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Notes on Piezoelectricity

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Abstract

These notes provide a pedagogical discussion of the physics of piezoelectricity. The exposition starts with a brief analysis of the classical (continuum) theory of piezoelectric phenomena in solids. The main subject of the notes is, however, a quantum mechanical analysis. We first derive the Fröhlich Hamiltonian as part of the description of the electron-phonon interaction. The results of this analysis are then employed to derive the equations of piezoelectricity. A couple of examples with the zinc blende and and wurtzite structures are presented at the end

I. INTRODUCTION

In these notes we consider the mathematical derivation of the equations that describe piezoelectricity in solids. The exposition starts with a brief overview of the classical (continuum) theory of piezoelectric phenomena in solids. We then proceed to develop a quantum mechanical description based on the Fröhlich Hamiltonian for the electron-phonon interaction. The results of this analysis are then employed to derive the corresponding equations for piezoelectricity. The document concludes with a calculation of the piezoelectric matix elements for the zinc blende and wurtzite structures.

II. CONTINUUM ANALYSIS OF PIEZOELECTRICITY[1]

The piezoelectric effect is the result of the interaction between the mechanical and electrical states in crystalline materials with no inversion symmetry. In particular, in piezoelectric bodies, when a mechanical force is applied a resulting internal charge is generated. Conversely, a mechanical strain is observed when an electric field is applied. The brothers Pierre and Jacques Curie were the first ones to report piezoelectricity.[2] The converse effect was mathematically deduced from thermodynamics by Gabriel Lippmann[3].

As mentioned above, the application of an electric field to a piezoelectric material results in internal strains. The concomitant stresses are proportional to the field itself. Conversely, the electric field that appears when the body is deformed is proportional to the strain. This observed linear relationship can be expressed as a constitutive equation, an example of which is the relationship between an electric field, $\mathbf{E}$, and the induced polarization, $\mathbf{P}$,

$$\mathbf{P} = \chi(\mathbf{E})\mathbf{E}, \tag{1}$$

where χ is the electric susceptibility. This quantity is characteristic of the material and, as indicated in Eq. (1), may be a function of the electric filed. When χ does not depend on $\mathbf{E}$, the relationship is linear. Experiment has shown that piezoelectric materials exhibit a linear constitutive relationship.

To derive the constitutive equations for piezoelectricity we start from linear elasticity theory.[4] Consider a body undergoing deformation and let $\mathbf{r}$ be the position vector (with components x_i, $i = 1, 2, 3$) of an arbitrary point before the deformation occurs; let $\mathbf{r}'$ be the position of the same point after the deformation has occurred. The displacement of this point is then given by the vector $\mathbf{u} = \mathbf{r}' - \mathbf{r}$, with components

$$u_i = x_i' - x_i. \tag{2}$$

Because the deformation is not necessarily uniform, we note that, in general, the displacement vector will be a function of position. When the body is deformed, the distances between pairs of points change. Take two points $\mathbf{r}^{(a)}$ and $\mathbf{r}^{(b)}$ before the deformation, so that $x_i^{(b)} = x_i^{(a)} + dx_i$. The distance between the points is $d\ell = [dx_1^2 + dx_2^2 + dx_3^2]^{1/2}$. After the deformation we have $x_i'^{(b)} = x_i'^{(a)} + dx_i'$, with a corresponding distance $d\ell' = [dx_1'^2 + dx_2'^2 + dx_3'^2]^{1/2}$.

We define the strain tensor, κ_{ij}, by the expression[5]

$$d\ell'^2 = d\ell^2 + 2\sum_{i,j=1}^{3} \kappa_{ij} dx_i dx_j. \tag{3}$$

It is not difficult to show[6] that

$$\kappa_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_{k=1}^{3} \frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}\right). \tag{4}$$

For small deformations, which is the case for most piezoelectric materials, the second order terms can be neglected to yield the strain tensor for linear elasticity,

$$\kappa_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \tag{5}$$

In linear elasticity one can show[7] that the relationship between the strain and stress tensors is given by

$$\sigma_{ij} = \left(\frac{\partial F}{\partial \kappa_{ij}}\right)_T, \tag{6}$$

where σ_{ij} is the stress tensor, F is the free energy per unit volume and the derivative is taken at constant temperature T. In an anisotropic dielectric medium (e.g., a crystal) the free energy is given by[8]

$$F = \tilde{F} + \frac{\mathbf{D}\cdot\mathbf{E}}{4\pi}, \tag{7}$$

where $\tilde{F}$ is the free energy thermodynamic potential for which the independent variable is $\mathbf{E}$ and $\mathbf{D}$ is the electric displacement vector, with components

$$D_i = D_{0i} + \sum_{j=1}^{3} \epsilon_{ij} E_j, \tag{8}$$

where $\mathbf{D}_0$ is a constant vector and ϵ_{ij} is the dielectric tensor. The resulting stress tensor[9] is

$$\sigma_{ij} = \frac{\partial \tilde{F}}{\partial \kappa_{ij}} + \frac{1}{8\pi}\left(E_i D_j + E_j D_i\right). \tag{9}$$

The piezoelectric effect is linear in the field; as a result, we can neglect the quadratic terms in Eq. (9), leading to

$$\sigma_{ij} = \left(\frac{\partial \tilde{F}}{\partial \kappa_{ij}}\right)_{T,\mathbf{E}}. \tag{10}$$

The thermodynamic relation for the differential $d\tilde{F}$ is[10]

$$d\tilde{F} = -SdT + \sum_{i,j=1}^{3} \sigma_{ij} d\kappa_{ij} - \frac{\mathbf{D}\cdot d\mathbf{E}}{4\pi}, \tag{11}$$

where S is the entropy. To calculate the dependence of the strain tensor on the electric field for a piezoelectric material it is more convenient to transform to a thermodynamic potential where the independent variables include the components of the stress tensor instead of those of the strain tensor. To do so we define a new thermodynamic potential:

$$\tilde{\Phi} = \tilde{F} - \sum_{i,j=1}^{3} \kappa_{ij}\sigma_{ij}. \tag{12}$$

The thermodynamic relation for the differential now becomes

$$d\tilde{\Phi} = -SdT - \sum_{i,j=1}^{3} \kappa_{ij} d\sigma_{ij} - \frac{\mathbf{D}\cdot d\mathbf{E}}{4\pi}, \tag{13}$$

We need to emphasize that this expression is only valid for piezoelectric materials.

We are ready now to derive the relationship between the strains and the electric field for piezoelectric crystals. The independent variables of the thermodynamic potential $\tilde{\Phi}$ are the temperature T, the components of the stress tensor, σ_{ij}, and the components of the electric field, E_i. Then, the displacement vector must also be a function of these independent variables. We can then do an expansion of $\mathbf{D}$ in terms of these independent variables. This has already been partly done in Eq. (8).

From experiment we know that the dominant terms are the linear terms, so it will be sufficient to just include constant and linear terms. There will be then, terms that are linear in the components of the stress tensor, which is a tensor of rank two. From tensor analysis we know that such a linear expansion takes the form $4\pi \sum_{jk} \gamma_{i,jk}\sigma_{jk}$ where the constant coefficients $\gamma_{i,jk}$ are the components of a tensor of rank three and the factor of 4π is introduced for convenience. Since the stress tensor is symmetrical, we may also assume that the tensor $\gamma_{i,jk}$, called the piezoelectric tensor, is also symmetrical in the last two indices,

$$\gamma_{i,kj} = \gamma_{i,jk}. \tag{14}$$

Adding the piezoelectric part to the expansion in Eq. (8) we obtain

$$D_i = D_{0i} + \sum_{j=1}^{3} \epsilon_{ij} E_j + 4\pi \sum_{j,k=1}^{3} \gamma_{i,jk}\sigma_{jk}. \tag{15}$$

The thermodynamic potential will have a corresponding set of terms. To see what they are consider the thermodynamic potential of a non-piezoelectric crystal in the absence of a field in the elastic approximation,

$$\tilde{\Phi} = \Phi = \Phi_0 - \frac{1}{2} \sum_{i,j,k,l=1}^{3} \mu_{ijkl}\sigma_{ij}\sigma_{kl}, \tag{16}$$

where Φ_0 is the thermodynamic potential of the undeformed body. The last term is the elastic energy.[11] The tensor μ_{ijkl} is the elastic constant tensor. For a piezoelectric system we must add the terms arising from the electrical and piezoelectric interactions,

$$\tilde{\Phi} = \Phi_0 - \frac{1}{2} \sum_{i,j,k,l=1}^{3} \mu_{ijkl}\sigma_{ij}\sigma_{kl} - \sum_{i=1}^{3} \left[\frac{1}{8\pi} \sum_{j=1}^{3} \epsilon_{ij} E_j - \frac{D_{0i}}{4\pi} - \sum_{j,k=1}^{3} \gamma_{i,jk}\sigma_{jk} \right] E_i, \tag{17}$$

To calculate the relationship between the electric field and the strain tensor we invoke Eq. (13). From the it we see that

$$\kappa_{ij} = -\left(\frac{\partial \tilde{\Phi}}{\partial \sigma_{ij}} \right)_{T,\mathbf{E}} = \sum_{k,l=1} \mu_{ijkl}\sigma_{kl} + \sum_{k=1}^{3} \gamma_{k,ij} E_k. \tag{18}$$

The first term on the right is the converse of Hooke's law, that is, the elastic contribution to the strain; the second term is the piezoelectric contribution. This is the final expression we are after. It says that the relationship between the electric field and the strain is linear, which is consistent with the experimental observations.

III. THE ELECTRON AND PHONON HAMILTONIANS

In this section we start the quantum mechanical analysis of the piezoelectric effect. From experimental observations and from the classical description given in the previous section we see that piezoelectricity is a phenomenon in which lattice distortions produce internal electric fields. The presence of internal electric fields means that there is charge separation in the piezoelectric crystal. Thus, a quantum mechanical description of this phenomenon necessarily involves the interaction between charges and phonons, which represent the ionic lattice distortions. To understand piezoelectricity from a quantum mechanical point of view we shall invoke the electron-phonon interaction. The electron-phonon interaction involves the density of the charges and the potential associated with the electric field. Thus, before we examine the electron and phonon Hamiltonians, let us calculate the charge density operator.

A. The charge density operator[12]

In many-body theory it is common to describe the wave function of the system by means of the occupation number representation. Thus, one writes $|n_1, n_2, \ldots\rangle$ for the wave function of a system in which the n_i are the occupation numbers of the single electron states $\phi_1, \phi_2, \ldots$ The single particle wave functions are assumed to be orthonormal and to form a complete set for the corresponding Hilbert space. In the case of electrons, given that they are fermions, in accordance with Pauli's principle, n_i can only take the values 0 and 1.

Associated with this representation one defines creation and annihilation operators, c_i^+ and c_i, respectively, by the expressions

$$c_i|n_1, n_2, \ldots, n_{i-1}, n_i, n_{i+1}, \ldots\rangle = \begin{cases} 0, & \text{if } n_i = 0, \\ (-1)^{N_i}|n_1, n_2, \ldots, n_{i-1}, 0, n_{i+1}, \ldots\rangle, & \text{if } n_i = 1, \end{cases} \tag{19}$$

$$c_i^+|n_1, n_2, \ldots, n_{i-1}, n_i, n_{i+1}, \ldots\rangle = \begin{cases} (-1)^{N_i}|n_1, n_2, \ldots, n_{i-1}, 1, n_{i+1}, \ldots\rangle, & \text{if } n_i = 0, \\ 0, & \text{if } n_i = 1, \end{cases} \tag{20}$$

with $N_i = \sum_{j=1}^{i-1} n_j$. The creation and annihilation operators obey the following anticommutation rules

$$\{c_i, c_j\} = c_i c_j + c_j c_i = 0, \tag{21}$$

$$\{c_i^+, c_j^+\} = c_i^+ c_j^+ + c_j^+ c_i^+ = 0, \tag{22}$$

$$\{c_i^+, c_j\} = c_i^+ c_j + c_j c_i^+ = \delta_{ij}, \tag{23}$$

where δ_{ij} is the Kroenecker delta. The creation operator c_i^+ acts on an $N-1$ electron wave function with no electrons in the single particle state ϕ_i and produces an N electron wave function with one electron in ϕ_i. Similarly, the annihilation operator c_i acts on and N electron wave function that has one electron in state ϕ_i and produces and $N-1$ electron wave function with no electrons in ϕ_i.

In periodic solids it is possible to solve the single particle Schrödinger equation for the functions $\phi_1, \phi_2, \ldots$ For simplicity, let us assume that the crystal has the shape of a cube of volume $\Omega = L^3$. One type of solution is given by plane waves of the form

$$\phi_\alpha(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}_\alpha \cdot \mathbf{r}}, \tag{24}$$

where the allowed values of $\mathbf{k}_\alpha$ are given by

$$\mathbf{k}_\alpha = \left(\frac{2\pi m_1}{L}, \frac{2\pi m_2}{L}, \frac{2\pi m_2}{L} \right), \tag{25}$$

in which the m_i are integers.

To construct operators acting on the electron wave functions using the occupation number representation we start with the solutions to the N electron Schrödinger equation. These solutions can be written as linear combinations of wave functions of the form

$$\Phi(\alpha_1, \alpha_2, \ldots, \alpha_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\alpha_1}(\mathbf{r}_1) & \phi_{\alpha_1}(\mathbf{r}_2) & \cdots & \phi_{\alpha_1}(\mathbf{r}_N) \\ \phi_{\alpha_2}(\mathbf{r}_1) & \phi_{\alpha_2}(\mathbf{r}_2) & \cdots & \phi_{\alpha_2}(\mathbf{r}_N) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \phi_{\alpha_N}(\mathbf{r}_1) & \phi_{\alpha_N}(\mathbf{r}_2) & \cdots & \phi_{\alpha_N}(\mathbf{r}_N) \end{vmatrix}, \tag{26}$$

where $\mathbf{r}_1, \mathbf{r}_1, \ldots, \mathbf{r}_N$ are the spatial coordinates of the N electrons. These wave functions are known as Slater determinants; they satisfy the antisymmetry conditions established by the Pauli principle, namely, that the exchange of any two fermions changes the sign of the wave function. Then, we can associate with each Slater determinant a wave function in the occupation number representation by making the assignment

$$|n_1, n_2, \ldots\rangle \leftrightarrow \Phi(\alpha_1, \alpha_2, \ldots, \alpha_N), \tag{27}$$

in which $n_{\alpha_1} = n_{\alpha_2} = \cdots = n_{\alpha_N} = 1$ and $n_i = 0$ for $i \neq \alpha_1, \alpha_2, \ldots, \alpha_N$. The wave functions $|n_1, n_2, \ldots\rangle$ are normalized, $\langle n_1, n_2, \ldots | n_1, n_2, \ldots\rangle = 1$, and form a complete basis set for the Hilbert space of N electron wave functions if the single particle functions form a complete basis set for the single particle Hilbert space. As a result, they satisfy the closure relationship,

$$\sum_{n_1, n_2, \ldots} |n_1, n_2, \ldots\rangle\langle n_1, n_2, \ldots | = 1. \tag{28}$$

Thus, if $\mathcal{V}$ is any operator containing the coordinates of any number of the N electrons we can write the identity

$$\mathcal{V} = \sum_{n_1, n_2, \ldots} \sum_{n'_1, n'_2, \ldots} |n_1, n_2, \ldots\rangle\langle n_1, n_2, \ldots | \mathcal{V} | n'_1, n'_2, \ldots\rangle\langle n'_1, n'_2, \ldots |. \tag{29}$$

The expression in the middle,

$$\langle n_1, n_2, \ldots | \mathcal{V} | n'_1, n'_2, \ldots\rangle = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Phi^*(\alpha_1, \alpha_2, \ldots, \alpha_N) \mathcal{V} \Phi(\alpha'_1, \alpha'_2, \ldots, \alpha'_N), \tag{30}$$

is the matrix element of the operator $\mathcal{V}$ with respect to the N electron states $|n_1, n_2, \ldots\rangle$ and $|n'_1, n'_2, \ldots\rangle$.

The standard definition on the charge density of particles located at positions $\mathbf{r}_i$ is

$$\rho(\mathbf{r}) = \sum_i Q_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{31}$$

where Q_i is the charge of the ith particle and $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function. For simplicity, we shall assume that all the particles have the same charge, $Q_i = Q$. Then, one can use Eq. (29) and the properties of the single particle functions, Eq. (24), to show[12] that the charge density operator is given by

$$\rho(\mathbf{r}) = \frac{Q}{\Omega} \sum_{\mathbf{k},\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}}. \tag{32}$$

B. The electron Hamiltonian[12]

The Hamiltonian in the Schrödinger equation for the electrons has the form

$$\mathcal{H}_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{en}(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} V_{ee}(|\mathbf{r}_i - \mathbf{r}_j|). \tag{33}$$

The first term is the kinetic energy of the electrons, in which $\hbar$ is Planck's constant divided by 2π and m is the mass of the electron; V_{en} is the nuclear attraction and V_{ee} is the electron-electron repulsion. The first two terms only contain single particle operators, the last term consists of two particle operators.

Rather than going through the details of the derivation of the electron Hamiltonian in terms of the occupation number representation, we will give the result here and refer the reader to the texts in Reference 12 in the bibliography for the proofs.

As we did in the previous section, we choose the single particle wave functions to be plane waves

$$\phi_\alpha(\mathbf{r}) = \frac{1}{\Omega} e^{i\mathbf{k}_\alpha\cdot\mathbf{r}}, \tag{34}$$

where $\mathbf{k}_\alpha$ is the wave vector and Ω is the volume of the crystal. Then the electron Hamiltonian is

$$\mathcal{H}_e = \sum_{\mathbf{k}} T_{\mathbf{k}} c^{+}_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{k},\mathbf{k}'} V_{en,\mathbf{k}\mathbf{k}'} c^{+}_{\mathbf{k}} c_{\mathbf{k}'} + \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} V_{ee,\mathbf{q}} c^{+}_{\mathbf{k}-\mathbf{q}} c^{+}_{\mathbf{k}'+\mathbf{q}} c_{\mathbf{k}'} c_{\mathbf{k}}, \tag{35}$$

where

$$T_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m}, \tag{36}$$

$$V_{en,\mathbf{k}\mathbf{k}'} = \frac{1}{\Omega} \int d\mathbf{r} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} V_{en}(\mathbf{r}), \tag{37}$$

$$V_{ee,\mathbf{q}} = \frac{1}{\Omega} \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} V_{ee}(\mathbf{r}). \tag{38}$$

C. The phonon Hamiltonian[12]

Phonons are collective excitations that correspond to the motion of atoms in solids. For our purposes, they represent the elastic distortions of the lattice present in piezoelectric phenomena. In the elastic approximation phonons can be described in terms of a set of harmonic oscillators that represent the vibrations of the atoms. The resulting collective excitations are bosons.

One can develop for bosons an occupation representation formalism similar to that of fermions. One of the main differences is that for bosons the occupation numbers can have the values $n_i = 0, 1, 2, 3, \ldots$ In this representation we can also define creation and annihilation operators, as we did in the case of fermions. We discuss these next in terms of harmonic oscillators.

In a harmonic oscillator, a particle of mass M moves in a potential energy $\frac{1}{2}M\omega^2\mathbf{R}^2$. The corresponding Hamiltonian is

$$\mathcal{H}_o = \frac{1}{2M}\sum_{i=1}^{3}\left[P_i^2 + (M\omega X_i)^2\right] = \frac{1}{2M}\sum_{i=1}^{3}\left[-\hbar^2\frac{\partial^2}{\partial X_i^2} + (M\omega X_i)^2\right], \tag{39}$$

where P_i is the ith component of the momentum vector and $\mathbf{R} = (X_1, X_2, X_3)$ is the position vector of the mass M. The components of position and momentum obey the commutation rules

$$[X_i, P_j] = X_i P_j - P_j X_i = i\hbar\delta_{ij}. \tag{40}$$

We define the creation and annihilations operators, a_i^+ and a_i, by the expressions

$$a_i^+ = \sqrt{\frac{1}{2\hbar M\omega}}\left(M\omega X_i - iP_i\right), \tag{41}$$

$$a_i = \sqrt{\frac{1}{2\hbar M\omega}}\left(M\omega X_i + iP_i\right) \tag{42}$$

with commutation relations

$$[a_i, a_j^+] = a_i a_j^+ - a_j^+ a_i = \delta_{ij}. \tag{43}$$

In terms of these operators the Harmonic oscillator Hamiltonian is

$$\mathcal{H}_o = \frac{1}{2}\hbar\omega\sum_{i=1}^{3}(a_i^+ a_i + a_i a_i^+) = \sum_{i=1}^{3}(\hat{n}_i + \frac{1}{2})\hbar\omega, \tag{44}$$

with $\hat{n}_i = a_i^+ a_i$; $\hat{n}_i$ is known as the number operator.

To find the phonon Hamiltonian let us consider first a simple crystal, namely a Bravais lattice, in which the separation vector between any two atoms can be written in the form

$$\mathbf{l} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3, \tag{45}$$

where the the m_i are integers and the $\mathbf{a}_i$ are the basis vectors of the lattice. We also define a reciprocal lattice of vectors $\mathbf{g}$ such that for each $\mathbf{l}$ there corresponds a $\mathbf{g}$ satisfying

$$e^{i\mathbf{g}\cdot\mathbf{l}} = 1. \tag{46}$$

We now refer the reader to the texts in Reference 12 for a proof that the phonon Hamiltonian for such a crystal takes the form

$$\mathcal{H}_p = \sum_{\mathbf{q},\mathbf{s}}\hbar\omega_{\mathbf{qs}}\left(a_{\mathbf{gs}}^+ a_{\mathbf{qs}} + \frac{1}{2}\right). \tag{47}$$

Here, $\mathbf{s}$ corresponds to three vectors $\mathbf{s}_1$, $\mathbf{s}_2$ and $\mathbf{s}_3$ that give the direction of polarization of the phonons. When one of the $\mathbf{s}_i$ is parallel to $\mathbf{q}$ we say that there can be longitudinally polarized phonons in the crystal. If $\mathbf{s} \cdot \mathbf{q} = 0$ we say that the phonons are transversely polarized. In Eq. (47), $\mathbf{q}$ is the wave vector of the phonons; it is always of the form $\mathbf{q} = \mathbf{g}_1 - \mathbf{g}_2$, where $\mathbf{g}_1$ and $\mathbf{g}_2$ are two reciprocal lattice vectors. The $\omega_{\mathbf{qs}}$ are the corresponding frequencies in the elastic approximation. The Hamiltonian of Eq. (47) is also valid for all crystals, not just for Bravais lattices. In general, such crystals have a basis of atoms associated with each point of the form $\mathbf{l} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3$.

The expression of Eq. (47) represents a set of uncoupled lattice vibrations; thus, its derivation[12] is accomplished by means of a transformation to normal modes in which the phonons with frequencies $\omega_{\mathbf{qs}}$ are uncoupled. The second term in the parenthesis represents the zero point energy and is often neglected when considering the interactions between phonons and electrons.

In three dimensions, the creation and annihilation operators in Eq. (47) can be defined in terms of the lattice displacements represented by a phonon of wave vector $\mathbf{q}$ with polarization vector $\mathbf{s}$. If M is the mass of the ions, $\mathbf{y}_{\mathbf{q}}$ and $\mathbf{p}_{\mathbf{q}}$ the Fourier transforms of the displacement and the momentum operators, then [compare to Eqs. (37) and (38)]

$$a_{\mathbf{qs}} = \frac{1}{\sqrt{2\hbar M\omega_{\mathbf{qs}}}}(M\omega_{\mathbf{qs}}\mathbf{y}_{\mathbf{q}} + i\mathbf{p}_{-\mathbf{q}}) \cdot \mathbf{s}, \tag{48}$$

$$a^{+}_{\mathbf{qs}} = \frac{1}{\sqrt{2\hbar M\omega_{\mathbf{qs}}}}(M\omega_{\mathbf{qs}}\mathbf{y}_{-\mathbf{q}} - i\mathbf{p}_{\mathbf{q}}) \cdot \mathbf{s}. \tag{49}$$

IV. THE FRÖHLICH HAMILTONIAN

We consider now the effect of the interaction between electrons and phonons. To do so we shall employ the Fröhlich Hamiltonian,[13] which consists of the bare electron, the bare phonon and the electron-phonon Hamiltonians. This is an approximate Hamiltonian that, nevertheless, includes all the effects necessary to explain the piezoelectric effect from a quantum mechanical point of view.

The description of the solution of the problem of phonons interacting with electrons requires that the Hamiltonian include three basic terms: (i) the bare electrons, (ii) the bare phonons, and (iii) the electron-phonon interaction, that is

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_p + \mathcal{H}_{ep}. \tag{50}$$

Although we have already described the Hamiltonians for the bare electrons and the bare phonons, it is convenient to make a further approximation for the Hamiltonian of the bare electrons.

A complete solution should start with the Hamiltonian of Eq. (**??**), which includes the long-range Coulomb interactions. We can explore, however, the effect of the electron-phonon interactions with a simpler model in which we accept the fact that the nuclei are surrounded by core electrons that are tightly associated with the positive charges of the nuclei. Moreover, the conduction electrons screen these ionic cores, so that, effectively, the ionic cores interact with each other and with the electrons only through a short-range screened potential. Under this assumption, we can write a Schrödinger equation for the single-electron states of the form[14]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U_0\right]\phi_{\mathbf{k}} = \mathcal{E}_{\mathbf{k}}\phi_{\mathbf{k}}, \tag{51}$$

where U_0 is a one-body potential. Bassani *et al.*[15] have shown that by properly defining U_0 the single-electron states are orthogonal to the ionic cores when they are in their equilibrium positions. Because of the periodicity of the potential U_0, to a good approximation, we can still take the single particle states to be the plane waves of Eq. (**??**). The bare electron Hamiltonian can then be written as

$$\mathcal{H}_e = \sum_{\mathbf{k}} \mathcal{E}_{\mathbf{k}} c^+_{\mathbf{k}} c_{\mathbf{k}}. \tag{52}$$

In addition, ignoring the zero point motion, the bare phonon Hamiltonian, Eq. (47), is

$$\mathcal{H}_p = \sum_{\mathbf{q},\mathbf{s}} \hbar\omega_{\mathbf{qs}} a^+_{\mathbf{gs}} a_{\mathbf{qs}}. \tag{53}$$

It remains to calculate the electron-phonon Hamiltonian, that is, the interaction Hamiltonian of the electrons with the screened ions. To this end, we assume that the corresponding potential, $V(|\mathbf{r}-\mathbf{R}|)$, only depends on the distance between the position of the electron, $\mathbf{r}$, and that of the screened ion, $\mathbf{R}$. This assumption is often referred to as the rigid ion approximation.

In the occupation number representation, the electron-phonon Hamiltonian becomes

$$\begin{aligned}\mathcal{H}_{ep} &= \sum_{\mathbf{k},\mathbf{k}',\mathbf{l}} \langle \mathbf{k}|V(|\mathbf{r}-\mathbf{l}-\mathbf{y}|)|\mathbf{k}'\rangle c^+_{\mathbf{k}} c_{\mathbf{k}'} \\ &= \sum_{\mathbf{k},\mathbf{k}',\mathbf{l}} e^{i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{l}+\mathbf{y})} V_{\mathbf{k}-\mathbf{k}'} c^+_{\mathbf{k}} c_{\mathbf{k}'}, \end{aligned} \tag{54}$$

where $\mathbf{y}$ is the small displacement of the ion from the equilibrium position $\mathbf{l}$ and

$$V_{\mathbf{q}} = \frac{1}{\Omega}\int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} V(\mathbf{r}). \tag{55}$$

Because the displacement of the ions from the equilibrium position is very small, $(\mathbf{k}'-\mathbf{k})\cdot\mathbf{y} \ll 1$, we can write

$$\begin{aligned} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{y}} &\approx 1 + i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{y} \\ &= 1 + \frac{i}{\sqrt{\Lambda}}(\mathbf{k}'-\mathbf{k})\cdot\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{l}}\mathbf{y}_{\mathbf{q}}, \end{aligned} \tag{56}$$

where $\mathbf{y}_{\mathbf{q}}$ is the Fourier transform of $\mathbf{y}$ and Λ is the number of unit cells in the volume of the crystal. Substitution into Eq. (53) yields

$$\begin{aligned} \mathcal{H}_{ep} &= \sum_{\mathbf{k},\mathbf{k}',\mathbf{l}} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} V_{\mathbf{k}-\mathbf{k}'} c^+_{\mathbf{k}} c_{\mathbf{k}'} + \sum_{\mathbf{k},\mathbf{k}',\mathbf{l}} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{l}} \left[\frac{i}{\sqrt{\Lambda}}(\mathbf{k}'-\mathbf{k})\cdot\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{l}}\mathbf{y}_{\mathbf{q}}\right] V_{\mathbf{k}-\mathbf{k}'} c^+_{\mathbf{k}} c_{\mathbf{k}'} \\ &= \mathcal{H}_{\text{Bloch}} + \mathcal{H}_{\text{disp}}. \end{aligned} \tag{57}$$

The first term is the Bloch Hamiltonian, which is independent of the lattice displacements from equilibrium; the second term gives the electron-phonon interaction proper. Because the wave vectors $\mathbf{k}$ and $\mathbf{k}'$ are differences of reciprocal lattice vectors, we can simplify the Bloch Hamiltonian further,

$$\mathcal{H}_{\text{Bloch}} = \Lambda \sum_{\mathbf{k},\mathbf{g}} V_{-\mathbf{g}} c^{+}_{\mathbf{k}-\mathbf{g}} c_{\mathbf{k}}, \tag{58}$$

where the $\mathbf{g}$ are reciprocal lattice vectors. For the displacement Hamiltonian we find that

$$\begin{aligned} \mathcal{H}_{\text{disp}} &= \frac{i}{\sqrt{\Lambda}} \sum_{\mathbf{k},\mathbf{k}',\mathbf{l},\mathbf{q}} e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{q})\cdot\mathbf{l}} [(\mathbf{k}'-\mathbf{k})\cdot\mathbf{y}_{\mathbf{q}}] V_{\mathbf{k}-\mathbf{k}'} c^{+}_{\mathbf{k}} c_{\mathbf{k}'} \\ &= i\sqrt{\Lambda} \sum_{\mathbf{k},\mathbf{k}'} [(\mathbf{k}'-\mathbf{k})\cdot\mathbf{y}_{\mathbf{k}-\mathbf{k}'}] V_{\mathbf{k}-\mathbf{k}'} c^{+}_{\mathbf{k}} c_{\mathbf{k}'}. \end{aligned} \tag{59}$$

We can now substitute Eqs. (48) and (49) in the second line to obtain

$$\mathcal{H}_{\text{disp}} = i \sum_{\mathbf{k},\mathbf{k}',\mathbf{s}} \left(\frac{\Lambda\hbar}{2M\omega_{\mathbf{k}-\mathbf{k}',\mathbf{s}}} \right)^{1/2} [(\mathbf{k}'-\mathbf{k})\cdot\mathbf{s}] V_{\mathbf{k}-\mathbf{k}'} (a^{+}_{\mathbf{k}-\mathbf{k}',\mathbf{s}} + a_{\mathbf{k}-\mathbf{k}',\mathbf{s}}) c^{+}_{\mathbf{k}} c_{\mathbf{k}'}, \tag{60}$$

where the summation now also includes the three polarization vectors.

For simplicity, we shall assume that the phonon spectrum is isotropic, so that the phonon will be either longitudinally or transversely polarized. Because for transverse phonons $(\mathbf{k}'-\mathbf{k})\cdot\mathbf{s} = 0$, only the longitudinal phonons enter in the electron-phonon interaction. We can also neglect the effects of $\mathcal{H}_{\text{Bloch}}$, the periodic potential of the stationary lattice. With these simplifications we are left with the Fröhlich Hamiltonian,

$$\mathcal{H} = \sum_{\mathbf{k}} \mathcal{E}_{\mathbf{k}} c^{+}_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{q},\mathbf{s}} \hbar\omega_{\mathbf{qs}} a^{+}_{\mathbf{gs}} a_{\mathbf{qs}} + \sum_{\mathbf{k},\mathbf{k}'} M_{\mathbf{kk}'} (a^{+}_{-\mathbf{q}} + a_{\mathbf{q}}) c^{+}_{\mathbf{k}} c_{\mathbf{k}'}, \tag{61}$$

with phonon wave vector $\mathbf{q} = \mathbf{k}-\mathbf{k}'$ and where the electron-phonon matrix element is defined by

$$M_{\mathbf{kk}'} = i \left(\frac{\Lambda\hbar}{2M\omega_{\mathbf{q}}} \right)^{1/2} |\mathbf{k}-\mathbf{k}'| V_{\mathbf{k}-\mathbf{k}'}. \tag{62}$$

If necessary, the wave number $\mathbf{q}$ may be reduced to the first Brillouin zone.

The last term in Eq. (61) is composed of two parts involving $a^{+}_{-\mathbf{q}} c^{+}_{\mathbf{k}} c_{\mathbf{k}'}$ and $a_{\mathbf{q}} c^{+}_{\mathbf{k}} c_{\mathbf{k}'}$. They may be represented by the diagrams shown in Fig. 1. In diagram (a) an electron is scattered from $\mathbf{k}'$ to $\mathbf{k}$ with the emission of a phonon of wave vector $\mathbf{k}'-\mathbf{k}$. The total momentum is conserved, unless the vector $\mathbf{k}'-\mathbf{k}$ lies outside the first Brillouin zone, in which case $\mathbf{q} = \mathbf{k}'-\mathbf{k}+\mathbf{g}$ for some vector $\mathbf{g}$ in the reciprocal lattice. This would be an example of an electron-phonon Umklapp process. In the second diagram, an electron with wave vector $\mathbf{k}'$ absorbs a phonon with wave vector $\mathbf{q}$ and is scattered into $\mathbf{k}$.

V. PIEZOELECTRICITY[16]

Piezoelectric solids are polar crystals that have heavy positive ions and lighter negative ions. As mentioned before, piezoelectricity arises from an interaction between charges and

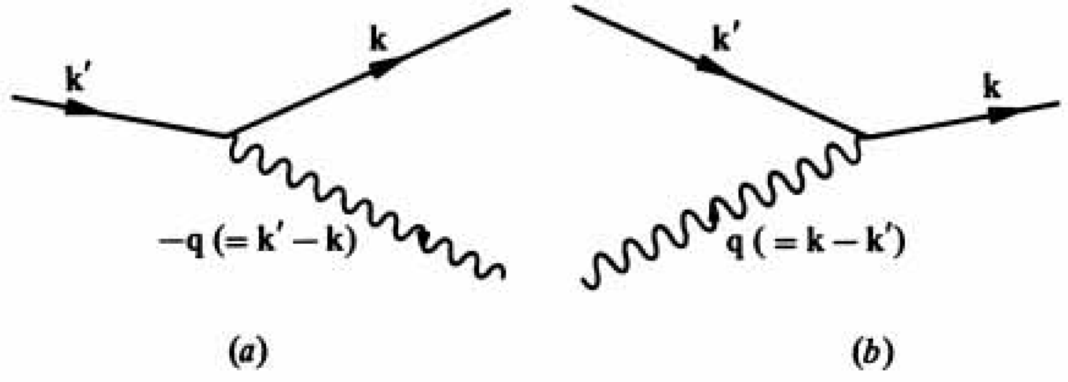

FIG. 1: (a) Emission and (b) absorption of a phonon in the Fröhlich Hamiltonian. Taken from P L Taylor, *A Quantum Approach to the Solid State* (Prentice Hall, Englewood Cliffs, New Jersey, 1970), p. 178.

phonons, in particular, acoustical phonons. In acoustical phonon modes all the ions tend to vibrate in the same direction, but they need not be displaced by the same amount. If the heavy ions move less than their lighter counterparts a polarization field is induced in the crystal. This is the origin of piezoelectricity.

A. Polar coupling to longitudinal acoustical phonons

Acoustical phonons with a transverse polarization do not couple strongly to the ions in the crystal because they do not produce a significant electric field when they vibrate. Acoustical longitudinal phonons couple effectively to the ions at long wavelengths. The atomic vibrations are along the direction $\mathbf{q}$ of the phonon wave vector, whereas for transverse phonons the vibrations are perpendicular to $\mathbf{q}$. The electrical polarization vector $\mathbf{P}_\mathbf{q}$ is set up in the direction of the vibration; it is parallel to $\mathbf{q}$ for longitudinal phonons and perpendicular for transverse phonons.

Roughly speaking, the magnitudes of these two polarization vectors are similar. However, the electric fields that are produced by these two types of oscillations are quite different. The field produced by longitudinal phonons is significant while that of the transverse phonons is negligible. To see this let us consider the first of Maxwell's equations,

$$\nabla \cdot \mathbf{D} = 4\pi\rho, \tag{63}$$

where $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ is the displacement vector and ρ the free charge density. In a polar crystal there are few free electrons so that the free charge density is zero and

$$\nabla \cdot \mathbf{D} = 0. \tag{64}$$

This implies[17] that

$$\mathbf{q} \cdot (\mathbf{E}_\mathbf{q} + 4\pi\mathbf{P}_\mathbf{q}) = 0. \tag{65}$$

For longitudinal modes both $\mathbf{E}_\mathbf{q}$ and $\mathbf{P}_\mathbf{q}$ are parallel to $\mathbf{q}$, which means that

$$\mathbf{E}_\mathbf{q} = -4\pi\mathbf{P}_\mathbf{q}. \tag{66}$$

The transverse phonons have their electric field perpendicular to $\mathbf{q}$. Photons also have their electric field perpendicular to $\mathbf{q}$. In fact, any excitation that is trying to produce a transverse electric field is just trying to produce photons. This process is very inefficient because photons go at the speed of light and phonons do not. As a result, only a small electric field is produced by the transverse excitation. This can be seen from Maxwell's equations,

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}, \tag{67}$$

$$\nabla \times \mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t}. \tag{68}$$

If these fields are generated by a phonon of wave vector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$ they are proportional to $e^{i\mathbf{q}\cdot\mathbf{r}-i\omega_{\mathbf{q}}t}$. Next, we note that the time derivatives give the original vector multiplied by $-i\omega_{\mathbf{q}}$. From electromagnetic theory we also have that $\mathbf{B} = \mu\mathbf{H}$, where μ is the magnetic permeability, which, for most piezoelectric materials, can be taken to be equal to one. Then, Eqs. (63) and (64) give

$$\mathbf{q} \times \mathbf{E} = \frac{\omega_{\mathbf{q}}}{c}\mathbf{H}, \tag{69}$$

$$\mathbf{q} \times \mathbf{H} = -\frac{\omega_{\mathbf{q}}}{c}\mathbf{D}. \tag{70}$$

Taking the cross product of Eq. (69) with $\mathbf{q}$ and substituting Eq. (70) we obtain

$$\mathbf{q} \times (\mathbf{q} \times \mathbf{E}_{\mathbf{q}}) = -\frac{\omega_{\mathbf{q}}^2}{c^2}(\mathbf{E}_{\mathbf{q}} + 4\pi\mathbf{P}_{\mathbf{q}}). \tag{71}$$

For transverse phonons $\mathbf{q}$ is perpendicular to $\mathbf{E}_{\mathbf{q}}$, so that $\mathbf{q} \times (\mathbf{q} \times \mathbf{E}_{\mathbf{q}}) = -\mathbf{q}^2\mathbf{E}_{\mathbf{q}}$, and

$$\mathbf{E}_{\mathbf{q}} = \frac{\omega_{\mathbf{q}}^2}{c^2\mathbf{q}^2 - \omega_{\mathbf{q}}^2}(4\pi\mathbf{P}_{\mathbf{q}}) \approx \frac{\omega_{\mathbf{q}}^2}{c^2\mathbf{q}^2}(4\pi\mathbf{P}_{\mathbf{q}}). \tag{72}$$

Here, we have used the fact that $c^2\mathbf{q}^2 \gg \omega_{\mathbf{q}}^2$ because the speed of light is so large. This shows that the electric field generated by a transverse phonon is very small. In fact, for acoustical phonons $\omega_{\mathbf{q}} = c_{\mathbf{q}}|\mathbf{q}|$, where $c_{\mathbf{q}}$ is of the order of the speed of sound in the crystal. Then, the ratio in Eq. (72) becomes $\omega_{\mathbf{q}}^2/c^2\mathbf{q}^2 \approx 10^{-10}$. Hence, the transverse electric fields can be neglected.

B. The electron-phonon interaction for a piezoelectric crystal

In section IV we derived the Frölich Hamiltoninan between free electrons (such as the conduction electrons in a metal) and the phonon. In the case of piezoelectric crystals, there are no free electrons to speak of and the electron-phonon interactions refers to the bound electrons in the ion cores. In fact, this interaction results from the displacements of the ions caused by the phonons. Next, we proceed to derive this interaction following the procedure used for the Frölich Hamiltoninan.

From the continuum treatment in Section II we recall that the strain tensor is given by Eq. (5). Let $\mathbf{u}(\mathbf{q})$ be the displacement created by a phonon of wave vector $\mathbf{q}$, so that

$$\mathbf{u}(\mathbf{q}, \mathbf{r}, t) = \mathbf{u}_0 e^{i\mathbf{q}\cdot\mathbf{r}-i\omega_{\mathbf{q}}t}. \tag{73}$$

From Eq. (5) the strain tensor is given by

$$\kappa_{jk}(\mathbf{q}) = \frac{i}{2}\left(u_j q_k + u_k q_j\right), \quad j,k = 1,2,3. \tag{74}$$

We can use Eq. (15) to find the electric field caused by this strain. To do so we need to rewrite that equation in terms of the strain tensor. We do this assuming that we are in the elastic regime, which should be the case for piezoelectricity on account of the very small displacements of the ions. We can then use Hooke's law,[18]

$$\sigma_{ij} = \sum_{k,l=1}^{3} C_{ijkl}\kappa_{kl}, \tag{75}$$

where, for elastic solids, $C_{ijkl} = K\delta_{ij}\delta_{kl} + 2\mu(\delta_{ik}\delta_{jl} - \delta_{ij}\delta_{kl}/3)$. The constants K and μ are the bulk modulus and the shear modulus, respectively. Substituting this expression into Eq. (15) leads to

$$D_i = \sum_{j=1}^{3}\epsilon_{ij}E_j + 4\pi\sum_{l,m=1}^{3}\Gamma_{i,lm}\kappa_{lm}, \tag{76}$$

with $\Gamma_{i,lm} = \sum_{j,k=1}^{3}\gamma_{i,jk}C_{jklm}$; $\Gamma_{i,lm}$ is also called the piezoelectric constant. For simplicity, we have set the constant displacement vector $\mathbf{D}_0$ equal to zero.

Because there are no free charges Eq. (64) is satisfied and we have

$$\sum_{i=1}^{3} q_i D_i = 0 = \sum_{i,j=1}^{3} q_i\epsilon_{ij}E_j(\mathbf{q}) + 4\pi\sum_{i,j,k=1}^{3} q_i\Gamma_{i,jk}\kappa_{jk}(\mathbf{q}). \tag{77}$$

Moreover, the transverse components of $\mathbf{E}(\mathbf{q})$ are negligible so we can write

$$E_j(\mathbf{q}) = \frac{q_j}{|\mathbf{q}|}|\mathbf{E}(\mathbf{q})|, \tag{78}$$

therefore

$$|\mathbf{E}(\mathbf{q})| = -\frac{4\pi|\mathbf{q}|\sum_{i,j,k=1}^{3} q_i\Gamma_{i,jk}\kappa_{jk}(\mathbf{q})}{\sum_{i,j=1}^{3} q_i\epsilon_{ij}q_j}. \tag{79}$$

In addition, the electric field can be written in terms of a potential $\mathbf{E} = -\nabla\Phi$. Because $\mathbf{E} \propto e^{i\mathbf{q}\cdot\mathbf{r}}$ we expect that $\Phi \propto e^{i\mathbf{q}\cdot\mathbf{r}}$ also, so that $|\mathbf{E}(\mathbf{q})| = -i|\mathbf{q}|\Phi(\mathbf{q})$ or

$$\begin{aligned}\Phi(\mathbf{q}) &= -\frac{4\pi i\sum_{i,j,k=1}^{3} q_i\Gamma_{i,jk}\kappa_{jk}(\mathbf{q})}{\sum_{i,j=1}^{3} q_i\epsilon_{ij}q_j} \\ &= \frac{2\pi\sum_{i,j,k=1}^{3} q_i\Gamma_{i,jk}\left(u_j q_k + u_k q_j\right)}{\sum_{i,j=1}^{3} q_i\epsilon_{ij}q_j}\end{aligned} \tag{80}$$

The denominator may be written as $q^2\hat{\mathbf{q}}\cdot\epsilon\cdot\hat{\mathbf{q}}$ where $q = |\mathbf{q}|$ and $\hat{\mathbf{q}}$ is a unit vector in the direction of the wave vector. Here, $\epsilon_0(\hat{\mathbf{q}}) = \hat{\mathbf{q}}\cdot\epsilon\cdot\hat{\mathbf{q}}$ is the longitudinal dielectric function of the anisotropic crystal.

In analogy to Eqs. (48) and (49) we can write

$$a_{\mathbf{q}} = \frac{1}{q\sqrt{2\hbar M\omega_{\mathbf{q}}}}(M\omega_{\mathbf{q}}\mathbf{u}_{\mathbf{q}} + i\mathbf{p}_{-\mathbf{q}}) \cdot \mathbf{q}, \tag{81}$$

$$a^{+}_{\mathbf{q}} = \frac{1}{q\sqrt{2\hbar M\omega_{\mathbf{q}}}}(M\omega_{\mathbf{q}}\mathbf{u}_{-\mathbf{q}} - i\mathbf{p}_{\mathbf{q}}) \cdot \mathbf{q}. \tag{82}$$

Solving for the displacement yields

$$(u_j q_k + u_k q_j) = 2\left(\frac{\hbar}{2M\omega_{\mathbf{q}}}\right)^{1/2}\frac{q_j q_k}{q}(a_{\mathbf{q}} + a^{+}_{-\mathbf{q}}). \tag{83}$$

The potential acting on the electrons bound to the ionic cores is obtained by summing over all the the phonon modes,

$$\Phi(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\Phi(\mathbf{q}). \tag{84}$$

That is, as expected, $\Phi(\mathbf{r})$ and $\Phi(\mathbf{q})$ are related by a Fourier transform. From electrostatics, the interaction energy is obtained by integrating this potential with the electronic charge density, $\rho(\mathbf{r})$,

$$\mathcal{H}_{ep} = \int d\mathbf{r}\rho(\mathbf{r})\Phi(\mathbf{r}) = Q\sum_{\mathbf{q}}\rho(\mathbf{q})\Phi(\mathbf{q}), \tag{85}$$

where [see Eq. (32)] $\rho(\mathbf{q}) = \int d\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}\rho(\mathbf{r}) = (Q/\Omega)\sum_{\mathbf{k}} c^{+}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}$. Substituting this expression plus Eqs. (80) and (83) into Eq. (85) gives the electron-phonon Hamiltonian,

$$\mathcal{H}_{ep} = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{k},\mathbf{q}}\mathcal{M}(\mathbf{q})c^{+}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}(a_{\mathbf{q}} + a^{+}_{-\mathbf{q}}), \tag{86}$$

with the piezoelectric matrix element given by

$$\mathcal{M}(\mathbf{q}) = \frac{4\pi Q\sum_{i,j,k=1}^{3}\Gamma_{i,jk}q_i q_j q_k}{q^3\epsilon_0(\hat{\mathbf{q}})}. \tag{87}$$

VI. EXAMPLES: ZINC BLENDE AND WURTZITE STRUCTURES

The piezoelectric constants $\Gamma_{i,jk}$ constitute a third rank tensor. The independent components are restricted by the symmetry of the point group to which the crystal belongs. The number of constants for each crystal group have been tabulated.[19]

As a first example of how to calculate the electron-phonon interaction we shall choose zinc blende, which belongs[20] to the cubic class $\bar{4}3m$. This structure has only one nonzero independent piezoelectric constant, namely, $\Gamma_{1,23} = \Gamma_{2,31} = \Gamma_{3,12}$ or, in terms of the x, y and z axes, $\Gamma_{x,yz} = \Gamma_{y,zx} = \Gamma_{z,xy}$. Because the structure is cubic, the longitudinal dielectric function $\epsilon_0(\hat{\mathbf{q}}) = \epsilon_0$ is isotropic. Then, the matrix element of Eq. (87) is

$$\mathcal{M}(\mathbf{q}) = 24\pi Q\left(\frac{\hbar}{2M\omega_{\mathbf{q}}}\right)^{1/2}\frac{\Gamma_{x,yz}q_x q_y q_z}{q^3\epsilon_0}. \tag{88}$$

As a second example, let us consider the wurtzite structure, which belongs[21] to the hexagonal group class $6mm$. The nonzero piezoelectric constants are $\Gamma_{3,11} = \Gamma_{3,22}$, $\Gamma_{1,31} = \Gamma_{2,23}$, and $\Gamma_{3,12}$. The piezoelectric matrix element is then

$$\mathcal{M}(\mathbf{q}) = 4\pi Q \left(\frac{\hbar}{2M\omega_{\mathbf{q}}}\right)^{1/2} \frac{\Gamma_{z,xy}q_z^3 + (2\Gamma_{x,zx} + \Gamma_{z,xx})(q_x^2 + q_y^2)q_z}{q^3\epsilon_0(\hat{\mathbf{q}})}. \qquad (89)$$

The dielectric tensor is no longer isotropic, so the longitudinal part $\epsilon_0(\hat{\mathbf{q}})$ depends on the angle θ which $\mathbf{q}$ makes with the z axis, so that $\epsilon_0(\hat{\mathbf{q}}) = \epsilon_{11}\sin^2\theta + \epsilon_{33}\cos^2\theta$.

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[1] This section is based on Section 17 of L Landau and E M Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Oxford, 1960), p. 73.

[2] J Curie and P Curie "Développement par compression de l'lectricité polaire dans les cristaux hémièdres à faces inclinées", *Bulletin de la Socité minérologique de France* **3**, 90 (1880).

[3] G Lippmann, "Principe de la conservation de l'électricité", *Annales de chimie et de physique* **24**, 145 (1881).

[4] L Landau and E M Lifshitz, *Theory of Elasticity, 2nd Edition* (Pergamon Press, Oxford, 1970), Chapter 1.

[5] A common notation for the strain tensor is ϵ_{ij}. However, we shall reserve this symbol for the dielectric tensor.

[6] Reference 4, p. 1.

[7] Reference 4, p. 9.

[8] Reference 1, Section 10.

[9] Reference 1, p. 71.

[10] Reference 1, p. 49; see also the discussion on p. 74 about the last term in this equation.

[11] A Sommefeld, *Mechanics of Deformable Bodies* (Academic Press, New York, 1964), p. 72. The expression in this page gives the energy in terms of the product of the strain and stress tensors. The formula in Eq. (16) is obtained from the relationship between the stress and the strain for an elastic solid, namely the converse of Hooke's law.

[12] The derivation of the charge density operator, the bare electron and bare phonon Hamiltonians can be found in books on many-body theory, such as, A L Fetter and J D Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971); G D Mahan, *Many-Particle Physics, 3rd Edition* (Kluwer Academic/Plenum Publishers, New York, 2000); S Raimes, *Many-Electron Theory* (North-Holland, Amsterdam, 1972); P L Taylor, *A Quantum Approach to the Solid State* (Prentice Hall, Englewood Cliffs, New Jersey, 1970).

[13] H Fröhlich, *Advances in Physics* **3**, 325 (1954).

[14] J R Schrieffer, *Theory of Superconductivity* (Westview Press, Boulder, Colorado, 1999), p. 95.

[15] F Bassani, J Robinson, B Goodman and J R Schrieffer, *Physical Review* **127**, 1969 (1962).

[16] G D Mahan, "Polarons in Heavily Doped Semiconductors," in *Polarons in Ionic Crystals and Polar Semiconductors, edited by J T Devreese* (North-Holand, Amsterdam, 1972), p. 553.

[17] For a proof of this expression see C Kittel, *Quantum Theory of Solids* (John Wiley & Sons, New York, 1963), Chapters 2 and 7. This can also be seen as follows. Because a phonon is a periodic vibration, the displacement vector generated by a phonon with wave vector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$ will be such that $\mathbf{D} \propto e^{i\mathbf{q}\cdot\mathbf{r} - i\omega_{\mathbf{q}}t}$. Then the divergence of this vector is $i\mathbf{q}\cdot\mathbf{D}$.

[18] Reference 4, p. 11.

[19] J F Nye, *Physical Properties of Crystals* (Oxford University Press, Oxford, 1969), p. 110.
[20] Reference 19, p. 129.
[21] Reference 19, p. 191.