

Chapter 4

Phonons



The ions forming the attractively acting lattice are not rigid. At least their oscillations around the rigid lattice positions have to be taken into account. These oscillations may be quantized and interpreted as bosonic particles called acoustical or optical phonons with typical spectra. Even a classical description of the phonons gives rise to important predictions as the Lyddane–Sachs–Teller formula. In a quantum mechanical approach to optical transitions assisted by phonons one may understand the Franck–Condon effect.

4.1 Lattice Oscillations

Until now we considered the ions as fixed positive point-like charges, positioned at the sites $\mathbf{R} + \boldsymbol{\xi}_s$ ($s = 1 \dots S$), where \mathbf{R} is a vector of the Bravais lattice, while $\boldsymbol{\xi}_s$ shows the position of a given ion within the elementary cell containing S ions. Actually, the ions are free to move away from their equilibrium positions with deviations $\mathbf{u}(\mathbf{R}, s)$ (here still classical!). For small deviations one may develop the potential energy \mathcal{U} of the lattice in a power series of these deviations. Up to a constant defining the ground state energy, the lowest term in this series must be quadratic, since the equilibrium corresponds to a stable minimum. Thus

$$\mathcal{U} = \frac{1}{2} \sum_{\mathbf{R}, s} \sum_{\mathbf{R}', s'} \Phi_{ss'}^{\mu\nu}(\mathbf{R} - \mathbf{R}') u^\mu(\mathbf{R}, s) u^\nu(\mathbf{R}', s') + \dots,$$

where $\Phi_{ss'}^{\mu\nu}(\mathbf{R} - \mathbf{R}')$ is a real symmetric

$$\Phi_{ss'}^{\mu\nu}(\mathbf{R}) = \Phi_{s's}^{\nu\mu}(-\mathbf{R})$$

positive defined matrix ($\Phi \geq 0$ means non-negative eigenvalues).
Since a constant shift does not change the energy

$$\sum_{\mathbf{R},s} \Phi_{ss'}^{\mu\nu}(\mathbf{R}) = \sum_{\mathbf{R},s} \Phi_{s's}^{\mu\nu}(\mathbf{R}) = 0.$$

One gets the classical Lagrange function $L = \mathcal{T} - U$ of the lattice by considering also the kinetic energy of the lattice

$$\mathcal{T} = \frac{1}{2} \sum_{\mathbf{R},s} m_s \dot{\mathbf{u}}(\mathbf{R}, s)^2,$$

where m_s is the mass of the ion designed with the index s .

In terms of discrete Fourier transforms

$$\mathbf{u}(\mathbf{R}, s) = \frac{v}{(2\pi)^3} \int_{BZ} d\mathbf{q} e^{i\mathbf{q}\mathbf{R}} \tilde{\mathbf{u}}_s(\mathbf{q}); \quad \tilde{\Phi}_{ss'}^{\mu\nu}(\mathbf{q}) = \frac{v}{(2\pi)^3} \int_{BZ} d\mathbf{q} e^{i\mathbf{q}\mathbf{R}} \Phi_{ss'}^{\mu\nu}(\mathbf{R})$$

retaining only the quadratic terms of the potential energy we have

$$L = \frac{v}{2(2\pi)^3} \int_{BZ} d\mathbf{q} \left\{ \sum_{s=1}^S \sum_{\mu} m_s \dot{\tilde{u}}_s^{\mu}(\mathbf{q})^* \dot{\tilde{u}}_s^{\mu}(\mathbf{q}) - \sum_{s,s'=1}^S \sum_{\mu,\nu} \tilde{u}_s^{\mu}(\mathbf{q})^* \tilde{\Phi}(\mathbf{q})_{ss'}^{\mu\nu} \tilde{u}_{s'}^{\nu}(\mathbf{q}) \right\}$$

with

$$\tilde{\Phi}(\mathbf{q})_{ss'}^{\mu\nu*} = \tilde{\Phi}(\mathbf{q})_{s's}^{\nu\mu}; \quad \tilde{\Phi}(\mathbf{q})_{ss'}^{\mu\nu*} = \tilde{\Phi}(-\mathbf{q})_{ss'}^{\mu\nu}; \quad \tilde{\Phi}(\mathbf{q}) \geq 0.$$

Absorbing the mass factor by

$$\tilde{\eta}_s^{\mu}(\mathbf{q}) \equiv \sqrt{m_s} \tilde{u}_s^{\mu}(\mathbf{q}); \quad \tilde{M}(\mathbf{q})_{ss'}^{\mu\nu} \equiv \frac{1}{\sqrt{m_s m_{s'}}} \tilde{\Phi}(\mathbf{q})_{ss'}^{\mu\nu}$$

we get

$$L = \frac{v}{2(2\pi)^3} \int_{BZ} d\mathbf{q} \left\{ \sum_{s=1}^S \sum_{\mu} \dot{\tilde{\eta}}_s^{\mu}(\mathbf{q})^* \dot{\tilde{\eta}}_s^{\mu}(\mathbf{q}) - \sum_{s,s'=1}^S \sum_{\mu,\nu} \tilde{\eta}_s^{\mu}(\mathbf{q})^* \tilde{M}(\mathbf{q})_{ss'}^{\mu\nu} \tilde{\eta}_{s'}^{\nu}(\mathbf{q}) \right\},$$

where the new matrix \tilde{M} has the same properties of symmetry, realness, and positiveness as $\tilde{\Phi}$.

This whole quadratic form may be brought to a diagonal one with the transformation that diagonalizes the potential energy, with positive eigenvalues $\omega_{\lambda}(\mathbf{q})^2$ and one may see that the Lagrangian describes a sum of oscillators of unit mass with eigenfrequencies $\omega_{\lambda}(\mathbf{q}) = \omega_{\lambda}(-\mathbf{q})$.

The quantization of the lattice corresponds therefore to the quantization of these oscillators. As it is well known, this leads to a quantum mechanical Hamiltonian that may be formulated in terms of the creation and annihilation operators $b_{\lambda\mathbf{q}}^\dagger$, $b_{\lambda\mathbf{q}}$ and the respective oscillator frequencies $\omega_\lambda(\mathbf{q})$. It is convenient to impose cyclical boundary conditions in order to deal with a discrete spectrum having the proper number of degrees of freedom. Then the quantized lattice Hamiltonian is

$$H = \sum_{\mathbf{q} \in BZ} \sum_{\lambda} \hbar \omega_{\lambda\mathbf{q}} b_{\lambda\mathbf{q}}^\dagger b_{\lambda\mathbf{q}}$$

with the bosonic commutation relations

$$\begin{aligned} [b_{\lambda\mathbf{q}}, b_{\lambda'\mathbf{q}'}] &= 0 \\ [b_{\lambda\mathbf{q}}, b_{\lambda'\mathbf{q}'}^\dagger] &= \delta_{\lambda,\lambda'} \delta_{\mathbf{q},\mathbf{q}'}. \end{aligned}$$

The quantized deviations from the equilibrium positions at their turn are

$$\mathbf{u}(\mathbf{R}, s) = \sum_{\mathbf{q}} \sum_{\lambda} e^{i\mathbf{q}\mathbf{R}} \sqrt{\frac{\hbar}{2m_s \omega_{\lambda,\mathbf{q}}}} \chi_s^{(\lambda)}(\mathbf{q}) (b_{\lambda,\mathbf{q}} + b_{\lambda,-\mathbf{q}}^\dagger),$$

where $\chi_s^{(\lambda)}(\mathbf{q})$ are the orthonormalized eigenfunctions of the Matrix \tilde{M}

$$\sum_{\nu, s'} \tilde{M}(\mathbf{q})_{s, s'} \chi_{s'}^{\nu(\lambda)}(\mathbf{q}) = \omega_{\lambda,\mathbf{q}}^2 \chi_s^{\mu(\lambda)}(\mathbf{q}); \quad (\lambda = 1, \dots, 3S).$$

Due to the invariance against a common translation discussed before it follows that

$$\sum_{s'=1}^S \tilde{M}(0)_{s, s'}^{\mu\nu} \sqrt{m_{s'}} = 0$$

and

$$\sum_{s=1}^S \sqrt{m_s} \tilde{M}(0)_{s s'}^{\mu\nu} = 0.$$

While the first equation shows that there are at least 3 eigenfrequencies that vanish at $\mathbf{q} = 0$, called acoustical modes, the second equation shows that if an eigenvalue does not vanish in the origin, then the eigenstate must fulfill the relation

$$\sum_{s=1}^S \sqrt{m_s} \chi_s^{(\lambda)}(0) = 0; \quad (\lambda = 4, \dots, 3S - 3)$$

or

$$\sum_{s=1}^S m_s \mathbf{u}_s^{(\lambda)}(0) = 0; \quad (\lambda = 4, \dots, 3S - 3).$$

This means that the center of mass by these oscillations, called optical modes, remains unchanged.

4.2 Classical Continuum Phonon-Model

In applications, it is useful to use a simplified continuum model for phonons with a simple phonon spectrum. The local deviations $\mathbf{u}(\mathbf{r})$ are defined then in every space point \mathbf{r} .

The prototype classical Lagrange function for acoustical phonons is

$$L_{acc} = \frac{m}{2v} \int d\mathbf{r} \sum_{\mu=1}^3 \left\{ \dot{u}_{\mu}(\mathbf{r})^2 + c^2 \sum_{\nu=1}^3 (\partial_{\nu} u_{\mu}(\mathbf{r}))^2 \right\}$$

or in Fourier transforms

$$L_{acc} = \frac{m}{2} \int d\mathbf{q} \sum_{\mu=1}^3 \left\{ \dot{\tilde{u}}_{\mu}(\mathbf{q})^* \dot{\tilde{u}}_{\mu}(\mathbf{q}) + c^2 q^2 \tilde{u}_{\mu}(\mathbf{q})^* \tilde{u}_{\mu}(\mathbf{q}) \right\}.$$

Obviously, here a linear acoustical phonon spectrum $\omega_{ac}(\mathbf{q}) = cq$ was assumed (with c being here the sound velocity in the medium).

To model optical phonons, one considers the classical Lagrange function

$$L_{opt} = \frac{m}{2v} \int d\mathbf{r} \sum_{\mu=1}^3 \left\{ \dot{u}_{\mu}(\mathbf{r})^2 - \omega_0^2 \tilde{u}_{\mu}(\mathbf{r})^2 \right\}$$

or in Fourier transforms

$$L_{opt} = \frac{m}{2} \int d\mathbf{q} \sum_{\mu=1}^3 \left\{ \dot{\tilde{u}}_{\mu}(\mathbf{q})^* \dot{\tilde{u}}_{\mu}(\mathbf{q}) - \omega_0^2 \tilde{u}_{\mu}(\mathbf{q})^* \tilde{u}_{\mu}(\mathbf{q}) \right\}.$$

Here the optical phonon spectrum was taken just to be constant $\omega_{opt}(\mathbf{q}) = \omega_0$. In both cases one must take into account that the total number of degrees of freedom (per volume!) should correspond to that of the crystal and therefore one cuts off the wave vectors by the Debye wave vector ($q < q_{Debye}$) defined by

$$\frac{4\pi}{3}q_{Debye}^3 \equiv \frac{1}{v}$$

with v being the volume of the elementary cell.

4.2.1 Optical Phonons in Polar Semiconductors

The optical lattice deviations lead to local electric dipoles. This local polarization in the classical continuum model is given by

$$\mathbf{P}(\mathbf{r}) = \frac{\kappa e}{v} \mathbf{u}(\mathbf{r}),$$

where κ is the polarizability of the elementary cell. The corresponding polarization charge density is

$$\rho_{pol}(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r}) = -\frac{\kappa e}{v} \nabla \cdot \mathbf{u}(\mathbf{r})$$

and the Poisson equation in the presence of a stationary external charge density $\rho_{ext}(\mathbf{r})$ looks as

$$\epsilon_\infty \nabla^2 V(\mathbf{r}) = -4\pi (\rho_{pol}(\mathbf{r}) + \rho_{ext}(\mathbf{r}))$$

with ϵ_∞ being the dielectric constant due to the electronic background. Alternatively, for low frequencies it will look as

$$\epsilon_0 \nabla^2 V(\mathbf{r}) = -4\pi \rho_{ext}(\mathbf{r}),$$

where ϵ_0 is the total dielectric constant. The notation stems from the assumption that at high frequencies only the light electrons contribute to the dielectric properties, while for low frequencies both the electrons and ions contribute. As we shall see, relating the polarization charge density to the potential allows for the identification of the total dielectric constant.

In the inhomogeneous situation due to the presence of an external charge density the Lagrange function contains supplementary Coulomb terms

$$L = \frac{m}{2v} \int d\mathbf{r} \sum_{\mu=1}^3 \left\{ \dot{u}^\mu(\mathbf{r})^2 - \omega_0^2 u^\mu(\mathbf{r})^2 \right\} - \frac{1}{\epsilon_\infty} \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left(\frac{1}{2} \nabla \mathbf{P}(\mathbf{r}) \nabla' \mathbf{P}(\mathbf{r}') - \nabla \mathbf{P}(\mathbf{r}) \rho_{ext}(\mathbf{r}') \right).$$

Now let us split the local deviations $\mathbf{u}(\mathbf{r})$ into longitudinal and transverse modes

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}_l(\mathbf{r}) + \mathbf{u}_t(\mathbf{r})$$

$$\mathbf{u}_l(\mathbf{r}) = -\nabla \int d\mathbf{r}' \frac{\nabla' \cdot \mathbf{u}(\mathbf{r}')}{4\pi |\mathbf{r} - \mathbf{r}'|}; \quad \nabla \mathbf{u}_t = 0; \quad \nabla \mathbf{u}_l = \nabla \mathbf{u}.$$

One gets the equations of motion for these modes through the Euler–Lagrange equations by using the identity

$$\nabla^2 \frac{1}{|\mathbf{r}|} = -4\pi \delta(\mathbf{r})$$

and they look as

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \mathbf{u}_t &= -\omega_{TO}^2 \mathbf{u}_t \\ \frac{\partial^2}{\partial t^2} \mathbf{u}_l &= -\omega_{LO}^2 \mathbf{u}_l + \frac{\kappa e}{m} \mathbf{E}_{ext} \end{aligned}$$

with

$$\omega_{TO}^2 \equiv \omega_0^2; \quad \omega_{LO}^2 = \omega_0^2 + \frac{4\pi \kappa^2 e^2}{\epsilon_\infty v m}.$$

In a stationary regime (thermal equilibrium) in the presence of a stationary external charge density it follows:

$$\mathbf{u}_l = \frac{\kappa e}{m \omega_{LO}^2} \mathbf{E}_{ext}$$

and

$$\rho_{pol} = -\frac{\kappa^2 e^2}{v m \omega_{LO}^2} \nabla \cdot \mathbf{E}_{ext} = -\frac{4\pi \kappa^2 e^2}{v m \omega_{LO}^2 \epsilon_\infty} \rho_{ext}; \quad (\epsilon_\infty \nabla \cdot \mathbf{E}_{ext} = 4\pi \rho_{ext}).$$

If one inserts this result into the Poisson equation, one may identify

$$\frac{\epsilon_\infty}{\epsilon_0} = 1 - \frac{4\pi \kappa^2 e^2}{v m \omega_{LO}^2 \epsilon_\infty} = \frac{1}{\omega_{LO}^2} \left(\omega_{LO}^2 - \frac{4\pi \kappa^2 e^2}{\epsilon_\infty v m} \right)$$

and one gets the Lyddane–Sachs–Teller relationship

$$\frac{\omega_{LO}}{\omega_{TO}} = \sqrt{\frac{\epsilon_0}{\epsilon_\infty}}.$$

Now let us introduce an arbitrary external time-dependent electromagnetic field $\mathbf{E}_{\text{ext}}(t)$. Then the equation of motion looks as

$$\frac{\partial^2}{\partial t^2} \mathbf{u}(t) = -\omega_0^2 \mathbf{u}(t) + \frac{\kappa e}{m} \mathbf{E}(t) \quad ,$$

whereby the electric field $\mathbf{E}(t)$ includes also the longitudinal field produced by the dipoles

$$\mathbf{E}(\mathbf{x}, t) = \mathbf{E}_{\text{ext}}(\mathbf{x}, t) + \nabla \int d\mathbf{x}' \frac{\nabla' P(\mathbf{x}', t)}{|\mathbf{x} - \mathbf{x}'|}.$$

Above we took into account that the interaction energy of our dipoles with the total electric field may be brought to the form $-\frac{\kappa e}{v} \int d\mathbf{x} \mathbf{u}(\mathbf{x}) \mathbf{E}(\mathbf{x}, t)$. After a Fourier transformation in the time variable t it follows for the frequency dependent susceptibility for both modes

$$\chi_{T,L}(k, \omega) = \frac{\alpha^2 e^2}{vm} \frac{1}{\omega_0^2 - \omega^2},$$

or for the frequency dependent dielectric function

$$\epsilon(\omega)_{L,T} = \epsilon_\infty \left(1 + \frac{4\pi \alpha^2 e^2}{\epsilon_\infty vm} \frac{1}{\omega_0^2 - \omega^2} \right) = \epsilon_\infty \frac{\omega_{LO}^2 - \omega^2}{\omega_{TO}^2 - \omega^2}.$$

4.2.2 Optical Eigenmodes

Starting from the above dielectric function we look now for possible electromagnetic eigenoscillations in such a medium. Since the system is homogeneous and isotropic, by using Fourier transforms it is useful to split the electromagnetic fields in their longitudinal, respectively, transverse parts. The Maxwell equations for the magnetic \mathbf{B} , respectively, electric field \mathbf{E} and the polarization \mathbf{P} look in their components as

$$\begin{aligned} B(k, \omega)_L &= 0 \\ B(k, \omega)_T &= \frac{ck}{\omega} E(k, \omega)_T \\ ik\epsilon_\infty E(k, \omega)_L &= -4\pi ikP(k, \omega)_L + 4\pi\rho^{\text{ext}}(k, \omega) \end{aligned}$$

$$(k^2 - \epsilon_\infty \frac{\omega^2}{c^2})E(k, \omega)_T = \frac{4\pi\omega^2}{c^2}P(k, \omega)_T - \frac{i4\pi\omega}{c^2}j^{ext}(k, \omega)_T.$$

With

$$\mathbf{P}(\mathbf{k}, \omega) = \frac{1}{4\pi} (\epsilon(\mathbf{k}, \omega) - \epsilon_\infty) \mathbf{E}(\mathbf{k}, \omega)$$

and the previously deduced dielectric function it follows that in the absence of external sources the homogeneous Maxwell equations still have non-vanishing solutions. For $\omega = \omega_{LO}$ there is a non-trivial longitudinal solution for any $k = |\mathbf{k}|$, while non-trivial transverse solutions exist only for ω, k pairs that are solutions of the equation

$$k^2 - \epsilon_\infty \frac{\omega^2}{c^2} \frac{\omega_{LO}^2 - \omega^2}{\omega_{TO}^2 - \omega^2} = 0$$

shown in Fig. 4.1. Such transverse fields are propagating mixed photon and LO-phonon modes.

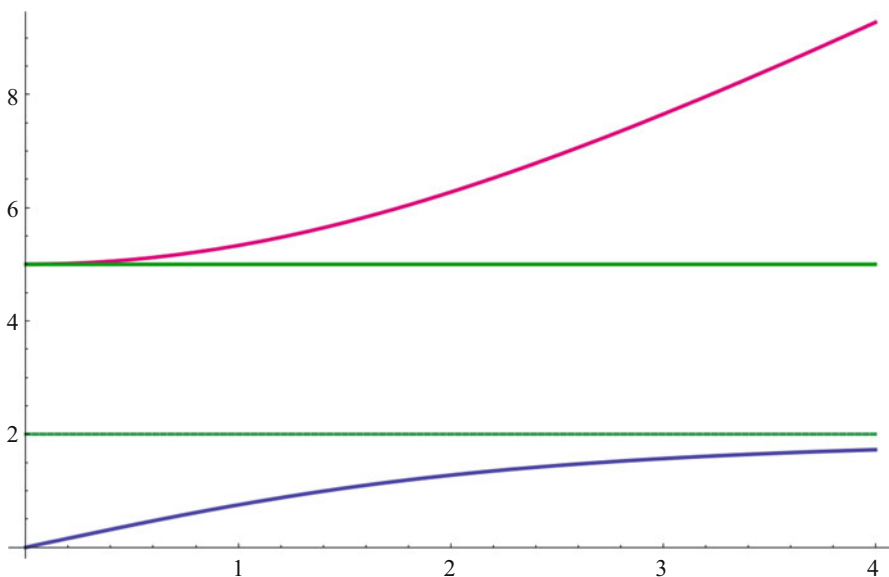


Fig. 4.1 Optical eigenmodes

4.2.3 The Electron–Phonon Interaction

4.2.3.1 The Franck–Condon Effect

Let us suppose that one has two localized electronic states of energies ε_1 and ε_2 on the same site and one of them is electrically neutral while the other one is electrically charged. In a polar semiconductor, this local charge density is coupled to the optical phonons. The energy of the system of electron and phonons (seen as a classical oscillator with coordinate Q) may be characterized schematically by the potential energies of the two states

$$E_1(Q) = \varepsilon_1 + \frac{1}{2}m(\dot{Q}^2 + \omega_{LO}^2 Q^2)$$

$$E_2(Q) = \varepsilon_2 + \frac{1}{2}m(\dot{Q}^2 + \omega_{LO}^2 Q^2) - gQ.$$

The energy of the second state may be rewritten as

$$E_2(Q) = \varepsilon_2 + \frac{1}{2}m \left(\dot{Q}^2 + \omega_{LO}^2 (Q - Q_0)^2 + \omega_{LO}^2 Q_0^2 \right),$$

where $m\omega_{LO}^2 Q_0 = g$. This means that the potential energy of the phonons gets shifted.

Now by photon absorption the system may undergo a transition from the minimum of the lower lying state on the higher branch outside the minimum of that branch. (The photon momentum may be neglected by these optical transitions!) Thereafter, follows a thermal relaxation (by emission of acoustical phonons) into the minimum of the upper branch and only later may follow a slower photon emission onto the lower branch again outside the minimum. This is the essence of the Franck–Condon effect showing a difference between the absorption and emission spectra (Stokes shift). It is illustrated in Fig. 4.2.

4.2.3.2 The Quantized Interaction of Electrons with Phonons

The interaction Hamiltonian of the electrons with the phonons is considered to be linear in the quantized lattice deviations, conserving the number of electrons and in the continuum model conserving also the momenta

$$H_{int} = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{q}} g_{\mathbf{q}} a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{q}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+).$$

Here Ω is the volume and the discretized wave vector \mathbf{q} is assumed to be smaller than the Debye wave vector $q < q_D$.

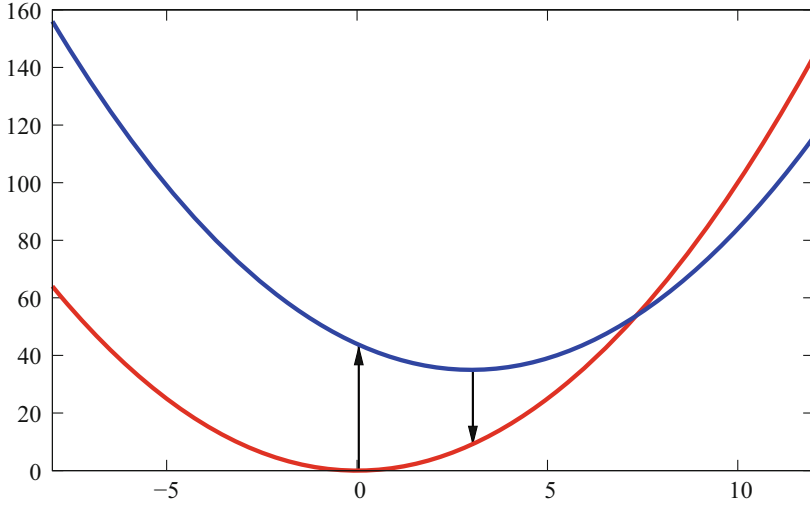


Fig. 4.2 Stokes shift

In the case of the optical phonons, analogously to the discussion in the frame of the classical continuum model one starts from the Coulomb interaction between the electron (or hole) charge density

$$\rho(\mathbf{x}) \equiv \pm e \psi^+(\mathbf{x}) \psi(\mathbf{x})$$

and the polarization charge density due to the optical deformation

$$-\frac{1}{\epsilon_\infty} \int d\mathbf{x}' \frac{\nabla \mathbf{P}(\mathbf{x}) \rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}.$$

Inserting the expression of the polarization in terms of the quantized lattice deviations one gets

$$g_q^2 = \alpha \frac{4\pi \hbar (\hbar \omega_0)^{3/2}}{(2m_e)^{1/2} q^2},$$

where instead of the coefficient $\frac{4\pi e^2 \kappa^2}{vm\omega_{LO}^2 \epsilon_\infty}$ one has introduced the dimensionless constant

$$\alpha = \frac{e^2}{\hbar} \left(\frac{m_e}{2\hbar\omega_0} \right)^{1/2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right).$$

The presence of the electron mass here is spurious. The coupling constant g_q itself does not depend on the electron mass.

In the case of the acoustic phonons one considers mostly the deformation potential model. This starts from the assumption that a slowly varying deformation in an isotropic medium causes a local variation of the band gap

$$\delta E_g(\mathbf{x}) \sim \nabla \mathbf{u}(\mathbf{x}).$$

This leads to

$$g_{\mathbf{q}} = G\sqrt{\hbar\omega_{\mathbf{q}}},$$

where $\omega_{\mathbf{q}} = c|\mathbf{q}|$ and G is a constant specific for the considered crystal. Of course, both models are highly idealized, but nevertheless, quite successful in predicting experimental phenomena.