7 Electron-phonon interactions. The polaron

In this section we will sketch the derivation of the Hamiltonian describing interactions of electrons with the quantized vibrations of the crystal lattice. As we have argued in section 5.5, excitations of the vibrations behave formally as particles. In the case of the crystal lattice vibrations such particles are called phonons. Interaction of electrons in a crystal with phonons is (among other factors like structure defects) responsible for a finite value of the electric conductivity (a nonzero resistance) of metals. We will use the formalism of creation and annihilation operators developed in previous chapters and apply it to an interesting problem of a polaron. This example will show some other features of the perturbation calculus.

7.1 Hamiltonian of the electrons and phonons

Consider first an electron moving in a crystal lattice. The lattice is a periodic structure consisting of elementary cells. Chosing some reference point (no matter which) in such a cell, the position of a cell in a crystal can be specified by a vector

$$\mathbf{N} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \ , \tag{7.1}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are three vectors characterizing the cell. Electrons move in a periodic potential which can be written as

$$V(\mathbf{r}) = \sum_{\mathbf{N}} V_0(\mathbf{r}-\mathbf{N}) \ . \tag{7.2}$$

where V_0 is the electrostatic potential produced at $\mathbf{r}$ by one elementary cell. In the absence of interactions with phonons and mutual repulsion the Hamiltonian of electrons takes the form

$$H_{\rm el} = \sum_{\lambda=1,2} \int d^3\mathbf{r}\ a^\dagger_\lambda(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right] a_\lambda(\mathbf{r}) \ . \tag{7.3}$$

One could as here also

$$H'_{\rm el} = \frac{1}{2}\sum_{\lambda_1\lambda_2=1}^{2} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2\ a^\dagger_{\lambda_1}(\mathbf{r}_1)a^\dagger_{\lambda_2}(\mathbf{r}_2)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}a_{\lambda_2}(\mathbf{r}_2)a_{\lambda_1}(\mathbf{r}_1)$$

but in this chapter we will neglect this interaction. If we solve the one-particle problem

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right] u_\kappa(\mathbf{r}) = E_\kappa u_\kappa(\mathbf{r}) \tag{7.4}$$

the Hamiltonian (7.3) can be written as

$$H_{\text{el}} = \sum_{\lambda=1,2}\sum_{\kappa} E_\kappa a^\dagger_{\kappa\lambda} a_{\kappa\lambda} \ . \tag{7.5}$$

From the ordinary Quantum Mechanics we know (or should know) that for a periodic potential of the form (7.2) the electron energies E_κ form allowed and forbidden bands of finite widths. In the allowed bands electrons behave essentially as free particles, possibly with an effective mass replacing its ordinary mass of 511 keV/c^2. The one-particle wave functions $u_\kappa(\mathbf{r})$ are then of the Bloch form $u(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{x}}\chi(\mathbf{r})$ where the $\mathbf{q}$ is the pseudomomentum restricted to the first Brillouin zone ($-\pi \leq \mathbf{q}\cdot\mathbf{a}_i \leq +\pi$ where $\mathbf{a}_i$ are the three vectors (7.1)) and the functions $\chi(\mathbf{r})$ are periodic $\chi(\mathbf{r}+\mathbf{N}) = \chi(\mathbf{r})$. We will approximate $\chi(\mathbf{r})$ by a constant factor and will neglect the difference between electron pseudomementum $\mathbf{q}$ and the ordinary momentum.

Next we consider lattice vibrations. Let each elementary cell consist of A atoms. Displacements of atoms from their equilibrium positions are described by the (generalized) coordinates $Z_{\mathbf{N},\alpha}$, where the subscript $\mathbf{N}$ gives the position of the cell and the subscript α labels $3A$ coordinates of A displaced atoms within the cell. The Lagrangian describing the harmonic motion[39] of atoms is

$$L = \frac{1}{2}\sum_{\mathbf{N},\alpha}\dot{Z}^2_{\mathbf{N},\alpha} - \frac{1}{2}\sum_{\mathbf{N},\alpha}\sum_{\mathbf{N}',\beta} V_{\mathbf{N},\alpha;\mathbf{N}',\beta}\ Z_{\mathbf{N},\alpha}\ Z_{\mathbf{N}',\beta} \tag{7.6}$$

where we have assumed that the coordinates $Z_{\mathbf{N},\alpha}$ are appropriately rescaled by mass factors. Since the crystal is periodic it must be possible to rewrite the above Lagrangian in the form

$$L = \frac{1}{2}\sum_{\mathbf{N},\alpha}\dot{Z}^2_{\mathbf{N},\alpha} - \frac{1}{2}\sum_{\mathbf{M},\alpha}\sum_{\mathbf{N},\beta} C^{\mathbf{M}}_{\alpha\beta}\ Z_{\mathbf{N},\alpha}\ Z_{\mathbf{N}+\mathbf{M},\beta} \tag{7.7}$$

[39] This might be, of course, only an approximation to a more complicated motion of atoms. For example, a term in the Lagrangian quartic in $Z_{\mathbf{N},\alpha}$ could be added and would lead to a phonon-phonon binary interaction.

i.e. making explicit that the interaction of atoms in two cells depends only of the relative position of these two cells. Moreover, by translational invariance the potential must be the same if we write it as

$$\frac{1}{2}\sum_{\mathbf{M}}\sum_{\mathbf{N}}\sum_{\alpha,\beta} C^{\mathbf{M}}_{\alpha\beta}\ Z_{\mathbf{N}-\mathbf{M},\alpha}\ Z_{\mathbf{N},\beta} = \frac{1}{2}\sum_{\mathbf{M}}\sum_{\mathbf{N}}\sum_{\alpha,\beta}\ C^{-\mathbf{M}}_{\alpha\beta} Z_{\mathbf{N}+\mathbf{M},\alpha}\ Z_{\mathbf{N},\beta}$$

from which it follows that $C^{\mathbf{M}}_{\alpha\beta} = C^{-\mathbf{M}}_{\beta\alpha}$

Assuming that the lattice is infinite, we seek the solution of the coupled Euler-Lagrange equations

$$\frac{d^2}{dt^2} Z^2_{\mathbf{N},\alpha} + \sum_{\mathbf{M},\beta} C^{\mathbf{M}}_{\alpha\beta}\ Z_{\mathbf{N}+\mathbf{M},\beta} = 0 \tag{7.8}$$

in the form

$$Z_{\mathbf{N},\alpha} = a_\alpha(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{N}}\ e^{-i\omega t}\ . \tag{7.9}$$

The possible vectors $\mathbf{K}$ should be restricted to the first Brillouin zone defined by

$$-\pi \leq \mathbf{K}\cdot\mathbf{a}_i \leq +\pi\ , \qquad i = 1,2,3 \tag{7.10}$$

since for $\mathbf{N}$ given by (7.1) only these values of $\mathbf{K}$ give distinct $Z_{\mathbf{N},\alpha}$ in (7.9). For such $\mathbf{K}$ we have

$$\mathcal{V}\int \frac{d^3\mathbf{K}}{(2\pi)^3}\ e^{i\mathbf{K}\cdot(\mathbf{N}-\mathbf{N}')} = \delta_{\mathbf{N},\mathbf{N}'} \tag{7.11}$$

where $\mathcal{V}$ is the volume of the elementary cell:

$$\mathcal{V} = |\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)|\ , \tag{7.12}$$

and

$$\mathcal{V}\sum_{\mathbf{N}} e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{N}} = (2\pi)^3\delta^{(3)}(\mathbf{K}-\mathbf{K}')\ . \tag{7.13}$$

Inserting (7.9) into (7.8) we find the condition

$$\sum_{\mathbf{M},\beta} C^{\mathbf{M}}_{\alpha\beta}\ e^{i\mathbf{K}\cdot\mathbf{M}}\ a_\beta(\mathbf{K}) \equiv \sum_{\beta}\gamma_{\alpha\beta}(\mathbf{K})\ a_\beta(\mathbf{K}) = \omega^2(\mathbf{K})\ a_\alpha(\mathbf{K})\ . \tag{7.14}$$

For a fixed vector $\mathbf{K}$ this condition has the form of a homogeneous linear equation. Therefore for each $\mathbf{K}$ there are $r = 1, \ldots, 3A$ eigenvectors $a^r_\beta(\mathbf{K})$ (each having $3A$ components), corresponding to $r = 1, \ldots, 3A$ real eigenvalues $\omega_r(\mathbf{K})$ of the Hermitian (as can be checked by using the property $C^{\mathbf{M}}_{\alpha\beta} = C^{-\mathbf{M}}_{\beta\alpha}$) matrix $\gamma_{\alpha\beta}(\mathbf{K})$.[40] We assume that all $\omega_r(\mathbf{K})$ are positive (if some of them are not positive, the Lagrangian (7.6) does not describe only harmonic oscilations) It is also easy to see that $\omega^2_r(-\mathbf{K}) = \omega^2_r(\mathbf{K})$. The $3A$ eigenvectors $a^r_\beta(\mathbf{K})$ of the matrix $\gamma_{\alpha\beta}(\mathbf{K})$ are orthogonal to each other

$$\sum_\alpha a^{r*}_\alpha(\mathbf{K})\ a^s_\alpha(\mathbf{K}) = \delta_{r,s}\ . \tag{7.15}$$

and form a complete set

$$\sum_{r=1}^{3A} a^r_\alpha(\mathbf{K})\ a^{r*}_\beta(\mathbf{K}) = \delta_{\alpha\beta} \tag{7.16}$$

Moreover, from (7.14) it follows that

$$a^{r*}_\alpha(\mathbf{K}) = a^r_\alpha(-\mathbf{K})\ . \tag{7.17}$$

The most general solution of the set of equations (7.8) reads

$$\begin{aligned} Z_{\mathbf{N},\alpha}(t) &= \mathcal{V}\sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3}\ C_r(\mathbf{K})\ a^r_\alpha(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{N}}\ e^{-i\omega_r(\mathbf{K})t} \\ &\equiv \mathcal{V}\sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3}\ Q_r(\mathbf{K},t)\ a^r_\alpha(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{N}} \end{aligned} \tag{7.18}$$

where $Q_r(\mathbf{K}, t)$ are the so-called normal coordinates. They can be obtained from the solution $Z_{\mathbf{N},\alpha}(t)$ with the help of the reciprocal relation

$$Q_r(\mathbf{K},t) = \sum_{\mathbf{N},\alpha} Z_{\mathbf{N},\alpha}(t)\ a^{r*}_\alpha(\mathbf{K})\ e^{-i\mathbf{K}\cdot\mathbf{N}}\ . \tag{7.19}$$

[40] In order to understand better what we are doing, recall the standard problem (solved at Fizyka II classes) of infinite line of masses m connected with springs. There is then only one $\omega(\mathbf{K})$, the so-called dispersion relation. If we however consider an infinite line consisting of masses m followed by masses M one finds that there are two different dispersion relations: one corresponding to the so-called acoustical vibrations and the other one corresponding to the so-called optical vibrations. Our $3A$ solutions $\omega_r(\mathbf{K})$ generalize this result to more degrees of freedom distributed periodically.

The Hamiltonian of the system

$$H = \frac{1}{2} \sum_{\mathbf{N},\alpha} P^2_{\mathbf{N},\alpha} + \frac{1}{2} \sum_{\mathbf{M},\alpha} \sum_{\mathbf{N},\beta} Z_{\mathbf{N},\alpha}\ C^{\mathbf{M}}_{\alpha\beta}\ Z_{\mathbf{N}+\mathbf{M},\beta} \tag{7.20}$$

where the canonical momenta $P_{\mathbf{N},\alpha} = \dot{Z}_{\mathbf{N},\alpha}$, expressed in terms of the normal coordinates reads

$$H = \frac{\mathcal{V}}{2} \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3} \left[\dot{Q}_r(\mathbf{K})\dot{Q}_r(-\mathbf{K}) + \omega_r^2(\mathbf{K}) Q_r(\mathbf{K}) Q_r(-\mathbf{K})\right]. \tag{7.21}$$

We quantize the system by promoting $Z_{\mathbf{N},\alpha}$ and $\dot{Z}_{\mathbf{N},\alpha}$ to operators and by imposing at $t = 0$ the commutation rule ($Z_{\mathbf{N},\alpha}$ and $\dot{Z}_{\mathbf{N},\alpha}$ become in this way time independent operators in the Schrödinger picture)

$$\left[Z_{\mathbf{N},\alpha},\ \dot{Z}_{\mathbf{N}',\beta}\right] = i\hbar\ \delta_{\mathbf{N},\mathbf{N}'}\ \delta_{\alpha\beta} \tag{7.22}$$

from which follows the commutation rule

$$\left[Q_r(\mathbf{K},t),\ \dot{Q}_{r'}(\mathbf{K}',t)\right] = i\hbar \frac{(2\pi)^3}{\mathcal{V}} \delta^{(3)}(\mathbf{K}+\mathbf{K}')\ \delta_{r,r'} \tag{7.23}$$

The annihilation and creation operators are defined as

$$A_r(\mathbf{K}) \equiv \sqrt{\frac{\mathcal{V}\omega_r(\mathbf{K})}{2\hbar}} \left[Q_r(\mathbf{K}) + \frac{i}{\omega_r(\mathbf{K})}\dot{Q}_r(\mathbf{K})\right], \tag{7.24}$$

$$A^\dagger_r(\mathbf{K}) \equiv \sqrt{\frac{\mathcal{V}\omega_r(-\mathbf{K})}{2\hbar}} \left[Q_r(-\mathbf{K}) - \frac{i}{\omega_r(-\mathbf{K})}\dot{Q}_r(-\mathbf{K})\right]. \tag{7.25}$$

It straightforward to find their commutation rules

$$\left[A_r(\mathbf{K}),\ A^\dagger_{r'}(\mathbf{K}')\right] = (2\pi)^3 \delta_{r,r'} \delta^{(3)}(\mathbf{K}-\mathbf{K}'), \tag{7.26}$$

$$[A_r(\mathbf{K}),\ A_{r'}(\mathbf{K}')] = 0, \qquad \left[A^\dagger_r(\mathbf{K}),\ A^\dagger_{r'}(\mathbf{K}')\right] = 0 \tag{7.27}$$

In terms of the creation and annihilation operators the Hamiltonian (7.21) takes the form

$$\begin{aligned} H_{\text{phon}} &= \frac{1}{2} \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3}\ \hbar\omega_r(\mathbf{K})\ \left[A^\dagger_r(-\mathbf{K})A_r(-\mathbf{K}) + A_r(\mathbf{K})A^\dagger_r(\mathbf{K})\right] \\ &= \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3}\ \hbar\omega_r(\mathbf{K})\ A^\dagger_r(\mathbf{K})A_r(\mathbf{K}) + \text{const}. \end{aligned} \tag{7.28}$$

(the constant is irrelevant and will be discarded.) The generalized coordinates (7.18) can be written as

$$Z_{\mathbf{N},\alpha} = \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3} \sqrt{\frac{\hbar\mathcal{V}}{2\omega_r(\mathbf{K})}} \left[A_r(\mathbf{K}) + A_r^\dagger(-\mathbf{K})\right] a_\alpha^r(\mathbf{K})\, e^{i\mathbf{K}\cdot\mathbf{N}} \tag{7.29}$$

$$= \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3} \sqrt{\frac{\hbar\mathcal{V}}{2\omega_r(\mathbf{K})}} \left[A_r(\mathbf{K})\; a_\alpha^r(\mathbf{K})\; e^{i\mathbf{K}\cdot\mathbf{N}} + A_r^\dagger(\mathbf{K})\; a_\alpha^{r*}(\mathbf{K})\; e^{-i\mathbf{K}\cdot\mathbf{N}}\right]$$

The eigenvectors of the Hamiltonian (7.28) are now obvious. If $|\Omega\rangle$ is a state annihilated by all operators $A_r(\mathbf{K})$ the energy eigenstates are

$$|\Omega\rangle, \quad A_r^\dagger(\mathbf{K})|\Omega\rangle, \quad A_{r_2}^\dagger(\mathbf{K}_2)A_{r_1}^\dagger(\mathbf{K}_1)|\Omega\rangle, \qquad \text{etc.} \tag{7.30}$$

and are said to be states of no, one, two, etc. phonons, respectively.

We consider now the coupling between electrons and phonons. To this end we will change slightly the notation. Let the k-th atom (of mass M_k) in the elementary cell be at position $\boldsymbol{\delta}_k$ with respect to the cell's reference point given by $\mathbf{N}$. The displacement of the k-th atom from its equilibrium position will be now given by the vector $\mathbf{Z}_{\mathbf{N},k}$. Due to the vibration of the crystall lattice atoms the potential energy (7.2) felt by an electron at a point $\mathbf{r}$ is changed by $\Delta V(\mathbf{r})$

$$V(\mathbf{r}) + \Delta V(\mathbf{r}) = \sum_{\mathbf{N}} \sum_{k=1}^{A} V_{0k}(\mathbf{r} - \mathbf{N} - \boldsymbol{\delta}_k - \mathbf{Z}_{\mathbf{N},\mathbf{k}})\ . \tag{7.31}$$

where V_{0k} is the electrostatic potential produced by the k-th atom. The assumption made here is that the displaced atom does not change its properties, i.e. that its electron cloud is displaced exactly in the same way as the nucleus. (We neglect the possibility that some of the electrons could be also displaced with respect to nucleus.) Hence,

$$\Delta V(\mathbf{r}) = -\sum_{\mathbf{N}} \sum_{k=1}^{A} \mathbf{Z}_{\mathbf{N},\mathbf{k}} \cdot \boldsymbol{\nabla} V_{0k}(\mathbf{r} - \mathbf{N} - \boldsymbol{\delta}_k) + \ldots \tag{7.32}$$

and we have to put it in the form of a second-quantized operator according to the standard rule:

$$H_{\mathrm{el-phon}} = \sum_\lambda \int d^3\mathbf{r}\; a_\lambda^\dagger(\mathbf{r})\; \Delta V(\mathbf{r})\; a_\lambda(\mathbf{r}) = \sum_\lambda \sum_{\kappa\kappa'} a_{\kappa\lambda}^\dagger\; V_{\kappa\kappa'}\; a_{\kappa'\lambda}\ , \tag{7.33}$$

where[41]

$$V_{\kappa\kappa'} = \int d^3\mathbf{r}\ u^*_{\kappa\lambda}(\mathbf{r})\ \Delta V(\mathbf{r})\ u_{\kappa'\lambda}(\mathbf{r}) \tag{7.34}$$

$$= -\sum_{\mathbf{N}}\sum_{k=1}^{A} \mathbf{Z}_{\mathbf{N},\mathbf{k}} \cdot \int d^3\mathbf{r}\ u^*_{\kappa\lambda}(\mathbf{r}) \boldsymbol{\nabla} V_{0k}(\mathbf{r}-\mathbf{N}-\boldsymbol{\delta}_k) u_{\kappa'\lambda}(\mathbf{r})$$

It is important to remember that $\mathbf{Z}_{\mathbf{N},\mathbf{k}}$ here are also operators but acting only on phononic vector states:

$$V_{\kappa\kappa'} = -\sum_{\mathbf{N}}\sum_{k=1}^{A}\sum_{r}\int \frac{d^3\mathbf{K}}{(2\pi)^3}\sqrt{\frac{\hbar\mathcal{V}}{2\omega_r(\mathbf{K})}}\Big[A_r(\mathbf{K})\ \mathbf{e}^r_k(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{N}} \tag{7.35}$$
$$+A^\dagger_r(\mathbf{K})\ \mathbf{e}^{r*}_k(\mathbf{K})\ e^{-i\mathbf{K}\cdot\mathbf{N}}\Big] \cdot \int d^3\mathbf{r}\ u^*_{\kappa\lambda}(\mathbf{r}) \boldsymbol{\nabla} V_0(\mathbf{r}-\mathbf{N}-\boldsymbol{\delta}_k)\ u_{\kappa'\lambda}(\mathbf{r})$$

where the vectors $\mathbf{e}^r_k(\mathbf{K})$, $k = 1,\dots,A$ replace the vectors $a^r_\alpha(\mathbf{K})$, $\alpha = 1,\dots,3A$ in (7.29) when we switch from $Z_{\mathbf{N},\alpha}$ to the vector notation $\mathbf{Z}_{\mathbf{N},k}$: $M_1^{-1/2}a^r_{\alpha=1,2,3} \to \mathbf{e}^r_1$, $M_2^{-1/2}a^r_{\alpha=4,5,6} \to \mathbf{e}^r_2$, etc.[42] This can be written in the general form

$$V_{\kappa\kappa'} = \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3}\Big[C^r_{\kappa\kappa'}(\mathbf{K})\ A_r(\mathbf{K}) + C^{r*}_{\kappa'\kappa}(\mathbf{K})\ A^\dagger_r(\mathbf{K})\Big] \tag{7.36}$$

in which the complicated factors $C^r_{\kappa\kappa'}$

$$C^r_{\kappa\kappa'}(\mathbf{K}) = -\sqrt{\frac{\hbar\mathcal{V}}{2\omega_r(\mathbf{K})}}\sum_{\mathbf{N}}\sum_{k=1}^{A}\mathbf{e}^r_k(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{N}}$$
$$\cdot\int d^3\mathbf{r}\ u^*_{\kappa\lambda}(\mathbf{r}) \boldsymbol{\nabla} V_0(\mathbf{r}-\mathbf{N}-\boldsymbol{\delta}_k)\ u_{\kappa'\lambda}(\mathbf{r})$$

depend on the specific physical problem (they summarize the information on the crystal and electron states in the crystal). The Hamiltonian of electron-phonon interactions takes the form

$$H_{\mathrm{el-phon}} = \sum_\lambda\sum_{\kappa\kappa'}\sum_r\int\frac{d^3\mathbf{K}}{(2\pi)^3}a^\dagger_{\kappa\lambda}\Big[C^r_{\kappa\kappa'}(\mathbf{K})\ A_r(\mathbf{K}) + C^{r*}_{\kappa'\kappa}(\mathbf{K})\ A^\dagger_r(\mathbf{K})\Big]a_{\kappa'\lambda} \tag{7.37}$$

[41] We assume that the interactions of electrons with the crystal lattice do not depend on electron spin.

[42] Recall, that because the kinetic term in the Lagrangian (7.6) has only 1/2 in front of its kinetic term, the coordinates $Z_{\mathbf{N},\alpha}$ have the dimension of $\sqrt{\text{mass}}\times$length.

and, after transition to the particle-hole description for electron annihilation and creation operators contains the elementary interactions represented by the following combination of operators:

$$\begin{array}{llll} A^\dagger a^\dagger a, & A^\dagger a^\dagger b^\dagger, & A^\dagger ba, & A^\dagger bb^\dagger, \\ Aa^\dagger a, & Aa^\dagger b^\dagger, & Aba, & Abb^\dagger, \end{array} \tag{7.38}$$

We assume that the phononic and electronic operators commute with each other. The total Hamiltonian of the system of electrons and phonons is given by the sum of (7.5), (7.28) and (7.37):

$$H_{\rm tot} = H_{\rm el} + H_{\rm phon} + H_{\rm el-phon} \ . \tag{7.39}$$

and the eigenstates of its unperturbed part $H_{\rm el} + H_{\rm phon}$ are the tensor products of electronic and phononic states. In some physical situations one can assume that some of the vibration modes r do not couple (or couple negligibly weakly) to electrons, i.e. that these vibrations do not modify appreciably the potential in which electrons move. One then sets $C^r_{\kappa\kappa'}(\mathbf{K}) = 0$ for there modes. In addition, at the phenomenological level one can assume any particular form of some $C^r_{\kappa\kappa'}$'s as functions of $\mathbf{K}$. This is in contrast to the relativistic case, in which Lorentz covariance of the S-matrix tightly constrains possible forms of interactions.

7.2 Electron effective mass in an ion crystal (the polaron)

The polaron problem is a an interesting example of calculations which can be easily performed in the theoretical framework developed in the preceding subsection. It also illustrates how physical considereations allow to select from all possible vibration modes the relevant one and to establish its coupling to electrons (the factors $C^r_{\kappa\kappa'}$).

An electron moving in a crystal whose elementary cells consist of one positively and one negatively charged ion (the so-called ion crystal) polarizes the sourrounding medium. This interaction affects the electron energy. The polarized region moves together with the electron forming the so-called polaron. Our task will be to compute the correction to the electron energy due to its interaction with the vibrations and to show that it can be accounted for as an additional shift of the electron mass.

To compute the mass shift we first note that in the absence of lattice vibrations (i.e. when the positions of the crystal atoms are fixed) the electron moves in a crystal in a periodic electrostatic potential. This interaction is formally taken into account as in formula (7.5), i.e. by chosing the appropriate basis of one-particle states $u_{\kappa\lambda}(\mathbf{r})$ and connecting the electron creation and annihilation operators with this basis. In the first approximation one can, however, modify the mass of the electron $M \to M \neq M_{\text{free el}}$ and take for $u_{\kappa\lambda}(\mathbf{r})$ the ordinary plane waves. The interaction of the electron with vibrations modifies further the electron mass and it is this further modification that we try to calculate here.

Let us assume that each elementary cell consists of $A = 2$ atoms (one positive and one negative ion). Therefore for each $\mathbf{N}$ there are two coordinate vectors $\mathbf{Z}_{\mathbf{N},+}$ and $\mathbf{Z}_{\mathbf{N},-}$ of the positive and negative ion, respectively, that is $3A = 6$ independent variables. There are therefore six different vibration modes (six different functions $\omega_r(\mathbf{K})$. Three of them represent the so-called acoustic modes for which $\omega_r(\mathbf{K}) \to 0$ as $\mathbf{K} \to 0$ (for $\mathbf{K} = 0$ these represent simply translations of the crystal as a whole in three possible directions). As for these modes both ions in each cell are displaced in the same direction, these modes have nothing to do with the polarization of the medium and we will ignore them. For the three other (the so-called optical) modes positive and negative ions in each cell are displaced in the opposite directions $\mathbf{Z}_{\mathbf{N},-} \approx -\mathbf{Z}_{\mathbf{N},+}$ creating some net polarization $\mathbf{P}(\mathbf{r})$. The frequencies of these modes do not vanish as $\mathbf{K} \to 0$.

In order to simplify the problem we will treat the crystal as a continuous distribution of matter, so that at each point $\mathbf{r}$ there is an elementary cell (in other words, we identify the vector $\mathbf{N}$ (7.1) with $\mathbf{r}$). We will also set $\mathbf{Z}_{\mathbf{N},-} = -\mathbf{Z}_{\mathbf{N},+}$ which will allow us to follow only $\mathbf{Z}_{\mathbf{N},+} \equiv \mathbf{Z}(\mathbf{r})$. Furthermore, we will perform our calculations in the approximation $\omega^r(\mathbf{K}) \approx \omega^r$ =const. In order to find the coupling of electrons to phonons responsible for the mass shift of the polaron we resort to a physical picture. The perturbation $\Delta V(\mathbf{r})$ in (7.31) can be viewed as due to the presence of a different from zero polarization charge density $\rho_{\text{pol}}(\mathbf{r})$ appearing as a result of the displacement of atoms. $\rho_{\text{pol}}(\mathbf{r})$ is in turn determined by the local polarization vector $\mathbf{P}(\mathbf{r})$:[43] $\rho_{\text{pol}} = -\boldsymbol{\nabla} \cdot \mathbf{P}$

[43] See "Feynman lectures on physics" vol. 2 chapter 10 for a lucid explanation: In a volume V the presence of a constant polarization $\mathbf{P}$ (polarization is simply given

Writing $\mathbf{E} = -\boldsymbol{\nabla}(\Delta V)$ and using the Maxwell equation $\boldsymbol{\nabla} \cdot \mathbf{E} = 4\pi\rho$ one gets

$$-\nabla^2(\Delta V(\mathbf{r})) = 4\pi(-\boldsymbol{\nabla} \cdot \mathbf{P}(\mathbf{r})) \ . \tag{7.40}$$

In such a picture the polarization vector $\mathbf{P}$ is proportional to the displacement $\mathbf{Z}(\mathbf{r})$ of the positive ions:

$$\mathbf{P}(\mathbf{r}) = \tilde{\eta}\ \mathbf{Z}(\mathbf{r}) = \tilde{\eta} \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3} \sqrt{\frac{\hbar \mathcal{V}}{2\omega_r(\mathbf{K})}} \Big[A_r(\mathbf{K})\ \mathbf{e}^r(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{r}} + A_r^\dagger(\mathbf{K})\ \mathbf{e}^{r*}(\mathbf{K})\ e^{-i\mathbf{K}\cdot\mathbf{r}}\Big] \tag{7.41}$$

and the polarization charge density is given by

$$\rho_{\rm pol}(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{P}(\mathbf{r}) = -i\tilde{\eta} \sum_r \int \frac{d^3\mathbf{K}}{(2\pi)^3} \sqrt{\frac{\hbar \mathcal{V}}{2\omega_r(\mathbf{K})}} \times \Big[A_r(\mathbf{K})\ \mathbf{K}\cdot\mathbf{e}^r(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{r}} - A_r^\dagger(\mathbf{K})\ \mathbf{K}\cdot\mathbf{e}^{r*}(\mathbf{K})\ e^{-i\mathbf{K}\cdot\mathbf{r}}\Big] \tag{7.42}$$

A good approximation to realistic situations is to assume that one of the vibration modes is longitudinal, i.e. has the vector $\mathbf{e}^r$ parallel to $\mathbf{K}$ and the other modes are transversal (usually the longitudinal mode has ω_r different than the other two modes). In such a situation it is only the longitudinal mode which contributes to the charge polarization density. This allows us to simplify the formula (7.42) to:

$$\rho_{\rm pol}(\mathbf{r}) = -i\eta \int \frac{d^3\mathbf{K}}{(2\pi)^3} |\mathbf{K}|\ \Big[A(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{r}} - A^\dagger(\mathbf{K})\ e^{-i\mathbf{K}\cdot\mathbf{r}}\Big] \tag{7.43}$$

where we have absorbed all irrelevant constants (including the constant by assumption ω_r of the longitudinal mode) into the redefinition $\tilde{\eta} \to \eta$. We have also suppressed the label r on creation and annihilation operators. Inverting now the laplacian in (7.40) we find

$$\Delta V(\mathbf{r}) = i4\pi\ \eta \int \frac{d^3\mathbf{K}}{(2\pi)^3} \frac{1}{|\mathbf{K}|} \Big[A(\mathbf{K})\ e^{i\mathbf{K}\cdot\mathbf{r}} - A^\dagger(\mathbf{K})\ e^{-i\mathbf{K}\cdot\mathbf{r}}\Big] \tag{7.44}$$

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by the number of positive or negative charges times the charge times the relative displacement $\mathbf{d}$ of opposite positive and negative charges) does not generate any charge density. However a nonconstant polarization produces the surface charge $\mathbf{n}\cdot\mathbf{P}$ on the boundary of the volume V ($\mathbf{n}$ is a vector normal to the surface). This is the charge that has left the volume V. Therefore the net charge generated inside the volume is $Q_{\rm pol} = -\int d\boldsymbol{\sigma}\cdot\mathbf{P}$, which, by Stokes theorem gives $\rho_{\rm pol} = -\boldsymbol{\nabla}\cdot\mathbf{P}$.

which, by using the plane waves normalized in a box of volume V (do not confuse with the volume of the elementary cell $\mathcal{V}$!) for electron wave functions $u_{\alpha\lambda}(\mathbf{r})$ in the formulae (7.33) and (7.34) gives rise to

$$H_{\mathrm{el-phon}} = \frac{1}{V} \sum_{\lambda} \sum_{\mathbf{p}_2} \sum_{\mathbf{p}_1} a^{\dagger}_{\mathbf{p}_2\lambda} a_{\mathbf{p}_1\lambda} \int d^3\mathbf{r}\; e^{-i\mathbf{p}_2\cdot\mathbf{r}}\; \Delta V(\mathbf{r})\; e^{i\mathbf{p}_1\cdot\mathbf{r}} \tag{7.45}$$

so that the total Hamiltonian describing the interaction we are interested in reads

$$\begin{aligned} H_{\mathrm{tot}} &= \sum_{\lambda} \sum_{\mathbf{p}} \frac{\hbar^2\mathbf{p}^2}{2M} a^{\dagger}_{\mathbf{p}\lambda} a_{\mathbf{p}\lambda} + \hbar\omega \int \frac{d^3\mathbf{K}}{(2\pi)^3} A^{\dagger}(\mathbf{K}) A(\mathbf{K}) \\ &+ i\alpha \sum_{\lambda} \sum_{\mathbf{p}} \int \frac{d^3\mathbf{K}}{(2\pi)^3} \frac{1}{|\mathbf{K}|} \left[A(\mathbf{K})\; a^{\dagger}_{\mathbf{p}-\mathbf{K}\lambda}\; a_{\mathbf{p}\lambda} - A^{\dagger}(\mathbf{K})\; a^{\dagger}_{\mathbf{p}+\mathbf{K}\lambda}\; a_{\mathbf{p}\lambda} \right] \end{aligned} \tag{7.46}$$

where now α stands for all constant factors and plays the role of the "coupling constant".

We want now to determine the energy of a single electron state $a^{\dagger}_{\mathbf{p}\lambda}|\Omega\rangle$. In zeroth order we obviously have

$$E^{(0)} = \frac{\hbar^2\mathbf{p}^2}{2M}\ . \tag{7.47}$$

The first order correction is evidently zero:

$$\Delta E^{(1)} = \langle\Omega| a_{\mathbf{p}\lambda} H' a^{\dagger}_{\mathbf{p}\lambda} |\Omega\rangle = 0 \tag{7.48}$$

and the first nontrivial correction is

$$\Delta E^{(2)} = \sum_n \frac{\langle\Omega| a_{\mathbf{p}\lambda} H' |n\rangle \langle n| H' a^{\dagger}_{\mathbf{p}\lambda} |\Omega\rangle}{E^{(0)} - E_n} \tag{7.49}$$

From the structure of H' it is clear that the only intermediate state which can appear here is $|n\rangle = |\mathbf{K}_1, \mathbf{p}_1\lambda_1\rangle$, so that

$$\sum_n \equiv \int \frac{d^3\mathbf{K}_1}{(2\pi)^3} \sum_{\mathbf{p}_1\lambda_1}$$

For such $|n\rangle$ we find

$$\begin{aligned} &\langle\mathbf{K}_1, \mathbf{p}_1\lambda_1 | H' | \mathbf{p}\lambda\rangle \\ &= i\alpha \langle\Omega| A(\mathbf{K}_1)\; a_{\mathbf{p}_1\lambda_1} \sum_{\lambda_2} \sum_{\mathbf{p}_2} \int \frac{d^3\mathbf{K}_2}{(2\pi)^3} \frac{1}{|\mathbf{K}_2|} A^{\dagger}(\mathbf{K}_2)\; a^{\dagger}_{\mathbf{p}_2-\mathbf{K}_2\lambda_2}\; a_{\mathbf{p}_2\lambda_2} a^{\dagger}_{\mathbf{p}\lambda} |\Omega\rangle \\ &= i\alpha \int \frac{d^3\mathbf{K}_2}{(2\pi)^3} \frac{1}{|\mathbf{K}_2|} \langle\Omega| A(\mathbf{K}_1)\; a_{\mathbf{p}_1\lambda_1} A^{\dagger}(\mathbf{K}_2)\; a^{\dagger}_{\mathbf{p}-\mathbf{K}_2\lambda} |\Omega\rangle = i\alpha \frac{1}{|\mathbf{K}_1|} \delta_{\mathbf{p}_1,\mathbf{p}-\mathbf{K}_1} \delta_{\lambda_1\lambda} \end{aligned}$$

Of course,

$$\langle \mathbf{p}\lambda | H' | \mathbf{K}_1, \mathbf{p}_1 \rangle = \langle \mathbf{K}_1, \mathbf{p}_1 \lambda_1 | H' | \mathbf{p}\lambda \rangle^* = -i\alpha \frac{1}{|\mathbf{K}_1|} \delta_{\mathbf{p}_1, \mathbf{p}-\mathbf{K}_1} \delta_{\lambda_1 \lambda}$$

We have therefore

$$\begin{aligned}
\Delta E^{(2)} &= \alpha^2 \sum_{\mathbf{p}_1 \lambda_1} \int \frac{d^3\mathbf{K}_1}{(2\pi)^3} \frac{1}{|\mathbf{K}_1|^2} \frac{\delta_{\lambda_1\lambda}\delta_{\lambda_1\lambda}\delta_{\mathbf{p}_1,\mathbf{p}-\mathbf{K}_1}\delta_{\mathbf{p}_1,\mathbf{p}-\mathbf{K}_1}}{\frac{\hbar^2\mathbf{p}^2}{2M} - \frac{\hbar^2\mathbf{p}_1^2}{2M} - \hbar\omega} \\
&= 2M\frac{\alpha^2}{\hbar^2} \int \frac{d^3\mathbf{K}_1}{(2\pi)^3} \frac{1}{\mathbf{K}_1^2\,[\mathbf{K}_1^2 - 2\mathbf{K}_1\cdot\mathbf{p} + 2M\omega/\hbar]}
\end{aligned}$$

In order to evaluate this integral, we use the standard Feynman trick allowing to combine deniminators:

$$\frac{1}{a\ b} = \int_0^1 \frac{dx}{[ax + b(1-x)]^2} \tag{7.50}$$

which here gives

$$\Delta E^{(2)} = -2M\frac{\alpha^2}{\hbar^2}\int_0^1 dx \int \frac{d^3\mathbf{K}_1}{(2\pi)^3} \frac{1}{[(\mathbf{K}_1 - x\mathbf{p})^2 - x^2\mathbf{p}^2 + 2xM\omega/\hbar]^2}$$

In agreement with our approach in this subsection, where we treat the distribution of ions in a crystal as continuous, we can assume that the integral over $d^3\mathbf{K}_1$ extends in fact to infinite values of $\mathbf{K}_1$. This allows us to shift the variables in the integral over $\mathbf{K}_1$ so that $\mathbf{K} = \mathbf{K}_1 - x\mathbf{p}$ and to write

$$\begin{aligned}
\Delta E^{(2)} &= -2M\frac{\alpha^2}{\hbar^2}\int_0^1 dx \int \frac{d^3\mathbf{K}}{(2\pi)^3} \frac{1}{[\mathbf{K}^2 - x^2\mathbf{p}^2 + 2xM\omega/\hbar]^2} \\
&= -2M\frac{\alpha^2}{\hbar^2}\frac{4\pi}{(2\pi)^3}\int_0^1 dx \int_0^\infty \frac{d\mathbf{K}\ \mathbf{K}^2}{[\mathbf{K}^2 + a^2]^2}
\end{aligned}$$

where $a^2 = -x^2\mathbf{p}^2 + 2xM\omega/\hbar$. Using the standard integral

$$\int_0^\infty \frac{z^{2m-1}dz}{(z^2+1)^{m+n}} = \frac{1}{2}\frac{\Gamma(n)\Gamma(m)}{\Gamma(n+m)} \tag{7.51}$$

we get

$$\Delta E^{(2)} = -M\frac{\alpha^2}{4\pi\hbar^2}\int_0^1 \frac{dx}{\sqrt{-x^2\mathbf{p}^2 + 2xM\omega/\hbar}}$$

Assuming for the moment that $-x^2\mathbf{p}^2 + 2xM\omega/\hbar > 0$ we can expand

$$\Delta E^{(2)} = -M\frac{\alpha^2}{4\pi\hbar^2}\sqrt{\frac{\hbar}{2M\omega}}\int_0^1 \frac{dx}{\sqrt{x}\sqrt{1-x\frac{\hbar\mathbf{p}^2}{2M\omega}}}$$

$$\approx -M\frac{\alpha^2}{4\pi\hbar^2}\sqrt{\frac{\hbar}{2M\omega}}\int_0^1 dx\left(x^{-1/2}+x^{1/2}\frac{\hbar\mathbf{p}^2}{4M\omega}+\ldots\right)$$

$$= -M\frac{\alpha^2}{4\pi\hbar^2}\sqrt{\frac{\hbar}{2M\omega}}2\left(1+\frac{1}{6}\frac{\hbar^2\mathbf{p}^2}{2M}\frac{1}{\hbar\omega}+\ldots\right)$$

Adding the zeroth order term we find the electron energy

$$E = -\frac{\beta^2}{2\pi\hbar\omega}+\frac{\hbar^2\mathbf{p}^2}{2M}\left(1+\frac{1}{6}\frac{\beta^2}{\hbar\omega}+\ldots\right) = -\frac{\beta^2}{2\pi\hbar\omega}+\frac{\hbar^2\mathbf{p}^2}{2M_{\text{eff}}}$$

where β^2 is some constant having dimension of energy and $M_{\text{eff}} = M(1-1\beta^2/6\hbar\omega)$. We see that as a result of the electron interaction with phonons its mass gets effectively shifted. (There is also a negative constant contribution but this is not important.)

The above calculation is valid provided $-x^2\mathbf{p}^2 + 2xM\omega/\hbar > 0$ as x varies between 0 and 1, this expression becomes negative for

$$\hbar^2\mathbf{p}^2/2M > \hbar\omega\ . \tag{7.52}$$

The correction to the electron energy is then complex suggesting that the electron state becomes unstable: the electron can loose kinetic energy decaying into an electron-phonon state. This can be checked by considering the energy conservation. As the energy of a single phonon equals $\hbar\omega$ (recall that we have approximated the phonon dispersion relation $\omega(\mathbf{K})$ by a constant ω so that the phonon energy does not depend on its quasimomentum $\mathbf{K}$) we ask for which values of $\mathbf{p}$ it is possible to satisfy the equation

$$\frac{\hbar^2\mathbf{p}^2}{2M} = \frac{\hbar^2(\mathbf{p}-\mathbf{K})^2}{2M}+\hbar\omega \tag{7.53}$$

that is,

$$\frac{\hbar^2\mathbf{p}\cdot\mathbf{K}}{M} = \frac{\hbar^2\mathbf{K}^2}{2M}+\hbar\omega$$

It is clear that this is possible only for positive $\mathbf{p}\cdot\mathbf{K}$. The minimal value of $\mathbf{p}^2$ allowed by this condition is obtained for $\mathbf{p}$ parallel to $\mathbf{K}$ and agrees with the one given by (7.52).

The rate w i.e. the probability per unit time that an electron will decay into an electron-phonon state can be computed by using the golden Fermi rule as

$$w = \sum_{\mathbf{p}_1,\lambda_1} \int \frac{d^3\mathbf{K}_1}{(2\pi)^3} \frac{2\pi}{\hbar} \left|\langle \mathbf{p}_1\lambda_1, \mathbf{K}_1|H'|\mathbf{p}\lambda\rangle\right|^2 \delta(E_f - E) \tag{7.54}$$

where $1/(2\pi)^3$ plays the role of the density of final (phononic) states. Inserting here the expression for the matrix element $\langle \mathbf{p}_1\lambda_1, \mathbf{K}_1|H'|\mathbf{p}\lambda\rangle$ already computed we find

$$\begin{aligned} w &= \sum_{\mathbf{p}_1,\lambda_1} \int \frac{d^3\mathbf{K}_1}{(2\pi)^3} \frac{2\pi}{\hbar} \left|\frac{\alpha}{|\mathbf{K}_1|}\delta_{\mathbf{p}_1,\mathbf{p}}\delta_{\lambda_1\lambda}\right|^2 \delta\left(\frac{\hbar^2(\mathbf{p}_1-\mathbf{K}_1)^2}{2M} + \hbar\omega - \frac{\hbar^2\mathbf{p}^2}{2M}\right) \\ &= \frac{2\pi}{\hbar}\int \frac{d^3\mathbf{K}_1}{(2\pi)^3}\frac{\alpha^2}{\mathbf{K}_1^2}\delta\left(\frac{\hbar^2\mathbf{K}_1^2}{2M} + \hbar\omega - \frac{\hbar^2\mathbf{p}\cdot\mathbf{K}_1}{M}\right) \\ &= \frac{4\pi^2}{\hbar}\alpha^2\int_0^\infty dK \int_{-1}^{+1} d\xi\ \delta\left(\frac{\hbar^2K^2}{2M} + \hbar\omega - \frac{\hbar^2|\mathbf{p}|K}{M}\xi\right) \end{aligned}$$

One can also compute the differential production rate i.e. the probability that the phonon is emitted in the infinitesimal solid angle $d\Omega$ in the direcion characterized by the angles (θ,ϕ) with respect to the direction of the momentum of the initial electron

$$\begin{aligned} \frac{dw}{d\Omega} &= \frac{2\pi}{\hbar}\alpha^2\int_0^\infty dK\ \delta\left(\frac{\hbar^2K^2}{2M} + \hbar\omega - \frac{\hbar^2|\mathbf{p}|K}{M}\cos\theta\right) \\ &= \frac{2\pi}{\hbar}\frac{\alpha^2}{\left|\frac{\hbar^2K_\theta}{M} - \frac{\hbar^2|\mathbf{p}|}{M}\cos\theta\right|} \end{aligned}$$

where K_θ is the solution of the equation

$$\frac{\hbar^2K^2}{2M} + \hbar\omega - \frac{\hbar^2|\mathbf{p}|K}{M}\cos\theta = 0$$