Der im Grenzübergang $F \to \infty$, $\gamma \to 0$ wegfallende Term ist ein direktes Maß für die Abweichung der Magnetisierung dünner Schichten von der des kompakten Materials. Diese Abweichung kann man merkwürdigerweise nicht als linearen Oberflächeneffekt deuten. Denn ein solcher würde einen Verlauf $\sim 1/F$ zeigen, während die Abweichung in (57 b) mit $F \to \infty$ schwächer gegen Null strebt als $1/F$.

Anhang II

Eine Monotonieeigenschaft der Magnetisierung

Abschließend soll noch auf eine Monotonieeigenschaft der Magnetisierung und auf ihre Konsequenzen für die durchgeführten Rechnungen hingewiesen werden.

Ersetzt man nämlich in (33) das Spektrum $\{E\}$ der Einspinwellenzustände durch ein anderes $\{E'\}$, für dessen Eigenwerte die Beziehung

$$E_\nu' \geqq E_\nu \quad \text{für alle } \nu \tag{61}$$

gelten soll, so ist auch $M'(T) \geqq M(T)$; die Magnetisierung ist also monoton „mit dem Spektrum“.

Die in Abschnitt III durchgeführten Näherungen für die Eigenwerte kommen nun gerade einer solchen Ersetzung des wahren Spektrums durch ein approximiertes gleich und für diese Ersetzung gilt (61). Denn sowohl $\Gamma_0{}^\lambda$ als auch e^ϱ ist überall größer als seine Schmiegungsparabel, durch die wir die $\boldsymbol{\lambda}$-Abhängigkeit der Eigenwerte erfaßten, und demzufolge liegen die quadratisch genäherten Energien über den exakt errechneten. Das gilt auch für die Approximationen für s_ν bzw. t_ν. Somit stellen die Formeln (57) — ebenso wie das Blochsche $T^{3/2}$-Gesetz für das kompakte Material — eine obere Grenze der Magnetisierungen dar, die sich bei Verwendung der wahren Eigenwerte in (33) ergeben würden.

Piezoelectric Polaron Effects in Regular Crystals

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Due to the interaction of an electron with both optical and acoustical modes in piezoelectric polar crystals, modified expressions for the self-energy and effective mass of the polaron are to be expected. The lattice vibrations are considered in the limit of large wave-length and an electrostatic approach to the interaction of charges in the lattice has been used. The Hamiltonian for a piezoelectric crystal of arbitrary lattice structure is given. With special reference to crystals of zincblende-type, approximate solutions for the self-energy and effective mass are found by thermodynamical pertubation theory. A numerical estimate for ZnS as a particularly favourable example, shows a negligible modification of the ground-state energy, but concerning the effective mass a contribution due to acoustical phonons of more than 50% of the optical-mode term.

In considering the interaction of electrons with the vibrating lattices of ionic crystals earlier investigations were restricted to the case of an electron within an isotropic polarizable medium. Then, in the limit of long waves, the electron strongly interacts with the optical modes only and we now know that for the behaviour of the resulting polaron the longitudinal optical mode is of particular importance. Looking upon the problem from the viewpoint of lattice dynamics of anisotropic crystals (or if we like an anisotropic polarizable continuum) it is evident, that such a simple treatment must break down in crystals without a centre of symmetry or with polar axes. It is the purpose of this note to extend the theory of polarons to such piezoelectric crystals. We start from the exact equations of motion for lattice waves of large wave-length and the Maxwell equations for the macroscopic electromagnetic fields within the crystals and write down the corresponding Hamiltonian. Because of the coupling between the displacements of the ions relative to each other and the displacement of the centre-of-gravity of each lattice cell established by a 3rd rank tensor (which is connected with the piezoelectric tensor) the acoustical vibrations can no longer be separated from the interaction Hamiltonian. In other words, the field of acoustical phonons cannot be considered as a conservative subsystem and therefore suppressed as in the usual treatment of the polaron problem.

Some simplifying assumptions will be introduced during the presented work, (1) only a slowly-moving electron will be considered, so that an electrostatic approach may be a good approximation; (2) we specialize to the simplest piezoelectric crystal with only one nonvanishing piezoelectric constant (zincblende structure). Even in this case the secular equation determining the frequency spectrum cannot be solved exactly except for some special directions of wave vector for the lattice vibrations. To arrive at some at least preliminary results we must consider the elastic vibrations of the solid as approximately isotropic. By perturbation theory we calculate expressions for the modified self energy and effective mass of the polaron due to the interaction with the acoustical phonons. We hope that some future work will be presented concerning the electrical conductivity or mobility of the piezoelectric polaron problem.

I. The Basic Equations

A detailed discussion of the lattice dynamics of ionic crystals can be found in the standard textbook by Born–Huang[1] and the article by Leibfried[2]. From the latter (pag. 214, formulae 68.1 – 68.4) the following set of equations is taken

$$\varrho \ddot{s}_i = \tilde{C}_{ik,mn}\, s_{k|mn} + \sum_\nu \tilde{C}^{\nu}_{ikm}\, u^{\nu}_{k|m}\,, \tag{1}$$

$$\varrho_\mu \ddot{u}_i^\mu = \sum_\nu \tilde{C}^{\mu\nu}_{ik}\, u^\nu_k - \tilde{C}^{\mu}_{kim}\, s_{k|m} + (\varrho^\mu_{\rm el}\,\delta_{ik} + b^\mu_{ik})\, E_k\,, \tag{2}$$

$$\operatorname{rot} \boldsymbol{H} = \frac{4\pi}{c}\dot{\boldsymbol{P}} + \frac{1}{c}\dot{\boldsymbol{E}} + \frac{4\pi e}{c}\boldsymbol{v}\,\delta(\boldsymbol{r}-\boldsymbol{r}_{\rm el})\,, \tag{3}$$

$$\operatorname{rot} \boldsymbol{E} = -\frac{1}{c}\dot{\boldsymbol{H}}\,, \tag{4}$$

$$\operatorname{div}(\boldsymbol{E} + 4\pi \boldsymbol{P}) = 4\pi e\,\delta(\boldsymbol{r}-\boldsymbol{r}_{\rm el})\,;\quad \operatorname{div}\boldsymbol{H} = 0\,, \tag{5}$$

$$P_i = \sum_\nu (b^\nu_{ik} + \varrho^\nu_{\rm el}\,\delta_{ik})\, u^\nu_k + r_{ik}\, E_k\,, \tag{6}$$

$$\varrho_\mu = M_\mu/V_z\,;\qquad \varrho^\mu_{\rm el} = Z\, e_\mu/V_z\,, \tag{7}$$

where the contribution of an extra electron (a point charge e) moving in the medium with constant velocity $\boldsymbol{v}$ is taken into account. For our purpose it is unnecessary to define the coupling coefficients $\tilde{C}_{ik,mn}$, $\tilde{C}^{\nu}_{ikm}$ etc. from the frequency dependent dynamical matrices occuring in lattice dynamics. At a later stage of the work we will eliminate these coefficients by comparison with appropriate phenomenological equations. Thus the final expressions will only contain well-defined physical quantities, the values of which may be taken from experiments. It will therefore be sufficient to explain the notation, which is exactly Leibfried's and to point out some slight differences compared with this author's treatment. Latin indices $i, k, l, \ldots = 1, 2, 3$ refer to cartesian coordinate axes. We use the summation convention with respect to the latin indices but not with respect to the greek indices, which denumerate the number of atoms contained in a lattice cell. The ions have masses M_μ, and charges $Z\, e_\mu$. V_z, ϱ stand for the cell volume and density of the crystal respectively. The equations of motion (1) and (2) arise from the one equation for the displacement vector s_i^μ by decomposing the latter into

$$s_i^\mu = s_i + u_i^\mu \quad \text{with} \quad \sum_\nu \varrho_\nu\, s_i^\nu = \varrho\, s_i\,;\quad \sum_\nu \varrho_\nu\, u_i^\nu = 0\,. \tag{8}$$

u_i^μ are the displacements of the several ions relative to the centre-of-gravity of a lattice cell, whose displacement vector is denoted by s_i. The s_i's correspond to the field of elastic displacements in the longwave limit. According to the continuum approximation both u_i^ν and s_i are functions of position $\boldsymbol{x}$. We use the abbreviation $s_{i|mn} \equiv \partial^2 s_i/\partial x_m\, \partial x_n$ etc. for spatial derivatives.

If electronic polarization is taken into account we arrive at eq. (6), thus extending eq. 68.3 of ref. [2], where only the polarization due to the displacements of ions relative to each other is considered. The first mentioned effect manifests itself in a modification of the ion displacement represented by terms $b^\mu_{ik}\, u^\mu_k$ and a term $r_{ik}\, E_k$ explicitly dependent on the macroscopic electric field (see ref. [1], § 35). Moreover there is a modification of the coupling coefficients, which we imagine to be included in the definition of these tensors. The coupling tensors $\tilde{C}^{\mu\nu}_{ik}$ etc. obey some usual symmetry relations (pag. 194, 195 of ref. [2]). For the coefficients b^μ_{ik}, r_{ik} we have

$$\sum_\nu b^\nu_{ik} = 0\,;\quad r_{ki} = r_{ik}\,. \tag{9}$$

Introducing the scalar and vector potential

$$\boldsymbol{E} = -(1/c)\,\dot{\boldsymbol{A}} - \operatorname{grad}\varphi\,,\qquad \boldsymbol{H} = \operatorname{rot}\boldsymbol{A}$$

resp. together with the Coulomb gauge $\operatorname{div}\boldsymbol{A} = 0$, the following set of equations can be derived from the Lagrangian density

$$\begin{aligned}\mathcal{L} = {} & \left(\frac{m^*}{2}v^2 + \frac{e}{c}\boldsymbol{A}\cdot\boldsymbol{v} - e\,\varphi\right)\delta(\boldsymbol{r}-\boldsymbol{r}_{\rm el}) \\ & + \frac{1}{8\pi}(\delta_{ik} + 4\pi\, r_{ik})\left(\frac{1}{c}\dot{A}_i + \frac{\partial\varphi}{\partial x_i}\right)\left(\frac{1}{c}\dot{A}_k + \frac{\partial\varphi}{\partial x_k}\right) \\ & - \frac{1}{8\pi}(\operatorname{rot}\boldsymbol{A})^2 - \sum_\nu (\varrho^\nu_{\rm el}\,\delta_{ik} + b^\nu_{ik})\, u^\nu_k\left(\frac{1}{c}\dot{A}_i + \frac{\partial\varphi}{\partial x_i}\right) \\ & + \frac{\varrho}{2}\dot{s}_i\,\dot{s}_i + \frac{1}{2}\sum_\nu \varrho_\nu\,\dot{u}^\nu_i\,\dot{u}^\nu_i + \frac{1}{2}\sum_{\mu,\nu}\tilde{C}^{\mu\nu}_{ik}\, u^\mu_i\, u^\nu_k \\ & - \frac{1}{2}\tilde{C}_{ik,mn}\, s_{i|m}\, s_{k|n} - \sum_\nu \tilde{C}^{\nu}_{ikm}\, u^\nu_k\, s_{i|m}\,.\end{aligned} \tag{10}$$

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[1] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Clarendon Press, Oxford 1962.

[2] G. Leibfried, Encyclopedia of Physics VII, 1, Springer-Verlag, Berlin 1955.

Writing down the EULER–LAGRANGE equations to deduce the MAXWELL equations and the dynamical equations for the lattice vibrations, we regard that the polarization vector (6) couples the field quantities $\boldsymbol{A}$, φ and u_i^μ. With the help of the conjugate momenta

$$\partial\mathcal{L}/\partial\dot{x}_i^{\text{el}} = m^*\,v_i + (e/c)\,A_i\,,$$
$$\partial\mathcal{L}/\partial\dot{u}_i^\mu = \varrho_\mu\,\dot{u}_i^\mu,$$
$$\partial\mathcal{L}/\partial\dot{s}_i = \varrho\,\dot{s}_i\,,$$
$$\frac{\partial\mathcal{L}}{\partial\dot{A}_i} = \frac{1}{4\,\pi\,c}\,(\delta_{ik} + 4\,\pi\,r_{ik})\,\left(\frac{1}{c}\,\dot{A}_k + \frac{\partial\varphi}{\partial x_k}\right) - \sum_\nu\,(\varrho_{\text{el}}^\nu\,\delta_{ik} + b_{ik}^\nu)\,\frac{1}{c}\,u_k^\nu$$

we can easily calculate the HAMILTONian density. Using (5) and the fact that divergences may be omitted from the HAMILTONian, we find the following expression most convenient for the subsequent considerations

$$\mathcal{H} = \frac{m^*}{2}\,v^2\,\delta(\boldsymbol{r} - \boldsymbol{r}_{\text{el}}) + \frac{1}{8\,\pi}\,(\delta_{ik} + 4\,\pi\,r_{ik})\,E_i\,E_k + \frac{1}{8\,\pi}\,\boldsymbol{H}^2 + \frac{1}{2}\sum_\nu \varrho_\nu\,\dot{u}_i^\nu\,\dot{u}_i^\nu - \frac{1}{2}\sum_{\mu,\nu}\tilde{C}_{ik}^{\mu\nu}\,u_i^\mu\,u_k^\nu + \sum_\nu \tilde{C}_{ikm}^{\nu}\,u_k^\nu\,s_{i|m} + \frac{\varrho}{2}\,\dot{s}_i\,\dot{s}_i + \frac{1}{2}\,\tilde{C}_{ik,\,mn}\,s_{i|m}\,s_{k|n}\,. \tag{11}$$

II. Specialization of the Bacic Equation to the Case of Cubic Symmetry

For convenience from now let us consider the simplest crystal structure $\bar{4}3\text{m}$ showing a piezoelectric effect determined by only one piezoelectric constant. Furthermore we assume that only two ions (or at least two aggregates of atoms) are contained in a lattice cell.

We recall that the total symmetrical tensor of 2nd rank is a scalar in cubic crystals, e. g. $r_{ik} = r\,\delta_{ik}$ and that a tensor of 4th rank obeying the relations

$$\tilde{C}_{ik,\,mn} = \tilde{C}_{ik,\,nm} = \tilde{C}_{ki,\,nm} = \tilde{C}_{mn,\,ik}\,,$$

has three independent components as is well-known from the theory of elasticity. Using (9), which means $b_{ik}^1 = -\,b_{ik}^2$ in our special case, a simple symmetry consideration shows that

$$b_{ik}^1 = -\,b\,\delta_{ik}$$

for a crystal of ZnS-structure. Similarly, by combining the general relations mentioned above

$$\tilde{C}_{ik}^{\mu\nu} = \tilde{C}_{ki}^{\nu\mu}\,;\ \sum_\nu \tilde{C}_{ik}^{\mu\nu} = 0\,,$$

$$C_{ikm}^{\nu} = -\,C_{kim}^{\nu} = \tilde{C}_{mki}^{\nu}\,;\ \sum_\nu \tilde{C}_{ikm}^{\nu} = 0$$

with appropriate symmetry operations of the group $\bar{4}3\text{m}$, we find

$$\tilde{C}_{ik}^{12} = \tilde{C}_{ik}^{21} = C_0\,\delta_{ik}$$

and $$\tilde{C}_{123}^{\,1} = \tilde{C}_{132}^{\,1} = \ldots = -\,C_{123}^{\,2} = C_1 \neq 0$$

for all permutations of the numbers 1, 2, 3 and zero otherwise. The last result is naturally the same as can be found for the piezoelectric tensor in ZnS-crystals.

Introducing the relative displacement

$$w_i = u_i^{\,2} - u_i^{\,1}$$

and the reduced mass

$$\overline{M} = \frac{M_1\,M_2}{M_1 + M_2} \quad \text{and} \quad \bar{\varrho} = \frac{\overline{M}}{V_z}$$

the HAMILTONian density writes

$$\mathcal{H} = \tfrac{1}{2}\,m^*\,v^2\,\delta(\boldsymbol{r} - \boldsymbol{r}_{\text{el}}) + \frac{1}{8\,\pi}\,(1 + 4\,\pi\,r)\,\mathbf{E}^2 + \frac{1}{8\,\pi}\,\boldsymbol{H}^2 + \tfrac{1}{2}\,\bar{\varrho}\,\dot{\boldsymbol{w}}^2 + \tfrac{1}{2}\,C_0\,\boldsymbol{w}^2 - 2\,C_1\,\boldsymbol{w}\cdot\boldsymbol{\epsilon} + \tfrac{1}{2}\,\varrho\,\dot{\mathbf{s}}^2 + \tfrac{1}{2}\,C_{ik,\,mn}\,s_{i|m}\,s_{k|n}\,, \tag{12}$$

where we have defined a quantity $\boldsymbol{\epsilon}$ by

$$\boldsymbol{\epsilon} = \tfrac{1}{2}\,[s_{2|3} + s_{3|2}\,,\ \ s_{3|1} + s_{1|3}\,,\ \ s_{1|2} + s_{2|1}]\,.$$

The term $-\,2\,C_1\,\boldsymbol{w}\cdot\boldsymbol{\epsilon}$ couples the elastic vibrations to the field of the relative displacements, thus preventing the omission of acoustical phonons from our HAMILTONian. This term gives modifications of the polaron properties due to the interaction with the acoustical branches.

Writing down the polarization vector

$$\boldsymbol{P} = \left(\frac{Z\,e}{V_z} + b\right)\boldsymbol{w} + r\,\mathbf{E} \tag{13}$$

and the equation of motion

$$\bar{\varrho}\,\ddot{w}_i = -\,C_0\,w_i + \tilde{C}_{kim}^{\,1}\,s_{k|m} + \left(\frac{Z\,e}{V_z} + b\right)E_i \tag{14}$$

we can follow the arguments of HUANG[1], which lead to

$$r = (\varepsilon_\infty - 1)/4\,\pi$$

for high frequencies ($\boldsymbol{w} = 0$), and to

$$C_0\,w_i = \tilde{C}_{kim}^{\,1}\,s_{k|m} + \left(\frac{Z\,e}{V_z} + b\right)E_i \tag{15}$$

under static conditions ($\ddot{w} = 0$). Substituting the last equation in (13) we find by comparison with the phenomenological relation

$$P_l = e_{l,\,km}\, s_{k\,|\,m} + a_{ls}\, E_s$$

the expressions

$$e_{14} \equiv e_{1,\,23} = \left(\frac{Z\,e}{V_z} + b\right) \frac{C_1}{C_0}\,, \tag{16}$$

$$\frac{\varepsilon_0 - \varepsilon_\infty}{4\,\pi} = \frac{1}{C_0} \left(\frac{Z\,e}{V_z} + b\right)^2 \tag{17}$$

for the piezoelectric tensor and the dielectric susceptibility $a_{ls} = (1/4\,\pi)\,(\varepsilon_{ls} - \delta_{ls})$. The usual procedure now consists in eliminating the term proportional to $w_{k\,|\,l}$ in the equations of motion (1) and comparing the resulting equations with the elastic equations for piezoelectric crystals. We will not enter into a further discussion of this point.

We now make use of the assumption already mentioned in the introduction. We neglect retardation effects, so that the Maxwell equations reduce to

$$\operatorname{div}(\boldsymbol{E} + 4\,\pi\,\boldsymbol{P}) = 4\,\pi\,e\,\delta(\boldsymbol{r} - \boldsymbol{r}_{\text{el}})\,; \quad \operatorname{rot} \boldsymbol{E} = 0\,, \tag{18}$$

which have the solution

$$\boldsymbol{E} = -\frac{1}{\varepsilon_\infty} \left\{ \operatorname{grad} \frac{e}{|\,r - r_{\text{el}}\,|} + 4\,\pi \left(\frac{Z\,e}{V_z} + b\right) \boldsymbol{w}_l \right\}. \tag{19}$$

By $\boldsymbol{w}_l$ we denote the irrotational part of $\boldsymbol{w}$.

Substituting the trial solutions

$$\boldsymbol{E} = \boldsymbol{E}_0 \quad \exp\{i(\boldsymbol{q} \cdot \boldsymbol{r} - \omega\,t)\}\,,$$
$$\boldsymbol{s} = \boldsymbol{e}(1) \exp\{i(\boldsymbol{q} \cdot \boldsymbol{r} - \omega\,t)\}\,,$$
$$\boldsymbol{w} = \boldsymbol{e}(2) \exp\{i(\boldsymbol{q} \cdot \boldsymbol{r} - \omega\,t)\}\,,$$

the system of equations (14), (18), and (1) reduces to the following

$$\omega^2\, e_i(1) = A_{ik}\, e_k(1) + B_{ik}\, e_k(2)\,, \tag{20 a}$$

$$\omega^2\, e_i(2) = \bar{C}_0\, e_i(2) - B_{ik}\, e_k(1) + R_{ik}\, e_k(2)\,. \tag{20 b}$$

In determining the vibration spectrum of the crystal, we may neglect the electric field due to the point charge and we have introduced the following abbreviations

$$A_{ik} = \frac{1}{\varrho}\, \tilde{C}_{ik,\,mn}\, q_m\, q_n \equiv \begin{bmatrix} A_1\, q_1^2 + A_2(q_2^2 + q_3^2) & A_3\, q_1\, q_2 & A_3\, q_1\, q_3 \\ A_3\, q_1\, q_2 & A_1\, q_2^2 + A_2(q_1^2 + q_3^2) & A_3\, q_2\, q_3 \\ A_3\, q_1\, q_3 & A_3\, q_2\, q_3 & A_1\, q_3^2 + A_2(q_1^2 + q_2^2) \end{bmatrix},$$

$$B_{ik} = \frac{i}{\sqrt{\varrho\,\bar{\varrho}}}\, \tilde{C}^{\,1}_{123} \begin{pmatrix} 0 & q_3 & q_2 \\ q_3 & 0 & q_1 \\ q_2 & q_1 & 0 \end{pmatrix}, \tag{21}$$

$$R_{ik} = \frac{4\,\pi(Z\,e/V_z + b)^2}{\bar{\varrho}(1 + 4\,\pi\,r)} \cdot \frac{q_i\, q_k}{q^2} \qquad \bar{C}_0 = \frac{1}{\bar{\varrho}}\, C_0\,.$$

For a later discussion it is useful to define the hypothetical frequencies

$$\omega_{0\text{t}} = \sqrt{\bar{C}_0} \quad \text{and} \quad \omega_{0\text{l}} = \omega_{0\text{t}} \sqrt{\varepsilon_0/\varepsilon_\infty} \tag{22}$$

as eigenvalues of (20 b), if the terms $B_{ik}\, e_k$ vanish.

For each of the six solutions $\omega^2_{q\sigma}$ ($\sigma = 1, 2, \ldots, 6$) of the secular determinant (20) yields a set of eigenvectors $e_i(\mu\,|\,{}^{q}_{\sigma})$ ($\mu = 1, 2$) which can be chosen such that

$$\sum_{u=1}^{2} e_i^*(\mu\,|\,{}^{\boldsymbol{q}}_{\sigma})\; e_i(\mu\,|\,{}^{\boldsymbol{q}}_{\sigma'}) = \delta_{\sigma\sigma'}\,,$$

$$\sum_{\sigma=1}^{6} e_i^*(\mu\,|\,{}^{\boldsymbol{q}}_{\sigma})\; e_l(\nu\,|\,{}^{\boldsymbol{q}}_{\sigma}) = \delta_{il}\, \delta_{\mu\nu}. \tag{23}$$

There exist only o few special values for the wave vector $\boldsymbol{q}$, where the exact solutions of the secular equations can be found. In general the tensor B_{ik}, which is responsible for the piezoelectric properties of the crystal causes the total eigenvector to be a 6-dimensional quantity for each fixed pair of values $\boldsymbol{q}$ and σ.

If detailed knowledge of the phonon polarizations is needed (as in our problem), one must try to solve the system (20) approximately (see Appendix).

Transforming to normal coordinates by the expansion

$$s_i = \sum_{\boldsymbol{q},\,\sigma} e_i(1\,|\,{}^{\boldsymbol{q}}_{\sigma})\; a_{\boldsymbol{q}\sigma} \cdot \frac{e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{\sqrt{\varrho\,V}}\,,$$

(periodic boundary conditions!)

$$w_i = \sum_{\boldsymbol{q},\,\sigma} e_i(2\,|\,{}^{\boldsymbol{q}}_{\sigma})\; a_{\boldsymbol{q}\sigma} \cdot \frac{e^{i\boldsymbol{r}\cdot\boldsymbol{q}}}{\sqrt{\bar{\varrho}\,V}}\,, \tag{24}$$

a straightforward calculation gives the following expressions for the Hamiltonian

$$H = \int \mathcal{H}\, \mathrm{d}\tau = \frac{m^*}{2}\, v^2 + \tfrac{1}{2} \sum_{\boldsymbol{q},\,\sigma} (\dot{a}^*_{\boldsymbol{q}\sigma}\, \dot{a}_{\boldsymbol{q}\sigma} + \omega^2_{\boldsymbol{q}\sigma}\, a^*_{\boldsymbol{q}\sigma}\, a_{\boldsymbol{q}\sigma})$$
$$- \frac{4\,\pi\,i\,e(b + Z\,e/V_z)}{\sqrt{\bar{\varrho}}\, V(1 + 4\,\pi\,r)} \sum_{\boldsymbol{q},\,\sigma} \frac{\boldsymbol{q} \cdot \boldsymbol{e}\,(2\,|\,{}^{\sigma}_{\boldsymbol{q}})}{q^2}\, a_{\boldsymbol{q}\sigma} \exp\{i\,\boldsymbol{q} \cdot \boldsymbol{r}_{\text{el}}\}\,.$$

The integration is over the periodicity volume of the crystal. Imposing the condition

$$\boldsymbol{e}^*(\mu\,|\,{}^{\boldsymbol{q}}_{\sigma}) = -\,\boldsymbol{e}(\mu\,|\,{}^{-\boldsymbol{q}}_{\sigma})$$

to the eigenvectors, we must have

$$a^*_{\boldsymbol{q}\sigma} = -\,a_{-\boldsymbol{q}\sigma}$$

to ensure reality of the expansions (24).

III. The Quantum-Mechanical Problem. Discussion of the Modified Hamiltonian

As usual we introduce normal coordinates $b_{\boldsymbol{q}\sigma}$ by defining

$$a_{\boldsymbol{q}\sigma} = \sqrt{\tfrac{1}{2}\hbar/\omega_{\boldsymbol{q}\sigma}}\,\{b_{\boldsymbol{q}\sigma} - b^*_{-\boldsymbol{q}\sigma}\}\,,$$
$$i\,\dot{a}_{\boldsymbol{q}\sigma} = \sqrt{\tfrac{1}{2}\hbar\cdot\omega_{\boldsymbol{q}\sigma}}\,\{b_{\boldsymbol{q}\sigma} + b^*_{-\boldsymbol{q}\sigma}\}$$

and then change to the quantum case by imposing boson commutation relations for the creation and destructive operators $b^+_{\boldsymbol{q}\sigma}$ and $b_{\boldsymbol{q}\sigma}$ resp. The term $\frac{1}{2}\,m^*\,v^2$ converts to the operator of the kinetic energy for a crsytal electrons in the effective mass approximation. Neglecting the zero-point energy of the field we finally arrive at

$$\begin{aligned}\hat{H} = -\frac{\hbar^2}{2\,m^*}\,\triangle + \sum_{\boldsymbol{q},\sigma} \hbar\,\omega_{\,\boldsymbol{q}\sigma} b^+_{\boldsymbol{q}\sigma} b_{\boldsymbol{q}\sigma} \\ + \sum_{\boldsymbol{q},\sigma}\{V_{\boldsymbol{q}\sigma}\,b_{\boldsymbol{q}\tau}\,e^{i\,\boldsymbol{q}\cdot\boldsymbol{r}} + V^+_{\boldsymbol{q}\sigma}\,b^+_{\boldsymbol{q}\sigma}\,e^{-i\,\boldsymbol{q}\cdot\boldsymbol{r}}\}\end{aligned} \tag{25}$$

with

$$V_{\boldsymbol{q}\sigma} = -4\,\pi\,i\sqrt{\frac{e^2\,\hbar}{2\,\gamma\,V\,\omega_{\boldsymbol{q}\sigma}}}\cdot\frac{\boldsymbol{q}\cdot\boldsymbol{e}\,(2\,|\,{}^{\boldsymbol{q}}_{\sigma})}{q^2}\,, \tag{26}$$

$$\frac{1}{\gamma} = \frac{\omega^2_{0l}}{4\,\pi}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right). \tag{27}$$

It is easy to show that (25) translates to the HAMILTONian of the optical polaron in the limit of a vanishing piezoelectric effect. In this case the eigenvectors $\boldsymbol{e}(2\,|\,{}^{\boldsymbol{q}}_{\sigma})$ do not contain any admixture from the acoustical branches. That is, the 6-dimensional vector space for the eigensolutions of (20) mentioned in II, decomposes into two 3-dimensional orthogonal subspaces. If we denote the three acoustical branches by $\sigma = 1, 2, 3$, we have $\boldsymbol{e}(2\,|\,{}^{\boldsymbol{q}}_{1,2,3}) \equiv 0$ and according to (20 b) (with $B_{ik} = 0$) there exist true longitudinal and transversal optical vibrations in this case. The resulting expression

$$V^{\text{opt.}}_{\boldsymbol{q},\,\text{long}} = -4\,\pi\,i\sqrt{\frac{e^2\,\hbar}{2\,\gamma\,V\,\omega_{\boldsymbol{q}l}}}\cdot\frac{1}{q} \tag{28}$$

completely agrees with the known result for the optical polaron, if the dispersion of the longitudinal optical mode is ignored.

The preceding remark can serve as starting point for a general discusion of the interaction term. The matrix element $V_{\boldsymbol{q}\sigma}$ contains the scalar product $\boldsymbol{q}\cdot\boldsymbol{e}(2\,|\,{}^{\boldsymbol{q}}_{\sigma})$. Due to the piezoelectric coupling of eqs. (20 a) and (20 b), it will generally not be true that only the longitudinal modes interact with the electron. Without solving the eqs. (20) it cannot be decided how large the several contributions will be.

Whereas it will yet be a good approximation to ignore the dispersion of the optical modes ($\sigma = 4, 5, 6$), the relation $\omega_{\boldsymbol{q}\sigma} \sim q$ ($\sigma = 1, 2, 3$) valid for small q has to be regarded for the acoustical phonons. Thus the interaction HAMILTONian splits into two characteristic terms, distinguishable by different $\boldsymbol{q}$-dependence. In addition to a term of type (28), there is one which is proportional to $q^{-1/2}$. The latter is in contrast, for example, to deformation potential coupling where $V_{\boldsymbol{q}} \sim q^{1/2}$.

IV. Self-Energy and Effective Mass of the Modified Polaron

As a simple application we have calculated the self energy and effective mass of the polaron using a thermodynamical second-order perturbation theory as has been done by KRIVOGLAZ and PEKAR [3] and OSAKA [4] (the latter using the FEYNMAN approach). We thus avoid some trouble due to the degeneracy of the unperturbed eigenstates of the total electron-phonon system, if acoustical phonons are taken into account.

The first nonvanishing correction to the partition function $Z = Z^{(0)} + Z^{(2)}$ is given by [3]

$$Z^{(2)} = \frac{\beta^2}{2}\,Z^{(0)}\sum_{\boldsymbol{q},\sigma}|\,V_{\boldsymbol{q}\sigma}|^2\int_0^1 \mathrm{d}v\,\exp\left\{-\beta\,\frac{\hbar^2\,q^2}{8\,m^*}\,(1-v^2)\right\}\frac{\cosh(\frac{1}{2}\,\beta\,\hbar\,\omega_{\boldsymbol{q}\sigma}v)}{\sinh(\frac{1}{2}\,\beta\,\hbar\,\omega_{\boldsymbol{q}\sigma})}\,, \tag{29}$$

where $Z^{(0)}$ is the partition function of the entire noninteracting system and $\beta = 1/k_{\text{B}}\,T$.

Assuming that at very low temperatures no internal degrees of freedom are excited and that the polaron energy spectrum of small total momentum $\boldsymbol{p}$ has the form

$$E(\boldsymbol{p}) = \varepsilon_0 + \varepsilon_2\,p^2 + \varepsilon_4\,p^4 + \dots\,; \qquad \varepsilon_2 = 1/2\,m_{\text{eff}}\,, \tag{30}$$

[3] M. A. KRIVOGLAZ and S. J. PEKAR, see Fortschr. d. Physik, 4. Sonderband, Akademie-Verlag, Berlin 1961.

[4] Y. OSAKA, Progr. Theor. Phys. **22**, 437 [1959].

we may calculate the corresponding partition function. We then identify various powers of β with the low-temperature expansion of (29), thus finding out expressions for the ground-state energy and the effective mass m_{eff}.

At very low temperatures we have $\beta \hbar \omega_{\boldsymbol{q}}^{\text{opt.}} \gg 1$ for optical vibrations and $\beta \hbar \omega_{\text{m}}^{\text{acoust.}} \gg 1$ (with respect to the DEBYE frequency ω_{m}) for the acoustical modes. Changing the sum over $\boldsymbol{q}$ into an integral over the first BRILLOUIN zone in (29), the upper limit may be taken as ∞ for the optical branches, but must be set equal to q_{m} for the acoustical vibrations, because otherwise the integral diverges. The low-temperature expansion of (29) yields

$$\begin{aligned} Z^{(2)} &= Z^{(2)}_{\text{opt.}} + Z^{(2)}_{\text{acoust.}} \\ &= Z^{(0)} \frac{\beta m^* V}{4 \pi^3 \hbar^2} \int\limits_0^{2\pi} \mathrm{d}\varphi \int\limits_0^{\pi} \sin\vartheta \, \mathrm{d}\vartheta \left[\int\limits_0^{\infty} q^2 \, \mathrm{d}q \sum_{\sigma=4}^{6} |V_{\boldsymbol{q}\sigma}|^2 \frac{1}{(q^2 + 2 m^* \omega_{\boldsymbol{q}\sigma}/\hbar)} \cdot \left\{ 1 + \frac{4 m^* q^2}{\beta \hbar^2 (q^2 + 2 m^* \omega_{\boldsymbol{q}\sigma}/\hbar)^2} \right\} \right. \\ &\qquad \left. + \int\limits_0^{q_{\text{m}}} q \, \mathrm{d}q \sum_{\sigma=1}^{3} |V_{\boldsymbol{q}\sigma}|^2 \frac{1}{(q + 2 m^* \omega_{\boldsymbol{q}\sigma}/\hbar q)} \cdot \left\{ 1 + \frac{4 m^*}{(q + 2 m^* \omega_{\boldsymbol{q}\sigma}/\hbar q)^2} \right\} \right], \end{aligned} \tag{31}$$

if an approximate v-integration is performed in (29).

In the appendix we have derived explicit expressions for the quantities $|V_{q\sigma}|^2$ under the following assumptions: (1) The piezoelectric coupling of equations (20) is small, so that the eigenfrequencies and eigenvectors may be calculated by perturbation theory. (2) The crystal will be considered as elastically isotropic. The latter assumption will not make any serious error in the order of magnitude of the effect we are going to estimate.

According to (A 9) the first sum on the right hand side of (31) reduces to only one term. For a constant longitudinal-optical frequency $\omega_{0\text{l}}$ (belonging to $q=0$) the resulting contribution $Z^{(2)}_{\text{opt.}}$ to $Z^{(2)}$ is equal to the known expression given in the equations (26) – (31) of ref. [3]. Using $\omega_{q\text{l},\text{t}} = c_{\text{l},\text{t}}\, q$, the abbreviation $q_{\text{l},\text{t}} = 2 m^* c_{\text{l},\text{t}}/\hbar$ ($c_{\text{l},\text{t}}$ the longitudinal and transverse velocity of sound respectively) and (A 12), it is easy to evaluate the contribution $Z^{(2)}_{\text{acoust.}}$:

$$\begin{aligned} Z^{(2)}_{\text{acoust.}} = \beta \frac{8 \pi m^* (4 e e_{14})^2 \omega_{\text{ot}}^2}{5 \gamma \hbar \omega_{\text{ol}}^4 \varrho (\varepsilon_0 - \varepsilon_\infty)} \cdot \left[\frac{4}{7 c_{\text{t}}} \left\{ \ln\left(\frac{q_{\text{m}} + q_{\text{t}}}{q_{\text{t}}}\right) + \frac{4 m^*}{\beta \hbar^2} \left[\frac{1}{q_{\text{t}}^2} - \frac{1}{(q_{\text{m}} + q_{\text{t}})^2} \right] \right\} \right. \\ \left. + \frac{3}{7 c_{\text{l}}} \left\{ \ln\left(\frac{q_{\text{m}} + q_{\text{l}}}{q_{\text{l}}}\right) + \frac{4 m^*}{\beta \hbar^2} \left[\frac{1}{q_{\text{l}}^2} - \frac{1}{(q_{\text{m}} + q_{\text{l}})^2} \right] \right\} \right]. \end{aligned} \tag{32}$$

For small q we can neglect ${}^{0}\omega_{q\text{t,l}}^2$ compared with ω_{ol}^2 in the denominators of (A 12). This leads immediately to the common factor ω_{ol}^{-4} in (32). The cofactor in (32) can be simplified considerably, if we substitute γ from (27) and use the relation (22).

The mean thermal energy $\bar{E}$ is given by
$$\bar{E} = -\frac{\partial \ln Z^{(0)}}{\partial \beta} - \frac{\partial Z^{(2)}}{\partial \beta}, \tag{33}$$

which reduces to

$$\bar{E}_0 = E_0^{(0)} - \alpha \hbar \omega_{0\text{l}} - \frac{2 (4 e e_{14})^2 m^*}{5 \hbar \varrho \varepsilon_0^2} \left\{ \frac{4}{7 c_{\text{t}}} \ln\left(\frac{q_{\text{m}}}{q_{\text{t}}}\right) + \frac{3}{7 c_{\text{l}}} \ln\left(\frac{q_{\text{m}}}{q_{\text{l}}}\right) \right\} \tag{34}$$

in the limit $T \to 0$. $E_0^{(0)}$ is the ground-state of the noninteracting entire system, $-\alpha \hbar \omega_{0\text{l}}$ gives the well-known depression of the ground-state energy due to the interaction of the electron with the longitudinal-optical mode. The last term stems from the contribution of acoustical phonons via piezoelectric coupling. Because $q_{\text{m}} \cong 10^8\ \text{cm}^{-1}$ and $q_{\text{l},\text{t}} \cong 10^6\ \text{cm}^{-1}$, we have $q_{\text{m}}/q_{\text{l},\text{t}} \gg 1$ and $q_{\text{l},\text{t}}$ is negligible compared with q_{m} in the logarithmic terms of (32).

Now the partition function for the decoupled polaron-phonon system with the energy spectrum (30) is given by

$$Z = \frac{Z^{(0)}}{(2 \varepsilon_2 m^*)^{3/2}} \left\{ 1 + \beta \hbar \omega_{0\text{l}} \alpha + \beta \frac{2 (4 e e_{14})^2 m^*}{5 \hbar \varrho \varepsilon_0^2} \left[\frac{4}{7 c_{\text{t}}} \ln\left(\frac{q_{\text{m}}}{q_{\text{t}}}\right) + \frac{3}{7 c_{\text{l}}} \ln\left(\frac{q_{\text{m}}}{q_{\text{l}}}\right) \right] - \frac{15}{4 \beta} \cdot \frac{\varepsilon_4}{\varepsilon_2^2} - \dots \right\}, \tag{35}$$

where we have taken into account that ε_0 is just the ground-state energy of the polaron (34). Thus by comparison with (32) adding the contribution of the optical mode we find the relation

$$\frac{1}{(2\,\varepsilon_2\,m^*)^{3/2}} = \left(\frac{m_{\text{eff}}}{m^*}\right)^{3/2} = = 1 + \frac{\alpha}{4} + \frac{2(4\,e\,e_{14})^2}{5\,\varrho\,\hbar\,\varepsilon_0^2} \cdot \left\{ \frac{4}{7\,c_{\text{t}}^3}\left(1 - \frac{q_{\text{t}}^2}{(q_{\text{m}}+q_{\text{t}})^2}\right) + \frac{3}{7\,c_{\text{l}}^3}\left(1 - \frac{q_{\text{l}}^2}{(q_{\text{m}}+q_{\text{l}})^2}\right\}.$$

Hence

$$\frac{m_{\text{eff}}}{m^*} \cong 1 + \frac{\alpha}{6} + \frac{4(4\,e\,e_{14})^2}{15\,\varrho\,\hbar\,\varepsilon_0^2}\left\{\frac{4}{7\,c_{\text{t}}^3} + \frac{3}{7\,c_{\text{l}}^3}\right\}, \tag{36}$$

where according to $q_{\text{l, t}}/q_{\text{m}} \ll 1$ the correction terms depending on $q_{\text{l, t}}$ and q_{m} have been omitted. In addition to the well-known contribution $\alpha/6$ we obtain a term, whose order of magnitude is essentielly determined by the elastic and piezoelectric properties of the crystal. Note that in our approximation the result (36) does not depend on the cut-off frequency ω_{m}.

We have evaluated exactly the same results by formal application of second-order RAYLEIGH–SCHRÖDINGER perturbation theory (for nondegenerate states) at $T = 0$, restricting to slow electrons with $k < \frac{1}{2}(q + q_{\text{l, t}})$, thus considering virtual transitions only. We have reproduced the thermodynamical perturbation theory because it does not suffer from the difficulties connected with the degeneracy of unperturbed eigenstates. More rigorous approaches are possible, but always much more elaborate.

As concluding considerations let us look at a numerical estimate of the two results (34) and (36). We choose ZnS as an example, because of the relatively large piezoelectric constant. Using the values $\varrho = 4{,}1$ g/cm³, $c_{\text{l}} = 4{,}79 \cdot 10^5$ cm/s, $c_{\text{t}} = 3{,}26 \cdot 10^5$ cm/s $|e_{14}| = 4{,}23 \cdot 10^4$ cgs-units, $\varepsilon_0 = 8$ we find that the energy depression due to acoustical phonons is negligibly small compared with[6] $-\alpha\,\hbar\,\omega_{0\text{l}}$. The values of $\alpha = 1{,}3$ and $\omega_{0\text{l}} = 7{,}3 \cdot 10^{13}$ s^{-1} can be taken from a table given by BROWN[5]. The contribution to the effective mass is, however, $0{,}13\,m^*$, which cannot be neglected compared with $\alpha\,m^*/6 = 0{,}22\,m^*$ for ZnS. The smallness of α and the piezoelectric contribution justifies the perturbational approach in this special case. There are of course other examples where the piezoelectric polaron effect is smaller than in ZnS, e. g. 4% in sodium-chlorate. However we believe that the contribution due to the piezoelectrically induced interaction of electrons and acoustical phonons might be important in other polar crystals too.

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Appendix

If we want to calculate the absolute square of the matrix element $V_{\boldsymbol{q}\sigma}$, that is, using (26),

$$|V_{\boldsymbol{q}\sigma}|^2 = \frac{(4\,\pi\,e)^2\,\hbar}{2\,\gamma\,V\,\omega_{\boldsymbol{q}\sigma}}\,\frac{1}{q^4}\,\left|\boldsymbol{q}\cdot\boldsymbol{e}\left(2\,\middle|\,{\boldsymbol{q} \atop \sigma}\right)\right|^2, \tag{A 1}$$

we must obtain an expression for the scalar product contained in (A 1). We try to get an approximate solution of the equations (20) considering the piezoelectric coupling as a perturbation.

Substituting[7]

$$\begin{aligned} \boldsymbol{e}(\mu\,|\,\sigma) &= {}^0\boldsymbol{e}(\mu\,|\,\sigma) + \varepsilon\,{}^1\boldsymbol{e}(\mu\,|\,\sigma), \quad (\mu = 1, 2), \\ \omega_\sigma &= {}^0\omega_\sigma + \varepsilon\,{}^1\omega_\sigma \end{aligned} \tag{A 2}$$

in eqs. (20) written down in an obvious matrix notation, we obtain for the 0th and 1st power of the expansion parameter ε:

$${}^0\omega_\sigma^2\,{}^0\boldsymbol{e}(1\,|\,\sigma) = \boldsymbol{A}\,{}^0\boldsymbol{e}(1\,|\,\sigma)\,, \tag{A 3 a}$$

$${}^0\omega_\sigma^2\,{}^0\boldsymbol{e}(2\,|\,\sigma) = \omega_{\text{ot}}^2\,{}^0\boldsymbol{e}(2\,|\,\sigma) + \boldsymbol{R}\,{}^0\boldsymbol{e}(2\,|\,\sigma), \tag{A 3 b}$$

$$\begin{aligned} {}^1\omega_\sigma^2\,{}^0\boldsymbol{e}(1\,|\,\sigma) + {}^0\omega_\sigma^2\,{}^1\boldsymbol{e}(1\,|\,\sigma) = \boldsymbol{A}\,{}^1\boldsymbol{e}(1\,|\,\sigma) \\ + \boldsymbol{B}\,{}^0\boldsymbol{e}(2\,|\,\sigma), \end{aligned} \tag{A 4 a}$$

$$\begin{aligned} {}^1\omega_\sigma^2\,{}^0\boldsymbol{e}(2\,|\,\sigma) + {}^0\omega_\sigma^2\,{}^1\boldsymbol{e}(2\,|\,\sigma) = \omega_{\text{ot}}^2\,{}^1\boldsymbol{e}(2\,|\,\sigma) \\ - \boldsymbol{B}\,{}^0\boldsymbol{e}(1\,|\,\sigma) + \boldsymbol{R}\,{}^1\boldsymbol{e}(2\,|\,\sigma). \end{aligned} \tag{A 4 b}$$

The unperturbed equations (A 3) yield solutions

$${}^0\boldsymbol{e}(1\,|\,\sigma = 1, 2, 3) \quad \text{and} \quad {}^0\boldsymbol{e}(2\,|\,\sigma = 4, 5, 6)$$

[but ${}^0\boldsymbol{e}(1\,|\,\sigma = 4, 5, 6) \equiv 0$ and ${}^0\boldsymbol{e}(2\,|\,\sigma = 1, 2, 3) \equiv 0$], which may each obey the usual orthonormality relations.

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[5] F. C. BROWN, in Polarons and Excitons, Scottish Universities' Summer School 1962, Oliver and Boyd, Edinburgh 1962.

[6] This result is perhaps not very astonishing. If we interpret the coupling constants as an average number of virtual phonons, we may at once refer to the smallness of the number of virtual acoustical phonons compared with the average number of virtual optical phonons.

[7] We omit the q-dependence of $e\left(\mu\,\middle|\,{b \atop \sigma}\right)$ and $\omega_{q\sigma}$ in the appendix.

By scalar multiplication with ${}^0\boldsymbol{e}(1\,|\,\sigma)$ or ${}^0\boldsymbol{e}(2\,|\,\sigma)$ in (A 4 a), (A 4 b) resp. it is easy to show that

$$ {}^1\omega_\sigma^2 = 0 \quad (\sigma = 1, 2, \ldots, 6). $$

We now multiply (A 4 a) by ${}^0\boldsymbol{e}(2\,|\,\sigma')$ $(\sigma' = 4, 5, 6)$ and (A 4 b) by ${}^0\boldsymbol{e}(1\,|\,\sigma')$ $(\sigma' = 1, 2, 3)$ and substitute the expansion

$$ {}^1\boldsymbol{e}(1\,|\,\sigma) = \sum_{\sigma'} a_{\sigma\sigma'}\,{}^0\boldsymbol{e}(1\,|\,\sigma'), \tag{A 5 a} $$

$$ {}^1\boldsymbol{e}(2\,|\,\sigma) = \sum_{\sigma'} b_{\sigma\sigma'}\,{}^0\boldsymbol{e}(2\,|\,\sigma'). \tag{A 5 b} $$

We then find the following values for the coefficients a and b

$$ a_{\sigma\sigma'} = \frac{({}^0\boldsymbol{e}\,(1\,|\,\sigma'),\ \boldsymbol{B}\,{}^0\boldsymbol{e}\,(2\,|\,\sigma))}{{}^0\omega_\sigma^2 - {}^0\omega_{\sigma'}^2} \left|\begin{array}{l} \sigma' = 1, 2, 3 \\ \sigma = 4, 5, 6 \end{array}\right. \tag{A 6 a} $$

$$ b_{\sigma\sigma'} = -\frac{({}^0\boldsymbol{e}\,(2\,|\,\sigma'),\ \boldsymbol{B}\,{}^0\boldsymbol{e}\,(1\,|\,\sigma))}{{}^0\omega_\sigma^2 - {}^0\omega_{\sigma'}^2} \left\{\begin{array}{l} \sigma = 1, 2, 3 \\ \sigma' = 4, 5, 6 \end{array}\right. \tag{A 6 b} $$

so that the final result for $\boldsymbol{e}(2\,|\,\sigma)$ becomes

$$ \boldsymbol{e}(2\,|\,\sigma) = \sum_{\sigma'=4}^{6} \frac{({}^0\boldsymbol{e}\,(2\,|\,\sigma'),\boldsymbol{B}\,{}^0\boldsymbol{e}\,(1\,|\,\sigma))}{{}^0\omega_{\sigma'}^2 - {}^0\omega_\sigma^2}\,{}^0\boldsymbol{e}(2\,|\,\sigma') \qquad (\sigma = 1, 2, 3), $$

$$ \boldsymbol{e}(2\,|\,\sigma) = {}^0\boldsymbol{e}(2\,|\,\sigma) \qquad (\sigma = 4, 5, 6). \tag{A 7} $$

We already know that the unperturbed system (A 3 b) has pure longitudinal and transverse vibrations. Let

$$ {}^0\boldsymbol{e}(2\,|\,\sigma = 4) \equiv {}^0\boldsymbol{e}(2\,|\,\text{long. opt.}) = \boldsymbol{q}^0 = \boldsymbol{q}/q; $$

${}^0\omega_4 = \omega_{01}$ and ${}^0\boldsymbol{e}$ $(2\,|\,\sigma = 5, 6)$ belong to the transverse optical modes; then we have from (A 7)

$$ \boldsymbol{q}^0\cdot\boldsymbol{e}(2\,|\,4) = 1; \qquad \boldsymbol{q}^0\cdot\boldsymbol{e}(2\,|\,5, 6) = 0, \tag{A 8} $$

$$ \boldsymbol{q}^0\cdot\boldsymbol{e}(2\,|\,\sigma) = \frac{({}^0\boldsymbol{e}\,(2\,|\,4),\ \boldsymbol{B}\,{}^0\boldsymbol{e}\,(1\,|\,\sigma))}{\omega_{\mathrm{ol}}^2 - {}^0\omega_\sigma} (\sigma = 1, 2, 3). $$

Returning to our polaron problem we state that in the foregoing approximation the electron interacts with the longitudinal optical mode and with all acoustical branches. Thus the absolute squares of the corresponding matrix elements are

$$ |V_{\boldsymbol{q}\mathrm{l}}^{\mathrm{opt.}}|^2 = \frac{(4\,\pi\,e)^2\,\hbar}{2\,\gamma\,V\,\omega_{\boldsymbol{q}\mathrm{l}}^{\mathrm{opt.}}}\cdot\frac{1}{q^2}, \tag{A 9} $$

$$ |V_{\boldsymbol{q}\mathrm{l}}^{\mathrm{acoust}}|^2 = \frac{(4\,\pi\,e)^2\,\hbar}{2\,\gamma\,V\,\omega_{\boldsymbol{q}\sigma}}\cdot\frac{1}{q^4}\,\frac{|q_i\,B_{ik}\,{}^0e_k(1\,|\,\sigma)|^2}{(\omega_{\mathrm{ol}}^2 - {}^0\omega_\sigma^2)^2} \qquad (\sigma = 1, 2, 3). \tag{A 10} $$

We will not be led to false results concerning the magnitude of the effects, if as a further approximation an elastic isotropic continuum is considered. We identify the longitudinal acoustical polarisation with ${}^0\boldsymbol{e}(1\,|\,\sigma = 1) \equiv \boldsymbol{q}^0$; the two other eigenvectors ${}^0e(1\,|\,\sigma = 2, 3)$ then belong to the degenerate transverse modes. The main advantage of the isotropic case is that with the help of the closure relation

$$ \sum_{\sigma=1}^{3} {}^0e_{\mathrm{i}}(1\,|\,\sigma)\,{}^0e_{\mathrm{l}}(1\,|\,\sigma) = \delta_{\mathrm{il}} $$

we always find

$$ \sum_{\sigma=1}^{3} F(\omega_{q\sigma})\,{}^0e_{\mathrm{i}}(1\,|\,\sigma)\,{}^0e_{\mathrm{l}}(1\,|\,\sigma) = F(\omega_{q\mathrm{t}})\,\delta_{\mathrm{il}} + [F(\omega_{q\mathrm{l}}) - F(\omega_{q\mathrm{t}})]\,{}^0e_{\mathrm{i}}(1\,|\,1)\,{}^0e_{\mathrm{l}}(1\,|\,1) \tag{A 11} $$

for any function F. Choosing $F(\omega_{q\sigma}) = f(\omega_{q\sigma})\,|V_{\boldsymbol{q}\sigma}^{\mathrm{acoust.}}|^2$ [$f(\omega_{q\sigma})$ another arbitrary function] we find with the help of (21), (16), (17), and (22) the relation

$$ \sum_{\sigma=1}^{3} f(\omega_{q\sigma})\,|V_{q\sigma}^{\mathrm{acoust.}}|^2 = \frac{(4\,\pi\,e)^2\,\hbar}{2\,\gamma\,V}\cdot\frac{16\,\pi\,e_{14}^2\,\omega_{0\mathrm{t}}^2}{\varrho\,(\varepsilon_0 - \varepsilon_\infty)}\cdot\left\{\frac{f(\omega_{q\mathrm{t}})}{\omega_{q\mathrm{t}}}\cdot\frac{q_1^2\,q_2^2 + q_1^2\,q_3^2 + q_2^2\,q_3^2}{q^4\,(\omega_{\mathrm{ol}}^2 - {}^0\omega_{q\mathrm{t}}^2)^2}\right. $$

$$ \left. + \frac{9\,(q_1\,q_2\,q_3)^2}{q^6}\left[\frac{f(\omega_{q\mathrm{l}})}{\omega_{q\mathrm{l}}}\cdot\frac{1}{(\omega_{\mathrm{ol}}^2 - {}^0\omega_{q\mathrm{l}}^2)^2} - \frac{f(\omega_{q\mathrm{t}})}{\omega_{q\mathrm{t}}}\cdot\frac{1}{(\omega_{\mathrm{ol}}^2 - {}^0\omega_{q\mathrm{t}}^2)^2}\right]\right\}, \tag{A 12} $$

which has been of importance in chapter IV.