

The theory of Polarons

Polarons and the electron-phonon interaction

The conduction electrons are strongly influenced by the ionic motion, thus leading to electron-phonon coupling. Some of the consequences of the coupling of electrons & phonons are:

1. Scattering of electrons from one state to another (ie k to k') leading to electrical resistivity.
2. Creation or absorption of phonons.
3. Giving rise to an attractive e-e interaction leading to superconductivity.
4. The electron drags along with it a part of the phonons (phonon cloud). This composite particle of electron plus phonon cloud is called a polaron.
5. The polaron is an example of a quasi particle, and has a heavier effective mass than an electron in a lattice.

energy band of interest is nondegenerate, spherical, and given by

$$(1) \quad \epsilon_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m^*};$$

here m^* is the effective mass of the conduction electron.

Let us now make a small uniform static deformation described by the strain components $e_{\mu\nu}$. The perturbed energy surface may be calculated in principle; it will be of the form

$$(2) \quad \epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) + C_{\mu\nu} e_{\mu\nu} + C'_{\mu\nu} k_\mu k_\nu e_{\mu\nu} + \dots,$$

to leading terms. In a semiconductor the k 's of interest are usually low, and we set $C'_{\mu\nu}$ aside. For a spherical energy surface in the unstrained crystal, it is not possible for $\epsilon(\mathbf{k})$ to be an odd function of the shear strain: we must therefore have $C_{\mu\nu} = 0$ for $\mu \neq \nu$. Because of the spin-orbit interaction we write for low k

$$(3) \quad \epsilon(\mathbf{k}) \cong \epsilon_0(\mathbf{k}) + C_1 \Delta,$$

where Δ is the dilation. Here $C_1 = \partial\epsilon(\mathbf{0})/\partial\Delta$ is a constant which may be determined in part by pressure measurements.

It is easily shown that for a free electron gas the constant C_1 has the value $-\frac{2}{3}\epsilon_F$, where ϵ_F is the fermi energy. The kinetic energy per electron is, at the fermi surface,

$$(5) \quad \epsilon_F = \frac{1}{2m} \left(\frac{3\pi^2 N}{\Omega} \right)^{2/3},$$

with N electrons in volume Ω . Thus

$$(6) \quad \frac{\delta\epsilon}{\epsilon_F} = -\frac{2\delta\Omega}{3\Omega} = -\frac{2}{3}\Delta,$$

or

$$(7) \quad \epsilon(k_F) = \epsilon_0(k_F) - \frac{2}{3}\epsilon_0(k_F)\Delta.$$

This result assumes that the charges move to keep each part of the

crystal electrically neutral—this is well satisfied for quasistatic perturbations of wavelength long in comparison with the screening length as defined in Chapter 6.

For acoustic phonons of long wavelength we assume that (3) may be generalized to read

$$(8) \quad \epsilon(\mathbf{k}, \mathbf{x}) = \epsilon_0(\mathbf{k}) + C_1 \Delta(\mathbf{x}),$$

with a similar generalization applying to (4). It is quite apparent that optical phonons are not covered by such a treatment; for one thing, the dilation is only related to acoustic phonons; for another, we have not included long-range electrostatic potentials which would arise from longitudinal optical phonon deformations.

In the Born approximation we are concerned with the matrix elements of $C_1\Delta(\mathbf{x})$ between the unperturbed one-electron Bloch states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$, with $|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{x}}u_{\mathbf{k}}(\mathbf{x})$, where $u_{\mathbf{k}}(\mathbf{x})$ has the periodicity of the lattice (Chapter 9). Using, from (2.84), the expansion of the dilation in phonon operators,

$$(9) \quad H' = \int d^3x \Psi^\dagger(\mathbf{x})C_1\Delta(\mathbf{x})\Psi(\mathbf{x}) = \sum_{\mathbf{k}'\mathbf{k}} c_{\mathbf{k}'}^\dagger c_{\mathbf{k}} \langle \mathbf{k}' | C_1\Delta | \mathbf{k} \rangle \\ = iC_1 \sum_{\mathbf{k}'\mathbf{k}} c_{\mathbf{k}'}^\dagger c_{\mathbf{k}} \sum_{\mathbf{q}} (2\rho\omega_{\mathbf{q}})^{-1/2} |\mathbf{q}| \left(a_{\mathbf{q}} \int d^3x u_{\mathbf{k}'}^* u_{\mathbf{k}} e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{x}} \right. \\ \left. - a_{\mathbf{q}}^\dagger \int d^3x u_{\mathbf{k}'}^* u_{\mathbf{k}} e^{i(\mathbf{k}-\mathbf{k}'-\mathbf{q})\cdot\mathbf{x}} \right),$$

where

$$(10) \quad \Psi(\mathbf{x}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \varphi_{\mathbf{k}}(\mathbf{x}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} u_{\mathbf{k}}(\mathbf{x}),$$

and the $a_{\mathbf{q}}^\dagger$, $a_{\mathbf{q}}$ refer to longitudinal phonons of wavevector \mathbf{q} . The product $u_{\mathbf{k}'}^*(\mathbf{x})u_{\mathbf{k}}(\mathbf{x})$ involves the periodic parts of the Bloch functions and is itself periodic in the lattice; thus the integrals in (9) vanish unless

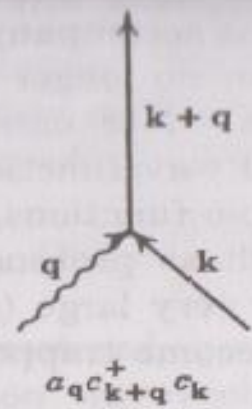
$$(11) \quad \mathbf{k} - \mathbf{k}' \pm \mathbf{q} = \begin{cases} 0 \\ \text{vector in the reciprocal lattice.} \end{cases}$$

For plane waves only the possibility zero exists, as here each $u_{\mathbf{k}}(\mathbf{x})$ is constant. In semiconductors at low temperatures the possibility zero may be the only process allowed energetically. If

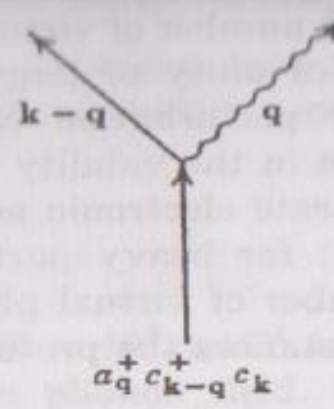
$$(12) \quad \mathbf{k} - \mathbf{k}' \pm \mathbf{q} = 0,$$

the scattering process is said to be a *normal* or *N* process. If

$$(13) \quad \mathbf{k} - \mathbf{k}' \pm \mathbf{q} = \mathbf{G},$$



Phonon absorption



Phonon emission

L.I

FIG. 1. Electron-phonon scattering processes in first order.

where \mathbf{G} is a vector in the reciprocal lattice, the scattering process is said to be an *umklapp* or *U* process. The classification of processes as normal or umklapp depends on the choice of Brillouin zone. By "vector in the reciprocal lattice" we always mean a vector connecting two lattice points of the reciprocal lattice.

Let us limit ourselves for the present to N processes, and for convenience we approximate $\int d^3x u_{\mathbf{k}}^* u_{\mathbf{k}}$ by unity. Then the deformation potential perturbation is

$$(14) \quad H' = iC_1 \sum_{\mathbf{k}\mathbf{q}} (2\rho\omega_{\mathbf{q}})^{-1/2} |\mathbf{q}| (a_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}}^+ c_{\mathbf{k}} - a_{\mathbf{q}}^+ c_{\mathbf{k}-\mathbf{q}}^+ c_{\mathbf{k}});$$

we may equally write this as

$$(15) \quad H' = iC_1 \sum_{\mathbf{k}\mathbf{q}} (2\rho\omega_{\mathbf{q}})^{-1/2} |\mathbf{q}| (a_{\mathbf{q}} - a_{-\mathbf{q}}^+) c_{\mathbf{k}+\mathbf{q}}^+ c_{\mathbf{k}}.$$

potential perturbation is

$$(14) \quad H' = iC_1 \sum_{\mathbf{kq}} (2\rho\omega_q)^{-1/2} |\mathbf{q}| (a_q c_{\mathbf{k}+\mathbf{q}}^+ c_{\mathbf{k}} - a_q^+ c_{\mathbf{k}-\mathbf{q}}^+ c_{\mathbf{k}});$$

we may equally write this as

$$(15) \quad H' = iC_1 \sum_{\mathbf{kq}} (2\rho\omega_q)^{-1/2} |\mathbf{q}| (a_q - a_{-\mathbf{q}}^+) c_{\mathbf{k}+\mathbf{q}}^+ c_{\mathbf{k}}.$$

The field operators describe the scattering processes shown in Fig. 1.

Before going further we should see what the limitations are on the strength of the coupling parameter C_1 in order that our separation of electron and phonon energies should make sense. The existence of the electron-phonon coupling H' (14) means that an electron in a state \mathbf{k} with no phonons excited cannot be an exact eigenstate of the system, but there will always be a cloud of virtual phonons accompanying the electron. The composite particle, electron plus lattice deformation, is called a *polaron*.^{*} The phonon cloud changes the energy of the

^{*} The term polaron is most often used for an electron plus the cloud of virtual optical phonons in ionic crystals.

electron. If the number of virtual phonons accompanying the electron is of the order of unity or larger, we can no longer trust the result of a first-order perturbation calculation. Nor can we then have much confidence in the validity of crystal wavefunctions written as a product of separate electronic and vibronic functions. This is not a trivial question: for heavy particles such as protons moving in the crystal the number of virtual phonons is very large (see Problem 1). In these circumstances the proton may become trapped locally in the crystal.

Phonon Cloud. Let us calculate by perturbation theory the number of virtual acoustic phonons accompanying a slow electron. We take as the unperturbed state of the phonon system the ground state in which no phonons are excited; the unperturbed state of the electronic system is taken as a Bloch state. Thus we write the unperturbed state of the total system as $|\mathbf{k}0\rangle$; the first-order perturbed state denoted by $|\mathbf{k}0\rangle^{(1)}$ is given by

$$(16) \quad |\mathbf{k}0\rangle^{(1)} = |\mathbf{k}0\rangle + \sum_{\mathbf{q}} |\mathbf{k} - \mathbf{q}; 1_{\mathbf{q}}\rangle \frac{\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}0 \rangle}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}}},$$

$$(16) \quad |\mathbf{k}0\rangle^{(1)} = |\mathbf{k}0\rangle + \sum_{\mathbf{q}} |\mathbf{k} - \mathbf{q}; 1_{\mathbf{q}}\rangle \frac{\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}0 \rangle}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}}},$$

where H' is the electron-phonon interaction. The total number of phonons $\langle N \rangle$ accompanying the electron is given by taking the expectation value of $\sum a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}}$ over the state $|\mathbf{k}0\rangle^{(1)}$. On summing over the squares of the admixture coefficients we have

$$(17) \quad \langle N \rangle = \sum_{\mathbf{q}} \frac{|\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}0 \rangle|^2}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}})^2}.$$

For the deformation potential interaction (14),

$$(18) \quad |\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}0 \rangle|^2 = \frac{C_1^2 |q|}{2\rho c_s},$$

where c_s is the longitudinal velocity of sound. Now, with m^* as the effective mass of the conduction electron,

$$(19) \quad \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}} = \frac{1}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2) - c_s q.$$

For a very slow electron we neglect k in comparison with q and then write the sum in (17) as an integral,

$$(20) \quad \langle N \rangle = \frac{2m^{*2} C_1^2}{(2\pi)^3 \rho c_s} \int d^3q \cdot \frac{q}{(q^2 + 2c_s m^* q)^2},$$

where the integral should be carried over the first Brillouin zone of the

longitudinal phonons. We shall for convenience take the integral over a sphere in q space out to a q_m chosen to enclose a number of modes equal to the number of atoms:

$$(21) \quad \langle N \rangle = \frac{1}{\pi^2} \frac{m^{*2} C_1^2}{\rho c_s} \int_0^{q_m} dq \frac{q}{(q + q_c)^2}$$

where, with \hbar restored, $q_c = 2m^*c_s/\hbar \approx 10^6 \text{ cm}^{-1}$ is essentially the electron Compton wavevector in the phonon field. The numerical estimate was made using $m^* = m$ and $c_s = 5 \times 10^5 \text{ cm/sec}$. The integral is standard:

$$(22) \quad \int_0^{q_m} dq \frac{q}{(q + q_c)^2} = \log \left(1 + \frac{q_m}{q_c} \right) - \frac{q_m}{q_m + q_c}$$

Because $q_m \approx 10^8 \text{ cm}^{-1}$, we have $q_m/q_c \gg 1$ and the value of the integral is approximately $\log(q_m/q_c)$. Now, with \hbar restored,

$$(23) \quad \langle N \rangle \cong \frac{1}{\pi^2} \frac{m^{*2} C_1^2}{\hbar^3 \rho c_s} \log(q_m/q_c)$$

Taking $C_1 \sim 5 \times 10^{-11} \text{ ergs}$; $m^* \sim 0.2 \times 10^{-27} \text{ gm}$; $\rho \sim 5$, $c_s \sim 5 \times 10^5 \text{ cm/sec}$; $(q_m/q_c) \sim 10^2$, we have $\langle N \rangle \sim 0.02$. In these conditions, which are perhaps typical for covalent semiconductors, the expectation value of the number of virtual phonons around each electron is very much smaller than unity. If we do not neglect k in comparison with q , we obtain the more complete result

$$(23) \quad \langle N \rangle \cong \frac{1}{\pi^2} \frac{m^{*2} C_1^2}{\hbar^3 \rho c_s} \log (q_m/q_c).$$

Taking $C_1 \sim 5 \times 10^{-11}$ ergs; $m^* \sim 0.2 \times 10^{-27}$ gm; $\rho \sim 5$, $c_s \sim 5 \times 10^5$ cm/sec; $(q_m/q_c) \sim 10^2$, we have $\langle N \rangle \sim 0.02$. In these conditions, which are perhaps typical for covalent semiconductors, the expectation value of the number of virtual phonons around each electron is very much smaller than unity. If we do not neglect k in comparison with q , we obtain the more complete result

$$(24) \quad \langle N \rangle = \frac{m^{*2} C_1^2}{(2\pi)^2 \rho c_s \hbar^3 k} \left\{ (q_c - 2k) \log \left| \frac{q_c - 2k}{q_m + q_c - 2k} \right| + (q_c + 2k) \log \left| \frac{q_m + q_c + 2k}{q_c + 2k} \right| \right\}.$$

Relaxation Time. We see from the form of the wavefunction $|\mathbf{k}0\rangle^{(1)}$ given by (16) that in the presence of the electron-phonon interaction the wavevector \mathbf{k} is not a constant of the motion for the electron alone, but the sum of the wavevectors of the electron and virtual phonon is conserved. Suppose an electron is initially in the state $|\mathbf{k}\rangle$; how long will it stay in the same state?

We calculate first the probability w per unit time that the electron in \mathbf{k} will absorb a phonon \mathbf{q} . If $n_{\mathbf{q}}$ is the initial population of the phonon state,

$$(25) \quad w(\mathbf{k} + \mathbf{q}; n_{\mathbf{q}} - 1 | \mathbf{k}; n_{\mathbf{q}}) = 2\pi |\langle \mathbf{k} + \mathbf{q}; n_{\mathbf{q}} - 1 | H' | \mathbf{k}; n_{\mathbf{q}} \rangle|^2 \delta(\epsilon_{\mathbf{k}} + \omega_{\mathbf{q}} - \epsilon_{\mathbf{k}+\mathbf{q}}).$$

$$(26) \quad |\langle \mathbf{k} + \mathbf{q}; n_q - 1 | H' | \mathbf{k}; n_q \rangle|^2 = \frac{C_1^2 q}{2\rho c_s} n_q.$$

The probability per unit time that an electron in \mathbf{k} will emit a phonon \mathbf{q} involves the matrix element through

$$(27) \quad |\langle \mathbf{k} - \mathbf{q}; n_q + 1 | H' | \mathbf{k}; n_q \rangle|^2 = \frac{C_1^2 q}{2\rho c_s} (n_q + 1).$$

The total collision rate W of an electron* in the state $|\mathbf{k}\rangle$ against a phonon system at absolute zero is, from (27) with $n_q = 0$,

$$(28) \quad W = \frac{C_1^2}{4\pi\rho c_s} \int_{-1}^1 d(\cos \theta_q) \int_0^{q_m} dq q^3 \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \omega_q).$$

Now the argument of the delta function is

$$(29) \quad \frac{1}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2) - c_s q = \frac{1}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2 - qq_c),$$

$$(29) \quad \frac{1}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2) - c_s q = \frac{1}{2m^*} (2\mathbf{k} \cdot \mathbf{q} - q^2 - qq_c),$$

where $q_c = 2m^*c_s$, as before. The minimum value of k for which the argument can be zero is

$$(30) \quad k_{\min} = \frac{1}{2}(q + q_c),$$

which for $q = 0$ reduces to

$$(31) \quad k_{\min} = \frac{1}{2}q_c = m^*c_s.$$

For this value of k the electron group velocity $v_g = k_{\min}/m^*$ is equal to c_s , the velocity of sound. Thus the threshold for the emission of phonons by electrons in a crystal is that the electron group velocity should exceed the acoustic velocity; this requirement resembles the Cerenkov threshold for the emission of photons in crystals by

* There is a simple connection between the first-order renormalization of the electron energy and the relaxation rate (28). The renormalized energy is

$$\varepsilon = \frac{k^2}{2m^*} + \sum_{\mathbf{q}} \frac{|\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}; 0_{\mathbf{q}} \rangle|^2}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}} - is}$$

where the limit $s \rightarrow +0$ is to be taken. By (1.34),

$$g(\varepsilon) = \pi \sum_{\mathbf{q}} |\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}; 0_{\mathbf{q}} \rangle|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}}).$$

On comparison with (28),

$$W = 2g(\varepsilon).$$

ELECTRON INTERACTION WITH LONGITUDINAL OPTICAL PHONONS

We expect electrons in ionic crystals to interact strongly with longitudinal optical phonons through the electric field of the polarization wave. This is a long-range coulomb interaction and is different from the deformation potential interaction. The interaction with transverse optical phonons will be less strong because of their smaller electric field, except at very low q where the electromagnetic coupling may be strong. Neglecting dispersion, the hamiltonian of the longitudinal optical phonons is approximately

$$(36) \quad H_0 = \omega_l \sum_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}},$$

where b^+ , b are boson operators. That is, we have N modes of different q , but with the identical frequency ω_l . Reference to (2.83) tells us that the dielectric polarization field is proportional to the optical phonon amplitude and will have the form

$$(37) \quad \mathbf{P} = F \sum_{\mathbf{q}} \boldsymbol{\epsilon}_{\mathbf{q}} (b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} + b_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q}\cdot\mathbf{x}}),$$

where $\boldsymbol{\epsilon}_{\mathbf{q}}$ is a unit vector in the direction of \mathbf{q} and F is a constant to be determined. We expand the electrostatic potential in the form

$$(38) \quad \varphi(\mathbf{x}) = \sum_{\mathbf{q}} (\varphi_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} + \varphi_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q}\cdot\mathbf{x}}),$$

whence

$$(39) \quad \mathbf{E} = -\text{grad } \varphi = -i \sum_{\mathbf{q}} \mathbf{q} (\varphi_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} - \varphi_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q}\cdot\mathbf{x}}).$$

But $\text{div } \mathbf{D} = 0$, so that $\mathbf{E} + 4\pi\mathbf{P} = 0$, or

$$(40) \quad \varphi_{\mathbf{q}} = -i4\pi F b_{\mathbf{q}}/q.$$

$$(40) \quad \varphi_{\mathbf{q}} = -i4\pi F b_{\mathbf{q}}/q.$$

We now want to evaluate the constant F in terms of the interaction energy $e^2/\epsilon r$ between two electrons in a medium of dielectric constant ϵ . Consider electrons at \mathbf{x}_1 and \mathbf{x}_2 which interact directly through the vacuum coulomb field and indirectly through the second-order perturbation of the optical phonon field. The desired form of the effective perturbation hamiltonian in first order is obtained as the expectation value of the potential energy operator $e \int d^3x \rho(\mathbf{x})\varphi(\mathbf{x})$ over the state $\Psi^+(\mathbf{x}_1)\Psi^+(\mathbf{x}_2)|\text{vac}\rangle$ which represents electrons localized at \mathbf{x}_1 and \mathbf{x}_2 , according to an extension of (5.124):

$$(41) \quad H'(\mathbf{x}_1, \mathbf{x}_2) = e\varphi(\mathbf{x}_1) + e\varphi(\mathbf{x}_2) \\ = -i4\pi F e \sum_{\mathbf{q}} q^{-1} (b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}_1} - b_{\mathbf{q}}^+ e^{-i\mathbf{q}\cdot\mathbf{x}_1} + b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}_2} - b_{\mathbf{q}}^+ e^{-i\mathbf{q}\cdot\mathbf{x}_2}).$$

Now at absolute zero the second-order energy perturbation caused by (41) is

$$(42) \quad H''(\mathbf{x}_1, \mathbf{x}_2) = -2 \sum_{\mathbf{q}} \frac{\langle 0|e\varphi(\mathbf{x}_1)|\mathbf{q}\rangle \langle \mathbf{q}|e\varphi(\mathbf{x}_2)|0\rangle}{\omega_{\mathbf{q}}},$$

where we have dropped products in \mathbf{x}_1 alone or \mathbf{x}_2 alone, as these are self-energy terms. The factor 2 arises from the interchange of \mathbf{x}_1 and \mathbf{x}_2 in the expression for the perturbation. Here the state $|0\rangle$ denotes

the vacuum phonon state; and $|q\rangle$ denotes the state with one optical phonon q excited virtually with energy ω_l . It is supposed in using (42) that the electrons are localized and that their state does not change in the interaction process. This problem is almost identical with the interaction problem in neutral scalar meson theory, without recoil.

It is easy to evaluate H'' from (41) and (42):

$$(43) \quad H''(\mathbf{x}_1, \mathbf{x}_2) = -\frac{2e^2(4\pi F)^2}{\omega_l} \sum_{\mathbf{q}} \frac{1}{q^2} e^{i\mathbf{q}\cdot(\mathbf{x}_1 - \mathbf{x}_2)};$$

but we have seen that when summed over all \mathbf{q}

$$(44) \quad \sum_{\mathbf{q}} \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{x}} = \frac{1}{|\mathbf{x}|},$$

so that in the ground state

$$(45) \quad H''(\mathbf{x}_1, \mathbf{x}_2) = -\frac{8\pi F^2}{\omega_l} \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|}.$$

so that in the ground state

$$(45) \quad H''(\mathbf{x}_1, \mathbf{x}_2) = -\frac{8\pi F^2}{\omega_l} \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|}.$$

This interaction is thus of the form of an attractive coulomb interaction between the charges e at \mathbf{x}_1 and \mathbf{x}_2 : it gives exactly the ionic contribution to the interaction. It thus accounts for the difference between $e^2/\epsilon_0 r$ and $e^2/\epsilon_\infty r$, where the dielectric constant ϵ_0 includes electronic and ionic polarizabilities, and ϵ_∞ includes only the electronic contribution. The ionic term lowers the energy of the system. We have

$$(46) \quad \frac{1}{\epsilon_0} = \frac{1}{\epsilon_\infty} - \frac{8\pi F^2}{\omega_l}.$$

In step (44) the sum was carried out over all \mathbf{q} ; actually the sum should only be over \mathbf{q} 's in the first Brillouin zone. The part of \mathbf{q} space we should have excluded may be seen to give by itself a screened coulomb interaction. On subtracting from $1/r$ a screened interaction we are left with a potential essentially $1/r$ at long distances, but flatter at distances within $1/q_m$, where q_m is on the zone boundary.

Polaron Cloud. We now solve in the weak coupling limit for the number of optical phonons which clothe an electron. From (16)

$$(47) \quad \langle N \rangle = \sum_{\mathbf{q}} \frac{|\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}; 0_{\mathbf{q}} \rangle|^2}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \omega_l)^2};$$

but now instead of the deformation potential (14) we have

$$(48) \quad H' = \int d^3x \, e\Psi^\dagger(\mathbf{x})\varphi(\mathbf{x})\Psi(\mathbf{x}) \\ = -i4\pi F e \sum_{\mathbf{k}q} q^{-1}(b_q c_{\mathbf{k}+q}^+ c_{\mathbf{k}} - b_q^+ c_{\mathbf{k}-q}^+ c_{\mathbf{k}}),$$

using (38) and (40) for $\varphi(\mathbf{x})$. Then

$$(49) \quad |\langle \mathbf{k} - \mathbf{q}; 1_q | H' | \mathbf{k}; 0_q \rangle|^2 = (4\pi e F)^2 / q^2,$$

and, neglecting $\mathbf{k} \cdot \mathbf{q}$ in comparison with q^2 ,

$$(50) \quad \langle N \rangle = 8e^2 F^2 (2m^*)^2 \int_0^\infty dq \frac{1}{(q^2 + q_p^2)^2},$$

where $q_p^2 = 2m^*\omega_l$; we have taken the upper limit as ∞ in the integration. For NaCl $q_p \approx 10^7 \text{ cm}^{-1}$ if m^* is taken as the electronic mass; thus q_p times the lattice constant is of the order of $\frac{1}{2}$.

The value of the integral in (50) is $\pi/4q_p^3$; with \hbar restored

$$(51) \quad \langle N \rangle = \frac{e^2}{4\hbar\omega_l} \left(\frac{2m^*\omega_l}{\hbar} \right)^{3/2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) = \frac{\alpha}{2};$$

this defines α , the dimensionless coupling constant commonly employed in polaron theory, after H. Fröhlich, H. Pelzer, and S. Zienau, *Phil. Mag.* **41**, 221 (1950). With m^* taken as the mass of the free electron, typical values of α calculated from the observed dielectric properties and infrared absorption of alkali halide crystals are:

	LiF	NaCl	NaI	KCl	KI	RbCl
α	5.25	5.5	4.8	5.9	6.1	6.4
$\langle N \rangle$	2.62	2.8	2.4	2.9	3.1	3.2

Thus for the alkali halides our estimate leads to $\langle N \rangle > 1$, so that the perturbation theory cannot be trusted to give valid quantitative results and more powerful methods are needed; we do, however, obtain an impression of the actual situation.

Polaron Effective Mass. The self-energy of a polaron for weak coupling is given in second-order perturbation theory as

$$(52) \quad \epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}}^0 - 2m^* \sum_{\mathbf{q}} \frac{|\langle \mathbf{k} - \mathbf{q}; 1_{\mathbf{q}} | H' | \mathbf{k}; 0_{\mathbf{q}} \rangle|^2}{q^2 - 2\mathbf{k} \cdot \mathbf{q} + q_p^2},$$

or, using the interaction (48) appropriate to the ionic crystal problem,

$$(53) \quad \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^0 = -8e^2 F^2 m^* \int_{-1}^1 d(\cos \theta) \int_0^{\infty} dq \frac{1}{q^2 - 2\mathbf{k} \cdot \mathbf{q} + q_p^2}.$$

Here we have used (49) and $q_p^2 = 2m^* \omega_l$.

The integral can be evaluated exactly, but for slow electrons ($k \ll q_p$) we might as well expand the integrand as

$$(54) \quad \frac{1}{1+x^2} \left(1 + \frac{2\eta\mu x}{1+x^2} + \frac{4\eta^2\mu^2 x^2}{(1+x^2)^2} + \dots \right),$$

with $x = q/q_p$; $\mu = \cos \theta$; $\eta = k/q_p$. The integral over $d\mu$ leaves (54) as

$$(55) \quad \frac{1}{1+x^2} \left(2 + \frac{8}{3}\eta^2 \frac{x^2}{(1+x^2)^2} + \dots \right);$$

after integrating over x from 0 to ∞ we have, using Dwight (122.3),

$$(56) \quad \epsilon_k - \epsilon_k^0 = -\alpha \left(\omega_l + \frac{1}{12m^*} k^2 + \dots \right),$$

so that the ground-state energy is depressed by $\alpha\omega_l$ by the electron-phonon interaction, and the total polaron kinetic energy is

$$(57) \quad \epsilon_{\text{kin}} = \frac{1}{2m^*} \left(1 - \frac{1}{3}\alpha \right) k^2.$$

For $\alpha \ll 1$, the mass of the polaron is

$$(58) \quad m_{\text{pol}}^* \cong m^* \left(1 + \frac{1}{3}\alpha \right),$$