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DIPLOMA THESIS

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Current Transmission Through a Vibrating Molecular Junction

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V Praze dne 9. prosince 2010

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Název práce: Průchod proudu vibrujícím molekulárním mústkem
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Abstrakt: V předložené práci studujeme průchod elektronu vibrujícím molekulárním mústkem interagujícím s přívodními vodiči za použití metody nerovnovážných Greenových funkcí. Použité Greenovy funkce využívávají kombinaci prvního kvantování k popisu vibračních hladin a druhého kvantování k popisu elektronových procesů. Zabýváme se změnou vibračního potenciálu mústku vyvolanou nabitím, stanovíme spektrální funkci a velikost protékajícího proudu. Potvrzujeme vliv Fermiho moře a Franck-Condonových faktorů na zúžení peaků. Procesy studujeme na modelu motivovaném molekulou bifenylu, kde zavádíme potenciál se dvěma mínimy a studujeme vliv kvazidegenerovaných energetických hladin. Ukazujeme vliv rostoucího momentu setrvačnosti molekuly na posuv peaků do oblastí určených Franck-Condonovými faktory.

Klíčová slova: nerovnovážná Greenova funkce, molekulární mústek

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Abstract: In the present work we study transmission of electron through vibrating molecular junction interacting with leads using a method of nonequilibrium Green functions. Our Green functions use combination of first quantization to treat vibrational levels and second quantization to treat electron processes. We treat the change of vibrational potential of junction induced by charging of junction, we find a spectral function and a magnitude of current through the junction. We confirm the effect of Fermi sea and Frack-Condon factors on sharpening of peaks. We study these processes on model motivated by biphenyl molecule, introducing double well potential and study an effect of quasidegenerate energy levels. We present the shift of peaks, resulting from an increase of moment of inertia, to positions determined by Franck-Condon factors.

Keywords: nonequilibrium Green function, molecular junction
Chapter 1

INTRODUCTION

Nanoelectronics is a term generally referring to electronic components smaller than 100 nm, for which quantum mechanical properties play an important role and have to be included in appropriate theory. This area covers nanofabrication, molecular electronics and one-dimensional nanowires. Short note should be put forward to introduce the matter, because each of these areas is somehow related to the problem studied.

Nanowires are chains of repeating molecules or atoms and generally can be considered one-dimensional. They are quite different from generic leads in terms of allowed energy levels (energy bands) and conductivity quantization, resulting from quantized energy levels.

Nanofabrication, most notably nanocircuitry, tries to bring today’s integrated circuits to nanoscale (in a sense mentioned above), integrating components, of which one example related to the work is single-electron transistor. The transistor is based on so called Coulomb blockade, an insulating barrier between two leads, which can be overcome by electron through a process of quantum tunneling. The tunneling process can be stimulated by turning on the switch voltage, thus, shifting energy levels in the island region. Part of this particular problem, tunneling of electron through vibrating junction, is studied in this work.

Major part of this work is a theoretical approach to molecular electronics phenomena. Molecular electronics, also called moletronics, is a branch of studies aiming to use individual molecules as building blocks for electronic devices either as passive components (like nanotubes) or active ones (molecular switches). Realizing limits of miniaturization of current semiconductor electronics, the extensive progress has been made in recent years in the area. The vision of single molecule replacing whole transistor, monoatomary conductors, and others have been a stimulation for a basic
research and partially also an industry.

Devices have been outlined theoretically already in 70’s and 80’s, such as molecular rectifier or single molecule transistor and logic gate. Practical experiments, however, were carried out with development of for example STM and AFM, which became instruments to manipulate with individual molecules. This was in mid 90’s; theoretical predictions were often experimentally confirmed on qualitative level, but quantitative analysis is lacking due to complications with setting up experiment with steady output values. On the part of passive components, devices like carbon nanotubes, fullerenes or polymeric conductors have been utilized.

In this thesis, we aim to follow the work of Flensberg [3]. In his work, he considered the change of conformation of molecular junction caused by charging of the junction with single electron; for accompanying change of harmonic vibrational potential he assumed mere coordinate shift of potential. At first, we will repeat his work to verify our results and prepared procedure. Going beyond his work, we will do several generalizations. We will introduce anharmonic, double well, potential, which will allow us to study influence of quasidegenerate energy levels. We will use simpler Green function with only one projector, not two as in his case. Using these generalizations, we will calculate steady state current through the junction and modify parameters of our model, to simulate a situation more realistic for molecules.
Chapter 2

THEORY

This chapter covers theory behind the utilized procedure with minor side-notes and short motivation at the beginning. Major thread develops onwards and is generally descriptive and explanatory. Problem solved in this thesis is current transport through molecular junction with one ionic electronic and vibronic state, while the molecule is in a thermal equilibrium with one of the leads. There is several approaches to this type of problems, scattering is major alternative. But our approach was based on nonequilibrium Green functions.

The studied system is an electronic-vibronic system of a single molecule with transport effects. It is necessary to consider nonequilibrium state invoked by chemical potentials difference on each side of the junction. For low bias voltage, this can be generally ignored, and IV characteristic can be calculated using equilibrium electronic structure of the junction; for stronger bias voltage maintaining elastic scattering, Landauer equation can be used.

It is convenient to state here, that some physical constants, such as \( \hbar \) are considered to be 1 and often are reintroduced in final results. The following section provides motivation for our work.

2.1 Tight binding model and Elastic Electron Scattering

Tight binding model is an approach to a periodic electronic structure. Despite it is not directly related to the method used in this work, analytical result obtained through this model can make a good comparison to the results obtained by our calculation. The model regards electrons as tightly bond to atom site in the solid
structure; whole crystal is then regarded as a lattice of separate nuclei, while interaction of different wavefunctions is limited.

For our purposes, it is enough to limit the scope to one-dimensional lattice and study behavior of one electron. Let us assume an electron is added to an atom (which therefore turns into ion) and non-zero amplitude of transfer to adjacent site exists. We may consider periodic position function

$$R_n = na, n \in \mathbb{N}$$

(2.1.0.1)

giving the distance from the site set as beginning, $a$ is lattice parameter, while $|\phi_n\rangle$ is state (atomic orbital or wavefunction in coordinate representation) localized at site $R_n$. Each site can be assigned its own energy $\epsilon_0$ and an energy given by the interaction with the nearest neighbours represented by parameter $\alpha$. We suppose for simplicity, that we are dealing with atoms of one kind with one electronic energy level and uniform $a = 1$, we can write Hamiltonian of whole system in localized orbital basis in form

$$H_c = \sum_i \epsilon_0 |\phi_i\rangle \langle \phi_i| - \alpha [ |\phi_i\rangle \langle \phi_{i+1}| + |\phi_{i+1}\rangle \langle \phi_i|].$$

(2.1.0.2)

It is rather easy to find a basis, in which this operator can be diagonalized. We try to find eigenfunctions of delocalized orbitals given as a linear combination of atomic localized orbitals $\psi_k = \sum_j c_{j,k} \phi_j$. Eigenvalue equation can be written in matrix form as

$$
\begin{pmatrix}
\ddots & & \\
\vdots & \epsilon_0 & -\alpha & 0 & \\
\cdots & -\alpha & \epsilon_0 & -\alpha & \\
0 & -\alpha & \epsilon_0 & \ddots & \\
& & \ddots & \ddots & 
\end{pmatrix}
\begin{pmatrix}
c_{1,k} \\
c_{2,k} \\
\vdots \\
0 \\
\vdots 
\end{pmatrix} = \begin{pmatrix}
\epsilon_k \\
\vdots \\
\vdots \\
\vdots 
\end{pmatrix} = \epsilon_k
$$

(2.1.0.3)

System yields a set of equations

$$\epsilon_0 c_{j,k} - \alpha (c_{j+1,k} + c_{j-1,k}) = \epsilon_k c_{j,k}$$

(2.1.0.4)

(in case we assume the chain is infinite, so there are no boundary conditions). It is easy to see, that plane wave solves the equation, so $c_{j,k} = e^{ijk}$. If we substitute back into the equation, the solution for eigenvalues is

$$\epsilon_0 e^{ik} - \alpha (e^{ik(j+1)} + e^{ik(j-1)}) = \epsilon_k e^{ik}$$

$$\epsilon_k = \epsilon_0 - 2\alpha \left( \frac{e^{ik} + e^{-ik}}{2} \right)$$

$$\epsilon_k = \epsilon_0 - 2\alpha \cos(k).$$

(2.1.0.5)
The last line is a dispersion relation for electron momentum and energy, it defines an energy band, the energies allowed for electrons to reach for given momenta. So electrons with momentum $k \in \langle -\pi, \pi \rangle$ will have energies $\epsilon_k \in \langle \epsilon_0 - 2\alpha, \epsilon_0 + 2\alpha \rangle$.

Situation changes a little bit, if an impurity is present. Electrons then scatter and transmission probability can be analytically calculated. The matrix equation is rather similar to (2.1.0.3), there are just three extra equations for the junction and surrounding atoms.

$$
\begin{pmatrix}
\ddots & \vdots & 0 \\
-\alpha & \epsilon_0 & -\beta & 0 \\
0 & -\beta & \epsilon_d & -\beta & 0 \\
0 & -\beta & \epsilon_0 & -\alpha \\
0 & \vdots & \ddots & \ddots & \ddots & \ddots
\end{pmatrix}
\begin{pmatrix}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\vdots
\end{pmatrix}
= \epsilon_k
\begin{pmatrix}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\vdots
\end{pmatrix}
(2.1.0.6)
$$

The situation is illustrated by figure 2.1, incident wave scatters resulting in transmitted and reflected wave. The amplitude of transmitted (reflected) wave is denoted as $t$ ($r$).

We have three equations for three unknowns. Situation can be even simplified, considering we can again use plane waves as decomposition coefficients and set junction site index $j = 0$, while numbering negative to the left and positive to the right. Equations then read

$$
\begin{align}
-\alpha(e^{-2ik} + re^{2ik}) + \epsilon_0(e^{-ik} + re^{ik}) - \beta c_0 &= \epsilon_k(e^{-ik} + re^{ik}) & (2.1.0.7a) \\
-\beta(e^{-ik} + re^{ik}) + \epsilon_d c_0 + \beta e^{ik} t &= \epsilon_k c_0 & (2.1.0.7b) \\
-\beta c_0 + \epsilon_0 e^{ik} t - \alpha e^{2ik} &= \epsilon_k t e^{ik} & (2.1.0.7c)
\end{align}
$$

These can be solved straightforwardly using (2.1.0.5), yielding results $t = 1 + \frac{r}{\alpha c_0}$ from first and third equation. The second equation leads to relations for
transmission amplitude \( t \) and transmission coefficient \( T = |t|^2 \).

\[
t = \frac{2i \sin(k) \frac{\beta^2}{\alpha}}{[\epsilon_k - \epsilon_d] + 2 \cos(k) \frac{\beta^2}{\alpha} + 2i \sin(k) \frac{\beta^2}{\alpha}} \tag{2.1.0.8}
\]

\[
T = |t|^2 = \frac{(2 \sin(k) \frac{\beta^2}{\alpha})^2}{[(\epsilon_k - \epsilon_d) + 2 \cos(k) \frac{\beta^2}{\alpha}]^2 + (2 \sin(k) \frac{\beta^2}{\alpha})^2} \tag{2.1.0.9}
\]

Where we have introduced a shortcut \( 2 \sin(k) \frac{\beta^2}{\alpha} \equiv \Gamma \). The last formula (2.1.0.9) generally holds for elastic electron scattering.

So far, we have supposed that \( \epsilon_d > \epsilon_0 \), but if energy on impurity site drops below the lower limit \( \epsilon_0 - 2 \alpha \cos(k) \) as given by (2.1.0.5), the electron gets below the band of allowed energies and is trapped on the site. In such case, we may assume \( k = i \kappa \) to be complex number. This leads to solutions

\[
c_j = ae^{-\kappa}, j < 0 \tag{2.1.0.10}
\]

\[
c_j = be^{\kappa}, j > 0 \tag{2.1.0.11}
\]

Carrying out the same procedure as we did with \( k \) real, for chain without impurity, leads us to a relation

\[
\epsilon_\kappa = \epsilon_0 - \alpha(e^\kappa + e^{-\kappa}) \tag{2.1.0.12}
\]

\[
\epsilon_\kappa = \epsilon_0 - \alpha \cosh(k)
\]

This value is always less than the minimal band energy given by (2.1.0.5). Now, three equations analogous to (2.1.0.6) are satisfied for \( a = b \). Choosing \( \kappa \) to satisfy equation \( \frac{\beta^2}{\alpha}(e^\kappa - e^{-\kappa}) = -[(\epsilon_k - \epsilon_d) + 2 \cos(k) \frac{\beta^2}{\alpha}] \), equation (2.1.0.12) can be reformulated using hyperbolic trigonometric identity as

\[
\epsilon_\kappa = \epsilon_d - \sqrt{4(\frac{\beta^2}{\alpha})^2 + [(\epsilon_k - \epsilon_d) + 2 \cos(k) \frac{\beta^2}{\alpha}]^2}. \tag{2.1.0.13}
\]

As we can see, energy is below the energy band. Following (2.1.0.10), coordinate probability of position of the bond electron is not strictly at the site, but exponentially decays with distance from it.

To conclude this section, we will carry out a similar calculation from other perspective. According to a general theory, analytic continuation of scattering amplitude beyond a band, where amplitude grows beyond limits, gives the energy of
bound state. The waves of bound state are already present on the site, they are not incoming, therefore, the ratio of incident and scattered amplitude goes to infinity.

Using trigonometric identity, we can rewrite (2.1.0.5) to form

\[ 2\frac{\beta^2}{\alpha} \sin(k) = \sqrt{4\left(\frac{\beta^2}{\alpha}\right)^2 - (\epsilon_k - \epsilon_d)^2}. \tag{2.1.0.14} \]

Amplitude of scattering \( r \) is then

\[ r = \frac{-[(\epsilon_k - \epsilon_d) + 2 \cos(k)\frac{\beta^2}{\alpha}]}{[(\epsilon_k - \epsilon_d) + 2 \cos(k)\frac{\beta^2}{\alpha} + i\sqrt{4\left(\frac{\beta^2}{\alpha}\right)^2 - (\epsilon_k - \epsilon_d)^2}}. \tag{2.1.0.15} \]

If we continue this relation beyond energies of band, i.e. \( |\epsilon_k - \epsilon_0| > 2\frac{\beta^2}{\alpha} \), we can make formal modification of denominator and rewrite (2.1.0.15) as

\[ r = \frac{-[(\epsilon_k - \epsilon_d) + 2 \cos(k)\frac{\beta^2}{\alpha}]}{[(\epsilon_k - \epsilon_d) + 2 \cos(k)\frac{\beta^2}{\alpha} + \sqrt{(\epsilon_k - \epsilon_d)^2 - 4\left(\frac{\beta^2}{\alpha}\right)^2}}. \tag{2.1.0.16} \]

The expected pole of the function for \( r \) is given by condition of denominator approaching zero, which yields the yields

\[ \epsilon_k = \epsilon_d \pm \sqrt{4\left(\frac{\beta^2}{\alpha}\right)^2 + [(\epsilon_k - \epsilon_d) + 2 \cos(k)\frac{\beta^2}{\alpha}]^2}, \tag{2.1.0.17} \]

which is the same as equation (2.1.0.13).[2, p. 238-243]

All theory introduced in this section was presented mainly to show simple analytical results and outline the problem of our study in simple terms. Obtained analytical results will be useful in comparison with solutions of our model using method of many-body green functions, which will be introduced in next section.
2.2 Green functions

More precisely, we will be dealing with many-body Green functions, which are an analogy of Green functions used to solve inhomogeneous partial differential equations under initial or boundary conditions. In many body physics, these functions are rather understood as correlators of field operators. These functions are essential tool for many-body systems, which cannot be solved exactly and perturbation solution has to be involved. Under these conditions, system Hamiltonian is usually separable into two parts

\[ H = H_0 + H^i. \] (2.2.0.18)

Where \( H_0 \) is exactly solvable part and \( H^i \) are all the remaining parts of original \( H \), which represent interactions among particles; latter can be solved by the perturbation approach of Green function formalism.

To better understand the decomposition of a Hamiltonian, we start with three different representations used in quantum mechanics. They differ in time dependence of operators and states. The most important for our needs is the interaction representation, which very much coincides with procedure outline in this short foreword.

2.2.1 Schrödinger representation

The Schrödinger representation follows from the equation of the same name

\[ i \frac{\partial}{\partial t} \psi(t) = H \psi(t), \] (2.2.1.1)

with operator solution giving time evolution of the wavefunction under initial condition

\[ \psi(t) = e^{-iHt}\psi(0), \] (2.2.1.2)

which is valid under two conditions:

- wavefunction \( \psi(t) \) is time dependent,
- operators, such as \( H \), are time independent.

2.2.2 Heisenberg representation

With expression (2.3.1.2) at hand, we can assume time-independent Hamiltonian and write

\[ \langle \psi(t)|O|\psi(t)\rangle = \langle \psi(0)|e^{iHt}Oe^{-iHt}|\psi(0)\rangle. \] (2.2.2.1)
This means, that the same solution for quantum mechanical problem can be obtained using Heisenberg picture under conditions:

- wave functions are time independent,
- operators are evolving in time and such evolution is given by \( O(t) = e^{iHt}O(0)e^{-iHt} \).

The last expression is equivalent to solving an equation of motion

\[
i \frac{\partial O(t)}{\partial t} = [O(t), H],
\]

which will be a common case in our study.\[7, \text{p. 66}\]

It is instructive to understand the equivalence of these two approaches in an intuitive way, given in Sakurai’s textbook \[8, \text{p. 87-88}\]. First of all, we note, that the operator in (2.3.1.2) is unitary and therefore the beam (state) represented by the wavefunction is merely rotating in Hilbert space. Second, we realize the difference between state kets and base kets. The base kets are eigenfunctions of operators and therefore, as operators do not change with time under Schrödinger picture, their eigenkets (base kets) remain unchanged as well.

The situation is different in Heisenberg picture, because operator evolution is given by

\[
A^{(H)}(t) = U^\dagger A(0)U,
\]

which has to coincide with Schrödinger picture at the beginning

\[
U^\dagger A(0)UU^\dagger |a\rangle = aU^\dagger |a\rangle,
\]

where \( a \) is eigenvalue, that belongs to eigenstate \( |a\rangle \) of operator \( A \). So the eigenvalues of \( A^{(H)} \) are

\[
A^{(H)}(U^\dagger |a\rangle) = a(U^\dagger |a\rangle).
\]

This gives us time dependence of Heisenberg picture operator base kets

\[
|a, t\rangle_H = U^\dagger |a\rangle,
\]

which, because of presence of \( U^\dagger = e^{iHt} \), rotates the opposite direction than Schrödinger state kets. In result, for example, expansion coefficients of state kets into base kets are the same in both pictures. Chapter cited provides slightly more details on the matter.
2.2.3 Interaction representation

This representation will be discussed more in depth, because it plays major role in our approach. In this picture, original Hamiltonian splits as outlined in equation (2.2.0.18), where $H_0$ is exactly solvable and $H^I$ bears (all or some) interaction. Both operators and wave functions are time dependent in this picture in following manner

$$O(t) = e^{iH_0 t}O(0)e^{-iH_0 t} \quad (2.2.3.1)$$

$$\psi(t) = e^{iH_0 t}e^{-iH_0 t}\psi(0) \quad (2.2.3.2)$$

We further assume $[H_0, V] \neq 0, V = H - H_0$; the problem would be trivial otherwise. It is obvious, that operators evolve in time according to $H_0$. In case of wave functions:

$$\frac{\partial}{\partial t}\psi(t) = ie^{iH_0 t}(H_0 - H)e^{-iH_0 t}\psi(0)$$

$$= -ie^{iH_0 t}V e^{-iH_0 t}\psi(0)$$

$$= -ie^{iH_0 t}V e^{-iH_0 t}(e^{iH_0 t}e^{-iH_0 t}\psi(0))$$

$$\frac{\partial}{\partial t}\psi(t) = -iV(t)\psi(t). \quad (2.2.3.3)$$

Now, we proceed to the main point in developing this formalism, which will allow us to build perturbation theory in a future. We note, that unitary evolution operator $U$ can be defined as

$$U(t) = e^{iH_0 t}e^{-iH_0 t}.$$ 

If it is derived by time, it satisfies (2.2.3.3) with initial condition $U(0) = 1$. The differential equation can be integrated:

$$U(t) - U(0) = -i \int_0^t dt_1 V(t_1)U(t_1)$$

$$\vdots$$

$$U(t) = \sum_{n=0}^{\infty} (-i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n V(t_1)V(t_2)\ldots V(t_n), \quad (2.2.3.4)$$

leading to infinite perturbation series.

At this point, time ordering operator $T$ should be introduced. It rearranges operators to act consecutively in time, while the last goes left. This notable concept can be written with a dignity using step function

$$T[V(t_1)V(t_2)] = \Theta(t_1 - t_2)V(t_1)V(t_2) + \Theta(t_2 - t_1)V(t_2)V(t_1). \quad (2.2.3.5)$$
Introducing time ordering into the equation (2.2.3.4) and realizing the simplex behaviour of integration (generating factorial term), we get

\[ U(t) = 1 + \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \int_0^t dt_1 \int_0^t dt_2 \cdots \int_0^t dt_n T[V(t_1)V(t_2)\ldots V(t_n)] \] (2.2.3.6)

\[ U(t) = T \exp \left( -i \int_0^t dt' V(t') \right). \]

Where the last line should be regarded only as a shortcut, a symbol for the whole series defined by (2.2.3.6), which is usually called the Dyson series. The sum structure of \( U(t) \) operator is in accordance with the aim of this development, i.e. to construct suitable perturbation formalism.
2.2.4 Equilibrium Green functions

With the Dyson expansion prepared, we will follow with simpler case of equilibrium Green functions. Formalism developed for such objects is very similar to formalism of nonequilibrium Green functions, which will be treated later.

For needs of the following section, we define second quantization operators

\[ \psi(x) = \sum_k u_k(x)c_k \]  
\[ \psi^\dagger(x) = \sum_k u^*_k(x)c_k^\dagger \]

where \( c_k(c_k^\dagger) \) annihilates (creates) a particle with momentum \( k \). These operators satisfy commutation (anti-commutation) relations for bosons (fermions)

\[ [c_k, c_{k'}^\dagger]_\pm = \delta_{k,k'} \]

according to standard conventions. The following section is derived from [4, p. 38,39].

Single particle Green function in the sense of quantum field theory can be understood as a propagator, it is an object, that moves a particle from state in one point to state in another point \((x,t) \rightarrow (x',t')\), while interactions on the way can be treated perturbationally, often using technique of Feynman diagrams.

First, we define time-ordered zero-temperature single-particle Green function

\[ G(x,t;x',t') = -i\frac{\langle \Psi_0|T\{\psi_H(x,t)\psi^\dagger_H(x',t')\}|\Psi_0\rangle}{\langle \Psi_0|\Psi_0\rangle} \]

In the equation, \( \Psi_0 \) is a ground state of the system (time independent), we still assume \( \hbar = 1 \). There is a slight difference for the time ordering operator \( T \) applied on field operators, comparing to equation (2.2.3.5):

\[ T[A(t_1)B(t_2)] = \Theta(t_1 - t_2)A(t_1)B(t_2) \mp \Theta(t_2 - t_1)B(t_2)A(t_1) \]

where minus sign refers to fermion operators and plus sign to boson. This is not present in (2.2.3.5), because then we assumed only quadratic potential operators.

Since field operators are in Heisenberg picture, we may solve the equation of motion by direct differentiation

\[ i\frac{\partial G(x,t;x',t')}{\partial t} = \delta(t-t')\frac{\langle \Psi_0|[\psi_H(x,t),\psi^\dagger_H(x',t')]|\Psi_0\rangle}{\langle \Psi_0|\Psi_0\rangle} - i\frac{\langle \Psi_0|T\{i\frac{\partial \psi_H(x,t)}{\partial t}\psi^\dagger_H(x',t')\}|\Psi_0\rangle}{\langle \Psi_0|\Psi_0\rangle} \]

(2.2.4.6)
Calculating the field operator relation in the first term on the right side, we find, it is a spatial delta function. As for the second term, we can solve the equation of motion; to make things more simple at this point, we consider a free particle Hamiltonian

\[
[\psi_H(x, t), H] = -\frac{\nabla^2_x}{2m}\psi_H(x, t). \tag{2.2.4.7}
\]

Combining all partial results, the free particle Green function has the form

\[
\left(i\frac{\partial}{\partial t} + \frac{\nabla^2_x}{2m}\right)G_0(x, t; x', t') = \delta(t - t')\delta(x - x'). \tag{2.2.4.8}
\]

This result closely resembles the Green function as is understood in mathematical sense. If we wanted to describe an influence of finite temperature, we would generalize Green function in this way:

\[
G(x, t; x', t') = -i\text{Tr}\{\varrho_T[\psi_H(x, t)\psi_H(x', t')]}\], \tag{2.2.4.9}
\]

where \(\varrho\) is density matrix operator.

We can also introduce four related auxiliary Green functions, namely retarded, advanced, lesser and greater, respectively:

\[
G^r(x, t; x', t') = -i\theta(t - t')\langle\{\psi(x, t), \psi^\dagger(x', t')\}\rangle \tag{2.2.4.10}
\]
\[
G^a(x, t; x', t') = i\theta(t' - t)\langle\{\psi(x, t), \psi^\dagger(x', t')\}\rangle \tag{2.2.4.11}
\]
\[
G^<(x, t; x', t') = i\langle\psi^\dagger(x', t')\psi(x, t)\rangle \tag{2.2.4.12}
\]
\[
G^>(x, t; x', t') = -i\langle\psi(x, t)\psi^\dagger(x', t')\rangle. \tag{2.2.4.13}
\]

We will provide at least brief interpretation of these functions at this place. A retarded Green function is used to calculate responses at time \(t\) to perturbation in earlier time \(t'\), situation for advanced Green function is analogous. Lesser Green function is called particle propagator, while greater Green function hole propagator, unlike retarded and advanced, these Green functions do not have singular inhomogeneous term. In equilibrium theory, all these functions are interconnected by fluctuation-dissipation theorem. Another important object, spectral function \(A(k, \omega)\) is related to these functions through following definition

\[
A(k, \omega) = i[G^r(k, \omega) - G^a(k, \omega)] = i[G^>(k, \omega) - G^<(k, \omega)], \tag{2.2.4.14}
\]

while it possesses following important properties

\[
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} A(\omega) = 1 \tag{2.2.4.15}
\]
\[
\int \frac{d^3k}{(2\pi)^3} A(k, \omega) = \varrho(\omega) \tag{2.2.4.16}
\]
To gain a little insight, spectral function can describe local spectrum of single-particle excitations. The calculation of such an object is not easy, but generally, the function in case of non-interacting particles has a form

\[ A(\omega) = 2\pi \delta(\omega - H). \]

The problem is, that delta function is not suitable operator for perturbations. In case of (2.2.0.18), the decomposition of \( \delta \) is unclear with regard to \( V \). Here, the following useful identity can be used

\[ 2\pi \delta(\omega - H) = i \left( \frac{1}{\omega - H + i0} - \frac{1}{\omega - H - i0} \right). \]  (2.2.4.17)

If we analyze the equality (derived from Sokhotski formula), we can see the first fraction is retarded Green function in frequency domain. To prove, a Fourier transformation back to time domain yields

\[ \int \frac{d\omega}{2\pi} e^{-i\omega \tau} \frac{1}{\omega - H + i0} = -i \Theta(\tau) e^{-iH \tau}, \]  (2.2.4.18)

where the right-hand side holds for non-interacting particles and time-independent Hamiltonian. This provides the idea of origin of equation (2.2.4.14)[6, p. 42].

The Green function

\[ G^R(\omega) = \frac{1}{\omega - H_0 - V + i0} \]

can be readily decomposed in the same fashion as geometrical series, just considering unperturbed Green function \( G^R_0(\omega) = (\omega - H_0 + i0)^{-1} \), we obtain

\[ G^R = G^R_0 + G^R_0 V G^R_0 + G^R_0 V G^R_0 V G^R_0 + \ldots. \]  (2.2.4.19)

This was a general introduction to equilibrium Green functions. In the next section, we will build a formalism for their perturbation, based on Dyson series introduced in section 2.2.3.

### 2.2.5 Perturbation Expansion of a Green function

We will continue from the end of section 2.2.3. We have defined the operator \( U(t) \) which allows us to evolve field operator from initial time to any future time. This object can be generalized to S-matrix, which provides evolution from any time \( t_1 \) to time \( t_2 \) simply as

\[ \psi(t_2) = U(t_2)U^\dagger(t_1)\psi(t_1) = S(t_2,t_1)\psi(t_1). \]  (2.2.5.1)
Taking derivative of the definition in respect to $t_1$ and solving in the same manner as (2.2.3.6), we can write

$$S(t_1, t_2) = Te^{-i\int_{t_1}^{t_2} dt' V(t')}.$$  

(2.2.5.2)

This operator will help us solve a problem in definition (2.2.4.4), an unknown ground state $|\Psi_0\rangle$, the property we want to obtain from the Green function.

First we assume

$$|\Psi_0\rangle = S(0, \infty)|\Phi_0\rangle,$$

where $|\Phi_0\rangle$ is non-interacting ground state. This is given by Gell-Mann and Low theorem [4, p. 44,45]. Equation (2.2.4.4) can be rewritten as

$$G(x, t; x', t') = -i \frac{\langle \Phi_0 | T \{S(\infty, -\infty) \psi_H(x, t) \psi_H^\dagger(x', t')\} | \Phi_0 \rangle}{\langle \Phi_0 | S(\infty, -\infty) | \Phi_0 \rangle}. \tag{2.2.5.3}$$

Where the phase-factor changes introduced by application of S-matrices cancel out. Expansion of S-matrix using (2.2.5.2) gives us $V(t_n)$ dependencies

$$S(\infty, -\infty) = \sum_{n=0}^{\infty} \frac{(-i)^{n+1} n!}{n!} \int_{-\infty}^\infty dt_1 dt_2 \ldots dt_n T[V(t_1)V(t_2)\ldots V(t_n)]. \tag{2.2.5.4}$$

With this perturbation, whole Green function can be rewritten into series

$$G(x, t; x', t') = -i \sum_{n=0}^{\infty} (-i)^n \int_{-\infty}^\infty dt_1 dt_2 \ldots dt_n \times \langle \Phi_0 | T \psi(x, t) \psi^\dagger(x', t') V(t_1)V(t_2)\ldots V(t_n) | \Phi_0 \rangle. \tag{2.2.5.5}$$

This summation goes over Feynmann diagrams which are topologically different and connected, non-connected diagrams cancel out with the denominator [4, p. 45]. At this point, we have reached desired perturbation equation to carry out approximative calculations of an equilibrium Green function. Next step would be to introduce nonequilibrium Green functions.

### 2.2.6 Nonequilibrium Green functions

Also called Contour ordered Green functions. As we could see in last section, the main ingredient for perturbations was S-matrix $S(\infty, -\infty)$, delivering the system from and forth asymptotic initial state – this is not possible in terms of nonequilibrium, because system just can’t reach the initial state again. However, formalism
of both approaches is very similar and this section will merely generalize previous result. Let’s start with slightly altered Hamiltonian

\[ H = H_0 + H^i + H'(t). \] (2.2.6.1)

As can be seen, time dependent term has been added. Nonequilibrium aspect can be perpetrated by outer electric field, light excitation etc. and is supposed to vanish for times \( t < t_0 \), which can be set as \( t_0 \to \infty \). Before the perturbation is turned on, we can describe system in thermal equilibrium by standard expression

\[ \varrho = \frac{e^{-\beta h}}{Tr[e^{-\beta h}]} , \] (2.2.6.2)

where \( h = H_0 + H^i \) is time-independent part of Hamiltonian. Our aim is to find the future value of any operator in Heisenberg picture (dependent on full Hamiltonian \( H \)), i.e. its time evolution

\[ \langle O(t) \rangle = Tr[\varrho(h)O_H(t)]. \] (2.2.6.3)

Note, that \( \varrho(h) \) is not dependent on \( H'(t) \), it is time-independent.

Our aim in treatment of nonequilibrium Green functions is to transform full Hamiltonian dependent operator \( O_H(t) \) to simple (quadratic) Hamiltonian solvable by Wick theorem \( O_{H_0} \); we need to transform away external rapid time dependence in \( H'(t) \) and complicated inter-particle interactions in \( H^i \). The first transformation

\[ O_H(t) = v_h^\dagger(t,t_0)O_h(t)v_h(t,t_0) \] (2.2.6.4)

gets rid of explicit time dependence, \( O_H \to O_h \). Evolution operator \( v_h(t,t_0) \) is governed by Hamiltonian \( H'_h \), which is an interaction representation of \( H'(t) \), i.e. an explicit time evolution in frame of \( h \) time evolution. Exactly speaking:

\[ v_h(t,t_0) = T \left( \exp \left[ -i \int_{t_0}^{t} dt' H'_{h}(t') \right] \right) \] (2.2.6.5)

\[ H'_h(t) = e^{ith(t-t_0)}H'(t)e^{-ith(t-t_0)}. \] (2.2.6.6)

At this point, we will make a little detour, rhetorically and literally alike. We will analytically continue the real time parameter into complex plane. In next few paragraphs, we will interrupt the explanation of transformations and introduce the concept, alternatively define the Green function and auxiliary functions.
So, in contour formalism, we may obtain the same result as in equation (2.2.6.4), if we use a contour ordered integral representing the Dyson expansion, and integrate over the enclosed contour

\[ O_H(t) = T_{C_t} \left( \exp \left[ -i \oint_{C_t} d\tau' H'_H(\tau') \right] O_h(t) \right), \tag{2.2.6.7} \]

where the contour is analytical continuation into complex plane running from \( t_0 \) to \( t \) and back again, while contour ordering operator \( T_{C_t} \) assures, that operators with later contour-integration parameter (i.e. analytically continued time) appear left in expansion.

With this in mind, we may define contour-ordered Green function

\[ G(1, 1') = -i \langle T_{C} [\psi_H(1) \psi_H^+(1')] \rangle. \tag{2.2.6.8} \]

The contour again starts and ends at \( t_0 \), but passes points \( 1 \equiv (x_1, t_1) \) and \( 1' \). The meaning of contour ordered function is equivalent to causal (time-ordered) Green function in equilibrium theory.

Since the concept of contour is novel to equilibrium theory of Green functions, it is advisable to introduce new treatment by following auxiliary Green functions, which depend on the branch of contour:

\[
G(1, 1') = \begin{cases} 
G_c(1, 1') & t_1, t_1' \in C_1 \\
G_{ac}(1, 1') & t_1, t_1' \in C_2 \\
G^>(1, 1') & t_1 \in C_2, t_1' \in C_1 \\
G^<(1, 1') & t_1 \in C_1, t_1' \in C_2 
\end{cases}
\tag{2.2.6.9} \]

\( C_1 \) is the first half of \( C \) and \( C_2 \) is a return path.

We may modify also retarded and advanced functions. All retarded, advanced, lesser and greater functions are strictly analogous in structure to equilibrium functions (2.2.4.10) and can be easily reconstructed. Time-ordered and antitime-ordered functions have the following structure:

\[
G_c(1, 1') = -i \langle T [\psi_H(1) \psi_H^+(1')] \rangle \\
= -i \Theta(t_1 - t_1') \langle \psi_H(1) \psi_H^+(1') \rangle + i \Theta(t_1' - t_1) \langle \psi_H^+(1') \psi_H(1) \rangle \tag{2.2.6.10} \\
G_{ac}(1, 1') = -i \langle \tilde{T} [\psi_H(1) \psi_H^+(1')] \rangle \\
= i \Theta(t_1 - t_1') \langle \psi_H^+(1') \psi_H(1) \rangle - i \Theta(t_1' - t_1) \langle \psi_H(1) \psi_H^+(1') \rangle. \tag{2.2.6.11} 
\]
Also, useful relations introduced for equilibrium functions still hold

\[ G_e + G_{ac} = G^< + G^> \]  \hspace{1cm} (2.2.6.12)
\[ G^r - G^a = G^> - G^<. \]  \hspace{1cm} (2.2.6.13)

We can now proceed to transform Green function into form, which can be tackled by contractions of Wick theorem. First, transformation \( H \rightarrow h \) gives us

\[ G(1, 1') = -i \langle T_C S_C^H \psi_h(1) \psi_h^\dagger(1') \rangle, \]  \hspace{1cm} (2.2.6.14)

using

\[ S_C^H = \exp \left[ \int_C d\tau H^i_h(\tau) \right]. \]  \hspace{1cm} (2.2.6.15)

Second step would be a transformation \( h \rightarrow H_0 \). We should note, that \( h \) is contained in all operators involved. Doing the necessary transformation gives

\[ G(1, 1') = -i \frac{\text{Tr} \{ \Theta_0 T_C S_C^i S_C' \psi_{H_0}(1) \psi_{H_0}^\dagger(1') \}}{\text{Tr} \{ \Theta_0 T_C S_C^i S_C' \}}, \]  \hspace{1cm} (2.2.6.16)

where

\[ \Theta_0 = \frac{e^{-\beta H_0}}{\text{Tr} \{ e^{-\beta H_0} \}} \]  \hspace{1cm} (2.2.6.17)
\[ S_C^i_v = \exp \left[ -i \int_{C_v} d\tau H^i_{H_0}(\tau) \right] \]  \hspace{1cm} (2.2.6.18)
\[ S_C' = \exp \left[ -i \int_C d\tau H_{H_0}'(\tau) \right], \]  \hspace{1cm} (2.2.6.19)

and contour \( C_v \) is the same as \( C \), yet after it returns to initial time \( t_0 \), integration proceeds to point in complex plane \((t_0, -\beta)\) to take into account turning on of interaction and subsequent change of thermal equilibrium. We can see, that the structure is very similar to that of equilibrium theory (2.2.5.3) and is wholly dependent on \( H_0 \), so as such is solvable by Wick theorem.

### 2.2.7 Dyson equation and Langreth theorem

In order to practically use (2.2.6.14), it is necessary to analytically continue function from complex contour back to real time axis. This can be done using Langreth theorem and its rules, which will be presented shortly.
But let us start with the Dyson equation, which reads

\[ G = G_0 + G_0 \Sigma G. \]  

(2.2.7.1)

Because the nonequilibrium expansion is formally the same as equilibrium, the Dyson equation can be rewritten as

\[ G(1, 1') = G_0(1, 1') + \int d^3x_2 \int_{C_v} d\tau_2 G_0(1, 2) U(2) G(2, 1') + \int d^3x_2 \int d^3x_3 \int_{C_v} d\tau_2 \int d\tau_3 G_0(1, 2) \Sigma(2, 3) G(3, 1'). \]  

(2.2.7.2)

Interactions are contained in \( \Sigma \), self-energy functional, which contains higher order Green functions arising from equation of motion technique, which is also used in our model. Short note about self-energy will be given at the end of this chapter.

The equation can be further simplified, if we consider approximation \( t_0 \to -\infty \) and adiabatical turning on of interaction. That makes contour \( C_v \to C \), discarding the information about transition from initial state to steady state.

The Dyson equation contains nontrivial multiplicative structure element of form

\[ C(t_1, t_1') = \int_C d\tau A(t_1, \tau) B(\tau, t_1'). \]  

(2.2.7.3)

To treat this obstacle, we may, for lesser function \( C^<(t_1, t_1') \), deform the integration contour into two in a manner, that first part \( C_1 \) contains only time \( t_1 \) (therefore, \( \tau < t_1', \forall \tau \in C_1 \)) and second part \( C_{1'} \) only \( t_1' \) (\( t_1 < \tau, \forall \tau \in C_{1'} \)). Under this circumstances, multiplicative term (2.2.7.3) can be rewritten as

\[ C^<(t_1, t_1') = \int_{C_1} d\tau A(t_1, \tau) B^<(\tau, t_1') + \int_{C_{1'}} d\tau A^<(t_1, \tau) B(\tau, t_1'). \]  

(2.2.7.4)

Then, if we split first integral in two

\[ \int_{C_1} d\tau A(t_1, \tau) B^<(\tau, t_1') = \int_{-\infty}^{t_1} dt A^>(t_1, t) B^<(t, t_1') + \int_{t_1}^{\infty} dt A^<(t_1, t) B^<(t, t_1') \]

\[ = \int_{-\infty}^{\infty} dt A^r(t_1, t) B^<(t, t_1'), \]  

(2.2.7.5)

exploiting retarded function definition. Carrying out the same procedure with second contour, we have final result

\[ C^<(t_1, t_1') = \int_{-\infty}^{\infty} dt [A^r(t_1, t) B^<(t, t_1') + A^<(t_1, t) B^a(t, t_1')]. \]  

(2.2.7.6)
Although the results might seem puzzling, the procedure as was presented is really simple and mechanical and can be easily modified for any kind and number of Green functions. Summary table of products can be found for example in Jauho’s textbook [4, p. 68].

2.2.8 Self-energy

Self-energy is an important concept in condensed-matter physics, which effectively represents a mean interaction with other particles in a matter. Explicit equation for self-energy can be obtained by multiplying equation (2.2.7.1) by $G^{-1}_0$ from the left and by $G^{-1}$ from the right. Procedure gives explicit equation for self-energy

$$\Sigma = G^{-1}_0 - G^{-1}. \quad (2.2.8.1)$$

The purpose of self-energy is to limit infinite perturbation expansion, however, given equation (2.2.8.1) shows, that self-energy itself contains an infinite expansion. Therefore, using this approach is choosing between Scylla and Charybdis; on the one side, we need to cut off Dyson infinite expansion, on the other side, there is no general approach how to choose important and highly contributing diagrams for self-energy. Generally speaking, the self-energy approach is sufficient only for weak coupling cases, where a good approximation can be obtained in few terms [7, p. 89]. We will return to the problem of determining significant terms during explanation of our specific model.

Before we proceed further, it would be instructive to study an example of resonant level model, which can be found in better detail in [4, p. 47, 48]. The model Hamiltonian has the form

$$H = \sum_p \epsilon_p a_p \dagger a_p + \epsilon_0 b \dagger b + \sum_p V_p(a_p \dagger b + b \dagger a_p) \quad (2.2.8.2)$$

and describes the continuum of states given by operators $a$ and discrete state given by $b$ operator, which is very similar to model we used, the electrons from the leads interacting with states of potential well. Following the equation of motion technique, we get the equations for retarded Green function

$$G^r(p, p', t) = -i \langle \{ a_p(t), a_{p'} \dagger (0) \} \rangle$$

$$[a_p, H] = \epsilon_p a_p + V_p b$$

$$i \frac{\partial}{\partial t} G^r(p, p', t) = \delta(t) \delta_{p, p'} - \epsilon_p G^r(p, p', t) + V_p \Gamma(p', t), \quad (2.2.8.3)$$

27
where $\Gamma(p', t) = -i\Theta(t)\langle b(t), a_{p'}^\dagger(0) \rangle$ is a new Green function with equation of motion,
\[
i \frac{\partial}{\partial t} \Gamma(p', t) = \epsilon_0 \Gamma(p', t) + \sum_{p''} V_{p'} G^r(p'', p', t),
\]
(2.2.8.4)

following from standard commutation relations. Introducing free Green function $g_0(t)$ for operator acting upon $\Gamma$, the equation (2.2.8.4) can be written in form of convolution. After that, doing a fourier transform into energy domain, we arrive to system of equations for two Green functions
\[
G^r_0(p, E) = \left[ E - \epsilon_p + i\delta \right]^{-1}
\]
\[
g^r_0(E) = \left[ E - \epsilon_0 + i\delta \right]^{-1}
\]
\[
G^r(p, p', E) = \delta_{p,p'} G^r_0(p, E) + G^r_0(p, E) V_p \Gamma(p', E)
\]
\[
\Gamma(p', E) = g^r_0(E) \sum_{p''} V_{p'} G^r(p'', p', E).
\]
(2.2.8.5)

$\Gamma(p', E)$ can be extracted from the equations yielding the final result
\[
G^r(p, p', E) = G^r_0(p, E) \delta_{p,p'} + G^r_0(p, E) \left[ \frac{V_p V_{p'}}{g^r_0(E)} \right]^{-1} - \sum_p V^2_p G^r_0(p, E) G^r_0(p', E).
\]
(2.2.8.6)

Let us draw our attention to the second term on the right side. The structure highly resembles the Dyson equation (2.2.7.1) in form of infinite series. Considering this, we may conclude, that result obtained is an approximation of self-energy, but the object truly is retarded T-matrix
\[
T_{p,p'} = \frac{V_p V_{p'}}{E - \epsilon_0 - \sum_{p'} \frac{V^2_{p'}}{E - \epsilon_{p'} + i\delta}}.
\]

To treat the matter little more systematically, first we consider fermion Green function $G_0$ and boson Green function $D_0$ in energy representation
\[
G_0(p, E) = \frac{1}{E - \epsilon_p + i\delta}
\]
(2.2.8.7)
\[
D_0(q, \omega) = \frac{2\omega_q}{\omega^2 - \omega^2_q + i\delta}.
\]
(2.2.8.8)

Now, we write electron-phonon interaction to the second order, considering just unperturbed fermion Green function and self-energy term, we can transform whole
S-matrix from time to energy domain term by term

\[ G(p, E) = G_0(p, E) + (-i)^2 \sum_q |M_q|^2 \int_{-\infty}^{\infty} dt e^{iE(t-t')} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \]

\[ \times G_0(p-t_1)G_0(p-q, t_1-t_2)G_0(p, t_2-t')D_0(q, t_1-t_2) \]  

(2.2.8.9)

\[ G(p, E) = G_0(p, E) + [G_0(p, E)]^2 \Sigma_1(p, E) + \ldots, \]  

(2.2.8.10)

where the one-phonon process electron self-energy gains form

\[ \Sigma_1(p, E) = i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_q |M_q|^2 D_0(q, \omega) G_0(p-q, E-\omega). \]  

(2.2.8.11)

If we continue with expansion to higher orders, bigger amount of contributing diagrams would generally provide a higher order self-energy. By summing the infinite series of all contributions, we can get another forms of Dyson equation, for electron in a band (2.2.8.12) and electron in Fermi sea at zero temperature (2.2.8.13)

\[ G(p, E) = \frac{G_0(p, E)}{1 - G_0(p, E)\Sigma(p, E)} \]  

(2.2.8.12)

\[ G(p, E) = \frac{1}{E - \epsilon_p + i\delta - \Sigma(p, E)} \]  

(2.2.8.13)

The infinitesimal part \(i\delta_p\) switches sign for conditions \(\epsilon_p > \mu\) or \(\epsilon_p < \mu\), where \(\mu\) is chemical potential. Considering imaginary part of noninteracting (without self-energy term) Green function \(\Im G_0(p, E)\), we find out it is non-vanishing under condition \(E = \epsilon_p\), therefore, \(\Im G_0(p, E)\) changes sign depending on \(E > \mu, E < \mu\).

For interacting case, imaginary part of self-energy \(i\Sigma_i\) also switches sign for breakpoint \(E = \mu\).

\[ \Sigma_i(p, E) < 0, \quad E > \mu \]
\[ \Sigma_i(p, E) > 0, \quad E < \mu. \]

This switching of sign of \(\delta_p\) is caused by distinction between electron \((\zeta_p > 0)\) and hole \((\zeta_p < 0)\) excitations, which is maintained even if interaction represented by self-energy takes place. For one-electron Green function, \(\Sigma_i < 0\), therefore, the imaginary part of denominator always has the same sign.
The phonon Green function, later using equation (2.2.8.8), is

\[
D(q, \omega) = \frac{D^{(0)}(q, E)}{1 - D^{(0)}(q, \omega) \pi(q, \omega)} \quad (2.2.8.14)
\]

\[
D(q, \omega) = \frac{2\omega q}{\omega^2 - \omega_q^2 + i\delta - 2\omega_q \pi(q, \omega)}, \quad (2.2.8.15)
\]

where \(\pi(q, \omega)\) is phonon self-energy, also called polarization operator, because self-energy effects are connected with polarization phonon causes in a medium.

The interpretation of self-energies is following. The imaginary part is causing damping of the particle motion, it is related to mean free path of an excitation. The real part is an energy shift of excitation and it may alter excitation’s mass or group velocity [7, p. 86-89].
2.3 Transport

This is the key part of whole theoretical development undergone in past sections, basis for the work. According to our future needs, only specific parts of transport and structures will be described in this place. In chapter dedicated to used model, more in-depth approach will be employed. Now, there is several aspects of transport to take care of, before we start with this section.

First of all, we will not consider magnetic field nor spin of electrons for this part. A nontrivial transport problem consists of heterostructure, i.e. leads and a junction, impurity or layer. Layer transport may be perpendicular, consisting of layers of semiconductors with different bands, where electron can be, under certain bias voltage, bound in quasibound state, thus enhancing otherwise suppressed current. Other case, the parallel transport, using a gate with adjustable potential to change the charge density in coulomb island in between the quantum point contacts disclosing the quantization of conductance.

As regarding the time, transport can be stationary or time-dependent. Main issue in this class of problems are interactions, which can be successfully tackled by nonequilibrium Green function technique. Subject has been studied extensively before, leading to Landauer formula, which relates conductance (and therefore current) to transmission coefficient of quantum mechanics (that is the reason why section 2.1 has been developed).

2.3.1 Hamiltonian

Because we cannot assume, that system will return to its initial state, nonequilibrium approach has to be used. System has evolved from remote past (when an initial state was prepared) to the point of interest and then back. Before we tackle the problem, we expect, that leads and a junction are decoupled in the beginning and in their own thermal equilibria. System is then coupled and perturbations are being calculated.

As mentioned before, it is advisable to separate system into leads (usually ideal, coupled to thermal bath) and the junction. This allows to write Hamiltonian in the form

\[ H = H_c + H_T + H_{cen} \] (2.3.1.1)

where \( H_c \) is Hamiltonian of leads (or contacts), \( H_{cen} \) is the junction (or central region) and \( H_T \) is tunneling Hamiltonian. Recalling diagonalization carried out in section one of this chapter, we can assume leads to be a tight binding model and
state Hamiltonian in terms of eigenvalues we obtained ibidem

\[ H_c = \sum_{k,\alpha \in L,R} \epsilon_{k\alpha} c_{k\alpha}^\dagger c_{k\alpha}. \]  

(2.3.1.2)

The Green functions for leads in decoupled state are

\[ g^{<}_{k\alpha}(t - t') = i \langle c_{k\alpha}^\dagger(t')c_{k\alpha}(t) \rangle \]
\[ = if(\epsilon_{k\alpha}) \exp[-i\epsilon_{k\alpha}(t - t')] \]  

(2.3.1.3)

\[ g^{\alpha,a}_{k\alpha}(t - t') = \mp i \Theta(\pm t \mp t') \langle \{ c_{k\alpha}(t), c_{k\alpha}^\dagger(t') \} \rangle \]
\[ = \mp i \Theta(\pm t \mp t') \exp[-i\epsilon_{k\alpha}(t - t')]. \]  

(2.3.1.4)

where \( f(\epsilon_{k\alpha}) = [1 + \exp\left(\frac{\epsilon_{k\alpha} - \mu_\alpha}{k_B T}\right)]^{-1} \) is an equilibrium Fermi-Dirac distribution.

An important aspect is, that coupling constant between the leads and an interacting region should depend on charge density determined self-consistently. If this is ignored (as in our model), we have

\[ H_T = \sum_{n,k,\alpha \in L,R} [V_{k\alpha,n} c_{k\alpha}^\dagger d_n + h.c.], \]  

(2.3.1.5)

where \( \{d_n^\dagger\} \) and \( \{d_n\} \) are single electron creation and annihilation operators for states \( |n\rangle \) forming junction complete orthonormal basis set. In our model, only one electronic state is considered.

Central region Hamiltonian depends on physical properties and chosen model. For now, we will limit our study to simple Hamiltonian of non-interacting levels and little more complex Hamiltonian with electron-phonon interaction

\[ H_{cen} = \sum_m \epsilon_m d_m^\dagger d_m \]  

(2.3.1.6)

\[ H^{el-ph}_{cen} = \epsilon_0 d^\dagger d + d^\dagger d \sum_q M_q[a_q^\dagger + a_{-q}] + \sum_q \hbar \omega_q a_q^\dagger a_q. \]  

(2.3.1.7)

In the equation (2.3.1.7), the first term represents bare electron energy, the second term describes the interaction, and the last term expresses pure phonon energy. We will omit electron-electron interactions for this part, as we will deal with single electron level in our model.

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2.3.2 Current

In this section, we will develop formula for current. First, current from left lead to central region will be taken into account, reduced Planck constant is, as before, taken $\hbar = 1$.

\[ J_L = -e\langle \dot{N}_L \rangle = -ie\langle [H, N_L] \rangle. \]  

(2.3.2.1)

The particle number operator $N_L = \sum_{k,\alpha \in L} c_{\alpha}^\dagger c_{\alpha}$. Since quadratic parts of Hamiltonian commute with $N_L$, we obtain

\[ J_L = ie \sum_{n, k, \alpha \in L} [V_{\alpha,n} \langle c_{\alpha}^\dagger d_n \rangle - V_{\alpha,n}^* \langle d_n c_{\alpha} \rangle]. \]  

(2.3.2.2)

From this expression, we can extract Green functions in obvious form

\[ G_{n,\alpha}^{<}(t - t') \equiv i\langle c_{\alpha}^\dagger(t') d_n(t) \rangle \]  

(2.3.2.3)

\[ G_{\alpha,n}^{<}(t - t') \equiv i\langle d_n(t') c_{\alpha}(t) \rangle \]  

(2.3.2.4)

The first function represents a transmission of an electron from molecule to the lead, the second one inverse process. Time diagonal of these functions gives the value of current. Further, these functions satisfy $G_{\alpha,n}^{<} = -[G_{n,\alpha}^{<}(t, t)]^*$ which leads to a simplified result

\[ J_L = 2e\Re\{ \sum_{n, k, \alpha \in L} V_{\alpha,n} G_{n,\alpha}^{<}(t, t) \}. \]  

(2.3.2.5)

As expression for $G_{n,\alpha}^{<}(t - t')$ is necessary, we may start our derivation with contour-ordered function for noninteracting case $G_{n,\alpha}(\tau, \tau')$, which can be obtained through equation of motion technique for time ordered Green function. So, using the equation, we come to

\[ -i \frac{\partial}{\partial t'} G_{n,\alpha}^t(t - t') = \epsilon_k G_{n,\alpha}^t(t - t') + \sum_m G_{nm}^t(t - t') V_{\alpha,m}^*, \]  

(2.3.2.6)

where $G_{mn}^t(t - t') = -i\langle T\{ d_{m}(t')d_n(t) \} \rangle$ is Green function for the junction. Should leads interaction be on, this procedure would generate higher order Green function involving lead operators and equations would not form a closed set.

We may introduce $[g_{\alpha}^t]^{-1} = (i \frac{\partial}{\partial t} + \epsilon_k)$ and multiply by $g_{\alpha}^t$ from the right; we get the contour-ordered Green function (because it has the same formal structure as time ordered Green functions, we just substitute $(t - t_1) \rightarrow (\tau, \tau_1)$)

\[ G_{n,\alpha}(\tau, \tau') = \sum_m \int_C d\tau_1 G_{nm}(\tau, \tau_1) V_{\alpha,m}^* g_{\alpha}(\tau_1, \tau). \]  

(2.3.2.7)
Using the analytical continuation rules from section 2.2.7 yields
\[ G_{n,k\alpha}^<(t-t') = \sum_m \int dt_1 V_{k\alpha,m}^*[G_{nm}^r(t-t_1)g_{k\alpha}^<(t_1-t') + G_{nm}^<(t-t_1)g_{k\alpha}^a(t_1-t')]. \]  
(2.3.2.8)

Green functions of uncoupled leads (2.3.1.3) were used. Doing Fourier transform, we obtain
\[ G_{n,k\alpha}^<(\epsilon) = \sum_m V_{k\alpha,m}^*[G_{nm}^r(\epsilon)g_{k\alpha}^<(\epsilon) + G_{nm}^<(\epsilon)g_{k\alpha}^a(\epsilon)]. \]  
(2.3.2.9)

getting current
\[ J_L = 2e \int \frac{d\epsilon}{2\pi} \Re\left\{ \sum_{n,m,k,\alpha} V_{k\alpha,n} V_{k\alpha,m}^*[G_{nm}^r(\epsilon)g_{k\alpha}^<(\epsilon) + G_{nm}^<(\epsilon)g_{k\alpha}^a(\epsilon)] \right\}. \]  
(2.3.2.10)

Desired formula can be further polished and under certain conditions rewritten into already mentioned Landauer equation.

First, we change summation over momentum to integration over energies, density of states \( \varrho_\alpha(\epsilon) \) and tunneling parameters \( V_{k\alpha,n}^*, V_{k\alpha,n} \) will form a function called level-width
\[ [\Gamma_L(\epsilon_k)]_{mn} = 2\pi \sum_{\alpha \in L} \varrho_\alpha(\epsilon_k)V_{\alpha,n}(\epsilon_k)V_{\alpha,m}^*(\epsilon_k). \]  
(2.3.2.11)

Second, we use definitions of decoupled leads Green functions (2.3.1.3) in energy domain and integrate over \( \epsilon_k \), while we keep in mind, that we take only real part of terms in parenthesis and realize \( G^< \in \mathbb{I} \) due to (2.3.2.3)
\[ \int \frac{d\epsilon_k}{2\pi} \Gamma_L(\epsilon_k)\Re[G_{nm}^r(\epsilon)2\pi i\delta(\epsilon - \epsilon_k)f_L(\epsilon_k) - G_{nm}^<(\epsilon)(\frac{1}{\epsilon - \epsilon_k} + i\pi\delta(\epsilon - \epsilon_k))]
\]
\[ = \Gamma_L(\epsilon_k)\Re[iG_{nm}^r(\epsilon) + \frac{iG_{nm}^<\epsilon}{2}] + \{\text{terms } \in \mathbb{I}\}
\]
\[ = \frac{i}{2} \Gamma_L^L(\epsilon)[(G_{nm}^r - G_{nm}^a)f_L(\epsilon) + G_{nm}^<\epsilon] \]  
(2.3.2.12)

The same procedure applies to current from the right lead \( J_R \). In a steady state, we can assume \( J = J_L = -J_R = \frac{J_L-J_R}{2} \) and directly obtain current formula
\[ J_{L(R)} = ie \int \frac{d\epsilon}{2\pi} \text{Tr} \left\{ \Gamma_L(\epsilon)[G_{nm}^r(\epsilon) + f_L(\epsilon)[G_{nm}^r(\epsilon) - G_{nm}^a(\epsilon)]\right\}
\]
\[ J = \frac{ie}{2} \int \frac{d\epsilon}{2\pi} \text{Tr}[(\Gamma_L(\epsilon) - \Gamma_R(\epsilon))G_{nm}^<(\epsilon) + [f_L(\epsilon)\Gamma_L^L(\epsilon) - f_R(\epsilon)\Gamma_R^L(\epsilon)][G_{nm}^r(\epsilon) - G_{nm}^a(\epsilon)]]. \]  
(2.3.2.13)
Typically, geometrical setting of a situation is not symmetrical, in that case (among other possibilities), coupling of junction to each lead is not the same, often one level-width is dominant over another and we can write

$$\Gamma_{mn}(\epsilon) = \lambda \Gamma_{mn}^R(\epsilon).$$

(2.3.2.14)

And because we can rewrite (2.3.2.13) in form $J \equiv xJ_L - (1-x)J_R$ and set $x = \frac{1}{1+\lambda}$, we finally obtain

$$J = ie \int \frac{d\epsilon}{2\pi} Tr \left( \Gamma_{mn}^R(\epsilon) \left\{ [\lambda x - (1 - x)] G_{nm}^{<}(\epsilon) \right. \\
+ [\lambda x f_L - (1 - x) f_R] (\epsilon) [G_{nm}^r(\epsilon) - G_{nm}^a(\epsilon)] \right\} \right)$$

(2.3.2.15)

$$J = ie \int \frac{d\epsilon}{2\pi} [f_L(\epsilon) - f_R(\epsilon)] T(\epsilon)$$

(2.3.2.16)

where $T(\epsilon)$ is, under certain conditions, $T(\epsilon)$ from Landauer formula. This analogy can, however, serve as a starting point for deriving more general formula.

$$T(\epsilon) = Tr \left\{ \frac{\Gamma_{mn}^L(\epsilon) \Gamma_{mn}^R(\epsilon)}{\Gamma_{mn}^L(\epsilon) + \Gamma_{mn}^R(\epsilon)} [G_{nm}^r(\epsilon) - G_{nm}^a(\epsilon)] \right\}.$$ 

(2.3.2.17)

This equation sums up the general theory for our future study. More detailed information about featured topics can be found in literature cited through the text.
Chapter 3

PROBLEM FORMULATION

In this section, the theory shall be narrowed to the point of our study. Specific equations will be derived and methods of solution described. We will introduce several subsections with supplementary explanation, which are not essential for development, but instructive.

The main subject of this thesis is a molecular junction connected with two ideal leads, which are in equilibrium with thermal bath. We have considered Green function of whole system and applied Dyson equation with self-energy term treating interaction with contacts. The evolutionary equations were obtained using equation of motion technique and then transformed into energy domain. The approach is mostly based on works of Karsten Flensberg [3] and Thomas Federiksen [1].

The main idea is to study the following situation: an electron passes through the energy level and occupies the molecular junction, turning molecule into an ion; creation of occupied electronic state causes conformational change of molecule, which is accompanied by a change of vibrational potential and an excitation of vibrational state. Under these circumstances, we want to study spectrum of the system and current through the system. In the first stage, we assumed harmonic potential with a shift induced by charging, following work of Flensberg [3]. In subsequent development, we attempted to model conformational change of biphenyl molecule.

3.1 General form of Hamiltonian

First of all, we state the problem in terms of Hamiltonian. We separate the system into several parts. It consists of two leads (electrodes) described by Hamiltonian $H_c$, which are connected to a single molecule — the junction — with Hamiltonian $H_m$. These two parts interact through tunneling Hamiltonian $H_T$. 
We consider Born-Oppenheimer approximation and separate electronic and vibrational states. We assume only one electronic level, so molecule can be in electronically unoccupied ground state $|\Psi_0\rangle$ or it can be ion with one electron $d^\dagger |\Psi_0\rangle$.

For electronic processes, we will use second quantization, but vibrational states will be treated by first quantization technique introduced shortly. The explicit form of Hamiltonian of whole system is:

$$H = H_m + H_c + H_T$$

$$H = h_0 d^\dagger d + h_1 d^\dagger d + \epsilon_0 d^\dagger d + \sum_{k,\alpha \in R,L} \epsilon_k c^\dagger_{k\alpha} c_{k\alpha} + \sum_{k,\alpha \in R,L} (V_{k\alpha} c^\dagger_{k\alpha} d + V^*_{k\alpha} d^\dagger_{k\alpha})$$

(3.1.0.1)

As for individual terms,

$$H_m = h_0 d^\dagger d + h_1 d^\dagger d + \epsilon_0 d^\dagger d$$

(3.1.0.2)

is a junction Hamiltonian, where the eigenstates of the first term $h_0 d^\dagger d$ are vibrational energy states of neutral molecule (the ordering of electron anihilation/creation operators implies zero, if acting on occupied molecule: $(h_0 d^\dagger d)|\Psi_0\rangle = 0$) and for the second $h_1 d^\dagger d$ are vibrational states of charged molecule (which undergone spatial change, if this operator acts on molecule in unoccupied electronic state, it yields zero due to ordering of electronic operators: $(h_1 d^\dagger d)|\Psi_0\rangle = 0$), where again $|\Psi_0\rangle$ stands for ground electronic state of the molecule. The last term, $\epsilon_0 d^\dagger d$ represents bare on-site electronic energy.

If we express first two terms in basis of their eigenstates, they satisfy the relations

$$h_0|v\rangle = \epsilon_v|v\rangle, \quad \langle v|v'\rangle = \delta_{v,v'}, \quad h_0 = \sum_{v'} \epsilon_{v'}|v'\rangle\langle v'| \quad (3.1.0.3a)$$

$$h_1|d\rangle = \epsilon_d|d\rangle, \quad \langle d|d'\rangle = \delta_{d,d'}, \quad h_1 = \sum_{d'} \epsilon_{d'}|d'\rangle\langle d'\rangle \quad (3.1.0.3b)$$

In case of LHO in second quantization, the $H_m$ Hamiltonian could read in simple form

$$h_0 = \Omega a^\dagger a, \quad h_1 = \Omega a^\dagger a + \lambda (a + a^\dagger)$$

(3.1.0.4)

where $\Omega$ is vibration energy, $a, a^\dagger$ are phonon annihilation/creation operators and $\lambda$ is electron-phonon coupling constant. We can see, that phonon could be either absorbed or emitted by electron.

The term

$$H_c = \sum_{k,\alpha \in R,L} \epsilon_k c^\dagger_{k\alpha} c_{k\alpha}$$

(3.1.0.5)
is a Hamiltonian of contacts (note equations developed in section 2.1) with appropriate electron annihilation/creation operators for given momentum \( k \) and either left or right lead \( \alpha \in L, R \). We assume, that leads themselves are noninteracting.

The last term is the most interesting, a tunneling Hamiltonian

\[
H_T = \sum_{k,\alpha \in R,L} \left( V_{k\alpha} c_{k,\alpha}^\dagger d + V_{k\alpha}^* d_{k,\alpha}^\dagger c_{k,\alpha} \right),
\]

which describes tunneling between the leads and the junction under coupling defined by \( V_{k,\alpha} \).

Several things can be clarified at this point:

| \( V_{k\alpha} \) | Contact-junction coupling vector will be generally approximated within \( \Gamma \) (see (2.3.2.11)) and will not be treated in detail any further. |
| \( H_c \) | Contacts will be treated within the self-energy term. |
| \( h_0, h_1 \) | These two Hamiltonians contain potential for neutral molecule and ion respectively, which is the key part of every distinct model. Apart from these, the rest of the \( H \) will be pretty much the same across models used. |

The Hamiltonian (3.1.0.1) will be used to derive an equation of motion for Green functions in next section.

### 3.1.1 Franck-Condon factors

When the molecule undergoes an electronic transition (i.e. it is occupied or left by an electron), it changes its spatial conformation and therefore, the vibronic state in ion \( d^\dagger \ket{\Psi_0} \) is in principle different from vibronic state in neutral molecule \( \ket{\Psi_0} \). Franck-Condon factors treat the probability of transition between individual vibronic states during electronic change. It turns out, that this probability is given by magnitude of a wave function overlap. It is easy to illustrate the origin of the idea from spectroscopical point of view.

Let us assume the probability of transition of oscillating dipole composed of electronic and nuclear part \( \mu = \mu_{el} + \mu_{nuc} \). The probability of transition from vibronic state \( \ket{n'} (\langle x | n' \rangle = \psi') \) to vibronic state \( \ket{n} (\langle x | n \rangle = \psi) \) is given by

\[
P_{\ket{n'}, \ket{n}} \sim \left| \int dx \psi'^* (x) \mu \psi (x) \right|^2 = |\langle \psi' | \mu | \psi \rangle|^2,
\]

(3.1.1.1)
where initial $|\psi'\rangle$ and final $|\psi\rangle$ wave functions can (under the Born-Oppenheimer approximation, which is mentioned in subsection 3.2.1) be decomposed into $\psi(x) = \psi_e(x)\psi_v(x)$, a product of electronic and vibrational wave function (eventually, we could assume also spin factorization etc.). Then, the probability is proportional

$$P_{|n'\rangle \rightarrow |n\rangle} \sim |\langle n'|V_{k,\alpha}|n\rangle|^2,$$

(3.1.1.3)

with the assumption that $V_{k,\alpha}$ is state-independent, we can write the product

$$P_{|n'\rangle \rightarrow |n\rangle} \sim |V_{k,\alpha}|^2|\langle n'|n\rangle|^2.$$

(3.1.1.4)

The second factor is the Franck-Condon factor.
3.2 Equation of motion

Since our Hamiltonian (3.1.0.1) does not contain any explicitly time dependent term as in (2.2.6.1), situation simplifies a little bit. To match appropriate parts between (3.1.0.1) and (2.2.6.1), we have quadratic Hamiltonian $H_m + H_c \equiv H_0$ and interaction Hamiltonian $H_T \equiv H^I$. We start with solving of noninteracting evolution for operators. Index $\alpha$ is dropped and can easily be reintroduced.

To use Heisenberg equation (2.3.1.3) we need to calculate commutation relations for noninteracting Hamiltonian (representing noninteracting evolution)

$$[c_k, H_0] = [c_k, H_d + H_c] = [c_k, H_c]$$

$$= [c_k, \sum_{k'} \epsilon_{k'} c_{k'}^\dagger c_{k'}]$$

$$= \sum_{k'} \epsilon_{k'} [c_k, c_{k'}^\dagger c_{k'}]$$

$$= \sum_{k'} \epsilon_{k'} \{c_k c_{k'}^\dagger c_{k'} - c_{k'}^\dagger c_{k'} c_k\}$$

$$= \sum_{k'} \epsilon_{k'} \{\delta_{k,k'} c_k\}$$

$$= \epsilon_k c_k(t)$$

$$c_k(t) = e^{-i\epsilon_k t} c_k(0) \quad (3.2.0.5)$$

The last line describes evolution of phase of leads operators from any initial time, without interaction with the molecule. Next, we calculate time evolution for electronic operators with projection operator (which will be needed in our model).

$$[d|v\rangle\langle d|, H_0] = [d|v\rangle\langle d|, H_m + H_c] = [d|v\rangle\langle d|, H_m]$$

$$= [d|v\rangle\langle d|, h_0 d^\dagger d + h_1 d^\dagger d + \epsilon_0 d^\dagger d]$$

$$= (-h_0|v\rangle\langle d|d + (h_1 + \epsilon_0)|v\rangle\langle d|d)$$

$$= (-\epsilon_v + \epsilon_d + \epsilon_0)|v\rangle\langle d|d$$

$$[d|v\rangle\langle d|](t) = e^{i(\epsilon_v - \epsilon_d - \epsilon_0) t} d(0)|v\rangle\langle d|(0) \quad (3.2.0.6)$$

$$[d^\dagger|d\rangle\langle v|](t) = e^{-i(\epsilon_v - \epsilon_d - \epsilon_0) t} d^\dagger(0)|v\rangle\langle d|(0) \quad (3.2.0.7)$$

It is easy to see, that creation operator has just inverse time evolution. Those are again the noninteracting time evolutions of operators. In the next step, we calculate
the interaction terms.

\[
[d|v⟩⟨d|, H^i] = [d|v⟩⟨d|, \sum_k V_k^* d^\dagger c_k]
\]
\[
= \sum_k [d|v⟩⟨d|, V_k^* d^\dagger c_k]
\]
\[
= \sum_{k,v',d'} [d|v⟩⟨d|, V_k^* d^\dagger c_k |v'⟩⟨v'|d'⟩⟨d'|]
\]
\[
= \sum_k \{ \sum_{v'} dd^\dagger \langle d|V_k^* |v'⟩|v⟩⟨v'⟩d^\dagger c_k + d^\dagger d \langle d'|V_k^* |v⟩|d'⟩⟨d|c_k \}
\]

(3.2.0.8)

Now, having necessary relations ready, we consider retarded Green function (2.2.4.10) with one time argument (because in a stationary state the Green function actually depends only on time difference)

\[
G_{vd}^r(t) = -i \Theta(t) \langle \{ |v⟩⟨d| d(t), d^\dagger \} \rangle
\]

(3.2.0.9)

and calculate the evolution equation

\[
\frac{\partial}{\partial t} G_{vd}^r(t) = \delta(t) \langle \{ |v⟩⟨d| d, d^\dagger \} \rangle
\]
\[
- i \Theta(t) \langle \{ |v⟩⟨d| d, H_0 \}, d^\dagger \rangle - i \Theta(t) \langle \{ |v⟩⟨d| d, H^i \}, d^\dagger \rangle
\]
\[
(i \frac{\partial}{\partial t} + \epsilon_v - \epsilon_d - \epsilon_0) G_{vd}^r(t) = \langle |v⟩⟨d| \rangle
\]
\[
- i \Theta(t) \langle \{ \sum_k \sum_{v'} dd^\dagger c_k \langle d|V_k^* |v'⟩|v⟩⟨v'⟩d^\dagger \rangle c_k
\]
\[
+ \sum_{d'} d^\dagger d \langle d'|V_k^* |v⟩|d'⟩⟨d| \rangle c_k \}
\]

(3.2.0.10)

We will calculate interaction term separately and then plug it back in equation
\[ \langle \{ |v\rangle \langle d | d', H' \}, d^\dagger \rangle = \{ \sum_k \{ \sum_{v'} dd' c_k \langle d | V_k^* | v' \rangle \langle v \rangle \langle v' \rangle \\
+ \sum_{d'} dd' c_k \langle d' | V_k^* | v \rangle \langle v' \rangle \langle d \rangle \rangle, d^\dagger \}\rangle \]
\[ = \{ \sum_k \{ \sum_{v'} (c_k - dd' c_k) \langle d | V_k^* | v' \rangle \langle v \rangle \langle v' \rangle \\
+ \sum_{d'} dd' c_k \langle d' | V_k^* | v \rangle \langle v' \rangle \langle d \rangle \rangle, d^\dagger \}\rangle \]
\[ = \{ \sum_k \{ \sum_{v'} c_k \langle d | V_k^* | v' \rangle \langle v \rangle \langle v' \rangle \\
- \{ dd' c_k \langle v' \rangle \langle v \rangle, d^\dagger \} \\
+ \{ d' d c_k \langle d' | V_k^* | v \rangle \langle v \rangle \langle d \rangle \rangle, d^\dagger \}\rangle \}
\[ = \{ \sum_k \{ \sum_{v'} \langle d | V_k^* | v' \rangle (c_k \langle v \rangle \langle v' \rangle, d^\dagger \} \\
- \{ d' d c_k \langle v' \rangle \langle v \rangle, d^\dagger \} \\
+ \sum_{d'} \langle d' | V_k^* | v \rangle \{ d' d c_k \langle d' \rangle \langle d \rangle \rangle, d^\dagger \}\rangle \}\]
so we can see, that tunneling term generated higher order Green functions. If we insert the expression back to equation (3.2.0.10), we obtain
\[ (i \frac{\partial}{\partial t} + \epsilon_v - \epsilon_d - \epsilon_0) G_{vd}(t) = \langle |v\rangle \langle d | \rangle + \sum_{v'} \langle \{ \sum_{v'} \langle d | V_k^* | v' \rangle (G_{k,v,v'}^r(t) - G_{d,k,v,v'}^r(t)) \\
+ \sum_{d'} \langle d' | V_k^* | v \rangle G_{d,k,d'd}^r(t) \rangle \rangle \] (3.2.0.11)

The defined objects are
\[ G_{k,v,v'}^r \equiv -i \Theta(t) \{ \langle c_k | v \rangle \langle v' \rangle, d^\dagger \} \] (3.2.0.12)
\[ G_{d,k,v,v'}^r \equiv -i \Theta(t) \{ \langle d' d c_k | v \rangle \langle v' \rangle, d^\dagger \} \] (3.2.0.13)
\[ G_{d,k,d'd}^r \equiv -i \Theta(t) \{ \langle d' d c_k | d' \rangle \langle d \rangle, d^\dagger \} \] (3.2.0.14)

Solving evolution equations for new Green funcitons is straightforward, but little tedious. We need to repeat the same steps as we did in previous cases. It is important to note, that number of particle operator acting on electronically-unoccupied
vibronic state gives zero, \( d^\dagger d|\psi\rangle = 0 \) (analogous for hole number operator and electronically-occupied state).

\[
[c_k|\psi\rangle \langle \psi'|, H_0] = [c_k|\psi\rangle \langle \psi'|, h_0 dd^\dagger + h_1 d^\dagger d + \epsilon_0 d^\dagger d + \sum_{k', k''} \epsilon_k c_{k'}^\dagger c_{k''}]
\]

\[
= [c_k|\psi\rangle \langle \psi'|, \sum_{\psi''} \epsilon_{\psi''}|\psi''\rangle \langle \psi''| dd^\dagger + \sum_{k'} \epsilon_{k'} c_{k'}^\dagger c_{k''}]
\]

\[
= c_k (\epsilon_{\psi'} - \epsilon_{\psi} + \epsilon_k)|\psi\rangle \langle \psi'|
\]

\[
= c_k (\epsilon_{\psi'} - \epsilon_{\psi} + \epsilon_k)|\psi\rangle \langle \psi'| \quad (3.2.0.15)
\]

Now, proceeding to process interaction term, we will ignore interaction vector \( V_k \), i.e. treat it as a real constant and not explicitly write it. This calculation takes some effort to regroup projectors and use anti-commutation relations to get result in suitable form, thus, some steps are not shown here.

\[
[c_k|\psi\rangle \langle \psi'|, H^i] = [c_k|\psi\rangle \langle \psi'|, \sum_{k', v', v'', d'} c_{k'}^\dagger d|v''\rangle \langle v''| d^\dagger d' \langle d' | v'' \rangle \langle v''|]\n\]

\[
= \sum_{k', v', v'', d'} \langle v''|d^\dagger d'\rangle [d'\langle d' | v'' \rangle \langle v''| - \langle d' | v'' \rangle \langle v''|] c_{k'}^\dagger c_{k'} d^\dagger d' \quad (3.2.0.16)
\]

From now on, we will ignore leads correlations and use a Hartree-Fock approximation to decompose three electron states into mean field and exchange interactions

\[
c_{k'}^\dagger c_k d \approx \langle c_{k'}^\dagger c_k d \rangle - \langle c_{k'}^\dagger d \rangle c_k \quad (3.2.0.17)
\]

\[
c_{k'} c_k d^\dagger \approx c_{k'} \langle c_k d^\dagger \rangle - c_k \langle c_{k'} d^\dagger \rangle. \quad (3.2.0.18)
\]

Further on, we will ignore exchange terms \( \langle c_k d^\dagger \rangle \) and \( \langle c_{k'}^\dagger d \rangle \), and consider only mean field energy. After these steps, equation (3.2.0.16) takes form

\[
[c_k|\psi\rangle \langle \psi'|, H^i] \approx \sum_{v'', d'} \langle v''|d^\dagger d'\rangle [d'\langle d' | v'' \rangle \langle v''| - \langle d' | v'' \rangle \langle v''|] c_{k'}^\dagger c_{k'} d^\dagger d' \quad (3.2.0.19)
\]

Putting all partial results together and reintroducing \( V_k \), equation of motion for \( G_{k,v'v''} \) is

\[
\left( \frac{i\partial}{\partial t} + \epsilon_{\psi'} - \epsilon_{\psi''} - \epsilon_k \right) G_{k,v'v''} = V_k \sum_{v'} \langle n_k|\psi''\rangle G_{v'v'v''}^r + V_k \sum_{d''} (1 - \langle n_k|\psi''\rangle) G_{v'd''v''}^r
\]

\[
+ \delta(t) \langle \{ c_k|\psi\rangle \langle \psi'|, d^\dagger \} \rangle \quad (3.2.0.20)
\]

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The same procedure can be applied to another generated higher order Green function. We begin with commutators:

\[ [d^4 dc_k | v \rangle \langle v'|, H_0] = [d^4 dc_k | v \rangle \langle v'|, h_0 dd^4 + h_1 d^4 d + \epsilon_0 d^4 d + \sum_{k'} \epsilon_{k'} c_{k'}^\dagger c_{k'}] \]

\[ = [d^4 dc_k | v \rangle \langle v'|, \sum_{v''} \epsilon_{v''} | v'' \rangle \langle v''| (1 - d^4 d) + \sum_{k'} \epsilon_{k'} c_{k'}^\dagger c_{k'}] \]

\[ = (\epsilon_k d^4 dc_k | v \rangle \langle v'|) + [d^4 dc_k | v \rangle \langle v'|, \sum_{v''} \epsilon_{v''} | v'' \rangle \langle v''|] \]

\[ = (\epsilon_v - \epsilon_v + \epsilon_k) d^4 dc_k | v \rangle \langle v'|, \quad (3.2.0.21) \]

where we used, that commutation with \( h_0 dd^4 \) yields zero. Interaction is then given by following equation (constant \( V_k \) was again temporarily omitted).

\[ [d^4 dc_k | v \rangle \langle v'|, H^i] = [d^4 dc_k | v \rangle \langle v'|, \sum_{k',v'',d''} c_{k'}^\dagger d | v'' \rangle \langle v''| d^4 d' | v' \rangle \langle v'|, d^4 d' | v'' \rangle \langle v''|] \]

\[ = \sum_{k',v'',d''} (c_{k'}^\dagger d c_k | v'' \rangle \langle v''| d^4 d' | v' \rangle \langle v'| - d^4 c_k c_k' | v \rangle \langle v' | d^4 d' | v'' \rangle \langle v''|) \]

\[ = \sum_{k',v'',d''} (c_{k'} c_k d | v'' \rangle \langle d^4 d' | v' \rangle \langle v' | - c_k c_k' d^4 d' | v'' \rangle \langle v''|) \]

\[ = (3.2.0.22) \]

which, after employing the same approximation as in case of equation (3.2.0.16), gives

\[ [d^4 dc_k | v \rangle \langle v'|, H^i] \approx \sum_{v''} \langle c_{k'}^\dagger c_k d | v'' \rangle | v'' \rangle \langle v'| \]

and once more, completing the equation gives us

\[ (\frac{\partial}{\partial t} + \epsilon_v - \epsilon_v - \epsilon_k) G_{d,k,vv'}(t) = \delta(t) \langle c_k d^4 | v \rangle \langle v'| + V_k \langle n_k \rangle \sum_{v''} \langle c_{k'}^\dagger c_k d | v'' \rangle G_{v'' v'}^{v'' v',} \quad (3.2.0.23) \]

Carrying out the procedure for the last Green function \( G^{v'}_{d,k,dd'} \) is analogous and the resulting equation is

\[ (\frac{\partial}{\partial t} + \epsilon_{d'} - \epsilon_{d} - \epsilon_k) G_{d,k,dd'}(t) = \delta(t) \langle c_k d^4 | d' \rangle \langle d'| + V_k \langle n_k \rangle \sum_{v''} \langle v'' | d^4 \rangle G_{v'' d'}^{v'' v',} \quad (3.2.0.24) \]
At this point, everything is ready to finish equation (3.2.0.11). To reintroduce $V_k$, if we inspect equations (3.2.0.16) and (3.2.0.22), we can see, that after approximations, there would be just $V_k$ left and no $V^*_k$. We have already assumed, that $V_k$ is basis independent, so we may extract it and combine with $V^*_k$ from previous tunneling term of equation (3.2.0.10). We started with the tunneling term from equation (3.2.0.10) and consecutively used equations (3.2.0.20), (3.2.0.23), and (3.2.0.24)

\[-i\Theta(t)\langle\{\sum_k V^*_k (\sum_{v'} dd^d c_k \langle d|v'\rangle|v\rangle + \sum_{d'} d^d c_k \langle d'|v\rangle|d\rangle, d^d\rangle\rangle\]

\[= \sum_k |V_k|^2 \left\{ \sum_{v'} \langle d|v'\rangle \left( i \frac{\partial}{\partial t} + \epsilon_v - \epsilon_{v'} - \epsilon_k \right)^{-1} \left[ \langle n_k \rangle \sum_{v''} \langle v''|d'\rangle G^r_{v''v'} - [V_k]^{-1} \delta(t) \langle c_k d^d|v'\rangle \right) \right\} \]

\[+ \sum_{d'} \langle d'|v\rangle \left( i \frac{\partial}{\partial t} + \epsilon_{d'} - \epsilon_d - \epsilon_k \right)^{-1} \left[ \langle n_k \rangle \sum_{v''} \langle v''|d'\rangle G^r_{v''d'} + [V_k]^{-1} \delta(t) \langle c_k d^d|v'\rangle \right) \]

\[+ \sum_{d'} \langle d'|v\rangle \left( i \frac{\partial}{\partial t} + \epsilon_{d'} - \epsilon_d - \epsilon_k \right)^{-1} \left[ (1 - \langle n_k \rangle) \sum_{d''} \langle v'|d''\rangle G^r_{v'v''} \right) \]

\[= \sum_k |V_k|^2 \left\{ \sum_{v'} \langle d|v'\rangle \left( i \frac{\partial}{\partial t} + \epsilon_v - \epsilon_{v'} - \epsilon_k \right)^{-1} \left[ (1 - \langle n_k \rangle) \sum_{d''} \langle v'|d''\rangle G^r_{v'v''} \right) \] \tag{3.2.0.25}

\[+ \sum_{d'} \langle d'|v\rangle \left( i \frac{\partial}{\partial t} + \epsilon_{d'} - \epsilon_d - \epsilon_k \right)^{-1} \left[ \langle n_k \rangle \sum_{v''} \langle v''|d'\rangle G^r_{v''d'} \right) \]

in the last step, we have combined all delta function terms through summing them over to same indexes with scalar products, e.g.

\[\sum_{v'} \langle d|v'\rangle \delta(t)\langle d^d c_k|v\rangle \langle v'\rangle = \delta(t)\langle d^d c_k|v\rangle \langle d\rangle.\]

Second and third delta function terms subtracted with anti-commutator delta function term.

Now, the tunneling term can be solved by solving for a delta function on the right side and convolving this solution with inhomogeneous right side. We introduce shortcut, as was announced before, $2\pi \sum_k |V_k|^2 = \Gamma$, and assumed, that level-band
is energy independent. So, the tunneling term in frequency domain is

$$
\sum_{v',d'} \langle d'|v'\rangle\langle v'|d''\rangle \Lambda_{v'v'}^h G_{vd'}^r + \sum_{v',d'} \langle d'|v\rangle\langle v'|d''\rangle \Lambda_{d'd}^e G_{v'd''}^r.
$$

(3.2.0.27)

The equation of motion for retarded Green function in frequency domain is

$$
(\omega + \epsilon_v - \epsilon_d - \epsilon_0)G_{vd}(\omega) = \langle \langle d \rangle \rangle + \sum_{v',d'} \langle d'|v'\rangle\langle v'|d''\rangle \Lambda_{v'v'}^h G_{vd'}^r + \sum_{v',d'} \langle d'|v\rangle\langle v'|d''\rangle \Lambda_{d'd}^e G_{v'd''}^r.
$$

(3.2.0.28)

### 3.2.1 Hartree and Fock terms

It former section, in equations (3.2.0.17) and (3.2.0.18), we have introduced Hartree-Fock factorization. In this place, a short note will be made about the approximation. This subsection is meant just to illustrate the concept of Hartree-Fock approach and intuitive interpretation of the terms.

The approximation starts with the assumption of Born-Oppenheimer approximation, which says, that overall state of system can be factorized into electronic and nuclear parts, i.e.

$$
|\psi\rangle = |\psi_{\text{nucleus}}\psi_{\text{electron}}\rangle = |\psi_{\text{nucleus}}\rangle \times |\psi_{\text{electron}}\rangle.
$$

In other words, it is assumed, that coordinate and vibrational changes in nucleus conformation are much slower than electronic change. As a result, nuclear degrees of freedom dependent on electronic energy only parametrically and electronic energy and wave function can be solved separately. This leads to Schrödinger equation in form

$$
[T_{\text{nuc}} + E_{\text{el}}(R)]\phi(R) = E\phi(R),
$$

where $T_{\text{nuc}}$ is nuclear kinetic energy and $E_{\text{el}}$ is parametric electronic field.

If we consider two-body system under Hartree-Fock approximation as an example, the terms present in equations (3.2.0.17) and (3.2.0.18) can be easily be illustrated. We will take only electronic interaction part of Hamiltonian, $d_i, d_i^\dagger$ are electronic annihilation/creation operators for electronic state $|i\rangle$ satisfying anticom-
Figure 3.1: Diagrams for Hartree mean field (a) and Fock exchange (b) interaction mutation relation.

\[
H_{ee} = \langle \Psi_0 | V_{ee} | \Psi_0 \rangle = \frac{1}{2} \sum_{i,j,k,l} \langle kl | \frac{e^2}{|x_1 - x_2|} | ij \rangle \langle \Psi_0 | d_k^\dagger d_l^\dagger d_j d_i | \Psi_0 \rangle
\]

\[
= \frac{1}{2} \sum_{i,j,k,l} \langle kl | \frac{e^2}{|x_1 - x_2|} | ij \rangle \times (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) n_i n_j
\]

\[
= \frac{1}{2} \sum_{i,j} \langle ij | \frac{e^2}{|x_1 - x_2|} | ij \rangle n_i n_j - \frac{1}{2} \sum_{i,j} \langle ij | \frac{e^2}{|x_1 - x_2|} | ji \rangle n_i n_j
\]

(3.2.1.1)

where \( | \Psi_0 \rangle \) is system electronic ground state and also it holds \( \langle d_i^\dagger d_i \rangle = n_i \). We used Wick theorem to evaluate the expression. In the last equation, we can identify terms mentioned before, the first is Coulomb repulsion local term (the mean field) and non-local exchange term, pictured in form of classical Feynman diagrams in figure 3.1. Closer inspection of terms shows us following [6, p. 54-56]: the Hartree term self-energy has form \( \Sigma^H(1,2) = e\phi(1)\delta(1,2) \) and is a scalar potential of mean density of electrons. In condensed state physics, diagram translates into equation

\[
e\phi(1) = -iV(1,\bar{1})G(1,\bar{1})
\]

\[
e\phi(1) = e\phi(t_1, x_1) = e^2 \int dx' \frac{n(t_1, x')}{|x_1 - x'|}.
\]

(3.2.1.2)

which is, in our case, the an average energy in leads in time \( t_1 \). For our assumption of semi-infinite chain, the value is constant.

As for the exchange term, we have

\[
\Sigma^F(1,2) = iV(1,2)G(1,2)
\]

\[
\Sigma^F(1,2) = - e^2 \frac{1}{|x_1 - x_2|} g(x_1, x_2, t) \delta(t_1, t_2).
\]

(3.2.1.3)

This more complicated term is ignored, as was stated before.
3.3 Self-energy

In equation (3.2.0.28), we can recognize the term corresponding to self-energy introduced in equation (3.2.0.27)

\[
G \Sigma + \Sigma G = \sum_{v',d'} \langle d'|v'\rangle \langle v'|d''\rangle \Lambda_{v'd'}^{h} G_{v'd''}^{r} + \sum_{v',d'} \langle d'|v\rangle \langle v|d''\rangle \Lambda_{d'd''}^{e} G_{v'd'}^{r}.
\]

The object is a key part of our calculations and in further paragraphs, we will see, that there is an elegant way how to determine its value. It represents a tunneling term, the term incorporating an interaction between junction and the leads, consisting of electron and hole contributions. Infinitesimal imaginary part was added to denominator to assure convergence of integral in positive imaginary infinity. Before we write an explicit form of Λ-function, we will go back to definition of Γ.

Origin of Γ lays in replacing of sum over momentum with integral over energies (which is reasonable, since we consider semi-infinite chain, so momentum can take almost any value):

\[
\sum_{k} |V_{k}|^2 \frac{\langle n_{k} \rangle}{E - \epsilon_{k}} = \int d\epsilon \sum_{k} \delta(\epsilon - \epsilon_{k}) |V_{k}|^2 \frac{\langle n(\epsilon) \rangle}{E - \epsilon} = \int d\epsilon \frac{\delta(\epsilon)}{2\pi \Gamma(\epsilon)} \frac{n(\epsilon)}{E - \epsilon},
\]

where we have introduced \( \Gamma(\epsilon) = 2\pi \sum_{k} \delta(\epsilon - \epsilon_{k}) |V_{k}|^2 \). Which we later approximated to be energy independent, in accordance with wide-band limit approximation. So now, we proceed with the Λ-function.

The following explicit form of Λ from equation (3.2.0.25) contains reintroduced numbering of leads

\[
\Lambda_{vl}^{\alpha}(\omega) = \int d\epsilon \frac{\delta(\epsilon)}{2\pi} \left( \frac{n_{\alpha}(\epsilon)}{1 - n_{\alpha}(\epsilon)} \right) \frac{1}{\omega + \epsilon_{v} - \epsilon_{l} + i\eta}.
\]

We need to evaluate integral in Λij, let’s say, the one for electrons. First, we use Sokhotsky formula and rewrite (3.3.0.20) as

\[
\int d\epsilon \frac{n_{\alpha}(\epsilon)}{E - \epsilon + i\eta} = -i\pi n_{\alpha}(E) + \varphi \int_{-\infty}^{\infty} d\epsilon \frac{n_{\alpha}(\epsilon)}{E - \epsilon},
\]

where we introduced \( E = \omega + \epsilon_{v} - \epsilon_{l} \).
This gives us the imaginary part of integral. Now, real part can be evaluated using Residue theorem (see [5, p. 79-93] for more details). To do that, we will analytically continue $\epsilon$ to complex place. First we set integration contour

$$\varphi_1 : \epsilon \in (-\infty, E - r) \cup (E + r, \infty), r \to 0^+, \quad (3.3.0.8)$$

$$\varphi_2 : \epsilon = re^{-i\theta}, \theta \in (0, \pi), r \to 0^+, \quad (3.3.0.9)$$

$$\varphi_3 : \epsilon = Re^{i\theta}, \theta \in (0, \pi), R \to \infty. \quad (3.3.0.10)$$

From definition, $\int_{\varphi_1} \frac{n_\alpha}{E - \epsilon} \equiv \varphi \int_{-\infty}^{\infty} \frac{n_\alpha}{E - \epsilon}$ in the limit $r \to 0^+$.

From Residue theorem follows

$$\oint_{\varphi_1 \cup \varphi_2 \cup \varphi_3} \frac{n_\alpha(\epsilon)}{E - \epsilon} = 2\pi i \sum_{r_{\text{res}}} \frac{n_\alpha(\epsilon)}{E - \epsilon}. \quad (3.3.0.11)$$

The part $\varphi_1$ is the desired quantity, therefore, we will inspect other two integration paths and the sum of residue to determine it. The easiest is part $\varphi_2$, a common expression in complex analysis:

$$\int_{\varphi_2} d\epsilon \frac{n_\alpha(\epsilon)}{E - \epsilon} = i\pi n_\alpha(E). \quad (3.3.0.12)$$
Integral over part $\varphi_3$ is slightly more challenging:

$$\int_{\varphi_3} \frac{n_\alpha(\epsilon)}{E - \epsilon} d\epsilon =$$

$$= - \int_{\varphi_3} \frac{n_\alpha(E - z)}{z} dz$$

$$= - \int_{\varphi_3} \frac{1}{1 + e^{\beta(E - z)}} \frac{1}{z} dz$$

$$= - \int_0^\pi \frac{1}{1 + e^{\beta(E - R\cos(\theta))}} \frac{1}{R\cos(\theta)} \Re e^{i\theta} d\theta$$

$$= - i \int_0^\pi \frac{1}{1 + e^{\beta(E - R\cos(\theta))}} d\theta$$

$$= - i \int_0^\pi \frac{1}{1 + e^{\beta E - \beta R\cos(\theta)}} d\theta$$

$$= - i \int_0^\pi \frac{1}{1 + e^{\beta E} \exp(-\beta R \cos(\theta)) \exp(-\beta i R \sin(\theta))} d\theta$$

$$= - i \int_0^\pi \frac{1}{1 + e^{\beta E} e^{-\beta R} \cos(\theta) - i e^{\beta E} e^{-\beta R} \sin(\theta)} \exp(\frac{\beta \epsilon}{2}) d\theta$$

$$= \left\{ \begin{array}{ll}
\theta \in (0, \frac{\pi}{2}) : e^{-\beta \tilde{R}} \rightarrow 0 & \Rightarrow \Re(I) = \frac{\pi}{2}, \Im(I) = 0 \\
\theta \in (\frac{\pi}{2}, \pi) : e^{-\beta \tilde{R}} \rightarrow \infty & \Rightarrow \Re(I) = 0, \Im(I) = 0 \\
\end{array} \right. $$

$$= - \frac{i\pi}{2}.$$

(3.3.0.13)

The key point is to realize the behaviour of $\tilde{R} = R \cos(\theta)$ through the contour and discuss the cases.

Finally, we will solve the sum of residues inside integration contour. These singularities are decided solely by Fermi-Dirac distribution, by condition

$$1 + e^{\beta \epsilon} = 0$$

$$\beta \epsilon = i\pi + 2i k \pi, k \in N$$

$$\epsilon = \frac{i\pi (2k + 1)}{\beta}$$

(3.3.0.14)

50
Once we determine value of residues, we can rewrite the sum into real and imaginary parts

\[
2\pi i \sum_{k=0}^{\infty} \frac{1}{E - \frac{i\pi(2k+1)}{\beta}} \left( \frac{1}{-\beta} \right) = -2\pi i \sum_{k=0}^{\infty} \frac{1}{\beta E - i\pi(2k + 1)} = \sum_{k=0}^{\infty} \frac{-2\pi i \beta E}{(\beta E)^2 + \pi^2(2k + 1)^2} + \frac{2\pi^2(2k + 1)}{(\beta E)^2 + \pi^2(2k + 1)^2}
\]

(3.3.0.15)

Imaginary part can be written in terms of elementary functions

\[
\sum_{k=0}^{\infty} \frac{-2\pi i \beta E}{(\beta E)^2 + \pi^2(2k + 1)^2} = -\frac{i\pi}{2} \tanh\left( \frac{\beta E}{2} \right)
\]

\[
= -\frac{i\pi}{2} \left[ \frac{e^{\beta E} - e^{-\beta E}}{e^{\beta E} + e^{-\beta E}} \right]
\]

\[
= -\frac{i\pi}{2} \left[ \frac{e^{\beta E} - 1}{e^{\beta E} + 1} \right]
\]

\[
= -\frac{i\pi}{2} \left[ 1 - \frac{2}{1 + e^{\beta E}} \right] = -\frac{i\pi}{2} + i\pi n_{\alpha}(E)
\]

(3.3.0.16)

The real part of the sum diverges, but workaround exists. Recalling equation (3.2.0.28) and noticing, that

\[
\sum_{v'} \langle d|v'\rangle \langle v'|d'\rangle = \langle d|d'\rangle = \delta_{dd'},
\]

and the same for second term, we can add a regularization term of divergent series, which will subtract with the same term added to regularize second \(\Lambda\)-function. Therefore, we can approximate the value of real part of the sum to any desired extend by adding up enough terms of following series

\[
\Re\{\Lambda_{vl}^e\} = \sum_{k=0}^{\infty} \frac{2\pi^2(2k + 1)}{(\beta E)^2 + \pi^2(2k + 1)^2} - \frac{2}{2k + 1} = \sum_{k=0}^{\infty} \frac{-2(\beta E)^2}{((\beta E)^2 + \pi^2(2k + 1)^2)(2k + 1)}
\]

(3.3.0.17)
If we now come back to complete contour integral (3.3.0.11) and input obtained results, we have
\[ \oint \frac{n_\alpha(\epsilon)}{E - \epsilon} = 2\pi i \sum_{res} n_\alpha(\epsilon) \]
\[ \varphi \int_{-\infty}^{\infty} d\epsilon \frac{n_\alpha(\epsilon)}{E - \epsilon} = \sum_{k=0}^{\infty} \frac{-2(\beta E)^2}{[(\beta E)^2 + \pi^2(2k+1)^2](2k+1)} - \frac{i\pi}{2} + i\pi n_\alpha(E) \]
\[ \varphi \int_{-\infty}^{\infty} d\epsilon \frac{n_\alpha(\epsilon)}{E - \epsilon} = \sum_{k=0}^{\infty} \frac{-2(\beta E)^2}{[(\beta E)^2 + \pi^2(2k+1)^2](2k+1)} \quad (3.3.0.18) \]

As we can see, imaginary parts compensate each other, and principal value integral is real as could be expected. Here we invoke new shortcut for principal value of integral
\[ \varphi \int_{-\infty}^{\infty} d\epsilon \frac{n_\alpha(\epsilon)}{E - \epsilon} = \sum_{k=0}^{\infty} \frac{-2(\beta E)^2}{[(\beta E)^2 + \pi^2(2k+1)^2](2k+1)} \quad (3.3.0.19) \]

It is useful to notice, that function \( \Psi(E) = \Psi(-E) \) has parity.

Complete and explicit form of \( \Lambda \)-functions is
\[ \Lambda^{\text{el}}_{\text{id}} = \sum_{\alpha} \left[ -i\Gamma_{\alpha} - \frac{1}{2} n_\alpha(\omega + \epsilon_l - \epsilon_d) + \frac{\Gamma_{\alpha}}{2\pi} \Psi(\omega + \epsilon_l - \epsilon_d) \right] \quad (3.3.0.20) \]
\[ \Lambda^{\text{el}}_{\text{vd}} = \sum_{\alpha} \left[ -i\Gamma_{\alpha} - \frac{1}{2} n_\alpha(-\omega + \epsilon_l - \epsilon_v) - \frac{\Gamma_{\alpha}}{2\pi} \Psi(\omega + \epsilon_v - \epsilon_l) \right] \quad (3.3.0.21) \]

### 3.3.1 Approximations to self-energy

To compare additional effects of a Fermi sea, the calculations are carried out also in approximations ignoring such effect, namely single particle approximation (SPA) and diagonal approximation of Dyson equation (DEA), which introduces only leading order of the Fermi sea. These approximations were introduced in [3] and will be introduced subsequently.

First of all, the SPA. In this approximation, the Fermi sea is completely ignored and real part of self-energy is zero, equation (3.2.0.28) can be solved analytically as
\[ G^{\text{r,SPA}}(\omega) = \sum_{v,d} |\langle v|d\rangle|^2 \frac{(1 - \bar{n})\langle v\rangle\langle v\rangle + \bar{n}\langle d\rangle\langle d\rangle}{\omega + \epsilon_v - \epsilon_d - \epsilon_0 + i\frac{\Gamma}{2}}. \quad (3.3.1.1) \]

Regarding the right side, we factorised vibrational and electronic parts, so that \( \bar{n} \) is average electron occupation. New introduced object, \( G^{r,SPA} = \sum_{v,d} \langle v|d\rangle G^{r,SPA}_{vd} \), is projector SPA Green function summed over the states.
We can make one step further, as was announced, and introduce first order of the Fermi sea in self-energy. The right side is treated in the same manner as in case of SPA. If we consider a solution near a resonance, it yields a condition \( \omega = \epsilon_0 - \epsilon_v + \epsilon_d \), where the Green function peaks. In this manner, we can choose the most important terms in equation (3.3.0.20), \( \sum_{\epsilon''} \epsilon_{v''} - \epsilon_d \approx \epsilon_v - \epsilon_d \approx \sum_{\epsilon''} \epsilon_v - \epsilon_d'' \), and therefore, we may assume \( v'' = v \) in electron term and \( d'' = d \) in hole term. This removes the summation index and self-energy has simpler form

\[
\Sigma_{vd}(\omega) = \sum_{d'} \Lambda_{d'd}^e(\omega)|\langle v|d'\rangle|^2 + \sum_{v'} \Lambda_{vv'}^h(\omega)|\langle v'|d'\rangle|^2.
\] (3.3.1.2)

The approximations described give us simplified Dyson equation

\[
G^{r,DEA}(\omega) = \sum_{vd} \frac{(1 - \bar{n})N_v + \bar{n}N_d}{\omega + \epsilon_v - \epsilon_d - \epsilon_0 - \Sigma_{vd}(\omega)}|\langle v|d\rangle|^2.
\] (3.3.1.3)

where \( N_i = e^{-\beta \epsilon_i} \) is Boltzman distribution of vibrational states in equilibrium. The difference between SPA and DEA is, that broadening by tunneling in (out) processes can be invoked only, if the state in lead is occupied (vacant).
3.4 Current condition

As we can see in section 2.3.2. in equation (2.3.2.13), we would need three Green functions to generally describe nonequilibrium current. From the later development in that section, it is obvious, that we can assume asymmetric situation and necessary equation simplifies into equation (2.3.2.16), which is the case we will consider in future development. We will assume, that molecule is very close to the left electrode, and therefore, in thermal equilibrium. This approximation allows us to calculate density of states matrices and use standard self-consistent approach. With spectral function given by the equation

\[ A_{vd}(\omega) = i[G^r_{vd}(\omega) - G^a_{vd}(\omega)] = i[G^<_{vd}(\omega) - G^>_{vd}(\omega)] \] (3.4.0.4)

the density of states is

\[ \rho_{vd} = \langle |v\rangle \langle d| \rangle = \int_{-\infty}^{\infty} A_{vd}(\omega) \frac{d\omega}{2\pi} \] (3.4.0.5)

\[ \rho_{vv'} = \langle dd' |v\rangle \langle v'| \rangle = \int_{-\infty}^{\infty} \sum_d \langle v'|d\rangle A_{vd}(\omega) n(-\omega) \frac{d\omega}{2\pi} \] (3.4.0.6)

\[ \rho_{dd'} = \langle d'd |d\rangle \langle d| \rangle = \int_{-\infty}^{\infty} \sum_v \langle v|d\rangle A_{vd'}(\omega) n(\omega) \frac{d\omega}{2\pi} \] (3.4.0.7)

where we can see, that (3.4.0.5) is right hand term to be self-consistently calculated.

Having stated all the introduction, we may proceed to implementation of techniques outlined.
Chapter 4

IMPLEMENTATION

In the following chapter, we will introduce and compare generally two models. The Flensberg’s model based on article [3] and similar model with anharmonic potential with near degenerate levels. The density of states and current will be calculated.

4.1 Shifted LHO model

This simple model follows the procedure outlined in section 3.1. The model introduces two basis sets, $|v\rangle$, the eigenstates of $h_0$ and $|d\rangle$ are eigenstates of $h_1$. We remind, that $h_0$ is not electronically occupied and $h_1$ is, so it has coordinates of potential shifted due to conformational change. Hamiltonians are given by equations

\begin{align}
  h_0 &= \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2x^2 \\
  h_1 &= \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2(x - g)^2
\end{align}

where $g$ is the shift — the electron-phonon coupling factor. In case of figures 4.1 and 4.2, the coupling factor was set to $g = 2$ and inverse temperature $\beta = 100$. Mentioned figures differ in parameter $\epsilon_0$, which introduces a bare electron on-site energy (see equation (3.1.0.2)). The parameter has an effect on occupation of electronic state in molecule because it effectively increases electronically occupied vibrational level energy $\epsilon_d$.

We performed a calculation of spectral function as noted in equation (3.4.0.4) for specific parameters with the results in figures 4.1 and 4.2. The results comply with those published in [3] and make a good starting point for further comparative calculations. We have carried out calculation for single particle approximation.
(SPA), diagonal approximation of Dyson equation (DEA) and full matrix solution according to equation (3.2.0.28). Energies $\epsilon$ in graphs are multiples the distance of two neighbouring equidistant LHO energies $\omega_0$.

Obvious symmetry in figure 4.1 is result of no bare electron energy, i.e. $\epsilon_0 = 0$. Therefore, ion transition just shifts the potential along the coordinate axis, i.e. it does not change vibronic energy levels, and inverse neutral state transition shifts the potential to the former place. Energy differences are then symmetrically distributed. The decrease magnitude of spectral lines for energies far from Fermi level is given by Franck-Condon factors.

We can notice, that the introduction of a Fermi sea introduces step-like structures, the cusps (marked by arrow in figure 4.2b), they arise, because the broadening can occur only, if tunneling is allowed by states occupation in a lead. Little dents (marked in figure 4.1d) have the same origin; the first local maximum is shifted off standard resonant position by real part of self-energy, then, one of fermi distribution terms in imaginary part of self-energy sum has the step, causing turn and leading to the second maximum.

Another thing is sharpening and towering of the peaks. That is a result of Franck-Condon factors. To explain the sharpening, we can start from DEA for each single element of self-energy sum independently, i.e. $v$ and $d$ are set.

$$
A_{vd}(\omega) = i(G^r_{vd} - G^a_{vd})
= i(G^r_{vd}[G^a_{vd}]^{-1}G^a_{vd} - G^r_{vd}[G^r_{vd}]^{-1}G^a_{vd})
= iG^r_{vd}(\Sigma^r_{vd} - \Sigma^a_{vd})G^a_{vd}
= iG^r_{vd}(i\Gamma_{vd})G^a_{vd}
\approx -\frac{\Gamma_{vd}}{\left(\omega + \epsilon_{vd} - \Delta_{vd} + \frac{i\Gamma_{vd}}{2}\right)\left(\omega + \epsilon_{vd} - \Delta_{vd} - \frac{i\Gamma_{vd}}{2}\right)}
\approx -\frac{\Gamma_{vd}}{[\omega + \epsilon_{vd} - \Delta_{vd}]^2 + \left[\frac{\Gamma_{vd}}{2}\right]^2}.
$$

(4.1.0.3)

We used shortcuts $\epsilon_{vd} \equiv \epsilon_v - \epsilon_d - \epsilon_0$, $\Delta_{vd} \equiv \Re \Sigma_{vd}$ and $\frac{\Gamma_{vd}}{2} \equiv -\Im \Sigma_{vd}$. To simplify notation, we also used

$$
\Gamma_{vd} = \Gamma \sum_l n(\omega + \epsilon_{vl})|\langle v|l\rangle|^2 + n(-\omega - \epsilon_{ld})|\langle l|d\rangle|^2,
$$

(4.1.0.4)

where $\Gamma$ is level-width, as was defined earlier. The summation over the leads should be also included, but its reintroduction is straightforward. We unified the summation
Figure 4.1: Spectral function of LHO potential with parameters \( \epsilon_0 = 0 \), and \( \Gamma = 0.5 \) for part (a), \( \Gamma = 1.0 \) for part (c). More detailed views of interval \((-2, 2)\) are also included (part (b) and (d)).

Figure 4.2: Spectral function of LHO potential with parameters \( \epsilon_0 = 1.5 \) and \( \Gamma = 0.5 \).
index as $l$ despite, in first Franck-Condon factor, it stands for electronically occupied vibrations and in second for unoccupied; this can be done, because sum goes over all vibronic states and we have assumed the same number of vibronic states in occupied and unoccupied cases.

This procedure shows, that when resonances are treated separately, term by term, equation (4.1.0.3) has the same form as equation derived in elastic scattering section, (2.1.0.9). The difference is, that level-width $\tilde{\Gamma}_{vd}$ is in this case modulated by a Fermi sea and Franck-Condon factors, as shown in equation (4.1.0.4).

To provide more plausible example, we may consider peak at $\omega = 0$, take into consideration $\epsilon_v - \epsilon_d = 0$ with $\epsilon_0 = 0$, and resonant occupation state $\bar{n} = \frac{1}{2}$. Real parts of self-energy subtract and we have

$$A(\omega) \approx \frac{|\langle 0 | 0 \rangle|^2 \Gamma}{\omega^2 + (\frac{|\langle 0 | 0 \rangle|^2 \Gamma}{2})^2}.$$  

(4.1.0.5)

Comparing with results for SPA, introduced Franck-Condon factors narrow and increase the magnitude of the peaks. In the next section treating double well potential, we will explain the origin of peaks in detail.

## 4.2 Double well potential

We would like to study more realistic situation. In real molecules, anharmonic potential are common, so we might choose one example of anharmonicity, double well potential with quasidegenerate levels.

$$h_0 = \frac{1}{2MI} \frac{\partial^2}{\partial \varphi^2} + 0.25(\cos(2\varphi) + 1)$$  

(4.2.0.6)

$$h_1 = \frac{1}{2MI} \frac{\partial^2}{\partial \varphi^2} + \cos(\varphi) + 1$$  

(4.2.0.7)

Potentials are more than just artificial. Besides it is intended to help us understand the effect of degeneration upon system, it can be used as a simple model of real situation. Imagine uncharged biphenyl in a weak electric field. Both aromatic cycles of molecule can rotate almost freely around the bond (barrier energy is very low), while equilibrium torsion angle is roughly $45^\circ$. However, if molecule is charged, shift in electronic structure brings equilibrium to about $90^\circ$ and barrier increases.

We have followed the idea of formerly introduced figures to discuss changes in the model, mainly due to degeneration of energy levels in electronically unoccupied
potential. The results for spectral function are presented in figures 4.3 and 4.4. The energy scale is in multiples of amplitude of cosine of ionic potential. Other parameters are $\beta = 100$ for inverse temperature and $MI = 4.0$ for moment of inertia. The figures differ in $\epsilon_0$, we can observe the same effect as we did in case of figures 4.1 and 4.2.

On this stage, we will take some time to explain the arising of the major peaks. At first, let’s remind, that very low temperature was assumed in our calculations and therefore Fermi-Dirac distribution is close to step function. For the junction it means, that mostly ground vibronic states are occupied and so, the lines in spectral function are transitions between excited vibronic states and ground state (transition to unoccupied state has peaks for $\omega > 0$ while to occupied $\omega < 0$). Following figure 4.5 illustrates the matter.

Values of figure 4.5 match values and settings in figure 4.3. In the middle part of picture, we can see three arrows indicating transitions from unoccupied states (either bound or semi-bound) to the ground occupied electronic state. We can see, that almost exclusively even-even transitions are allowed, as others are suppressed by Franck-Condon factors and conservation of symmetry of wave function. The arrows indicate transitions $\{|v_2\rangle, |v_4\rangle, |v_6\rangle\} \rightarrow |d_0\rangle$ with energies appropriate to the peaks for $\omega < 0$. Three dashed arrows to the right indicate transition $\{|d_0\rangle, |d_2\rangle, |d_4\rangle\} \rightarrow |v_0\rangle$, while $|d_0\rangle \rightarrow |v_0\rangle$ is tunneling long-lived transition and is responsible for the main peak, therefore, the main peak is slightly slanted to the positive $\omega$, all these transitions are translated into peaks for $\omega > 0$. The last arrow to mention is the dotted arrow to the right, this is $|d_1\rangle \rightarrow |v_1\rangle$, an odd-odd transition, only significant transition of this kind. The appropriate peak for this is marked by an arrow in figure 4.3b.

Closer inspection of figures 4.3 and 4.4 discloses the same effects as in case of LHO potential, namely cusps and narrowing of the peaks. A special effect, exclusive for systems with degeneration, can be further observed. As we have mentioned in general discussion, even parity of electronic-occupied ground state leads to disappearance of odd-state (of unoccupied electronic state) peaks due to Franck-Condon factors. On the graphs, however, we may note, that the peaks do not disappear altogether, but spectral lines are just very weak. We have pointed out such a peak in figure 4.3b, now, other odd-odd peaks have been marked by an arrow in figure 4.4a. Also, of course, rather substantial difference between potentials removes the symmetry observed for LHO potentials. Further, molecule tends to be in unoccupied state, because of bigger phase-space of unoccupied electronic states.

To conclude this section, figure 4.6 illustrates density of states for system in figures 4.3a and 4.4. Note, that presence of odd-parity states is in absolute accordance
Figure 4.3: Spectral function of double well potential with parameters $\epsilon_0 = 0$, and $\Gamma = 0.2$ for part (a), $\Gamma = 0.5$ for part (c). More detailed views of interval $(-1, 1)$ are also included (part (b) and (d)).

Figure 4.4: Spectral function of double well potential with parameters $\epsilon_0 = 0.5$ and $\Gamma = 0.2$. 
Figure 4.5: Transitions between electronic states with different vibronic states. Black solid lines are potentials, blue lines and numbers belong to vibronic states of ground electronic state, red lines and numbers to vibronic states of occupied electronic state, dashed lines are even states and dotted lines are odd states, arrows represent major calculated transitions.
with our markings in figures mentioned. Also note, that with the bare electron on-site energy introduced, ground unoccupied state becomes overwhelmingly prevailing.

### 4.3 Current comparison

Since main aim of this work was to calculate the current, at this point, it would be instructive to go back to introduced equation and illustrate, how is current actually evaluated. We have used the approximation outlined in section 3.4, assuming that the molecule is in thermal equilibrium with left lead, and that their chemical potentials are equal, and further $\mu_L = 0$. Since molecule is much closer to the left lead, it holds that coupling constant $\Gamma_L \gg \Gamma_R$. We have held the potential of the left lead $\mu_L = 0$
and induced a voltage by changing the potential on the right lead $\mu_R$.

Examining the equation for current, we can see, that the difference between Fermi-Dirac distribution creates a characteristic function (an integration window) for integration of part of Spectral function for energies belonging to such interval. As the distributions difference would extend beyond limits (i.e. voltage would grow beyond limits), we would integrate over whole spectral function and reach

$$J_{\text{max}} = ie \int \frac{d\epsilon}{2\pi} \Gamma_R [f_L(\epsilon) - f_R(\epsilon)] A(\epsilon) = ie \Gamma_R, \quad (4.3.0.8)$$

which would be the maximal current. Since we keep left lead potential at the same value, we may never reach the full current, however, in the figure 4.7, we refer to the integrated current in terms of share of maximal current.

It is important to note, that LHO positive and negative current is symmetrical, as we would expect from the spectral function. With the same argument it is obvious, that double well potential current is not symmetrical. Our expectation about zero current at zero voltage and negative current for negative voltage are met. It is all easy to see from the equation used.

Figure 4.7: Comparison of current for LHO potential and double well potential.
4.4 Way to molecules

To conclude this chapter, we present spectral functions calculated for higher moments of inertia (ranging to 150), therefore being better approximation to molecules. The figure 4.8 shows the trend of increasing inertia to smooth out the peaks. As it increases, the potential well fills with increasing number of states with smaller energy differences, therefore equilibrium density of states gives reasonable occupation probabilities even to non-ground states; particularly the degeneration of states $|v_0\rangle, |v_1\rangle$ becomes more obvious, as their energies merge, and their occupation probabilities are almost equal. The energies of ground vibronic states are lower, deeper in the potential well, and therefore much better localised.

First of all we notice, that zero-energy peak disappeared. This is result of Franck-Condon factors. If we recall, that these factors are overlaps of vibronic wave functions, it is obvious, that overlap of much better localized ground state wave functions are minimal. The reason, why spectral densities gather approximately around $\epsilon \approx -0.5$ and $\omega \approx 1$ is following: as mentioned, ground states are localized narrowly around potential minima, it means near rotational angles $\phi_v = \frac{\pi}{2}, \frac{3\pi}{2}, \phi_d = \pi$, on the other side, the most probable angle for the excited system to be in is turning point, where angular momentum is zero. So, the resonance condition follows, when these two points coincide, i.e. the turning angle with the potential minima.

So for the $\epsilon \approx -0.5$, wave functions of $|v\rangle$ are just under the edge of potential, having turning point at $\phi = \pi$, because the energy difference is lower compare to other peak, system has less $|d\rangle$ states to fall into and therefore, the peak is higher and narrower. The case of $\epsilon \approx 1$ is analogous, at that energy, turning angles are $\phi = \frac{\pi}{2}, \frac{3\pi}{2}$, which coincide with unoccupied minima. System has more states to transit to (especially two degenerate ground states $|v_0\rangle, |v_1\rangle$), so the peak is lower but wider.

Obviously, the secondary peak structure upon two major peaks are transitions between states close to major ones. It is also interesting to note, that Franck-Condon factors smooth out the narrow tall peaks caused by Fermi sea near zero energy.
Figure 4.8: Spectral function for molecules with increasing moment of inertia.
Chapter 5

CONCLUSIONS

Through progress of this work, we have put in the effort to consecutively explain the general theory of non-equilibrium Green functions and apply it on the problem of transport through single-vibration molecular junction. The equation of motion technique was utilized to derive the Green function of the system. To close the system of equations, we used mean-field (or Hartree-Fock) approximation suggested by Flensberg. We calculated spectral function and explained the origin of observed features. At first, we applied our equations to harmonic potential model of Flensberg to verify the implementation. Later, we have modified a model to feature double well potential with quasidegenerate energy levels and studied newly introduced effects. We used obtained spectral functions and calculated current in asymmetric setup, where a junction was in equilibrium with one lead. As part of discussion, we attempted to show relation between our method and elastic electron scattering.

The last stage of this work is meant to foreshadow possible extension of these calculations. Even though we have mentioned biphenyl molecule as a motivation for introduction of degenerate potential, it was necessary to use very small moment of inertia in order to carry out the calculation. With an increase of moment of inertia, the number of bound states increases rapidly, requiring a big number of basis functions to converge. Since computational demands scale with number of states like $N^6$, it is not plausible to continue with a wild enlargement of the basis set and new approximations and approach have to be explored.

Also, many interesting thing were not exploited, like calculation of a current with junction in true nonequilibrium, consideration of exchange term in self-energy equations, more than one vibronic and electronic state in the junction, spin degrees of freedom etc. All these matters could be studied in future work.
Bibliography


