Thesis

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Chapter 1

Froehlich Polaron

1.1 Electrons in crystals

The study of electrons inside a solid crystal is an important field due to their role in the determination of transport and optical properties of such materials.

Multiple experiments involving X-ray or electron scattering from suitable solid samples have demonstrated that a crystalline solid, whether a metal, an insulator or a semiconductor, is described a periodic arrangement of atoms consisting of a unit cell (usually the primitive one, defined as the smallest unit cell possible in a determined material) with a suitable atomic basis: some examples are Iron (Fe), described by a BCC (Body-Centered Cubic) unit cell with a single Fe atom basis, rock salt (NaCl), described by by a FCC (Face-Centered Cubic) unit cell with a basis composed of one Na atom and one Cl atom, and crystalline silicon (Si), which is characterized by the diamond structure, an FCC structure with a basis composed of 2 silicon atoms (geometrically different from that seen in rock salt).

Given the periodic nature of crystal structures, it is natural to consider the electrostatic potential generated by the crystal to be periodic too. Such is the basic assumption which underlies the treatment of electrons in crystals, that was first described by Felix Bloch in his famous 1928 paper *Uber die Quantenmechanikder Elektronen in Kristallgittern* [1].

The model proposed by Bloch assumed independent electrons (no electron-electron interactions terms): each electron behaves as if only an average contribution to the potential from the other electrons (with the same periodicity of the lattice) exists, thus retrieving an **effective one-electron potential**.

The resulting Hamiltonian for the single independent electron is:

$$\mathrm{H}\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{1.1.1}$$

where $V(r)$ is a periodic potential with the lattice periodicity, given a lattice translation vector

$$\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \qquad n_1, n_2, n_3 \quad \text{integers}, \tag{1.1.2}$$

with $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ primitive translation vectors. Therefore, we have

$$V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r}) \tag{1.1.3}$$

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This means that the potential can be expanded in Fourier series

$$V(\mathbf{K}) = \sum_{\mathbf{K}} V_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{1.1.4}$$

and is consequently useful to expand the wavefunction in the same way. For this reason the Born-von Karman boundary conditions are applied [2]

$$\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r}), \qquad i = 1, 2, 3. \tag{1.1.5}$$

where $N_i \mathbf{a}_i$ is a chosen vector such that $V(r + N_i a_i) = V(\mathbf{r})$ (it is a translation vector for the lattice). This is a normalizing condition for the wavefunction which corresponds to taking N_i unit cell in each direction and periodically repeating them. In this way it is possible to write the wavefunction in the following way:

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{1.1.6}$$

Going back to the periodic potential $U(\mathbf{r})$ we observe that the Fourier terms $U_{\mathbf{K}}$ are related to $U(\mathbf{r})$ by

$$U_{\mathbf{K}} = \frac{1}{V} \int_{cell} dr\, e^{-i\mathbf{K}\cdot\mathbf{r}} U(\mathbf{r}) \tag{1.1.7}$$

with V unit cell volume and $\mathbf{K}$ reciprocal lattice vector (vector in k-space such that $e^{i\mathbf{K}\cdot\mathbf{a}_i} = 1$). If it is assumed that the potential $V(\mathbf{r})$ is real and $V(-\mathbf{r}) = V(\mathbf{r})$ (valid for every Bravais lattice) it follows that the coefficients $U_{\mathbf{K}}$ are real.
Substituting in 1.1.1 we obtain:

$$(\mathrm{H} - E)\psi(\mathbf{r}) = \sum_{\mathbf{q}} \left(\frac{\hbar^2}{2m} q^2 - E \right) c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + \sum_{\mathbf{K}\mathbf{q}'} U_{\mathbf{K}} c_{\mathbf{q}'-\mathbf{K}} e^{i\mathbf{q}'\cdot\mathbf{r}} = 0, \tag{1.1.8}$$

which yields the following result:

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - E \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} c_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0. \tag{1.1.9}$$

From this equation it becomes clear that for a fixed k only the coefficients $c_{\mathbf{k}}, c_{\mathbf{k}-\mathbf{K}}, \ldots$ whose wavevector differs from $\mathbf{k}$ by a reciprocal lattice vector are coupled. In this way the original problem has been divided in N independent equations for each allowed value of $\mathbf{k}$ (in the first Brillouin zone, the primitive unit cell in the reciprocal space).
Going back to the expansion 1.1.6 the wavefunction now becomes:

$$\psi_k(r) = \sum_{K} c_{k-K} e^{i(k-K)\cdot r}, \tag{1.1.10}$$

which can be recast as

$$\psi_k(r) = e^{ik\cdot r} \sum_{K} c_{k-K} e^{-iK\cdot R}; \tag{1.1.11}$$

in this form it is easy to recognize that

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{R}} \tag{1.1.12}$$

has the periodicity of the (reciprocal) Bravais lattice.
The shape of the Bloch wavefunction as stated in the Bloch theorem is thus retrieved

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \tag{1.1.13}$$

and its square modulus (from which important properties such as charge distribution follow) $|\psi_{\mathbf{k}}(\mathbf{r})|^2$ has the periodicity of the lattice.
The new Hamiltonian eigenvalues equation using Bloch wavefunction reads

$$\mathrm{H}_{\mathbf{k}} u_{n\mathbf{k}} = \left(\frac{\hbar^2}{2m} \left(\frac{1}{i}\nabla + \mathbf{k} \right)^2 + U(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = E_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}), \tag{1.1.14}$$

which yields a different energy eigenvalue for each $\mathbf{k}$ in the first Brillouin zone. The index n arises from the fact that for each $\mathbf{k}$ value infinite discrete solutions to the eigenvalue equation exist, in the same as in the particle in a box problem. Going to the thermodynamic limit ($N_i \to \infty$ for each component i) the entire first Brillouin zone is sampled and the typical band structure of the solids is recovered.
All the methods employed in solid state calculations rely on this "simple" equation to determine band structures, granted analytical form of the periodic potential $U(\mathbf{r})$ can be retrieved.
The most used and effective computation method is **Density Functional Theory** [3] or **DFT** for short, which does not directly compute the eigenvalue equation for each single k and n value, which would be impossible since the potential $U(\mathbf{r})$ is a many-body object that includes electron-electon interactions, but rather computes all the physical quantities of interest starting from the ground state charge density $\rho_0(\mathbf{r})$. This is made possible by the two Hohenberg-Kohn theorems [4], which respectively state that the external potential (the periodic $U(\mathbf{r})$ from the electron point of view) is uniquely determined up to a constant by the ground state charge density $\rho_0(\mathbf{r})$ and that this density can be computed variationally by minimizing a suitable functional $F[\rho]$.
Nevertheless, the functional $F[\rho]$ exact form is unknown: for this reason the **Kohn-Sham scheme** [5] is used. The idea at the basis of this practical setup is to substitute the real interacting system (many-body) with an auxiliary non-interacting one (single particle) which has the same ground state as the original. In this system the total potential $V(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_{ee}(\mathbf{r})$ is replaced with an effective potential $V_{eff}(\mathbf{r})$ defined as

$$U_{eff}(\mathbf{r}) = U_{ion}(\mathbf{r}) + U_H(\mathbf{r}) + U_{xc}(\mathbf{r}), \tag{1.1.15}$$

where U_{ion} is the ionic potential, often modelled using pseudopotentials [6], $U_H(\mathbf{r})$ is the Hartree term, the electrostatic potential due to the mean field distribution of all the other electrons, and $U_{xc}(\mathbf{r})$ the exchange-correlation term, an approximate potential which includes Pauli exclusion principle (exchange), higher order electron-electron interactions (correlation) and many body corrections to kinetic energy. The exchange-correlation

term is usually computed using **LDA** (Local Density Approximation) or **GGA** (Generalized Gradient Approximation), both based on the the Uniform Electron Gas (UEG) [7]. Despite the inevitable approximations, DFT calculations are able to provide extremely accurate band structure calculations with few drawbacks, such as inaccurate gap estimations in insulators and semiconductors.
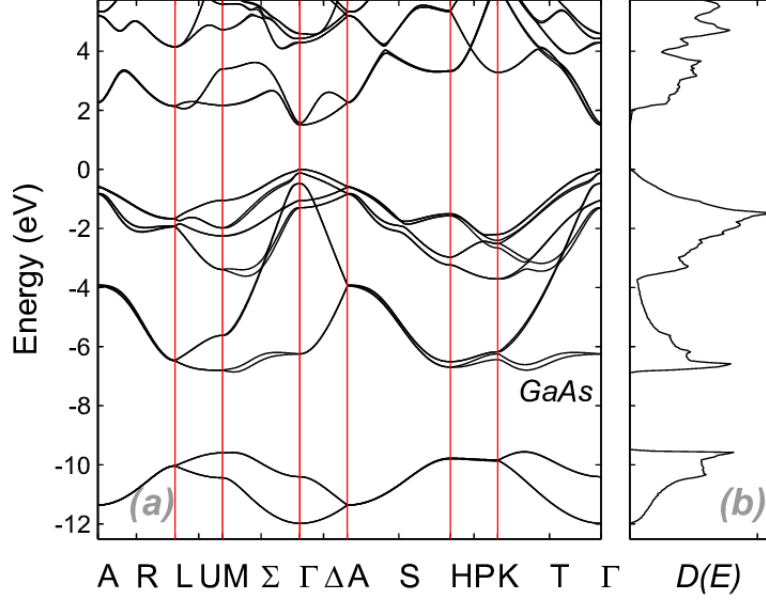

Figure 1.1: DFT calculated low-temperature GaAs Wurtzite structure with relative DOS [8].

As it can be seen in Figure 1.1 for GaAs, at the band extrema (at the edge between the allowed band states and the forbidden gap) the bands have a quadratic dispersion akin to that of a free electron: an electron in these regions only feel a very weak external potential $U(\mathbf{r})$ and can be considered as free provided that the free electron mass m is substituted with an effective mass m^* which takes into account the potential acting on it.
In a general case the effective mass is a tensorial quantity (bands are anisotropic in general with respect to the wavevector) and their value can be computed with

$$m_{ij}^{*-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}, \qquad (1.1.16)$$

provided that the quadratic approximation is valid. This approximation is really useful when calculating quantities near band extrema, providing an effective description of an otherwise complex interaction.

1.2 The polaron problem: the Froehlich model

The treatment described up until now for electrons in solids relies on a basic assumption: electro dynamics is much faster than ion dynamics. This is the so-called **Born-Oppenheimer approximation**, which assumes that the motion of the much heavier

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ions is slow compared to the fast dynamics of the electrons (the characteristic time are of the order of ps for ions and fs for electrons). As a result, electrons are considered to respond instantaneously to changes in the positions of the ions, allowing the separation of electronic and ionic degrees of freedom in the analysis. Given M ions and n electrons the wavefunction $\Psi(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_n)$ with $\mathbf{R}_\alpha$ ionic positions and $\mathbf{r}_i$ electron positions can be decomposed in the following way:

$$\Psi(\mathbf{R}_1, ..., \mathbf{R}_M, \mathbf{r}_1, ..., \mathbf{r}_n) = \chi(\mathbf{R}_1, ..., \mathbf{R}_M)\psi(\mathbf{r}_1, ..., \mathbf{r}_n), \qquad (1.2.1)$$

and only the electronic wavefunction $\psi(\mathbf{r}_1, ..., \mathbf{r}_n)$ is taken into consideration, decoupling ionic degrees of freedom and treating ionic potential as a constant energy surface $U_{ion}(\mathbf{r})$. This approximation, although extremely effective in computing electronic bands, fails by design to describe systems where there is a strong coupling between electrons and ions (for example electron-phonon interaction).

Such is the case of polar crystals: in these materials single electrons at the bottom of the conduction band (or holes at the top of the valence band) couple to the strongly polarized ions and distort the unit cell: an electron-phonon interaction is thus present in the lattice and the electron properties (such as energy and effective mass) are renormalized due to this coupling [9].

The basic assumption of the Froehlich model is that the polaron is "large", namely the characteristic size of the polaron (electron together with its phonon cloud) is much larger than the lattice constant a. In this way it is possible to ignore the atomic details of the actual material and treat it as a uniform dielectric medium.

It is assumed that the electron which takes part in the formation of the polaron lies at the bottom of the valence band, in this way it is expected to have a quadratic energy dispersion characterized (as already seen in 1.1.16) by an effective mass

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m^*}, \qquad (1.2.2)$$

where the effective mass m^* encapsulates all the interactions due to crystal structure (for a hole polaron the dispersion is similar considering a negative effective mass).

Given the fact that we are dealing with the large polaron model, it is possible to treat the material as an homogeneous continuum which is polarized by the excess charge (the conduction electron). We also assume that the material is isotropic. Let $\mathbf{P}(\mathbf{r})$ be the electric polarization at the point $\mathbf{r}$, the total electric field is then:

$$\begin{aligned} \mathbf{D}(\mathbf{r}) &= \epsilon_0 \mathbf{E}(\mathbf{r}) + 4\pi \mathbf{P}(\mathbf{r}), \\ \mathbf{D}(\mathbf{r}) &= \epsilon \mathbf{E}(\mathbf{r}). \end{aligned} \qquad (1.2.3)$$

The only free charge present in the material is the conduction electron in excess, this means that $\mathbf{D}(\mathbf{r})$ is completely determined by it:

$$\begin{aligned} D(\mathbf{r}, \mathbf{r}_{el}) &= -\nabla \frac{e}{|\mathbf{r} - \mathbf{r}_{el}|}, \\ \nabla \cdot \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) &= 4\pi \delta(\mathbf{r} - \mathbf{r}_{el}), \end{aligned} \qquad (1.2.4)$$

with $\mathbf{r}_{el}$ the coordinate of the conduction electron. Developing the equations the following relation is obtained:

$$4\pi \mathbf{P}(\mathbf{r}) = \left(1 - \frac{1}{\epsilon}\right) \mathbf{D}(\mathbf{r}). \qquad (1.2.5)$$

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$\mathbf{P}(\mathbf{r})$ is the total polarization, which has the contribution both from electrons and from ionic displacements, since only the second contribution is relevant in our treatment, a method to tell apart this two contributions is needed.

To obtain this we imagine a system where a field is slowly applied and then rapidly switched off [10]: only electrons are able to keep up with the variation of the field. A formula connecting polarization and $\mathbf{D}$ (dropping the $\mathbf{r}$ dependence for simplicity since an isotropic and homogeneous medium is assumed) is then retrieved as

$$4\pi\delta\mathbf{P} = -\left(1 - \frac{1}{\epsilon_\infty}\right)\mathbf{D}, \tag{1.2.6}$$

it is then obtained the lattice contribution to the polarization:

$$4\pi\mathbf{P}_{lat} = 4\pi(\mathbf{P} - \delta\mathbf{P}) = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\mathbf{D}. \tag{1.2.7}$$

We know consider a model for the polar crystal lattice: we assume it to be constituted of individual oscillating discrete dipoles located at fixed sites of the crystal with characteristic frequency ω. The energy of each one of these oscillators is

$$\frac{M}{2}(\dot{q}^2 + \omega^2 q^2). \tag{1.2.8}$$

The next step is to move from a discrete set of fixed oscillators to a continuum of dipoles: it is assumed that the dipoles are not coupled. Defining the effective charge as e^*, the following substitution is made:

$$e^*\mathbf{q}_n \to \mathbf{P}_{lat}(\mathbf{r}), \tag{1.2.9}$$

which relates the dipole moment to the polarization field. We also write the following relation:

$$\frac{M}{e^{*2}} = \gamma d^3 r, \tag{1.2.10}$$

where $M = nd^3r$ is the mass density of the medium.

It is now possible to define the kinetic and potential energy of the freely oscillating polarization field:

$$\begin{aligned} T &= \int \frac{\gamma}{2}\dot{\mathbf{P}}_{lat}^2(\mathbf{r})d^3r, \\ V &= \int \frac{\gamma\omega^2}{2}\mathbf{P}_{lat}^2(\mathbf{r})d^3r. \end{aligned} \tag{1.2.11}$$

We identify ω with the optical phonon frequency ω_{LO}, but the constant γ has not yet been given a physical definition. For this reason we consider the interaction between electrons and dipole moment, which is given by

$$e\frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}\mathbf{P}_{lat}, \tag{1.2.12}$$

which, using a continuous charge distribution and the polarization field, becomes

$$\rho(\mathbf{r})d^3r\frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}\mathbf{P}_{lat}(\mathbf{r}')d^3r'. \tag{1.2.13}$$

The interaction energy E_I is thus

$$E_I = \iint \rho(\mathbf{r}) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \mathbf{P}_{lat}(\mathbf{r}') d^3 r d^3 r'. \tag{1.2.14}$$

The Lagrangian is then built as follows:

$$L = T - U - E_I \tag{1.2.15}$$

and the equation of motion are found solving the Lagrange equations

$$\frac{d}{dt} \frac{\delta L}{\delta \dot{P}_{lat_i}} - \frac{\delta L}{\delta P_{lat_i}} = 0 \tag{1.2.16}$$

for $i = 1, 2, 3$. The explicit formula of the equation of motion is:

$$\gamma(\ddot{\mathbf{P}}_{lat}(\mathbf{r}') + \omega^2 \mathbf{P}_{lat}(\mathbf{r}')) = - \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \rho(\mathbf{r}) d^3 r \tag{1.2.17}$$

keeping fixed $\rho(\mathbf{r})$. The term on the right side is simply the dielectric displacement $\mathbf{D}(\mathbf{r}')$ and, in the static limit, the equation simplifies to

$$\gamma \omega^2 \mathbf{P}_{lat}(\mathbf{r}') = \mathbf{D}(\mathbf{r}'). \tag{1.2.18}$$

Comparing this equation with 1.2.7, the value of γ is obtained:

$$\gamma = \frac{4\pi}{\omega^2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)^{-1}. \tag{1.2.19}$$

It is now time to define the full complete polaron Hamiltonian. We start by defining the free electron term (the interaction lies inside the effective mass m^*), considering that the electron charge density operator is defined as:

$$\rho(\mathbf{r}) = -e\psi^\dagger(\mathbf{r})\psi(\mathbf{r}) \tag{1.2.20}$$

using the second quantization formalism with field operators, then the electron kinetic term is

$$H_{el} = \int \psi^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m^*} \nabla^2 \right) \psi(\mathbf{r}) d^3 r. \tag{1.2.21}$$

If we use a suitable basis for the field operator

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \tag{1.2.22}$$

with V (unit cell) volume, then 1.2.21 becomes

$$H_{el} = \sum_{\mathbf{k}} \frac{k^2}{2m^*} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, \tag{1.2.23}$$

with $c_{\mathbf{k}}^\dagger$ and $c_{\mathbf{k}}$ creation and annihilation operators for the free electron.
We now turn our attention to the polarization field, taking into account that it can be modelled as an harmonic oscillator a form similar to 1.2.21 can be recovered (P_{lat} is substituted by P in the following equations):

$$H_{ph} = \int \left(\frac{1}{2\gamma}\mathbf{\Pi}^2(\mathbf{r}) + \frac{\gamma}{2}\omega^2\mathbf{P}^2(\mathbf{r}) \right) d^3r, \tag{1.2.24}$$

where $\mathbf{\Pi}(\mathbf{r})$ is the conjugate momentum to $\mathbf{P}(\mathbf{r})$.
Using the canonical substitution for the operator $\mathbf{P}(\mathbf{r})$

$$\mathbf{P}(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{q}}\sqrt{\frac{\hbar}{2\gamma\omega}}\frac{\mathbf{q}}{q}e^{i\mathbf{q}\cdot\mathbf{r}}(a_{\mathbf{q}} - a_{-\mathbf{q}}^\dagger) \tag{1.2.25}$$

and the corresponding one for $\mathbf{\Pi}(\mathbf{r})$ we obtain the equation for a quantum harmonic oscillator:

$$H_{ph} = \hbar\omega\sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}}, \tag{1.2.26}$$

with $a_{\mathbf{q}}^\dagger$ and $a_{\mathbf{q}}$ bosonic phononic creation and annihilation operators.
Using the same formalism, the interaction term is instead written in the following way:

$$H_{EPC} = \iint \psi^\dagger(\mathbf{r})\psi(\mathbf{r})\frac{e}{|\mathbf{r} - \mathbf{r}'|}(-\nabla_{\mathbf{r}'}\cdot\mathbf{P})(\mathbf{r}')d^3r\,d^3r', \tag{1.2.27}$$

using the same substitution in 1.2.25 for $\mathbf{P}(\mathbf{r})$ the following form is obtained:

$$H_{EPC} = \int \psi^\dagger(\mathbf{r})\psi(\mathbf{r})\left[4\pi i\left(\frac{e^2\hbar}{2\gamma\omega V}\right)^{1/2}\sum_{\mathbf{q}}\frac{1}{q}(a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} - a_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}})d^3r\right]. \tag{1.2.28}$$

The term is simplified even more if we substitute the electron field operator using 1.2.25, then the final form of the coupling term is reached

$$H_{EPC} = \sum_{\mathbf{k},\mathbf{q}}(V_{\mathbf{w}}c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}}a_{\mathbf{w}} + V_{\mathbf{w}}^* c_{\mathbf{k}-\mathbf{q}}^\dagger c_{\mathbf{k}}a_{\mathbf{q}}^\dagger), \tag{1.2.29}$$

where the coupling parameter is given as

$$V_{\mathbf{q}} = -4\pi i\left(\frac{e^2}{2\hbar\gamma\omega V}\right)^{1/2}\frac{1}{q}. \tag{1.2.30}$$

It is possible to rewrite the coupling parameter in terms of the dimensionless coupling strength α:

$$V_{\mathbf{q}} = i\left(\frac{4\pi\alpha}{V}\right)^{1/2}\frac{1}{q},$$
$$\alpha = \frac{2\pi e^2}{\hbar\gamma\omega}\sqrt{\frac{2m^*\omega}{\hbar}} = \frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2}{\hbar\omega}\sqrt{\frac{2m^*\omega}{\hbar}}. \tag{1.2.31}$$

If we now identify ω with ω_{LO} angular frequency of the longitudinal optical phonon modes (the modes that effectively couple with the electron), we obtain the final form of the Froehlich Hamiltonian:

$$H^{Fr} = \sum_{\mathbf{k}} \frac{k^2}{2m^*} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \hbar\omega_{LO} \sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{\mathbf{k},\mathbf{q}} (V_q c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}} a_{\mathbf{q}} + V_q^* c_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}} a_{\mathbf{q}}^\dagger) \qquad (1.2.32)$$

where we have dropped the coupling parameter dependence on $\mathbf{q}$ direction since it only depends on its modulus.

The main assumptions of this model are:

- Free electron with quadratic dispersion (up to a *scalar* effective mass m^*).

- Dispersionless optical mode with frequency ω_{LO}.

- "Large" polaron, with characteristic dimension d much greater than lattice parameter a (continuum approximation).

In this form the model correctly describes only a handful of real materials and it mainly serves as a toy model (we will breafly mention how it can be solved at weak coupling with perturbation theory and at strong coupling variationally), however we will focus on the **Diagrammatic Monte Carlo Method**, a computational method that is capable of solving the polaron problem using some tricks. We will also see how some of the main limitations of the model (namely the scalar effective mass m^* and the single phonon mode ω_{LO}) can be lifted without lifting the main assumption (the large polaron approximation). It will be illustrated in particular the case of an anisotropic band with effective mass $m^*(\hat{\mathbf{k}})$ and multiple dispersionless optical modes ω_{LO_j}, already capable of modelling valence band minima in a wide range of materials.

1.2.1 Weak coupling limit: perturbation theory

In the weak coupling regime it is possible to apply perturbation theory to the Froehlich Hamiltonian, for this treatment a slightly modified Hamiltonian with respect to the one seen in 1.2.32 will be used [11]:

$$H^{Fr} = -\frac{\nabla^2}{2m^*} + \omega_{LO} \sum_{\mathbf{q}} (a_{\mathbf{q}}^\dagger a_{\mathbf{q}}) + \sum_{\mathbf{q}} (V_{\mathbf{q}} a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + V_{\mathbf{q}}^* a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}). \qquad (1.2.33)$$

We will respectively define the non-interacting Hamiltonian H_0^{Fr} and the interaction term H_I^{Fr} as

$$\begin{aligned}
H_0^{Fr} &= -\frac{\nabla^2}{2m^*} + \omega_{LO} \sum_{\mathbf{q}} (a_{\mathbf{q}}^\dagger a_{\mathbf{q}}), \\
H_I^{Fr} &= \sum_{\mathbf{q}} (V_{\mathbf{q}} a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + V_{\mathbf{q}}^* a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}).
\end{aligned} \qquad (1.2.34)$$

The quantum state of the non-interacting electron is described by $|\mathbf{k}\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$, while for the non interacting phonons it is possible to define the average number of excitations

$\langle a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}} \rangle = \langle n_{\mathbf{q}} \rangle$, which is equal to 0 at the ground state The total wavefunction of the non-interacting system then becomes:

$$|\mathbf{k}, 0\rangle = e^{i\mathbf{k} \cdot \mathbf{r}}|0\rangle. \tag{1.2.35}$$

The first excited state to which the ground non-interacting state can jump to is the one with electron wavevector $\mathbf{k} - \mathbf{q}$ and one phonon $n_{\mathbf{q}} = 1$, total energy is:

$$\frac{(\mathbf{k} + \mathbf{q})^2}{2m^*} + \omega_{LO} = \frac{k^2}{2m^*}, \tag{1.2.36}$$

the corresponding wavefunction is

$$|\mathbf{k} - \mathbf{q}, 1\rangle = e^{i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r}}|1\rangle. \tag{1.2.37}$$

At first order perturbation theory there is no correction to the energy, we then need to go to second order. We consider the matrix element

$$\langle \mathbf{k} - \mathbf{q}, 1|H_I^{Fr}|\mathbf{k}, 0\rangle = V_{\mathbf{q}}^*, \tag{1.2.38}$$

second order perturbation theory energy then becomes:

$$E_{\mathbf{k}P} = \frac{k^2}{2m^*} - \sum_{\mathbf{q}} \frac{|V_{\mathbf{q}}|^2}{(\mathbf{k} - \mathbf{q})^2/2m^* + \omega_{LO} - k^2/2m^*}, \tag{1.2.39}$$

evaluating the sum over the q wavevectors we arrive at

$$E_{\mathbf{k}P} = \frac{k^2}{2m^*} - \frac{\alpha \omega_{LO} \sqrt{2m^* \omega_{LO}}}{k} \arcsin \frac{k}{\sqrt{2m^* \omega_{LO}}}, \tag{1.2.40}$$

which for $k \ll \sqrt{2m^* \omega_{LO}}$ yields

$$E_{\mathbf{k}P} = \frac{k^2}{2m^*} - \alpha \omega_{LO}. \tag{1.2.41}$$

The polaron effective mass m_P^* is given by:

$$m_P^* = \frac{m^*}{\left(1 - \frac{\alpha}{6}\right)}. \tag{1.2.42}$$

From the equation it clearly results that the polaron effective mass diverges for $\alpha \to 6^-$ and is negative for $\alpha > 6$. This clearly signals that perturbation theory does not correctly describe the physical system at strong couplings.

1.2.2 Strong coupling limit: variational treatment

For the strong coupling case a different approach is taken: the main assumption of this model is a localized polaron wavefunction with a gaussian form [12], the Froehlich Hamiltonian is recast in order to write the phonon operators as displacement and conjugate moment operators:

$$Q_{\mathbf{q}} = \frac{1}{\sqrt{2}}\left(a_{\mathbf{q}} + a_{-\mathbf{q}}^{\dagger}\right), \qquad P_{\mathbf{q}} = -\frac{i}{\sqrt{2}}\left(a_{\mathbf{q}} - a_{-\mathbf{q}}^{\dagger}\right), \tag{1.2.43}$$

so that the Hamiltonian in 1.2.32 can be rewritten as

$$H^{Fr} = \frac{p^2}{2m^*} + \frac{\omega_{LO}}{2} \sum_{\mathbf{q}} \left(P_{\mathbf{q}}^2 + Q_{\mathbf{q}}^2 \right) + \sum_{\mathbf{q}} V_{\mathbf{q}} Q_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}. \qquad (1.2.44)$$

A wavefunction with dependence both on the electron position $\mathbf{r}$ and the lattice displacement $Q_{\mathbf{q}}$ is needed, for this reason the following gaussian ansatz is used:

$$\Phi(\mathbf{r}, Q_{\mathbf{q}}) = \phi(\mathbf{r}) \Psi_n(Q_{\mathbf{q}} + \delta Q_{\mathbf{q}}),$$
$$\phi(r) = \left(\frac{\beta}{\sqrt{\pi}} \right)^{3/2} e^{-\frac{\beta^2}{2} r^2}, \qquad (1.2.45)$$

with β variational parameter, Ψ_n the harmonic oscillator wavefunction and $\delta Q_{\mathbf{q}}$ displacement to be calculated.
We now need to take the expectation value of the Hamiltonian operator:

$$H(Q_{\mathbf{q}}) = \langle \phi(r) | H | \phi^*(r) \rangle = \int \phi(r) H \phi(r) d^3 r, \qquad (1.2.46)$$

the terms with $\mathbf{r}$ dependence are respectively evaluated as:

$$\int \phi^*(\mathbf{r}) \frac{p^2}{2m^*} \phi(\mathbf{r}) d^3 r = \frac{3\beta^2}{4m^*},$$
$$\int \phi^*(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \phi(\mathbf{r}) d^3 r = e^{-q^2/4\beta^2}. \qquad (1.2.47)$$

The following result is thus obtained:

$$H(Q_{\mathbf{q}}) = \frac{3\beta^2}{4m^*} + \frac{\omega_{LO}}{2} \sum_{\mathbf{q}} (P_{\mathbf{q}}^2 + Q_{\mathbf{q}}^2) + \sum_{\mathbf{q}} L_{\mathbf{q}} Q_{\mathbf{q}}, \qquad L_{\mathbf{q}} = V_{\mathbf{q}} e^{-q^2/4\beta^2}. \qquad (1.2.48)$$

To cancel out the linear term in $Q_{\mathbf{q}}$ it is important to choose the right equilibrium displacement $\delta Q_{\mathbf{q}}$ as

$$\delta Q_{\mathbf{q}} = \frac{L_{\mathbf{q}}}{\omega_{LO}}, \qquad (1.2.49)$$

which yields the Hamiltonian

$$H(Q_{\mathbf{q}}) = \frac{\omega_{LO}}{2} \sum_{\mathbf{q}} \left[P_{\mathbf{q}}^2 + (Q_{\mathbf{q}} + \delta Q_{\mathbf{q}})^2 \right] + \frac{3\beta}{4m^*} - \frac{1}{2\omega_{LO}} \sum_{\mathbf{q}} L_{\mathbf{q}}^2$$
$$= \frac{\omega_{LO}}{2} \sum_{\mathbf{q}} \left[P_{\mathbf{q}}^2 + (Q_{\mathbf{q}} + \delta Q_{\mathbf{q}})^2 \right] + E(\beta). \qquad (1.2.50)$$

The three different terms have precise physical meanings: the first term describes the harmonic oscillation of phonons around their new equilibrium position $(Q_{\mathbf{q}} + \delta Q_{\mathbf{q}})$, the second term represents the kinetic energy of the electron in the gaussian formalism, the

third one the interaction energy between the electron and the phonons. To variationally retrieve the lowest energy the β parameter is minimized, we have:

$$
\frac{1}{2\omega_{LO}} \sum_{\mathbf{q}} L_{\mathbf{q}}^2 = \alpha \left(\frac{\beta^2 \omega_{LO}}{m^* \pi} \right)^{1/2},
$$

$$
E(\beta) = \frac{3\beta^2}{4m^*} - \alpha \left(\frac{\beta^2 \omega_{LO}}{m^* \pi} \right)^{1/2}.
$$

(1.2.51)

If we calculate the derivative with respect to β and we minimize it the following result is obtained:

$$
\frac{dE}{d\beta} = \frac{3\beta}{2m^*} - \alpha \left(\frac{\omega_{LO}}{m^* \pi} \right)^{1/2} = 0,
$$

(1.2.52)

which yields a value for β_0:

$$
\beta_0 = \frac{\alpha}{3} 2m^* \left(\frac{\omega_{LO}}{m^* \pi} \right)^{1/2}.
$$

(1.2.53)

Using this result the minimum energy $E(\beta_0)$ is:

$$
E(\beta_0) = -\frac{\alpha^2 \omega_{LO}}{3\pi} = -0.106 \alpha^2 \omega_{LO},
$$

(1.2.54)

with a quadratic dependence on the coupling strength α different from that found using perturbation theory (linear).

A more refined treatment of the strong coupling limit [13] yields the following result:

$$
\lim_{a \to \infty} E_0(\alpha) = -\omega_{LO} \left[-0.1085 \alpha^2 + 2.836 + O(1/\alpha^2) \right],
$$

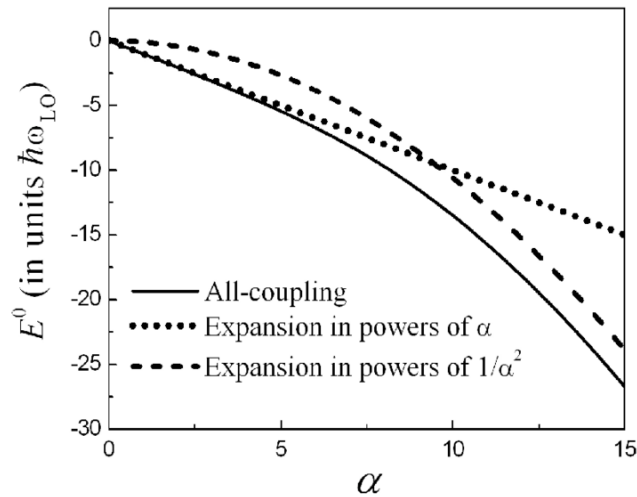(1.2.55)

not so different from our obtained result.

Figure 1.2: Computed polaron energy using perturbation theory, strong coupling theory and all coupling Feynman technique [14].

1.2.3 Froehlich Hamiltonian with degenerate bands and multiple phonon modes

The Hamiltonian in 1.2.32 only describes an extremely limited number of real cases, namely a non-degenerate isotropic electron band with effective mass m^* coupled to a single LO phonon mode. Although this relatively simple model is already quite challenging, some of its assumptions can be relaxed to obtain a more general framework.

Here we will be describing the **generalized Froehlich cubic model**: while mantaining some core simplification already seen in the original Froehlich model such as an isotropic dielectric tensor ϵ_0 and ϵ_∞ together with a phonon dispersion ω_{jLO} which does not depend on the wavevector direction (an even more general model not restrained to the cubic case is described in [15]) $\hat{k}$, it is still a quite relevant and useful model since it can be used to describe multiple materials such as various oxides (BaO, CaO, MgO), II-VI compounds (CdS, CdSe, ZnS, ZnTe) and III-V compounds (AlAs, GaAs, GaN, GaP) [16].
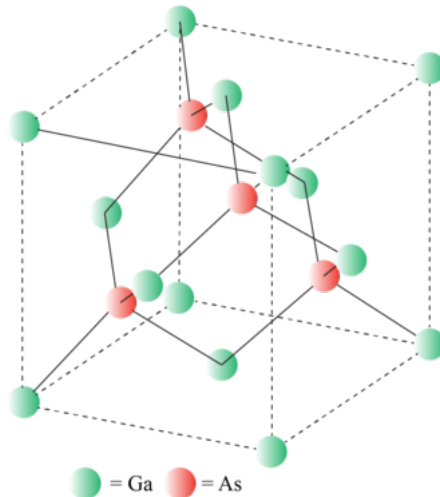

Figure 1.3: GaAs crystal structure, the cubic structure of the zincblende unit cell is here clearly displayed.

We start by defining the new electron term:

$$H_{el}^{cFr} \sum_{\mathbf{k}n} \frac{\sigma k^2}{2m_n^*(\hat{k})} c_{\mathbf{k}n}^\dagger c_{\mathbf{k}n}, \tag{1.2.56}$$

where the sum has been extended to n bands degenerate at the extremum, $\sigma = \pm 1$ depending on the fact that an electron or a hole polaron is taken into consideration, $m_n^*(\hat{k})$ is the new effective mass depending on band index n and wavevector direction $\hat{k}$ (a tensorial quantity in general).

We also want to extend our Hamiltonian to tackle the case of multiple LO phonon modes

present in the material, to this aim we define the following phonon term:

$$H_{ph}^{cFr} = \sum_{\mathbf{q}j} \hbar\omega_{jLO} a_{\mathbf{q}j}^{\dagger} a_{\mathbf{q}j}, \tag{1.2.57}$$

where the index j represents the different LO modes.

The electron-phonon coupling term gets redefined as:

$$H_{EPC}^{cFr} = \sum_{\mathbf{k}nn',\mathbf{q}j} c_{\mathbf{k+q}n'}^{\dagger} c_{\mathbf{k}n} \left[V^{cFr}(\mathbf{k}nn',\mathbf{q}j) a_{\mathbf{q}j} + V^{*cFr}(\mathbf{k}nn',\mathbf{q}j) a_{-\mathbf{q}j}^{\dagger} \right]. \tag{1.2.58}$$

It should be noted that the new electron-phonon coupling term includes interband transitions (from n to n'). The new coupling strength $V^{cFr}(\mathbf{k}nn',\mathbf{q}j)$ is found to be

$$V^{cFr}(\mathbf{k}nn',\mathbf{q}j) = \frac{i}{q}\frac{4\pi}{\Omega_0}\left(\frac{1}{2\omega_{jLO}V_{BvK}}\right)^{1/2}\frac{p_{jLO}}{\epsilon_\infty} \times \sum_m s_{n'm}(\hat{k}')s_{nm}^*(\hat{k}), \tag{1.2.59}$$

with Ω_0 volume of the primitive unit cell, V_{BvK} volume of the Born-von Karman unit cell, p_{jLO} phonon mode polarities, linked to Born effective charges and ionic dielectric tensor ϵ_0 [17] and computed as $p_{jLO}(\hat{q}) = \sum_\nu Z_\nu^* e_\nu(\hat{q})$ isotropic in cubic system, and the s tensors, symmetry dependent unitary matrices which represent specific bands (and have the same symmetry group).
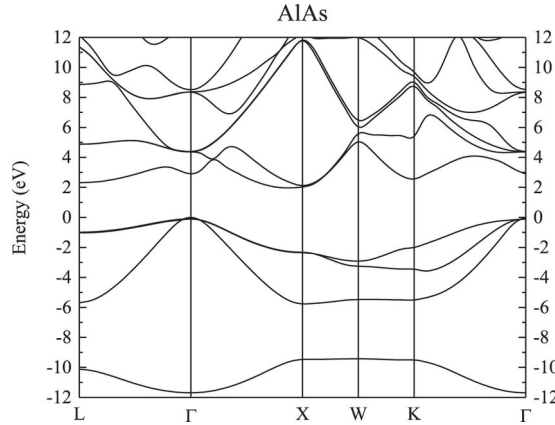

Figure 1.4: DFT calculated AlAs band structure [18], the conduction band minimum is on the high symmetry line Δ between Γ and X.

In our case of interest we restrict to just one anisotropic non-degenrate electron band, which is an accurate model for the conduction band minimum of the materials cited before (usually located somewhere between Γ and X along the Δ line), in this case the interaction strength simplifies to:

$$V^{cFr}(qj) = \frac{i}{q}\frac{4\pi}{\Omega_0}\left(\frac{1}{2\omega_{jLO}V_{BvK}}\right)^{1/2}\frac{p_{jLO}}{\epsilon_\infty}, \tag{1.2.60}$$

and the full Hamiltonian reads:

$$H^{cFr} = \sum_{\mathbf{k}} \frac{\sigma k^2}{2m^*(\hat{k})} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} + \sum_{\mathbf{q}j} \hbar\omega_{jLO} a_{\mathbf{q}j}^{\dagger} a_{\mathbf{q}j} + \sum_{\mathbf{k},\mathbf{q}j} c_{\mathbf{k+q}}^{\dagger} c_{\mathbf{k}} \left[V^{cFr}(qj)a_{\mathbf{q}} + V^{*cFr}(qj)a_{-\mathbf{q}}^{\dagger} \right]. \tag{1.2.61}$$

The effective mass $m^*(\hat{k})$ dependence on the wavevector $\mathbf{q}$ direction is expressed in the following way:

$$\frac{1}{m^*(\hat{k})} = \frac{\hat{k}_x^2}{m_x^*} + \frac{\hat{k}_y^2}{m_y^*} + \frac{\hat{k}_z^2}{m_z^*}, \tag{1.2.62}$$

with m_x^*, m_y^* and m_z^* effective mass values on the three cartesian axes.

Alternatively, the following formula for the electron energy as a function of k can be employed:

$$\epsilon(\mathbf{k}) = \frac{\sigma}{2} \left(\frac{k_x^2}{m_x^*} + \frac{k_y^2}{m_y^*} + \frac{k_z^2}{m_z^*} \right). \tag{1.2.63}$$

Chapter 2

The Froehlich polaron: Feynman diagrams

In order to deeply understand a many-body system such as the Froehlich polaron it is necessary to use a more powerful formalism derived from quantum field theory, we will first breafly describe Green's functions as an effective mean to describe meaningful quantities of our system and we will then shift to the **Matsubara imaginary time** formalism, much more useful in the context of Diagrammatic Monte Carlo. At the end of this journey the connection between the Froehlich polaron and Feynman diagrams will be explicated. In this section of the thesis we will use the convention $\hbar = 1$.

2.1 Green's function formalism

Green functions are useful objects to perturbatively solve systems that are really hard to correctly treat in any other way [19].
If we take for example a time-dependent Schroedinger equation in the following way:

$$[i\partial_t - H_0(\mathbf{r}) - V(\mathbf{r})]\,\psi(\mathbf{r}, t) = 0, \tag{2.1.1}$$

with the non-interacting diagonizable term H_0 and the perturbation V. It is possible to define the corresponding Green's functions as:

$$
\begin{aligned}
[i\partial_t - H_0(\mathbf{r})]\,G_0(\mathbf{r}, \mathbf{r}'; t, t') &= \delta(\mathbf{r} - \mathbf{r}')\delta(t - t'), \\
[i\partial_t - H_0(\mathbf{r}) - V(\mathbf{r})]\,G(\mathbf{r}, \mathbf{r}'; t, t') &= \delta(\mathbf{r} - \mathbf{r}')\delta(t - t').
\end{aligned}
\tag{2.1.2}
$$

We can define $G_0^{-1}(\mathbf{r}; t')$ and $G^{-1}(\mathbf{r}; t)$ as:

$$
\begin{aligned}
G_0^{-1}(\mathbf{r}; t) &= i\partial_t - H_0(\mathbf{r}), \\
G^{-1}(\mathbf{r}; t) &= i\partial_t - H_0(\mathbf{r}) - V(\mathbf{r}),
\end{aligned}
\tag{2.1.3}
$$

The Schroedinger equation can then be recast as

$$\left[G_0^{-1}(\mathbf{r}, t) - V(\mathbf{r})\right]\psi(\mathbf{r}, t) = 0 \tag{2.1.4}$$

and it is possible to rewrite the system as an integral equation

$$\psi(\mathbf{r}, t) = \psi^0(\mathbf{r}, t) + \int d^3r' \int dt' G_0(\mathbf{r}, \mathbf{r}'; t, t') V(\mathbf{r}') \psi(\mathbf{r}', t') \tag{2.1.5}$$

which can be solved iteratively. In fact:

$$\begin{aligned}
\psi &= \psi^0 + G_0 V \psi^0 + G_0 V G_0 V \psi^0 + G_0 V G_0 V G_0 V \psi^0 + ... \\
&= \psi^0 + (G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + ...) V \psi_0.
\end{aligned} \tag{2.1.6}$$

Noting that 2.1.5 can be also written as:

$$\psi(\mathbf{r}, t) = \psi^0(\mathbf{r}, t) + \int d^3r' \int dt' G(\mathbf{r}, \mathbf{r}'; t, t') V(\mathbf{r}') \psi^0(\mathbf{r}', t'), \tag{2.1.7}$$

it is possible to identify G with

$$\begin{aligned}
G &= G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + ... \\
&= G_0 + G_0 V (G_0 + G_0 V G_0 + ...),
\end{aligned} \tag{2.1.8}$$

and the well-known **Dyson equation** is retrieved:

$$G = G_0 + G_0 V G. \tag{2.1.9}$$

The one described above is the **single particle Green's function**, also called propagator since it "propagates" the wavefunction: in fact, if the wavefunction is known at time t' the wavefunction at a later time can be obtained in the following way:

$$\psi(\mathbf{r}, t) = \int d^3r' \int dt' G(\mathbf{r}t, \mathbf{r}'t') \psi(\mathbf{r}'t'), \tag{2.1.10}$$

which is a solution to 2.1.3. The Green's function can also be written as

$$G(\mathbf{r}t, \mathbf{r}'t') = -\theta(t - t') \langle \mathbf{r} | e^{-iH(t-t')} | \mathbf{r}' \rangle, \tag{2.1.11}$$

and is more precisely known as the **retarded Green's function**.

Focusing now on a many-body system the Green's function is defined as

$$G^R(\mathbf{r}\sigma t, \mathbf{r}'\sigma't') = -i\theta(t - t') \langle [\psi_\sigma(\mathbf{r}, t), \psi_{\sigma'}^\dagger(\mathbf{r}', t')]_{B,F} \rangle, \tag{2.1.12}$$

where $[,]_{B,F}$ is the commutator $[,]$ for bosons and the anticommutator $\{,\}$ for fermions. In the case of translation-invariant system (such as lattices) Green's functions can only depend on $\mathbf{r} - \mathbf{r}'$ and it is natural to adopt the usual $\mathbf{k}$ formalism:

$$G^R(\mathbf{r} - \mathbf{r}', \sigma t, \sigma' t') = \frac{1}{V} \sum_\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} G^R(\mathbf{k}, \sigma t, \sigma' t'), \tag{2.1.13}$$

$$G^R(\mathbf{k}, \sigma t, \sigma' t') = -i\theta(t - t') \langle [a_{\mathbf{k}\sigma}, a_{\mathbf{k}'\sigma'}^\dagger]_{B,F} \rangle.$$

The goal is now to find explicit expressions for the various Green's function of relevance, in the special case of a free electron the Hamiltonian assumes the simple form

$$H = \sum_{\mathbf{k}\sigma} \epsilon(k) c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}, \tag{2.1.14}$$

and the time dependence of the creation/annihilation operators is simply defined as

$$c_{\mathbf{k}\sigma}(t) = e^{iHt} c_{\mathbf{k}\sigma} e^{-iHt} = c_{\mathbf{k}\sigma} e^{-i\xi_k t}. \tag{2.1.15}$$

The retarded Green's function then becomes:

$$G^R(\mathbf{k}\sigma, t - t') = -i\theta(t - t') e^{-i\xi_k(t-t')}. \tag{2.1.16}$$

2.2   Perturbation theory for Green's functions

Given an Hamiltonian which can be written as a sum of two terms

$$H = H_0 + V, \tag{2.2.1}$$

where H_0 is diagonizable and V is an interaction term which can be treated perturbatively, we want to obtain a perturbative expansion of the Green's function. The issue with this approach is that in the expression for a generic Green's function it is require to take the expectation value over a ground state ($\langle \cdot \rangle$) which is not known, namely the ground state of the interacting system.

It is thus important to link the ground state of the interacting system to the ground state of the non-interacting one, to this mean we introduce **adiabatic switching on of the interaction** [20].

The core feature of this method is turning a time-independent problem into a time-dependent one by slowly switching on the perturbation, the Hamiltonian is transformed in the following way:

$$H_\alpha(t) = H_0 + V e^{-\alpha|t|}, \qquad \alpha > 0, \tag{2.2.2}$$

such that the system is non-interacting for $t \to \pm\infty$ and goes back to 2.2.1 for $t \to \infty$,

$$\lim_{t \to \pm\infty} H_\alpha(t) = H_0, \qquad \lim_{t \to 0} H_\alpha(t) = H. \tag{2.2.3}$$

In this setup, it is natural to suppose that the ground state of the interacting system $|\Phi_0\rangle$ evolves continuously starting from the ground state of the non-interacting one $|\Psi_0\rangle$.

We introduce the Dirac representation the operators, for the interaction term of the Hamiltonian we have

$$V_I e^{-\alpha|t|} = e^{iH_0 t} V e^{-iH_0 t} e^{-\alpha|t|}, \tag{2.2.4}$$

the time-evolution operator in the Dirac representation is written as

$$U_{I\alpha}(t, t_0) = \sum_{n_0}^{\infty} \frac{1}{n!} (-i)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t} dt_n e^{-\alpha(|t_1| + \dots + |t_n|)} T_t \left[V_I(t_1) \cdots V_I(t_n) \right], \tag{2.2.5}$$

and defines the evolution of the system in the following way:

$$|\psi_{I\alpha}(t)\rangle = U_{I\alpha}(t, t_0)|\psi_{I\alpha}(t_0)\rangle. \tag{2.2.6}$$

The equation of motion is obtained as

$$i\frac{d}{dt}|\psi_{I\alpha}(t)\rangle = e^{-\alpha|t|} V_I(t)|\psi_{I\alpha}(t)\rangle, \tag{2.2.7}$$

from this it follows that

$$i\frac{d}{dt}|\psi_{I\alpha}(t \pm \infty)\rangle = 0, \tag{2.2.8}$$

which means that the state is time-independent. We can thus take the ground state of the non-interacting system as the ground state for the interacting system when $t \to \pm\infty$, the expression at the two times can differ up to a phase factor:

$$|\psi_{I\alpha}(t \to -\infty)\rangle = |\Psi_0\rangle, \qquad |\psi_{I\alpha}(t \to \infty)\rangle = e^{i\phi}|\Psi_0\rangle. \tag{2.2.9}$$

It is now possible to link the non-interacting ground state at $t \to -\infty$ with the interacting one at t using the time-evolution operator

$$|\psi_{I\alpha}(t)\rangle = U_I(t, -\infty)|\Psi_0\rangle, \qquad (2.2.10)$$

at $t = 0$ the interaction is completely switched on. Moreover, if the switching on is performed really slowly (adiabatically) it can be excluded that the wavefunction $|\psi_{I\alpha}(t)$ depends on the parameter α and the exact ground state should be computed starting from the non-interacting ground state.

However, since it is required that $\alpha > 0$, there is no certainty that the limit

$$|\Phi_0\rangle = \lim_{\alpha \to 0} |\psi_{I\alpha}(0)\rangle \qquad (2.2.11)$$

exists, and in fact it does not exist.

For this reason the **Gell-Mann-Low theorem** [21] is used, which is a theorem that fixes the eigenstate which evolves from the non-interacting ground state during the adiabatic switching on of the interaction.

The statement of the theorem is the following: given a state

$$\lim_{\alpha \to 0} \frac{U_{I\alpha}(0, -\infty)|\Psi_0\rangle}{\langle \Psi_0 | U_{I\alpha, -\infty} | \Psi_0 \rangle} = \lim_{\alpha \to 0} \frac{|\psi_{I\alpha}(0)\rangle}{\langle \Psi_0 | \psi_{I\alpha}(0)\rangle} \qquad (2.2.12)$$

which exists for every order of the perturbation theory, then this state is an eigenstate $|\Phi_0\rangle$ of the full Hamiltonian H_0.

The importance of this system consists on the fact that it fixes the eigenstate during its evolution starting from the non-interacting ground state, a further important assumption is thus the requirement that no crossings of the states occur during their evolution from the free states. This is not a problem in our case since in the Froehlich Hamiltonian no transitions of this type occur, differently from what happens, for example, in superconductivity.

Since Green's functions are defined as expectation values of Heisenberg operators, these expectation values should be evaluated over the ground state (at $T = 0$), Using Gell-Mann-Low theorem it was demonstrated that the ground state of the interacting system $|\Phi_0\rangle$ can be retrieved from the non interacting one $|\Psi_0\rangle$, the normalized ground state is

$$|\Phi_0\rangle_{norm} = \frac{|\Phi_0\rangle}{(\langle \Phi_0 | \Phi_0 \rangle)^{1/2}}. \qquad (2.2.13)$$

Given a generic Green's function (in terms of the parameter α)

$$G_\alpha(\mathbf{k}t, \mathbf{k}'t') = -i\langle T_t c_\mathbf{k}(t) c_{\mathbf{k}'}^\dagger(t')\rangle, \qquad (2.2.14)$$

the creation and annihilation operators in the Heisenberg representation can be cast in the interaction one:

$$c_{\alpha\mathbf{k}}(t) = U_{I\alpha}(0, t) c_{I\alpha\mathbf{k}}(t) U_{I\alpha}(t, 0). \qquad (2.2.15)$$

The expectation value of the Heisenberg operator can now be computed:

$$\begin{aligned}
{}_{norm}\langle \Psi_0 | c_\mathbf{k}(t) c_{\mathbf{k}'}^\dagger(t') | \Psi_0 \rangle_{norm} &= \frac{\langle \Psi_0 | c_{\alpha \to 0 \mathbf{k}} c_{\alpha \to 0 \mathbf{k}'}^\dagger | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \\
&= \lim_{\alpha \to 0} \frac{\langle \Psi_0 | U_{I\alpha}(+\infty, t) c_{I\mathbf{k}}(t) U_{I\alpha}(t, t') c_{I\mathbf{k}'}^\dagger(t') U_{I\alpha}(t', -\infty) | \Psi_0 \rangle}{\langle \Psi_0 | U_{I\alpha}(+\infty, -\infty) | \Psi_0 \rangle}.
\end{aligned} \qquad (2.2.16)$$

Using this formula it is possible to perturbatively treat any Green's function by expanding it in a power series.

Given a generic Heisenberg operator $A(t)$ and the power expansion for the time-evolution operator in 2.2.5 we may write:

$$_{norm}\langle\Psi_0|A(t)|\Psi_0\rangle_{norm} = \lim_{\alpha\to 0}\frac{1}{\langle\Psi_0|U_{I\alpha}(+\infty,-\infty)|\Psi_0\rangle}\sum_{n=0}^{+\infty}\frac{1}{n!}(-i)^n \cdot$$
$$\int_{-\infty}^{+\infty}dt_1\cdots\int_{-\infty}^{+\infty}dt_n e^{-\alpha(|t_1|+...+|t_n|)}\langle\Psi_0|T\left(V_I(t_1)\cdots V_I(t_n)\right)|\Psi_0\rangle. \tag{2.2.17}$$

It is then possible to compare 2.2.17 with 2.2.5 to obtain the following identity:

$$\sum_{n=0}^{+\infty}\frac{1}{n!}(-i)^n\int_{-\infty}^{+\infty}dt_1\cdots\int_{-\infty}^{+\infty}dt_n e^{-\alpha(|t_1|+...+|t_n|)}T_t\left(V_I(t_1)\cdots V_I(t_n)A(t)\right) =$$
$$=U_{I\alpha}(+\infty,t)A(t)U_{I\alpha}(t,-\infty). \tag{2.2.18}$$

The same argument can be made for a single particle Green's function, obtaining a similar expansion:

$$iG(\mathbf{k},t,t') = \sum_{n=0}^{+\infty}\frac{1}{n!}(-i)^n\int_{-\infty}^{+\infty}dt_1\cdots\int_{-\infty}^{+\infty}dt_n\cdot$$
$$e^{-\alpha(|t_1|+...+|t_n|)}\langle\Psi_0|T_t\left(V_I(t_1)\cdots V_I(t_n)c_{\mathbf{k}}(t)c_{\mathbf{k}}^\dagger(t')\right)|\Psi_0\rangle. \tag{2.2.19}$$

2.3 Matsubara formalism for imaginary time Green's functions

The usual Green's functions are complex objects that are not fit to be used in the Diagrammatic Monte Carlo method since they provides negative values that cannot be easily sampled from a distribution without losing precision.

For this reason we now describe the imaginary time formalism for Green's functions, which is also useful to evaluate system that are at non-zero temperature. The relevant substitution is:

$$it \to \tau, \tag{2.3.1}$$

the retarded Green's function previously defined in 2.1.13 thus becomes the following Matsubara Green's function:

$$G(\mathbf{k},\sigma\tau,\sigma'\tau') = -\theta(\tau-\tau')\langle[a_{\mathbf{k}\sigma},a_{\mathbf{k}'\sigma'}^\dagger]_{B,F}\rangle \tag{2.3.2}$$

where the thermal average $\langle A(\tau)B(\tau')\rangle$ is defined as:

$$\begin{cases}\langle\Psi_0|A(\tau)B(\tau')|\Psi_0\rangle & T=0, \\ \frac{1}{Z}Tr\left[e^{-\beta H}A(\tau)B(\tau')\right] & T>0.\end{cases} \tag{2.3.3}$$

where Ψ_0 is the ground state and Z the partition function.

Given a system with a Hamiltonian characterized by a diagonizable term H_0 and a perturbation $V(\tau)$, we can define the imaginary time Heisenberg picture for an operator A as

$$A(\tau) = e^{-\tau H} A e^{\tau H}, \tag{2.3.4}$$

and similarly the imaginary time interaction picture as

$$A_I(\tau) = e^{\tau H_0} A e^{-\tau H_0}. \tag{2.3.5}$$

We can define the imaginary time time-evolution operator in the interaction picture as

$$U_I(\tau, \tau') = e^{\tau H_0} e^{-(\tau - \tau')H} e^{-\tau' H_0}, \tag{2.3.6}$$

an explicit expression for the interaction picture time-evolution operator in the imaginary time formalism is found in analogy with the real time counterpart

$$\frac{\partial}{\partial \tau} U_I(\tau, \tau') = e^{\tau H_0}(H_0 - H)e^{-(\tau - \tau')H}e^{-\tau' H_0} = -V_I(\tau)U_I(\tau, \tau'), \tag{2.3.7}$$

which can be solved iteratively:

$$
\begin{aligned}
U_I(\tau, \tau') &= \sum_{n=0}^{\infty} \frac{1}{n!}(-1)^n \int_{\tau'}^{\tau} d\tau_1 ... \int \tau'^{\tau} d\tau_n T_\tau \left[V_I(\tau_1)...V_I(\tau_n) \right] \\
&= T_\tau \exp\left(-\int_{\tau'}^{\tau} d\tau_1 V_I(\tau_1) \right),
\end{aligned}
\tag{2.3.8}
$$

where T_τ is the τ ordering operator.

It is also important to stress that the partition function Z is naturally treated in the imaginary time formalism, in fact:

$$e^{-\beta H} = e^{-\beta H_0} U_I(\beta, 0) = e^{-\beta H_0} T_\tau exp\left(-\int_0^\beta d\tau_1 V_I(\tau_1) \right), \tag{2.3.9}$$

and we have

$$
\begin{aligned}
\langle T_\tau A(\tau) B(\tau') \rangle &= \frac{1}{Z} Tr \left[e^{-\beta H} T_\tau (A(\tau) B(\tau')) \right] \\
&= \frac{1}{Z} Tr \left[e^{-\beta H_0} U_I(\beta, 0) T_\tau (U_I(0, \tau) A_I(\tau) U_I(\tau, \tau') B_I(\tau') U_I(\tau', 0)) \right] \\
&= \frac{1}{Z} Tr \left[e^{-\beta H_0} T_\tau (U_I(\beta, 0) A_I(\tau) B_I(\tau')) \right] \\
&= \frac{\langle T_\tau U_I(\beta, 0) A_I(\tau) B_I(\tau') \rangle_0}{\langle U_I(\beta, 0) \rangle_0},
\end{aligned}
\tag{2.3.10}
$$

where the expectation value is taken on the non-interacting system, in agreement with the previously found result for $T = 0$.

We now go back to the definition of single particle Green's functions in imaginary time formalism, we can define them both in real space and in $\mathbf{k}$ space:

$$
\begin{aligned}
G(\mathbf{r}t, \mathbf{r}'t') &= -\langle T_\tau \left(\psi(\mathbf{r}, \tau), \psi^\dagger(\mathbf{r}', \tau') \right) \rangle, \\
G(\mathbf{k}\tau, \mathbf{k}'\tau') &= -\langle T_\tau \left(c_\mathbf{k}(\tau) c_{\mathbf{k}'}^\dagger(\tau') \right) \rangle,
\end{aligned}
\tag{2.3.11}
$$

neglecting the spin σ degree of freedom (not relevant for our treatment).

In the non-interacting case the Matsubara single particle Green's functions can be valued in the same way as the retarded Green's functions, in fact:

$$H_0 = \sum_{\mathbf{k}} \xi_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}, \tag{2.3.12}$$

and the creation/annihilation operators in the Heisenberg picture read

$$c_{\mathbf{k}}(\tau) = e^{\tau H_0} c_{\mathbf{k}} e^{-\tau H_0} = c_{\mathbf{k}} e^{-\xi_{\mathbf{k}}\tau}, \qquad c_{\mathbf{k}}^{\dagger}(\tau) = e^{\tau H_0} c_{\mathbf{k}}^{\dagger} e^{-\tau H_0} = c_{\mathbf{k}}^{\dagger} e^{\xi_{\mathbf{k}}\tau}. \tag{2.3.13}$$

The non-interacting Matsubara Green's function is then defined as

$$\begin{aligned}
G_0(\mathbf{k}, \tau, \tau') &= -\langle T_\tau \left(c_{\mathbf{k}}(\tau) c_{\mathbf{k}}^{\dagger}(\tau') \right) \rangle \\
&= -\theta(\tau - \tau')\langle c_{\mathbf{k}}(\tau) c_{\mathbf{k}}^{\dagger}(\tau') \rangle - (\pm)_{B,F}\theta(\tau' - \tau)\langle c_{\mathbf{k}}^{\dagger}(\tau') c_{\mathbf{k}}(\tau) \rangle \\
&= -\left[\theta(\tau - \tau')\langle c_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} \rangle - (\pm)_{B,F}\theta(\tau' - \tau)\langle c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \rangle \right] e^{-\xi_{\mathbf{k}}(\tau - \tau')}.
\end{aligned} \tag{2.3.14}$$

2.4 Equation of motion and Wick's theorem

For a general Green's function the process to find its expression goes through the equation of motion technique, for a general operator in the imaginary time formalism the time derivative is

$$\partial_\tau A(\tau) = \partial(\tau) \left(e^{\tau H} A e^{-\tau H} \right) = e^{\tau H}[H, A] e^{-\tau H} = [H, A](\tau), \tag{2.4.1}$$

if we derivate with respect to imaginary time a Matsubara Green's function the following result is obtained:

$$-\frac{\partial}{\partial \tau} \left(T_\tau \langle A(\tau) B(\tau') \rangle \right) = \delta(\tau - \tau') \langle (AB - (\pm)_{B,F} BA) \rangle + \langle T_\tau ([H, A](\tau) B(\tau')) \rangle, \tag{2.4.2}$$

which for the single particle Green's function in momentum space becomes

$$-\frac{\partial}{\partial \tau} G(\mathbf{k}\tau, \mathbf{k}'\tau') = \delta(\tau - \tau')\delta_{\mathbf{k}\mathbf{k}'} + \langle T_\tau \left([H, c_{\mathbf{k}}](\tau) c_{\mathbf{k}'}^{\dagger}(\tau') \right) \rangle. \tag{2.4.3}$$

In the case of a Green's function for a non-interacting system G_0 with an Hamiltonian $H_0 = \sum_{\mathbf{k}\mathbf{k}'} t_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}'}$ this equation simplifies to

$$-\frac{\partial}{\partial \tau} G_0(\mathbf{k}\tau, \mathbf{k}'\tau') = \delta(\tau - \tau')\delta_{\mathbf{k}\mathbf{k}'} + \sum_{\mathbf{k}''} t_{\mathbf{k}\mathbf{k}''} G_0(\mathbf{k}''\tau, \mathbf{k}'\tau'), \tag{2.4.4}$$

and the solution is found as previously defined.

We now introduce **Wick's theorem**, an important result which states that higher order (greater than 1) Green's functions for non-interacting systems $G_0^{(n)}$ can be factorized into products of single particle Green's functions G_0.

The n-particle Green's function is defined as:

$$G_0^{(n)}(\nu_1\tau_1, \cdots, \nu_n\tau_n; \nu_1'\tau_1', \cdots \nu_n'\tau_n') = (-1)^n \langle T_\tau \left[c_{I\nu_1}(\tau_1) \cdots c_{I\nu_n}(\tau_n) c_{I\nu_n'}^{\dagger}(\tau_n') \cdots c_{I\nu_1'}^{\dagger}(\tau_1') \right] \rangle. \tag{2.4.5}$$

This expression is quite complicated and difficult to handle, we first define an easier notation to handle all the operators:

$$l_j(\gamma_j) = \begin{cases} c_{I\nu_j}(\tau_j) & \in [0, n], \\ c^{\dagger}_{I\nu'_{2n+1-j}}(\tau'_{2n+1-j}) & \in [n+1, 2n], \end{cases} \tag{2.4.6}$$

and we define the permutation of the $2n$ operators as:

$$P(l_1(\gamma_1) \cdots l_{2n}(\gamma_{2n})) = l_{P1}(\gamma_{P1}) \cdots l_{P_{2n}}(\gamma_{P_{2n}}), \tag{2.4.7}$$

with P_j j-th variable in the permutation P.

The correct order of permutation depends on the the time arguments ordering, for this reason it is possible to rewrite 2.4.5 taking into account these considerations:

$$G_0^{(n)}(j_1 \cdots j_{2n}) = (-1)^n \sum_{P \in S_{2n}} (\pm)^P_{B,F} \theta(\gamma_{P_1} - \gamma_{P_2}) \cdots \theta(\gamma_{P_{n-1}} - \gamma_{P_n}) \times \langle l_{P_1}(\gamma_{P_1}) \cdots l_{P_{2n}}(\gamma_{P_{2n}}) \rangle. \tag{2.4.8}$$

We can now take the derivative with respect to one of the time variables of $G_0^{(n)}$ and use the equation of motion:

$$\left[-\frac{\partial}{\partial \tau_1} G^{(n)_0}\right]_{2nd-term} = -(-1)^n \langle T_\tau \left[H_0, c_{I\nu_1}(\tau_1) \cdots c_{I\nu_n}(\tau_n) c^{\dagger}_{I\nu_n}(\tau'_n) \cdots c^{\dagger}_{I\nu_1}(\tau'_1)\right] \rangle \tag{2.4.9}$$

We know focus on the case where τ_i is next to τ'_j, two terms like this are present in 2.4.8, one where $\tau_i < \tau'_j$ and one where $\tau_i > \tau'_j$ (the permutation order is obviously different). The Green's function is written as

$$G_0^{(n)} = \left[\cdots \theta(\tau_i - \tau'_j) \cdots\right] \langle \cdots c_{I\nu_i}(\tau_i) c^{\dagger}_{I\nu'_j}(\tau'_j) \cdots \rangle$$
$$(\pm)_{B,F}[\cdots \theta(\tau'_j - \tau_i) \cdots] \langle \cdots c^{\dagger}_{I\nu'_j}(\tau'_j) c_{I\nu_i}(\tau_i) \rangle. \tag{2.4.10}$$

Differentiating these two terms with respect to τ_i gives two contributions from the heavy-side function $\theta(\cdot)$:

$$-\left[\frac{\partial}{\partial \tau_i} G_0^{(n)}\right]_{1st-term} = \left(\left[\cdots\right] \langle \cdots c_{I\nu_i}(\tau_I) c^{\dagger}_{I\nu'_j}(\tau'_j) \cdots \rangle\right.$$
$$\left.(\mp)_{B,F}[\cdots] \langle \cdots c^{\dagger}_{\nu'_j}(\tau'_j) c_{\nu_i}(\tau_i) \cdots \rangle\right) \delta(\tau_i - \tau'_j). \tag{2.4.11}$$

We now observe that

$$\left[c_{\nu_i}(\tau_i), c^{\dagger}_{\nu'_j}(\tau_i)\right]_{B,F} = \delta_{\nu_i, \nu'_j}, \tag{2.4.12}$$

in the same way, for a couple of terms $c_{\nu_i}(\tau_i)$ and $c_{\nu_j}(\tau_i)$:

$$\left[c_{\nu_i}(\tau_i), c_{\nu_j}(\tau_i)\right]_{B,F} = 0, \tag{2.4.13}$$

and the same is true for two creation operators.

In this way the number of creation and annihilation operators has been reduced by one

each and we have demonstrated that a n order Green's function can written in terms of a $n-1$ Green's functions (which is a sum of different terms). For fermionic Green's functions, the sign of G_0^{n-1} depends on the specific τ_j'. Apart from that, the equation of motion is now:

$$G_{0i}^{-1}G_0^{(n)} = \sum_{j=1}^{n} \delta_{\nu_i,\nu_j'}\delta(\tau_i - \tau_j')(\pm 1)_{B,F}^x G_0^{(n-1)}(\underbrace{\nu_1\tau_1,\cdots,\nu_n\tau_n}_{\text{without } i};\underbrace{\nu_1'\tau_1',\cdots,\nu_n'\tau_n'}_{\text{without } j}). \quad (2.4.14)$$

The sign $(-1)^x$ for fermions is determined as $(-1)^{n-i+n-j} = (-1)^{-(i+j)} = (-1)^{i+j}$ due to the fact that it is required that the annihilation operator $c_{I\nu_i}(\tau_i)$ is moved i positions to the right while the creation operator $c_{\nu_j'}^\dagger(\tau_j')$ is moved j positions to the left.

It is now possible to write the explicit decomposition of the n-order Green's function into a sum of n $(n-1)$-order ones:

$$G_0^{(n)} = \sum_{i=0}^{n}(\pm)_{B,F}^{i+j} G_0(\nu_1\tau_1,\nu_j'\tau_j')G_0^{(n-1)}(\underbrace{\nu_1\tau_1,\cdots,\nu_n\tau_n}_{\text{without } i};\underbrace{\nu_1'\tau_1',\cdots,\nu_n'\tau_n'}_{\text{without } j}). \quad (2.4.15)$$

It is clear from the obtained result that this method can be naturally generalized to iteratively obtain any non-interacting n-order Green's function as sum of terms only containing products of single particle non-interacting Green's functions, the final result of Wick's theorem is thus obtained:

$$G_0^{(n)}(1,\cdots,n;n',\cdots,1') = \begin{vmatrix} G_0(1,1') & \cdots & G_0(1,n') \\ \vdots & \ddots & \vdots \\ G_0(n,1') & \cdots & G_0(n,n') \end{vmatrix}_{B,F}, \qquad i \equiv (\nu_i,\tau_i) \quad (2.4.16)$$

where the result is given as a determinant for fermions and as a permanent for bosons.

2.5   Green's functions for the Froehlich Hamiltonian

We may now consider the Froehlich Hamiltonian previously defined in 1.2.61 using the new imaginary time formalism, defining the non-interacting Hamiltonian H_0^{cFr} as

$$H_0^{cFr} = \sum_{\mathbf{k}} \frac{\sigma k^2}{2m(\hat{k})} c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + \sum_{\mathbf{q}j} \omega_{LO} a_{\mathbf{q}j}^\dagger a_{\mathbf{q}j}. \quad (2.5.1)$$

Since our model consists of a single electron (hole) in the minimum (maximum) of the conduction (valence) band interacting with a cloud of phonon, we may consider our system to be at zero temperature and the ground state wavefunction $|\Psi_0\rangle$ to be the vacuum:

$$|\Psi_0\rangle = |0\rangle, \qquad \langle\cdot\rangle = \langle 0|\cdot|0\rangle \quad (2.5.2)$$

It is then possible to explicitly compute the electron free propagator using 2.3.14:

$$\begin{aligned} G_0(\mathbf{k},\tau,\tau') &= -\left[\theta(\tau-\tau')\langle 0|c_{\mathbf{k}}c_{\mathbf{k}}^\dagger|0\rangle + \theta(\tau'-\tau)\langle 0|c_{\mathbf{k}}^\dagger c_{\mathbf{k}}|0\rangle\right] e^{k^2/2m(\hat{k})(\tau-\tau')} \\ &= -\theta(\tau-\tau')e^{(k^2/2m(\hat{k}))(\tau-\tau')}, \end{aligned} \quad (2.5.3)$$

which for $\tau' = 0$ becomes

$$G_0(\mathbf{k}, \tau) = -\langle 0|c_{\mathbf{k}}(\tau)c_{\mathbf{k}}^\dagger|0\rangle = -e^{-(k^2/2m(\hat{k}))\tau}, \qquad \tau \geq 0. \qquad (2.5.4)$$

The Matsubara Green's function for a free electron propagator assumes the simple form of an exponential function, which can be easily sampled.
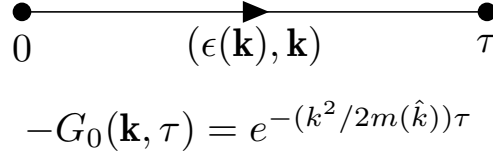

$$-G_0(\mathbf{k}, \tau) = e^{-(k^2/2m(\hat{k}))\tau}$$

Figure 2.1: Feynman diagram of the free electron propagator together with its Green's function.

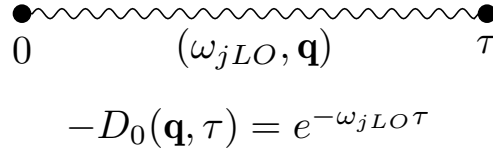$$-D_0(\mathbf{q}, \tau) = e^{-\omega_{jLO}\tau}$$

Figure 2.2: Feynman diagram of the free phonon propagator together with its Green's function.

In the same way, it is possible to find an explicit form for the phonon free propagator:

$$D_0(\mathbf{q}j, \tau) = -\langle 0|a_{\mathbf{q}}(\tau)a_{\mathbf{q}}^\dagger|0\rangle = -e^{-\omega_{jLO}\tau}, \qquad \tau \geq 0, \qquad (2.5.5)$$

which is again a simple exponential function. We now take into consideration the interaction part of the Froehlich Hamiltonian:

$$V = \sum_{\mathbf{k},\mathbf{q}j} c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}} \left[V_{\mathbf{q}}^{cFr} a_{\mathbf{q}} + V_{\mathbf{q}}^{*cFr} a_{-\mathbf{q}}^\dagger \right], \qquad (2.5.6)$$

The basic Feynman diagram that describes this interaction is an interaction between two free electron propagators (one with momentum $\mathbf{k}$ gets annihilated and one with momentum $\mathbf{k} + \mathbf{q}$ gets created) and a free phonon propagator which can either be annihilated (momentum $\mathbf{q}$) or created (momentum $-\mathbf{q}$), the strength of the interaction at the vertex is given by $|V_{\mathbf{q}}|$.
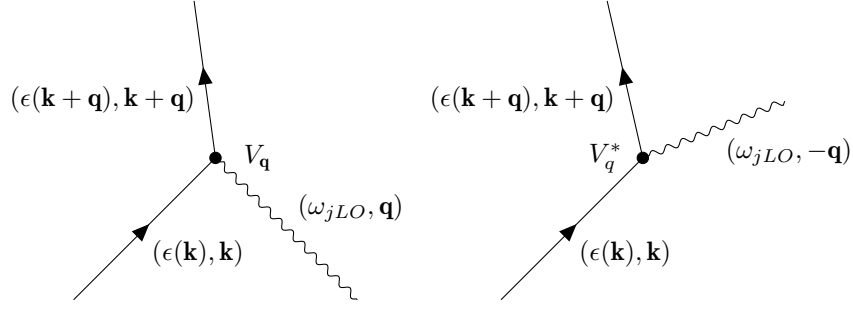
Figure 2.3: Feynman diagrams of the electron-phonon interaction.

We have now obtained the fundamental building blocks which can be used to obtain the total Green's function for the Froehlich polaron $G(\mathbf{k}, \tau)$, a generic one-electron Matsubara Green's function for the polaron is written as

$$G(\mathbf{k}, \tau - \tau') = -\langle c_{\mathbf{k}}(\tau)c_{\mathbf{k}}^{\dagger}(\tau')\rangle = -\langle 0|c_{\mathbf{k}}(\tau)c_{\mathbf{k}}^{\dagger}(\tau')|0\rangle. \qquad (2.5.7)$$

The creation and annihilation operators here defined do not have the simple form described above for the free propagators, it is thus necessary to use the interaction picture:

$$c_{I\mathbf{k}}(\tau) = e^{\tau H_0^{cFr}}c_{\mathbf{k}}e^{-\tau H_0^{cFr}}, \qquad c_{I\mathbf{k}}^{\dagger}(\tau) = e^{\tau H_0^{cFr}}c_{\mathbf{k}}^{\dagger}e^{-\tau H_0^{cFr}}. \qquad (2.5.8)$$

In the interaction picture it is possible to perturbatively treat the Green's function following 2.1.9:

$$\langle 0|c_{\mathbf{k}}(\tau)c_{\mathbf{k}}^{\dagger}(\tau')|0\rangle = \langle 0|U_I(0,\tau)c_{I\mathbf{k}}(\tau)U_I(\tau,\tau')c_{I\mathbf{k}}^{\dagger}U_I(\tau',0) \qquad (2.5.9)$$

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