Long wavelength properties of electron-TO-phonon interactions in polar crystals

Aleksandr Pishtshev
Institute of Physics, University of Tartu, Riiia 142, 51014 Tartu, Estonia

Theoretical analysis dealing with the interaction of electrons with the polar long-wavelength transverse optical (TO) vibrations is presented. The theory is based on the model of a polar crystal with classical potentials, which takes into account the electronic polarizability effects. A significant enhancement of the strength of the electron-TO-phonon interaction in ferroelectrics is found. A microscopic justification of this effect is given. A bridge that relates the interaction of electrons with the polar long-wavelength TO modes of the lattice vibrations to the long-range dipole-dipole interaction is established. As an application of our analysis, a new equation representing the relationship between the electron-TO-phonon interaction constant and material parameters is obtained.

PACS numbers: 63.20.-e; 63.20.kd; 77.84.-s
Keywords: Electron-phonon interaction; optical lattice vibrations; polar crystals

I. INTRODUCTION

In the lattice dynamics of a polar crystal, there are two characteristic features, which give evidence that the interaction of electrons with the polar long-wavelength optical modes should be necessarily taken into account. The first feature is related to the existence of dipole moments associated with optical vibrational modes. The second one concerns with the difference in long-range fields given by longitudinal and transverse optical modes at the zone center [1]. In general, the long-wavelength optical vibrations in polar crystals are responsible for the presence of an electric field [1]. As it is well-known, the generation of this field results from the displacement of the ions and is modified by electronic polarizabilities. This modifies the forces and affects the optical phonon frequencies. On the other hand, the anomalously large Born effective charges, which give giant LO-TO splittings in ferroelectric compounds [2], are associated with the existence of an anomalously large dipole-dipole interaction [3]. The long-wavelength optical phonons, therefore, appear to be a key factor for relating electronic and lattice (structural) properties.

It is important to emphasize that electron-phonon coupling has the fundamental significance in the understanding of various physical properties of polar compounds (e.g., [4, 5]). However, to the best of our knowledge, most comprehensive information regarding the interactions between electrons and optical phonons is primarily concerned with the theoretical and experimental studies related to longitudinal optical (LO) phonons (e.g., [4–9] and references therein). As regards transverse optical (TO) vibrations, with only a few exceptions [10, 11], no attempts have been made to consider consistently the problem of determining the electron-TO-phonon (el-TO-ph) interactions in polar crystals with due account for their particular polar properties. This question is of considerable practical importance for the vibronic theory (e.g., [12–15] and references therein) in which the coupling between electrons and the zone-center TO vibrations is the driving force of a ferroelectric instability, and where the strength of this coupling should be especially strong [16]. Moreover, the new developments of the vibronic theory concerning different properties of oxide ferroelectrics and multiferroics [13, 15, 17, 19] increased the interest in the understanding of the nature of the el-TO-ph interactions. Thus, this raises the issue of very little theoretical knowledge about the el-TO-ph interaction constants in polar compounds, and the present paper is aimed at filling this gap.

In this paper, using characteristic parameters of a polar crystal in an explicit way, we study the main features of the el-TO-ph interaction. The novel aspects of our work are based on a first-principles treatment of the role of the el-TO-ph interaction. In particular, we demonstrate that, in polar materials, the el-TO-ph coupling is essentially influenced by the features of the Coulomb interaction between electrons and the lattice ions. We also give a microscopic justification of a significant enhancement of the el-TO-ph interaction strength in ferroelectrics compounds. Within a first-principles methodology, we show how to link the interaction of electrons with the polar long-wavelength TO phonons to the long-range dipole-dipole interaction. This, in turn, provides a nontrivial relationship between the el-TO-ph interaction constants and the macroscopic material parameters, such as dipole oscillator strengths and the forbidden gap. The relationship gives us a practical framework for estimations of the values of the el-TO-ph interaction constants in a polar material for which no data have been available so far.
In the more general context of understanding displacive structural instabilities our results can be used to probe deeper into the nature of the ferroelectric phase transition, and, in particular, to discover what factors related to material properties may be responsible for the strength of the el-TO-ph interaction in polar insulators.

II. THEORETICAL MODELING

A. Basic set-up of physical model and the main features

As our focus is the el-TO-ph interaction, we shall be interested in finding the change in the electronic charge density induced by a polar TO vibration of a long wavelength. In order to consider the problem at the atomic level, we represent a polar crystal by a model based on classical potentials and contributions of the electronic polarization effects through the relative displacements of the electronic shells \[10\] (see also \[20, 21\]). Within the standard procedure of the dipole approximation (expanding to first order in the ionic and electronic displacements, entering into the \(q\)-representation, and going to the normal coordinates \(u_{qj}\)), the perturbation of the host crystal due to interactions with the polar lattice TO vibrations (\(q_j\)) is given by:

\[
\delta U_{ext}^r = N^{-1/2} \sum_{q,j} V_{qj}(r) u_{qj} \tag{1}
\]

where \(V_{qj}(r) = v P(q_j) \cdot F_q(r)\),

\[
F_q(r) = -ie \sum_{G \neq 0} \frac{G}{|q + G|^2} e^{i(q + G) \cdot r}, \tag{2}
\]

\(P(q_j)\) is an amplitude of the dipole polarization (dipole moment per unit volume) associated with the polar TO mode \[1\]. \(G\) denotes the reciprocal lattice vector, \(v\) is the volume of the unit cell, and \(N\) is their number. The derivation of Eq. (1) accounts also for the fact that in the long-wavelength limit one can take the corresponding Fourier transformation of the Coulomb potential to be independent of ion’s position in the unit cell. The accuracy of this approximation was investigated previously in \[10, 11\].

Equation (1) is exactly the one that we shall use to study the interaction of electrons with the polar TO lattice vibrations in the long-wavelength limit. Before presenting the results themselves, let us emphasize the most important key points which characterize the model as a consistent, systematic and workable framework.

The first is that Eq. (1) accounts for the changes in ion properties that are caused by changes in its environment, and, hence, in accordance with \[21\] includes not only pairwise electron-ion interactions but also many-body effects. This follows from the accounting for an electronic contribution \((P^{(e)}(q_j))\) in the dipole polarization: \(P(q_j) = P^{(i)}(q_j) + P^{(e)}(q_j)\). This contribution is connected with the distortion of the electronic charge distribution (e.g., \[22\]). The corresponding ionic contribution \(P^{(i)}(q_j)\) is related with the displacements of the ions participating in the TO vibrations \[1\]: \(P^{(i)}(q_j) = v^{-1} \sum_j (Z_j e / \sqrt{M_j}) w(s, q_j)\) where \(Z_j e\) denotes the effective charge \[23\] of an ion with the mass \(M_j\) placed in the cite \(s\), and \(w(s, q_j)\) is the polarization vector of the normal TO vibration. At \(q = 0\), the both polarization components satisfy the following relations \[1, 10\]:

\[
P^{(i)}(0j) = \frac{3}{\epsilon_{\infty} + 2} P(0j), \quad P^{(e)}(0j) = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} P(0j) \tag{3}
\]

where \(\epsilon_{\infty}\) is the electronic (static-high-frequency) dielectric permittivity.

Attention should next be directed to the long-wavelength nature of the quantity \(F_q(r)\) standing in Eq. (1). On the one hand, in a polar crystal it defines the electric field at a point \(r\) inside the bulk as a part of the internal field associated with the TO phonon displacement \[10\] (we recall that the microscopic electric field excited in the crystal has components \(q + G\) for all reciprocal-lattice vectors). On the other hand, at \(q = 0\), \(F_q(r)|_{q=0} = F_0(r)\) can be represented as (\(l\) denotes lattice vectors):

\[
F_0(r) = -\nabla \left( \sum_l \frac{e}{|r - l|} \right) = -\nabla \phi_e(r). \tag{4}
\]

It is seen from Eq. (4) that, in accordance with \[24, 25\], the quantity \(F_0\) is a field generated by the Coulomb electrostatic potential \(\phi_e(r)\) which is connected (at given boundary conditions) through the Poisson equation with a
charge distribution $\delta_{\rho_e}(r) = e \sum \delta(r - l)$. This result, in turn, suggests a macroscopic characterization for the quantity $V_{qj}(\mathbf{r})$ given in Eq. (1) as follows: it comes in the form of an electrostatic contribution which interrelates the dipole polarization associated with the polar long-wavelength TO mode and the electric field caused by the reaction of the electron subsystem to the relevant “external” perturbation. In this connection, we also note that both the resulting shift of the electron density and the effect of the dipole polarization appear to be clear signatures of the strength of the el-TO-ph interaction.

The third important point is that interaction in the form (1) may be responsible for the softening of the lattice subsystem. Clearly, this is the case of the vibronic theory [12 - 14]. Following closely Ref. [20], we observe that local change in the electron density distribution will generate an imbalance with respect to the corresponding density of the positive background. As a result, there will be a restoring force that will tend to compensate this density imbalance. As it argued in [20], such asymmetry effect will initiate distortions of the ions and the redistribution of charge, eventually leading to a decrease in the total energy, and to a match between the symmetry of the ionic arrangement and that of the electron density distribution.

### B. Model for electron-TO phonon interaction

The starting point is a generic model of an insulator consisting of the occupied valence and empty conduction bands separated by a forbidden gap. Keeping in mind correctness in the description of an insulating state, we assume that the wave functions ($\psi_{\sigma k}$) and energies ($E_{\sigma}(k)$) are the set of one-particle Bloch eigenfunctions and eigenvalues corresponding to the band structure, which are determined within the framework of DFT-LDA methods with the correct accounting for the quasiparticle effects by means of many-body perturbation theory [27].

Equation (1), providing a basis for studying the el-TO-ph interaction, corresponds in the second-quantization formalism to the Hamiltonian

$$H_{el-ph} = N^{-1/2} \sum_{\sigma,\sigma',j} \sum_{k,q} g_{\sigma\sigma'}(k,q) a_{\sigma k}^{+} a_{\sigma' k+q} a_{qj}$$

which characterizes the dynamic mixing of an electron state |$\sigma k>$ with another state |$\sigma'(k - q)>$ caused by the TO phonon. Here $a^{+}$ ($a$) are the creation (annihilation) operators for electronic states in the valence and conduction bands ($\sigma, \sigma'$), $g_{\sigma\sigma'}(k,q)$ denotes the matrix elements of the el-TO-ph interaction defined at the equilibrium high-symmetry configuration of the lattice by

$$g_{\sigma\sigma'}(k,q) = <\sigma k| V_{qj}(\mathbf{r}) |\sigma'(k - q)> .$$

Expression (6) involves both interband ($\sigma \neq \sigma'$) and intraband ($\sigma = \sigma'$) matrix elements. In the long-wavelength limit, the intraband matrix elements vanish due to inversion symmetry and, correspondingly, the coupling of electrons and TO lattice vibrations is completely characterized by the interband matrix elements.

In the context of first-principles features/attributes belonging to the model, it is worth to emphasize the following aspects: (i) The electronic states are periodic in space and delocalized over the entire unit cell; in systems with a gap infinitesimal displacements affect all the states uniformly [28], (ii) the valence and conduction (excited) states can mix under these displacements [14], (iii) the energetics of the interaction of electrons with the long-wavelength polar TO lattice vibrations is strongly affected by energetics of the lattice electronic distribution, (iv) the effect of the dipole polarization is to change the center of force between a ”shell” of an ion’s electrons and the other force centers in the crystal [29], (v) like the electron-gas model of Gordon and Kim [30], the corresponding interaction energy is a function of changes in the electron charge densities, and (vi) as seen from Eq. (1), these changes are represented by distortions of charge density owing to electric field gradients at certain lattice sites of a polar crystal.

Our intermediate goal here has been to offer a detailed, microscopically realistic framework that could be used for quantitative investigations of the el-ph interaction in a polar crystal. In order to achieve the objectives of the present work further study in this direction is divided into two main steps: The first is a comparative first-principles analysis of the contribution of Eq. (5) into the lattice dynamics of TO lattice vibrations; the second handles the interband matrix elements, and develops formulas allowing us to estimate el-TO-ph interaction strengths in terms of macroscopic material parameters for a wide range of polar dielectrics.
III. ELECTRON-PHONON INTERACTION AND TO LATTICE VIBRATIONS

A. On the dynamics of TO lattice vibrations

We begin the present section by reviewing the main properties of the electronic contribution into the dynamics of lattice vibrations. Then we calculate the relevant electronic contribution given by Eq. (5). Our task is to compare this contribution with the corresponding results of microscopic lattice dynamics \[31, 33\] with regard to the long-wavelength polar TO phonons. For this purpose, within the adiabatic approximation, we consider the dynamics of the TO vibrations in terms of the matrix elements of the el-TO-ph interaction determined by Eq. (6).

A key feature of the electron subsystem is that it provides a link between an electronic energy and an equilibrium charge density due to the presence of the electron-ion potential in a system (e.g., \[12, 14, 31, 34, 35\]). This implies that, by studying the lattice dynamics, one can acquire fundamental information on the role of the electron-phonon interactions in a given material.

We expect the “normal” part \(\tilde{\omega}^2_{qj}\), which may be regarded as the bare TO phonon frequency with respect to the el-TO-ph coupling, to be free of softening anomalies. As usual (e.g., \[12, 36\]), it is assumed that \(\tilde{\omega}^2_{qj}\) also involves contributions from the phonon-phonon interactions, which are needed to describe the dependence of the TO phonon frequency on temperature.

We can obtain the corresponding electronic contribution \(\Delta \omega^2_{qj}\) in the following way. The first step is to employ the linear density response function matrix (the dielectric susceptibility) \(\chi\) that relates a variation of the electronic density (the charge response) \(\delta \rho\) to the perturbation potential \(\delta v_{ext}\) as follows \[37, 38\]:

\[
\delta \rho = \tilde{\chi} \delta v_{ext}, \quad \tilde{\chi}^{-1} \equiv \tilde{I} + \tilde{v}_c \tilde{\chi}
\]

(7)

where \(\tilde{\chi}^{-1}\) denotes the inverse dielectric matrix, \(\tilde{I}\) is the identity matrix, and \(\tilde{v}_c\) is the bare Coulomb interaction. Note that perturbation \(\tilde{\chi}\) modifies the ground-state values and therefore induces \(\delta \tilde{\rho}\). As stated by the DFT formalism, both \(\tilde{\chi}\) and the potential \(\delta v_{ext}\) itself are unique functionals of the electronic density.

Since the Coulomb and electron-phonon interactions cause the phonon propagator to be fully renormalized (e.g., \[39\]), the second step is to represent the real part of the TO phonon self-energy to the lowest-order in \(g^2\) as the corresponding harmonic term, and to account for the contributions of the Coulomb interaction among electrons. Using microscopic expressions for matrix elements \(g_{\sigma \sigma'}(k, q)\) given by Eq. (3), by the last step, we write the equation for \(\Delta \omega^2_{qj}\) in the following form:

\[
\Delta \omega^2_{qj} = 4\pi v \sum_{\alpha, \beta} B_{\alpha \beta}(q) P_{\alpha}(qj) P_{\beta}(qj)
\]

(8)

where

\[
B_{\alpha \beta}(q) = \frac{v}{4\pi e^2} \sum_{G, G' \neq 0} G_{\alpha} v_c(q + G) \chi_{el}(q + G, q + G') v_c(q + G') G'_{\beta},
\]

(9)

\[
\chi_{el} = \frac{\Pi_0}{\tilde{I} - \tilde{v}_c \Pi_0}, \quad v_c(q + G) = \frac{4\pi e^2}{v |q + G|^2},
\]

(10)

\[
\Pi_0(q + G, q + G') = -\frac{1}{N} \sum_{\sigma, \sigma'} \sum_k \frac{f_{\sigma}(k) - f_{\sigma'}(k + q)}{E_{\sigma'}(k + q) - E_{\sigma}(k)} \times \int \tilde{\psi}_{\sigma}^* e^{i(q + G) r} \tilde{\psi}_{\sigma'}^* e^{-i(q + G') r'} \tilde{\psi}_{\sigma} e^{i(k + q) r} \tilde{\psi}_{\sigma'} e^{-i(k + q) r'} .
\]

(11)

Here the matrix elements of the microscopical dielectric susceptibility of the electron subsystem \(\chi_{el}(q + G, q + G')\) are expressed in the random phase approximation in terms of polarization operator \(\Pi_0 \[37, 40, 42\], and \(f\) are the occupation numbers.
B. Consistency with first-principles considerations

In this and next section, we shall show that our results given by Eqs. (8)-(11) are consistent with first-principles considerations. This will allow us to establish a bridge that relates the interaction of electrons with the polar long-wavelength TO modes of the lattice vibrations to the long-range dipole-dipole interaction.

Within the framework of our comparative analysis, it seems to be useful to take into account three important points:
(i) We deal with the long-wavelength TO phonons, i.e., in fact, with the analytical part of the harmonic force constants. The remaining non-analytic part only affects the LO phonon frequencies, and therefore determines the LO-TO splitting at the Γ point.
(ii) The unique feature of the force constants is that they can be decomposed into a sum of two independent terms [31, 34, 35]: the direct ionic and electronic contributions. The electronic contribution, which represents indirect interactions via the electron subsystem, is the focus of our discussion because involves the detailed information on the el-TO-ph interaction.
(iii) The long-wavelength behavior of the force constants can also be represented in terms of the balance between the short-range repulsive and long-range Coulomb forces associated with the short-range and long-range dipole-dipole interactions, respectively [3, 32, 33, 43]. The long-range contribution is represented by the interplay of the Born transverse effective charge tensors. It is a key quantity in polar compounds because favors the ferroelectric distortion, while its direct competitor (the short-range contribution) tends to suppress the ionic displacements and to provide the stability of the high-symmetry configuration.

Note that, in the context of the present work, the above pair-wise separabilities of the force constants will be particularly instructive for comparison purposes. For instance, by matching different pieces of information contained in the dynamical matrix, we could recognize relevant aspects of the el-TO-ph interaction.

We start our comparison procedure by noting that within the microscopic theory of lattice vibrations the Fourier transforms of the harmonic force constants are expressed through the matrix elements of the susceptibility function χ_{cl}(q + G, q + G') (e.g., [31, 44, 45]). By performing a comparison of Eqs. (8) and (9) with those from [31], we can ensure that the expression for B_{αβ}(q), which is written in terms of the microscopic electronic dielectric susceptibilities and the Coulomb potentials, describes the corresponding electronic contribution to the square of the TO phonon frequency Ω_{0j}^2 (i.e., the contribution which uniquely involves the χ_{cl}(q + G, q + G') matrix elements with both G and G' different from zero). Due to the microscopic formulation of the el-TO-ph interaction given by [35], this result is general and independent on the particular details of the interaction of electrons with the polar long-wavelength TO vibrations. This implies that fundamental property of B_{αβ}(q) is that it represents, in accordance with [31, 32, 45], the electron mediated part of the long-range Coulomb interaction.

C. Relevance to the long-range dipole-dipole interaction

As the second step of the comparison procedure, it is appropriate to compare equations (8) and (9) with the corresponding results of lattice dynamics theories [1, 22, 31, 33] related to polar insulators. For this purpose let us inspect the long-wavelength limit of Eqs. (8) and (9) in more detail.

Observe that one of the characteristic features of Eq. (8) represents the interplay of the polarization amplitudes P_{α}(0j) and P_{β}(0j) which, as in [33], can be characterized by the second rank tensor S_{αβ}(j) = 4πv P_{α}(0j)P_{β}(0j). The quantities S_{αβ}(j) are defined as dipole oscillator strengths for the given zone-center TO vibration and correspond to the contributions of the TO vibrational modes in the infrared (IR) part of the Lorentz model of the dielectric matrix ϵ_{αβ} (e.g., [10, 31, 46]):

\[ (ε_ω)_{αβ} = (ε_∞)_{αβ} + \sum_j \frac{S_{αβ}(j)}{Ω_{0j}^2 - ω^2}. \]  

(12)

It is easy to show, using the definition of P_{α}^{(0)}(0j) together with (3), that the dipole oscillator strengths S_{αβ}(j) can be represented in terms of the TO mode effective charge:

\[ S_{αβ}(j) = \frac{4πe^2}{v} \left( \sum_s Z_s^* w_{α}(s,0j) \right) \left( \sum_t Z_t w_{β}(t,0j) \right). \]  

(13)

Here the result of each such summation in the round brackets is called the TO mode effective charge [2] (which corresponds to the dipolar activity of the zone-center TO phonons and is a measure of the intensities of IR-active modes), Z_s^* are the Born transverse dynamical effective charges defined as [1, 32, 33, 48] Z_s^* = (ε_∞ + 2)/3 Z_s.
After substituting for the product $P_a(0j)P_b(0j)$, Eq. (8) becomes

$$\Delta \omega_{0j}^2 = \sum_{\alpha,\beta} B_{\alpha\beta}(0) S_{\alpha\beta}(j)$$

(14)

where the tensor $B_{\alpha\beta}(0)$ is defined from Eq. (9) at $q = 0$ by

$$B_{\alpha\beta}(0) = -\frac{\nu}{4\pi\epsilon^2} \sum_{G,G' \neq 0} G_\alpha v_c(G) \chi_{el}(G,G') v_c(G') G_\beta$$

(15)

and $\chi_{el}(G,G') = \lim_{q \rightarrow 0} \chi_{el}(q + G, q + G')$. By using the representation of the susceptibility function $\chi_{el}(G,G')$ in terms of matrix elements of the microscopic polarizability tensor $a_{\gamma\eta}(G,G')$ [49],

$$\chi_{el}(G,G') = -\sum_{\gamma\eta} G_\gamma a_{\gamma\eta}(G,G') G_\eta'$$

Eq. (15) becomes

$$B_{\alpha\beta}(0) = -\frac{4\pi\epsilon^2}{\nu} \sum_{G,G' \neq 0} G_\alpha G_\gamma \frac{a_{\gamma\eta}(G,G') G_\eta' G_{\beta}}{|G|^2}.$$  

(16)

The set of equations (14)-(16), which we have rigorously derived, allows us to analyse the relevance of our model to long-range dipole forces. We shall now prove this relevance by comparing with the results of the previous theoretical studies of lattice dynamical models (e.g., [1, 23, 33]).

Note first that, in polar insulators, in the limit of zero wave-vector the displacement of charges from their equilibrium positions creates dipoles, which interact with long-range forces [1]. The associated long-range dipole-dipole interaction can be characterized by the coupling of the Born transverse dynamical effective charges $Z_\alpha^* Z_\beta^*$, i.e., by the product $P_a(0j)P_b(0j)$. Secondly, this interaction can be characterized by assigning the dipole polarization an external moment [50]. With the use of results of [1, 10], for the case of the cubic (or tetrahedral) lattice symmetry, $S_{\alpha\beta}(j)$ represents the long-range dipole-dipole interaction [51].

As a comparison parameter, it is reasonable to choose the product $P_a(0j)P_b(0j)$ that measures the long-range dipole-dipole interaction [51]. With the use of results of [1, 10], for the case of the cubic (or tetrahedral) lattice symmetry, in dipole approximations, the counterpart of Eq. (14) can be represented in terms of the product $P_a(0j)P_b(0j)$ (or $S_{\alpha\beta}(j)$) as follows:

$$\Delta \omega_{0j}^2 = -4\pi\nu \sum_{\alpha,\beta} \frac{\delta_{\alpha\beta}}{\epsilon_{\infty} + 2} P_a(0j) P_b(0j) = -\sum_{\alpha,\beta} \frac{\delta_{\alpha\beta}}{\epsilon_{\infty} + 2} S_{\alpha\beta}(j).$$

(18)

Eq. (17) is obtained by a direct comparison of Eqs. (14) and (18).

In the last step of our comparison analysis, we find that equations (14) and (17) are identical to the results derived within the exact accounting of the dipole-dipole interaction in lattice dynamics [33]. This identity directly implies that the product $B_{\alpha\beta}(0)P_a(0j)P_b(0j)$ represents the regular at the $q = 0$ contribution of the long-range dipole forces. This allows us to conclude that, within the framework of TO vibration mode dynamics, the model originally specified by Eqs. (1), (2), (5) and (6) matches the microscopic approach proposed and developed for polar crystals in [32, 33]. This is a novel result of principal importance: we showed and confirmed the correspondence between two descriptions of dynamics of the zone-centre TO vibrational mode - one in terms of the el-TO-ph interaction and the other in terms of the long-range regular at the $q = 0$ part of the dipole-dipole interaction [32, 33]. Moreover, Eq. (14) clearly demonstrates the equivalence of the interpreting power of both descriptions, and therefore can serve as a link between the two approaches.
Thus, we have shown above that microscopic formulation of the el-TO-ph interaction given by (6) provides results consistent with first-principles considerations. We finish this section with a few important remarks. Firstly, it should be noted that, as follows from the foregoing analysis, the interaction of electrons with the polar zone-centre TO phonons is directly associated with the long-range Coulomb interaction. Secondly, the magnitude of the destabilizing contribution \((B_{\alpha\beta}(0) < 0)\) determined by Eq. (14) will rise steeply in polar materials. This will lead to significant softening of the zone-centre TO vibrational mode frequency \(\Omega_0\). The third remark is concerned with strong sensitivity of calculated (at \(q = 0\)) frequencies \([14]\) to the dipole oscillator strengths: this is the manifestation of the fact that the zone-centre TO vibrational modes exceptionally strongly can be coupled to valence band electrons.

Our findings give a clear understanding of the role of the el-TO-ph interaction in the conversion of \(\Omega_0\) to the ferroelectric soft-mode. Eq. (14) shows how changes in the electron density (or the changes in the electronic states) induced by the local displacements are sufficient to yield a considerable softening of the TO phonons around the \(\Gamma\) point. In the context of structural dynamical instability the dipole oscillator strengths \(S_{\alpha\beta}(j)\) as enhancement factors in Eq. (14) can serve as an important macroscopic measure for probing how close the system may be to the ferroelectric instability.

In the next section, we specify our treatment of the el-TO-ph interaction to the case of ferroelectric crystals, and derive the corresponding effective Hamiltonian, which would characterize the interband scatterings of the bond electrons due to the zone-center TO phonons.

IV. ON ELECTRON-TO-PHONON COUPLING IN FERROELECTRICS

A. Parametrization of electron-TO phonon coupling at \(q = 0\)

The microscopic approach considered above is quite general; in the present section, we show how simplifications allow us to deduce a reduced model of el-TO-ph interaction.

The starting point is Eqs. (8)-(11) in which we set \(q = 0\). The main complication in executing the limit \(q \to 0\) in the matrix elements of \(\hat{\chi}_{el}\) is that one needs to exclude the relevant contributions associated with the electronic displacements (these contributions are included in the definition of \(g^2_{\sigma'\sigma}\)). This problem is solved in two steps: (i) by finding a change of the electronic charge density associated with interaction (11) and (ii) by applying Eqs. (7) in a similar way as was described in [32] regarding the analysis on the internal electric field effects. Acting in this manner, and taking into account Eqs. (3), we obtain that in the long-wavelength limit, the reduced susceptibility \(\hat{\chi}_{el}^0\) turns out to be related to \(\hat{\chi}_{el}\) by the following equation:

\[
q \to 0 : \quad \hat{\chi}_{el} = \frac{3}{\epsilon_\infty + 2} \hat{\chi}_{el}^0. \tag{19}
\]

With all of these considerations and assuming that in insulators \((f_\sigma(k) - f_\sigma'(k)) = 1\), we can write the long-wavelength limit of Eqs. (8) in terms of the el-TO-ph interaction \(g_{\sigma\sigma'}(k,0j) \equiv g^0_{\sigma\sigma'}(k)\) as follows:

\[
\Delta \omega_{0j}^2 = -\frac{3}{\epsilon_\infty + 2} \sum_{\sigma \neq \sigma'} \sum_k \frac{|g^0_{\sigma\sigma'}(k)|^2}{|E_{\sigma'}(k) - E_\sigma(k)|^2}, \tag{20}
\]

\[
|g^0_{\sigma\sigma'}(k)|^2 = \frac{e^2}{2} \sum_{\sigma,\sigma'} P_{\sigma}(0j) P_{\sigma'}(0j) \sum_{G,G' \neq 0} G_{\alpha}(G) v_\sigma(G) G_{\beta}^* v_{\sigma'}(G') \times \int \psi^*_{\sigma k} e^{ig_{Gr}} \psi_{\sigma' k} d\tau \int \psi^*_{\sigma' k} e^{-ig_{Gr}'} \psi_{\sigma k} d\tau'. \tag{21}
\]

The remarkable property of Eq. (20) is that it can be represented as a product of two independent factors, \((\lambda')^2 \times \Pi_0(0)\), one of which, \((\lambda')^2 = |g^0|^2 [(\epsilon_\infty + 2)/3]^{-1}\), characterizes an effective interaction of electrons with polar zone-centre TO vibrations. The other, \(\Pi_0(0)\), is the so-called non-interacting susceptibility. Following the vibronic theory prescription (e.g., [12]), this allows us to constitute a reduced one-parameter version of the el-TO-ph Hamiltonian \([5]\) in the following model form:

\[
H_{el-ph}^{(red)} = N^{-1/2} \sum_{\sigma \neq \sigma'} \sum_k \lambda_{\sigma\sigma'}(k) a^\dagger_{\sigma k} g_{\sigma' k} u_{0j}. \tag{22}
\]
First-principles justification of Eq. (22) is an important result of the present work. We refer to this equation as a vibronic-type model since it involves the interband coupling between electrons and the zone-centre TO phonons. According to [12, 13], such coupling forms the basis of the vibronic theory. Due to the successful mapping of the original microscopic model [15] onto the effective model given by (22), it became clear why, by introducing the constants $\lambda'$ as model parameters, it is, in principle, possible within the framework of the vibronic theory to study the lattice and electronic properties of polar materials. Besides, Eq. (20) shows the new meaning of the el-TO-ph coupling constant, the square of which is inversely related to the local field factor ($\epsilon_\infty + 2)/3$. Since local fields and their effects become more prominent in compounds with a mixed ionic-covalent character of chemical bonds (e.g., [37, 52, 53]), this would certainly imply the important improvement in the applicability of the standard vibronic Hamiltonian. Note that a similar renormalization occurs in the theory of surface polarization modes [3].

From a physical point of view, Eq. (22) represents the Fröhlich-type long-range electron-lattice dynamic hybridization of the electronic bands of opposite parities, which takes into account the relevant $s$, $p$, and $d$-channels (e.g., [12–15] and references therein). For instance, as applied to a family of high polar crystals such as the ferroelectric ABO$_3$ perovskite oxides, hybridization (22) involves significant mixing between the filled O 2p and the empty d$^0$ (Ti$^{4+}$, Nb$^{5+}$, Zr$^{4+}$, Ta$^{5+}$, Mo$^{6+}$, W$^{6+}$, etc.) electronic states caused by the IR-active TO F$_{1u}$ soft vibrations [13, 18, 54].

For the last several decades, the model of type (22) was a useful prototype for intensive studies of various properties of both typical insulating perovskites [13, 17, 54, 57] and the A$^{IV}$B$^{VI}$ narrow-gap semiconductors and their alloys [58–62]. It was recently demonstrated to be applicable to give a theoretical description of the ferroelectricity found in BiFeO$_3$-type multiferroics [18, 19].

B. Evaluation of electron-TO-phonon coupling at $q = 0$

In order to evaluate the el-TO-ph coupling in the long wavelength limit, we first examine the Fröhlich-type expression for the amplitude of the interband el-TO-ph interaction $g_{\sigma\sigma'}(k, q)$. This can be accomplished in a similar way as in the case of the scattering of an electron due to LO phonons [10]. Let us fix $j$. Denoting the amplitude by $|g_{\sigma\sigma'}(k)| = \lim_{q \to 0} \left| g_{\sigma\sigma'}(k, q) \right|^2$ and using the evaluation of the dipole oscillator strengths of the TO modes $S_{\sigma\beta}(j)$, we can obtain:

$$|g_{\sigma\sigma'}(k)| \approx \Delta\Omega_{LT} \sqrt{\frac{\mu \epsilon_\infty}{4\pi}} \left| \sigma \epsilon_0 F_{0}(r) \sigma' \right|,$$

where, according to [63], we introduced for the given polarization a difference between the longitudinal ($\Omega_{LO}$) and the transverse ($\Omega_{TO}$) frequencies (the LO-TO splitting) provided in terms of $\Delta\Omega_{LT} = (\Omega_{LO}^2 - \Omega_{TO}^2)^{1/2}$ (i.e., the difference in long-range fields given by longitudinal and transverse modes as $q \to 0$).

From Eq. (23), one can draw the following important inferences: First of all, note that dynamic hybridization described by (22) leads to an asymmetric charge distribution, which corresponds to the internal electric field $F_0(r)$. This field, in turn, provides, due to Eq. (4), the long-range character of the el-TO-ph coupling at the $\Gamma$ point. Secondly, the magnitude of the splitting $\Delta\Omega_{LT}$ serves as an enhancement factor of the matrix elements of $F_0(r)$. Therefore, in the long-wavelength limit, the el-TO-ph interaction in polar crystals is distinguished from that of most other dielectrics by the following features: (i) it is long-range, (ii) it is controlled by the internal electric field and (iii) it is essentially sensitive to values of the LO-TO difference (i.e., the polar strength of long-wavelength optical vibrational modes). Eq. (23) can serve as an indicative of the strength of the el-TO-ph coupling in polar materials. In particular, large values of $|g_{\sigma\sigma'}(k)|$ occur when $\Delta\Omega_{LT}$ is large: for example, the experimental difference between the corresponding LO and TO modes in the ferroelectric BaTiO$_3$ is about 530 cm$^{-1}$ [64] to be compared with the values of 100, 69, and 48 cm$^{-1}$ obtained for the differences in the compounds NaCl, KCl, and RbCl, respectively [65].

In a polar lattice, the LO-TO splitting depends generally on Born’s transverse dynamical effective charge $Z^*$ of the lattice ions and the screening of the Coulomb interaction, which depends on the electronic dielectric permittivity $\epsilon_\infty$ [2]: $\Delta\Omega_{LT} \propto |Z^*|^2/\epsilon_\infty$. Thus, one can conclude that the presence of anomalously large Born’s effective charges is the key signature that the interband el-TO-ph coupling is essentially strong in a ferroelectric material. This result corresponds to the main assumption of the vibronic theory [12, 15] regarding the existence of sufficiently strong interband el-TO-ph coupling in displacive ferroelectrics. The strength of the interband el-TO-ph interaction can therefore serve as a direct indicator of the extent to which a crystal lattice is close to a possible ferroelectric instability. Further details concerned with the quantitative characteristics of the electron-TO-phonon coupling are given in our separate paper [10].
C. Electron-TO-phonon coupling via macroscopic parameters

As shown in the present work, one can associate the interaction between electrons and the polar long-wavelength TO phonons with the long-range dipole-dipole interaction. This link, which was not anticipated by previous theoretical considerations, helps us to express the strength of the el-TO-ph interaction via macroscopic parameters of a polar crystal.

Let us introduce the bare constant $g_{0j}$ which represents the effective $k$-independent interband el-TO-ph interaction defined by a proper average of the squared el-TO-ph matrix elements over the given electronic states:

$$
 g_{0j}^2 = \sum_{\sigma'>\sigma} \frac{1}{2N} \sum_k |g_{\sigma'\sigma}(k)|^2 \frac{E_g}{|E_{\sigma'}(k) - E_{\sigma}(k)|} 
$$

where $E_g$ is a bond-gap energy. Accounting for local-fields effects-induced partial screening of the bare el-TO-ph interaction is described by the renormalization:

$$
 g_{0j}^2 \rightarrow \bar{g}_j^2 = 3g_{0j}^2/(\epsilon_\infty + 2).
$$

As follows from Eqs. (14) and (17), the contribution of the linear el-TO-ph interaction to the square of the zone-centre TO vibrational mode frequency $\Omega_{0j}^2$ can be represented as the product of two macroscopic quantities: the quantity $B_{\alpha\beta}(0)$ which accounts for the corresponding electronic contribution, and the dipole oscillator strengths $S_{\alpha\beta}(j)$ associated with the given TO vibration. The bare constant of the el-TO-ph interaction $g_{0j}$ can thus be determined from matching Eq. (20) and Eq. (14) together. As a result, we obtain the following relationship ($S(j) = \sum_{\alpha} S_{\alpha\alpha}(j)$):

$$
 g_{0j}^2 = \frac{1}{12} E_g M_j S(j).
$$

Eq. (26) is an important result of the present work. It relates, for each zone-center TO vibration of the branch $j$ and of the reduced mass $M_j$, the bare constant of the el-TO-ph coupling at the $\Gamma$ point, $g_{0j}$, with the macroscopic material constants, the values of which can be obtained from experiment. Employing the relevant information from the IR spectra concerning the IR-active optical phonons and the dielectric function behavior in the far-IR spectral range, and using Eqs. (26) and (25) in combination with the experimental data for $\epsilon_\infty$ and $E_g$, we can directly evaluate the el-TO-ph coupling constants for polar materials of interest.

A more detailed demonstration of the practical usefulness of Eq. (26) together with numerical results for a wide number of selected polar insulators and semiconductors, can be found in our separate publication [16]. In particular, calculations of the interband el-TO-ph interaction constants and the further comparative analysis showed that the large interband el-TO-ph interaction is a special microscopic feature of the ferroelectric materials. In contrast, in non-ferroelectrics, as it was demonstrated, the strength of the el-TO-ph interaction is not necessarily high enough due to their lower polar nature.

V. CONCLUSIONS

In this paper, focusing mostly on the fundamental contribution of electron subsystem to the dynamics of polar long-wavelength TO vibrations and using a first-principles methodology, we provided a systematic description of the el-TO-ph interaction in a polar insulator. The study is based on the model of a polar crystal with classical potentials, which takes into account the electronic polarizability effects. By analyzing the electronic contribution to the TO vibrational mode in terms of the el-TO-ph coupling, we established a bridge which allowed us a) to link the model under consideration to the microscopic lattice dynamics and b) in the long wavelength limit, to relate the interaction of electrons with polar TO vibrations to the long-range dipole-dipole interaction. Our results highlight the importance of the el-TO-ph interaction for the genesis of the long-wavelength TO vibrations in ferroelectrics, thereby giving fundamental support at the microscopic level for the applicability of the vibronic theory. Within a first-principles methodology, we found and explained the significant increase of the constants of the el-TO-ph coupling in ferroelectric materials, showed how the el-TO-ph interaction constants might be dependent on macroscopic material parameters, and obtained analytical equations allowing us to estimate el-TO-ph interaction strengths in a wide range of polar dielectrics. In particular, it was proved that the zone-center TO vibrational mode effective charge $Z^*$ can be considered to be the key macroscopic parameter of the el-TO-ph coupling strength. In materials where the el-TO-ph coupling is operative, it can be verified by spectroscopy measurements of the IR-active TO mode.
Acknowledgements

The author would like to thank N. Kristoffel for helpful discussions, A. Sherman for attention to this work. The work was supported by the Estonian Science Foundation grants No. 6918 and No. 7296.

[1] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Oxford Univ. Press, Oxford, 1954.
[2] W. Zhong, R. D. King-Smith, D. Vanderbilt, Phys. Rev. Lett. 72 (1994) 3618.
[3] Ph. Ghosez, J. P. Michenaud, X. Gonze, Phys. Rev. B58 (1998) 6224.
[4] J. L. M. van Mechelen, D. van der Marel, C. Grimaldi, A. B. Kuzmenko, N. P. Armitage, N. Reyren, H. Hagemann, I. I. Mazin, Phys. Rev. Lett. 100 (2008) 226403.
[5] J. T. Devreese, S. N. Klimin, J. L. M. van Mechelen, D. van der Marel, Phys. Rev. B81 (2010) 125119.
[6] W.A. Harrison, Electronic Structure and Properties of Solids. The Physics of Chemical Bond, W.H. Freeman and Company, San Francisco, 1980.
[7] P. Y. Yu, M. Cardona, Fundamentals of Semiconductors, Physics and Materials Properties, Springer-Verlag, Berlin, 2005.
[8] A. S. Alexandrov, in: A. S. Alexandrov (Ed.), Polarons in Advanced Materials, Springer Series in Materials Science vol. 103, Canopus and Springer, Bristol, 2007, pp. 257-310.
[9] V. L. Vinetskii, M. A. Itskovskii, L. S. Kukushkin, Fiz. tverd. Tela 13 (1971) 76.
[10] I. I. Mazin, R. E. Cohen, Ferroelectrics 194 (1997) 263.
[49] S. K. Sinha, Phys. Rev. 177 (1969) 1256.
[50] G. D. Mahan, Phys. Rev. 153 (1967) 983.
[51] K. Iishi, Am. Mineral. 63 (1967) 1190.
[52] M. Posternak, R. Resta, A. Baldereschi, Phys. Rev. B 50 (1994) 8911.
[53] K. Tkacz-Śmiech, A. Koleżyński, W. S. Ptak, J. Phys. Chem. Solids 61 (2000) 1847.
[54] P. Konsin, B. Sorkin, Ferroelectrics 257 (2001) 269; Ferroelectrics 270 (2002) 399; Ferroelectrics 283 (2003) 23; Ferroelectrics 320 (2005) 69.
[55] N. Ohnishi, Ferroelectrics 45 (1982) 229.
[56] T. Hidaka, Phys. Rev. B48 (1993) 9313.
[57] A. Bussmann-Holder, Ferroelectrics 206 (1998) 47; Physica C 364-365 (2001) 665.
[58] H. Kawamura, in: W. Zawadski (Ed.), Narrow Gap Semiconductors Physics and Applications, Springer, Berlin/Heidelberg, 1980, pp. 470-494.
[59] K. Murase, Ferroelectrics 35 (1981) 67.
[60] P. Konsin, Fiz. Tverd. Tela 24 (1982) 1321 (Engl. transl.: Sov. Phys. Solid State 24 (1982) 750); Ferroelectrics 45 (1982) 45.
[61] K. Sakai, Phys. Rev. B34 (1986) 8019.
[62] O. B. Maksimenko, A. S. Mishchenko, J. Phys.: Condens. Matter 9 (1997) 5561.
[63] K. W. Lee, W. E. Pickett, Phys. Rev. B 68 (2003) 085308.
[64] S.-Y. Kuo, W.-Y. Liao, W.-F. Hsieh, Phys. Rev. B 64 (2001) 224103.
[65] G. Raunio, S. Rolandson J. Phys. C: Solid State Phys. 3 (1970) 1013; Phys. Rev. B 2 (1970) 2098.