Brisbane, Queensland 4072, Australia*

<sup>4</sup>*Department of Physics and Astronomy, Alma Mater Studiorum, Università di Bologna, Bologna 40127, Italy*

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Describing electron-phonon interactions in a solid requires knowledge of the electron-phonon matrix elements in the Hamiltonian. State-of-the-art first-principles calculations for the electron-phonon interaction are limited to the one-electron-one-phonon matrix element, which is suitable for harmonic materials. However, there is no first-principles theory for one-electron-two-phonon interactions, which occur in anharmonic materials with significant electron-phonon interaction such as halide perovskites and quantum paraelectrics. Here we derive an analytical expression for the long-range part of the one-electron-two-phonon matrix element, written in terms of microscopic quantities that can be calculated from first principles. We show that the long-range one-electron-two-phonon interaction is described by the derivative of the phonon dynamical matrix with respect to an external electric field. We calculate the quasiparticle energy of a large polaron including one-electron-two-phonon interaction and show that it can be written in terms of a one-electron-two-phonon spectral function  $\mathcal{T}_{\alpha\beta}(\omega)$ . We demonstrate how to calculate this spectral function and its temperature dependence for the benchmark materials LiF and KTaO<sub>3</sub>, where it turns out that the effect is very small. The first-principles framework developed in this article is general, paving the way for future calculations of one-electron-two-phonon interactions in materials where the effect may be larger.

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## I. INTRODUCTION

Electrons in a crystalline solid can interact with the lattice vibrations of the nuclei. This electron-phonon interaction is responsible for a wide range of interesting properties of materials, including formation of polarons [1–10], band-gap renormalization [11–13], conventional superconductivity [14–17], and contributions to the electrical conductivity [18–21]. In general, the Hamiltonian describing a coupled electron-phonon system consists of three contributions: the Hamiltonian of the electron system  $\hat{H}_{\text{el}}$ , the Hamiltonian of the phonon system  $\hat{H}_{\text{ph}}$ , and a term  $\hat{H}_{\text{el-ph}}$  that describes how electrons and phonons interact with each other.

Many treatments of a coupled electron-phonon system rely on the harmonic approximation, where the Hamiltonian is expanded up to lowest order in the ionic displacements. This means the phonon Hamiltonian  $\hat{H}_{\text{ph}}$  is approximated up to second order in the ionic displacements. Additionally, the electron-phonon interaction  $\hat{H}_{\text{el-ph}}$  is approximated up to first order: This is known as linear electron-phonon interaction. In the harmonic approximation, the Hamiltonian is entirely described by three inputs:  $\hat{H}_{\text{el}}$  depends only on the electron bands  $\epsilon_{\mathbf{k},n}$ ,  $\hat{H}_{\text{ph}}$  depends only on the phonon bands  $\omega_{\mathbf{q},\nu}$ , and  $\hat{H}_{\text{el-ph}}$  only depends on the electron-phonon matrix element  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$  [see also Sec. II, (2)–(4)]. This formulation can be applied in several different contexts. For example, one could choose analytic models for the electron bands, phonon bands, and electron-phonon matrix elements: In particular, the Fröhlich [3] and Holstein Hamiltonian [4,5] are both

special cases of this formulation. On the other hand, keeping  $\epsilon_{\mathbf{k},n}$ ,  $\omega_{\mathbf{q},\nu}$ , and  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$  as general functions allows one to interface the Hamiltonian with first-principles calculations. Indeed, they can represent the electron bands, phonon bands, and electron-phonon matrix elements of a specific material, which can be calculated with a first-principles code such as the Vienna Ab-initio Simulation Package (VASP) [22–24], Quantum ESPRESSO [25,26], ABINIT [27,28], EPW [29], or Perturbo [30].

Physically, the electron-phonon matrix element  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$  can be split into a long-range and a short-range contribution. In polar materials,  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$  has a  $|\mathbf{q}|^{-1}$  divergence around  $\mathbf{q} \approx \mathbf{0}$ , due to the appearance of nonzero Born effective charges: This allows long-wavelength phonons to generate macroscopic electric fields, which couple to the electrons. The  $|\mathbf{q}|^{-1}$  divergence is the long-range contribution. It is the basis for the Fröhlich Hamiltonian [3], and, in general, it has a semianalytic expression which was first calculated in Ref. [31]. In some contexts, the long-range electron-phonon interaction dominates the short-range interaction, which can then be neglected: Most notably, this happens in the large polaron problem, where the electron wave function spans numerous unit cells. Then, the electron only interacts with the  $\mathbf{q} \approx \mathbf{0}$  phonon modes, which are the modes whose momentum  $\hbar\mathbf{q}$  is nonzero but very small with respect to the edge of the Brillouin zone [3,7].

For anharmonic materials, the ionic displacements can be large, and higher-order terms in the ionic displacements should be added to both  $\hat{H}_{\text{ph}}$  and  $\hat{H}_{\text{el-ph}}$ . The higher-order terms

in  $\hat{H}_{\text{ph}}$  are due to phonon anharmonicity and manifest themselves as three-phonon interaction, four-phonon interactions, etc. The higher-order terms in  $\hat{H}_{\text{el-ph}}$  are known as nonlinear electron-phonon interactions: They are expected to be important for materials with strong electron-phonon interaction and strong anharmonicity. Examples of such materials include the quantum paraelectrics SrTiO<sub>3</sub> and KTaO<sub>3</sub> [32–36], halide perovskites [37–40], and high-pressure hydrides [41–49]. The treatment of phonon anharmonicity is well known in the literature [50,51] and can be tackled on the first-principles level with codes such as Phono3Py [52,53] or SSCHA [54]. However, the nonlinear electron-phonon interaction has been much less studied in the literature. The main obstacle for a general treatment is the increased complexity of the nonlinear electron-phonon matrix elements. Even for the one-electron-two-phonon interaction, which is the lowest-order nonlinear term, there is no general theory or code available for a practical calculation of the matrix element  $g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$ . Therefore, almost all literature treatments of nonlinear electron-phonon interaction that the authors are aware of start from a simplified model: either from a Holstein-type lattice Hamiltonian [55–70] or from a model Hamiltonian for one-electron-two-phonon interaction in SrTiO<sub>3</sub> [33,70–76]. Both of these Hamiltonians include phenomenological parameters, which makes them incompatible with a full first-principles approach. Notable exceptions are the first-principles calculation of renormalized electronic quantities based on adiabatic supercell approaches [77–80], the first-principles treatment of conventional superconductivity in MgB<sub>2</sub> based on a second-order expansion of the deformation potential [81,82], and the first-principles theory of nonlinear electron-phonon interaction for conventional superconductivity in anharmonic metals such as PdH [83]. Of these three treatments, only the last one provides a way to obtain the one-electron-two-phonon matrix element. However, it is limited to metals, where only the short-range part of the electron-phonon interaction is considered because the long-range part is essentially suppressed due to very large screening. A theory for the long-range electron-phonon interaction in semiconductors, due to the generation of a macroscopic electric field, is still lacking.

In this article, we provide a general theory of long-range one-electron-two-phonon interaction that can be combined with first-principles calculations. We propose a derivation for the long-range part of the nonlinear electron-phonon interaction, which we use to find the semianalytic expression for the long-range part of the one-electron-two-phonon interaction matrix element in arbitrary materials. This derivation contains the result in Ref. [31] for the first-order long-range interaction as a special case and can be straightforwardly generalized to arbitrary order. The only anharmonic quantity that appears is the derivative of the phonon dynamical matrix with respect to an external electric field, which plays a similar role as the Born effective charge tensor in the one-electron-one-phonon interaction [31]. As a demonstration for the theory presented in this article, we then use this matrix element to calculate the quasiparticle energy shifts  $\Delta\varepsilon_{\mathbf{k},n}$  of a large polaron. We show that the result only depends on well-known harmonic quantities and a new one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$ , which represents the strength of the long-range

nonlinear interaction in a material. We explicitly show how to calculate  $\mathcal{T}(\omega)$  from first principles for the benchmark material LiF and KTaO<sub>3</sub> at finite temperatures.

This paper is structured as follows. In Sec. II, we analytically derive an expression for the long-range part of the one-electron-two-phonon interaction in terms of quantities that can be calculated from first principles. In Sec. III, we use this matrix element to calculate the ground-state energy and effective mass of a polaron in a material that only has long-range electron-phonon interaction, including the one-electron-two-phonon interaction up to lowest order. In Sec. IV, we calculate the one-electron-two-phonon matrix element from first principles for LiF and KTaO<sub>3</sub> and build a framework to analyze the strength of the one-electron-two-phonon interaction and to reconstruct where its main contributions originate from. We also calculate the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  at finite temperatures and show that it grows larger as the temperature increases, in contrast with the equivalent one-electron-one-phonon spectral function which is independent of temperature. We discuss the results and conclude in Sec. V.

## II. ANALYTICAL DERIVATION OF THE LONG-RANGE ELECTRON-PHONON MATRIX ELEMENTS

### A. Definition of the electron-phonon Hamiltonian

Consider a crystalline material where the electrons interact with the phonons of the lattice. The Hamiltonian for such a system is given by:

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}}. \quad (1)$$

If we limit ourselves to terms that are quadratic in the phonon coordinates, and electron-electron interactions are neglected, then the three terms that appear in this Hamiltonian are given by [13]:

$$\hat{H}_{\text{el}} = \sum_{\mathbf{k},n} \epsilon_{\mathbf{k},n} \hat{c}_{\mathbf{k},n}^\dagger \hat{c}_{\mathbf{k},n}, \quad (2)$$

$$\hat{H}_{\text{ph}} = \sum_{\mathbf{q},\nu} \hbar\omega_{\mathbf{q},\nu} \left( \hat{a}_{\mathbf{q},\nu}^\dagger \hat{a}_{\mathbf{q},\nu} + \frac{1}{2} \right), \quad (3)$$

$$\begin{aligned} \hat{H}_{\text{el-ph}} = & \sqrt{\frac{\Omega_0}{\Omega}} \sum_{\mathbf{k},\mathbf{q},n,m,\nu} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{A}_{\mathbf{q},\nu} \hat{c}_{\mathbf{k}+\mathbf{q},m}^\dagger \hat{c}_{\mathbf{k},n} \\ & + \frac{\Omega_0}{\Omega} \sum_{\mathbf{k},\mathbf{q}_1,\mathbf{q}_2} \sum_{m,n,\nu_1,\nu_2} g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) \hat{A}_{\mathbf{q}_1,\nu_1} \hat{A}_{\mathbf{q}_2,\nu_2} \\ & \times \hat{c}_{\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2,m}^\dagger \hat{c}_{\mathbf{k},n}. \end{aligned} \quad (4)$$

Here  $\hat{c}_{\mathbf{k},n}^\dagger$  and  $\hat{c}_{\mathbf{k},n}$  are the fermionic electron operators which create and annihilate an electron in a Bloch state  $|\psi_{\mathbf{k},n}\rangle$  with crystal momentum  $\hbar\mathbf{k}$  in band  $n$  and  $\hat{A}_{\mathbf{q},\nu} := \hat{a}_{\mathbf{q},\nu} + \hat{a}_{-\mathbf{q},\nu}^\dagger$ , where  $\hat{a}_{\mathbf{q},\nu}^\dagger$  and  $\hat{a}_{\mathbf{q},\nu}$  are the bosonic phonon operators which create and annihilate a phonon with crystal momentum  $\hbar\mathbf{q}$  in branch  $\nu$ .  $\Omega_0$  and  $\Omega$  represent the volume of the unit cell and the system volume, respectively. We will also introduce a Born-von Kármán supercell of volume  $\Omega_{\text{sc}}$  for first-principles calculations. Throughout this article, it is always assumed that  $\Omega \gg \Omega_{\text{sc}} \gg \Omega_0$ . The

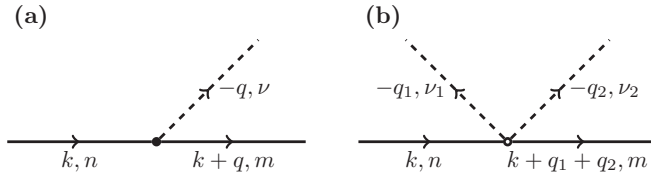


FIG. 1. Feynman diagrams of electron-phonon interactions that will be considered in this article. (a) Linear one-electron-one-phonon interaction with vertex factor  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$ . (b) Nonlinear one-electron-two-phonon interaction with vertex factor  $g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$ .  $k = (\mathbf{k}, \omega)$  and  $q = (\mathbf{q}, \omega')$  represent four-momenta,  $m$  and  $n$  represent electron bands, and  $\nu$  represents a phonon branch.

assumption  $\Omega_{sc} \gg \Omega_0$  is necessary for convergence of the first-principles calculations, and the assumption  $\Omega \gg \Omega_{sc}$  is the thermodynamic limit, which implies that the sums over the momenta  $\mathbf{k}, \mathbf{q}$  can be interpreted as integrals over the first Brillouin zone (1BZ). The Feynman diagrams for the one-electron-one-phonon and one-electron-two-phonon interactions are shown in Fig. 1; the electron-phonon matrix elements  $g_{mn\nu}(\mathbf{k}, \mathbf{q})$  and  $g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  respectively contain all the physics of these interactions. It is worth pointing out that the one-electron-two-phonon matrix element is written as  $g_{mn\nu_1\nu_2}^{DW}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  in Ref. [13]. The superscript DW can be traced back to the fact that the one-electron-two-phonon interaction is often only used to treat the Debye-Waller term in the self-energy [12,13,84]. In the Debye-Waller term,  $g_{mn\nu\nu}(\mathbf{k}, \mathbf{q}, -\mathbf{q})$  can be approximated by an expression that contains two one-electron-one-phonon matrix elements [84], but this is no longer true for the general one-electron-two-phonon matrix element  $g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$ . Since we apply the one-electron-two-phonon interaction beyond only the Debye-Waller diagram in this article, we will also drop the superscript DW from the notation.

### B. Classical derivation of the long-range electron-ion Hamiltonian

The central goal of this article is to find expressions for the long-range parts of the electron-phonon matrix elements, which are due to the classical electrostatic interaction between the electric field  $\mathcal{E}$  of the electrons and the polarization field  $\mathbf{P}$  of the ions in the material. For the one-electron-one-phonon interaction, these expressions have been derived already [3,31]: Here a derivation is presented that can be generalized to higher orders in the phonon coordinates. To do this, we start from a rather general Hamiltonian of the ionic lattice. Let us write the lattice basis vectors as  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ , such that the lattice vectors  $\boldsymbol{\ell}$  and supercell lattice vectors  $\mathbf{T}$  are defined as:

$$\boldsymbol{\ell} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3, \quad m_j \in \{0, 1, \dots, N_j - 1\}, \quad (5)$$

$$\mathbf{T} = n_1N_1\mathbf{a}_1 + n_2N_2\mathbf{a}_2 + n_3N_3\mathbf{a}_3, \quad n_j \in \mathbb{Z}. \quad (6)$$

This splits the crystal into supercells of size  $N_1 \times N_2 \times N_3$ , each of which is labeled by a unique supercell vector  $\mathbf{T}$ . A unique unit cell can be labeled by  $\boldsymbol{\ell} + \mathbf{T}$ , one lattice vector and one supercell vector. This unit cell contains  $N$  atoms, which are labeled with an index  $\kappa \in \{1, \dots, N\}$ . The equilibrium

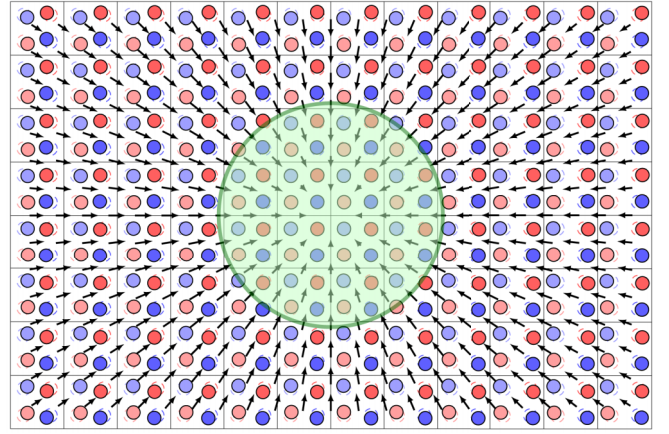


FIG. 2. Schematic drawing of a large polaron in a crystalline solid. When the electron wave function is much larger than the size of the unit cell, the electric field due to the electron can be treated approximately as a constant external electric field in the unit cell.

positions of these atoms within the unit cell are denoted as  $\boldsymbol{\tau}_\kappa$ . As the ions move, they will be brought out of their equilibrium positions to a new position  $\mathbf{T} + \boldsymbol{\ell} + \boldsymbol{\tau}_\kappa + \mathbf{u}_\kappa(\boldsymbol{\ell} + \mathbf{T})$ , where  $\mathbf{u}_\kappa(\boldsymbol{\ell} + \mathbf{T})$  is the instantaneous displacement of atom  $\kappa$  in cell  $\boldsymbol{\ell} + \mathbf{T}$ . Then, the general Hamiltonian of this lattice can be written as:

$$H = \sum_{\kappa\alpha} \sum_{\boldsymbol{\ell}, \mathbf{T}} \frac{P_{\kappa\alpha}^2(\boldsymbol{\ell} + \mathbf{T})}{2m_\kappa} + \tilde{E}_0, \quad (7)$$

where  $\alpha \in \{x, y, z\}$  denotes Cartesian directions,  $m_\kappa$  is the mass of atom  $\kappa$ , and  $P_{\kappa\alpha}(\boldsymbol{\ell} + \mathbf{T}) = m_\kappa \dot{u}_{\kappa\alpha}(\boldsymbol{\ell} + \mathbf{T})$  is its momentum. Furthermore,  $\tilde{E}_0$  is an interaction energy that depends only on the ionic displacements  $\mathbf{u}_{\kappa\alpha}(\boldsymbol{\ell} + \mathbf{T})$  and the macroscopic electric displacement field  $\mathbf{D}(\mathbf{r})$ . The change in  $\tilde{E}_0$  due to a change  $\delta u$  in the ionic positions and a change  $\delta \mathbf{D}$  in the electric displacement field satisfies ([85], Sec. 10):

$$\delta \tilde{E}_0 = - \sum_{\kappa\alpha} \sum_{\boldsymbol{\ell}, \mathbf{T}} m_\kappa \ddot{u}_{\kappa\alpha}(\boldsymbol{\ell} + \mathbf{T}) \delta u_{\kappa\alpha}(\boldsymbol{\ell} + \mathbf{T}) + \int_{\Omega} \mathcal{E}_{\text{tot}}(\mathbf{r}) \cdot \delta \mathbf{D}(\mathbf{r}) d^3\mathbf{r}, \quad (8)$$

where  $\mathcal{E}_{\text{tot}}(\mathbf{r})$  is the macroscopic electric field in the material. The general Hamiltonian in Eq. (7) is too difficult to treat computationally for a system in the thermodynamic limit. To simplify this Hamiltonian, we make a key assumption, which is inspired by an observation in the large polaron problem in Fig. 2. For a large polaron, the electron wave function is very delocalized over the crystal, and the electric field generated by the electron will be approximately constant on the scale of a unit cell or even a supercell. This approximation becomes exact in the large polaron limit. In the more general context of electron-phonon interaction, the same assumption can be made: For the long-range interaction a constant external electric displacement field  $\mathbf{D}$  can be assumed, and any spatial variations in this field should be included in the short-range interaction. With this assumption, the relevant Hamiltonian to study is the Hamiltonian of a single supercell, which then

takes the following form:

$$H_{\text{sc}} = \sum_{\kappa\alpha} \sum_{\ell} \frac{P_{\kappa\alpha}^2(\ell)}{2m_{\kappa}} + E_0(\{\mathbf{u}_{\kappa}(\ell)\}, \mathbf{D}), \quad (9)$$

$$\delta E_0 = - \sum_{\kappa\alpha} \sum_{\ell, \mathbf{T}} m_{\kappa} \ddot{u}_{\kappa\alpha}(\ell) \delta u_{\kappa\alpha}(\ell) + \Omega_{\text{sc}} \boldsymbol{\varepsilon}_{\text{tot}} \cdot \delta \mathbf{D}. \quad (10)$$

The total Hamiltonian is then approximately given by summing the Hamiltonians for all of the supercells  $\mathbf{T}$ , where we take the supercell average for the externally applied field  $\mathbf{D}(\mathbf{T})$ :

$$H \approx \sum_{\mathbf{T}} H_{\text{sc}}(\mathbf{T}), \quad (11)$$

$$\mathbf{D}(\mathbf{T}) := \frac{1}{\Omega_{\text{sc}}} \int_{\Omega_{\text{sc}}(\mathbf{T})} \mathbf{D}(\mathbf{r}) d^3 \mathbf{r}. \quad (12)$$

This approximation is valid if the supercell is large enough,  $\Omega_{\text{sc}} \gg \Omega_0$ , such that the interactions between atoms in neighboring supercells are negligible. By making the simplification in Eq. (11), all supercells in the system will decouple, and only a single supercell must be treated under the application of a constant electric field. This is computationally possible with first-principles theory.

So far, the  $\mathbf{D}$  dependence of  $E_0$  was kept general. However, in practice, the external electric field is small, and  $E_0$  may be expanded in orders of  $\mathbf{D}$ . In this article, we will expand  $E_0$  up to second order in  $\mathbf{D}$ , which gives the following expression for the supercell Hamiltonian in Eq. (9):

$$\begin{aligned} H_{\text{sc}} \approx & \sum_{\kappa\alpha, \ell} \frac{P_{\kappa\alpha}^2(\ell)}{2m_{\kappa}} + E_0(\{\mathbf{u}_{\kappa}(\ell)\})|_{\mathbf{D}=0} \\ & + \mathbf{D} \cdot \left. \frac{\partial E_0(\{\mathbf{u}_{\kappa}(\ell)\})}{\partial \mathbf{D}} \right|_{\mathbf{D}=0} \\ & + \mathbf{D} \cdot \left. \frac{\partial^2 E_0(\{\mathbf{u}_{\kappa}(\ell)\})}{\partial \mathbf{D} \partial \mathbf{D}} \right|_{\mathbf{D}=0} \cdot \mathbf{D} + O(\mathbf{D}^3). \end{aligned} \quad (13)$$

Each of the expansion coefficients is still a function of the ionic displacements  $\mathbf{u}_{\kappa}(\ell)$ . We will additionally neglect this ionic dependence for the second-order term and write  $\left. \frac{\partial^2 E_0(\{\mathbf{u}_{\kappa}(\ell)\})}{\partial \mathbf{D} \partial \mathbf{D}} \right|_{\mathbf{D}=0} \approx \left. \frac{\partial^2 E_0}{\partial \mathbf{D} \partial \mathbf{D}} \right|_{\mathbf{D}=\mathbf{u}_{\kappa}(\ell)=0}$ . Later, the first-order term in  $\mathbf{D}$  will lead to all of the one-electron- $n$ -phonon interactions. Therefore, approximating the  $O(\mathbf{D}^2)$  term and neglecting all terms of  $O(\mathbf{D}^3)$  and higher will not affect the results for the one-electron- $n$ -phonon interactions, which are the primary focus of this article.

We can give names to the expansion coefficients in  $\mathbf{D}$ , such that they will correspond to physically relevant quantities. Let us define the electron energy  $H_{\text{KS}}$ , phonon potential energy  $E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell)\})$ , ionic polarization  $\mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell)\})$ , and dielectric tensor  $\boldsymbol{\varepsilon}_{\infty}$  as follows:

$$H_{\text{KS}} := E_0(\{\mathbf{0}\})|_{\mathbf{D}=0}, \quad (14)$$

$$E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell)\}) := E_0(\{\mathbf{u}_{\kappa}(\ell)\})|_{\mathbf{D}=0} - H_{\text{KS}}, \quad (15)$$

$$\mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell)\}) := - \frac{\varepsilon_0}{\Omega_{\text{sc}}} \boldsymbol{\varepsilon}_{\infty} \cdot \left. \frac{\partial E_0(\{\mathbf{u}_{\kappa}(\ell)\})}{\partial \mathbf{D}} \right|_{\mathbf{D}=0}, \quad (16)$$

$$\boldsymbol{\varepsilon}_{\infty}^{-1} := \left. \frac{\varepsilon_0}{\Omega_{\text{sc}}} \frac{\partial^2 E_0}{\partial \mathbf{D} \partial \mathbf{D}} \right|_{\mathbf{D}=\mathbf{u}_{\kappa}(\ell)=0}. \quad (17)$$

$H_{\text{KS}}$  represents the energy of the system without external electric field and with all ions in their equilibrium positions. After quantization,  $H_{\text{KS}}$  will take the role of the Kohn-Sham Hamiltonian. With the definitions in Eqs. (15)–(17), the supercell Hamiltonian Eq. (9) can be written as:

$$\begin{aligned} H_{\text{sc}} \approx & H_{\text{KS}} + \sum_{\kappa\alpha, \ell} \frac{P_{\kappa\alpha}^2(\ell)}{2m_{\kappa}} + E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell)\}) \\ & - \frac{\Omega_{\text{sc}}}{\varepsilon_0} \mathbf{D} \cdot \boldsymbol{\varepsilon}_{\infty}^{-1} \cdot \mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell)\}) + \frac{\Omega_{\text{sc}}}{2\varepsilon_0} \mathbf{D} \cdot \boldsymbol{\varepsilon}_{\infty}^{-1} \cdot \mathbf{D}. \end{aligned} \quad (18)$$

So far, this derivation is written in terms of the ground-state energy  $E_0$ , which is a function of the electric displacement field  $\mathbf{D}$ . In the first principles literature, it is far more common to define the electric enthalpy  $E$ , which is a function of the external electric field  $\boldsymbol{\varepsilon}$  [86,87]:

$$E(\{\mathbf{u}_{\kappa}(\ell)\}, \boldsymbol{\varepsilon}) = E_0(\{\mathbf{u}_{\kappa}(\ell)\}, \mathbf{D}) - \Omega_{\text{sc}} \boldsymbol{\varepsilon} \cdot \mathbf{P}_{\text{ext}}, \quad (19)$$

where  $\mathbf{P}_{\text{ext}} = \mathbf{D} - \varepsilon_0 \boldsymbol{\varepsilon}$  is the polarization in the case where all the ions are stationary. Many useful quantities can be calculated as derivatives of the electric enthalpy. For example, in Appendix A, it is proven that the quantities defined in Eqs. (15) and (16) can also be written directly in terms of (derivatives of) the electric enthalpy:

$$H_{\text{KS}} = E(\{\mathbf{0}\})|_{\boldsymbol{\varepsilon}=0}, \quad (20)$$

$$E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell)\}) = E(\{\mathbf{u}_{\kappa}(\ell)\})|_{\boldsymbol{\varepsilon}=0} - H_{\text{KS}}, \quad (21)$$

$$\mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell)\}) = - \left. \frac{1}{\Omega_{\text{sc}}} \frac{\partial E}{\partial \boldsymbol{\varepsilon}} \right|_{\boldsymbol{\varepsilon}=0}, \quad (22)$$

and that  $\boldsymbol{\varepsilon}_{\infty}$ , defined through Eq. (17), defines a relation between  $\mathbf{D}$  and  $\boldsymbol{\varepsilon}$  in the usual way [88]:

$$\mathbf{D} = \varepsilon_0 \boldsymbol{\varepsilon}_{\infty} \cdot \boldsymbol{\varepsilon}. \quad (23)$$

To describe the one-electron-one-phonon interaction one also needs the Born effective charge tensor, which is defined from the electric enthalpy as follows [88]:

$$\mathbf{Z}_{\kappa} = - \left. \frac{1}{e} \frac{\partial^2 E}{\partial \boldsymbol{\varepsilon} \partial \mathbf{u}_{\kappa}(\ell)} \right|_{\mathbf{u}_{\kappa}(\ell)=\boldsymbol{\varepsilon}=0} = \frac{\Omega_{\text{sc}}}{e} \left. \frac{\partial \mathbf{P}_{\text{ion}}}{\partial \mathbf{u}_{\kappa}(\ell)} \right|_{\mathbf{u}_{\kappa}(\ell)=0}, \quad (24)$$

which is independent of  $\ell$  because of the translation invariance of the crystal. Finally, to describe the phonon properties, one requires the harmonic force constants  $\Phi_{\kappa\alpha, \kappa'\beta}(\ell)$  and the dynamical matrix  $\mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q})$ , as well as their dependence on the constant external electric field  $\boldsymbol{\varepsilon}$ :

$$\Phi_{\kappa\alpha, \kappa'\beta}(\ell' - \ell; \boldsymbol{\varepsilon}) = \left. \frac{\partial^2 E(\{\mathbf{u}_{\kappa}(\ell)\}, \boldsymbol{\varepsilon})}{\partial u_{\kappa\alpha}(\ell) \partial u_{\kappa'\beta}(\ell')} \right|_{\mathbf{u}_{\kappa}(\ell)=0}, \quad (25)$$

$$\mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}; \boldsymbol{\varepsilon}) = \frac{1}{\sqrt{m_{\kappa} m_{\kappa'}}} \sum_{\ell} \Phi_{\kappa\alpha, \kappa'\beta}(\ell; \boldsymbol{\varepsilon}) e^{i\mathbf{q} \cdot \ell}. \quad (26)$$

The dynamical matrix can be diagonalized to yield the phonon eigenvectors  $e_{\kappa\alpha, v}(\mathbf{q}; \boldsymbol{\varepsilon})$  and the squares of the phonon frequencies  $\omega_v^2(\mathbf{q}; \boldsymbol{\varepsilon})$ :

$$\sum_{\kappa'\beta} \mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}; \boldsymbol{\varepsilon}) e_{\kappa'\beta, v}(\mathbf{q}; \boldsymbol{\varepsilon}) = \omega_v^2(\mathbf{q}; \boldsymbol{\varepsilon}) e_{\kappa\alpha, v}(\mathbf{q}; \boldsymbol{\varepsilon}). \quad (27)$$

Unless otherwise indicated, throughout this section we use the d-type convention for the phonon eigenvectors (see, e.g.,

Ref. [89], Sec. 2.3), and we assume the Born-Huang convention  $e_{\kappa\alpha,\nu}^*(\mathbf{q}; \mathcal{E}) = e_{\kappa\alpha,\nu}(-\mathbf{q}; \mathcal{E})$  [90]. The dependence on the electric field is naturally included from the electric field dependence of the electric enthalpy. When  $\mathcal{E} = \mathbf{0}$ , the definitions in Eqs. (25) and (26) reduce to the literature definitions of the force constants  $\Phi_{\kappa\alpha,\kappa'\beta}(\ell' - \ell)$ , the dynamical matrix  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$ , the phonon frequencies  $\omega_{\mathbf{q},\nu}$ , and the phonon eigenvectors  $e_{\kappa\alpha,\nu}(\mathbf{q})$  [88,89].

$\mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\})$  can arbitrarily be written as a volume average of dipoles associated with each atom  $(\kappa, \ell)$  in the supercell:

$$\mathbf{P}_{\text{ion}}(\mathbf{T}) = \frac{1}{\Omega_{\text{sc}}} \sum_{\kappa,\ell} \mathbf{p}_\kappa(\ell + \mathbf{T}). \quad (28)$$

Doing this for every supercell  $\mathbf{T}$  allows us to define a position-dependent polarization field  $\mathbf{P}_{\text{ion}}(\mathbf{r})$ , defined by placing the dipoles  $\mathbf{p}_\kappa(\ell + \mathbf{T})$  at the equilibrium positions of the atoms  $(\kappa, \ell + \mathbf{T})$ :

$$\mathbf{P}_{\text{ion}}(\mathbf{r}) := \sum_{\kappa,\ell,\mathbf{T}} \mathbf{p}_\kappa(\ell + \mathbf{T}) \delta(\mathbf{r} - \mathbf{T} - \ell - \boldsymbol{\tau}_\kappa). \quad (29)$$

This field is defined in such a way that taking the volume average over a supercell  $\Omega_{\text{sc}}$  yields the correct ionic polarization for that supercell, analogously to the definition for  $\mathbf{D}(\mathbf{T})$  in Eq. (12):

$$\mathbf{P}_{\text{ion}}(\mathbf{T}) = \frac{1}{\Omega_{\text{sc}}} \int_{\Omega_{\text{sc}}(\mathbf{T})} \mathbf{P}_{\text{ion}}(\mathbf{r}) d^3\mathbf{r}. \quad (30)$$

The Fourier transform of  $\mathbf{P}_{\text{ion}}(\mathbf{r})$  is given by:

$$\mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G}) = \frac{1}{\Omega} \sum_{\kappa,\ell,\mathbf{T}} \mathbf{p}_\kappa(\ell + \mathbf{T}) e^{-i\mathbf{q}\cdot(\ell+\mathbf{T})} e^{-i(\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\tau}_\kappa}, \quad (31)$$

where  $\mathbf{G}$  is a reciprocal lattice vector. In Sec. II C, we will derive explicit expressions for the dipoles  $\mathbf{p}_\kappa(\ell + \mathbf{T})$  from the derivatives of the electric enthalpy. The choices of how to write  $\mathbf{P}_{\text{ion}}$  as a sum of dipoles, and how to associate these dipoles with a position, are arbitrary. However, only the low-momentum components of  $\mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G})$  will appear in the final results. In this limit with  $\mathbf{q} + \mathbf{G} \rightarrow \mathbf{0}$ , any choice of dipoles  $\mathbf{p}_\kappa(\ell + \mathbf{T})$  that satisfies Eq. (28) will lead to the same result for Eq. (31): Therefore, the arbitrariness has no physical relevance. We make the above choices because they are implicitly made in Ref. [31] for the harmonic problem, where  $\mathbf{p}_\kappa(\ell + \mathbf{T}) = e\mathbf{Z}_\kappa \cdot \mathbf{u}_\kappa(\ell + \mathbf{T})$ . By making the same choices, we will eventually obtain the same result for the long-range one-electron-one-phonon matrix element.

Next, the Hamiltonian  $H$  on the full system can be recovered by summing up the supercell Hamiltonians  $H_{\text{sc}}(\mathbf{T})$  over all supercell vectors  $\mathbf{T}$ . In Eq. (18) for the supercell Hamiltonian, both  $\mathbf{D}(\mathbf{T})$  and  $\mathbf{P}_{\text{ion}}(\mathbf{T})$  depend on the specific supercell, so:

$$\begin{aligned} H = & H_{\text{KS}} + \sum_{\mathbf{T}} \left[ \sum_{\kappa\alpha,\ell} \frac{P_{\kappa\alpha}^2(\ell + \mathbf{T})}{2m_\kappa} + E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell + \mathbf{T})\}) \right] \\ & - \sum_{\mathbf{T}} \frac{\Omega_{\text{sc}}}{\epsilon_0} \mathbf{D}(\mathbf{T}) \cdot \boldsymbol{\epsilon}_\infty^{-1} \cdot \mathbf{P}_{\text{ion}}(\mathbf{T}) \\ & + \sum_{\mathbf{T}} \frac{\Omega_{\text{sc}}}{2\epsilon_0} \mathbf{D}(\mathbf{T}) \cdot \boldsymbol{\epsilon}_\infty^{-1} \cdot \mathbf{D}(\mathbf{T}). \end{aligned} \quad (32)$$

This can be written in terms of the continuous field  $\mathbf{D}(\mathbf{r})$  by substituting the definitions for  $\mathbf{D}(\mathbf{T})$  and  $\mathbf{P}(\mathbf{T})$  in Eq. (12) and Eq. (30) and by using that  $\mathbf{D}(\mathbf{r}) \approx \mathbf{D}(\mathbf{r}')$  when  $\mathbf{r}$  and  $\mathbf{r}'$  are in the same supercell. Then, a short calculation yields:

$$\begin{aligned} H = & H_{\text{KS}} + \sum_{\mathbf{T}} \left[ \sum_{\kappa\alpha,\ell} \frac{P_{\kappa\alpha}^2(\ell + \mathbf{T})}{2m_\kappa} + E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell + \mathbf{T})\}) \right] \\ & - \frac{1}{\epsilon_0} \int_{\Omega} \mathbf{D}(\mathbf{r}) \cdot \boldsymbol{\epsilon}_\infty^{-1} \cdot \mathbf{P}_{\text{ion}}(\mathbf{r}) d^3\mathbf{r} \\ & + \frac{1}{2\epsilon_0} \int_{\Omega} \mathbf{D}(\mathbf{r}) \cdot \boldsymbol{\epsilon}_\infty^{-1} \cdot \mathbf{D}(\mathbf{r}) d^3\mathbf{r}. \end{aligned} \quad (33)$$

This Hamiltonian describes an ionic lattice interacting with a macroscopic electric displacement field  $\mathbf{D}(\mathbf{r})$ . In the case of long-range electron-phonon interaction, this electric displacement field is due to  $N_{\text{el}}$  electrons. If these electrons are moving slowly enough, then their electric field must be longitudinal, which means the electric field can be described through the electrostatic potential:

$$\mathcal{E} = -\nabla\phi(\mathbf{r}). \quad (34)$$

The connection between  $\mathbf{D}$  and  $\mathcal{E}$ , described in Eq. (23), then tells us that the electric displacement field must be equal to:

$$\mathbf{D}(\mathbf{r}) = -\epsilon_0 \boldsymbol{\epsilon}_\infty \cdot \nabla\phi(\mathbf{r}). \quad (35)$$

Combining this with Maxwell's first equation yields the anisotropic Poisson equation for the scalar potential:

$$\nabla \cdot (\boldsymbol{\epsilon}_\infty \nabla\phi(\mathbf{r})) = \frac{e}{\epsilon_0} \sum_{j=1}^{N_{\text{el}}} \delta(\mathbf{r} - \mathbf{r}_{\text{el},j}). \quad (36)$$

This equation can be solved by transforming to Fourier space: The derivation can be found in Ref. [31]. The final result for the electric displacement field of the electrons is

$$\mathbf{D}(\mathbf{r}) = -\frac{ie}{\Omega} \sum_{\mathbf{Q} \neq \mathbf{0}} \frac{\boldsymbol{\epsilon}_\infty \cdot \mathbf{Q}}{\mathbf{Q} \cdot \boldsymbol{\epsilon}_\infty \cdot \mathbf{Q}} \rho_{\mathbf{Q}} e^{-i\mathbf{Q}\cdot\mathbf{r}}, \quad (37)$$

where the sum over  $\mathbf{Q}$  is over the entire reciprocal space and the dimensionless density operator of the electrons  $\rho_{\mathbf{Q}}$  is defined in the usual way:

$$\rho_{\mathbf{Q}} = \sum_{j=1}^{N_{\text{el}}} e^{i\mathbf{Q}\cdot\mathbf{r}_{\text{el},j}}. \quad (38)$$

Equation (37) can be used back in Eq. (33) to find a fairly general expression for the classical electron-phonon Hamiltonian. The integrals are straightforward; one should only remember to remove the self-interaction of the electrons. The result is as follows:

$$H = H_{\text{KS}} + H_{\text{ph}} + H_{\text{el-ph}} + H_{\text{el-el}}, \quad (39)$$

$$H_{\text{ph}} = \sum_{\kappa\alpha,\ell,\mathbf{T}} \frac{P_{\kappa\alpha}^2(\ell + \mathbf{T})}{2m_\kappa} + E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell + \mathbf{T})\}), \quad (40)$$

$$H_{\text{el-ph}} = \frac{ie}{\epsilon_0} \sum_{\kappa,\ell,\mathbf{T}} \sum_{\mathbf{Q} \neq \mathbf{0}} \frac{\mathbf{Q} \cdot \mathbf{P}_{\text{ion}}(\mathbf{Q})}{\mathbf{Q} \cdot \boldsymbol{\epsilon}_\infty \cdot \mathbf{Q}} \rho_{\mathbf{Q}}, \quad (41)$$

$$H_{\text{el-el}} = \frac{e^2}{2\Omega\epsilon_0} \sum_{\mathbf{Q} \neq \mathbf{0}} \frac{\rho_{\mathbf{Q}}\rho_{-\mathbf{Q}} - \rho_0}{\mathbf{Q} \cdot \boldsymbol{\epsilon}_\infty \cdot \mathbf{Q}}, \quad (42)$$

where we recall that  $\mathbf{P}_{\text{ion}}(\mathbf{Q})$  is defined in Eq. (31). Equation (42) is the well-known Coulomb interaction between the electrons. The focus of this article is on the electron-phonon interaction, and we will only be interested in single-electron properties: Therefore, for the remainder of the article, we will ignore the Coulomb interaction  $H_{\text{el-e}}$ . However, note that  $H_{\text{el-e}}$  can always be added to the Hamiltonian if desired.

The above Hamiltonian is classical but can be readily written in first quantization by promoting  $H_{\text{KS}}$ ,  $\rho_{\mathbf{Q}}$ ,  $\mathbf{u}_{\kappa}(\ell + \mathbf{T})$ , and  $\mathcal{P}_{\kappa}(\ell + \mathbf{T})$  to operators. It can also be written in second quantization, following the recipe provided in Ref. [91], Sec. 1.2. Let us introduce the fermionic operators  $\hat{c}_{\mathbf{k},n}^{\dagger}$  and  $\hat{c}_{\mathbf{k},n}$ , which create and annihilate an eigenstate  $|\psi_{\mathbf{k},n}\rangle$  of the Kohn-Sham Hamiltonian  $H_{\text{KS}}$  with corresponding energies  $\epsilon_{\mathbf{k},n}$ . Then, the second quantization expressions for  $\hat{H}_{\text{KS}}$  and  $\hat{\rho}_{\mathbf{Q}}$  are as follows [91]:

$$\hat{H}_{\text{KS}} = \sum_{\mathbf{k},n} \epsilon_{\mathbf{k},n} \hat{c}_{\mathbf{k},n}^{\dagger} \hat{c}_{\mathbf{k},n}, \quad (43)$$

$$\hat{\rho}_{\mathbf{q}+\mathbf{G}} = \sum_{\mathbf{k},m,n} \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle \hat{c}_{\mathbf{k}+\mathbf{q},m}^{\dagger} \hat{c}_{\mathbf{k},n}, \quad (44)$$

where  $\mathbf{Q} = \mathbf{q} + \mathbf{G}$  is written as the sum of a reciprocal lattice vector  $\mathbf{G}$  and a lattice wave vector  $\hbar\mathbf{q}$  in the first Brillouin zone. With these expressions, the Hamiltonian becomes

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}}, \quad (45)$$

$$\hat{H}_{\text{el}} = \sum_{\mathbf{k},n} \epsilon_{\mathbf{k},n} \hat{c}_{\mathbf{k},n}^{\dagger} \hat{c}_{\mathbf{k},n}, \quad (46)$$

$$\hat{H}_{\text{ph}} = \sum_{\kappa\alpha,\ell,\mathbf{T}} \frac{\mathcal{P}_{\kappa\alpha}^2(\ell + \mathbf{T})}{2m_{\kappa}} + E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell + \mathbf{T})\}), \quad (47)$$

$$\begin{aligned} \hat{H}_{\text{el-ph}} &= \frac{ie}{\epsilon_0} \sum_{\mathbf{k},\mathbf{q},m,n} \sum_{\mathbf{G} \neq -\mathbf{q}} \frac{(\mathbf{q} + \mathbf{G}) \cdot \mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G})}{(\mathbf{q} + \mathbf{G}) \cdot \boldsymbol{\epsilon}_{\infty} \cdot (\mathbf{q} + \mathbf{G})} \\ &\times \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle \hat{c}_{\mathbf{k}+\mathbf{q},m}^{\dagger} \hat{c}_{\mathbf{k},n}. \end{aligned} \quad (48)$$

This Hamiltonian is the furthest one can go without assuming anything about the  $\{\mathbf{u}_{\kappa}(\ell + \mathbf{T})\}$  dependence of  $E_{\text{ph}}$  or  $\mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G})$ . Respectively, these would be assumptions about the phonon anharmonicity and about the electron-phonon anharmonicity.

Each of the terms in the above Hamiltonian has a clear meaning. Equation (46) is the electron Hamiltonian with all ions in the equilibrium positions, and in the absence of an external electric field. Equation (47) is the phonon Hamiltonian in the absence of an external electric field or, equivalently, in the absence of electron-phonon coupling. It contains the entire energy landscape  $E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell + \mathbf{T})\})$  and is therefore valid up to arbitrary orders of anharmonicity. Finally, Eq. (48) is the long-range electron-phonon interaction: It contains all the processes where one electron interacts with the phonons. This is again up to arbitrary orders of anharmonicity, since  $\mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G})$  and  $\mathbf{p}_{\kappa}(\ell + \mathbf{T})$  are ultimately defined from the general ionic polarization  $\mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell + \mathbf{T})\})$ .

Note that the derivation requires that  $\mathbf{P}_{\text{ion}}$  is approximately constant over the size of a supercell. Therefore, for self-consistency, we must assume that  $\mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G})$  only consists of low-momentum components. In particular, the resulting electron-phonon Hamiltonian Eq. (48) is only valid in the

limit  $\mathbf{q} + \mathbf{G} \rightarrow \mathbf{0}$ . This is how one can define the long-range limit for the electron-phonon interaction in general: Only the momentum appearing in  $\rho_{\mathbf{q}+\mathbf{G}}$  must be small, but all other momenta can be arbitrarily large. Throughout this article, we will frequently take the long-range limit in several expressions for self-consistency.

### C. Expansion in the ion coordinates

Equation (41) for the electron-phonon interaction is not useful until one has a useful expression for the dipoles  $\mathbf{p}_{\kappa}(\ell + \mathbf{T})$ . Such an expression can be obtained by expanding  $\mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell)\})$  in terms of the ionic displacements  $\mathbf{u}_{\kappa}(\ell)$ . In this article we focus on the one-electron-two-phonon interaction and ignore phonon anharmonicity, so  $E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell + \mathbf{T})\})$  and  $\mathbf{P}_{\text{ion}}(\{\mathbf{u}_{\kappa}(\ell)\})$  are both expanded up to second order. The first-order derivatives of  $E_{\text{ph}}(\{\mathbf{u}_{\kappa}(\ell + \mathbf{T})\})$  are zero since the derivatives are evaluated at the equilibrium positions of the ions, and its second-order derivatives are the harmonic force constants defined in Eq. (25). Therefore, the phonon Hamiltonian  $H_{\text{ph}}$  from Eq. (40) can be written in the following form:

$$\begin{aligned} H_{\text{ph}} &= \sum_{\kappa\alpha,\ell,\mathbf{T}} \frac{\mathcal{P}_{\kappa\alpha}^2(\ell + \mathbf{T})}{2m_{\kappa}} + \frac{1}{2} \sum_{\kappa\alpha,\kappa'\beta,\ell,\ell',\mathbf{T}} u_{\kappa\alpha}(\ell + \mathbf{T}) \\ &\times \Phi_{\kappa\alpha,\kappa'\beta}(\ell - \ell') u_{\kappa'\beta}(\ell' + \mathbf{T}), \end{aligned} \quad (49)$$

where it is assumed that the supercell is large enough so that the force constants are zero when the two ions do not belong to the same supercell. This is the usual harmonic lattice Hamiltonian: Its further treatment can be found in the literature [13,92]. Here the main steps are outlined. The Hamiltonian can be written in second quantization in terms of phonon ladder operators  $\hat{a}_{\mathbf{q},v}$ ,  $\hat{a}_{\mathbf{q},v}^{\dagger}$ , if the ionic displacements and momenta are written as follows [13]:

$$\begin{aligned} u_{\kappa\alpha}(\ell + \mathbf{T}) &= \sqrt{\frac{\Omega_0}{\Omega}} \sum_{\mathbf{q},v} \sqrt{\frac{\hbar}{2m_{\kappa}\omega_{\mathbf{q},v}}} (\hat{a}_{\mathbf{q},v} + \hat{a}_{-\mathbf{q},v}^{\dagger}) \\ &\times e_{\kappa\alpha,v}(\mathbf{q}) e^{i\mathbf{q}\cdot(\ell+\mathbf{T})}, \end{aligned} \quad (50)$$

$$\begin{aligned} \mathcal{P}_{\kappa\alpha}(\ell + \mathbf{T}) &= \frac{1}{i} \sqrt{\frac{\Omega_0}{\Omega}} \sum_{\mathbf{q},v} \sqrt{\frac{\hbar m_{\kappa} \omega_{\mathbf{q},v}}{2}} (\hat{a}_{\mathbf{q},v} - \hat{a}_{-\mathbf{q},v}^{\dagger}) \\ &\times e_{\kappa\alpha,v}(\mathbf{q}) e^{i\mathbf{q}\cdot(\ell+\mathbf{T})}, \end{aligned} \quad (51)$$

and the bosonic commutation relations  $[\hat{a}_{\mathbf{q},v}, \hat{a}_{\mathbf{q}',v'}^{\dagger}] = \delta_{\mathbf{q},\mathbf{q}'} \delta_{v,v'}$  are imposed. Substituting Eqs. (50) and (51) into Eq. (49) and using the definitions in Eqs. (26) and (27) yields the familiar expression for the harmonic phonon Hamiltonian in second quantization:

$$\hat{H}_{\text{ph}} = \sum_{\mathbf{q},v} \hbar\omega_{\mathbf{q},v} \left( \hat{a}_{\mathbf{q},v}^{\dagger} \hat{a}_{\mathbf{q},v} + \frac{1}{2} \right). \quad (52)$$

This is precisely Eq. (3), where the phonon frequencies are obtained in the usual way from the diagonalization of the dynamical matrix.

To expand  $\mathbf{P}_{\text{ion}}$ , recall that it is defined as an electric field derivative of the energy according to Eq. (22). Therefore, the expansion coefficients can be written as derivatives of the energy, where it is again assumed that the supercell is large

enough so that the derivatives are zero when the ions do not belong to the same supercell:

$$\begin{aligned} \mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell + \mathbf{T})\}) \approx & -\frac{1}{\Omega_{\text{sc}}} \sum_{\kappa\alpha, \ell, \mathbf{T}} u_{\kappa\alpha}(\ell + \mathbf{T}) \frac{\partial^2 E}{\partial \boldsymbol{\mathcal{E}} \partial u_{\kappa\alpha}(\ell + \mathbf{T})} \Big|_{\mathbf{u}_\kappa(\ell) = \boldsymbol{\mathcal{E}} = \mathbf{0}} \\ & - \frac{1}{2\Omega_{\text{sc}}} \sum_{\kappa\alpha, \kappa'\beta, \ell, \ell', \mathbf{T}} u_{\kappa\alpha}(\ell + \mathbf{T}) u_{\kappa'\beta}(\ell' + \mathbf{T}) \frac{\partial^3 E}{\partial \boldsymbol{\mathcal{E}} \partial u_{\kappa\alpha}(\ell + \mathbf{T}) \partial u_{\kappa'\beta}(\ell' + \mathbf{T})} \Big|_{\mathbf{u}_\kappa(\ell + \mathbf{T}) = \boldsymbol{\mathcal{E}} = \mathbf{0}}. \end{aligned} \quad (53)$$

These derivatives can be written in terms of the Born effective charge tensor and the harmonic force constants using Eqs. (24) and (25):

$$\mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell + \mathbf{T})\}) \approx \frac{1}{\Omega_{\text{sc}}} \sum_{\kappa, \ell, \mathbf{T}} e\mathbf{Z}_\kappa \cdot \mathbf{u}_\kappa(\ell + \mathbf{T}) - \frac{1}{2\Omega_{\text{sc}}} \sum_{\kappa\alpha, \kappa'\beta, \ell, \ell', \mathbf{T}} u_{\kappa\alpha}(\ell + \mathbf{T}) \frac{\partial \Phi_{\kappa\alpha, \kappa'\beta}(\ell' - \ell; \boldsymbol{\mathcal{E}})}{\partial \boldsymbol{\mathcal{E}}} \Big|_{\boldsymbol{\mathcal{E}} = \mathbf{0}} u_{\kappa'\beta}(\ell' + \mathbf{T}). \quad (54)$$

This also provides a natural definition for the ionic dipoles  $\mathbf{p}_\kappa(\ell)$  in Eq. (28), such that  $\mathbf{P}_{\text{ion}}$  is the volume average of these dipoles in the supercell:

$$\mathbf{p}_\kappa(\ell + \mathbf{T}) \approx e\mathbf{Z}_\kappa \cdot \mathbf{u}_\kappa(\ell + \mathbf{T}) - \frac{1}{2} \sum_{\alpha, \kappa'\beta, \ell'} u_{\kappa\alpha}(\ell + \mathbf{T}) \frac{\partial \Phi_{\kappa\alpha, \kappa'\beta}(\ell' - \ell; \boldsymbol{\mathcal{E}})}{\partial \boldsymbol{\mathcal{E}}} \Big|_{\boldsymbol{\mathcal{E}} = \mathbf{0}} u_{\kappa'\beta}(\ell' + \mathbf{T}). \quad (55)$$

Note here that the first term is a standard expression for the ionic dipole moment, which is used in the harmonic derivation in Ref. [31]. It will lead to the one-electron-one-phonon interaction, and the central quantity that controls it is the Born effective charge tensor  $\mathbf{Z}_\kappa$ . The second term is the next-higher order, which will lead to the one-electron-two-phonon interaction. This derivation immediately clarifies that  $\frac{\partial \Phi_{\kappa\alpha, \kappa'\beta}(\ell' - \ell; \boldsymbol{\mathcal{E}})}{\partial \boldsymbol{\mathcal{E}}} \Big|_{\boldsymbol{\mathcal{E}} = \mathbf{0}}$  will be the central quantity that will control the one-electron-two-phonon interaction. Although we will be satisfied with the second-order expansion in this article, this idea is easily extended to higher orders by including higher-order derivatives of the ionic coordinates in (54). It can straightforwardly be seen that the central quantity that controls the one-electron- $n$ -phonon interaction would be the electric field derivative of the  $n$ -phonon matrix elements, as defined in, e.g., Ref. [50].

To find an expression for the long-range electron-phonon Hamiltonian, Eq. (55) and Eq. (50) should be substituted into Eq. (41). The calculation is straightforward; only the main steps are presented here. First,  $\mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G})$  is calculated with Eq. (31), Eq. (50), and Eq. (55), which gives:

$$\begin{aligned} \mathbf{P}_{\text{ion}}(\mathbf{q} + \mathbf{G}) = & \frac{e}{\sqrt{\Omega\Omega_0}} \sum_{\kappa v} \sqrt{\frac{\hbar}{2m_\kappa\omega_{\mathbf{q},v}}} \mathbf{Z}_\kappa \cdot \mathbf{e}_{\kappa,v}(\mathbf{q}) e^{-i(\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\tau}_\kappa} (\hat{a}_{\mathbf{q},v} + \hat{a}_{-\mathbf{q},v}^\dagger) \\ & - \frac{ie}{2\Omega} \sum_{\mathbf{q}', v, v'} \mathbf{Y}_{v_1 v_2}(\mathbf{q}', \mathbf{q} + \mathbf{G}) (\hat{a}_{\mathbf{q}'-\mathbf{q},v} + \hat{a}_{\mathbf{q}'-\mathbf{q},v}^\dagger) (\hat{a}_{\mathbf{q}',v} + \hat{a}_{-\mathbf{q}',v}^\dagger), \end{aligned} \quad (56)$$

where the auxiliary vector  $\mathbf{Y}_{v_1 v_2}(\mathbf{q}', \mathbf{q} + \mathbf{G})$  is defined as:

$$\mathbf{Y}_{v_1 v_2}(\mathbf{q}', \mathbf{q} + \mathbf{G}) := \frac{1}{ie} \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}'-\mathbf{q},v_1}} \frac{\hbar}{2\omega_{\mathbf{q}',v_2}}} \sum_{\kappa\alpha, \kappa'\beta} e^{-i(\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\tau}_\kappa} e_{\kappa\alpha, v_1}(\mathbf{q} - \mathbf{q}') \frac{\partial \mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}')}{\partial \boldsymbol{\mathcal{E}}} e_{\kappa'\beta, v_2}(\mathbf{q}'). \quad (57)$$

Here the shorthand notation  $\frac{\partial \mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}')}{\partial \boldsymbol{\mathcal{E}}} := \frac{\partial \mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}; \boldsymbol{\mathcal{E}})}{\partial \boldsymbol{\mathcal{E}}} \Big|_{\boldsymbol{\mathcal{E}} = \mathbf{0}}$  was introduced for the derivative at zero electric field: We will use this shorthand notation throughout the article. Now, Eq. (56) can be substituted back into Eq. (48) for the electron-phonon interaction. This yields a Hamiltonian of the form Eq. (4), with the following expressions for the electron-phonon matrix elements:

$$g_{mnv}^{(\text{long})}(\mathbf{k}, \mathbf{q}) = \frac{ie^2}{\varepsilon_0\Omega_0} \sum_{\mathbf{G} \neq -\mathbf{q}} \sum_{\kappa} \sqrt{\frac{\hbar}{2m_\kappa\omega_{\mathbf{q},v}}} \frac{(\mathbf{q} + \mathbf{G}) \cdot \mathbf{Z}_\kappa \cdot \mathbf{e}_{v,\kappa}(\mathbf{q})}{(\mathbf{q} + \mathbf{G}) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q} + \mathbf{G})} \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot(\mathbf{r}-\boldsymbol{\tau}_\kappa)} | \psi_{\mathbf{k},n} \rangle, \quad (58)$$

$$g_{mnv_1 v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = \frac{e^2}{2\varepsilon_0\Omega_0} \sum_{\mathbf{G} \neq -\mathbf{q}_1 - \mathbf{q}_2} \frac{(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}) \cdot \mathbf{Y}_{v_1 v_2}(\mathbf{q}_2, \mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G})}{(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G})} \langle \psi_{\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2,m} | e^{i(\mathbf{q}_1+\mathbf{q}_2+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle. \quad (59)$$

Equation (58) is the literature result for the long-range part of the one-electron-one-phonon matrix element [13,31]. This confirms that the derivation presented in this section is a generalization of current literature theory, which can be applied to arbitrary orders of anharmonicity.

We explicitly write the superscript “(long)” in Eqs. (58) and (59) to indicate that these are not the full electron-

phonon matrix elements but only the long-range parts. Recall from the discussion at the end of Sec. II B that the long-range part can be identified as the  $\mathbf{Q} \rightarrow \mathbf{0}$  limit of whichever wave vector  $\mathbf{Q}$  is in the density operator or, equivalently, in the electron matrix element in Eqs. (58) and (59). For the one-electron-one-phonon matrix element this is  $\mathbf{q} + \mathbf{G}$ , and for the one-electron-two-phonon matrix element

it is  $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}$ , so:

$$\lim_{\mathbf{q}+\mathbf{G}\rightarrow\mathbf{0}} g_{mnv}(\mathbf{k}, \mathbf{q}) = g_{mnv}^{(\text{long})}(\mathbf{k}, \mathbf{q}), \quad (60)$$

$$\lim_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{G}\rightarrow\mathbf{0}} g_{mnv_1v_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = g_{mnv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2). \quad (61)$$

The limit  $\mathbf{G} \rightarrow \mathbf{0}$  in these expressions should be understood as follows: In the sums over  $\mathbf{G}$  that appear in Eqs. (58) and (59), one may always neglect any term that has  $\mathbf{G} \neq \mathbf{0}$  without changing the physical results. In practice, the sum over  $\mathbf{G}$  is only necessary when interpolating the entire electron-phonon matrix element [31], which is outside the scope of this article.

By definition, Eq. (58) is only valid in the  $\mathbf{q} + \mathbf{G} \rightarrow \mathbf{0}$  limit, and Eq. (59) is only valid in the  $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G} \rightarrow \mathbf{0}$  limit. Therefore, for self-consistency, these limits should be taken in Eqs. (58) and (59) as well. For the one-electron-two-phonon interaction, this is easily done by replacing  $\mathbf{Y}_{v_1v_2}(\mathbf{q}_2, \mathbf{q}_1 + \mathbf{G})$  with  $\mathbf{Y}_{v_1v_2}(\mathbf{q}_2, \mathbf{0}) := \mathbf{Y}_{v_1v_2}(\mathbf{q}_2)$ , which is

given by:

$$\begin{aligned} \mathbf{Y}_{v_1v_2}(\mathbf{q}) &:= \frac{1}{ie} \sqrt{\frac{\hbar}{2\omega_{\mathbf{q},v_1}} \frac{\hbar}{2\omega_{\mathbf{q},v_2}}} \sum_{\kappa\alpha,\kappa'\beta} e_{\kappa\alpha,v_1}^*(\mathbf{q}) \\ &\times \frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}} e_{\kappa'\beta,v_2}(\mathbf{q}). \end{aligned} \quad (62)$$

For the one-electron-one-phonon interaction, it is convenient to introduce the mode polarities  $\mathbf{p}_v(\hat{\mathbf{q}})$ , which are used in the generalized Fröhlich model for the one-electron-one-phonon interaction [93]. They are defined as:

$$\mathbf{p}_v(\hat{\mathbf{q}}) := \sum_{\kappa} \frac{\mathbf{Z}_{\kappa} \cdot \mathbf{e}_{\kappa,v}(\hat{\mathbf{q}})}{\sqrt{m_{\kappa}}}. \quad (63)$$

In general, they may depend on the direction  $\hat{\mathbf{q}}$  along which we take the  $\mathbf{q} \rightarrow \mathbf{0}$  limit. Similarly, the phonon frequencies in the  $\mathbf{q} \rightarrow \mathbf{0}$  limit can still have a nonanalytic dependence on  $\hat{\mathbf{q}}$  [93], so we write the phonon frequencies around  $\Gamma$  as  $\omega_{\hat{\mathbf{q}},v}$ .

Taking the above-mentioned limits in Eqs. (58) and (59) yields find the final expressions for the long-range electron-phonon matrix elements:

$$g_{mnv}^{(\text{long})}(\mathbf{k}, \mathbf{q}) = \frac{ie^2}{\varepsilon_0\Omega_0} \sqrt{\frac{\hbar}{2\omega_{\hat{\mathbf{q}},v}}} \sum_{\mathbf{G}\neq-\mathbf{q}} \frac{(\mathbf{q} + \mathbf{G}) \cdot \mathbf{p}_v(\hat{\mathbf{q}})}{(\mathbf{q} + \mathbf{G}) \cdot \boldsymbol{\varepsilon}_{\infty} \cdot (\mathbf{q} + \mathbf{G})} \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle, \quad (64)$$

$$g_{mnv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = \frac{e^2}{2\varepsilon_0\Omega_0} \sum_{\mathbf{G}\neq-\mathbf{q}_1-\mathbf{q}_2} \frac{(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}) \cdot \mathbf{Y}_{v_1v_2}(\mathbf{q}_2)}{(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}) \cdot \boldsymbol{\varepsilon}_{\infty} \cdot (\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G})} \langle \psi_{\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2,m} | e^{i(\mathbf{q}_1+\mathbf{q}_2+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle. \quad (65)$$

Note that Eqs. (64) and (65) look very similar in this form and that the role of  $\mathbf{Y}_{v_1v_2}(\mathbf{q})$  in the one-electron-two-phonon interaction is analogous to the role of the mode polarities  $\mathbf{p}_v(\hat{\mathbf{q}})$  in the one-electron-one-phonon interaction.

We end this section with several remarks surrounding the long-range limit. Most notably, for the one-electron-one-phonon interaction, the long-range limit is identical to the continuum limit, which is also obtained by letting  $\mathbf{q} \rightarrow \mathbf{0}$  for all phonon properties. However, this is no longer the case for the one-electron-two-phonon interaction: We only require that  $\mathbf{q}_1 \approx -\mathbf{q}_2$ , which leaves the phonon wave vector  $\mathbf{q}_2$  completely free. This is reflected in Eq. (65), where  $\mathbf{Y}_{v_1v_2}(\mathbf{q}_2)$  still depends on one phonon momentum which is free to explore the entire Brillouin zone. In contrast,  $\mathbf{p}_v(\hat{\mathbf{q}})$  is only evaluated very close to the  $\Gamma$  point at  $\mathbf{q} = \mathbf{0}$ . One must therefore be careful to not confuse the continuum limit  $\mathbf{q}_1, \mathbf{q}_2 \rightarrow \mathbf{0}$  with the long-range limit  $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G} \rightarrow \mathbf{0}$  when working with the one-electron-two-phonon interaction. For example, the model of Ref. [94] is derived in the continuum limit instead of the long-range limit, which is an additional hidden assumption of the model.

The long-range limit can be seen in terms of a series expansion of the full electron-phonon matrix elements  $g_{mnv}(\mathbf{k}, \mathbf{q})$  and  $g_{mnv_1v_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  as a function of the variables  $\mathbf{Q} = \mathbf{q} + \mathbf{G}$  and  $\mathbf{Q} = \mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}$ , respectively. Then, the long-range part represents the lowest-order term in the expansion, the dipole contribution, which is a  $1/|\mathbf{Q}|$  divergence in both cases. The next-order term would be a quadrupole contribution, a term of order  $|\mathbf{Q}|^0$  but which may have a nonanalytic angular

dependence around  $\mathbf{Q} = \mathbf{0}$ . This term is known for the one-electron-one-phonon interaction [95–98], but it will not be considered further in this article.

Finally, note that for cubic materials with a single nondegenerate conduction band that only interacts with a single dispersionless longitudinal optical (LO) phonon branch, Eq. (64) reduces to the well-known Fröhlich interaction [3,31]. This interaction is often used on its own to describe large polarons, where it is assumed that the long-range interaction dominates over the short-range interaction, so that  $g_{mnv}(\mathbf{k}, \mathbf{q}) \approx g_{mnv}^{(\text{long})}(\mathbf{k}, \mathbf{q})$ . For the remainder of this article, we make the same assumption for the one-electron-two-phonon interaction and assume that  $g_{mnv_1v_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) \approx g_{mnv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  for a large polaron. In the next section, we will calculate the effect of the one-electron-two-phonon interaction on the ground-state energy of a large polaron. While the theory appears to be general, it is essential to apply it only to materials that host large polarons, where contributions to the ground-state energy from short-range interactions are negligible. In contrast, for other types of materials, such as metals or those hosting small polarons, short-range effects become important and must be properly taken into account.

### III. WEAK-COUPLING TREATMENT OF THE NONLINEAR ELECTRON-PHONON HAMILTONIAN

#### A. Weak-coupling electron self-energy

With the Hamiltonian Eqs. (1)–(4) and with Eq. (64) and Eq. (65) for the electron-phonon matrix elements ready, we

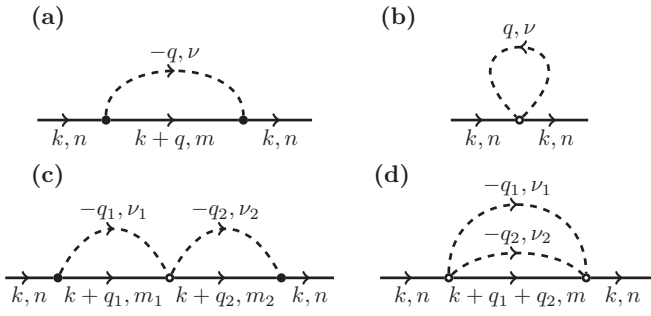


FIG. 3. Lowest-order self-energy diagrams that will be considered in this article. Diagrams (a) and (b) are the Fan-Migdal and Debye-Waller diagrams. Only diagrams (a) and (d) give significant contributions when the short-range one-electron-two-phonon interaction is neglected.  $k = (\mathbf{k}, \omega)$  and  $q = (\mathbf{q}, \omega')$  represent four-momenta,  $m$  and  $n$  represent electron bands, and  $\nu$  represents a phonon branch.

can proceed to investigate the effect of the long-range one-electron-two-phonon interaction on a physically interesting quantity. One of the most fundamental properties is the renormalization of the electron energies to quasiparticle energies  $\tilde{\epsilon}_{\mathbf{k},n}$ . They are found as the poles of the electron Green's function  $G_{mn}(\mathbf{k}, \omega)$ , which satisfies the following Dyson equation [13,91]:

$$G_{mn}^{-1}(\mathbf{k}, \omega) = G_{mn}^{(0)-1}(\mathbf{k}, \omega) + \Sigma_{mn}^{-1}(\mathbf{k}, \omega). \quad (66)$$

Here  $G_{mn}^{(0)}(\mathbf{k}, \omega)$  is the free electron Green's function, given in terms of the Fermi-Dirac distribution  $n_F(E)$  as follows [91]:

$$G_{mn}^{(0)}(\mathbf{k}, \omega) = \delta_{mn} \left( \frac{1 - n_F(\epsilon_{\mathbf{k},n})}{\omega - \frac{\epsilon_{\mathbf{k},n}}{\hbar} + i\delta} + \frac{n_F(\epsilon_{\mathbf{k},n})}{\omega - \frac{\epsilon_{\mathbf{k},n}}{\hbar} - i\delta} \right), \quad (67)$$

and  $\Sigma_{mn}(\mathbf{k}, \omega)$  is the self-energy of the electron. Often, the electron-phonon interaction is small enough that it is sufficient to obtain the quasiparticle energies up to lowest order in the self-energy. In this case, which is equivalent to Rayleigh-Schrödinger perturbation theory, the quasiparticle energy renormalization  $\Delta\epsilon_{\mathbf{k},n} := \tilde{\epsilon}_{\mathbf{k},n} - \epsilon_{\mathbf{k},n}$  is given by [13]:

$$\Delta\epsilon_{\mathbf{k},n} \approx \hbar \Sigma_{nn} \left( \mathbf{k}, \frac{\epsilon_{\mathbf{k},n}}{\hbar} \right) + O(\Sigma^2). \quad (68)$$

The self-energy itself can be obtained from a diagrammatic expansion ([91], Secs. 2–3). Here the perturbation is a sum of the one-electron-one-phonon and one-electron-two-phonon interactions, so one must build diagrams using both vertices in Fig. 1. In this article, we will consider all diagrams that have at most two one-electron-one-phonon vertices, and at most two one-electron-two-phonon vertices. This leaves the four unique self-energy diagrams which have been depicted in Fig. 3. The diagram in Fig. 3(a) is the Fan-Migdal diagram, which is the only diagram that would remain if no one-electron-two-phonon interaction was present. The diagram in Fig. 3(b) is the Debye-Waller diagram. Both of these diagrams are well known in the literature [13] and are the usual self-energy diagrams that are kept when treating the one-electron-one-phonon interaction: In that context, the Debye-Waller diagram is rewritten in terms of  $g_{mn\nu}(\mathbf{k}, \mathbf{0})$  using the rigid ion approx-

imation [13,84]. The diagrams in Fig. 3(c) and Fig. 3(d) are new: They both contain the one-electron-two-phonon vertex  $g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$ , for which the expression in Eq. (65) can be used.

We note that the choice of which diagrams to include in the expansion is somewhat arbitrary, because it is more difficult to define what “lowest order in the electron-phonon interaction” means when more than one interaction is present. For example, one might define the order of the diagram as the number of its interaction vertices, which indicates how many times the macroscopic electric field of the electron interacts with the phonons. By this metric, the diagrams in Fig. 3(a) and Fig. 3(d) have the same order. However, one might also define the order of the diagram by their number of phonon lines or, equivalently, the order of the ionic displacements. By this metric, the diagram in Fig. 3(d) is of higher order than the diagram in Fig. 3(a) and a self-consistent expansion that includes this diagram should also include all diagrams with four one-electron-one-phonon interactions. In the theory of this section, we choose to limit ourselves to the diagrams in Fig. 3 for the sake of simplicity and novelty, since results for the higher-order one-electron-one-phonon processes already exist in the literature [99–101]. In practice, the decision of which diagrams to include should be based on the strength of the interaction vertices, which can change significantly from material to material. As a concrete example, the one-electron-one-phonon interaction strength is strong in LiF and the higher-order one-electron-one-phonon processes may not be neglected. Therefore, when we calculate the polaron energy for LiF in Sec. IV, we will use the literature result from Ref. [99] that includes diagrams with up to six one-electron-one-phonon interactions.

The diagrams in Fig. 3 can be written as integrals over Green's functions using the Feynman rules (Ref. [91], Sec. 2.8). We follow the method and conventions in Ref. [102] to determine the prefactors for each diagram. Every one-electron-one-phonon vertex corresponds to a factor  $\sqrt{\frac{\Omega_0}{\Omega}} \frac{1}{\hbar} g_{mn\nu}(\mathbf{k}, \mathbf{q})$ , and every one-electron-two-phonon vertex corresponds to a factor  $\frac{\Omega_0}{\Omega} \frac{2}{\hbar} g_{mn\nu_1\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$ . The additional factor 2 comes from the fact that the conventional factor  $\frac{1}{2!}$  from Ref. [102] is missing from the Hamiltonian in Eq. (4). Every electron line corresponds to the usual electron Green's function from Eq. (67), and every phonon line corresponds to the usual phonon Green's function  $D_{\nu\nu'}^{(0)}(\mathbf{q}, \omega)$  [91]:

$$D_{\nu\nu'}^{(0)}(\mathbf{q}, \omega) = (1 + n_B(\omega_{\mathbf{q},\nu})) \frac{2\omega_{\mathbf{q},\nu} \delta_{\nu\nu'}}{\omega^2 - (\omega_{\mathbf{q},\nu} - i\delta)^2} - n_B(\omega_{\mathbf{q},\nu}) \frac{2\omega_{\mathbf{q},\nu} \delta_{\nu\nu'}}{\omega^2 - (\omega_{\mathbf{q},\nu} + i\delta)^2}, \quad (69)$$

where  $n_B(\omega)$  is the Bose-Einstein distribution. Finally, each diagram must be divided by a combinatorial factor, equal to the number of symmetries that leaves the diagram invariant according to the rules in Ref. [102]. This combinatorial factor is 1 for the diagrams in Figs. 3(a)–3(c) and 2 for the diagrams in Figs. 3(b)–3(d). Following these rules, the contribution of each of the diagrams in Fig. 3 can be

written as follows:

$$\Sigma_{nm}^{(a)}(\mathbf{k}, \omega) = i \frac{\Omega_0}{\Omega} \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \sum_{\mathbf{q}, v, m} |g_{mv}(\mathbf{k}, \mathbf{q})|^2 G_{mm}^{(0)}(\mathbf{k} + \mathbf{q}, \omega + \omega_1) D_{vv}^{(0)}(\mathbf{q}, -\omega_1), \quad (70)$$

$$\Sigma_{nm}^{(b)}(\mathbf{k}, \omega) = i \frac{\Omega_0}{\Omega} \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \sum_{\mathbf{q}, v} g_{mv}(\mathbf{k}, -\mathbf{q}, \mathbf{q}) D_{vv}^{(0)}(-\mathbf{q}, \omega_1), \quad (71)$$

$$\begin{aligned} \Sigma_{nm}^{(c)}(\mathbf{k}, \omega) = & -2 \frac{\Omega_0^2}{\Omega^2} \frac{1}{\hbar^3} \sum_{m_1, m_2} \sum_{v_1, v_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \int_{-\infty}^{+\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{+\infty} \frac{d\omega_2}{2\pi} G_{m_1 m_1}^{(0)}(\mathbf{k} + \mathbf{q}_1, \omega + \omega_1) G_{m_2 m_2}^{(0)}(\mathbf{k} + \mathbf{q}_2, \omega + \omega_2) \\ & \times D_{v_1 v_1}^{(0)}(\mathbf{q}_1, -\omega_1) D_{v_2 v_2}^{(0)}(\mathbf{q}_2, -\omega_2) g_{m_1 n v_1}(\mathbf{k}, \mathbf{q}_1) g_{m_2 m_1 v_1 v_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) g_{m_2 n v_2}^*(\mathbf{k}, \mathbf{q}_2), \end{aligned} \quad (72)$$

$$\begin{aligned} \Sigma_{nm}^{(d)}(\mathbf{k}, \omega) = & -2 \frac{\Omega_0^2}{\Omega^2} \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \sum_{\mathbf{q}_1, \mathbf{q}_2, v_1, v_2, m} |g_{mv_1 v_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)|^2 \\ & \times G_{mm}^{(0)}(\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2, \omega + \omega_1) D_{v_1 v_1}^{(0)}(-\mathbf{q}_1, -\omega_1 + \omega_2) D_{v_2 v_2}^{(0)}(-\mathbf{q}_2, -\omega_2). \end{aligned} \quad (73)$$

We are interested in the case where there is only long-range electron-phonon interaction, e.g., in the case of a large polaron. In Appendix B, it is shown that in this case, the diagrams in Eqs. (71) and (72) have negligible contributions compared to the other two diagrams. Therefore, from here onward, we will only consider the ‘‘Fan-Migdal-like’’ diagrams of Fig. 3(a) and Fig. 3(d) for the self-energy:

$$\Sigma_{nm}(\mathbf{k}, \omega) = \Sigma_{nm}^{(a)}(\mathbf{k}, \omega) + \Sigma_{nm}^{(d)}(\mathbf{k}, \omega). \quad (74)$$

In Eq. (70) and Eq. (73) for these two terms, the integrals over the frequencies  $\omega_1$  and  $\omega_2$  can be performed exactly. First, note that the free phonon Green’s function can be written as  $D_{vv'}^{(0)}(\mathbf{q}, \omega) = \mathcal{D}_0(\omega_{\mathbf{q}, v}, \omega) \delta_{vv'}$ , where

$$\mathcal{D}_0(\omega', \omega) = (1 + n_B(\omega')) \frac{2\omega'}{\omega^2 - (\omega' - i\delta)^2} - n_B(\omega') \frac{2\omega'}{\omega^2 - (\omega' + i\delta)^2}. \quad (75)$$

Then, the following identity can be used in Eq. (73), which can be proven using complex contour integration on the upper half plane:

$$\begin{aligned} i \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \mathcal{D}_0(\omega_{\mathbf{q}_1, v_1}, \omega - \omega') \mathcal{D}_0(\omega_{\mathbf{q}_2, v_2}, \omega') = & [1 + n_B(\omega_{\mathbf{q}_1, v_1}) + n_B(\omega_{\mathbf{q}_2, v_2})] \mathcal{D}_0(\omega_{\mathbf{q}_1, v_1} + \omega_{\mathbf{q}_2, v_2}, \omega) \\ & + |n_B(\omega_{\mathbf{q}_2, v_2}) - n_B(\omega_{\mathbf{q}_1, v_1})| \mathcal{D}_0(|\omega_{\mathbf{q}_1, v_1} - \omega_{\mathbf{q}_2, v_2}|, \omega). \end{aligned} \quad (76)$$

The remaining integrals over  $\omega_1$  are both of the following form:

$$i \int_{-\infty}^{+\infty} \frac{d\omega_1}{2\pi} G_{mm}^{(0)}(\mathbf{k}, \omega + \omega_1) \mathcal{D}_0(\omega', -\omega_1) = \frac{1 - n_F(\epsilon_{\mathbf{k}, n}) + n_B(\omega')}{\omega - \omega' - \frac{\epsilon_{\mathbf{k}, n}}{\hbar} + i\delta} + \frac{n_B(\omega') + n_F(\epsilon_{\mathbf{k}, n})}{\omega + \omega' - \frac{\epsilon_{\mathbf{k}, n}}{\hbar} + i\delta}. \quad (77)$$

This identity can also be proven by complex contour integration on the upper half plane. It only holds after moving all the poles to the lower half plane after performing the integration, which means that the resulting self-energy will be the retarded one. This is a standard result at finite temperatures [13,91]; this distinction will not be relevant in the remainder of this article.

By using the above two integral identities in Eq. (70) and Eq. (73), the lowest-order self-energy from Eq. (74) can be written in the following form:

$$\Sigma_{nm}(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \alpha^2 F_{\mathbf{k}, n}(\varepsilon, \omega') \left[ \frac{1 - n_F(\varepsilon) + n_B(\omega')}{\hbar\omega - \hbar\omega' - \varepsilon + i\delta} + \frac{n_F(\varepsilon) + n_B(\omega')}{\hbar\omega + \hbar\omega' - \varepsilon + i\delta} \right] d\varepsilon d\omega'. \quad (78)$$

In the above expression, the two-argument Eliashberg function  $\alpha^2 F_{\mathbf{k}, n}(\varepsilon, \omega)$  is defined as follows:

$$\begin{aligned} \alpha^2 F_{\mathbf{k}, n}(\varepsilon, \omega) := & \frac{1}{\hbar} \sum_{v, m} \frac{1}{\Omega_{1\text{BZ}}} \int_{1\text{BZ}} |g_{mv}(\mathbf{k}, \mathbf{q})|^2 \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q}, m}) \delta(\omega - \omega_{\mathbf{q}, v}) d^3 \mathbf{q} \\ & + \frac{2}{\hbar} \sum_{v_1, v_2, m} \frac{1}{\Omega_{1\text{BZ}}^2} \int_{1\text{BZ}} \int_{1\text{BZ}} |g_{mv_1 v_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)|^2 \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2, m}) \\ & \times \left( [1 + n_B(\omega_{\mathbf{q}_1, v_1}) + n_B(\omega_{\mathbf{q}_2, v_2})] \delta(\omega - \omega_{\mathbf{q}_1, v_1} - \omega_{\mathbf{q}_2, v_2}) \right. \\ & \left. + |n_B(\omega_{\mathbf{q}_2, v_2}) - n_B(\omega_{\mathbf{q}_1, v_1})| \delta(\omega - |\omega_{\mathbf{q}_1, v_1} - \omega_{\mathbf{q}_2, v_2}|) \right) d^3 \mathbf{q}_1 d^3 \mathbf{q}_2. \end{aligned} \quad (79)$$

Here the sums over  $\mathbf{q}$  have been replaced with integrals over the first Brillouin zone using the usual substitution  $\sum_{\mathbf{q}} \rightarrow \frac{\Omega}{(2\pi)^3} \int_{\text{1BZ}} d^3\mathbf{q}$  [103], and  $\Omega_{\text{1BZ}} = \frac{(2\pi)^3}{\Omega_0}$  is the volume of the first Brillouin zone [103].

Equation (78) is the literature expression for the Fan-Migdal self-energy [13]. The one-electron-two-phonon contribution from the diagram in Fig. 3(d) only enters the self-energy through an additional term in the Eliashberg function. Indeed, the first line of Eq. (79) is the familiar definition of the Eliashberg function for the one-electron-one-phonon Hamiltonian [13]. The other term is of a similar form but is directly due to the one-electron-two-phonon interaction. Curiously, this additional term is temperature dependent through the Bose-Einstein distributions: This temperature dependence comes directly from the integral identity in Eq. (76).

## B. The one-electron-two-phonon spectral function

Let us now consider the case where the long-range interaction is dominant over the short-range interaction, such as in the case of a large polaron. In this case, we may approximate the Eliashberg function by using the long-range electron-phonon matrix elements from Eqs. (64) and (65) in its definition from Eq. (79). Furthermore, because the one-electron-one-phonon matrix element is dominated by processes where  $\mathbf{q} + \mathbf{G} \approx \mathbf{0}$ , we may replace the phonon frequencies  $\omega_{\mathbf{q},\nu}$  in the first term with  $\omega_{\hat{\mathbf{q}},\nu}$ , the phonon frequencies around the  $\Gamma$  point. Analogously, the one-electron-two-phonon matrix element is dominated by processes where  $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G} \approx \mathbf{0}$ , so we may set  $\omega_{\mathbf{q}_1,\nu_1} \approx \omega_{-\mathbf{q}_2,\nu_1} = \omega_{\mathbf{q}_2,\nu_1}$  in the second term. This yields:

$$\begin{aligned} \alpha^2 F_{\mathbf{k},n}(\varepsilon, \omega) &\approx \frac{1}{\hbar} \sum_{\nu,m} \frac{1}{\Omega_{\text{1BZ}}} \int_{\text{1BZ}} |g_{m\nu}^{(\text{long})}(\mathbf{k}, \mathbf{q})|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q},m}) \delta(\omega - \omega_{\hat{\mathbf{q}},\nu}) d^3\mathbf{q} \\ &+ \frac{2}{\hbar} \sum_{\nu_1,\nu_2,m} \frac{1}{\Omega_{\text{1BZ}}^2} \int_{\text{1BZ}} \int_{\text{1BZ}} |g_{m\nu_1\nu_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q}_1+\mathbf{q}_2,m}) \\ &\times \left( [1 + n_B(\omega_{\mathbf{q}_2,\nu_1}) + n_B(\omega_{\mathbf{q}_2,\nu_2})] \delta(\omega - \omega_{\mathbf{q}_2,\nu_1} - \omega_{\mathbf{q}_2,\nu_2}) \right. \\ &\left. + |n_B(\omega_{\mathbf{q}_2,\nu_2}) - n_B(\omega_{\mathbf{q}_2,\nu_1})| \delta(\omega - |\omega_{\mathbf{q}_2,\nu_1} - \omega_{\mathbf{q}_2,\nu_2}|) \right) d^3\mathbf{q}_1 d^3\mathbf{q}_2. \end{aligned} \quad (80)$$

Substituting Eqs. (64) and (65) into this expression yields, after a short calculation:

$$\begin{aligned} \alpha^2 F_{\mathbf{k},n}(\varepsilon, \omega) &\approx \frac{e^2}{\varepsilon_0 \Omega_0} \frac{1}{\Omega_{\text{1BZ}}} \int_{\text{1BZ}} \sum_{\mathbf{G}_1, \mathbf{G}_2 \neq -\mathbf{q}} \frac{(\mathbf{q} + \mathbf{G}_1) \cdot (\mathcal{R}(\omega, \hat{\mathbf{q}}) \mathbf{I} + \mathcal{T}(\omega)) \cdot (\mathbf{q} + \mathbf{G}_2)}{[(\mathbf{q} + \mathbf{G}_1) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q} + \mathbf{G}_1)][(\mathbf{q} + \mathbf{G}_2) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q} + \mathbf{G}_2)]} \\ &\times \left( \sum_m \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q},m}) \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G}_2) \cdot \mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G}_1) \cdot \mathbf{r}} | \psi_{\mathbf{k},n} \rangle \right) d^3\mathbf{q}, \end{aligned} \quad (81)$$

where we have introduced the following two dimensionless spectral functions, which represent the contributions from the one-electron-one-phonon and one-electron-two-phonon interactions, respectively:

$$\mathcal{R}(\omega, \hat{\mathbf{q}}) := \frac{e^2}{2\varepsilon_0 \Omega_0 \omega} \sum_{\nu} |\hat{\mathbf{q}} \cdot \mathbf{p}_\nu(\hat{\mathbf{q}})|^2 \delta(\omega - \omega_{\hat{\mathbf{q}},\nu}) \quad (82)$$

$$\mathcal{T}_{\alpha\beta}(\omega) := \frac{e^2}{2\hbar\varepsilon_0 \Omega_0} \sum_{\nu_1,\nu_2} \frac{1}{\Omega_{\text{1BZ}}} \int_{\text{1BZ}} Y_{\nu_1\nu_2,\alpha}(\mathbf{q}) Y_{\nu_1\nu_2,\beta}^*(\mathbf{q}) \left( [1 + n_B(\omega_{\mathbf{q},\nu_1}) + n_B(\omega_{\mathbf{q},\nu_2})] \delta(\omega - \omega_{\mathbf{q},\nu_1} - \omega_{\mathbf{q},\nu_2}) \right. \\ \left. + |n_B(\omega_{\mathbf{q},\nu_2}) - n_B(\omega_{\mathbf{q},\nu_1})| \delta(\omega - |\omega_{\mathbf{q},\nu_1} - \omega_{\mathbf{q},\nu_2}|) \right) d^3\mathbf{q}. \quad (83)$$

In the common case where  $\omega_{\hat{\mathbf{q}},\nu} = \omega_\nu$  does not depend on the direction  $\hat{\mathbf{q}}$  (e.g., in cubic materials), the function  $\mathcal{R}(\omega, \hat{\mathbf{q}})$  is simply a sum of delta peaks  $\delta(\omega - \omega_\nu)$ . This is due to the long-range approximation. In practice, it means that  $\mathcal{R}(\omega, \hat{\mathbf{q}})$  is merely a function to simplify notation: It cannot be calculated or plotted numerically.

By contrast, the one-electron-two-phonon spectral function  $\mathcal{T}_{\alpha\beta}(\omega)$  is an important quantity that can be calculated from first principles. Indeed, recalling the definition of  $Y_{\nu_1\nu_2,\alpha}(\mathbf{q})$  in Eq. (62), one only requires the phonon frequencies, phonon eigenvectors, and the  $\mathcal{E}$  derivative of the dynamical matrix to calculate  $\mathcal{T}_{\alpha\beta}(\omega)$ . It is the only new quantity in Eq. (81): All other quantities are known, harmonic literature quantities. The intuitive meaning for  $\mathcal{T}_{\alpha\beta}(\omega)$  is more clear in the

zero-temperature limit, where  $n_B(\omega) = 0$ :

$$\begin{aligned} \mathcal{T}_{\alpha\beta}(\omega) &= \frac{e^2}{2\hbar\varepsilon_0 \Omega_0} \sum_{\nu_1,\nu_2} \frac{1}{\Omega_{\text{1BZ}}} \int_{\text{1BZ}} Y_{\nu_1\nu_2,\alpha}(\mathbf{q}) \\ &\times Y_{\nu_1\nu_2,\beta}^*(\mathbf{q}) \delta(\omega - \omega_{\mathbf{q},\nu_1} - \omega_{\mathbf{q},\nu_2}) d^3\mathbf{q}. \end{aligned} \quad (84)$$

$\mathcal{T}_{\alpha\beta}(\omega)$  can be interpreted as the total strength of all the one-electron-two-phonon processes where  $\mathbf{q}_1 \approx -\mathbf{q}_2$  and the total phonon energy is  $\hbar\omega$ . Because  $\mathcal{T}_{\alpha\beta}(\omega)$  is a dimensionless quantity, its value for a material will roughly indicate how strong we expect the one-electron-two-phonon interaction to be for that material.

$\mathcal{T}_{\alpha\beta}(\omega)$  is a real and symmetric  $3 \times 3$  tensor, which is a function of a single variable  $\omega$ . Furthermore,  $\mathcal{T}_{\alpha\beta}(\omega) = 0$  unless  $\omega \in [0, 2\omega_{\max}]$ , where  $\omega_{\max}$  is the maximum phonon frequency of the material. This makes it possible to tabulate the one-electron-two-phonon spectral function for a given material. Additionally,  $\mathcal{T}_{\alpha\beta}(\omega)$  follows all the symmetries of the material. Expressed mathematically, if  $\mathcal{G}$  is the point group of the material under consideration, then for every symmetry  $\mathbf{R} \in \mathcal{G}$  of the material, the matrix  $\mathcal{T}(\omega)$  must satisfy:

$$\mathcal{T}(\omega) = \mathbf{R}^{-1} \cdot \mathcal{T}(\omega) \cdot \mathbf{R}. \quad (85)$$

In particular, for any orthorhombic material this implies that  $\mathcal{T}_{\alpha\beta}(\omega)$  is diagonal, and for any cubic material the one-electron-two-phonon spectral function is a scalar:

$$\mathcal{T}_{\alpha\beta}(\omega) = \mathcal{T}(\omega)\delta_{\alpha\beta} \quad (\text{cubic materials}). \quad (86)$$

For the remainder of this section, it is assumed that  $\mathcal{T}_{\alpha\beta}(\omega)$  is an input parameter that has been calculated elsewhere. In Sec. IV, it is shown how to calculate  $\mathcal{T}(\omega)$  in practice from first principles for the cubic materials LiF and KTaO<sub>3</sub>.

### C. Quasiparticle energy shifts

With the one-electron-two-phonon spectral function defined, we now return to Eq. (81) for the Eliashberg function. It can be simplified considerably by making appropriate approximations. First, recall that due to the long-range approximation, it is allowed to neglect any term with a nonzero reciprocal lattice vector. Here we keep only the terms where  $\mathbf{G}_1 = \mathbf{G}_2$  in Eq. (81). Then, in Appendix C, we show that the sum over  $m$  simplifies drastically, and the result no longer depends on the electronic states:

$$\sum_m \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q},m}) \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle = \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q},n}). \quad (87)$$

This gives the following expression for the Eliashberg function:

$$\alpha^2 F_{\mathbf{k},n}(\varepsilon, \omega) \approx \frac{e^2}{\varepsilon_0 \Omega_0} \sum_{\mathbf{G} \neq -\mathbf{q}} \frac{1}{\Omega_{1\text{BZ}}} \int_{1\text{BZ}} \frac{(\mathbf{q} + \mathbf{G}) \cdot [\mathcal{R}(\omega, \hat{\mathbf{q}}) \mathbf{I} + \mathcal{T}(\omega)] \cdot (\mathbf{q} + \mathbf{G})}{[(\mathbf{q} + \mathbf{G}) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q} + \mathbf{G})]^2} \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q},n}) d^3 \mathbf{q}. \quad (88)$$

The combination of integral over the first Brillouin zone  $\Omega_{1\text{BZ}}$  and the sum over reciprocal lattice vectors  $\mathbf{G}$  can be written as an integral over the entire reciprocal space, with an integration variable  $\mathbf{q} + \mathbf{G} = \mathbf{Q}$ . Using  $\Omega_0 \Omega_{1\text{BZ}} = (2\pi)^3$ , this yields:

$$\alpha^2 F_{\mathbf{k},n}(\varepsilon, \omega) \approx \frac{e^2}{\varepsilon_0 (2\pi)^3} \int \frac{\mathbf{Q} \cdot [\mathcal{R}(\omega, \hat{\mathbf{Q}}) \mathbf{I} + \mathcal{T}(\omega)] \cdot \mathbf{Q}}{(\mathbf{Q} \cdot \boldsymbol{\varepsilon}_\infty \cdot \mathbf{Q})^2} \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{Q},n}) d^3 \mathbf{Q}. \quad (89)$$

This expression for the Eliashberg function can be combined with Eq. (68) and Eq. (78) to find an expression for the temperature-dependent quasiparticle energy shifts  $\Delta\varepsilon_{\mathbf{k},n}$ :

$$\Delta\varepsilon_{\mathbf{k},n} = \frac{\hbar e^2}{\varepsilon_0 (2\pi)^3} \iint_0^{+\infty} \frac{\mathbf{Q} \cdot (\mathcal{R}(\omega, \hat{\mathbf{Q}}) \mathbf{I} + \mathcal{T}(\omega)) \cdot \mathbf{Q}}{[\mathbf{Q} \cdot \boldsymbol{\varepsilon}_\infty \cdot \mathbf{Q}]^2} \left[ \frac{1 - n_F(\varepsilon_{\mathbf{k}+\mathbf{Q},n}) + n_B(\omega)}{\varepsilon_{\mathbf{k},n} - \varepsilon_{\mathbf{k}+\mathbf{Q},n} - \hbar\omega + i\delta} + \frac{n_F(\varepsilon_{\mathbf{k}+\mathbf{Q},n}) + n_B(\omega)}{\varepsilon_{\mathbf{k},n} - \varepsilon_{\mathbf{k}+\mathbf{Q},n} + \hbar\omega + i\delta} \right] d^3 \mathbf{Q} d\omega. \quad (90)$$

where the lower bound for the  $\omega$  integral was changed from  $-\infty$  to 0 because both  $\mathcal{R}(\omega, \hat{\mathbf{Q}})$  and  $\mathcal{T}(\omega)$  are zero when  $\omega < 0$ . This expression can be evaluated once the electronic bands  $\varepsilon_{\mathbf{k},n}$  are known, for example after a first-principles calculation. In the remainder of this section, we will instead evaluate Eq. (90) by choosing appropriate model expressions for the electronic bands in the context of a large polaron.

### D. Ground-state energy in the generalized Fröhlich model

The generalized Fröhlich Hamiltonian was introduced in Ref. [93]. Its only assumptions are that the electron-phonon interaction is dominated by the long-range interaction as in Eqs. (64) and (65), that the conduction band minimum is located at  $\Gamma$ , and that all quantities are evaluated near  $\Gamma$ . In particular, it is assumed that only the electron bands around the conduction band minimum are important, and these bands are replaced by a parabolic approximation:

$$\varepsilon_{\mathbf{k},n} \approx \varepsilon_c + \frac{\hbar^2 |\mathbf{k}|^2}{2m_n^*(\hat{\mathbf{k}})}. \quad (91)$$

Here  $\varepsilon_c$  is the minimum energy of the conduction band at  $\Gamma$ . We are neglecting any band with  $\varepsilon_{0,n} \neq \varepsilon_c$ ; in other words,

we are only keeping those bands which are degenerate at the conduction band minimum. The degree of degeneracy at the conduction band minimum is denoted by  $n_{\text{deg}}$ .

With Eq. (91), it is possible to calculate the ground-state energy  $E_0$  of a large polaron, which is the energy shift of the conduction band bottom due to the electron-phonon interaction. It is equivalent to the conduction band zero-point renormalization in band-gap renormalization theory [93]. For simplicity, we evaluate the ground-state energy at temperature zero, such that  $n_B(\omega) = 0$ . Furthermore, we assume that the material is either undoped or that the doping concentration of the material is very low, so that  $E_F \lesssim \varepsilon_c$  and  $n_F(\varepsilon_{\mathbf{k},n}) \approx 0$ . Under those approximations, the ground-state energy can be obtained from Eq. (90) as follows:

$$E_0 = -\frac{1}{n_{\text{deg}}} \sum_{n=1}^{n_{\text{deg}}} \frac{\hbar e^2}{\varepsilon_0 (2\pi)^3} \iint_0^{+\infty} \frac{\mathbf{Q} \cdot [\mathcal{R}(\omega, \hat{\mathbf{Q}}) \mathbf{I} + \mathcal{T}(\omega)] \cdot \mathbf{Q}}{(\mathbf{Q} \cdot \boldsymbol{\varepsilon}_\infty \cdot \mathbf{Q})^2} \times \frac{1}{\frac{\hbar^2 |\mathbf{Q}|^2}{2m_n^*(\hat{\mathbf{Q}})} + \hbar\omega} d^3 \mathbf{Q} d\omega. \quad (92)$$

The integral over  $\mathbf{Q}$  can be split into a radial integral over  $Q^2 dQ$  and an angular integral  $d^2 \hat{\mathbf{q}}$  over the unit

sphere  $S^2$ :

$$E_0 = -\frac{1}{n_{\text{deg}}} \sum_{n=1}^{n_{\text{deg}}} \frac{\hbar e^2}{\varepsilon_0 (2\pi)^3} \int_{S^2} \int_0^{+\infty} \frac{\hat{\mathbf{q}} \cdot [\mathcal{R}(\omega, \hat{\mathbf{q}}) \mathbf{I} + \mathcal{T}(\omega)] \cdot \hat{\mathbf{q}}}{(\hat{\mathbf{q}} \cdot \boldsymbol{\varepsilon}_\infty \cdot \hat{\mathbf{q}})^2} \times \left[ \int_0^{+\infty} \frac{dQ}{\frac{\hbar^2 Q^2}{2m_n^*(\hat{\mathbf{q}})} + \hbar\omega} \right] d^2 \hat{\mathbf{q}} d\omega. \quad (93)$$

The integral over  $Q$  can now be evaluated analytically, which yields:

$$E_0 = -\frac{1}{n_{\text{deg}}} \sum_{n=1}^{n_{\text{deg}}} \frac{e^2}{(4\pi)^2 \varepsilon_0} \sqrt{\frac{2}{\hbar}} \int_0^{+\infty} \int_{S^2} \frac{\mathcal{R}(\omega, \hat{\mathbf{q}}) + \hat{\mathbf{q}} \cdot \mathcal{T}(\omega) \cdot \hat{\mathbf{q}}}{\sqrt{\omega} (\hat{\mathbf{q}} \cdot \boldsymbol{\varepsilon}_\infty \cdot \hat{\mathbf{q}})^2} \times \sqrt{m_n^*(\hat{\mathbf{q}})} d\omega d^2 \hat{\mathbf{q}}. \quad (94)$$

The one-electron-one-phonon contribution can still be simplified, because the  $\omega$  integral over Eq. (82) for  $\mathcal{R}(\omega, \hat{\mathbf{q}})$  can be performed analytically:

$$\int_{-\infty}^{+\infty} \frac{\mathcal{R}(\omega, \hat{\mathbf{q}})}{\sqrt{\omega}} d\omega = \frac{e^2}{2\varepsilon_0 \Omega_0} \sum_{\nu} \frac{|\hat{\mathbf{q}} \cdot \mathbf{p}_\nu(\hat{\mathbf{q}})|^2}{\omega_{\hat{\mathbf{q}}, \nu}^{\frac{3}{2}}}. \quad (95)$$

Similarly, in the one-electron-two-phonon contribution, nothing depends on  $\omega$  other than  $\mathcal{T}(\omega)$ , so the one-electron-two-phonon spectral function only enters the ground-state energy through the following moment:

$$\mathcal{T}_{-\frac{1}{2}} := \int_0^{+\infty} \frac{\mathcal{T}(\omega)}{\sqrt{\omega}} d\omega. \quad (96)$$

With these two integrals, the ground-state energy can be written in its final form as a sum of the one-electron-one-phonon and one-electron-two-phonon contributions:

$$E_0 = E_0^{(1e1ph)} + E_0^{(1e2ph)}, \quad (97)$$

$$E_0^{(1e1ph)} = -\sum_{\nu} \sum_{n=1}^{n_{\text{deg}}} \left( \frac{e^2}{4\pi \varepsilon_0} \right)^2 \frac{\hbar}{\sqrt{2} \Omega_0 n_{\text{deg}}} \int_{S^2} \frac{\sqrt{m_n^*(\hat{\mathbf{q}})}}{(\hbar \omega_{\hat{\mathbf{q}}, \nu})^{\frac{3}{2}}} \times \frac{|\hat{\mathbf{q}} \cdot \mathbf{p}_\nu(\hat{\mathbf{q}})|^2}{(\hat{\mathbf{q}} \cdot \boldsymbol{\varepsilon}_\infty \cdot \hat{\mathbf{q}})^2} d^2 \hat{\mathbf{q}}, \quad (98)$$

$$E_0^{(1e2ph)} = -\sum_{n=1}^{n_{\text{deg}}} \frac{e^2}{4\pi \varepsilon_0 n_{\text{deg}}} \sqrt{\frac{2}{\hbar}} \frac{1}{4\pi} \int_{S^2} \frac{\hat{\mathbf{q}} \cdot \mathcal{T}_{-\frac{1}{2}} \cdot \hat{\mathbf{q}}}{(\hat{\mathbf{q}} \cdot \boldsymbol{\varepsilon}_\infty \cdot \hat{\mathbf{q}})^2} \times \sqrt{m_n^*(\hat{\mathbf{q}})} d^2 \hat{\mathbf{q}}. \quad (99)$$

Equation (98) is the literature expression for the weak-coupling ground-state energy in the generalized Fröhlich model [93]. We have shown here that the one-electron-two-phonon interaction gives a contribution that can similarly be written as an angular average over  $d^2 \hat{\mathbf{q}}$ . Perhaps most interestingly, it shows that the  $-\frac{1}{2}$  moment of the one-electron-two-phonon spectral function has a physical meaning: It controls the strength of the contribution to the ground-state energy. Combining Eqs. (96) and (83), we can find another useful expression for this moment at

temperature zero:

$$\left( \mathcal{T}_{-\frac{1}{2}} \right)_{\alpha\beta} = \frac{e^2}{2\hbar \varepsilon_0 \Omega_0} \sum_{\nu_1, \nu_2} \frac{1}{\Omega_{1BZ}} \times \int_{1BZ} \frac{Y_{\nu_1 \nu_2, \alpha}(\mathbf{q}) Y_{\nu_1 \nu_2, \beta}^*(\mathbf{q})}{\sqrt{\omega_{\mathbf{q}, \nu_1} + \omega_{\mathbf{q}, \nu_2}}} d^3 \mathbf{q}. \quad (100)$$

This moment is a  $3 \times 3$  matrix; for cubic materials it is even a simple scalar. Therefore,  $\mathcal{T}_{-\frac{1}{2}}$  is a useful quantity to tabulate for many materials to quantify the strength of the one-electron-two-phonon interaction in that material. A downside is that  $\mathcal{T}_{-\frac{1}{2}}$  is no longer dimensionless but has the same units as  $\sqrt{\omega}$ . If desired, then one could calculate and tabulate  $\mathcal{T}_{-\frac{1}{2}}/\sqrt{\omega_{\text{ref}}}$  for some reference frequency  $\omega_{\text{ref}}$ , such as the maximum phonon frequency in the system.

### E. Polaron energy and effective mass in a Fröhlich-type material

Finally, we investigate the one-electron-two-phonon interaction in the case of a material that satisfies all the assumptions of the Fröhlich Hamiltonian. In particular, we assume that the material has cubic symmetry and that it only has two atoms in the unit cell so that there is only a single longitudinal optical phonon branch. Additionally, we assume that the conduction band is not degenerate at its minimum, so that the electron band can be written as:

$$\epsilon_{\mathbf{k}, c} \approx \epsilon_c + \frac{\hbar^2 |\mathbf{k}|^2}{2m^*}. \quad (101)$$

Since this model describes a cubic material, the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  is a scalar function, as discussed in Eq. (86). The dielectric tensor  $\boldsymbol{\varepsilon}_\infty = \varepsilon_\infty \mathbf{I}$  also becomes a scalar in this case. The one-electron-one-phonon function  $\mathcal{R}(\omega, \hat{\mathbf{q}})$  also simplifies considerably. Indeed, in this model, the mode polarities  $\hat{\mathbf{q}} \cdot \mathbf{p}_\nu(\hat{\mathbf{q}})$  are zero for all phonon branches except for the LO branch, whose mode polarity we write as  $p_{LO}$  [104]:

$$\hat{\mathbf{q}} \cdot \mathbf{p}_\nu(\hat{\mathbf{q}}) = p_{LO} \delta_{\nu, LO}. \quad (102)$$

This simplifies  $\mathcal{R}(\omega, \hat{\mathbf{q}})$  to a single delta peak:

$$\mathcal{R}(\omega, \hat{\mathbf{q}}) = \alpha \frac{4\pi \varepsilon_0 \varepsilon_\infty^2}{e^2} \frac{(\hbar \omega_{LO})^2}{\sqrt{2\hbar \omega_{LO} m^*}} \delta(\omega - \omega_{LO}), \quad (103)$$

where the Fröhlich coupling constant  $\alpha$  is defined as [104]:

$$\alpha := \frac{4\pi}{\Omega_0} \sqrt{\frac{\hbar m^*}{2\omega_{LO}}} \left( \frac{e^2}{4\pi \varepsilon_0 \varepsilon_\infty \hbar \omega_{LO}} \right)^2 |p_{LO}|^2. \quad (104)$$

The polaron energy shift  $\Delta \epsilon_{\mathbf{k}, c}$  in the conduction band can now be calculated from Eq. (90) in terms of  $\alpha$  and  $\mathcal{T}(\omega)$ . Just like in Sec. III D, we assume temperature zero and a very low doping concentration, such that we may write  $n_B(\omega) = n_F(\epsilon_{\mathbf{k}, c}) = 0$ . Using this, Eq. (86), and Eq. (103) in Eq. (90) gives the following expression for the polaron energy

shift:

$$\Delta\epsilon_{\mathbf{k},c} = -\frac{\hbar e^2}{\epsilon_0 \epsilon_\infty^2 (2\pi)^3} \int_0^{+\infty} \left[ \alpha \frac{4\pi \epsilon_0 \epsilon_\infty^2}{e^2} \frac{(\hbar\omega_{\text{LO}})^2}{\sqrt{2\hbar\omega_{\text{LO}} m^*}} \delta(\omega - \omega_{\text{LO}}) + \mathcal{T}(\omega) \right] \left( \int \frac{1}{\frac{\hbar^2 |\mathbf{k} + \mathbf{Q}|^2}{2m^*} - \frac{\hbar^2 |\mathbf{k}|^2}{2m^*} + \hbar\omega - i\delta} \frac{d^3 \mathbf{Q}}{|\mathbf{Q}|^2} \right) d\omega. \quad (105)$$

The remaining integral over  $\mathbf{Q}$  also appears in the treatment of the Fröhlich Hamiltonian. It can be performed analytically and yields (see Eqs. (7.10), (7.15), and (7.23) in Ref. [91]):

$$\int \frac{1}{\frac{\hbar^2 |\mathbf{k} + \mathbf{Q}|^2}{2m^*} - \frac{\hbar^2 |\mathbf{k}|^2}{2m^*} + \hbar\omega - i\delta} \frac{d^3 \mathbf{Q}}{|\mathbf{Q}|^2} = 2\pi^2 \frac{2m^*}{\hbar^2 |\mathbf{k}|} \arcsin \left( \sqrt{\frac{\hbar}{2m^* \omega}} |\mathbf{k}| \right). \quad (106)$$

With the above integral, the quasiparticle energy of the conduction band can be written as:

$$\epsilon_{\mathbf{k},c} - \epsilon_c = \frac{\hbar^2 |\mathbf{k}|^2}{2m^*} - \hbar\omega_{\text{LO}} \alpha \frac{\arcsin \left( \sqrt{\frac{\hbar}{2m^* \omega_{\text{LO}}}} |\mathbf{k}| \right)}{\sqrt{\frac{\hbar}{2m^* \omega_{\text{LO}}}} |\mathbf{k}|} - \frac{e^2}{4\pi \epsilon_0 \epsilon_\infty^2} \frac{2m^*}{\hbar |\mathbf{k}|} \int_0^{+\infty} \mathcal{T}(\omega) \arcsin \left( \sqrt{\frac{\hbar}{2m^* \omega}} |\mathbf{k}| \right) d\omega. \quad (107)$$

For a slow-moving polaron, this energy band can be expanded up to order  $|\mathbf{k}|^2$ , which yields:

$$\epsilon_{\mathbf{k},c} \approx \epsilon_c + E_0 + \frac{\hbar^2 |\mathbf{k}|^2}{2m_{\text{pol}}} + O(|\mathbf{k}|^4), \quad (108)$$

where the ground-state energy  $E_0$  and polaron effective mass  $m_{\text{pol}}$  are given by:

$$E_0 = -\alpha \hbar\omega_{\text{LO}} - \frac{e^2}{4\pi \epsilon_0 \epsilon_\infty^2} \sqrt{\frac{2m^*}{\hbar}} \int_0^{+\infty} \frac{\mathcal{T}(\omega)}{\sqrt{\omega}} d\omega, \quad (109)$$

$$\frac{m^*}{m_{\text{pol}}} = 1 - \frac{\alpha}{6} - \frac{1}{6\hbar} \frac{e^2}{4\pi \epsilon_0 \epsilon_\infty^2} \sqrt{\frac{2m^*}{\hbar}} \int_0^{+\infty} \frac{\mathcal{T}(\omega)}{\omega^{\frac{3}{2}}} d\omega. \quad (110)$$

When there is no one-electron-two-phonon interaction,  $\mathcal{T}(\omega) = 0$  and these formulas reduce to the well-known weak-coupling results for the Fröhlich Hamiltonian (Eqs. (2.20)–(2.22) in Ref. [100] or Eq. (7.28) in Ref. [91]). The one-electron-two-phonon interaction simply adds contributions to the polaron ground-state energy and inverse effective mass, and these contributions can be written in terms of  $\mathcal{T}(\omega)$ . As in the previous section, the contribution to the polaron energy only depends on the moment  $\mathcal{T}_{-\frac{1}{2}}$  of the one-electron-two-phonon spectral function. Equation (110) shows that the effective polaron mass depends on a different moment:

$$\mathcal{T}_{-\frac{3}{2}} = \int_0^{+\infty} \frac{\mathcal{T}(\omega)}{\omega^{\frac{3}{2}}} d\omega. \quad (111)$$

This moment represents the strength of the one-electron-two-phonon interaction in the context of the polaron mass, so it may also be useful to tabulate alongside  $\mathcal{T}_{-\frac{1}{2}}$ .

Note that Eqs. (109) and (110) have been derived in the weak-coupling approximation, since we only kept the lowest-order diagrams in our diagrammatic expansion in Fig. 3. As discussed in Sec. III A, this approximation is only valid when the one-electron-one-phonon interaction is sufficiently small. For the case with only one-electron-one-phonon interaction, more accurate results are known. Besides the all-coupling result obtained with the path integral method [11], the perturbation series in  $\alpha$  for the polaron energy and effective mass

are known up to higher orders in  $\alpha$  [99,100]:

$$\frac{E_0}{\hbar\omega_{\text{LO}}} = -\alpha - 0.015920\alpha^2 - 0.000806\alpha^3 - O(\alpha^4), \quad (112)$$

$$\frac{m^*}{m_{\text{pol}}} = 1 - \frac{\alpha}{6} - 0.00415\alpha^2 - O(\alpha^3). \quad (113)$$

Therefore, one should only use Eqs. (109) and (110) when  $\alpha \lesssim 1$ , and when  $\mathcal{T}(\omega)$  is similarly appropriately small.

## IV. FIRST-PRINCIPLES APPLICATION TO LITHIUM FLUORIDE AND POTASSIUM TANTALATE

### A. The dynamical matrix derivative

In Sec. III it was shown how to calculate the lowest-order effect of the long-range one-electron-two-phonon interaction on the electron quasiparticle energies. The result was written in terms of a one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  which depends on the material. In this section, we show how to calculate  $\mathcal{T}(\omega)$  from first principles, using the finite-displacement method to calculate phonon properties  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$  and  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \boldsymbol{\epsilon}}$ . As a benchmark example, this method is applied to two polar semiconductors: LiF, a cubic material with the rock salt structure and with significant long-range one-electron-one-phonon interaction, and  $\text{KTaO}_3$ , a cubic quantum paraelectric with the perovskite structure and non-negligible anharmonicity [105]. The electron polaron in LiF is a large polaron [7], and LiF has one atom of Li and one atom of F in its primitive unit cell, so the one-electron-one-phonon Hamiltonian reduces to the Fröhlich Hamiltonian. This will make it easy to quantitatively compare our numerical results for the one-electron-two-phonon interaction with those for the one-electron-one-phonon interaction. For  $\text{KTaO}_3$ , the situation is slightly different. Because it has more than two atoms in its primitive unit cell, and because the electron band structure is degenerate around the conduction band minimum, the one-electron-one-phonon Hamiltonian reduces to the generalized Fröhlich Hamiltonian instead. However, because  $\text{KTaO}_3$  has cubic symmetry, it can still be shown that the results from lowest-order perturbation theory in

Eqs. (97)–(99) reduce to:

$$E_0 = E_0^{(1e1ph)} + E_0^{(1e2ph)}, \quad (114)$$

$$E_0^{(1e1ph)} = -\frac{2\pi}{\Omega_0} \left( \frac{e^2}{4\pi\epsilon_0\epsilon_\infty} \right)^2 \sqrt{\frac{2m^*}{\hbar}} \sum_{\mathbf{v}} \frac{|p_{\mathbf{v}}|^2}{\omega_{\mathbf{v}}^3}, \quad (115)$$

$$E_0^{(1e2ph)} = -\frac{e^2}{4\pi\epsilon_0\epsilon_\infty^2} \sqrt{\frac{2m^*}{\hbar}} \int_0^{+\infty} \frac{\mathcal{T}(\omega)}{\sqrt{\omega}} d\omega, \quad (116)$$

where  $p_{\mathbf{v}} := \hat{\mathbf{q}} \cdot \mathbf{p}_{\mathbf{v}}(\hat{\mathbf{q}})$ , and the single effective band mass  $m^*$  is given by a square-root average over all angles and all degenerate bands at the conduction band minimum [104]:

$$\sqrt{m^*} = \frac{1}{4\pi n_{\text{deg}}} \sum_{n=1}^{n_{\text{deg}}} \int_{S^2} \sqrt{m_n^*(\hat{\mathbf{q}})} d^2\hat{\mathbf{q}}. \quad (117)$$

With this definition of a single effective band mass, the contribution in Eq. (116) due to the one-electron-two-phonon interaction is precisely the same as in Eq. (109). Therefore, we can set up the same computational framework for both materials: In this framework, the one-electron-one-phonon interaction is treated from the generalized Fröhlich Hamiltonian (which reduces to the usual Fröhlich Hamiltonian for LiF), and the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  can be calculated as a scalar.

We use the finite displacement method as implemented in PhonoPy [52,53] to calculate the required dynamical matrices. PhonoPy uses the c-type convention [89] for the dynamical matrix; therefore, expressions in this section will be written in the c-type convention as well. Note that Eq. (62) for  $\mathbf{Y}_{\nu_1\nu_2}(\mathbf{q})$  is invariant if we change between the c-type and d-type convention with the method described in Ref. [89], Sec. 2.3; therefore, this change of convention has no influence on the one-electron-two-phonon theory derived in the previous sections.

In the finite displacement method, first-principles calculations are performed on an  $N \times N \times N$  supercell with one atom slightly displaced in order to find an approximation for the force constants  $\Phi_{\kappa\alpha,\kappa'\beta}(\boldsymbol{\ell})$ ; an approximation for the dynamical matrix  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$  is then obtained through Eq. (26). If the first-principles calculation is performed with an electric

field  $\mathcal{E}$ , then  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; \mathcal{E})$  is automatically calculated as long as the first-principles calculation includes the effect of the electric field in the Hellman-Feynman forces. We note that first-principles calculations with an electric field are possible through the modern theory of polarization [86,106], which circumvents the issue that the electric field introduces a non-periodic potential. The electric field derivative can then be calculated via the central difference approximation:

$$\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}_z} \approx \frac{\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; \mathcal{E}\mathbf{e}_z) - \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; -\mathcal{E}\mathbf{e}_z)}{2\mathcal{E}} + O(\mathcal{E}^3). \quad (118)$$

Here the value of  $\mathcal{E}$  should be chosen appropriately: small enough such that the central difference approximation holds and large enough such that the effect of the electric field is larger than the numerical precision of the calculations. Only the derivative in the  $z$  direction is needed, since LiF and KTaO<sub>3</sub> are cubic materials.

Both LiF and KTaO<sub>3</sub> possess an inversion center which takes all atoms to an equivalent position. In this case, the c-type dynamical matrix  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$  is real, and its derivative  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}}$  is purely imaginary. This property is proven in Appendix D. Therefore, in the particular cases of LiF and KTaO<sub>3</sub>, the following expression for the derivative of the dynamical matrix is numerically more stable:

$$\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}_z} \approx \text{Im} \left[ \frac{\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; \mathcal{E}\mathbf{e}_z) - \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; -\mathcal{E}\mathbf{e}_z)}{2\mathcal{E}} \right] + O(\mathcal{E}^3). \quad (119)$$

The finite displacement method provides an approximation to the dynamical matrix which improves as the supercell size  $N$  increases. In particular, the method is exact for all commensurate points  $\mathbf{q}_c$ , which are the wave vectors in the Brillouin zone which satisfy  $e^{i\mathbf{q}_c \cdot \mathbf{T}} = 1$  for all supercell lattice vectors  $\mathbf{T}$  [52]. For all other  $\mathbf{q}$  points, the standard technique is to use Fourier interpolation, which is implemented by default in PhonoPy [52,53]. The dynamical matrix is interpolated from the values at the commensurate points  $\mathbf{q}_c$  with the following expression [52]:

$$\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) \approx \sum_{\mathbf{q}_c} \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}_c) \left( \frac{1}{N_c} \sum_{\boldsymbol{\ell} \in \Omega_{\text{sc}}} \frac{1}{\#\{\mathbf{T}_{\kappa\kappa',\boldsymbol{\ell}}\}} \sum_{\mathbf{T} \in \{\mathbf{T}_{\kappa\kappa',\boldsymbol{\ell}}\}} e^{i(\mathbf{q}-\mathbf{q}_c) \cdot (\mathbf{T} + \boldsymbol{\ell} + \boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_\kappa)} \right). \quad (120)$$

Here  $N_c = N^3$  is the number of commensurate points in the Brillouin zone,  $\{\mathbf{T}_{\kappa\kappa',\boldsymbol{\ell}}\}$  is the set of supercell vectors that minimizes  $|\mathbf{T} + \boldsymbol{\ell} + \boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_\kappa|$ , and  $\#\{\mathbf{T}_{\kappa\kappa',\boldsymbol{\ell}}\}$  is the number of supercell vectors in that set. The factor between brackets only depends on the geometry of the unit cell: It has no dependence on the electric field. Therefore, one can straightforwardly take the electric field derivative of Eq. (120) to find the Fourier interpolation rule for the derivative of the dynamical matrix:

$$\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}_z} \approx \sum_{\mathbf{q}_c} \frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}_c)}{\partial \mathcal{E}_z} \left( \frac{1}{N_c} \sum_{\boldsymbol{\ell} \in \Omega_{\text{sc}}} \frac{1}{\#\{\mathbf{T}_{\kappa\kappa',\boldsymbol{\ell}}\}} \sum_{\mathbf{T} \in \{\mathbf{T}_{\kappa\kappa',\boldsymbol{\ell}}\}} e^{i(\mathbf{q}-\mathbf{q}_c) \cdot (\mathbf{T} + \boldsymbol{\ell} + \boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_\kappa)} \right). \quad (121)$$

In practice,  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}_c)}{\partial \mathcal{E}_z}$  is calculated at the commensurate points using Eq. (119), and then interpolated to arbitrary  $\mathbf{q}$  points using Eq. (121).

Since the  $\Gamma$  point is always a commensurate point, Eqs. (120) and (121) only work in practice if the dynamical matrix is well defined in  $\Gamma$ . This is not the case in polar materials, where the dynamical matrix has a nonanalytic contribution around  $\Gamma$  [52,88]:

$$\begin{aligned} \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{\text{NAC}}(\mathbf{q}) &= \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \frac{e^2}{\varepsilon_0 \Omega_0} \sum_{\mathbf{G} \neq -\mathbf{q}} \sum_{\gamma,\delta} \frac{Z_{\gamma,\kappa\alpha}(q_\gamma + G_\gamma)(q_\delta + G_\delta) Z_{\delta,\kappa'\beta}}{(\mathbf{q} + \mathbf{G}) \cdot \mathbf{e}_\infty \cdot (\mathbf{q} + \mathbf{G})} e^{i\mathbf{G} \cdot (\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'})} \\ &\quad - \frac{\delta_{\kappa\kappa'}}{\sqrt{m_\kappa m_{\kappa'}}} \frac{e^2}{\varepsilon_0 \Omega_0} \sum_{\kappa''} \sum_{\mathbf{G} \neq 0} \sum_{\gamma,\delta} \frac{Z_{\gamma,\kappa\alpha} G_\gamma G_\delta Z_{\delta,\kappa''\beta}}{\mathbf{G} \cdot \mathbf{e}_\infty \cdot \mathbf{G}} e^{i\mathbf{G} \cdot (\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa''})}. \end{aligned} \quad (122)$$

For the dynamical matrix, the treatment of the nonanalytic contribution is implemented in PhonoPy [52,53]. For the derivative of the dynamical matrix, it would have to be implemented from scratch. The nonanalytic contribution to the derivative of the dynamical matrix  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{\text{NAC}}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}}$  can be obtained from Eq. (122) by taking a derivative with respect to the electric field  $\boldsymbol{\mathcal{E}}$ . This requires knowledge of the following two tensors:

$$\frac{\partial Z_{\beta,\kappa\alpha}}{\partial \mathcal{E}_\gamma} = -\frac{1}{e} \frac{\partial^3 E}{\partial u_{\kappa\alpha} \partial \mathcal{E}_\beta \partial \mathcal{E}_\gamma} = \frac{\Omega_0 \varepsilon_0}{e} \frac{\partial \chi_{\beta\gamma}}{\partial u_{\kappa\alpha}}, \quad (123)$$

$$\frac{\partial \varepsilon_{\alpha\beta}^{(\infty)}}{\partial \mathcal{E}_\gamma} = -\frac{1}{\varepsilon_0} \frac{\partial^3 E}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta \partial \mathcal{E}_\gamma} = 2\chi_{\alpha\beta\gamma}^{(2)}. \quad (124)$$

Respectively,  $\frac{\partial \chi_{\beta\gamma}}{\partial u_{\kappa\alpha}}$  and  $\chi_{\alpha\beta\gamma}^{(2)}$  are the Raman susceptibility tensor and the nonlinear optical susceptibility of the material [107]. In Appendix D, it is shown that both of these tensors are zero in materials with an inversion center that takes every atom to an equivalent position. Therefore, in the specific case of LiF and KTaO<sub>3</sub>,  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{\text{NAC}}(\mathbf{q}_c)}{\partial \boldsymbol{\mathcal{E}}}$  is analytic in  $\Gamma$ , so that Eq. (121) can be used without any further corrections.

## B. First-principles setup

All the first-principles calculations in this article have been performed using the VASP [22–24]. Calculations in VASP were performed using the Perdew-Burke-Ernzerhof functional for solids [108] with a plane-wave basis cutoff of 800 eV. The default projector augmented wave pseudopotentials were used for all calculations: The valence electron configurations and energy cutoffs of these pseudopotentials can be found in Table I. Unit-cell calculations for LiF and KTaO<sub>3</sub> were performed using a  $12 \times 12 \times 12$   $\Gamma$ -centered  $\mathbf{k}$  grid and an  $8 \times 8 \times 8$  Monkhorst-Pack  $\mathbf{k}$  grid, respectively. The energy convergence tolerance was set to a strict value of  $10^{-10}$  eV,

TABLE I. Valence electron configurations and plane-wave energy cutoffs of the pseudopotentials used for the first principles calculations in this article.

Element	Valence configuration	Energy cutoff
Li	$1s^2 2s^2$	499.034 eV
F	$2s^2 2p^5$	400 eV
K	$3s^2 3p^6 4s^1$	259.264 eV
Ta	$5p^6 5d^4 6s^1$	223.667 eV
O	$2s^2 2p^4$	400 eV

in order to accurately evaluate the finite difference derivative with respect to  $\boldsymbol{\mathcal{E}}$ . The calculations with a finite electric field were performed at  $\mathcal{E} = 0.01 \frac{\text{V}}{\text{\AA}}$  for LiF and at  $\mathcal{E} = 0.005 \frac{\text{V}}{\text{\AA}}$  for KTaO<sub>3</sub>. These calculations were performed in VASP v6.5.0, since earlier versions do not include the effect of the electric field in the Hellman-Feynman forces.

The PhonoPy package [52,53] was used to generate the required supercells and displacements for VASP calculations, and for the postprocessing step of generating the dynamical matrices  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{\text{NAC}}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}}$  from the Hellman-Feynman forces output by VASP. Calculations are performed on different supercell sizes, from  $2 \times 2 \times 2$  to  $6 \times 6 \times 6$  for LiF and from  $2 \times 2 \times 2$  to  $4 \times 4 \times 4$  for KTaO<sub>3</sub>, to ensure that the results for  $\mathcal{T}(\omega)$  are converged with respect to the size of the supercell. For supercell calculations, the  $\mathbf{k}$  grid was appropriately scaled to maintain a constant scaling density. Phonon frequencies are reported as cycle frequencies in THz; one should multiply by  $2\pi$  to obtain the radial frequency in  $10^{12} \frac{\text{rad}}{\text{s}}$ .

KTaO<sub>3</sub> contains a heavy tantalum atom with significant spin-orbit coupling. The spin-orbit coupling splits off one of the three degenerate electron bands at the conduction band minimum [109], leaving only a twofold degeneracy. Therefore, we include spin-orbit coupling in the unit cell calculations for the electron bands, from which we calculate the effective band mass  $m^*$  via equation Eq. (117) with  $n_{\text{deg}} = 2$ . However, we do not include spin-orbit coupling in the supercell calculations, since the inclusion of spin-orbit coupling does not significantly change the phonon frequencies in KTaO<sub>3</sub> [110]. Instead, we perform calculations on larger supercell sizes, which is necessary for an accurate prediction of  $\mathcal{T}(\omega)$  as we shall show in Sec. IV D.

Note that PhonoPy automatically performs a symmetry analysis in order to reduce the number of required calculations, but this symmetry analysis is performed using only the input structure; it is unaware that the electric field breaks all symmetries along the  $z$  direction. To include this effect in the symmetry analysis, all calculations were performed with one of the atoms moved by a very small amount  $\delta = 10^{-9}$  in the  $z$  direction. For example, the FCC lattice of the rock salt structure remains unchanged:

$$\mathbf{a}_1 = 0\mathbf{e}_x + \frac{a}{2}\mathbf{e}_y + \frac{a}{2}\mathbf{e}_z, \quad (125)$$

$$\mathbf{a}_2 = \frac{a}{2}\mathbf{e}_x + 0\mathbf{e}_y + \frac{a}{2}\mathbf{e}_z, \quad (126)$$

$$\mathbf{a}_3 = \frac{a}{2}\mathbf{e}_x + \frac{a}{2}\mathbf{e}_y + 0\mathbf{e}_z, \quad (127)$$

TABLE II. Comparison of harmonic material parameters with experimental values [111–119], for LiF (left) and KTaO<sub>3</sub> (right). For LiF, we also compare with the first-principles calculations in Ref. [8].  $a$  is the lattice parameter of the conventional unit cell,  $m^*/m_{\text{el}}$  is the electron band mass expressed in units of the electron mass,  $\omega_{\text{LO}}$  is the LO phonon frequency at  $\Gamma$  (LiF has one LO phonon branch at  $\Gamma$ , KTaO<sub>3</sub> has three),  $\varepsilon(0)$  and  $\varepsilon_\infty$  are the static and high-frequency dielectric constants, and  $\alpha$  is the Fröhlich coupling constant.

LiF	Experiments	Sio <i>et al.</i> [8]	This article
$a$	4.02 Å [111]	4.058 Å	4.004 Å
$m^*/m_{\text{el}}$		0.88	0.88
$\omega_{\text{LO}}$	19.60 THz [112]	18.62 THz	19.25 THz
$\varepsilon(0)$	9.036 [113]	10.62	9.051
$\varepsilon_\infty$	1.92 [114]	2.04	2.086
$\alpha$		4.92	4.52
KTaO <sub>3</sub>			
	Experiments		This article
$a$	3.989 Å [115]		3.99 Å
$m^*/m_{\text{el}}$	0.2-0.6 [116,117]		0.40
$\omega_{\text{LO1}}$	5.59 THz [118]		5.14 THz
$\omega_{\text{LO2}}$	12.52 THz [118]		11.93 THz
$\omega_{\text{LO3}}$	24.90 THz [118]		23.80 THz
$\varepsilon_\infty$	4.592 [119]		5.514

but the atomic positions are given by:

$$\boldsymbol{\tau}_1 = 0\mathbf{e}_x + 0\mathbf{e}_y + 0\mathbf{e}_z, \quad (128)$$

$$\boldsymbol{\tau}_2 = \frac{a}{2}\mathbf{e}_x + \frac{a}{2}\mathbf{e}_y + \left(\frac{1}{2} + \delta\right)a\mathbf{e}_z. \quad (129)$$

Table II shows several material parameters of LiF and KTaO<sub>3</sub> which are relevant for the Fröhlich one-electron-one-phonon interaction, calculated with the first-principles setup described in this section. The values of these material parameters are sufficiently close to the experimental values [111–114] and to the values calculated in Ref. [8].

### C. The one-electron-two-phonon strengths $|Y_{\nu_1\nu_2,z}(\mathbf{q})|^2$

Sections IV A and IV B describe the first-principles setup which allows us to calculate  $\omega_{\mathbf{q},\nu}$ ,  $\mathbf{e}_{\mathbf{q},\nu}(\mathbf{q})$ , and  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}_z}$  at arbitrary  $\mathbf{q}$  points. This allows us to straightforwardly calculate  $Y_{\nu_1\nu_2,z}(\mathbf{q})$  with Eq. (62). This quantity will roughly indicate the strength of the one-electron-two-phonon interaction, where the two phonons belong to branches  $\nu_1, \nu_2$  and have momenta  $\mathbf{q}_1 \approx -\mathbf{q}$  and  $\mathbf{q}_2 \approx \mathbf{q}$ .

In order to plot  $Y_{\nu_1\nu_2,z}(\mathbf{q})$ , we should choose an appropriate high-symmetry path through the Brillouin zone. The phonon frequencies  $\omega_{\mathbf{q},\nu}$  follow all the cubic symmetries, so they may be plotted on a high-symmetry path through the irreducible Brillouin zone. For example, in LiF, we may take the path suggested in Ref. [120]:

$$\Gamma - X - W - K - \Gamma - L - U - W - L - K | U - X, \quad (130)$$

which is shown in Fig. 4(a). However, it is important to realize that  $Y_{\nu_1\nu_2,z}(\mathbf{q})$  does not follow the same symmetry as the phonon frequencies  $\omega_{\mathbf{q},\nu}$ . The electric field derivative breaks the symmetry along the  $z$  direction. Therefore, it makes more

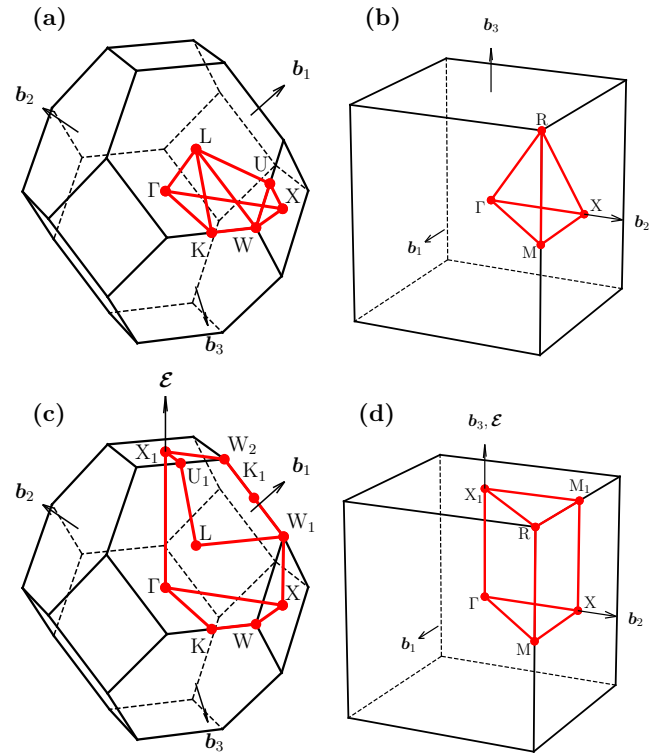


FIG. 4. The face-centered cubic and simple cubic Brillouin zones and two possible high-symmetry paths. [(a) and (b)] The standard paths from Ref. [120], appropriate for a cubic cell. [(c) and (d)] More appropriate paths for the system with an applied electric field  $\mathcal{E} = \mathcal{E}\mathbf{e}_z$ , based on the paths for tetragonal systems from Ref. [120].

sense to use a high-symmetry path that is appropriate for a tetragonal unit cell rather than for a cubic unit cell. We choose the path shown in Fig. 4(c):

$$\Gamma - X - W - K - \Gamma - X_1 - U_1 - L - W_1 - W_2 - X_1 | X - W_1. \quad (131)$$

This path is the suggested path for a tetragonal body-centered cell [120], after transforming the coordinates to a tetragonal face-centered cell and then setting the dimensions of the unit cell equal to each other. In this path, we have introduced the labels  $X_1, U_1, W_1, K_1,$  and  $W_2$  for points that would be equivalent to the  $X, U, W,$  and  $K$  points in a cubic cell but represent distinct points when the  $z$  symmetry is broken. This means that the phonon frequencies are equal in, e.g.,  $X$  and  $X_1$ , but  $Y_{\nu_1\nu_2,z}(\mathbf{q})$  in those two points may be different.

We find a similar path for KTaO<sub>3</sub> in an analogous way: We start from the suggested path for the simple tetragonal lattice from Ref. [120] and then set the dimensions of the unit cell equal to each other and introduce new names for the labels based on those of the simple cubic lattice. This yields the following path:

$$\Gamma - X - M - \Gamma - X_1 - M_1 - R - X_1 | X - M_1 | M - R. \quad (132)$$

The new labels are  $X_1$  and  $M_1$ , which represent points that have the same phonon frequencies as  $X$  and  $M$  but not necessarily the same value of  $Y_{\nu_1\nu_2,z}(\mathbf{q})$ .

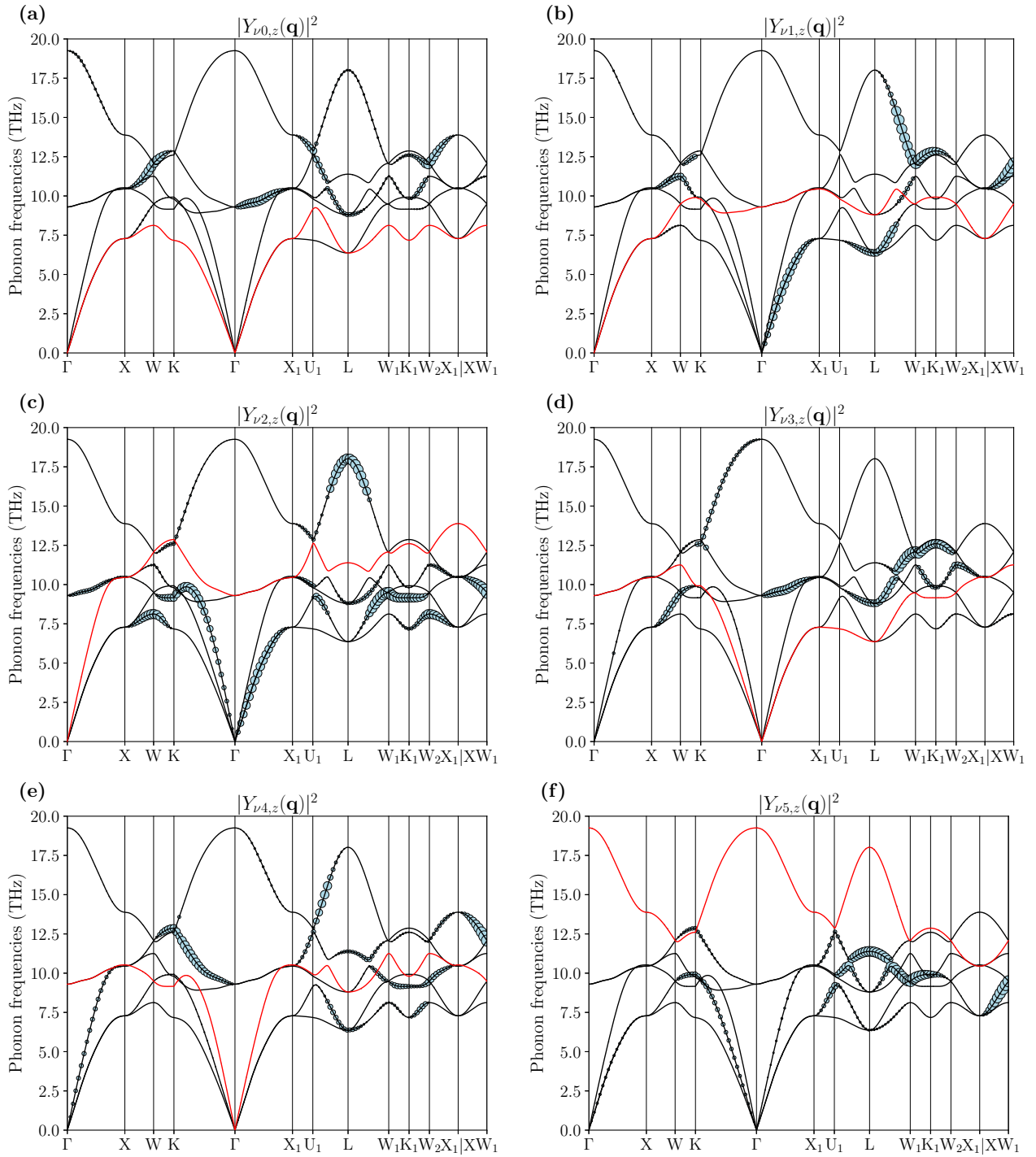


FIG. 5. Relative strength of the one-electron-two-phonon interaction  $|Y_{\nu_1\nu_2,z}(\mathbf{q})|^2$  in LiF along the path shown in Fig. 4(b), calculated on a  $6 \times 6 \times 6$  supercell. The area of each circle is proportional to  $|Y_{\nu_1\nu_2,z}(\mathbf{q})|^2$ , where  $\nu_1$  is the branch the circle is on and  $\nu_2$  is a fixed branch which is highlighted in red. The largest circle in this plot corresponds to  $|Y_{\nu_1\nu_2,z}(\mathbf{q})|^2 = 7.79 \times 10^{-7} \text{ \AA}^2$ .

Figure 5 shows the plot of  $|Y_{\nu_1\nu_2,z}(\mathbf{q})|^2$  for LiF along a high-symmetry path shown in Fig. 4(b). There seem to be some pairs of branches that have much more interaction than other pairs of branches. For example, on the  $\Gamma - X_1$  line, the transverse optical (TO) branches have significantly more interaction with the transverse acoustic (TA) branches than with the longitudinal bands. There also seems to be more interaction between the two highest-energy bands around the  $L$  point;

these are predominantly LO and longitudinal acoustic (LA) bands, although as we will discuss in Sec. IV E, these labels are no longer exact. Finally, note that there is no one-electron-two-phonon interaction when  $\nu_1 = \nu_2$ . This is visible in Fig. 5 as the fact that there are no circles on the red branches. This is due to the fact that LiF possesses an inversion center that takes all atoms to an equivalent position, which is proven in Appendix D. Figure 5 shows all the separate contributions to

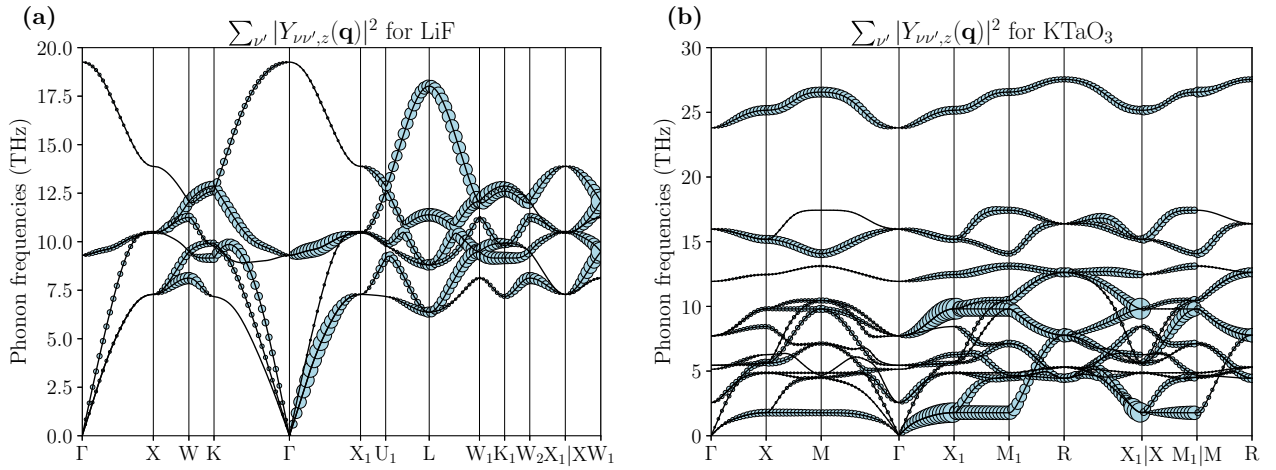


FIG. 6. Plot of the sum of contributions to  $|Y_{\nu\nu',z}(\mathbf{q})|^2$ , as defined in equation Eq. (133). The one-electron-two-phonon interaction has contributions from all over the Brillouin zone. Branches with very small circles do not participate in the one-electron-two-phonon interaction at all. The largest circles correspond to a value of  $\sum_{\nu\nu'} |Y_{\nu\nu',z}(\mathbf{q})|^2 = 1.53 \times 10^{-6} \text{ \AA}^2$  in (a) and a value of  $\sum_{\nu\nu'} |Y_{\nu\nu',z}(\mathbf{q})|^2 = 1.11 \times 10^{-4} \text{ \AA}^2$  in (b).

the one-electron-two-phonon strengths but requires a number of subplots equal to the number of phonon branches. This makes it impractical to make similar figures for materials with more atoms in the unit cell, such as KTaO<sub>3</sub> which would require 15 subfigures. To summarize the key info in a single plot, we overlap all the subplots in Fig. 5 and add up the areas of the overlapping circles. This corresponds to plotting the following quantity on top of the phonon branches  $\omega_{\mathbf{q},\nu}$ :

$$\sum_{\substack{\nu' \text{ degenerate} \\ \text{with } \nu}} \sum_{\nu''} |Y_{\nu\nu'',z}(\mathbf{q})|^2. \quad (133)$$

Figure 6 shows a plot of this quantity for both LiF and KTaO<sub>3</sub>. Whenever a branch in this figure has no circles on it, or the circles are very small, it does not participate in the long-range one-electron-two-phonon interaction with any other branch. The most notable occurrences are all the branches on the  $\Gamma$  - X line or the longitudinal branches on the  $\Gamma$  - X<sub>1</sub> line.

The most striking feature of Fig. 6 is that the one-electron-two-phonon interaction gets contributions from everywhere in the Brillouin zone. In fact, one can see that the contribution from  $\Gamma$  itself is exactly zero for both LiF and KTaO<sub>3</sub>. This is in stark contrast with the one-electron-one-phonon long-range interaction, whose contributions from around  $\Gamma$  dominate the other contributions. This is related to how the long-range approximation  $\mathbf{q}_1 + \mathbf{q}_2 \approx \mathbf{0}$  is no longer equivalent to the continuum approximation  $\mathbf{q}_1, \mathbf{q}_2 \approx \mathbf{0}$ , as discussed at the end of Sec. II. The reason that there is no contribution from  $\Gamma$  is again the inversion center that takes all atoms to an equivalent position, which is present in both LiF and KTaO<sub>3</sub>. In Appendix D, we present a simple symmetry argument which shows that  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{0})}{\partial \mathcal{E}} = \mathbf{0}$  if such an inversion center is present, which immediately implies that  $|Y_{\nu_1\nu_2,z}(\mathbf{q})|^2$  is zero for all phonon branches.

#### D. The one-electron-two-phonon spectral function

The one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  at zero temperature can be calculated from  $Y_{\nu_1\nu_2,z}(\mathbf{q})$  using

Eqs. (84) and (86). The expression in Eq. (84) features an integral over  $\mathbf{q}$  where the integrand is a delta function, similarly to the phonon density of states. We compute this integral numerically using the smearing method, where the delta function is replaced by a Gaussian peak with a finite width  $\sigma$ :

$$\begin{aligned} \mathcal{T}(\omega) \approx & \frac{e^2}{2\hbar\epsilon_0\Omega_0} \sum_{\nu_1,\nu_2} \frac{1}{\Omega_{1\text{BZ}}} \int_{1\text{BZ}} |Y_{\nu_1\nu_2,z}(\mathbf{q})|^2 \\ & \times \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(\omega-\omega_{\mathbf{q},\nu_1}-\omega_{\mathbf{q},\nu_2})^2}{2\sigma^2}} d^3\mathbf{q}. \end{aligned} \quad (134)$$

The integral over  $\mathbf{q}$  is then computed on a fine grid using the composite trapezoid method.  $\sigma$  should be chosen as small as possible but large enough such that the variation of  $\omega_{\mathbf{q},\nu_1} + \omega_{\mathbf{q},\nu_2}$  on the fine  $\mathbf{q}$  grid is less than  $\sigma$ . The results in this section are reported for  $\sigma = 0.1$  THz, which require a  $128 \times 128 \times 128$  fine  $\mathbf{q}$  grid for convergence. Once  $\mathcal{T}(\omega)$  has been calculated, the moments  $\mathcal{T}_n$  can also be calculated through:

$$\mathcal{T}_n := \int_0^{+\infty} \mathcal{T}(\omega)\omega^n d\omega. \quad (135)$$

Table III shows the moments  $\mathcal{T}_{-\frac{1}{2}}$  and  $\mathcal{T}_{-\frac{3}{2}}$ , which are required in Eqs. (109) and (110) for the polaron energy and effective mass. It also shows the moment  $\mathcal{T}_{-1}$  because it is a naturally dimensionless quantity and is therefore a useful summary of the entire spectrum.

Figure 7 shows the calculated one-electron-two-phonon spectrum  $\mathcal{T}(\omega)$ . The most important remark is that  $\mathcal{T}(\omega)$  and its moments are on the order of  $10^{-4}$  in LiF and on the order of  $10^{-3}$  in KTaO<sub>3</sub>. Since the one-electron-one-phonon interaction is of order 1, as we shall see when calculating the polaron ground-state energies, we can conclude that the long-range one-electron-two-phonon interaction is essentially negligible in both LiF and KTaO<sub>3</sub>. This means that the resulting polaron properties like  $E_0$  or  $m_{\text{pol}}$  will not be particularly interesting, since they will be essentially the same as the harmonic properties. Regardless, it is still interesting to focus on some of

TABLE III. Moments of  $\mathcal{T}(\omega)$ , calculated through equation Eq. (135) with the data from Fig. 7. All moments are evaluated with a  $128 \times 128 \times 128$  grid of interpolated  $\mathbf{q}$  points and a smearing of  $\sigma = 0.1$  THz. The moments were multiplied with appropriate powers of the frequencies in Table II in order to make them dimensionless.

Supercell	LiF			KTaO <sub>3</sub>		
	$\frac{1}{\sqrt{\omega_{LO}}}\mathcal{T}_{-\frac{1}{2}}$	$\mathcal{T}_{-1}$	$\sqrt{\omega_{LO}}\mathcal{T}_{-\frac{3}{2}}$	$\frac{1}{\sqrt{\omega_{LO3}}}\mathcal{T}_{-\frac{1}{2}}$	$\mathcal{T}_{-1}$	$\sqrt{\omega_{LO3}}\mathcal{T}_{-\frac{3}{2}}$
$2 \times 2 \times 2$	0.000097	0.000097	0.000097	0.001900	0.002372	0.003113
$3 \times 3 \times 3$	0.000108	0.000105	0.000104			
$4 \times 4 \times 4$	0.000111	0.000108	0.000107	0.001903	0.002313	0.002945
$5 \times 5 \times 5$	0.000111	0.000108	0.000106			
$6 \times 6 \times 6$	0.000111	0.000108	0.000107			

the more detailed aspects of  $\mathcal{T}(\omega)$  and its calculation, which provides valuable insights for further calculations.

The calculations were performed on different supercells. For KTaO<sub>3</sub>, the phonon spectrum contains imaginary modes on the  $3 \times 3 \times 3$  supercell, so we only have data for the  $2 \times 2 \times 2$  and  $4 \times 4 \times 4$  supercells. On the contrary, we have much more data for LiF, which shows that  $\mathcal{T}(\omega)$  converges rapidly with respect to the size of the supercell. The results are fully converged for a  $6 \times 6 \times 6$  supercell, but even for a  $4 \times 4 \times 4$  supercell, the results are sufficiently converged for most practical applications at a fraction of the computational cost. The  $3 \times 3 \times 3$  supercell is overall also very good but fails to predict the precise height of the second peak. The spectral function for the  $2 \times 2 \times 2$  supercell is not quantitatively reliable, but it roughly matches the general two-peak structure. In KTaO<sub>3</sub>, the result on the  $2 \times 2 \times 2$  supercell is already quite reliable, although it misses the peak around 22 THz. The moments  $\mathcal{T}_n$  also converge rapidly, with a precision of three significant digits on the  $4 \times 4 \times 4$  supercell and a correct order-of-magnitude estimate on the  $2 \times 2 \times 2$  supercell.

In LiF,  $\mathcal{T}(\omega)$  is nonzero in a broad region between 10 THz  $< \omega < 30$  THz, with two peaks as the most prominent features. The lower bound of 10 THz  $\sim \omega_{TO}$  appears because Fig. 5 shows that there is very little interaction when  $\nu_1$  and  $\nu_2$  are both acoustic branches, so the interaction at the

lowest frequency occurs when  $\nu_1$  is acoustic and  $\nu_2$  is a TO branch (or vice versa). The upper bound of 30 THz is lower than the theoretical maximum  $2\omega_{\max} = 2\omega_{LO} = 38.5$  THz. This is because LiF has no interaction when  $\nu_1 = \nu_2$ , so we must look at the highest two branches that still have any interaction. This happens at the L point, where the sum of the two highest phonon frequencies is  $18.0 + 11.4 = 29.4$  THz. At frequencies higher than this, we must therefore have  $\mathcal{T}(\omega) = 0$ .

In KTaO<sub>3</sub>, the most noticeable interaction in Fig. 6(b) is on the  $\Gamma - X_1 - M_1$  line, coming from the (mostly TA) lowest mode with frequency  $\sim 2$  THz and a (mostly TO) intermediate mode with frequency  $\sim 10$  THz. This accounts for a significant contribution to the peak at  $\sim 12$  THz which is visible in Fig. 7. Other than this, the one-electron-two-phonon spectral function in KTaO<sub>3</sub> has many more peaks at higher frequencies, which are hard to attribute to specific pairs of branches due to the many phonon bands all providing contributions from all over the Brillouin zone.  $\mathcal{T}(\omega)$  becomes zero around 44 THz, again well before the theoretical maximum value of  $2\omega_{\max} = 55.1$  THz. The reason is the same as in LiF: there is no interaction when  $\nu_1 = \nu_2$ , and the highest phonon branch is well separated from the second highest one.

The moments  $\mathcal{T}_{-\frac{1}{2}}$  and  $\mathcal{T}_{-\frac{3}{2}}$  from Table III can be used in Eqs. (109) and (110) to calculate the polaron ground-state

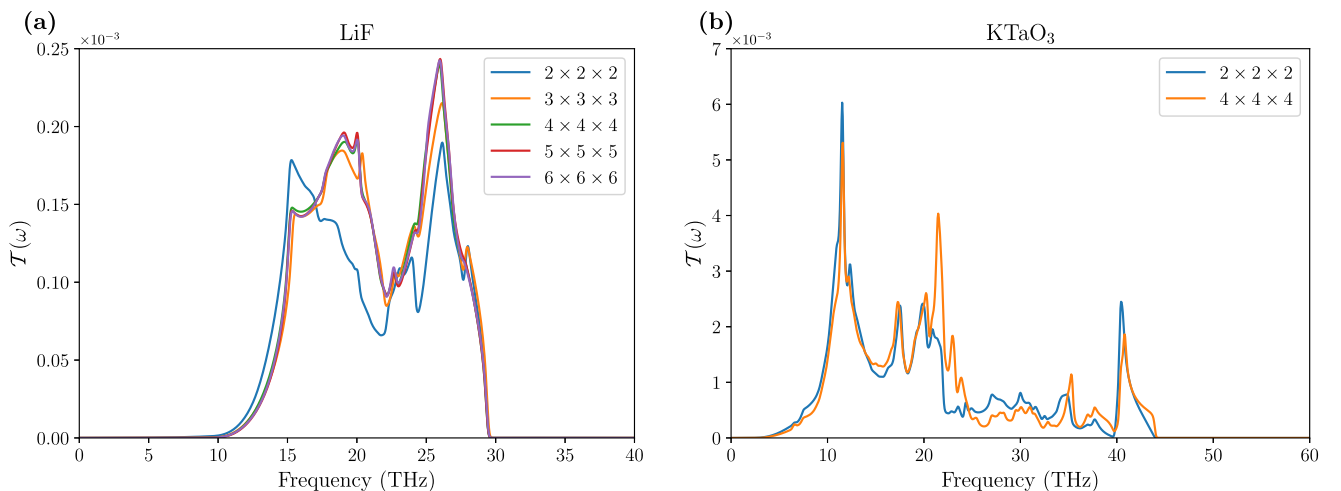


FIG. 7. One-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  at zero temperature of (a) LiF and (b) KTaO<sub>3</sub>, calculated from first principles using Eq. (134) with  $\sigma = 0.1$  THz and a  $128 \times 128 \times 128$  fine  $\mathbf{q}$  grid. The spectral function converges rapidly with respect to the supercell size. The actual value of  $\mathcal{T}(\omega)$  is very small, indicating that long-range one-electron-two-phonon interaction is negligible in LiF and KTaO<sub>3</sub>.

energy  $E_0$  and effective mass  $m_{\text{pol}}$ . For the one-electron-one-phonon interaction, we use Eqs. (112) and (113) instead because  $\alpha = 4.52$  is too large to use lowest-order perturbation theory, as also discussed in Sec. III A. This yields the following values:

$$E_0 = -0.392279 \text{ eV} - 0.000050 \text{ eV} = -0.392 \text{ eV}, \quad (136)$$

$$\frac{m^*}{m_{\text{pol}}} = 1 - 0.669274 - 0.000101, \quad \Leftrightarrow m_{\text{pol}} = 2.662 m_{\text{e1}}. \quad (137)$$

In both cases, we have separately written the two terms in Eqs. (109) and (110) that come from the one-electron-one-phonon and one-electron-two-phonon interactions. The one-electron-two-phonon interaction contributes around 0.01% of the total contribution, so the rounded results are unchanged. For  $\text{KTaO}_3$ , we find a similar conclusion for the ground-state energy. In order to use equation Eq. (115) for the one-electron-one-phonon contribution, we need values for the mode polarities  $|p_\nu|^2$ . We calculated these to be  $|p_{\text{LO1}}|^2 = 0.00184 \text{ (a.m.u.)}^{-1}$ ,  $|p_{\text{LO2}}|^2 = 0.278 \text{ (a.m.u.)}^{-1}$ , and  $|p_{\text{LO3}}|^2 = 3.24 \text{ (a.m.u.)}^{-1}$  for the LO branches; all other mode polarities are zero. With the other values from Table II and the value of  $\mathcal{T}_{-\frac{1}{2}}$  from Table III, the  $\text{KTaO}_3$  polaron ground-state energy can be calculated as:

$$E_0 = -0.119432 \text{ eV} - 0.000092 \text{ eV} = -0.119 \text{ eV}. \quad (138)$$

The relative contribution of the one-electron-two-phonon interaction to the ground-state energy is almost an order of magnitude larger in  $\text{KTaO}_3$  than in LiF. However, this is still not large enough to be relevant compared to the one-electron-one-phonon contribution.

It seems that in LiF and  $\text{KTaO}_3$ , at  $T = 0 \text{ K}$ , the long-range one-electron-two-phonon interaction is negligible with respect to the one-electron-one-phonon interaction. This is a material-specific property: In other materials the one-electron-two-phonon interaction may be larger. The results presented in this section serve as a proof of principle, showing that it is indeed possible to calculate  $\mathcal{T}(\omega)$  for real materials from first principles.

### E. Longitudinal/transverse and acoustic/optical distinction

In Fig. 5, one can see that around  $\Gamma$ , there is significantly more interaction between the TA-TO branches than between any other pair of branches. It would be useful to track the separate contributions of the LA, LO, TA, and TO branches to  $\mathcal{T}(\omega)$ , but outside  $\Gamma$ , the phonon branches no longer uniquely fall into one of these four categories. Therefore, a mathematical measure is required that tracks how longitudinal/transverse and acoustic/optical a branch is. For every branch  $(\mathbf{q}, \nu)$ , let us define real weights  $P_{\mathbf{q},\nu}^{(\lambda)}$  with  $\lambda \in \{\text{LA, TA, LO, TO}\}$ , that tell us how longitudinal/transverse and acoustic/optical that branch is at that point:

$$P_{\mathbf{q},\nu}^{(\text{TA})} = \sum_{\kappa\alpha,\kappa'\beta} e_{\kappa\alpha,\nu}^*(\mathbf{q}) e_{\kappa'\beta,\nu}(\mathbf{q}) \frac{\sqrt{m_\kappa m_{\kappa'}}}{\sum_{\kappa''} m_{\kappa''}} (\delta_{\alpha\beta} - \hat{q}_\alpha \hat{q}_\beta), \quad (139)$$

$$P_{\mathbf{q},\nu}^{(\text{LA})} = \sum_{\kappa\alpha,\kappa'\beta} e_{\kappa\alpha,\nu}^*(\mathbf{q}) e_{\kappa'\beta,\nu}(\mathbf{q}) \frac{\sqrt{m_\kappa m_{\kappa'}}}{\sum_{\kappa''} m_{\kappa''}} \hat{q}_\alpha \hat{q}_\beta, \quad (140)$$

$$P_{\mathbf{q},\nu}^{(\text{TO})} = \sum_{\kappa\alpha,\kappa'\beta} e_{\kappa\alpha,\nu}^*(\mathbf{q}) e_{\kappa'\beta,\nu}(\mathbf{q}) \left( \delta_{\kappa\kappa'} - \frac{\sqrt{m_\kappa m_{\kappa'}}}{\sum_{\kappa''} m_{\kappa''}} \right) \times (\delta_{\alpha\beta} - \hat{q}_\alpha \hat{q}_\beta), \quad (141)$$

$$P_{\mathbf{q},\nu}^{(\text{LO})} = \sum_{\kappa\alpha,\kappa'\beta} e_{\kappa\alpha,\nu}^*(\mathbf{q}) e_{\kappa'\beta,\nu}(\mathbf{q}) \left( \delta_{\kappa\kappa'} - \frac{\sqrt{m_\kappa m_{\kappa'}}}{\sum_{\kappa''} m_{\kappa''}} \right) \hat{q}_\alpha \hat{q}_\beta. \quad (142)$$

Because of the orthogonality of the phonon eigenvectors, we immediately find that these weights are normalized:

$$\sum_{\lambda} P_{\mathbf{q},\nu}^{(\lambda)} = 1. \quad (143)$$

Figure 8 shows the weights  $P_{\mathbf{q},\nu}^{(\lambda)}$  superimposed on the phonon spectrum  $\omega_{\mathbf{q},\nu}$  for LiF. Around  $\Gamma$  the characters TA, LA, TO, LO uniquely describe each band, but outside of  $\Gamma$  most bands have a mix of at least two characters.

We can use the weights defined in Eqs. (139)–(142) to define separate contributions of  $\mathcal{T}(\omega)$  that each tell us how much the longitudinal/transverse and the acoustic/optical branches are contributing. Because the weights sum up to one, these contributions can be defined as follows:

$$\mathcal{T}(\omega) = \sum_{\lambda_1 \lambda_2} \mathcal{T}^{(\lambda_1, \lambda_2)}(\omega), \quad (144)$$

$$\mathcal{T}^{(\lambda_1, \lambda_2)}(\omega) = \frac{e^2}{2\hbar\epsilon_0\Omega_0} \sum_{\nu_1, \nu_2} \frac{1}{\Omega_{1\text{BZ}}} \int_{1\text{BZ}} |Y_{\nu_1\nu_2,z}(\mathbf{q})|^2 \times P_{\mathbf{q},\nu_1}^{(\lambda_1)} P_{\mathbf{q},\nu_2}^{(\lambda_2)} \delta(\omega - \omega_{\mathbf{q},\nu_1} - \omega_{\mathbf{q},\nu_2}) d^3\mathbf{q}. \quad (145)$$

Similarly, we may define the separate contributions to the moments  $\mathcal{T}_n$ :

$$\mathcal{T}_n^{(\lambda_1, \lambda_2)} := \int_0^{+\infty} \mathcal{T}^{(\lambda_1, \lambda_2)}(\omega) \omega^n d\omega. \quad (146)$$

Because  $\mathcal{T}^{(\lambda_1, \lambda_2)}(\omega) = \mathcal{T}^{(\lambda_2, \lambda_1)}(\omega)$ , this method distinguishes a total of 10 different contributions. Figure 9 shows these 10 different contributions and how they add up to form the full  $\mathcal{T}(\omega)$  of Fig. 7. In LiF, there are two contributions that are larger than the others, which also roughly explains why  $\mathcal{T}(\omega)$  has two main peaks. The first peak is largely due to TA-TO interactions, and the second peak is largely due to LA-LO and TA-TO interactions. It seems that in LiF the one-electron-two-phonon interaction is largest when one of the phonons is optical and the other is acoustic. However, note that even though the LA-LO and TA-TO contributions are the largest ones, together they only provide less than half of the total  $\mathcal{T}(\omega)$ , so all branches must be considered for a quantitative prediction. In  $\text{KTaO}_3$ , we may see that a significant contribution to the peak at 12 THz indeed comes from the interaction of the TA branch with a TO branch, as noted in the previous section. Overall, a large contribution seems to be coming from branches with TO weight, but this is likely due to the fact that 8 of the 15 phonon branches in  $\text{KTaO}_3$  are TO branches.

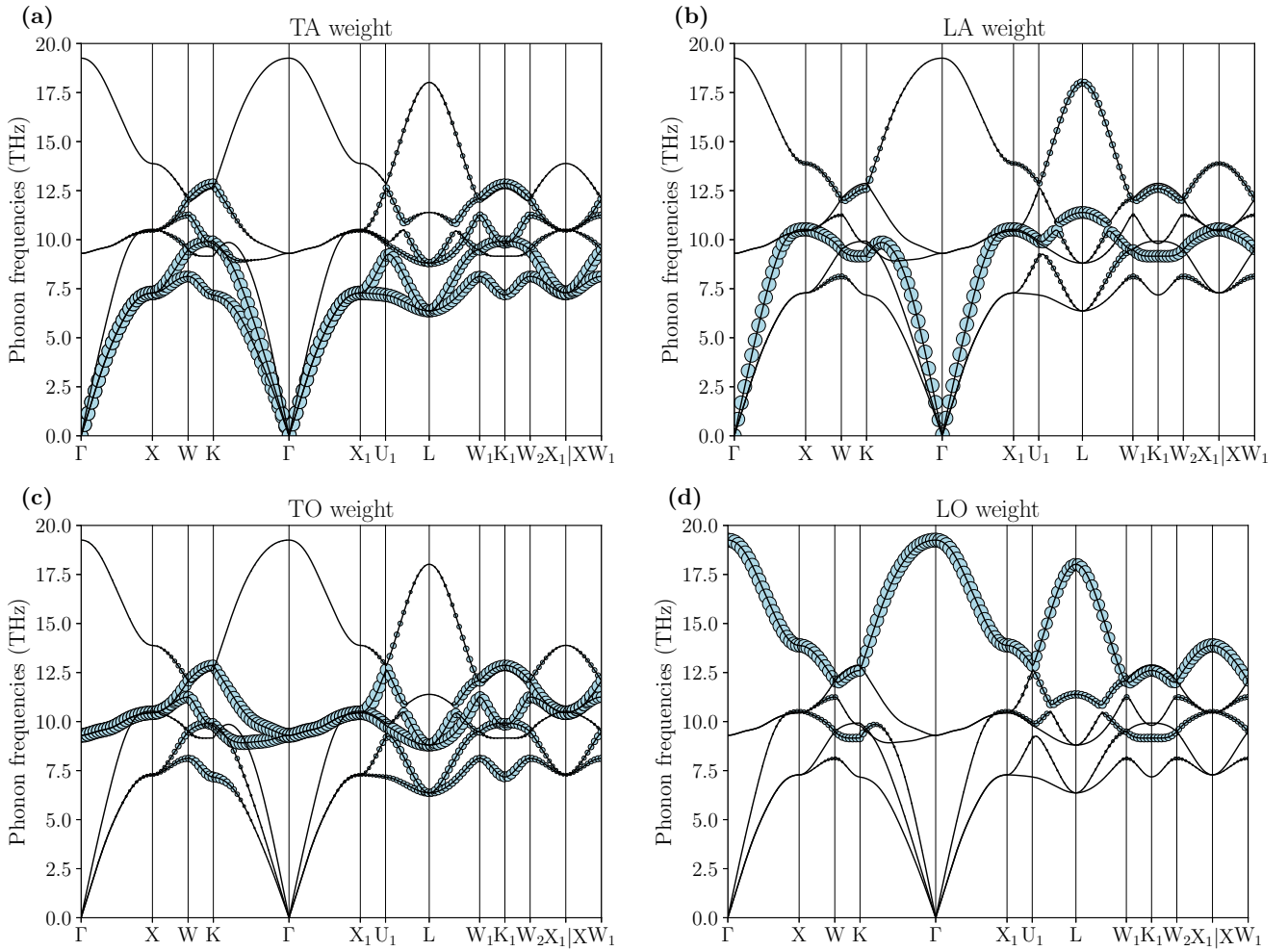


FIG. 8. (a) Transverse acoustic, (b) longitudinal acoustic, (c) transverse optical, and (d) longitudinal optical weights of the phonon bands in LiF, calculated on a  $6 \times 6 \times 6$  supercell. For each frequency  $\omega_{\mathbf{q},\nu}$ , a circle is drawn with an area proportional to  $P_{\mathbf{q},\nu}^{(l)}$  as defined in Eqs. (139)–(142). The phonon branches were plotted along the low-symmetry path of Fig. 4(b), to facilitate comparison with Fig. 5.

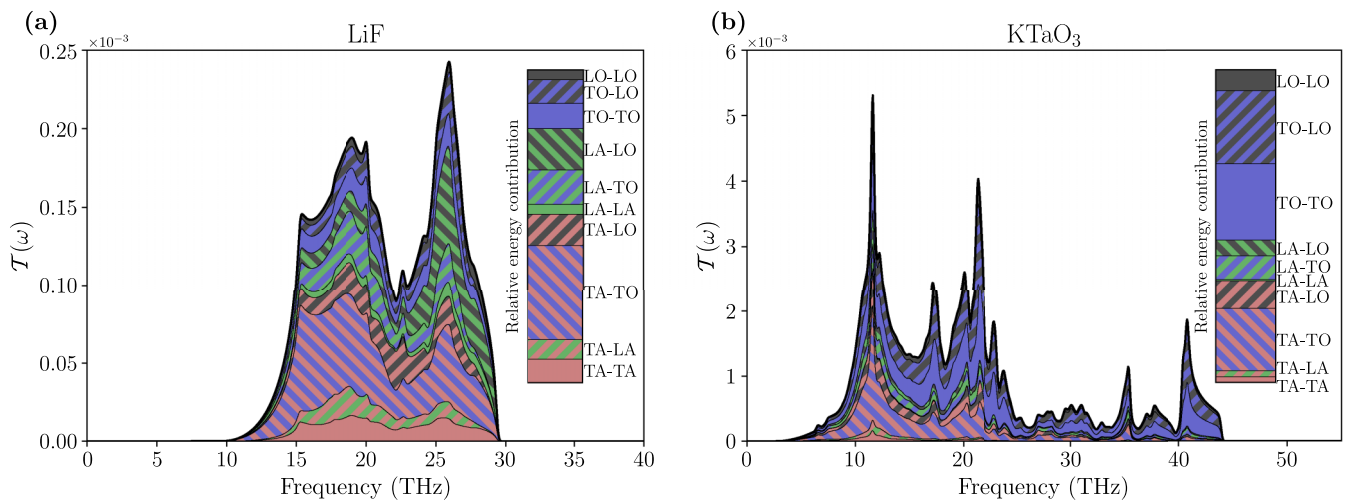


FIG. 9. The different longitudinal/transverse and acoustic/optical contributions of the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$ , as defined by Eq. (145): (a) in LiF on a  $6 \times 6 \times 6$  supercell and (b) in KTaO<sub>3</sub> on a  $4 \times 4 \times 4$  supercell. The inset shows the relevant contributions to the moment  $\mathcal{T}_{-1/2}$ , as defined in Eq. (146). Calculations were performed with a  $128 \times 128 \times 128$   $\mathbf{q}$  grid and a smearing of  $\sigma = 0.1$  THz.

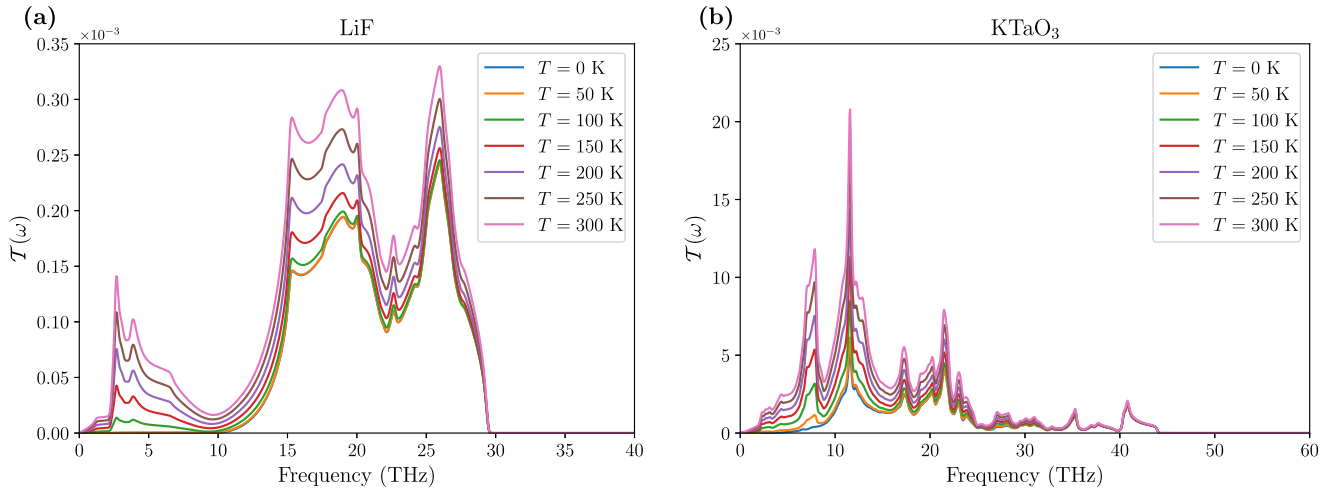


FIG. 10. Temperature dependence of the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  at zero temperature of (a) LiF and (b) KTaO<sub>3</sub>, calculated from first principles using Eq. (147) with  $\sigma = 0.1$  THz and a  $128 \times 128 \times 128$  fine  $\mathbf{q}$  grid. The temperature dependence is larger in KTaO<sub>3</sub> because the phonon branches that participate in the one-electron-two-phonon interaction have lower energy than in LiF.

#### F. Temperature dependence of the one-electron-two-phonon spectral function

So far, we have only calculated the one-electron-two-phonon spectral function at temperature zero, for the sake of simplicity. We may also calculate it at finite temperatures by applying the smearing method to Eq. (83):

$$\mathcal{T}(\omega) := \frac{e^2}{2\hbar\epsilon_0\Omega_0} \sum_{v_1, v_2} \frac{1}{\Omega_{1BZ}} \int_{1BZ} |Y_{v_1 v_2, z}(\mathbf{q})|^2 \frac{1}{\sqrt{2\pi}\sigma} \times \left( [1 + n_B(\omega_{\mathbf{q}, v_1}) + n_B(\omega_{\mathbf{q}, v_2})] e^{-\frac{(\omega - \omega_{\mathbf{q}, v_1} - \omega_{\mathbf{q}, v_2})^2}{2\sigma^2}} + |n_B(\omega_{\mathbf{q}, v_2}) - n_B(\omega_{\mathbf{q}, v_1})| e^{-\frac{(\omega - |\omega_{\mathbf{q}, v_1} - \omega_{\mathbf{q}, v_2}|)^2}{2\sigma^2}} \right) d^3\mathbf{q}. \quad (147)$$

Here  $n_B(\omega)$  is simply the Bose-Einstein distribution function, which introduces a dependence on the temperature  $T$ :

$$n_B(\omega) = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}. \quad (148)$$

Evaluating Eq. (147) is computationally no more difficult than evaluating Eq. (134), since  $n_B(\omega)$  is analytically known. Because  $n_B(\omega) > 0$  when  $\omega > 0$ , increasing the temperature will always make  $\mathcal{T}(\omega)$  larger and therefore increase the effect of the one-electron-two-phonon interaction. In particular, we expect the temperature effects to be most significant for low-frequency phonon branches, since this means  $n_B(\omega_{\mathbf{q}, v})$  will be larger in Eq. (147).

This is precisely what we see in Fig. 10, which shows the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  for both LiF and KTaO<sub>3</sub>. In LiF, most of the long-range one-electron-two-phonon interaction originates from high-frequency phonon branches, as we showed in Fig. 6. Therefore, the one-electron-two-phonon spectral function does not even visibly change in Fig. 10(a) when increasing the temperature to 50 K. At  $T = 300$  K, which corresponds to  $\omega = \frac{k_B T}{\hbar} = 6.25$  THz, enough of the phonon branches are thermally activated to see a noticeable increase in the one-electron-two-phonon spectral function. As

argued in Sec. IV D, the peak at  $\sim 12$  THz in KTaO<sub>3</sub> has a significant contribution from the lowest phonon mode with frequency  $\omega \sim 2$  THz. This mode is thermally activated at much lower temperatures, which explains why the height of this peak increases with temperature much faster. On the contrary, the spectral function at higher frequencies is almost unaffected by temperature because none of the phonon modes are thermally activated in this region at 300 K.

A noticeable additional feature of the one-electron-two-phonon spectral functions in Fig. 10 is the appearance of a peak at low frequencies, which is only present at finite temperatures. This peak is due to the second term in Eq. (147), which gives a contribution to the one-electron-two-phonon spectral function at the difference  $|\omega_{\mathbf{q}, v_2} - \omega_{\mathbf{q}, v_1}|$  of the two phonon frequencies, rather than at the sum. This contribution naturally shows up at lower frequencies. In KTaO<sub>3</sub>, we can once again explain this with the contribution on the  $\Gamma - X_1 - M_1$  line with two phonon branches of frequencies  $\omega \sim 2$  THz and  $\omega \sim 10$  THz, which yields the finite-temperature peak at  $\omega \sim 8$  THz.

Table IV shows the moments of the one-electron-two-phonon spectral function for LiF and KTaO<sub>3</sub>, calculated from the data in Fig. 10. It is clearly visible that the moments increase faster as a function of temperature in KTaO<sub>3</sub> than in LiF, due to the lower phonon frequencies. The low-frequency finite-temperature peak of the one-electron-two-phonon spectral function also causes a significant increase in the moments, since they are all calculated with a negative power and therefore favor contributions at lower frequencies. This is most clearly visible in LiF, where the moment  $\mathcal{T}_{-\frac{3}{2}}$  is more than twice as large as the moment  $\mathcal{T}_{-\frac{1}{2}}$  at 300 K.

Note that although higher temperatures favor the one-electron-two-phonon interaction compared to the one-electron-one-phonon interaction, the former is still negligible in LiF and KTaO<sub>3</sub> at room temperatures. The contribution of the one-electron-two-phonon interaction to the polaron ground-state energy was three to four orders of magnitude lower than that of the one-electron-one-phonon interaction, and the temperature effects increase the one-electron-two-

TABLE IV. Moments of  $\mathcal{T}(\omega)$ , calculated through equation Eq. (135) with the data from Fig. 7. All moments are evaluated with a  $128 \times 128$  grid of interpolated  $\mathbf{q}$  points and a smearing of  $\sigma = 0.1$  THz. The moments were multiplied with appropriate powers of the frequencies in Table II in order to make them dimensionless.

Temperature	LiF			KTaO <sub>3</sub>		
	$\frac{1}{\sqrt{\omega_{LO}}}\mathcal{T}_{-\frac{1}{2}}$	$\mathcal{T}_{-1}$	$\sqrt{\omega_{LO}}\mathcal{T}_{-\frac{3}{2}}$	$\frac{1}{\sqrt{\omega_{LO3}}}\mathcal{T}_{-\frac{1}{2}}$	$\mathcal{T}_{-1}$	$\sqrt{\omega_{LO3}}\mathcal{T}_{-\frac{3}{2}}$
0 K	0.000111	0.000108	0.000107	0.001903	0.002313	0.002945
100 K	0.000121	0.000126	0.000145	0.002938	0.004128	0.006592
200 K	0.000169	0.000204	0.000311	0.005038	0.007656	0.013475
300 K	0.000231	0.000298	0.000498	0.007315	0.011383	0.020539

phonon contribution by less than an order of magnitude. Regardless, it provides an important piece of information when looking for materials with significant one-electron-two-phonon interaction: In this case, it is beneficial to look at materials with low phonon frequencies, since the temperature effects will be much larger in those materials. Indeed,  $\mathcal{T}_{-\frac{3}{2}}$  increases by an order of magnitude in KTaO<sub>3</sub> when increasing the temperature from 0 K to 300 K, due to the stronger contributions from the low-frequency phonon modes.

## V. CONCLUSIONS AND OUTLOOK

The central result of this article is the analytical derivation of the long-range one-electron-two-phonon matrix element  $g_{mn\nu_1\nu_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  in Eq. (65), written in terms of quantities that are accessible via first-principles calculations. It was shown that the key quantity that controls the strength of the long-range one-electron-two-phonon matrix element is  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}}$ , the derivative of the dynamical matrix with respect to an external electric field. This quantity is not implemented in standard first-principles codes, so we computed it using finite differences by calculating the dynamical matrix under a small positive and negative electric field. In principle, it should also be possible to calculate  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}}$  using density functional perturbation theory with the use of the  $2n+1$ -theorem, similarly to the methods described in Refs. [107,121].

For a large polaron treated up to lowest order in the electron-phonon interactions, it was shown that the one-electron-two-phonon interaction only enters the self-energy through a  $3 \times 3$  spectral function  $\mathcal{T}_{\alpha\beta}(\omega)$ . This spectral function is a useful target quantity for first-principle calculations. It is expected that  $\mathcal{T}_{\alpha\beta}(\omega)$  enters other electron-phonon quantities that only depend on the Fan-Migdal-like diagram in Fig. 3(d): Such quantities might include the superconducting Eliashberg function  $\alpha^2F(\omega)$  [17] and the optical polaron conductivity [20,122].

As a benchmark, we calculated the one-electron-two-phonon spectral function  $\mathcal{T}(\omega)$  for LiF and KTaO<sub>3</sub>. The framework developed in Sec. IV for extracting the one-electron-two-phonon strength is applicable to any material. It can be used to determine the relative contributions from different phonon branches and from different parts of the Brillouin zone. This guides the construction of model Hamiltonians, where only a few phonon branches with dominant contributions are included in the Hamiltonian. The results for

LiF show that  $\mathcal{T}(\omega)$  has contributions from all over the Brillouin zone, which means that a simple model Hamiltonian that gives quantitative predictions for LiF cannot be constructed. It also means that it is not possible to make the continuum approximation for an accurate description of the long-range one-electron-two-phonon interaction.

The one-electron-two-phonon interaction in LiF and KTaO<sub>3</sub> turns out to be small. Going forward, it will be more interesting to calculate  $\mathcal{T}_{\alpha\beta}(\omega)$  for more anharmonic materials, since they naturally have larger phononic displacements. In such materials, it is common to describe the phonons with an effective anharmonic dynamical matrix  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}^{(\text{anh})}(\mathbf{q})$ , which is calculated from the entire ionic landscape with a method such as SSCHA [54]. Since the full electron-phonon interaction Eq. (48) originally comes from the electric field derivative of the entire ionic landscape through Eq. (22), one might capture the higher-order electron-phonon effects within the same approximations by replacing  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \mathcal{E}}$  with  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{(\text{anh})}(\mathbf{q})}{\partial \mathcal{E}}$  in the theory of this article, e.g., in Eq. (62).

Looking ahead, SrTiO<sub>3</sub> is a material where the calculation of  $\mathcal{T}(\omega)$  might be interesting. There is already a model Hamiltonian for one-electron-two-phonon coupling to the soft TO mode, which was first proposed in Refs. [71,72] using arguments similar to the ones proposed in Sec. II. This Hamiltonian was used to study the superconductivity [73,74] and resistivity [75] of SrTiO<sub>3</sub>. However, the Hamiltonian features a phenomenological parameter  $g_2$ , which cannot be calculated from first principles. Calculating  $\mathcal{T}(\omega)$  for SrTiO<sub>3</sub> is challenging because of its strong phonon anharmonicity and electronic correlations that require a beyond-DFT treatment [36], but it would provide a fully *ab initio* description of the long-range one-electron-two-phonon interaction without phenomenological parameters.

Halide perovskites such as CsPbI<sub>3</sub> or MAPbI<sub>3</sub> [38] are also promising, since they are expected to have much stronger long-range than short-range coupling [40]. Additionally, they have relatively low phonon frequencies of less than 5 THz [123,124]: As discussed in Sec. IV F, this will make the one-electron-two-phonon spectral function much larger at room temperature. It has already been shown that the higher-order electron-phonon interactions are necessary to find the correct temperature dependence for the band-gap renormalization at ambient temperatures in these materials [37]. A first-principles calculation of  $\mathcal{T}(\omega)$  in CsPbI<sub>3</sub> or MAPbI<sub>3</sub> might reproduce this result and explain it in more detail.

Equation (65) for the long-range one-electron-two-phonon matrix element  $g_{mnv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  contains a  $1/|\mathbf{q}_1 + \mathbf{q}_2|$  divergence, similarly to the  $1/|\mathbf{q}|$  divergence in the one-electron-one-phonon matrix element. The analytic expression of this divergence is used when interpolating the full one-electron-one-phonon matrix element [13,31]. Therefore, once it becomes computationally feasible to calculate the full one-electron-two-phonon matrix element  $g_{mnv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  from first principles, knowledge of Eq. (65) for  $g_{mnv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2)$  will also be necessary for robust interpolation.

### ACKNOWLEDGMENTS

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### DATA AVAILABILITY

The first-principles data and postprocessing code used to generate Figs. 5–10 are publicly available online [125]. The data that support the findings of this article are openly available [125].

### APPENDIX A: THE ELECTRIC ENTHALPY AND ITS DERIVATIVES

The electric enthalpy is defined from the ground-state energy through Eq. (19), which we reproduce here for clarity:

$$E(\{\mathbf{u}_\kappa(\ell)\}, \mathcal{E}) = E_0(\{\mathbf{u}_\kappa(\ell)\}, \mathbf{D}) - \Omega_{\text{sc}} \mathcal{E} \cdot \mathbf{P}_{\text{ext}}. \quad (\text{A1})$$

The main issue with defining derivatives of the electric enthalpy in the context of this article, is that this definition is not a Legendre transform. This is because  $\mathcal{E}$  represents only the external electric field, whereas the canonically conjugate variable  $\frac{\partial E_0}{\partial \mathbf{D}} := \mathcal{E}_{\text{tot}}$  represents the total electric field inside the material. In the context of this article, the polarization  $\mathbf{P}_{\text{ion}}$  creates an internal electric field  $\mathcal{E}_{\text{int}}$  in the material when the ions are not in their equilibrium positions. This means that:

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{int}} + \mathcal{E}. \quad (\text{A2})$$

Therefore, the definition for the electric enthalpy, as written in Eq. (19), actually defines a function  $E(\{\mathbf{u}_\kappa(\ell)\}, \mathcal{E}, \mathbf{D})$  where both arguments  $\mathcal{E}$  and  $\mathbf{D}$  are still present. In many literature definitions of the electric enthalpy [86,87], it is implicitly assumed that  $\mathcal{E}_{\text{int}} = \mathbf{0}$ . In this case, one has  $\frac{\partial E_0}{\partial \mathbf{D}} = \mathcal{E}$ , and the definition Eq. (19) for the electric enthalpy is indeed a Legendre transform. Then, the electric enthalpy becomes a pure function of  $\mathcal{E}$ , with no further  $\mathbf{D}$  dependence.

The problem of the dependence on both  $\mathcal{E}$  and  $\mathbf{D}$  can be circumvented by assuming a connection between the two. Indeed, they both represent an external field, so intuitively one might expect that they are related. This connection will be Eq. (23): Let us motivate this connection here. In this article,

we assume an optically linear material, where the response of the electric displacement field  $\mathbf{D}$  to a homogeneous electric field  $\mathcal{E}_{\text{tot}}$  is defined by the dielectric function  $\epsilon(\omega)$ :

$$\mathbf{D}(\omega) = \epsilon_0 \epsilon(\omega) \cdot \mathcal{E}_{\text{tot}}(\omega). \quad (\text{A3})$$

Suppose  $\omega$  lies in the frequency range where it is low enough to not cause any transitions between the electronic levels but fast enough so that the ions are too slow to follow the oscillation and are therefore almost stationary:  $\mathbf{u}_\kappa(\ell) = \mathbf{0}$ . This limit is usually denoted as  $\epsilon_\infty$ , and therefore  $\epsilon_\infty$  can be formally defined as:

$$\mathbf{D} = \epsilon_0 \epsilon_\infty \cdot \mathcal{E}_{\text{tot}}, \quad \text{when } \mathbf{u}_\kappa(\ell) = \mathbf{0}. \quad (\text{A4})$$

When all ions are in their equilibrium positions,  $\mathcal{E}_{\text{int}} = \mathbf{0}$  and we have that  $\mathcal{E}_{\text{tot}} = \mathcal{E}$ . Therefore, we may also write:

$$\mathbf{D} = \epsilon_0 \epsilon_\infty \cdot \mathcal{E}. \quad (\text{A5})$$

This is Eq. (23) from the main part of the article.

The above connection between  $\mathbf{D}$  and  $\mathcal{E}$  can be used to eliminate the  $\mathbf{D}$  dependence in the electric enthalpy from Eq. (19). First, we note that  $\mathbf{P}_{\text{ext}}$  in this expression is defined as the polarization when all ions are in their equilibrium positions. In this case, the only electric fields are  $\mathbf{D}$  and  $\mathcal{E}$ , and the standard definition of the polarization density  $\mathbf{P}$  may be used to write:

$$\mathbf{P}_{\text{ext}} = \mathbf{D} - \epsilon_0 \mathcal{E}. \quad (\text{A6})$$

Now, if Eq. (19) is combined with the definition Eq. (A6) of  $\mathbf{P}_{\text{ext}}$  and the expanded expression of the ground-state energy  $E_0$  from Eq. (18), then the electric enthalpy can be written as:

$$\begin{aligned} E(\{\mathbf{u}_\kappa(\ell)\}, \mathcal{E}; \mathbf{D}) &\approx H_{\text{KS}} + E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell)\}) \\ &- \frac{\Omega_{\text{sc}}}{\epsilon_0} \mathbf{D} \cdot \epsilon_\infty^{-1} \cdot \mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\}) \\ &+ \frac{\Omega_{\text{sc}}}{2\epsilon_0} \mathbf{D} \cdot \epsilon_\infty^{-1} \cdot \mathbf{D} - \Omega_{\text{sc}} \mathcal{E} \cdot (\mathbf{D} - \epsilon_0 \mathcal{E}). \end{aligned} \quad (\text{A7})$$

However, the  $\mathbf{D}$  dependence can be eliminated in favor of  $\mathcal{E}$  by using Eq. (23). This gives the following expression for the electric enthalpy:

$$\begin{aligned} E(\{\mathbf{u}_\kappa(\ell)\}, \mathcal{E}) &\approx H_{\text{KS}} + E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell)\}) - \Omega_{\text{sc}} \mathcal{E} \cdot \mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\}) \\ &- \frac{\Omega_{\text{sc}} \epsilon_0}{2} \mathcal{E} \cdot (\epsilon_\infty - 2\mathbf{I}) \cdot \mathcal{E}. \end{aligned} \quad (\text{A8})$$

If the  $\mathcal{E}$  dependence is defined like this, then the first-order derivative with respect to the electric field can be read off immediately:

$$\mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\}) = - \frac{1}{\Omega_{\text{sc}}} \left. \frac{\partial E}{\partial \mathcal{E}} \right|_{\mathcal{E}=\mathbf{0}}. \quad (\text{A9})$$

This is the definition Eq. (22) as presented in the main part of the article. Note that even for optically nonlinear materials, the above argument still holds: Any higher-order terms in  $\mathcal{E}$  that would need to be added to Eq. (23) would only give contributions to Eq. (A8) of at least second order in  $\mathcal{E}$ . These contributions do not contribute to the above definition of  $\mathbf{P}_{\text{ion}}$ .

We must also prove that  $\boldsymbol{\varepsilon}_\infty$  as defined from Eq. (A4) is equivalent to the definition in Eq. (17). This can be proven by rederiving the relation between  $\mathbf{D}$  and  $\boldsymbol{\mathcal{E}}_{\text{tot}}$  from the ground-state energy  $E_0$ . According to Eq. (10), we have that:

$$\boldsymbol{\mathcal{E}}_{\text{tot}} = \frac{1}{\Omega_{\text{sc}}} \frac{\partial E_0}{\partial \mathbf{D}}. \quad (\text{A10})$$

Now note that we assume an optically linear material, which means that the ground-state energy can always be written in the form of Eq. (18):

$$E_0(\{\mathbf{u}_\kappa(\ell)\}, \mathbf{D}) \approx H_{\text{KS}} + E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell)\}) - \mathbf{D} \cdot \mathbf{A} \cdot \mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\}) + \frac{1}{2} \mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}, \quad (\text{A11})$$

where we have temporarily defined the shorthand matrix  $\mathbf{A}$ :

$$\mathbf{A} := \left. \frac{\partial^2 E_0}{\partial \mathbf{D} \partial \mathbf{D}} \right|_{\mathbf{u}_\kappa(\ell) = \mathbf{D} = \mathbf{0}}, \quad (\text{A12})$$

and  $E_{\text{ph}}(\{\mathbf{u}_\kappa(\ell)\})$  and  $\mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\})$  are only functions of the ionic displacements  $\mathbf{u}_\kappa(\ell)$ , as defined through Eq. (15) and Eq. (16). If we use Eq. (A10) to calculate the total electric field from Eq. (A11), then this gives:

$$\boldsymbol{\mathcal{E}}_{\text{tot}} = \frac{1}{\Omega_{\text{sc}}} \mathbf{A} \cdot (\mathbf{D} - \mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\})), \quad (\text{A13})$$

$$\Leftrightarrow \mathbf{D} = \Omega_{\text{sc}} \mathbf{A}^{-1} \cdot \boldsymbol{\mathcal{E}}_{\text{tot}} + \mathbf{P}_{\text{ion}}(\{\mathbf{u}_\kappa(\ell)\}). \quad (\text{A14})$$

If this expression is evaluated at  $\mathbf{u}_\kappa(\ell) = \mathbf{0}$ , then the second term is zero, and we can compare directly with Eq. (A4) of  $\boldsymbol{\varepsilon}_\infty$  to find that:

$$\left. \frac{\partial^2 E_0}{\partial \mathbf{D} \partial \mathbf{D}} \right|_{\mathbf{u}_\kappa(\ell) = \mathbf{D} = \mathbf{0}} = \frac{\Omega_{\text{sc}}}{\varepsilon_0} \boldsymbol{\varepsilon}_\infty^{-1}, \quad (\text{A15})$$

and this is exactly the definition as presented in Eq. (17).

Finally, Eqs. (20) and (21) for  $H_{\text{KS}}$  and  $E_{\text{ph}}$  are trivial, since they are defined at  $\boldsymbol{\mathcal{E}} = \mathbf{0}$ . In the case of no external electric field, the ground-state energy  $E_0$  and electric enthalpy  $E$  are

$$g_{mmv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = \begin{cases} \frac{e^2}{2\varepsilon_0\Omega_0} \frac{(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{Y}_{v_1v_2}(\mathbf{q}_2)}{(\mathbf{q}_1 + \mathbf{q}_2) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q}_1 + \mathbf{q}_2)} \langle \psi_{\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2, m} | e^{i(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{r}} | \psi_{\mathbf{k}, n} \rangle & \text{if } \mathbf{q}_1 + \mathbf{q}_2 \neq \mathbf{0}, \\ 0 & \text{if } \mathbf{q}_1 + \mathbf{q}_2 = \mathbf{0}. \end{cases} \quad (\text{B3})$$

The one-electron-two-phonon matrix element only enters Eq. (B1) as  $g_{mmv_1v_2}^{(\text{long})}(\mathbf{k}, -\mathbf{q}, \mathbf{q})$ . However, by the above definition, one immediately has that  $g_{mmv_1v_2}^{(\text{long})}(\mathbf{k}, -\mathbf{q}, \mathbf{q}) = 0$ . This means the long-range interaction does not contribute to the Debye-Waller self-energy, as mentioned in the main text. Note that a similar argument can be used to show that  $g_{mmv_1v_2}^{(\text{long})}(\mathbf{k}, \mathbf{0}) = \mathbf{0}$ , which implies that  $\Sigma_{nn}^{(b)}(\mathbf{k}, \omega) = 0$  is also true in the commonly used rigid-ion approximation for the Debye-Waller self-energy (see, e.g., Eqs. (195)–(198) in Ref. [13]).

## 2. The other diagram

For the self-energy contribution in Eq. (B2), the argument is less straightforward. The proof is divided into two big steps. In the first step, we study how the expression changes if we make the exchange of the labels  $1 \leftrightarrow 2$  and show that this

equal to each other, meaning that the definitions in Eqs. (14) and (15) carry over directly to the electric enthalpy.

## APPENDIX B: NEGLIGIBLE DIAGRAMS

In the diagrammatic expansion for the self-energy in Sec. III A, we have neglected the following two contributions to the self-energy, which respectively come from the diagrams in Figs. 3(b) and 3(c):

$$\Sigma_{nn}^{(b)}(\mathbf{k}, \omega) = i \frac{\Omega_0}{\Omega} \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \sum_{\mathbf{q}, v} g_{nmv_1v_2}(\mathbf{k}, -\mathbf{q}, \mathbf{q}) \times D_{vv}^{(0)}(-\mathbf{q}, \omega_1), \quad (\text{B1})$$

$$\Sigma_{nn}^{(c)}(\mathbf{k}, \omega) = -2 \frac{\Omega_0^2}{\Omega^2} \frac{1}{\hbar^3} \sum_{m_1, m_2} \sum_{v_1, v_2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \int_{-\infty}^{+\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{+\infty} \frac{d\omega_2}{2\pi} \times G_{m_1 m_1}^{(0)}(\mathbf{k} + \mathbf{q}_1, \omega + \omega_1) \times G_{m_2 m_2}^{(0)}(\mathbf{k} + \mathbf{q}_2, \omega + \omega_2) D_{v_1 v_1}^{(0)}(\mathbf{q}_1, -\omega_1) \times D_{v_2 v_2}^{(0)}(\mathbf{q}_2, -\omega_2) g_{m_1 n v_1}(\mathbf{k}, \mathbf{q}_1) \times g_{m_2 m_1 v_1 v_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) g_{m_2 n v_2}^*(\mathbf{k}, \mathbf{q}_2). \quad (\text{B2})$$

In this Appendix, we show that these terms are either zero or very small when we use the long-range expressions from Eqs. (64) and (65) for the matrix elements.

### 1. The Debye-Waller diagram

For the Debye-Waller self-energy  $\Sigma_{nn}^{(b)}(\mathbf{k}, \omega)$ , the argument is simple. One only needs the one-electron-two-phonon matrix element, which is given by Eq. (65). Because it is defined in the  $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G} \rightarrow \mathbf{0}$  limit, it is allowed to neglect all terms in the sum which have  $\mathbf{G} \neq \mathbf{0}$ . This gives the following approximate expression for the one-electron-two-phonon matrix element:

essentially comes down to taking the complex conjugate of all the matrix elements in this expression. In the second step, we prove that each of the matrix elements is approximately purely imaginary if we focus only on the long-range interaction. Combining those two properties will eventually yield the property  $\Sigma_{nn}(\mathbf{k}, \omega) \approx -\Sigma_{nn}(\mathbf{k}, \omega)$ , which is only possible when  $\Sigma_{nn}(\mathbf{k}, \omega) \approx 0$ .

The first step is to study the exchange of the labels  $1 \leftrightarrow 2$ . If this substitution is performed in Eq. (B2), then the first two lines remain completely unchanged. Therefore, one should only check how the matrix elements change under this substitution. The one-electron-one-phonon matrix elements change as:

$$g_{m_1 n v_1}(\mathbf{k}, \mathbf{q}_1) g_{m_2 n v_2}^*(\mathbf{k}, \mathbf{q}_2) \leftrightarrow g_{m_2 n v_2}(\mathbf{k}, \mathbf{q}_2) g_{m_1 n v_1}^*(\mathbf{k}, \mathbf{q}_1), \quad (\text{B4})$$

which is the same as taking a complex conjugate. The one-electron-two-phonon matrix element changes as:

$$g_{m_2 m_1 \nu_1 \nu_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) \leftrightarrow g_{m_1 m_2 \nu_2 \nu_1}(\mathbf{k} + \mathbf{q}_2, -\mathbf{q}_2, \mathbf{q}_1). \quad (\text{B5})$$

Equation (4) for the Hamiltonian immediately implies the symmetry property  $g_{m\nu\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = g_{m\nu\nu_2}(\mathbf{k}, \mathbf{q}_2, \mathbf{q}_1)$ . With this symmetry property, the right-hand side can be rewritten as:

$$g_{m_2 m_1 \nu_1 \nu_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) \leftrightarrow g_{m_1 m_2 \nu_1 \nu_2}(\mathbf{k} + \mathbf{q}_2, \mathbf{q}_1, -\mathbf{q}_2). \quad (\text{B6})$$

Finally, we use that the one-electron-two-phonon matrix element must satisfy the following condition such that the Hamiltonian in Eq. (4) is Hermitian:

$$g_{m\nu\nu_2}^*(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = g_{m\nu\nu_2}(\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2, -\mathbf{q}_1, -\mathbf{q}_2). \quad (\text{B7})$$

Then, the right-hand side of the substitution changes as:

$$g_{m_2 m_1 \nu_1 \nu_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) \leftrightarrow g_{m_2 m_1 \nu_1 \nu_2}^*(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2). \quad (\text{B8})$$

Again, the exchange  $1 \leftrightarrow 2$  simply gives a complex conjugate. Combining all of this, we find a second valid expression for  $\Sigma_{mm}(\mathbf{k}, \omega)$  through the substitution  $1 \leftrightarrow 2$ :

$$\begin{aligned} \Sigma_{mm}(\mathbf{k}, \omega) = & -\frac{2\Omega_0^2}{\hbar^3 (2\pi)^8} \sum_{m_1 m_2} \sum_{\nu_1, \nu_2} \int_{\text{1BZ}} d^3 \mathbf{q}_1 \int_{\text{1BZ}} d\mathbf{q}_2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \\ & \times G_{m_1 m_1}^{(0)}(\mathbf{k} + \mathbf{q}_1, \omega + \omega_1) G_{m_2 m_2}^{(0)}(\mathbf{k} + \mathbf{q}_2, \omega + \omega_2) \mathcal{D}_0(\omega_{\mathbf{q}_1, \nu_1}, -\omega_1) \mathcal{D}_0(\omega_{\mathbf{q}_2, \nu_2}, -\omega_2) \\ & \times (g_{m_1 \nu_1}(\mathbf{k}, \mathbf{q}_1) g_{m_2 m_1 \nu_1 \nu_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) g_{m_2 \nu_2}^*(\mathbf{k}, \mathbf{q}_2))^*. \end{aligned} \quad (\text{B9})$$

This is the same expression as Eq. (B2), but where all the electron-phonon matrix elements have been complex conjugated. In fact, Eq. (B2) and Eq. (B9) can be added together to introduce a real part into the expression:

$$\begin{aligned} \Sigma_{mm}(\mathbf{k}, \omega) = & -\frac{2\Omega_0^2}{\hbar^3 (2\pi)^8} \sum_{m_1 m_2} \sum_{\nu_1, \nu_2} \int_{\text{1BZ}} d^3 \mathbf{q}_1 \int_{\text{1BZ}} d\mathbf{q}_2 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 G_{m_1 m_1}^{(0)}(\mathbf{k} + \mathbf{q}_1, \omega + \omega_1) \\ & \times G_{m_2 m_2}^{(0)}(\mathbf{k} + \mathbf{q}_2, \omega + \omega_2) \mathcal{D}_0(\omega_{\mathbf{q}_1, \nu_1}, -\omega_1) \mathcal{D}_0(\omega_{\mathbf{q}_2, \nu_2}, -\omega_2) \\ & \times \text{Re}[g_{m_1 \nu_1}(\mathbf{k}, \mathbf{q}_1) g_{m_2 m_1 \nu_1 \nu_2}(\mathbf{k} + \mathbf{q}_1, -\mathbf{q}_1, \mathbf{q}_2) g_{m_2 \nu_2}^*(\mathbf{k}, \mathbf{q}_2)]. \end{aligned} \quad (\text{B10})$$

This expression essentially says that this diagram for the self-energy must be real with respect to complex conjugation of only the electron-phonon matrix elements.

The second step of the proof is to show that the relevant limits of the electron-phonon matrix elements are all purely imaginary. The long-range approximation for the one-electron-one-phonon matrix elements in Fig. 3(c) implies that both phonon momenta must separately be very small:  $\mathbf{q}_1 \approx \mathbf{q}_2 \approx \mathbf{0}$ . In that case, the relevant limit of the electron-phonon matrix elements are as follows:

$$\lim_{|\mathbf{q}| \rightarrow 0} g_{m\nu}(\mathbf{k}, \mathbf{q}) = \frac{ie^2}{\varepsilon_0 \Omega_0} \sqrt{\frac{\hbar}{2\omega_{\hat{\mathbf{q}}, \nu}}} \frac{\mathbf{q} \cdot \mathbf{p}_\nu(\hat{\mathbf{q}})}{\mathbf{q} \cdot \boldsymbol{\varepsilon}_\infty \cdot \mathbf{q}} \langle \psi_{\mathbf{k}, m} | \psi_{\mathbf{k}, n} \rangle, \quad (\text{B11})$$

$$\lim_{\mathbf{q}_1, \mathbf{q}_2 \rightarrow 0} g_{m\nu\nu_2}(\mathbf{k}, \mathbf{q}_1, \mathbf{q}_2) = \frac{e^2}{2\varepsilon_0 \Omega_0} \frac{(\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{Y}_{\nu_1, \nu_2}(\hat{\mathbf{q}}_2)}{(\mathbf{q}_1 + \mathbf{q}_2) \cdot \boldsymbol{\varepsilon}_\infty \cdot (\mathbf{q}_1 + \mathbf{q}_2)} \langle \psi_{\mathbf{k}, m} | \psi_{\mathbf{k}, n} \rangle, \quad (\text{B12})$$

where  $\mathbf{Y}_{\nu_1, \nu_2}(\hat{\mathbf{q}})$  is defined as the  $\mathbf{q} \rightarrow \mathbf{0}$  limit of  $\mathbf{Y}_{\nu_1, \nu_2}(\mathbf{q})$ , which may still depend on the direction  $\hat{\mathbf{q}}$ . The Bloch states can be chosen such that they are orthonormal: Therefore, the electron matrix elements in Eqs. (B11) and (B12) are real. Alternatively, a proof similar to the one in Appendix C can be used to show that the sums over  $m_1, m_2$  that appear in Eq. (B10) no longer contain the Bloch states. This means one only needs to investigate whether  $\mathbf{p}_\nu(\hat{\mathbf{q}})$  and  $\mathbf{Y}_{\nu_1, \nu_2}(\hat{\mathbf{q}}_2)$  are real or imaginary. This can be done by investigating the dynamical matrix  $\mathcal{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}; \boldsymbol{\varepsilon})$  around  $\Gamma$ . The following property of the dynamical matrix follows immediately from its definition in Eq. (26):

$$\mathcal{D}_{\kappa\alpha, \kappa'\beta}^*(\mathbf{q}; \boldsymbol{\varepsilon}) = \mathcal{D}_{\kappa\alpha, \kappa'\beta}(-\mathbf{q}; \boldsymbol{\varepsilon}). \quad (\text{B13})$$

This immediately implies that  $\mathcal{D}_{\kappa\alpha, \kappa'\beta}(\hat{\mathbf{q}}; \boldsymbol{\varepsilon})$  is real, since it is defined in the  $|\mathbf{q}| \rightarrow \mathbf{0}$  limit and the nonanalytic contribution from Eq. (122) is real. This means that the usual dynamical

matrix  $\mathcal{D}_{\kappa\alpha, \kappa'\beta}(\hat{\mathbf{q}})$ , as well as its electric field derivative  $\frac{\partial \mathcal{D}_{\kappa\alpha, \kappa'\beta}(\hat{\mathbf{q}})}{\partial \boldsymbol{\varepsilon}}$ , are real and symmetric. Therefore, we can choose the phonon eigenvectors to be real:

$$e_{\kappa\alpha, \nu}(\hat{\mathbf{q}}) = e_{\kappa\alpha, \nu}^*(\hat{\mathbf{q}}) = e_{\kappa\alpha, \nu}(-\hat{\mathbf{q}}). \quad (\text{B14})$$

Equation (63) then immediately implies that the mode polarities  $\mathbf{p}_\nu(\hat{\mathbf{q}})$  are real. The same argument can be made for  $\mathbf{Y}_{\nu_1, \nu_2}(\hat{\mathbf{q}})$ :

$$\begin{aligned} \mathbf{Y}_{\nu_1, \nu_2}(\hat{\mathbf{q}}) = & \frac{1}{ie} \sqrt{\frac{\hbar}{2\omega_{\hat{\mathbf{q}}, \nu_1}} \frac{\hbar}{2\omega_{\hat{\mathbf{q}}, \nu_2}}} \sum_{\kappa\alpha} \sum_{\kappa'\beta} e_{\kappa\alpha, \nu_1}^*(\hat{\mathbf{q}}) \\ & \times \frac{\partial \mathcal{D}_{\kappa\alpha, \kappa'\beta}(\hat{\mathbf{q}})}{\partial \boldsymbol{\varepsilon}} e_{\kappa'\beta, \nu_2}(\hat{\mathbf{q}}). \end{aligned} \quad (\text{B15})$$

Here everything is real except for the factor  $i$  in front. This means  $\mathbf{Y}_{\nu_1, \nu_2}(\hat{\mathbf{q}})$  is purely imaginary in general. Combining this with Eqs. (B11) and (B12) shows that each of the

one-electron-one-phonon and one-electron-two-phonon matrix elements are purely imaginary, as mentioned earlier.

The proof can be completed as follows. Equation (B10) features the real part of a product of three electron-phonon matrix elements. Due to the long-range limit, the dominant contribution to the integrals must come from the region with  $\mathbf{q}_1 \approx \mathbf{q}_2 \approx \mathbf{0}$ . In this region, each of the electron-phonon matrix elements is purely imaginary, so the real part of this product will be zero. If one uses Eqs. (64) and (65) instead of Eqs. (B11) and (B12) for the long-range electron-phonon matrix elements in Eq. (B10), then this argument only holds approximately. However, it still provides a reason to neglect this diagram compared to the Fan-Migdal-like diagram in Fig. 3(d), where the argument of this Appendix does not work because the long-range approximation in that diagram implies  $\mathbf{q}_1 + \mathbf{q}_2 \approx \mathbf{0}$  instead of  $\mathbf{q}_1 \approx \mathbf{q}_2 \approx \mathbf{0}$ .

### APPENDIX C: SUM OVER BLOCH STATES

In this Appendix, it is shown that:

$$\lim_{\mathbf{q}+\mathbf{G} \rightarrow \mathbf{0}} \sum_m \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},m}) \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \times \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle = \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},n}). \quad (\text{C1})$$

The argument is quite short. First, because the Bloch states are eigenstates of a Hermitian Hamiltonian with the corresponding eigenvalues  $\epsilon_{\mathbf{k},m}$ , the matrix elements in Eq. (C1) are zero unless  $m$  and  $n$  represent states with the same energy. Therefore,  $\epsilon_{\mathbf{k}+\mathbf{q},m}$  can be replaced with  $\epsilon_{\mathbf{k}+\mathbf{q},n}$  under the sum to obtain:

$$\lim_{\mathbf{q}+\mathbf{G} \rightarrow \mathbf{0}} \sum_m \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},m}) \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle = \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},n}) \sum_m \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle. \quad (\text{C2})$$

Furthermore, the Bloch states are complete and normalized:

$$\sum_m | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \langle \psi_{\mathbf{k}+\mathbf{q},m} | = \hat{1}. \quad (\text{C3})$$

Then, one finds that:

$$\lim_{\mathbf{q}+\mathbf{G} \rightarrow \mathbf{0}} \sum_m \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},m}) \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q},m} \rangle \langle \psi_{\mathbf{k}+\mathbf{q},m} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle = \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},n}) \langle \psi_{\mathbf{k},n} | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \psi_{\mathbf{k},n} \rangle, \quad (\text{C4})$$

$$= \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},n}) \langle \psi_{\mathbf{k},n} | \psi_{\mathbf{k},n} \rangle, \quad (\text{C5})$$

$$= \delta(\varepsilon - \epsilon_{\mathbf{k}+\mathbf{q},n}), \quad (\text{C6})$$

where the final step used the fact that the Bloch states are normalized.

### APPENDIX D: EFFECT OF AN INVERSION CENTER WITH $R(\kappa) = \kappa$

The components of the dynamical matrix  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; \boldsymbol{\mathcal{E}})$  are not all independent of each other: They are linked to each other by symmetry constraints. Suppose  $(\mathbf{R}, \boldsymbol{\tau})$  is an element of the space group of the material, consisting of a rotation  $\mathbf{R}$  followed by a translation  $\boldsymbol{\tau}$ . Then, this symmetry imposes the following constraint on the dynamical matrix:

$$\mathcal{D}_{\kappa\kappa'}(\mathbf{q}, \boldsymbol{\mathcal{E}}) = \mathbf{R}^{-1} \cdot \mathcal{D}_{R(\kappa)R(\kappa')}(\mathbf{R} \cdot \mathbf{q}, \mathbf{R} \cdot \boldsymbol{\mathcal{E}}) \cdot \mathbf{R}. \quad (\text{D1})$$

This expression is only valid in the c-type convention, which we assume throughout this Appendix. Here the index  $R(\kappa)$  is the new index that the atom  $\kappa$  is taken to after applying the symmetry  $(\mathbf{R}, \boldsymbol{\tau})$ , up to a lattice translation  $\boldsymbol{\ell}$ . Mathematically,  $R(\kappa)$  is defined as:

$$\mathbf{R} \cdot \boldsymbol{\tau}_\kappa + \boldsymbol{\tau} = \boldsymbol{\tau}_{R(\kappa)} + \boldsymbol{\ell}. \quad (\text{D2})$$

In LiF, the two atoms are distinguishable, so all symmetries  $(\mathbf{R}, \boldsymbol{\tau})$  of the material must automatically satisfy  $R(\kappa) = \kappa$ ; otherwise,  $(\mathbf{R}, \boldsymbol{\tau})$  would not be a symmetry of the material.

This is not true in general: For example, in the cubic perovskite structure  $\text{ABX}_3$ , the three X ions may be scrambled by some of the rotations. Regardless, some of the symmetry elements may still satisfy  $R(\kappa) = \kappa$ . For example, the inversion center in the cubic perovskite structure still takes all atoms to an equivalent site up to a lattice translation and therefore satisfies  $R(\kappa) = \kappa$ .

In this Appendix, we study some properties of the dynamical matrix  $\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}; \boldsymbol{\mathcal{E}})$  for a material that possesses an inversion center that satisfies  $R(\kappa) = \kappa$ . This includes both LiF and  $\text{KTaO}_3$ , the two materials studied in this article. The inversion center is represented by the space group operation  $(-\mathbf{I}, \mathbf{0})$ , so according to Eq. (D1), a material with such an inversion center necessarily satisfies:

$$\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}, \boldsymbol{\mathcal{E}}) = \mathcal{D}_{\kappa\alpha,\kappa'\beta}(-\mathbf{q}, -\boldsymbol{\mathcal{E}}). \quad (\text{D3})$$

This property may now be used to prove several useful theorems about the material parameters that are present in this article.

#### 1. Imaginary dynamical matrix derivative

Equation (D3) can be used to prove that  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}}$  is purely imaginary. From the definition Eq. (26), it immediately follows that the dynamical matrix satisfies

the following property:

$$\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}, \boldsymbol{\mathcal{E}}) = \mathcal{D}_{\kappa\alpha,\kappa'\beta}^*(-\mathbf{q}, \boldsymbol{\mathcal{E}}). \quad (\text{D4})$$

Combining this with Eq. (D3) shows that:

$$\mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}, \boldsymbol{\mathcal{E}}) = \mathcal{D}_{\kappa\alpha,\kappa'\beta}^*(\mathbf{q}, -\boldsymbol{\mathcal{E}}), \quad (\text{D5})$$

in all materials with an inversion center that satisfies  $R(\kappa) = \kappa$ . Evaluating this property at  $\boldsymbol{\mathcal{E}} = \mathbf{0}$  immediately yields that the dynamical matrix is real. Taking the derivative with respect to  $\boldsymbol{\mathcal{E}}$  on both sides yields that  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}}$  is purely imaginary. It should be emphasized that these properties are only true in the c-type convention.

Note that if we evaluate Eq. (D4) in  $\mathbf{q} = \mathbf{0}$ , then it follows the dynamical matrix must be real in the  $\Gamma$  point, regardless of the strength of the electric field. Together with the property that the dynamical matrix derivative must be purely imaginary, this implies that:

$$\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{0})}{\partial \boldsymbol{\mathcal{E}}} = \mathbf{0}. \quad (\text{D6})$$

In other words, there is no one-electron-two-phonon interaction in  $\Gamma$ , which can be seen in Figs. 5 and 6.

## 2. No one-electron-two-phonon interaction when $\omega_{\mathbf{q},\nu_1} = \omega_{\mathbf{q},\nu_2}$

In Fig. 5, it can be noticed that there is no one-electron-two-phonon interaction in LiF when  $\nu_1 = \nu_2$ . Here, it is shown that this is true for any material with an inversion center that satisfies  $R(\kappa) = \kappa$ . First, we need the following alternative expression for  $\mathbf{Y}_{\nu_1\nu_2}(\mathbf{q})$ , which can be straightforwardly derived by taking the  $\boldsymbol{\mathcal{E}}$  derivative of Eq. (27) and inserting the result into Eq. (62):

$$\mathbf{Y}_{\nu_1\nu_2}(\mathbf{q}) = \frac{1}{ie} \sqrt{\frac{\hbar}{2\omega_{\mathbf{q},\nu_1}} \frac{\hbar}{2\omega_{\mathbf{q},\nu_2}}} \left[ \frac{\partial \omega_{\mathbf{q},\nu_1}^2}{\partial \boldsymbol{\mathcal{E}}} \delta_{\nu_1\nu_2} + (\omega_{\mathbf{q},\nu_2}^2 - \omega_{\mathbf{q},\nu_1}^2) \times \sum_{\kappa\alpha} e_{\kappa\alpha,\nu_1}^*(\mathbf{q}) \frac{\partial e_{\kappa\alpha,\nu_2}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}} \right]. \quad (\text{D7})$$

This expression is written in terms of the electric field derivatives of the phonon frequencies and eigenvectors. Equations (D3) and (D4) are properties for the dynamical matrix, but they also hold for its eigenvalues, such that:

$$\left. \begin{aligned} \omega_\nu(\mathbf{q}, \boldsymbol{\mathcal{E}}) &= \omega_\nu(-\mathbf{q}, -\boldsymbol{\mathcal{E}}) \\ \omega_\nu(\mathbf{q}, \boldsymbol{\mathcal{E}}) &= \omega_\nu(-\mathbf{q}, \boldsymbol{\mathcal{E}}) \end{aligned} \right\} \Rightarrow \omega_\nu(\mathbf{q}, \boldsymbol{\mathcal{E}}) = \omega_\nu(\mathbf{q}, -\boldsymbol{\mathcal{E}}). \quad (\text{D8})$$

From the final property it is immediately clear that  $\frac{\partial \omega_{\mathbf{q},\nu_1}^2}{\partial \boldsymbol{\mathcal{E}}} = \mathbf{0}$ . Therefore, for materials with an inversion center that satisfies  $R(\kappa) = \kappa$ , Eq. (D7) reduces to:

$$\mathbf{Y}_{\nu_1\nu_2}(\mathbf{q}) = \frac{1}{ie} \sqrt{\frac{\hbar}{2\omega_{\mathbf{q},\nu_1}} \frac{\hbar}{2\omega_{\mathbf{q},\nu_2}}} (\omega_{\mathbf{q},\nu_2}^2 - \omega_{\mathbf{q},\nu_1}^2) \times \sum_{\kappa\alpha} e_{\kappa\alpha,\nu_1}^*(\mathbf{q}) \frac{\partial e_{\kappa\alpha,\nu_2}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}}. \quad (\text{D9})$$

In this expression, the factor  $(\omega_{\mathbf{q},\nu_2}^2 - \omega_{\mathbf{q},\nu_1}^2)$  makes it clear that  $\mathbf{Y}_{\nu_1\nu_2}(\mathbf{q}) = \mathbf{0}$  when  $\nu_1 = \nu_2$ , or more generally for two degenerate branches.

## 3. No nonanalytic contribution for the dynamical matrix derivative

In Sec. IV A of the main text, it was shown that the nonanalytic contribution to the derivative of the dynamical matrix  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{\text{NAC}}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}}$  requires knowledge of the Raman susceptibility tensor  $\frac{\partial \chi_{\beta\gamma}}{\partial u_{\kappa\alpha}}$  and the nonlinear optical susceptibility  $\chi_{\alpha\beta\gamma}^{(2)}$ , which were defined in Eqs. (123) and (124). In general, if the material has a space group symmetry  $(\mathbf{R}, \boldsymbol{\tau})$ , then these two tensors satisfy the following symmetry constraints:

$$\frac{\partial \chi_{\beta\gamma}}{\partial u_{\kappa\alpha}} = \sum_{\alpha'\beta'\gamma'} R_{\alpha'\alpha} R_{\beta'\beta} R_{\gamma'\gamma} \frac{\partial \chi_{\beta'\gamma'}}{\partial u_{R(\kappa)\alpha'}}, \quad (\text{D10})$$

$$\chi_{\alpha\beta\gamma}^{(2)} = \sum_{\alpha'\beta'\gamma'} R_{\alpha'\alpha} R_{\beta'\beta} R_{\gamma'\gamma} \chi_{\alpha'\beta'\gamma'}^{(2)}. \quad (\text{D11})$$

Therefore, if the material has an inversion center  $R_{\alpha\alpha'} = -\delta_{\alpha\alpha'}$  that satisfies  $R(\kappa) = \kappa$ , then it imposes the following conditions:

$$\frac{\partial \chi_{\beta\gamma}}{\partial u_{\kappa\alpha}} = -\frac{\partial \chi_{\beta\gamma}}{\partial u_{\kappa\alpha}}, \quad (\text{D12})$$

$$\chi_{\alpha\beta\gamma}^{(2)} = -\chi_{\alpha\beta\gamma}^{(2)}, \quad (\text{D13})$$

which is only possible if both tensors are zero. Therefore, we find that  $\frac{\partial \mathcal{D}_{\kappa\alpha,\kappa'\beta}^{\text{NAC}}(\mathbf{q})}{\partial \boldsymbol{\mathcal{E}}} = 0$  in such materials. This means the Fourier interpolation for the derivative of the dynamical matrix can be performed with Eq. (121), without subtracting and adding a nonanalytic contribution.

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