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TITOLO TESI

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ii

Sommario

Abstract in italiano

iv

Abstract

Abstract in English

Acknowledgements

Contents

Chapter 1

Introduction

1.1 Historical overview

Lev Landau was the first to propose the concept of an auto-localized in a crystal in a 1933 paper [**terhaar1965**]. The idea was developed by Pekar, who considered a single electron interacting with a dielectric medium [**pekar1946**, **pekar1947**]. This interaction was shown to cause an enhancement of the effective mass and a localization of the wavefunction [**landau1948**]. The Landau-Pekar model gives a quantum mechanical description of the electron and a classical description of the medium. A full quantum mechanical description was then developed by Fröhlich [**frohlich1950**] and Holstein [**holstein1959**], who formalized the distinction between large and small polarons. A description of these models is given in **??**.

1.2 Landau-Pekar model

The electron is described by a wavefunction $\Psi(\boldsymbol{r})$ moving in a dielectric continuum medium. The static potential of the crystal is taken into account associating at the electron an effective mass m^* (see Section 1.4.2). If we allow the medium to be polarized, the energy of the system is given by the kinetic energy of electron plus the energy of the electromagnetic field

$$E = \frac{\hbar^2}{2m^*} \int \mathrm{d}\boldsymbol{r} |\boldsymbol{\nabla}\psi(\boldsymbol{r})|^2 + \frac{1}{2} \int \mathrm{d}\boldsymbol{r} \boldsymbol{E} \cdot \boldsymbol{D} \tag{1.1}$$

$\boldsymbol{D}$ can expressed using Gauss law $\boldsymbol{\nabla} \cdot \boldsymbol{D} = \rho = -e|\psi(\boldsymbol{r}|^2$, or equivalently

$$\boldsymbol{D} = -\frac{e}{4\pi} \boldsymbol{\nabla} \int \mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r})|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1.2}$$

Remembering that for a dielectric medium $\boldsymbol{D} = \varepsilon_0 \epsilon^0 \boldsymbol{E}$, where ε_0 is the vacuum permittivity and ϵ^0 the static dielectric constant, we obtain for the electrostatic energy

$$\frac{1}{2} \int \mathrm{d}\boldsymbol{r} \boldsymbol{E} \cdot \boldsymbol{D} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{\epsilon^0} \int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r})|^2 |\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1.3}$$

In the previous expression, $\boldsymbol{E}$ includes contributions both from the displacement of the ions and of the electric screening of the electrons. The latter effect is already taken into account by the effective mass in the expression of the kinetic energy. Since the ions have a much larger mass than the electrons, they will not contribute to the high-frequency dielectric constant ϵ^∞. Removing this contribution, Eq. (1.3) becomes

$$\frac{1}{2} \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{E} \cdot \boldsymbol{D} = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{\epsilon^0} - \frac{1}{\epsilon^\infty} \right) \int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r})|^2 |\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1.4}$$

If we define $1/\kappa = 1/\epsilon^\infty - 1/\epsilon^0$, we can rewrite the total energy as a functional of ψ

$$E[\psi] = \frac{\hbar^2}{2m^*} \int \mathrm{d}\boldsymbol{r}\, |\boldsymbol{\nabla}\psi(\boldsymbol{r})|^2 - \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\kappa} \int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r})|^2 |\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1.5}$$

Following a variational approach, this functional can be minimized to find the polaron ground state energy. To do so, we must include a normalization constraint. This is done with the help of a Lagrange multiplier ε

$$E[\psi, \varepsilon] = \frac{\hbar^2}{2m^*} \int \mathrm{d}\boldsymbol{r}\, |\boldsymbol{\nabla}\psi(\boldsymbol{r})|^2 - \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\kappa} \int \mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r})|^2 |\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|}$$
$$- \varepsilon \left(\int \mathrm{d}\boldsymbol{r}\, |\psi(\boldsymbol{r})|^2 - 1 \right) \quad (1.6)$$

Minimizing with respect to ψ^* and ε, we obtain a Schrödinger-type equation

$$\left(-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\kappa} \int \mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \right) \psi(\boldsymbol{r}) = \varepsilon \psi(\boldsymbol{r}) \tag{1.7}$$

The Lagrange multiplier ε has the dimension of an energy, but it not exactly the polaron ground state energy. Projecting Eq. (1.7) onto ψ^* and confronting the result with Eq. (1.6), we obtain a ground state energy E_0

$$E_0 = \varepsilon + \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\kappa} \int \mathrm{d}\boldsymbol{r}' \frac{|\psi(\boldsymbol{r})|^2 |\psi(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{1.8}$$

Equation (1.7) is not known to have an exact solution. However, given the similarity with the hydrogen atom Hamiltonian, we can use as a trial wavefunction $(\pi r_p^3)^{-1/2} e^{-r/r_p}$ and minimize E with respect to r_p. As in the hydrogen atom, the kinetic term minimization favours larger r_p (delocalized states) and the potential term favours smaller r_p (localized states). Performing the minimization [**alexandrov2010**], r_p is found to be

$$r_p = \frac{16}{5} \frac{\kappa}{m^*/m_e} a_0 \tag{1.9}$$

where m_e is the mass of the electron and a_0 the Bohr radius. The value of the ground state energy is

$$E_0 = -\frac{50}{512} \alpha^2 \hbar \omega_{\mathrm{LO}} \tag{1.10}$$

where ω_{LO} is the characteristic frequency of longitudinal optical phonon (see Section 1.4.3) and

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{m^*}{2\hbar\omega_{\mathrm{LO}}}\frac{1}{\kappa}} \tag{1.11}$$

Despite its simplicity, the Landau-Pekar model provides simple formulas for the polaron ground state, radius and effective mass [**landau1948**]. However, to have polaron bound states, κ must be positive, which implies $\epsilon^0 > \epsilon^\infty$. This is true only for polar crystals, but polarons are observed in non-polar crystals as well. Moreover, this model carries an intrinsic contradiction. Treating the medium as a continuum requires the polaron to be large, but formally justified results can only be obtained in the strong coupling regime, a situation improbable for real materials.

1.3 Second quantization

1.3.1 Occupation number representation

In condensed matter physics we often have to deal with systems of many particles. We can describe such a system starting from the wavefunctions of the single particles $|k\rangle$, where the particle is in the eigenstate of eigenvalue k of an operator $\hat{K}$. We suppose this set of vectors to be orthonormal. We could initially write the total state vector as the product of the single ones.

$$|\Psi\rangle = |k_1\rangle |k_2\rangle \dots |k_N\rangle \tag{1.12}$$

However, the former expression does not take into account the indistinguishability of quantum particles. In fact, the physics of the system must be invariant under the exchange of two particles. This is possible only if $|\Psi\rangle$ is symmetric or antisymmetric for the exchange of two particles. The former case is true for bosons, the latter for fermions.

In order to satisfy this condition, we have to modify Eq. (1.12). An appropriate linear combination of the products of the single kets, compatible with the symmetry constraints required by Bose and Fermi statistics is given by

$$|\Psi\rangle = |k_1, k_2, \dots, k_N\rangle = \sqrt{\frac{1}{N!}}\sum_P \xi^P |P[k_1]\rangle |P[k_2]\rangle \dots |P[k_N]\rangle \tag{1.13}$$

where the sum is extended to all the $N!$ permutations P of $k_1, k_2, \dots k_N$. $\xi = 1$ for bosons and $\xi = -1$ for fermions, so that for fermions $\xi^P = 1$ for even permutations and $\xi^P = -1$ for odd permutations. This construction assures that the total wavefunction is symmetric for the exchange of two bosons and antisymmetric for the exchange of two fermions. It is important to notice that Eq. (1.13) has an ambiguity in the phase of the final vector. To remove it, we chose the permutation to be even when $k_1 < k_2 < \dots k_N$.

It is useful to compute the product of a base bra and a base ket of two total state

vectors.

$$\langle m_1, \ldots, m_N | k_1, \ldots, k_N \rangle = \frac{1}{N!}$$
$$= \sum_P \sum_{P'} \xi^{P+P'} \langle P[m_1] | \langle P[m_2] | \ldots \langle P[m_N] | \times | P'[k_1] \rangle | P'[k_2] \rangle \ldots | P'[k_N] \rangle$$
$$= \sum_{P''} \xi^{P''} \langle m_1 | P''[k_1] \rangle \ldots \langle m_N | P''[k_N] \rangle$$
$$= \begin{vmatrix} \langle m_1 | k_1 \rangle & \langle m_1 | k_2 \rangle & \ldots & \langle m_1 | k_N \rangle \\ \langle m_2 | k_2 \rangle & \langle m_2 | k_2 \rangle & \ldots & \langle m_2 | k_N \rangle \\ \ldots & \ldots & \ldots & \ldots \\ \langle m_N | k_1 \rangle & \langle m_N | k_2 \rangle & \ldots & \langle m_N | k_N \rangle \end{vmatrix}_\xi \quad (1.14)$$

where $| \cdot |_{\xi=-1}$ represents a determinant and $| \cdot |_{\xi=1}$ a permanent (a determinant with all positive signs). Given the orthonormality of the single state kets, the only terms of the sum that differ from zero are the ones where

$$P''\{k_1, \ldots, k_N\} = \{m_1, \ldots, m_N\} \quad (1.15)$$

If a state is made of n_j bosons in the state k_j, the norm squared of the state vector will be equal to the total number of identical permutations

$$\langle k_1, \ldots, k_N | k_1, \ldots, k_N \rangle = n_1! n_2! \ldots n_N! \quad (1.16)$$

Thus, the normalized state vector is

$$|k_1, \ldots, k_N \rangle_n = \frac{1}{\sqrt{n_1! n_2! \ldots n_N!}} |k_1, \ldots, k_N \rangle \quad (1.17)$$

The case of fermions is easier, since n_j can either be 1 or 0. Thus, there is only one identical permutation and the state is already normalized.

Given the indistinguishability of the particles, a simpler way to describe this state vector is using only the number n_j of particles that are in the state k_j.

$$|n_1, n_2, \ldots n_i, \ldots \rangle = |k_1, \ldots, k_N \rangle_n \quad (1.18)$$

where k_j is repeated n_j times. This eliminates the inconvenience of having multiple kets describing the same state as we had before. This representation is called occupation number representation, and the kets are said to be elements of the Fock space.

Two special cases of states in the Fock space are the following. The vacuum state

$$|0, 0, \ldots 0 \rangle = |\mathbf{0}\rangle \quad (1.19)$$

is a state with no particles in any single-particle states. The second is

$$|0, 0, \ldots, n_i = 1, \ldots \rangle = |k_i\rangle \quad (1.20)$$

where there is exactly one particle in the k_i state.

1.3.2 Creation and annihilation operators

Now that we have defined the base kets, we can introduce two operators that are used to transform the kets. We define the *creation operator* as

$$\hat{a}_i^{\dagger}|k_1, k_2, \ldots\rangle = |k_i, k_1, k_2, \ldots\rangle \tag{1.21}$$

Below we show several properties that derive from these definition, but its essential role can be understood applying it to the vacuum state.

$$\hat{a}_i^{\dagger}|\mathbf{0}\rangle = |k_i\rangle \tag{1.22}$$

Its effect is to add a particle in k_i state to the system. It is easy to interpret its adjoint as an *annihilation operator*, in fact

$$1 = \langle k_i|k_i\rangle = \langle \mathbf{0}|\hat{a}_i\hat{a}_i^{\dagger}|\mathbf{0}\rangle = \langle \mathbf{0}|\hat{a}_i|k_i\rangle \tag{1.23}$$

which implies that

$$\hat{a}_i|k_i\rangle = |\mathbf{0}\rangle \tag{1.24}$$

We now try to prove these properties on a general base ket. We consider the transition matrix element

$$\mathcal{A} = \langle m_1, \ldots, m_{N-1}|\hat{a}_i|k_1, \ldots, k_N\rangle =$$
$$= \langle k_1, \ldots, k_N|\hat{a}_i^{\dagger}|m_1, \ldots, m_{N-1}\rangle^* = \langle k_1, \ldots, k_N|k_i, m_1, \ldots, m_{N-1}\rangle^* \tag{1.25}$$

using Eq. (1.14)

$$\mathcal{A} = \begin{vmatrix} \langle k_1|k_i\rangle & \langle k_1|m_1\rangle & \ldots & \langle k_1|m_{N-1}\rangle \\ \langle k_2|k_i\rangle & \langle k_2|m_1\rangle & \ldots & \langle k_2|m_{N-1}\rangle \\ \ldots & \ldots & \ldots & \ldots \\ \langle k_N|k_i\rangle & \langle k_N|m_1\rangle & \ldots & \langle k_N|m_{N-1}\rangle \end{vmatrix}_\xi^* \tag{1.26}$$

and developing it along the first column

$$\mathcal{A} = \left(\sum_{j=1}^{N} \xi^{j+1} \langle k_j|k_i\rangle \begin{vmatrix} \langle k_1|m_1\rangle & \ldots & \langle k_1|m_{N-1}\rangle \\ \langle k_2|m_1\rangle & \ldots & \langle k_2|m_{N-1}\rangle \\ \ldots & (\text{no } k_j) & \ldots \\ \langle k_N|m_1\rangle & \ldots & \langle k_N|m_{N-1}\rangle \end{vmatrix}_\xi \right)^*$$

$$= \sum_{j=1}^{N} \xi^{j+1} \langle k_i|k_j\rangle \langle k_1, \ldots (\text{no } k_j), k_N|m_1, \ldots, m_{N-1}\rangle^*$$

$$= \sum_{j=1}^{N} \xi^{j+1} \delta_{k_i k_j} \langle m_1, \ldots, m_{N-1}|k_1, \ldots (\text{no } k_j), k_N\rangle \tag{1.27}$$

Confronting it with Eq. (1.25) we conclude

$$\hat{a}_i \left| k_1, \dots, k_N \right\rangle = \sum_{j=1}^{N} \xi^{j+1} \left\langle k_i | k_j \right\rangle \left| k_1, \dots (\text{no } k_j), k_N \right\rangle$$

$$= \sum_{j=1}^{N} \xi^{j+1} \delta_{k_i k_j} \left| k_1, \dots (\text{no } k_j), k_N \right\rangle \quad (1.28)$$

If k_i is not present in $\left| k_1, \dots, k_N \right\rangle$, $\delta_{k_i k_j} = 0$ and overall $\hat{a}_i \left| k_1, \dots, k_N \right\rangle = 0$. On the other hand, if k_i is included in the ket n_i times, there will be n_i non-null terms in the sum.

In the case of bosons,

$$\hat{a}_i \left| k_1, \dots, k_N \right\rangle = n_i \left| k_1, \dots (\text{one less } k_i), k_N \right\rangle \quad (1.29)$$

We can use Eq. (1.18) to express the last relation in the occupation number representation.

$$\hat{a}_i \left| n_1, n_2, \dots, n_i, \dots \right\rangle = \hat{a}_i \left| k_1, \dots, k_N \right\rangle_n$$

$$= \hat{a}_i \left(\prod_{j=1}^{N} \sqrt{n_j!} \right)^{-1} \left| k_1, \dots, k_N \right\rangle = n_i \left(\prod_{j=1}^{N} \sqrt{n_j!} \right)^{-1} \left| k_1, \dots (\text{one less } k_i), k_N \right\rangle$$

$$= \sqrt{n_i} \left| k_1, \dots (\text{one less } k_i), k_N \right\rangle_n = \sqrt{n_i} \left| n_1, n_2, \dots, n_i - 1, \dots \right\rangle \quad (1.30)$$

The same argument, developed for the creation operator $\hat{a}_i^\dagger$, leads to

$$\hat{a}_i^\dagger \left| n_1, n_2, \dots, n_i, \dots \right\rangle = \sqrt{n_i + 1} \left| n_1, n_2, \dots, n_i + 1, \dots \right\rangle \quad (1.31)$$

For fermions, the occupation numbers can either be 1 or 0. The creation operator $\hat{a}_i^\dagger$ returns a phase factor of 0 if $n_i = 1$ and ± 1 if $n_i = 0$ The annihilation operator $\hat{a}_i$ does the opposite.

It is useful defining a new operator, the number operator $\hat{N}_i = \hat{a}_i^\dagger \hat{a}_i$. If we apply it to base ket of a system made of bosons

$$\hat{N}_i \left| n_1, n_2, \dots, n_i, \dots \right\rangle = \hat{a}_i^\dagger \hat{a}_i \left| n_1, n_2, \dots, n_i, \dots \right\rangle$$

$$= \hat{a}_i^\dagger \sqrt{n_i} \left| n_1, n_2, \dots, n_i - 1, \dots \right\rangle = n_i \left| n_1, n_2, \dots, n_i, \dots \right\rangle \quad (1.32)$$

1.3.3 Commutation relations

Applying $\hat{a}_k^\dagger \hat{a}_{k'}^\dagger$ on a base ket, using Eq. (1.21)

$$\hat{a}_{k'}^\dagger \hat{a}_k^\dagger \left| k_1, k_2, \dots \right\rangle = \left| \psi_{k'} k, k_1, k_2, \dots \right\rangle$$

$$= \xi \left| k \psi_{k'}, k_1, k_2, \dots \right\rangle = \hat{a}_k^\dagger \hat{a}_{k'}^\dagger \left| k_1, k_2, \dots \right\rangle \quad (1.33)$$

We have proven the (anti)commutation relation

$$[\hat{a_k}^\dagger, \hat{a_{k'}}^\dagger]_\xi = 0 \tag{1.34}$$

where $[A, B]_1 = \{A, B\} = AB + BA$ and $[A, B]_{-1} = AB - BA$. We see that for bosons the creation operators always commute, while for fermions they anti-commute.

Let's now investigate the commutator of a creation and an annihilation operator. Using Eq. (1.21) and Eq. (1.28)

$$\hat{a_{k'}}\hat{a_k}^\dagger |k_1, k_2, \ldots\rangle = \hat{a_{k'}} |k, k_1, k_2, \ldots\rangle$$
$$= \langle \psi_{k'}|k\rangle |k_1, k_2, \ldots\rangle + \sum_j \xi^j \langle \psi_{k'}|k_j\rangle |k, k_1, k_2, (\text{no } k_j) \ldots\rangle \tag{1.35}$$

$$\hat{a_k}^\dagger \hat{a_{k'}} |k_1, k_2, \ldots\rangle = \hat{a_k}^\dagger \sum_j \xi^{j+1} \langle \psi_{k'}|k_j\rangle |k_1, k_2, (\text{no } k_j) \ldots\rangle$$
$$= \sum_j \xi^{j+1} \langle \psi_{k'}|k_j\rangle |k, k_1, k_2, (\text{no } k_j) \ldots\rangle \tag{1.36}$$

thus

$$(\hat{a_{k'}}\hat{a_k}^\dagger - \xi\hat{a_k}^\dagger\hat{a_{k'}}) = \langle \psi_{k'}|k\rangle |k_1, k_2, \ldots\rangle \tag{1.37}$$

and

$$[\hat{a_{k'}}, \hat{a_k}^\dagger]_\xi = \langle \psi_{k'}|k\rangle = \delta_{kk'} \tag{1.38}$$

The former equation is of fundamental importance in second quantization formalism. If we have a set of single-state base kets $|k\rangle$ and we define a creation and annihilation operator that satisfy Eq. (1.38), we obtain multi-particle base kets $|k_1, k_2, \ldots\rangle$ that automatically satisfy the symmetry condition of Fermi and Bose statistics. The kets can then be expressed in the more compact occupation number representation $|n_{k_1}, n_{k_2}, \ldots\rangle$.

1.3.4 Dynamical variables

We now investigate how operators different from the ones we have already encountered can be expressed in second quantization [sakurai2020]. We focus our discussion on additive single-particle operator. Examples are momentum, kinetic energy or single body potentials. In these cases, the total value of the operator is simply the sum over all the particles.

Given an operator $\hat{K}$ of eigenkets $|k_i\rangle$ and a state vector

$$|\Psi\rangle = |n_1, n_2, \ldots\rangle \tag{1.39}$$

the result of applying $\hat{K}$ to $|\Psi\rangle$ is simply

$$\hat{K}|\Psi\rangle = \left(\sum_i n_i k_i\right) |\Psi\rangle \tag{1.40}$$

Confronting this expression with the definition of the number operator expressed in Eq. (1.32) we can write $\hat{K}$ as

$$\hat{K} = \sum_i k_i N_i = \sum_i k_i \hat{a}_i^\dagger \hat{a}_i \tag{1.41}$$

It could happen that we have a state ket expressed in base different from the eigenkets of our operator of interest. If we suppose this base to be formed by $|l_j\rangle$, using completeness

$$|k_i\rangle = \sum_j |l_j\rangle \langle l_j|k_i\rangle \tag{1.42}$$

It makes then sense to write

$$\hat{a}_i^\dagger = \sum_j \hat{b}_j^\dagger \langle l_j|k_i\rangle \tag{1.43}$$

which implies

$$\hat{a}_i = \sum_j \hat{b}_j \langle k_i|l_j\rangle \tag{1.44}$$

where operators $\hat{b}_j^\dagger$ and $\hat{b}_j$ create and annihilate the single-particle states $|l_j\rangle$. The result of applying Eq. (1.43) on the vacuum state is then

$$\hat{a}_i^\dagger |\mathbf{0}\rangle = \sum_j \hat{b}_j^\dagger \langle l_j|k_i\rangle |\mathbf{0}\rangle = \sum_j |l_j\rangle \langle l_j|k_i\rangle = |k_i\rangle \tag{1.45}$$

in agreement with Eq. (1.42).

We are now ready to express the operator $\hat{K}$ in the basis $|l_j\rangle$.

$$\hat{K} = \sum_i k_i \hat{a}_i^\dagger \hat{a}_i = \sum_i k_i \sum_{mn} \hat{b}_m^\dagger \hat{b}_n \langle l_m|k_i\rangle \langle k_i|l_n\rangle$$

$$= \sum_{mn} \hat{b}_m^\dagger \hat{b}_n \sum_i \langle l_m|k_i\rangle k_i \langle k_i|l_n\rangle = \sum_{mn} \hat{b}_m^\dagger \hat{b}_n \langle l_m| \left[\hat{K} \sum_i |k_i\rangle\langle k_i| \right] |l_n\rangle$$

$$= \sum_{mn} \langle l_m| \hat{K} |l_n\rangle \hat{b}_m^\dagger \hat{b}_n \tag{1.46}$$

This allow us to write every additive operator in terms of the creation and annihilation operators. It is then possible to write the Hamiltonian for a non-interacting system of particles, where the potential and the kinetic energy satisfy the additivity requirement, as

$$\hat{H} = \sum_{mn} \langle l_m| \hat{T} + \hat{V}_1 |l_n\rangle \hat{b}_m^\dagger \hat{b}_n \tag{1.47}$$

where V_1 is the non-interacting (single particle) potential and $\hat{T}$ the kinetic energy.

1.4 Electrons and phonons in crystals

In this section we will briefly describe how free electrons and phonons behave in a crystal, starting with a description of a crystal lattice. The interaction between two electrons and two phonons will not be considered. The electron-phonon interaction will be discussed in the following section.

1.4.1 Crystal lattice

Solid state physics deals with materials made of huge numbers of atoms, of the order of the Avogadro number. We have just developed a mathematical formalism (second quantization) with which it is possible to treat such systems. However, it is clearly impossible to solve the equations for a general N-body system. Luckily, X-ray diffraction experiments showed that many solids exhibit particular symmetry properties, useful to simplify the problem.

Many solids, called crystals, are composed by the repetition in space of an identical unit cell. The unit cell is defined as the smallest repeating unit having the full symmetry of the crystal structure [**westBasicSolidState1999**]. Each unit cell is place on a point of a Bravais lattice. The Bravais lattice, also referred to as space lattice, describes the geometric arrangement of the lattice points [**lernerEncyclopediaPhysicsVolumes2005**]. Given any two points of the lattice, described by the vectors $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$, the difference between them is

$$\boldsymbol{R}_1 - \boldsymbol{R}_2 = \boldsymbol{R}_n \tag{1.48}$$

with $\boldsymbol{R}_n = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3$. The three vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ are called basis vectors and n_1, n_2, n_3 are integers. The position of a single atom in the crystal can then be expressed as the position in the unit cell $\boldsymbol{\tau}_a j$ plus the position of the lattice point $\boldsymbol{R}_n$

$$\boldsymbol{R}_n^a = \boldsymbol{R}_n + \boldsymbol{\tau}_a \tag{1.49}$$

Given the symmetry of the system, every property $f(\boldsymbol{r})$ of the lattice is invariant under a translation of a lattice vector $\boldsymbol{R}_n$

$$f(\boldsymbol{r} + \boldsymbol{R}_n) = f(\boldsymbol{r}) \tag{1.50}$$

We will see that applying this principle to the potential generated by the ions of the crystal will have important implications on the description of the electrons.

Associated to the Bravais lattice, there is a second one called reciprocal lattice. It is defined by three other basis vectors $\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3$, with

$$\boldsymbol{b}_1 = \frac{2\pi}{\Omega} \, \boldsymbol{a}_2 \times \boldsymbol{a}_3 \qquad \boldsymbol{b}_2 = \frac{2\pi}{\Omega} \, \boldsymbol{a}_3 \times \boldsymbol{a}_1 \qquad \boldsymbol{b}_3 = \frac{2\pi}{\Omega} \, \boldsymbol{a}_1 \times \boldsymbol{a}_2 \tag{1.51}$$

where $\Omega = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3$ is the volume of a unit cell. A vector in the reciprocal lattice is usually written as $\boldsymbol{G}_m = m_1 \boldsymbol{a}_1 + m_2 \boldsymbol{b}_2 + m_3 \boldsymbol{b}_3$, where m_1, m_2, m_3 are integers. From Eq. (1.51) it is easy to see that the product of a basis Bravais lattice vector $\boldsymbol{a}_i$ and a basis reciprocal lattice vector $\boldsymbol{b}_j$ is

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi \delta_{ij} \tag{1.52}$$

1.4.2   Electrons in crystals

The simplest model of electrons in a solid is the Sommerfield model. It was developed by Arnold Sommerfeld in 1928 [**sommerfeldZurElektronentheorieMetalle1928**], combining the Drude model [**drude1900a**] with Fermi-Dirac statistics. The electrons are treated as quantum non-interacting free particles, which implies that the wavefunctions are plane waves

$$\psi_{\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{1.53}$$

The energy is entirely kinetic, thus the dispersion relation is

$$\epsilon_{\boldsymbol{k}} = \frac{\hbar k^2}{2m} \tag{1.54}$$

Despite its simplicity, this model is surprisingly good at describing a vast number of physical phenomena. Examples are the Wiedemann–Franz law [**jones1985**], electrons heat capacity and electrical conductivity. However, it does not give any explanation for the different properties of conductors, insulators and semiconductors.

To correctly describe the properties of electrons, we have to take into account the potential generated by the ions in the crystal. The interaction is entirely electrical, so the potential is the well known Coulomb potential

$$V_{e-N} = \sum_{i=1}^{N_e} \sum_{j=1}^{N_N} \frac{1}{4\pi\epsilon_0} \frac{-Z_j e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_j|} \tag{1.55}$$

where the first sum is extended on all the electrons and the second on the nuclei. It is convenient to divide the electrons in inner core electrons and valence electrons. The formers are tightly bound to the nucleus and occupy closed inner shells. They do not interact with other atoms of the crystal, so the nucleus together with its core electrons can be treated as a positive ion. The valence electrons belong to non-closed shells and form chemical bonds with other atoms. Despite this description of electrons being apparently simpler, the potential of interaction between valence electrons and ions cannot be treated as simple Coulomb potential anymore.

To overcome the complexity of solving a many-body Schrödinger equation with a long range electromagnetic interaction, we leverage the symmetry of the crystal. Recalling our previous discussion, we know the potential of the ions to be translationally invariant:

$$V_{e-I}(\boldsymbol{r} + \boldsymbol{R}_n) = V_{e-I}(\boldsymbol{r}) \tag{1.56}$$

where r is the position of the electron and R_n is a Bravais lattice vector. The Schrödinger equation for the periodic potential V_{e-I} is then

$$\hat{H}_{\text{Bloch}}\Psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{e-I}\right)\Psi = \epsilon\Psi \tag{1.57}$$

Block proved in 1929 [**bloch1929**] that the solutions of this problem are the Bloch functions $\Psi_{n\boldsymbol{k}}$:

$$\hat{H}_{\text{Block}}\Psi_{n\boldsymbol{k}} = \epsilon_n(\boldsymbol{k})\Psi_{n\boldsymbol{k}} \quad \rightarrow \quad \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) = u_{n\boldsymbol{k}}(r)e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{1.58}$$

where u is a function with the same periodicity of V_{e-I}, $\boldsymbol{k}$ is a wavevector and n is the band index. The plane wave solution showed in Eq. (1.53) is a simple case where V_{e-I} and u are constant. An important consequence of the Bloch theorem is that the solutions to the Schrödinger equation, even if they are not plane waves, can still be indexed with the quantum number $\boldsymbol{k}$, along with the band index n.

Expanding $\epsilon_n(\boldsymbol{k})$ around $\boldsymbol{k} = 0$, for an isotropic energy band,

$$\epsilon_n(\boldsymbol{k}) = \epsilon_n(\boldsymbol{0}) + \frac{\hbar k^2}{2m^*} + \mathcal{O}(k^3) \tag{1.59}$$

where m^* is the effective mass, defined as

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon}{\partial k^2} \tag{1.60}$$

Expression (1.59) is formally identical to Eq. (1.54) with m^* in place of m. For small values of k electrons can then be treated as free particles of mass m^*. The final non-interacting electron Hamiltonian can be rewritten in second quantization as

$$\hat{H}_{\text{el}} = \sum_{n\boldsymbol{k}} \epsilon_{n\boldsymbol{k}} \hat{c}_{n\boldsymbol{k}}^\dagger \hat{c}_{n\boldsymbol{k}} \tag{1.61}$$

1.4.3 Phonons

So far, we have treated a crystal as a collection of ions fixed in a lattice and non-interacting valence electrons. However, the atoms are not really fixed. The crystal is held together by the bonds between the atoms. We can write the corresponding potential as

$$V_{I-I}(\boldsymbol{R}_1, \boldsymbol{R}_2, \dots) = \frac{1}{2} \sum_{ij} v_{I-I}(|\boldsymbol{R}_i - \boldsymbol{R}_j|) \tag{1.62}$$

where the sum is extended to all the ions, and we have implicitly assumed the potential to be dependent only on the distance between the ions. The positions of the atoms in the lattice

$$\boldsymbol{R}_n^a = \boldsymbol{R}_n + \boldsymbol{\tau}_a \tag{1.63}$$

are now interpreted as the equilibrium positions of the potential (1.62). Whereas the actual positions are given by

$$\boldsymbol{R}_n^a(t) = \boldsymbol{R}_n^a + \delta\boldsymbol{R}_n^a(t) \tag{1.64}$$

Expanding (1.62) in a Taylor series up to the second order, we can treat the system in the harmonic approximation. In this form, the Hamiltonian is not separable. Making a canonical change of coordinate from the position space to the reciprocal space, we can decouple the Hamiltonian into a sum of non-interacting Hamiltonians [**cohenFundamentalsCondensedMatter**]. Thus, the vibrational modes are described

as a collection of bosonic quasi-particles called phonons. The final Hamiltonian for a crystal with r atoms per unit cell in d dimensions, expressed in second quantization is

$$\hat{H}_{\text{ph}} = \sum_{\lambda\boldsymbol{q}} \hbar\omega_{\lambda\boldsymbol{q}} \left(\hat{b}^{\dagger}_{\lambda\boldsymbol{q}} \hat{b}_{\lambda\boldsymbol{q}} + \frac{1}{2} \right) \tag{1.65}$$

where $\boldsymbol{q}$ is the wavevector, $\lambda = (0, 1, \dots rd)$ the branch index, ω the eigenfrquencies and $\hat{b}^{\dagger}$ and $\hat{b}$ the creation and annihilation operators. The system has a non-zero energy ground state

$$E_0 = \sum_{\lambda\boldsymbol{q}} \frac{1}{2} \hbar\omega_{\lambda\boldsymbol{q}} \tag{1.66}$$

The relation between the displacement and the creation and annihilation operators is

$$\delta\boldsymbol{R}^a_n = \sum_{\boldsymbol{q}\lambda} A^a_{\boldsymbol{q}\lambda} \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} e^{i\boldsymbol{q}\cdot\boldsymbol{R}^a_n} (\hat{b}_{\boldsymbol{q}\lambda} + \hat{b}^{\dagger}_{-\boldsymbol{q}\lambda}) \tag{1.67}$$

where $\hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda}$ is the polarization vector and

$$A^a_{\boldsymbol{q}\lambda} = \sqrt{\frac{\hbar}{2M_a N \omega_{\boldsymbol{q}\lambda}}} \tag{1.68}$$

where M_a is mass of the ath atom and N the number of atoms. The polarization vector is used to describe the direction of the displacement $\delta\boldsymbol{R}^a_n$ with respect to the direction of propagation $\boldsymbol{q}$. We have transversal phonons if $\boldsymbol{q} \cdot \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} = 0$ and longitudinal phonons if $\boldsymbol{q} \times \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} = 0$

To generalize [**cohenFundamentalsCondensedMatter**], we have considered a Hamiltonian

$$\hat{H} = \sum_i \hat{H}_i(\boldsymbol{r}_i, \boldsymbol{p}_i) + \sum_{ij} \hat{H}_{ij}(\boldsymbol{r}_i, \boldsymbol{p}_i, \boldsymbol{r}_j, \boldsymbol{p}_j) \tag{1.69}$$

and after a canonical change of coordinates, we have transformed it in

$$\hat{H} = E_0 + \sum_{\boldsymbol{q}} E_{\boldsymbol{q}} \hat{c}^{\dagger}_{\boldsymbol{q}} \hat{c}_{\boldsymbol{q}} + \Delta E \tag{1.70}$$

The first term, E_0 is the ground state energy, the second describe a system of non-interacting particles and the third is the residual energy. This method is valid as long as $\Delta E_{\boldsymbol{q}} << E_{\boldsymbol{q}}$. In the case of phonons, $\Delta E = 0$ because we made a harmonic approximation. The non-harmonic terms would describe the interaction between phonons, which would result in $\Delta E \neq 0$.

1.4.4   Electron-phonon interaction

Now that we have described electrons and phonons, we can investigate how they interact with each other [**cohenFundamentalsCondensedMatter**, **tempere**]. Their

interaction is of vital importance in solid state physics. It influences transport proper-
ties in metals and mobility and optical properties in semiconductors and polar crystals
[**tempere**]. Our discussion starts with a periodic potential $V(\boldsymbol{r})$ perturbed from its
equilibrium position

$$V(\boldsymbol{r}, t) = \sum_{l,a} V_a(\boldsymbol{r} - \boldsymbol{R}_l^a(t)) \tag{1.71}$$

where l is an index of lattice points and a of atoms in the unit cell. $\boldsymbol{R}_l^a(t)$ is the position
of the atom, and it is given by Eq. (1.64):

$$\boldsymbol{R}_l^a(t) = \boldsymbol{R}_l^a + \delta\boldsymbol{R}_l^a(t) \tag{1.72}$$

For typical vibrations, it can be shown that the displacements $\xi = |\delta\boldsymbol{R}_l^a(t)|$ are much
smaller than the atomic spacing d. In particular

$$\frac{\xi}{d} \simeq \left[\frac{m}{M}\right]^{\frac{1}{4}} \tag{1.73}$$

and the phonon energy E_{ph} scales as

$$\frac{E_{\mathrm{ph}}}{E_{\mathrm{el}}} \simeq \left(\frac{m}{M}\right)^{\frac{1}{2}} \tag{1.74}$$

where E_{el} is the electron energy, m the electron mass and M the atomic mass. Given this
scaling consideration, we can assume the general band structure of the crystal not to be
modified. However, the interaction with the phonons can slightly modify it. This results
in a modification of the electron effective mass, of the order of the phonon energies.

Using the assumption of small displacements, we can expand the potential in Eq. (1.71)
in a Taylor series.

$$V(\boldsymbol{r}, t) = \sum_{l,a} V_a(\boldsymbol{r} - \boldsymbol{R}_l^a - \delta\boldsymbol{R}_l^a(t)) \simeq \sum_{l,a} \left[V_a(\boldsymbol{r} - \boldsymbol{R}_l^a) + \delta\boldsymbol{R}_l^a(t) \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} V_a(\boldsymbol{r} - \boldsymbol{R}_l^a)\right] \tag{1.75}$$

Terms of higher orders take into account anharmonic oscillations, which were already
neglected in the study of phonon Hamiltonian. The term $V_a(\boldsymbol{r} - \boldsymbol{R}_l^a)$ does not depend
on the deviations of atoms from the equilibrium positions. In fact, it is the periodic
potential considered in the study of electrons.

The total Hamiltonian of the system can be written as the sum of three terms

$$\hat{H} = \hat{H}_{\mathrm{el}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{el\text{-}ph}} \tag{1.76}$$

where $\hat{H}_{\mathrm{el}}$ and $\hat{H}_{\mathrm{ph}}$ are given by Eq. (1.61) and Eq. (1.65). The last term describes the
electron-phonon contribution, and it can be identified with

$$\hat{H}_{\mathrm{el\text{-}ph}} = \sum_{l,a} \delta\boldsymbol{R}_l^a(t) \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} V_a(\boldsymbol{r} - \boldsymbol{R}_l^a) \tag{1.77}$$

We can use Eq. (1.67) to rewrite it expanding the displacements in phonon coordinates

$$\hat{H}_{\text{el-ph}} = \sum_a \sum_{\boldsymbol{q}\lambda} A^a_{\boldsymbol{q}\lambda} \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} \cdot \left(\sum_l e^{i\boldsymbol{q}\cdot\boldsymbol{R}^a_l} \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} V_a(\boldsymbol{r} - \boldsymbol{R}^a_l) \right) (\hat{b}_{\boldsymbol{q}\lambda} + \hat{b}^\dagger_{-\boldsymbol{q}\lambda}) \tag{1.78}$$

where $A^a_{\boldsymbol{q}\lambda}$ is given by Eq. (1.68), $\hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda}$ is the polarization vector, $\boldsymbol{q}$ the momentum of the phonon and $\hat{b}^\dagger_{-\boldsymbol{q}\lambda}$ and $\hat{b}_{\boldsymbol{q}\lambda}$ the phonon creation and annihilation operators.

The electron part of the previous expression is still written in the language of first quantization. Using Eq. (1.47), we can express it in a second-quantized form. Suppressing the band indices and using the extended zone scheme, so that $\boldsymbol{k}'$ and $\boldsymbol{k}$ are not limited to the first Brillouin zone,

$$\hat{H}_{\text{el-ph}} = \sum_{\boldsymbol{k}'\boldsymbol{k}} \langle \boldsymbol{k}' | \, \hat{H}_{\text{el-ph}} \, | \boldsymbol{k} \rangle \, \hat{c}^\dagger_{\boldsymbol{k}'} \hat{c}_{\boldsymbol{k}} = \sum_{\boldsymbol{k}'\boldsymbol{k}} \sum_{\boldsymbol{q}\lambda} M^\lambda_{\boldsymbol{k}\to\boldsymbol{k}'}(\boldsymbol{q}) \hat{c}^\dagger_{\boldsymbol{k}'} \hat{c}_{\boldsymbol{k}} (\hat{b}_{\boldsymbol{q}\lambda} + \hat{b}^\dagger_{-\boldsymbol{q}\lambda}) \tag{1.79}$$

where the electron-phonon matrix M is defined by Eq. (1.78). The previous expression can be interpreted as the transition of an electron from the state $|\boldsymbol{k}\rangle$ to the state $|\boldsymbol{k}'\rangle$ with either the creation of a phonon of momentum $-\boldsymbol{q}$ or the annihilation of a phonon of momentum $\boldsymbol{q}$. The matrix element $M^\lambda_{\boldsymbol{k}\to\boldsymbol{k}'}(\boldsymbol{q})$ gives the mechanical amplitude of such a process.

In order to evaluate M, we need to compute $\langle \boldsymbol{k}' | \, \hat{H}_{\text{el-ph}} \, | \boldsymbol{k} \rangle$. We start with a Fourier transform of the potential

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{q}} V_a(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{1.80}$$

where the atomic form factor is given by

$$V_a(\boldsymbol{q}) = \frac{1}{\Omega_a} \int e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} V_a(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} = \frac{wN}{\Omega} \int e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} V_a(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \tag{1.81}$$

Ω_a is the volume of a unit cell, Ω the volume of the crystal, N the number of unit cells and w the number of atoms per unit cell. We compute the gradient of the potential $\boldsymbol{\nabla}_{\boldsymbol{r}} V_a(\boldsymbol{r})$ expressed as a Fourier series, and we evaluate it at $\boldsymbol{r} - \boldsymbol{R}^a_l$

$$\boldsymbol{\nabla}_{\boldsymbol{r}} V_a(\boldsymbol{r} - \boldsymbol{R}^a_l) = \frac{i}{wN} \sum_{\boldsymbol{q}'} \boldsymbol{q}' e^{i\boldsymbol{q}'\cdot\boldsymbol{r}} V_a(\boldsymbol{r}) e^{-i\boldsymbol{q}'\cdot\boldsymbol{R}^a_l} \tag{1.82}$$

Equation (1.78) can now be rewritten using Eq. (1.82) as

$$\hat{H}_{\text{el-ph}} = \frac{i}{wN} \sum_{la\lambda} \sum_{\boldsymbol{q}\boldsymbol{q}'} A^a_{\boldsymbol{q}\lambda} \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} \cdot \boldsymbol{q}' e^{i\boldsymbol{q}'\cdot\boldsymbol{r}} e^{i(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{R}^a_l} V_a(\boldsymbol{q}') (\hat{b}_{\boldsymbol{q}\lambda} + \hat{b}^\dagger_{-\boldsymbol{q}\lambda}) \tag{1.83}$$

We know that

$$\sum_l e^{i(\boldsymbol{q}-\boldsymbol{q}')\cdot\boldsymbol{R}^a_l} = N\delta(\boldsymbol{q} - \boldsymbol{q}' + \boldsymbol{G}) \tag{1.84}$$

where $\boldsymbol{G}$ is a vector of the reciprocal lattice. Then, most of the terms of the previous expression are zero, and we obtain

$$
\begin{aligned}
&\langle \boldsymbol{k}' | \, \hat{H}_{\text{el-ph}} \, | \boldsymbol{k} \rangle \\
&= \frac{i}{w} \sum_{a\lambda\boldsymbol{q}} A^a_{\boldsymbol{q}\lambda} \sum_{\boldsymbol{G}} e^{-i\boldsymbol{G}\cdot\boldsymbol{\tau}_a} V_a(\boldsymbol{q}+\boldsymbol{G}) \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} \cdot (\boldsymbol{q}+\boldsymbol{G})(\hat{b}_{\boldsymbol{q}\lambda}+\hat{b}^\dagger_{-\boldsymbol{q}\lambda}) \langle \boldsymbol{k}' | \, e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \, | \boldsymbol{k} \rangle \quad (1.85)
\end{aligned}
$$

where we have used $\boldsymbol{G} \cdot \boldsymbol{R}_l = 2\pi n$, with n integer, to simplify the sum over l. Finally, inserting this result in Eq. (1.79), we obtain an expression for the matrix element

$$
M^\lambda_{\boldsymbol{k}\to\boldsymbol{k}'}(\boldsymbol{q}) = \frac{i}{w} \sum_{a\boldsymbol{G}} \sqrt{\frac{\hbar}{2M_a N \omega_{\boldsymbol{q}\lambda}}} e^{-i\boldsymbol{G}\cdot\boldsymbol{\tau}_a} V_a(\boldsymbol{q}+\boldsymbol{G}) \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} \cdot (\boldsymbol{q}+\boldsymbol{G}) \langle \boldsymbol{k}' | \, e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \, | \boldsymbol{k} \rangle \quad (1.86)
$$

We can compute the matrix element for a simple case where the initial and final state of the electron are plane waves. In this case,

$$
\langle \boldsymbol{k}' | \, e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} \, | \boldsymbol{k} \rangle = \delta_{\boldsymbol{k}',\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}} \quad (1.87)
$$

and

$$
M^\lambda_{\boldsymbol{k}\to\boldsymbol{k}'}(\boldsymbol{q}) = \frac{i}{w} \sum_{a\boldsymbol{G}} \sqrt{\frac{\hbar}{2M_a N \omega_{\boldsymbol{q}\lambda}}} e^{-i\boldsymbol{G}\cdot\boldsymbol{\tau}_a} V_a(\boldsymbol{q}+\boldsymbol{G}) \hat{\boldsymbol{\epsilon}}^a_{\boldsymbol{q}\lambda} \cdot (\boldsymbol{q}+\boldsymbol{G}) \delta_{\boldsymbol{k}',\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}} \quad (1.88)
$$

The scattering process that we have explained earlier is now more clear. An electron of momentum $\hbar\boldsymbol{k}$ is scattered in an electron of momentum $\hbar(\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G})$ by the emission of a phonon of momentum $-\boldsymbol{q}$ or the absorption of a phonon of momentum $\boldsymbol{q}$. We can identify two processes: the normal (N) process, where $\boldsymbol{G}=0$, and the umklapp (U) process, where $\boldsymbol{G}\neq 0$. In the normal process $\boldsymbol{k}'=\boldsymbol{k}+\boldsymbol{q}$, and assuming $w=1$,

$$
M^\lambda_{\boldsymbol{k}\to\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{q}) = i\sqrt{\frac{\hbar}{2M_a N \omega_{\boldsymbol{q}\lambda}}} V_a(\boldsymbol{q}) \hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}\lambda} \cdot \boldsymbol{q} \quad (1.89)
$$

It is clear that in this type of process, only longitudinal phonons contribute to the scattering, since for transversal phonons $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}\lambda} \cdot \boldsymbol{q} = 0$.

The electrons are affected by deformations of the lattice in several ways [**kittel1987**]. The main effects of the coupling between electrons and phonons are:

- the scattering of electrons from a state $\boldsymbol{k}$ to a state $\boldsymbol{k}'$, resulting in electrical resistivity;

- the absorption or creation of phonons;

- the creation of an attractive force between electrons, which is essential to explain superconductivity;

- the electrons carry a lattice polarization field with them. The particle resulting from the combination of the electron and the polarization field is called *polaron*, and it has a larger effective mass than the electron alone.

In the next chapter, and in the rest of the thesis, we will focus on this last type of interaction.

Chapter 2

The polaron problem

2.1 Fröhlich polarons

We have already anticipated in Section a simple model for polarons (the Landau-Pekar model). We are now ready to improve that first simple model, taking now into account a more precise mechanics of the lattice polarization. In this section we will discuss the Fröhlich Hamiltonian, derived by Fröhlich in 1950 [**frohlich1950**]. This Hamiltonian is appropriate to describe polarons in ionic crystals and polar semiconductors. In these materials we expect electrons to interact strongly with longitudinal optical phonons through the electric field produced by the polarization of the lattice. The contribution of transversal phonons is expected to be negligible because of the smaller electric field they produce.

2.1.1 Derivation of the Fröhlich Hamiltonian

In this section we derive the Fröhlich Hamiltonian following the approach described by Kittel [**kittel1987**]. We assume the longitudinal phonons to be dispersionless (with frequency ω_{LO}) and we treat the polarizable medium as continuum.

In an ionic crystal, the polarization $\boldsymbol{P}$ can be considered as the sum of two components: the optical polarization $\boldsymbol{P}_o$ and the infra-red polarization $\boldsymbol{P}_{\mathrm{ir}}$. The former is due to the displacement of bound electrons and it is characterized by a resonance frequency in the optical or ultra-violet region; the latter is due to the displacement of ions and its resonance frequency is in the infra-red region. Given the slow velocities of the electrons that we are going to consider, the optical polarization is always excited at its static value. Thus, given the absence of a dependence on the velocity of the electron, the optical polarization $\boldsymbol{P}_o$ is of no interest to us, since it does not modify the energy of the electron between different states. On the other hand, this does not apply to the infra-red polarization, because of its lower resonance frequency. At long distances from the electric charge (placed at $\boldsymbol{r}_0$), $\boldsymbol{P}_{\mathrm{ir}}$ can be obtained subtracting the optical polarization $\boldsymbol{P}_o$ from the total polarization $\boldsymbol{P}$. Thus, it can be derived from an electric potential $V(\boldsymbol{r})$ by

$$4\pi \boldsymbol{P}_{\mathrm{ir}}(\boldsymbol{r}) = \boldsymbol{\nabla} V(\boldsymbol{r}) \tag{2.1}$$

where

$$V(\boldsymbol{r}) = \left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right) \frac{e}{|\boldsymbol{r} - \boldsymbol{r}_0|} \tag{2.2}$$

The infra-red polarization is proportional to the amplitude of the displacement of the ions. Generalizing Eq. (1.67) for a generic point $\boldsymbol{r}$, we can express the displacement in the point $\boldsymbol{r}$ as

$$\boldsymbol{\xi}(\boldsymbol{r}) = \sum_{\boldsymbol{q}} A\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger) \tag{2.3}$$

where we have dropped the indices a and λ because we are considering atoms of the same mass and phonons of the same branch. Moreover, A does not depend on $\boldsymbol{q}$ because the phonons are assumed to be dispersionless. Since we are considering only longitudinal phonons, the polarization vector $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}}$ must be parallel to $\boldsymbol{q}$. However, we cannot simply suppose $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}} = \hat{\boldsymbol{q}}$. In fact, we have to guarantee that $\boldsymbol{\xi}(\boldsymbol{r})$ is real:

$$\boldsymbol{\xi}^\dagger(\boldsymbol{r}) = \sum_{\boldsymbol{q}} A\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}}^\dagger e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} (\hat{b}_{\boldsymbol{q}}^\dagger + \hat{b}_{-\boldsymbol{q}}) = \sum_{\boldsymbol{q}} A\hat{\boldsymbol{\epsilon}}_{-\boldsymbol{q}}^\dagger e^{i\boldsymbol{q}\cdot\boldsymbol{r}} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger) = \boldsymbol{\xi}(\boldsymbol{r}) \tag{2.4}$$

This implies $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}}^\dagger = \hat{\boldsymbol{\epsilon}}_{-\boldsymbol{q}}$, and then $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{q}} = i\hat{\boldsymbol{q}}$.

As we anticipated, $\boldsymbol{P}_{\text{ir}}$ is proportional to the amplitude of the displacement

$$\boldsymbol{P}_{\text{ir}} = F\boldsymbol{\xi}(\boldsymbol{r}) = iF \sum_{\boldsymbol{q}} A\hat{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger) \tag{2.5}$$

where F is a constant to be determined. We expand also the electric potential in a Fourier series

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{q}} V(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{2.6}$$

and we compute the gradient

$$\boldsymbol{\nabla} V(\boldsymbol{r}) = i \sum_{\boldsymbol{q}} \boldsymbol{q} V(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{2.7}$$

Using Eq. (2.1) and comparing Eq. (2.5) with Eq. (2.7), we find

$$V(\boldsymbol{q}) = 4\pi \frac{FA}{q} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger) \tag{2.8}$$

We now want to express the constant F in terms of the interaction energy of two electrons in a polarizable material of dielectric constant ϵ. We consider two electrons completely localized in two points $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The electrons will interact directly through the vacuum electric field and indirectly through a perturbation induced by the optical phonon field. The interaction Hamiltonian is given by the sum of the potential of the two electrons

$$H_{\text{el-el}} = -eV(\boldsymbol{r}_1) - eV(\boldsymbol{r}_2) = 4\pi e FA \sum_{\boldsymbol{q}} q^{-1} (e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1} + e^{i\boldsymbol{q}\cdot\boldsymbol{r}_2}) (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger)$$

$$= 4\pi e FA \sum_{\boldsymbol{q}} q^{-1} \left[\hat{b}_{\boldsymbol{q}} (e^{i\boldsymbol{q}\cdot\boldsymbol{r}_1} + e^{i\boldsymbol{q}\cdot\boldsymbol{r}_2}) + \hat{b}_{\boldsymbol{q}}^\dagger (e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_1} + e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_2}) \right] \tag{2.9}$$

where in the second line we have changed the sign of $\boldsymbol{q}$ in the second term, using the fact that the sum is extended over all $\boldsymbol{q}$. The second-order energy perturbation caused by the previous Hamiltonian is given by

$$\Delta E = -\sum_{\boldsymbol{q}} \frac{\langle 0 | H_{\text{el-el}} | \boldsymbol{q} \rangle \langle \boldsymbol{q} | H_{\text{el-el}} | 0 \rangle}{\hbar \omega_{\text{LO}}} \tag{2.10}$$

where $|0\rangle$ and $|\boldsymbol{q}\rangle$ are respectively states with no phonons and a single LO phonon in the state $\boldsymbol{q}$ with energy $\hbar \omega_{\text{LO}}$. Inserting Eq. (2.9) in the previous expression and dropping the terms with $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ alone, which are self-energy terms,

$$\begin{aligned} \Delta E &= -2 \sum_{\boldsymbol{q}} \frac{\langle 0 | eV(\boldsymbol{r}_1) | \boldsymbol{q} \rangle \langle \boldsymbol{q} | eV(\boldsymbol{r}_2) | 0 \rangle}{\hbar \omega_{\text{LO}}} \\ &= -2 \frac{(4\pi e F A)^2}{\hbar \omega_{\text{LO}}} \sum_{\boldsymbol{q}} q^{-2} \langle 0 | e^{i\boldsymbol{q} \cdot \boldsymbol{r}_1} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{\boldsymbol{q}}^{\dagger}) | \boldsymbol{q} \rangle \langle \boldsymbol{q} | e^{-i\boldsymbol{q} \cdot \boldsymbol{r}_2} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{\boldsymbol{q}}^{\dagger}) | 0 \rangle \\ &= -2 \frac{(4\pi e F A)^2}{\hbar \omega_{\text{LO}}} \sum_{\boldsymbol{q}} q^{-2} \langle \boldsymbol{q} | e^{i\boldsymbol{q} \cdot \boldsymbol{r}_1} | \boldsymbol{q} \rangle \langle \boldsymbol{q} | e^{-i\boldsymbol{q} \cdot \boldsymbol{r}_2} | \boldsymbol{q} \rangle \\ &= -2 \frac{(4\pi e F A)^2}{\hbar \omega_{\text{LO}}} \sum_{\boldsymbol{q}} \frac{e^{i\boldsymbol{q} \cdot (\boldsymbol{r}_1 - \boldsymbol{r}_2)}}{q^2} \end{aligned} \tag{2.11}$$

Knowing that, when summed over all $\boldsymbol{q}$,

$$\sum_{\boldsymbol{q}} \frac{4\pi}{q^2} e^{i\boldsymbol{q} \cdot \boldsymbol{r}} = \Omega \frac{1}{|\boldsymbol{r}|} \tag{2.12}$$

where Ω is the volume of the region of interest, we can rewrite the perturbation energy as

$$\Delta E = -\frac{8\pi \Omega A^2 F^2}{\hbar \omega_{\text{LO}}} \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{2.13}$$

The form of this interaction is exactly the same of an attractive Coulomb potential between two charges placed at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The origin of this attraction is the polarization of the ions of the medium. Thus, the factor

$$-\frac{8\pi \Omega A^2 F^2}{\hbar \omega_{\text{LO}}} \tag{2.14}$$

gives exactly the contribution of the ions to the dielectric constant. Since the static dielectric constant ϵ^0 includes both the contribution of ions and of the electrons, and the high-frequency dielectric constant ϵ^∞ only the contribution of the electrons, we can express Eq. (2.14) as

$$\frac{1}{\epsilon^0} = \frac{1}{\epsilon^\infty} - \frac{8\pi \Omega A^2 F^2}{\hbar \omega_{\text{LO}}} \tag{2.15}$$

The electric potential is then given by

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{q}} V(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} = \sum_{\boldsymbol{q}} \left[\frac{2\pi e^2 \hbar \omega_{\text{LO}}}{\Omega q^2}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)\right]^{1/2}(\hat{b}_{\boldsymbol{q}} + \hat{b}^\dagger_{-\boldsymbol{q}}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \qquad (2.16)$$

and writing it in a fully second-quantized form, we find

$$\hat{H}_{\text{el-ph}} = \sum_{\boldsymbol{k}'\boldsymbol{k}} \sum_{\boldsymbol{q}} \left[\frac{2\pi e^2 \hbar \omega_{\text{LO}}}{\Omega q^2}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)\right]^{1/2} \langle \boldsymbol{k}' | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | \boldsymbol{k}\rangle (\hat{b}_{\boldsymbol{q}\lambda} + \hat{b}^\dagger_{-\boldsymbol{q}\lambda}) \hat{c}^\dagger_{\boldsymbol{k}'} \hat{c}_{\boldsymbol{k}} \qquad (2.17)$$

Confronting the previous expression with Eq. (1.79), we can identify the interaction matrix

$$M_{\boldsymbol{k}\to\boldsymbol{k}+\boldsymbol{q}} = \left[\frac{2\pi e^2 \hbar \omega_{\text{LO}}}{\Omega q^2}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)\right]^{1/2} \qquad (2.18)$$

which is more commonly written as

$$M_{\boldsymbol{q}} = \frac{\hbar \omega_{\text{LO}}}{|\boldsymbol{q}|}\left(\frac{\hbar}{2m\omega_{\text{LO}}}\right)^{1/4}\left(\frac{4\pi\alpha}{\Omega}\right)^{1/2} \qquad (2.19)$$

where α is the dimsensionless Fröhlich coupling constant, defined as

$$\alpha = \frac{e^2}{\hbar}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)\sqrt{\frac{m}{2\hbar\omega_{\text{LO}}}} \qquad (2.20)$$

where m is the electron band mass.

The interaction of the electrons with the lattice described by Eq. (2.19) has multiple effects. Some consequences we may expect are:

- The electron band energy is decreased, because part of the energy is used to produce phonons.

- The effective mass of the electron is increases, because the electron has to deform the lattice while moving.

- The mobility of the electron is modified, because the polaron experiences scattering effects different from the ones of a free electron.

We can analyse quantitatively the first of these two effects using approximation techniques. We will do it in the next two sections, applying perturbation theory and variational methods to the Fröhlich Hamiltonian.

2.1.2   Weak coupling: perturbation theory

Polarons are often divided in two classes: large and small. The name is due to their effective radius l_p, which is defined as the effective radius of the polarized area. If l_p is greater than the interatomic distance d, the polaron is said to be large; on the contrary,

if $l_p \lesssim d$, the polaron is said to be small. In the former case, the coupling is usually weak ($\alpha < 1$), in the latter it is strong ($\alpha > 1$). In the weak-coupling regime, it is possible to use perturbation theory to derive some properties of large polarons.

The total Hamiltonian is

$$
\begin{aligned}
\hat{H} &= \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}} \\
&= \sum_{\bm{k}} \frac{\hbar^2 \bm{k}^2}{2m} + \sum_{\bm{q}} \hbar\omega_{\text{LO}} \left(\hat{b}_{\bm{q}}^{\dagger} \hat{b}_{\bm{q}} + \frac{1}{2} \right) + \sum_{\bm{kq}} M_{\bm{q}} \hat{c}_{\bm{k}-\bm{q}}^{\dagger} \hat{c}_{\bm{k}} (\hat{b}_{\bm{q}} + \hat{b}_{-\bm{q}}^{\dagger})
\end{aligned} \tag{2.21}
$$

where $M_{\bm{q}}$ is given by Eq. (2.19)

$$
M_{\bm{q}} = \frac{\hbar\omega_{\text{LO}}}{|\bm{q}|} \left(\frac{\hbar}{2m\omega_{\text{LO}}} \right)^{1/4} \left(\frac{4\pi\alpha}{\Omega} \right)^{1/2} \tag{2.22}
$$

and it is supposed to be small ($\alpha < 1$). The unperturbed Hamiltonian

$$
\hat{H}^{(0)} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} \tag{2.23}
$$

has plane waves $|\bm{k}\rangle$ as eigenfcuntions for the single electron part and many-body basis kets $|n_1 \ldots n_{\bm{q}} \ldots\rangle$ as eigenfunctions for the phonon part. The full eigenkets are given by the composition of the two parts $|\bm{k}; \{n_{\bm{q}}\}\rangle = |\bm{k}\rangle |n_1 \ldots n_{\bm{q}} \ldots\rangle$. The energy of this state is

$$
E_{\bm{k},\{n_{\bm{q}}\}}^{(0)} = \frac{\hbar^2 \bm{k}^2}{2m} + \hbar\omega_{\text{LO}} \sum n_{\bm{q}} \tag{2.24}
$$

and the ground state is given by an electron with $\bm{k} = 0$ and the vacuum state $|0\rangle$ for the phonon part. First-order perturbation theory results in no energy shift, since

$$
\langle \bm{k}| \langle 0| (\hat{b}_{\bm{q}} + \hat{b}_{-\bm{q}}^{\dagger}) |0\rangle |\bm{k}\rangle = 0 \tag{2.25}
$$

Going to second order

$$
\Delta E_{\bm{k}}^{(2)} = \sum_a \frac{\langle \bm{k}; 0| \hat{H}_{\text{el-ph}} |a\rangle \langle a| \hat{H}_{\text{el-ph}} |\bm{k}; 0\rangle}{E_{\bm{k}} - E_a} \tag{2.26}
$$

where $keta$ is an excited state. The only states that contribute with non-null terms are states composed by an electron and a single phonon of wavevector $\bm{q}$. The electron is scattered by the phonon in a state of wavevector $\bm{k} - \bm{q}$. The kets $|a\rangle$ are thus of the form $|\bm{k} - \bm{q}; n_{\bm{q}} = 1\rangle$, with energy

$$
E_a = \frac{\hbar^2}{2m} (\bm{k} - \bm{q})^2 + \hbar\omega_{\text{LO}} = \frac{\hbar^2 \bm{k}^2}{2m} - \frac{\hbar^2 \bm{k} \cdot \bm{q}}{m} + \frac{\hbar^2 \bm{q}^2}{2m} + \hbar\omega_{\text{LO}} \tag{2.27}
$$

The shift in the energy is then

$$
\Delta E_{\bm{k}} = - \sum_{\bm{q}} \frac{|M_{\bm{q}}|^2}{\hbar\omega_{\text{LO}} + \frac{\hbar^2}{2m} q^2 - \frac{\hbar^2}{m} \bm{k} \cdot \bm{q}} \tag{2.28}
$$

We may denote

$$|M_{\boldsymbol{q}}|^2 = \frac{C}{q^2} \tag{2.29}$$

where

$$C = (\hbar\omega_{\mathrm{LO}})^2 \left(\frac{\hbar}{2m\omega_{\mathrm{LO}}}\right)^{1/2} \left(\frac{4\pi\alpha}{\Omega}\right) \tag{2.30}$$

Defining $\mu = \frac{\boldsymbol{k}\cdot\boldsymbol{q}}{|\boldsymbol{k}||\boldsymbol{q}|}$, we can convert the sum in Eq. (2.28) in an integral,

$$\sum_{\boldsymbol{q}} \rightarrow \frac{\Omega}{(2\pi)^3} \int \mathrm{d}\boldsymbol{q} = \frac{\Omega}{(2\pi)^3} \int 2\pi q^2 \mathrm{d}q \mathrm{d}\mu \tag{2.31}$$

then,

$$\Delta E_{\boldsymbol{k}} = -\frac{\Omega}{(2\pi)^2} \int_{-1}^{1} \mathrm{d}\mu \int_{0}^{q_{\mathrm{BZ}}} \mathrm{d}q \frac{C}{\hbar\omega_{\mathrm{LO}} + \frac{\hbar^2}{2m}q^2 - \frac{\hbar^2}{m}kq\mu} \tag{2.32}$$

where the integral is extended until the boundary of the first Brillouin zone. Although the integral in Eq. (2.32) may be exactly solved, we can gain some insights on the main physical meaning by developing it in powers of k and letting $q_{\mathrm{BZ}} \to \infty$. Choosing an appropriate set of units, so that $\hbar = \omega_{\mathrm{LO}} = 2m = 1$,

$$\Delta E_{\boldsymbol{k}} = -\frac{\alpha}{\pi} \left[2\int_0^\infty \mathrm{d}q \frac{1}{1+q^2} + 4k^2 \int_{-1}^{1} \mathrm{d}\mu \int_0^\infty \mathrm{d}q \frac{q^2\mu^2}{(1+q^2)^3} \right] = -\alpha - \frac{\alpha}{6}k^2 \tag{2.33}$$

and plugging back the standard units,

$$\Delta E_{\boldsymbol{k}} = -\alpha\hbar\omega_{\mathrm{LO}} - \frac{\alpha}{6}\frac{\hbar^2}{2m}k^2 \tag{2.34}$$

Finally, the perturbed energy is

$$E_{\boldsymbol{k}} = -\alpha\hbar\omega_{\mathrm{LO}} + \left(1 - \frac{\alpha}{6}\right)\frac{\hbar^2}{2m}k^2 \tag{2.35}$$

where the factor on the right can be interpreted as an electron with a new effective mass $m^* = m/(1 - \alpha/6)$. The band energy is shifted down by an overall factor of $\alpha\hbar\omega_{\mathrm{LO}}$ and the effective mass of the electron is increased. This is a reasonable conclusion: the electron digs itself a hole in the lattice potential, lowering its energy, and it has to carry the deformation along its path, resulting in a bigger effective mass.

2.1.3   Strong coupling: variational analysis

In the strong coupling regime, perturbation theory cannot be applied. However, it is possible to use a different approximation method: variational analysis. When the coupling is strong, we expect the electron to dig itself a deeper hole in the lattice potential. The electron will then localize inside the hole. In this regime, we can suppose the polaron

wavefunction to be composed of two factors: an unknown phonon wavefunction $|\phi_{\mathrm{ph}}\rangle$ and an electron wavefunction $|\psi_{\mathrm{el}}\rangle$. The latter is assumed to have the shape of a gaussian

$$\psi(\boldsymbol{r}) = \frac{1}{r_p^{3/2}} e^{-\frac{r^2}{2r_p^2}} \tag{2.36}$$

where r_p is the effective radius of the polaron, which we use as variational parameter. According to variational theory, we have to minimize the functional

$$\langle \phi_{\mathrm{ph}} | \langle \psi_{\mathrm{el}} | \hat{H} | \psi_{\mathrm{el}} \rangle | \phi_{\mathrm{ph}} \rangle \tag{2.37}$$

where $\hat{H}$ is the Frohlich Hamiltonian

$$\hat{H} = \sum_{\boldsymbol{k}} \frac{\hbar^2 \boldsymbol{k}^2}{2m} + \sum_{\boldsymbol{q}} \hbar\omega_{\mathrm{LO}} \left(\hat{b}_{\boldsymbol{q}}^\dagger \hat{b}_{\boldsymbol{q}} + \frac{1}{2} \right) + \sum_{\boldsymbol{kq}} M_{\boldsymbol{q}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger) \tag{2.38}$$

and M is the usual interaction matrix derived in Eq. (2.19). In the natural units introduced in the previous section, the Hamiltonian becomes

$$\hat{H} = \sum_{\boldsymbol{k}} \boldsymbol{k}^2 + \sum_{\boldsymbol{q}} \left(\hat{b}_{\boldsymbol{q}}^\dagger \hat{b}_{\boldsymbol{q}} + \frac{1}{2} \right) + \sum_{\boldsymbol{kq}} M_{\boldsymbol{q}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} (\hat{b}_{\boldsymbol{q}} + \hat{b}_{-\boldsymbol{q}}^\dagger) \tag{2.39}$$

Using the kinetic energy

$$E_{\mathrm{kin}} = \langle \psi_{\mathrm{el}} | \boldsymbol{k}^2 | \psi_{\mathrm{el}} \rangle = \frac{3}{2r_p^2} \tag{2.40}$$

and the electron density

$$\rho_{\boldsymbol{k}} = \langle \psi_{\mathrm{el}} | e^{i\boldsymbol{k}\cdot\boldsymbol{r}} | \psi_{\mathrm{el}} \rangle = e^{-k^2 r_p^2/4} \tag{2.41}$$

we find

$$\langle \psi_{\mathrm{el}} | \hat{H} | \psi_{\mathrm{el}} \rangle = E_{\mathrm{kin}} + \sum_{\boldsymbol{q}} \left[\hat{b}_{\boldsymbol{q}}^\dagger \hat{b}_{\boldsymbol{q}} + \frac{1}{2} + M_{\boldsymbol{q}} \rho_{\boldsymbol{k}} \hat{b}_{\boldsymbol{q}} + M_{\boldsymbol{q}}^* \rho_{\boldsymbol{k}}^* \hat{b}_{\boldsymbol{q}}^\dagger \right] \tag{2.42}$$

Ignoring the phonon ground state energy and completing the square, we find

$$\langle \psi_{\mathrm{el}} | \hat{H} | \psi_{\mathrm{el}} \rangle = E_{\mathrm{kin}} + \sum_{\boldsymbol{q}} \left(\hat{b}_{\boldsymbol{q}}^\dagger + M_{\boldsymbol{q}} \rho_{\boldsymbol{q}} \right) \left(\hat{b}_{\boldsymbol{q}} + M_{\boldsymbol{q}}^* \rho_{\boldsymbol{q}}^* \right) - \sum_{\boldsymbol{q}} |M_{\boldsymbol{q}} \rho_{\boldsymbol{q}}|^2 \tag{2.43}$$

The second term is easily uunnderstandable as a displaced harmonic oscillator. The equilibrium position is shifted from zero by $M_{\boldsymbol{q}} \rho_{\boldsymbol{q}}$. This is precisely the effect of the polarization induced by the electron. It is clear that the minimum of the functional will correspond to the vacuum state of the displaced operator. In this state, the energy is simply

$$E_{\mathrm{var}} = \langle \psi_{\mathrm{el}} | \hat{H} | \psi_{\mathrm{el}} \rangle = E_{\mathrm{kin}} - \sum_{\boldsymbol{q}} |M_{\boldsymbol{q}} \rho_{\boldsymbol{q}}|^2 = \frac{3}{2r_p^2} \tag{2.44}$$

2.2 Holstein Hamiltonian