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Molecular Transport

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Definitions and conventions

In this paper I will use some definitions and conventions that will be used in this paper. Most of them are explained here.

All the calculations are done in atomic units. This means $c = \hbar = m_e = e = 1$. This greatly reduces the number of constants that have to be carried around with every equation.

Some notation conventions:

- $\partial_a = \partial/\partial a$, the partial derivative
- $\dot{r} = \partial_t r$, the time derivative
- $r' = \partial_x r$, the space derivative
- $\beta = [k_B T]^{-1}$, the inverse temperature
- $[A, B] = AB - BA$, the commutator
- $\{A, B\} = AB + BA$, the anti-commutator
- $\delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{cases}$, the Kronecker delta
- $\delta(t_1, t_2)$ the Dirac delta function *on the contour*
- $\theta(t_1, t_2)$ the step function *on the contour*

Further I will use bold face type setting to indicate matrices.

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Chapter 1

Introduction

Since the conductance through a single molecule has been measured, the interest in the molecular transport problem has been greatly increased [1]. Lot of groups have directed their research on the problem. The problem has mainly been treated by the Landauer–Büttiker formalism [2, 3], but this formalism is limited to describing non-interacting electrons in a steady state. Recently it has been treated by non-equilibrium Green’s functions in such a way that the time-dependent current could be calculated but it has still been done in a partitioned approach [4]. The device and the two leads are treated as separate systems at a different chemical potential. To simulate the switch on, the leads are brought in contact with the molecule and a current starts to flow. This is not realistic, since the device is before the switch on already in an equilibrium together with the leads. Instead, the equilibrium for the whole system should be calculated and then the bias voltage should be switched on [5]. Due to electron correlations and de-phasing the system might show memory effects, which makes it uncertain if the steady state current of the two approaches is the same.

In my thesis I will concentrate on the molecular transport problem for non-interacting particles. This will exclude the study of memory effects due to electron correlations. Memory effects will only appear due to de-phasing. For semi-infinite leads the occupied orbitals cover a continuous energy spectrum, which ensures that switch on effects do not effect the steady state current. For finite sized leads however the spectrum is discrete and complete de-phasing is not assured.

Although electron correlations are excluded in this thesis, they can be included using Time Dependent Density Functional Theory (TDDFT) [6]. TDDFT is an exact theory which describes interacting many-particle systems in terms of non-interacting particles. This makes the study of molecular transport for non-interacting particles very useful.

The thesis consists of two parts. The first part will treat the problem by using non-equilibrium Green’s functions, which enables an analytic treatment and the use of semi-infinite leads by the self energy Σ . The first chapter is devoted to the definitions and properties of the Green’s functions in the hope to make the material understandable for non-experts in the non-equilibrium Green’s function technique. However, I limited the description to only the necessary elements to treat the molecular transport problem. Green’s functions are much more versatile and references are given for the reader who wants to know more about them. Some knowledge is assumed on second quantization and complex analysis.

The second chapter deploys the Green’s functions to treat the molecular transport problem for a simple model system. An equation for the time-dependent current is obtained and some results are shown.

The second part focusses on solving the problem by solving the time-dependent Schrödinger equation. Unfortunately the formulation of the problem in terms the Schrödinger equation makes it impossible to include semi-infinite leads. Therefore the leads will have a finite size and de-phasing might not be complete. The first chapter deals with the formalism required to do numerical calculations with the

Schrödinger equation. The next chapter shows a simple application to the 2 level system.

The following chapter deals with a 1 dimensional model, to simulate the transport problem. The two leads are simulated by placing a barrier in a box with infinite walls. Then at some time the potential is raised in one of the region and particles start to flow to the other side of the box. I will show some results and draw some conclusions.

The last chapter treats a 3 dimensional model. The barrier has now the shape of a sheet throughout the box. This will be a much better model, since the current flowing through the device can spread through the volume. Therefore the current density will fall of as $\sim 1/r^2$ and become zero at infinity. In this model there is also a local potential included to simulate the device. Unfortunately only few results are available and there was not enough time to evaluate them thoroughly.

All the calculations are done in atomic units, i.e. $c = \hbar = m_e = e = 1$. More conventions are explained just after the title page.

Chapter 2

Non-equilibrium Green's functions

This chapter deals with a number of basic principles of Green's functions which are necessary to calculate the time-dependent current in a molecular transport system. Therefore the description is quite limited and not all possibilities of the Green's functions are explained. The Green's functions are only treated for non-interacting particle system, but they can also be written for systems where the particles do interact. For interacting systems especially Green's functions turn out to be a very good tool to describe the system properties. For more information on equilibrium Green's functions see [13, 14, 15, 16] and for information on non-equilibrium Green's functions see [8, 9, 10, 11, 12, 5].

Further it is assumed that the reader is familiar with second quantization and complex analysis. For more information about second quantization most of the solid state books will do, for example [14, 17]. More information about complex analysis can be found in any mathematical book about this subject such as [23].

2.1 The evolution operator

In this section we will introduce the evolution operator $\hat{U}(t, t')$ and its properties are derived from the Schrödinger equation. At the end the Heisenberg operator is defined and we use it to obtain the expectation value for an operator for an equilibrium system in the grand canonical ensemble. The evolution operator will be used in the next chapter to define the Green's function on the Keldysh contour.

The time-dependent Schrödinger equation (TDSE), $i\partial_t\Psi(\mathbf{r}, t) = \hat{H}(t)\Psi(\mathbf{r}, t)$, is basically just a first order differential equation in time t . Usually it is very easy for these equations to find a solution, but the Schrödinger equation involves an operator which is generally time-dependent. However, formally there is no problem to solve the equation. We are looking for a solution of the form

$$\Psi(t) = \hat{U}(t, t')\Psi(t'), \quad (2.1)$$

which defines the evolution operator $\hat{U}(t, t')$. It is a mapping of a function at t' to t . The most obvious property of the evolution operator is: $\hat{U}(t, t) = 1 \quad \forall t$. Other properties can be obtained by differentiating equation 2.1 with respect to t and using the TDSE

$$i\partial_t\hat{U}(t, t')\Psi(t') = \hat{H}(t)\hat{U}(t, t')\Psi(t'). \quad (2.2)$$

Since equation 2.2 has to hold for every $\Psi(t')$ it reduces to

$$i\partial_t\hat{U}(t, t') = \hat{H}(t)\hat{U}(t, t'). \quad (2.3)$$

In a similar way one can find a property for the derivative of the evolution operator with respect to t'

$$i\partial_{t'}\hat{U}(t, t') = -\hat{U}(t, t')\hat{H}(t'). \quad (2.4)$$

So the evolution operator satisfies the following relations

$$\hat{U}(t, t) = 1 \quad (2.5)$$

$$i\partial_t \hat{U}(t, t') = \hat{H}(t) \hat{U}(t, t') \quad (2.6)$$

$$i\partial_{t'} \hat{U}(t, t') = -\hat{U}(t, t') \hat{H}(t') \quad (2.7)$$

These relations completely define the properties of the evolution operator. The differential equation 2.6 can be transformed to an integral integration

$$\hat{U}(t, t') - \hat{U}(t', t') = \int_{t'}^t dt_1 \partial_{t_1} \hat{U}(t_1, t') = -i \int_{t'}^t dt_1 \hat{H}(t_1) \hat{U}(t_1, t'). \quad (2.8)$$

So we obtain a recursive equation which defines $\hat{U}(t, t')$

$$\hat{U}(t, t') = 1 - i \int_{t'}^t dt_1 \hat{H}(t_1) \hat{U}(t_1, t'). \quad (2.9)$$

By iterating this expression an equation for $\hat{U}(t, t')$ can be found in terms of $\hat{H}(t)$ only:

$$\begin{aligned} \hat{U}(t, t') &= 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \dots \int_{t'}^{t_{n-1}} dt_n \hat{H}(t_1) \dots \hat{H}(t_n) \\ &= 1 + \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \dots \int_{t'}^{t_{n-1}} dt_n \begin{cases} \mathcal{T} [\hat{H}(t_1) \dots \hat{H}(t_n)] & \text{for } t \geq t' \\ \tilde{\mathcal{T}} [\hat{H}(t_1) \dots \hat{H}(t_n)] & \text{for } t \leq t' \end{cases} \end{aligned} \quad (2.10)$$

where in the last step the time-ordered product and its anti-chronological counter part are used

$$\mathcal{T} [\hat{O}(t_1) \dots \hat{O}(t_n)] = \sum_P \theta(t_{P(1)} - t_{P(2)}) \dots \theta(t_{P(n-1)} - t_{P(n)}) \hat{O}(t_{P(1)}) \dots \hat{O}(t_{P(n)}) \quad (2.11)$$

$$\tilde{\mathcal{T}} [\hat{O}(t_1) \dots \hat{O}(t_n)] = \sum_P \theta(t_{P(1)} - t_{P(2)}) \dots \theta(t_{P(n-1)} - t_{P(n)}) \hat{O}(t_{P(n)}) \dots \hat{O}(t_{P(1)}), \quad (2.12)$$

where P runs over all permutations of the numbers $1 \dots n$. The time-ordered product orders the operators by time with the latest time on the left and for the anti-chronological time-ordered product the latest time is on the right. Formally the sum can be written as an exponential:

$$\hat{U}(t, t') = \mathcal{T} \exp \left[-i \int_{t'}^t d\tau \hat{H}(\tau) \right] \text{ for } t \geq t' \quad (2.13)$$

$$\hat{U}(t, t') = \tilde{\mathcal{T}} \exp \left[-i \int_{t'}^t d\tau \hat{H}(\tau) \right] \text{ for } t \leq t'. \quad (2.14)$$

From numerical point of view this kind of formalism is useless since the time-ordering is very expensive to calculate. However, for time-independent Hamiltonians the time-ordering can be dropped and the integral can be evaluated explicitly. This gives the better known result

$$\hat{U}(t, t') = e^{-i(t-t')\hat{H}} \quad (2.15)$$

It is not specified that the evolution operator has to work on the wave function as is assumed in the Schrödinger picture. One can equally well put the time dependence in the operators and connect the evolution operator to the operators, which is generally known as the Heisenberg picture

$$\langle \hat{O} \rangle(t) = \langle \Psi(t) | \hat{O} | \Psi(t) \rangle = \langle \Psi | \hat{U}(t_0, t) \hat{O} \hat{U}(t, t_0) | \Psi \rangle = \langle \Psi | \hat{O}(t) | \Psi \rangle. \quad (2.16)$$

This equation suggests some time contour starting from t_0 where the system is described by the state $|\Psi\rangle$. It then goes to t where the operator acts and then goes back again to t_0 .

With the use of equations 2.6 and 2.7, the Schrödinger equation can now be rewritten in an equation of motion for the operator

$$\begin{aligned} i\partial_t \hat{O}(t) &= i\partial_t \hat{U}(t_0, t) \hat{O} \hat{U}(t, t_0) = \hat{U}(t_0, t) \hat{O} \hat{H}(t) \hat{U}(t, t_0) - \hat{U}(t_0, t) \hat{H}(t) \hat{O} \hat{U}(t, t_0) \\ &= \hat{U}(t_0, t) [\hat{O}, \hat{H}(t)] \hat{U}(t, t_0) \end{aligned} \quad (2.17)$$

We will now derive the expectation value of an observable for an equilibrium system in the grand canonical ensemble. The system in its equilibrium is described by the Hamiltonian

$$\hat{H}_0 = \hat{T} + \hat{V} - \mu \hat{N}, \quad (2.18)$$

where μ is the chemical potential and \hat{N} is the particle number operator. The expectation value of an observable for some eigen state $|\Psi_i\rangle$ with an energy E_i , $\langle \hat{O} \rangle_i(t)$, is given by equation 2.16. In the grand canonical ensemble the expectation value of an operator is written as a weighted average of the observable over the whole ensemble:

$$\langle \hat{O} \rangle(t) = \frac{\sum_i e^{-\beta E_i} \langle \hat{O} \rangle_i(t)}{\sum_i e^{-\beta E_i}}, \quad (2.19)$$

where the chemical potential was already in the definition of the Hamiltonian. Note the ambiguity in the notation of the expectation value with respect to the whole ensemble and for the state i .

Combining these two equations we can write the expectation value as:

$$\begin{aligned} \langle \hat{O} \rangle(t) &= \frac{\sum_i e^{-\beta E_i} \langle \Psi_i | \hat{O}(t) | \Psi_i \rangle}{\sum_i e^{-\beta E_i} \langle \Psi_i | \Psi_i \rangle} = \frac{\sum_i \langle \Psi_i | e^{-\beta E_i} \hat{O}(t) | \Psi_i \rangle}{\sum_i \langle \Psi_i | e^{-\beta E_i} | \Psi_i \rangle} \\ &= \frac{\sum_i \langle \Psi_i | e^{-\beta \hat{H}_0} \hat{O}(t) | \Psi_i \rangle}{\sum_i \langle \Psi_i | e^{-\beta \hat{H}_0} | \Psi_i \rangle} = \frac{\text{Tr} \{ e^{-\beta \hat{H}_0} \hat{O}(t) \}}{\text{Tr} \{ e^{-\beta \hat{H}_0} \}}, \end{aligned} \quad (2.20)$$

where we have written \hat{H}_0 to indicate the Hamiltonian that describes equilibrium of the system and have introduced the trace in the last step. The trace of an operator is defined as

$$\text{Tr} \{ \hat{A} \} = \sum_i \langle \Psi_i | \hat{A} | \Psi_i \rangle, \quad (2.21)$$

where $\{|\Psi_i\rangle\}$ is a complete set in Fock space.

2.2 Green's function on the Keldysh contour

In this section we will define the Green's function on the Keldysh contour. The Keldysh contour does not run only over the real time axis, but has also a part on the imaginary axis, which describes the initial conditions of the system in a very elegant way. Finally anti-periodic boundary conditions will be derived for the Green's function.

As explained in the previous section, the expectation value for an operator in the grand canonical ensemble can be written as

$$\langle \hat{O} \rangle(t) = \frac{\text{Tr} \left\{ e^{-\beta \hat{H}_0} \hat{U}(t_0, t) \hat{O} \hat{U}(t, t_0) \right\}}{\text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\}}, \quad (2.22)$$

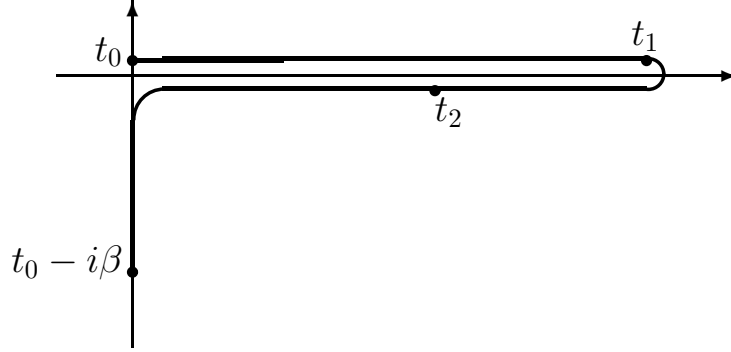


Figure 2.1: Keldysh contour. Forward and backwards parts are on the real time axis, but they are plotted slightly of the axis to display the two branches more clearly. In this case t_1 is earlier than t_2 on the contour, although t_1 is later than t_2 in real time.

where the hamiltonian \hat{H}_0 describes the system in its equilibrium state at $t = t_0$. The operator $e^{-\beta\hat{H}_0}$ can be regarded as the evolution operator in imaginary time

$$\hat{U}(t_0 - i\beta, t_0) = e^{-\beta\hat{H}_0}. \quad (2.23)$$

This allows us to write the expression for the expectation value of the operator as

$$\langle \hat{O} \rangle(t) = \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \hat{U}(t_0, t) \hat{O} \hat{U}(t, t_0) \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} \quad (2.24)$$

If the expression is read from right to left, the system evolves from t_0 to t where the operator acts. Then it evolves back from t to t_0 and finally evolves along the imaginary axis to $t_0 - i\beta$. Therefore it is convenient to define a contour C as shown in figure 2.1, which was originally introduced by Keldysh [7]. In this case there is only one time $t = t_1 = t_2$.

Equation 2.24 can now be rewritten in terms of integrals over the contour

$$\langle \hat{O} \rangle(t) = \frac{\text{Tr} \left\{ \mathcal{T}_C \left[\exp(-i \int_C dt' \hat{H}(t')) \hat{O}(t) \right] \right\}}{\text{Tr} \left\{ \mathcal{T}_C \left[\exp(-i \int_C dt' \hat{H}(t')) \right] \right\}}, \quad (2.25)$$

where the exponential is defined by its expansion

$$\mathcal{T}_C \left[\exp(-i \int_C dt' \hat{H}(t')) \hat{O}(t) \right] \equiv \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_C dt_1 \dots dt_n \mathcal{T}_C \left[\hat{O}(t) \hat{H}(t_1) \dots \hat{H}(t_n) \right] \quad (2.26)$$

and the contour ordered product is defined as

$$\mathcal{T}_C \left[\hat{A}_1(t_1) \dots \hat{A}_n(t_n) \right] \equiv \sum_P \theta(t_{P(1)}, t_{P(2)}) \dots \theta(t_{P(n-1)}, t_{P(n)}) \hat{A}_{P(1)}(t_{P(1)}) \dots \hat{A}_{P(n)}(t_{P(n)}) \quad (2.27)$$

Here we have used $\theta(t_1, t_2)$ which is the contour step function. It is just a generalization of the normal step function θ , but now defined for the contour

$$\theta(t_1, t_2) = \begin{cases} 1 & \text{if } t_1 \text{ is later on the contour than } t_2 \\ 0 & \text{otherwise} \end{cases} \quad (2.28)$$

The one-particle Green's function can be defined on the contour as

$$\begin{aligned} G_{ij}(t_1, t_2) &\equiv \frac{1}{i} \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \mathcal{T}_C [\hat{c}_i(t_1) \hat{c}_j^\dagger(t_2)] \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} \\ &= -i \langle \mathcal{T}_C [\hat{c}_i(t_1) \hat{c}_j^\dagger(t_2)] \rangle, \end{aligned} \quad (2.29)$$

where $\hat{c}_i^\dagger(t_1)$ and $\hat{c}_i(t_2)$ are the usual creation and annihilation operators for fermions which obey the usual anti-commutation relations

$$\{\hat{c}_i, \hat{c}_j\} = \{\hat{c}_i^\dagger, \hat{c}_j^\dagger\} = 0 \quad \{\hat{c}_i, \hat{c}_j^\dagger\} = \delta_{ij}. \quad (2.30)$$

Note that the Green's function has two time arguments that are ordered on the contour, t_1 and t_2 (see fig. 2.1).

The Green's function can be split into two parts

$$G_{ij}(t_1, t_2) = \theta(t_1, t_2) G_{ij}^>(t_1, t_2) + \theta(t_2, t_1) G_{ij}^<(t_1, t_2), \quad (2.31)$$

where the greater and lesser Green's function ($G_{ij}^>(t_1, t_2)$ and $G_{ij}^<(t_1, t_2)$) are defined as

$$G_{ij}^>(t_1, t_2) \equiv -i \langle \hat{c}_i(t_1) \hat{c}_j^\dagger(t_2) \rangle \quad (2.32)$$

$$G_{ij}^<(t_1, t_2) \equiv i \langle \hat{c}_j^\dagger(t_2) \hat{c}_i(t_1) \rangle \quad (2.33)$$

The Green's function has anti-periodic boundary conditions. These can be derived by considering the Green's function at $t_1 = t_0 - i\beta$ and using the cyclic property of the trace

$$\begin{aligned} G_{ij}(t_0 - i\beta, t_2) &= \frac{1}{i} \frac{\text{Tr} \left\{ \hat{c}_i \hat{U}(t_0 - i\beta, t_2) \hat{c}_j^\dagger \hat{U}(t_2, t_0) \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} \\ &= \frac{1}{i} \frac{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_2) \hat{c}_j^\dagger \hat{U}(t_2, t_0) \hat{c}_i \right\}}{\text{Tr} \left\{ \hat{U}(t_0 - i\beta, t_0) \right\}} = -G_{ij}(t_0, t_2) \end{aligned} \quad (2.34)$$

A similar property can be found for the other time-coordinate $G_{ij}(t_1, t_0) = -G_{ij}(t_1, t_0 - i\beta)$.

2.3 Green's function calculated from the Schrödinger equation

We will now derive an expression for the Green's function from the Schrödinger equation. This equation will be used in the next section to illustrate the correspondence between the Green's function for the Schrödinger equation and the Keldysh Green's function.

The Schrödinger equation does not involve any temperature, so we can limit ourselves to the real time axis. Consider a non-interacting system described by the Hamiltonian

$$\hat{H}(t) = \sum_{i,j} h_{ij}(t) \hat{c}_i^\dagger \hat{c}_j, \quad (2.35)$$

where the matrix $h_{ij}(t)$ is the one-particle hamiltonian in the chosen basis $\{\phi\}$

$$h_{ij}(t) = \langle \phi_i | \hat{H}(t) | \phi_j \rangle = \langle \phi_i | \hat{T} + \hat{V}(t) | \phi_j \rangle - \mu \delta_{ij} = h_{ji}^*(t), \quad (2.36)$$

where \hat{T} is the kinetic energy operator, $\hat{V}(t)$ is the external potential and μ is the chemical potential. The fermion creation and annihilation operators (\hat{c}_i^\dagger and \hat{c}_i) obey the usual anti-commutation relations (eq. 2.30). The greater and lesser Green's functions \mathbf{G}^\lessgtr are still defined by equations 2.32 and 2.33 and the retarded and advanced Green's function $\mathbf{G}^{R,A}$ can be defined as

$$\mathbf{G}^R(t_1, t_2) \equiv \theta(t_1 - t_2) [\mathbf{G}^>(t_1, t_2) - \mathbf{G}^<(t_1, t_2)] \quad (2.37)$$

$$\mathbf{G}^A(t_1, t_2) \equiv -\theta(t_2 - t_1) [\mathbf{G}^>(t_1, t_2) - \mathbf{G}^<(t_1, t_2)]. \quad (2.38)$$

Since \hat{c}_i^\dagger and \hat{c}_i are operators, we can use equation 2.17 to obtain equation of motions for them. First consider the commutators of the creation and annihilation operators with the Hamiltonian. Using the identity $[A, BC] = \{A, B\}C - B\{A, C\}$ we obtain

$$[\hat{c}_i, \hat{H}(t)] = \sum_{j,k} h_{jk}(t) [\hat{c}_i, \hat{c}_j^\dagger \hat{c}_k] = \sum_i h_{ij}(t) \hat{c}_j \quad \text{and} \quad [\hat{c}_i^\dagger, \hat{H}(t)] = -\sum_i \hat{c}_j^\dagger h_{ji}(t) \quad (2.39)$$

So the equation of them become

$$i\partial_t \hat{c}_i(t) = \sum_j h_{ij}(t) \hat{c}_j(t) \quad \text{and} \quad i\partial_t \hat{c}_i^\dagger(t) = -\sum_j \hat{c}_j^\dagger(t) h_{ji}(t) \quad (2.40)$$

It is possible from these equations to express \mathbf{G}^\lessgtr in terms of $\mathbf{G}^{R,A}$. Therefore we separate the time-dependent part from $\hat{c}_i^\dagger(t)$ and $\hat{c}_i(t)$ by introducing the evolution matrix $S_{ij}(t)$

$$\hat{c}_i^\dagger(t) = \sum_j \hat{c}_j^\dagger S_{ji}^\dagger(t) \quad \text{and} \quad \hat{c}_i(t) = \sum_j S_{ij}(t) \hat{c}_j \quad (2.41)$$

The evolution matrix $\mathbf{S}(t)$ satisfies the Schrödinger equation

$$i\partial_t \mathbf{S}(t) = \mathbf{h}(t) \mathbf{S}(t), \quad (2.42)$$

with the obvious boundary condition $\mathbf{S}(0) = \mathbf{1}$.

Note that these equations define a connection between the evolution operator $\mathbf{S}(t)$ and the evolution operator $\hat{U}(t_1, t_2)$ defined in equation 2.1. For the operator \hat{c}_i the relation can be expressed as

$$\sum_j S_{ij}(t) \hat{c}_j = \hat{U}(t_0, t) \hat{c}_i \hat{U}(t, t_0), \quad (2.43)$$

where t_0 is defined as the time from where the systems evolution is calculated. As similar equation can also be written for \hat{c}_i^\dagger .

So the lesser and the greater Green's functions in these expansions for the creation and annihilation operator become

$$G_{ij}^>(t_1, t_2) = -i \sum_{k,l} S_{ik}(t_1) \langle \hat{c}_k \hat{c}_l^\dagger \rangle S_{lj}^\dagger(t_2) \quad (2.44)$$

$$G_{ij}^<(t_1, t_2) = i \sum_{k,l} S_{ik}(t_1) \langle \hat{c}_k^\dagger \hat{c}_l \rangle S_{lj}^\dagger(t_2). \quad (2.45)$$

The retarded and advanced Green's function can be expressed solely in the evolution operator $\mathbf{S}(t)$

$$\begin{aligned} G_{ij}^R(t_1, t_2) &\equiv \theta(t_1 - t_2) [G_{ij}^>(t_1, t_2) - G_{ij}^<(t_1, t_2)] = -i\theta(t_1 - t_2) \sum_{k,l} S_{ik}(t_1) \langle \{\hat{c}_k, \hat{c}_l^\dagger\} \rangle S_{lj}^\dagger(t_2) \\ &= -i\theta(t_1 - t_2) \sum_k S_{ik}(t_1) S_{kj}^\dagger(t_2) \end{aligned} \quad (2.46)$$

$$\begin{aligned} G_{ij}^A(t_1, t_2) &\equiv -\theta(t_2 - t_1) [G_{ij}^>(t_1, t_2) - G_{ij}^<(t_1, t_2)] = i\theta(t_2 - t_1) \sum_{k,l} S_{ik}(t_1) \langle \{\hat{c}_k, \hat{c}_l^\dagger\} \rangle S_{lj}^\dagger(t_2) \\ &= i\theta(t_2 - t_1) \sum_k S_{ik}(t_1) S_{kj}^\dagger(t_2) \end{aligned} \quad (2.47)$$

With the use of these equations, the time-dependence can be expressed by the retarded and advanced Green's function. Equations 2.44 and 2.45 can be rewritten in terms of their initial form $\mathbf{G}^{\lessgtr}(0, 0)$

$$\mathbf{G}^{\lessgtr}(t_1, t_2) = \mathbf{G}^R(t_1, 0) \mathbf{G}^{\lessgtr}(0, 0) \mathbf{G}^A(0, t_2) \quad (2.48)$$

The term $\mathbf{G}^{\lessgtr}(0, 0)$ contains only information of the initial state at $t = 0$.

2.4 Using the Keldysh formalism

In this section we will show how to use the Keldysh formalism for the simple example of a non-interacting system. We will derive an equation which is exactly the same as equation 2.48 derived in the previous section for the Schrödinger equation. This shows that at least for non-interacting systems both give the same results.

For a simple Hamiltonian which is diagonal $H_0(t) = \sum_i \epsilon_i(t) \hat{c}_i^\dagger \hat{c}_i$, the Green's function can be calculated exactly. The evolution matrix $\mathbf{S}^0(t)$ can be simply written as

$$S_{ij}^0(t) = \delta_{ij} e^{-i \int_0^t dt' \epsilon_i(t')} \quad (2.49)$$

Further it is derived in the appendix A.1 that

$$\langle \hat{c}_i^\dagger \hat{c}_j \rangle_0 = \frac{\text{Tr} \left\{ e^{-\beta \hat{H}_0} \hat{c}_i^\dagger \hat{c}_j \right\}}{\text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\}} = \frac{\delta_{ij}}{e^{\beta \epsilon_i} + 1} = \delta_{ij} f(\epsilon_i) \quad \text{and} \quad \langle \hat{c}_i \hat{c}_j^\dagger \rangle_0 = \delta_{ij} (1 - f(\epsilon_i)), \quad (2.50)$$

where $f(\epsilon)$ is the usual Fermi distribution function. In accordance with equations 2.32 and 2.33 we can write the Green's functions as

$$g_{ij}^<(t_1, t_2) = i \langle \hat{c}_i^\dagger(t_2) \hat{c}_j(t_1) \rangle_0 = i \delta_{ij} f(\epsilon_i) e^{-i \int_{t_2}^{t_1} dt' \epsilon_i(t')} \quad (2.51)$$

$$g_{ij}^>(t_1, t_2) = -i \langle \hat{c}_i(t_1) \hat{c}_j^\dagger(t_2) \rangle_0 = -i \delta_{ij} (1 - f(\epsilon_i)) e^{-i \int_{t_2}^{t_1} dt' \epsilon_i(t')}, \quad (2.52)$$

It is easy to show by inserting the Green's function $\mathbf{g}(t_1, t_2) = \theta(t_1, t_2) \mathbf{g}^>(t_1, t_2) + \theta(t_2, t_1) \mathbf{g}^<(t_1, t_2)$ into the Schrödinger equation that it satisfies the equation of motion

$$[i\partial_{t_1} - \epsilon(t_1)] g_{ij}(t_1, t_2) = \delta(t_1, t_2) \delta_{ij} \quad \text{and} \quad [-i\partial_{t_2} - \epsilon(t_2)] g_{ij}(t_1, t_2) = \delta(t_1, t_2) \delta_{ij}. \quad (2.53)$$

That is why it is called a Green's function. The Green's function $\mathbf{G}(t_1, t_2)$ for a hamiltonian with off-diagonal elements $\hat{H}(t) = \hat{H}_0(t) + \sum_{i,j} V_{ij}(t) \hat{c}_i^\dagger \hat{c}_j$ however satisfies the equations

$$[i\partial_{t_1} - \epsilon(t_1)] G_{ij}(t_1, t_2) = \delta(t_1, t_2) \delta_{ij} + V_{ik}(t_1) G_{kj}(t_1, t_2) \quad (2.54)$$

$$[-i\partial_{t_2} - \epsilon(t_2)] G_{ij}(t_1, t_2) = \delta(t_1, t_2) \delta_{ij} + G_{ik}(t_1, t_2) V_{kj}(t_2) \quad (2.55)$$

Combining equations 2.53, 2.54 and 2.55, $\mathbf{G}(t_1, t_2)$ can be expressed in terms of $\mathbf{g}(t_1, t_2)$ in an integral form

$$\mathbf{G}(t_1, t_2) = \mathbf{g}(t_1, t_2) + \int_C dt' \mathbf{g}(t_1, t') \mathbf{V}(t') \mathbf{G}(t', t_2) = \mathbf{g}(t_1, t_2) + \int_C dt' \mathbf{G}(t_1, t') \mathbf{V}(t') \mathbf{g}(t', t_2) \quad (2.56)$$

where the C indicates that the integral has to be taken along the contour. Note that the time variables are now on the contour, so the Kronecker delta is only 1 when both times are equal *on the contour*.

Consider now a time t_1 later than t_2 on the contour. The Green's function can then be written as $\mathbf{G} = \mathbf{G}^>$. The Green's function satisfies the equation (see appendix A.2)

$$\begin{aligned} \mathbf{G}^>(t_1, t_2) &= \mathbf{g}^>(t_1, t_2) + \int_0^\infty dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') \mathbf{G}^>(t', t_2) + \int_0^\infty dt' \mathbf{g}^>(t_1, t') \mathbf{V}(t') \mathbf{G}^A(t', t_2) \\ &\quad - i \int_0^\beta d\tau \mathbf{g}^\lceil(t_1, \tau) \mathbf{V}(\tau) \mathbf{G}^\lceil(\tau, t_2), \end{aligned} \quad (2.57)$$

where we introduced the symbols \lceil and \lrcorner to denote

$$a^\lceil(t, \tau) = a^<(t, t_0 - i\tau) \quad (2.58)$$

$$a^\lrcorner(\tau, t) = a^>(t_0 - i\tau, t). \quad (2.59)$$

The retarded and advanced Green's functions are defined as in equations 2.37 and 2.38. The expression can be written in a even more condensed form by introducing

$$a \cdot b = \int_0^\infty dt' a(t') b(t') \quad (2.60)$$

$$a \star b = -i \int_0^\beta d\tau a(\tau) b(\tau). \quad (2.61)$$

The equation for the greater Green's function can now be written as

$$\mathbf{G}^>(t_1, t_2) = \mathbf{g}^>(t_1, t_2) + [\mathbf{g}^R \cdot \mathbf{V} \cdot \mathbf{G}^>](t_1; t_2) + [\mathbf{g}^> \cdot \mathbf{V} \cdot \mathbf{G}^A](t_1; t_2) + [\mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner](t_1; t_2). \quad (2.62)$$

This can be rewritten as

$$(\mathbf{1} - \mathbf{g}^R \cdot \mathbf{V}) \cdot \mathbf{G}^> = \mathbf{g}^> \cdot [\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^A] + \mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner, \quad (2.63)$$

where we dropped the time arguments for shorter notation. Using the identity $(\mathbf{1} - \mathbf{g}^R \cdot \mathbf{V}) = \mathbf{g}^R \cdot (\mathbf{G}^R)^{-1}$ (eq. A.14 rewritten) we can write this as

$$\mathbf{g}^R \cdot (\mathbf{G}^R)^{-1} \cdot \mathbf{G}^> = \mathbf{g}^> \cdot [\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^A] + \mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner \quad (2.64)$$

This equation can be solved by multiplying on both sides with $\mathbf{G}^R \cdot (\mathbf{g}^R)^{-1} = (\mathbf{1} + \mathbf{G}^R \cdot \mathbf{V})$,

$$\begin{aligned} \mathbf{G}^> &= \mathbf{G}^R \cdot (\mathbf{g}^R)^{-1} \cdot \mathbf{g}^> [\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^A] + \mathbf{G}^R \cdot (\mathbf{g}^R)^{-1} \cdot \mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner \\ &= (\mathbf{1} + \mathbf{G}^R \cdot \mathbf{V}) \cdot \mathbf{g}^> [\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^A] + (\mathbf{1} + \mathbf{G}^R \cdot \mathbf{V}) \cdot \mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner. \end{aligned} \quad (2.65)$$

Using the relations $\mathbf{g}^> = \mathbf{g}^R(t_1, 0) \mathbf{g}(0, 0) \mathbf{g}^A(0, t_2)$, $\mathbf{g}^\lceil(t, \tau) = \mathbf{g}^R(t, 0) \mathbf{g}^\lceil(0, \tau)$ and equation 2.56, the equation can be simplified to

$$\mathbf{G}^>(t_1, t_2) = \mathbf{G}^R(t_1, 0) \mathbf{g}^>(0, 0) \mathbf{G}^A(0, t_2) + \mathbf{G}^R(t_1, 0) [\mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner](0; t_2). \quad (2.66)$$

A similar treatment for $\mathbf{G}^<$ gives as similar result

$$\mathbf{G}^<(t_1, t_2) = \mathbf{G}^R(t_1, 0) \mathbf{g}^<(0, 0) \mathbf{G}^A(0, t_2) + \mathbf{G}^R(t_1, 0) [\mathbf{g}^\lceil \star \mathbf{V} \star \mathbf{G}^\lrcorner](0; t_2). \quad (2.67)$$

Note that the second part of these equations contains the contributions to the Green's functions $\mathbf{G}^{\lessgtr}(t_1, t_2)$ due to the initial conditions. If for some reason the last term becomes zero for $t \rightarrow \infty$, the steady state solution will be independent of initial state.

Using equation 2.56 and then using $\mathbf{g}^\Gamma(\tau, t) = \mathbf{g}^\Gamma(\tau, 0)\mathbf{g}^A(0, t)$ the Green's function $\mathbf{G}^\Gamma(\tau, t)$ can be written as

$$\begin{aligned} \mathbf{G}^\Gamma(\tau, t) &= \mathbf{g}^\Gamma(\tau, t) + \left[\mathbf{g}^\Gamma \cdot \mathbf{V} \cdot \mathbf{G}^A \right] (\tau; t) + \left[\mathbf{g} \star \mathbf{V} \star \mathbf{G}^\Gamma \right] (\tau; t) \\ \Rightarrow \left[(\mathbf{1} - \mathbf{g} \star \mathbf{V}) \star \mathbf{G}^\Gamma \right] (\tau; t) &= \mathbf{g}^\Gamma(\tau, 0) \left[\mathbf{g}^A \cdot (\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^A) \right] (0; t) = \mathbf{g}^\Gamma(\tau, 0)\mathbf{G}^A(0, t) \end{aligned} \quad (2.68)$$

The left hand of this equation contains the term $(\mathbf{1} - \mathbf{g} \star \mathbf{V}) = \mathbf{g} \cdot \mathbf{G}^{-1}$, which we can get rid of by multiplying on both sides with $\mathbf{G} \cdot \mathbf{g}^{-1} = (\mathbf{1} + \mathbf{G} \cdot \star \mathbf{V})$

$$\mathbf{G}^\Gamma(\tau, t) = \mathbf{G}^\Gamma(\tau, 0)\mathbf{G}^A(0, t) \quad (2.69)$$

Using this result, we rewrite equations 2.66 and 2.67 as

$$\begin{aligned} \mathbf{G}^{\lessgtr}(t_1, t_2) &= \mathbf{G}^R(t_1, 0) \left(\mathbf{g}^{\lessgtr}(0, 0) + [\mathbf{g}^\Gamma \star \mathbf{V} \star \mathbf{G}^\Gamma](0; 0) \right) \mathbf{G}^A(0, t_2) \\ &= \mathbf{G}^R(t_1, 0)\mathbf{G}^{\lessgtr}(0, 0)\mathbf{G}^A(0, t_2), \end{aligned} \quad (2.70)$$

which is exactly the same equation as equation 2.48. This assures that the Green's function on the Keldysh contour agrees with the Schrödinger equation.

2.5 Observables

From the definition of the Green's functions it is clear that the density is given by

$$n_i(t) = -iG_{ii}^<(t, t) \quad (2.71)$$

Taking the derivative to t , we obtain the change in particle numbers which can be related to the current

$$\begin{aligned} \frac{d}{dt}n_i(t) &= -i\frac{d}{dt}G_{ii}(t, t) = -i \left[\partial_t G_{ii}^<(t, t') + \partial_{t'} G_{ii}^<(t, t') \right]_{t=t'} \\ &= -\sum_k \left[V_{ik}(t)G_{ki}^<(t, t) - G_{ik}^<(t, t)V_{ki}(t) \right]. \end{aligned} \quad (2.72)$$

Since $V_{ik}^* = V_{ki}$ and $G_{ij}^{\lessgtr*}(t_1, t_2) = -G_{ji}^{\lessgtr}(t_2, t_1)$, the equation can be rewritten as

$$\frac{d}{dt}n_i(t) = 2 \sum_k \text{Re} \{ G_{ik}^<(t, t)V_{ki}(t) \} \quad (2.73)$$

Chapter 3

Resonant tunneling system

In this section the current response of a noninteracting resonant tunneling system is calculated by Keldysh Green's function technique. It is the same derivation of the resonant tunneling system treated in [5], but more comment is included. This will be especially helpful for readers that are not used to the formulation. The study will be limited to a steplike modulation only.

To study transport we will assume a model system consisting of two leads and a central device. For the sake of simplicity the central device will be modeled by a single level. In principle the model can be extended for more level systems, but the analytical treatment becomes very cumbersome since for the one level device the equations are already quite lengthy. The total hamiltonian of the system in equilibrium can be written as:

$$\hat{H}_0 = \sum_{k\alpha} \epsilon_{k\alpha} \hat{c}_{k\alpha}^\dagger \hat{c}_{k\alpha} + \epsilon_0 \hat{c}_0^\dagger \hat{c}_0 + \sum_{k\alpha} V_{k\alpha} \left[\hat{c}_{k\alpha}^\dagger \hat{c}_0 + \hat{c}_0^\dagger \hat{c}_{k\alpha} \right] - \mu \left(\sum_{k\alpha} \hat{c}_{k\alpha}^\dagger \hat{c}_{k\alpha} + \hat{c}_0^\dagger \hat{c}_0 \right) \equiv \sum_{m,n} h_{m,n} \hat{c}_m^\dagger \hat{c}_n, \quad (3.1)$$

where $\alpha = L, R$ denotes the left and right leads and m and n are collective indices for $k\alpha$ and 0. The system is assumed to be in thermal equilibrium at a given temperature β^{-1} and chemical potential μ before the perturbation

$$\hat{H}_U(t) = \sum_{k\alpha} U_{k\alpha}(t) \hat{c}_{k\alpha}^\dagger \hat{c}_{k\alpha} + U_0(t) \hat{c}_0^\dagger \hat{c}_0 \quad (3.2)$$

is switched on. The current from a lead α to the central region can be calculated by taking the derivative of the particle number of that lead. An expression for the time derivative of the density was already obtained in section 2.5. By summing the time derivatives of the densities of all the levels of one lead and multiplying by the charge, we obtain the current from that particular lead

$$\begin{aligned} J_\alpha(t) &= e \sum_k \frac{d}{dt} n_{k\alpha}(t) = 2e \sum_k \text{Re} \left\{ G_{0,k\alpha}^<(t, t) \right\} V_{k\alpha} \\ &= 2e \sum_k \text{Re} \left\{ \mathbf{G}^R(t, 0) \mathbf{G}^<(0, 0) \mathbf{G}^A(0, t) \right\} V_{k\alpha}, \end{aligned} \quad (3.3)$$

where $V_{k\alpha}$ is chosen to be real.

The matrix $\mathbf{G}^<(0, 0)$ can be written as

$$\mathbf{G}^<(0, 0) = if(\mathbf{h}) = \int_\Gamma \frac{d\zeta}{2\pi} \frac{f(\zeta) e^{\eta\zeta}}{\zeta - \mathbf{h}} = \int_\Gamma \frac{d\zeta}{2\pi} f(\zeta) e^{\eta\zeta} \mathbf{R}(\zeta), \quad (3.4)$$

where Γ is the contour surrounding all the Matsubara frequencies $\omega_n = i(2n+1)\pi/\beta$ (see fig. A.1) and η is an infinitesimal number to ensure convergence. More information about writing $\mathbf{G}^<(0,0)$ as an integral over the contour Γ can be found in appendix A.3. Further we defined the frequency dependent matrix $\mathbf{R}(z) = [z - \mathbf{h}]^{-1}$.

When integrating along the contour Γ , the frequency is either below or above the real axis. Since the retarded Green's function is analytic in the upper half-plane and the advanced Green's function is analytic in the lower half-plane, we can identify

$$\mathbf{R}(\zeta) = \mathbf{G}^R(\zeta) \quad \text{if } \text{Im}(\zeta) > 0 \quad \text{and} \quad \mathbf{R}(\zeta) = \mathbf{G}^A(\zeta) \quad \text{if } \text{Im}(\zeta) < 0 \quad (3.5)$$

This expression $\mathbf{G}^<(0,0)$ can be used to define the kernel

$$Q_\alpha(\zeta, t) \equiv \sum_k \left(\mathbf{G}^R(t, 0) \frac{1}{\zeta - \mathbf{h}} \mathbf{G}^A(0, t) \right)_{0, k\alpha} V_{k\alpha}. \quad (3.6)$$

The current can now be written as

$$J_\alpha(t) = 2e \text{Re} \left\{ \int_\Gamma \frac{d\zeta}{2\pi} f(\zeta) e^{\eta\zeta} Q_\alpha(\zeta, t) \right\}. \quad (3.7)$$

To simulate the applied bias voltage, we will assume a sudden switch on at $t = 0$, i.e. $\mathbf{U}(t) = \theta(t)\mathbf{U}$. The retarded and advanced Green's functions obey the equation of motion

$$i\partial_t \mathbf{G}^{R/A}(t, t') = \mathbf{1}\delta(t - t') + \mathbf{H}(t)\mathbf{G}^{R/A}(t, t') \quad (3.8)$$

We now want to find an expression for $\mathbf{G}^R(t, 0)$, so set the time argument $t' = 0$. The Hamiltonian after the switch on can be written as $\hat{H} = \hat{H}_0 + \hat{H}_U$, containing the time-independent matrix elements $\tilde{\epsilon}_0 = \epsilon_0 + U_0$, $\tilde{\epsilon}_{k\alpha} = \epsilon_{k\alpha} + U_{k\alpha}$ and $V_{k\alpha}$. The retarded Green's functions therefore can be rewritten as

$$i\partial_t G_{0,0}^R(t, 0) = \delta(t) + \tilde{\epsilon}_0 G_{0,0}^R(t, 0) + \sum_{k\alpha} V_{k\alpha} G_{k\alpha,0}^R(t, 0) \quad (3.9)$$

and

$$i\partial_t G_{k\alpha,0}^R(t, 0) = \tilde{\epsilon}_{k\alpha} G_{k\alpha,0}^R(t, 0) + V_{k\alpha} G_{0,0}^R(t, 0) \quad (3.10)$$

The easiest way to calculate these Green's functions is by introducing auxiliary diagonal Green's functions \mathbf{g}^R that satisfy the equations of motion

$$i\partial_t g_0^R(t) = \delta(t) + \tilde{\epsilon}_0 g_0^R(t) \quad \text{and} \quad i\partial_t g_{k\alpha}^R(t) = \delta(t) + \tilde{\epsilon}_{k\alpha} g_{k\alpha}^R(t). \quad (3.11)$$

The retarded Green's function can be expressed in these auxiliary Green's functions as

$$G_{0,0}^R(t, 0) = g_0^R(t) + \sum_{k\alpha} V_{k\alpha} \int_{-\infty}^{\infty} dt' g_0^R(t - t') G_{k\alpha,0}^R(t, 0), \quad (3.12)$$

$$G_{k\alpha,0}^R(t, 0) = V_{k\alpha} \int_{-\infty}^{\infty} dt' g_{k\alpha}^R(t - t') G_{0,0}^R(t, 0). \quad (3.13)$$

Since the expressions contain convolution time integrals, it is convenient to rewrite everything in the frequency domain. The diagonal Green's functions have the simple form

$$g_0^R(\omega) = \frac{1}{\omega - \tilde{\epsilon}_0 + i\eta} \quad \text{and} \quad g_{k\alpha}^R(\omega) = \frac{1}{\omega - \tilde{\epsilon}_{k\alpha} + i\eta}. \quad (3.14)$$

The retarded Green's function $\mathbf{G}^R(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \mathbf{G}^R(t, 0)$, however, is written as

$$G_{0,0}^R(\omega) = g_0^R(\omega) + \sum_{k\alpha} V_{k\alpha} g_0^R(\omega) G_{k\alpha,0}^R(\omega) \quad \text{and} \quad G_{k\alpha,0}^R(\omega) = V_{k\alpha} g_{k\alpha}^R(\omega) G_{0,0}^R(\omega). \quad (3.15)$$

A similar analysis for the advanced Green's function $\mathbf{G}^A(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \mathbf{G}^A(0, t)$ yields a similar expression

$$G_{0,0}^A(\omega) = g_0^A(\omega) + \sum_{k\alpha} V_{k\alpha} g_0^A(\omega) G_{k\alpha,0}^A(\omega) \quad \text{and} \quad G_{k\alpha,0}^A(\omega) = V_{k\alpha} g_{k\alpha}^A(\omega) G_{0,0}^A(\omega), \quad (3.16)$$

where the diagonal Green's function $\mathbf{g}^A(\omega)$ can be written as

$$g_0^A(\omega) = \frac{1}{\omega - \tilde{\epsilon}_0 - i\eta} \quad \text{and} \quad g_{k\alpha}^A(\omega) = \frac{1}{\omega - \tilde{\epsilon}_{k\alpha} - i\eta}. \quad (3.17)$$

Combining the expressions in 3.15 and 3.16, we obtain

$$G_{0,0}^{R/A}(\omega) = g_0^{R/A}(\omega) + g_0^{R/A}(\omega) \sum_{k\alpha} V_{k\alpha}^2 g_{k\alpha}^{R/A}(\omega) G_{0,0}^{R/A}(\omega) = g_0^{R/A}(\omega) + g_0^{R/A}(\omega) \Sigma^{R/A}(\omega) G_{0,0}^{R/A}(\omega), \quad (3.18)$$

where we defined the self-energy

$$\Sigma^{R/A}(\omega) = \sum_{\alpha} \Sigma_{\alpha}^{R/A}(\omega) = \sum_{k\alpha} V_{k\alpha}^2 g_{k\alpha}^{R/A} = \sum_{k\alpha} \frac{V_{k\alpha}^2}{\omega - \tilde{\epsilon}_{k\alpha} \pm i\eta}. \quad (3.19)$$

The self-energy describes the effect of the leads on the local level. The electron on the device is not only limited to its own level but it can hop to the leads. This is expressed as a change of the energy of the device level. The device component of the retarded and advanced Green's function can now be written as

$$G_{0,0}^{R/A}(\omega) = \frac{1}{(g_0^{R/A}(\omega))^{-1} - \Sigma^{R/A}(\omega)} = \frac{1}{\omega - \tilde{\epsilon}_0 - \Sigma^{R/A}(\omega) \pm i\eta} \quad (3.20)$$

A similar evaluation for $G_{k\alpha,k'\alpha'}^{R/A}(\omega)$ holds

$$\begin{aligned} G_{k\alpha,k'\alpha'}^{R/A}(\omega) &= \delta_{k\alpha,k'\alpha'} g_{k\alpha}^{R/A}(\omega) + g_{k\alpha}^{R/A}(\omega) V_{k\alpha} G_{0,k'\alpha'}^{R/A}(\omega) \\ &= \delta_{k\alpha,k'\alpha'} g_{k\alpha}^{R/A}(\omega) + g_{k\alpha}^{R/A}(\omega) V_{k\alpha} G_{0,0}^{R/A}(\omega) V_{k'\alpha'} g_{k'\alpha'}^{R/A}(\omega). \end{aligned} \quad (3.21)$$

3.1 Steady state current

We will assume that the levels in the leads are shifted by an equal amount $U_{k\alpha} = U_{\alpha}$. The steady state current is defined as

$$J_{\alpha}^S \equiv \lim_{t \rightarrow \infty} J_{\alpha}(t) \quad (3.22)$$

We see from equation 3.7 that it is needed to calculate the limit of the kernel $Q_{\alpha}(\zeta, t)$ for t to infinity. To calculate $\lim_{t \rightarrow \infty} Q_{\alpha}(\zeta, t)$, we have to evaluate the matrix elements $G_{0,0}^R(t, 0)$ and $G_{0,k\alpha}^R(t, 0)$ of the retarded Green's function and the two contractions $\sum_k G_{0,k\alpha}^A(0, t) V_{k\alpha}$ and $\sum_k G_{k'\alpha',k\alpha}^A(0, t) V_{k\alpha}$ for t goes

to infinity. Assuming that $\Sigma_\alpha^{R/A}(\omega)$ is a smooth function, one can use the Riemann-Lebesgue lemma to obtain

$$\lim_{t \rightarrow \infty} G_{0,0}^R(t, 0) = \lim_{t \rightarrow \infty} \sum_k G_{0,k\alpha}^A(0, t) V_{k\alpha} = 0, \quad (3.23)$$

$$\lim_{t \rightarrow \infty} G_{0,k\alpha}^R(t, 0) = \lim_{t \rightarrow \infty} -i V_{k\alpha} e^{-i\tilde{\epsilon}_{k\alpha} t} G_{0,0}^R(\tilde{\epsilon}_{k\alpha}), \quad (3.24)$$

$$\lim_{t \rightarrow \infty} \sum_k G_{k'\alpha', k\alpha}^A(0, t) V_{k\alpha} = \lim_{t \rightarrow \infty} i V_{k'\alpha'} e^{i\tilde{\epsilon}_{k'\alpha'} t} [\delta_{\alpha', \alpha} + G_{0,0}^A(\tilde{\epsilon}_{k'\alpha'}) \Sigma_\alpha^A(\tilde{\epsilon}_{k'\alpha'})] \quad (3.25)$$

Substituting these equations in the kernel and doing careful analysis, one obtains

$$\lim_{t \rightarrow \infty} Q_\alpha(\zeta, t) = \int \frac{d\epsilon}{2\pi} \frac{\Gamma_\alpha(\epsilon)}{\zeta - \epsilon + U_\alpha} G_{0,0}^R(\epsilon) + \sum_{\alpha'} \int \frac{d\epsilon}{2\pi} \frac{\Gamma_{\alpha'}(\epsilon)}{\zeta - \epsilon + U_{\alpha'}} |G_{0,0}^R(\epsilon)|^2 \Sigma_\alpha^A(\epsilon), \quad (3.26)$$

where

$$\Gamma_\alpha(\epsilon) \equiv -2\text{Im} [\Sigma_\alpha^R(\epsilon)] = 2\pi \sum_k \delta(\epsilon - \tilde{\epsilon}_{k\alpha}) V_{k\alpha}^2. \quad (3.27)$$

For more details on the derivation of equation 3.26, see appendix A.4. The expression for the kernel contains a simple pole structure. Using the same transformation as in equation 3.4 backwards, we can write for the steady state current

$$J_R^S = -e \int \frac{d\epsilon}{2\pi} \frac{\Gamma_R(\epsilon) \Gamma_L(\epsilon)}{[\epsilon - \tilde{\epsilon}_0 - \Lambda(\epsilon)]^2 + [\Gamma(\epsilon)/2]^2} [f(\epsilon - U_L) - f(\epsilon - U_R)] = -J_L^S, \quad (3.28)$$

where $\Lambda(\epsilon) = \text{Re}[\Sigma^R(\epsilon)]$ is the Hilbert transform of $\Gamma(\epsilon) = \sum_\alpha \Gamma_\alpha(\epsilon)$:

$$\Lambda(\omega) = P \int \frac{d\omega'}{2\pi} \frac{\Gamma(\omega')}{\omega - \omega'} \quad (3.29)$$

Note that the bias voltage U_α is not only in the Fermi distribution function, but also in the self energy which is expressed in the quantities Γ and Λ . The dependence of the self-energy on the bias voltage is physical, since when the energy levels in the leads are shifted the hopping between the device and the leads will be altered, so the self-energy has to change.

This is the same result as Jauho and co-workers [9, 4] obtained for the steady state current. They used a partitioned approach where the two leads are each in its own equilibrium at different chemical potentials μ_R and μ_L and temperatures β_R^{-1} and β_L^{-1} . The undisturbed leads have the equilibrium conditions μ and β . The energy levels in the leads have to be shifted by $\mu_\alpha - \mu$ in order to preserve charge neutrality. This corresponds to the applied bias voltage $U_\alpha = \mu_\alpha - \mu$. To obtain a current between the two regions, the contacts are switched on. Due to the difference in chemical potential electrons will flow to the other side. By tuning $\beta_R = \beta_L = \beta$, the current is given by equation 3.28.

3.2 Time-dependent current in the wide-band limit

The calculation of the steady state current was possible due to the long time behaviour of the various Green's functions in equation 3.3. However, to calculate the time-dependent current, the structure of the retarded (advanced) self-energy needs to be specified. Here we will consider the so called 'wide-band limit'. The lead spectral functions are assumed to be constant $\Gamma_\alpha \equiv 2\gamma_\alpha$ and hence from equation 3.29 $\Lambda_\alpha = 0$. This assumption has the advantage that $\mathbf{G}_{0,0}^R(\omega)$ has a simple pole structure which simplifies the calculations slightly. Since the zero-point of the energy can be chosen at will, we can choose $\epsilon_0 = 0$

without loss of generality. For the sake of simplicity we will assume $U_0 = 0$. The derivation of the time-dependent current is done in appendix A.5. Here, only the final result for the time-dependent current is given

$$J_\alpha(t) = J_\alpha^S - 4e\gamma_\alpha e^{-\gamma t} \int \frac{d\omega}{2\pi} f(\omega) \left[U_\alpha \text{Im} \left\{ \frac{e^{i(\omega+U_\alpha)t}}{(\omega+i\gamma)(\omega+U_\alpha+i\gamma)} \right\} + \sum_{\alpha'} \gamma_{\alpha'} U_{\alpha'} \frac{U_{\alpha'} e^{-\gamma t} + 2\omega \cos[(\omega+U_{\alpha'})t] + 2\gamma \sin[(\omega+U_{\alpha'})t]}{[\omega^2 + \gamma^2][(\omega+U_{\alpha'})^2 + \gamma^2]} \right], \quad (3.30)$$

where J_α^S is the steady state current as given in equation 3.28 and $\gamma = \gamma_R + \gamma_L$. It is easily checked that the long time behaviour ($t \rightarrow \infty$) gives the steady state current of equation 3.28. More information about the calculation can be found in the article [5].

In the article it is stated that a more physical and compact way of writing can be deployed by noting that the particle number in the central device $\langle n_0 \rangle$ may be written as

$$J_R(t) + J_L(t) = e \frac{d}{dt} \langle n_0 \rangle. \quad (3.31)$$

The equation for the time-dependent current can then be written as

$$J_R(t) = J_R^S + e \frac{\gamma_R}{\gamma} \frac{d}{dt} \langle n_0 \rangle - 4e \frac{\gamma_R \gamma_L}{\gamma} e^{-\gamma t} \int \frac{d\omega}{2\pi} \text{Im} \left\{ \frac{f(\omega)}{\omega+i\gamma} \left[U_R \frac{e^{i(\omega+U_R)t}}{\omega+U_R+i\gamma} - U_L \frac{e^{i(\omega+U_L)t}}{\omega+U_L+i\gamma} \right] \right\}. \quad (3.32)$$

The current for the left lead $J_L(t)$ is obtained by interchanging $R \leftrightarrow L$ in the expression. Therefore, $J_R(t) \neq -J_L(t)$ for any finite time, even in the symmetric case $\gamma_R = \gamma_L$. The time-dependent current clearly differs from the one obtained by Jauho and co-workers [4] in the partitioned scheme. The difference are the terms that describe the contact for negative times. It is verified by Stefanucci and Almladh [5] that by discarding these terms the time-dependent current reduces to the one obtained in the partitioned scheme. These terms disappear in the long time limit and the steady state result is the same for both approaches.

Unfortunately the current can not be determined by these two equations, since the equations have 3 unknowns, and there are in fact only two independent equations. The term $d/dt \langle n_0 \rangle(t)$ can not be determined from these equations. Since $J_R(0) = -J_L(0)$, it is possible to determine the initial value $\partial_t \langle n_0 \rangle(0) = 0$. However, any function which satisfies this condition will be correct for this set of equations. So one needs an explicit equation for $\partial_t \langle n_0 \rangle(t)$. This can be simply obtained using equation 3.31 and plugging in equation 3.30. After simple algebraic manipulations one obtains

$$\frac{d}{dt} \langle n_0 \rangle = -4e^{-\gamma t} \int \frac{d\omega}{2\pi} f(\omega) \times \sum_{\alpha} \gamma_{\alpha} U_{\alpha} \frac{\gamma U_{\alpha} (e^{-\gamma t} - \cos[(\omega+U_{\alpha})t]) + (\omega(\omega+U_{\alpha}) + \gamma^2) \sin[(\omega+U_{\alpha})t]}{[\omega^2 + \gamma^2][(\omega+U_{\alpha'})^2 + \gamma^2]} \quad (3.33)$$

The lack of conditions can also be checked by writing equation 3.32 in a matrix form

$$\begin{pmatrix} c_R - 1 & c_R \\ c_L & c_L - 1 \end{pmatrix} \begin{pmatrix} J_R(t) \\ J_L(t) \end{pmatrix} = \begin{pmatrix} d - s \\ s - d \end{pmatrix}, \quad (3.34)$$

where we defined

$$s \equiv J_R^S = -J_L^S \quad (3.35)$$

$$c_\alpha \equiv \frac{\gamma_\alpha}{\gamma} \quad (3.36)$$

$$d \equiv -4e^{\frac{\gamma_R\gamma_L}{\gamma}}e^{-\gamma t} \int \frac{d\omega}{2\pi} \text{Im} \left\{ \frac{f(\omega)}{\omega + i\gamma} \left[U_R \frac{e^{i(\omega+U_R)t}}{\omega + U_R + i\gamma} - U_L \frac{e^{i(\omega+U_L)t}}{\omega + U_L + i\gamma} \right] \right\} \quad (3.37)$$

When we calculate the determinant of the matrix we obtain

$$\left| \begin{pmatrix} c_R - 1 & c_R \\ c_L & c_L - 1 \end{pmatrix} \right| = (c_R - 1)(c_L - 1) - c_R c_L = 1 - c_L - c_R = 0 \Rightarrow c_R + c_L = 1. \quad (3.38)$$

But this was already clear from the definition of γ , so the equations are not linear independent from each other. This implies that the equations can not be solved unambiguously and an extra condition will be required.

The equation for the time-dependent current can be further simplified by assuming that one of the two leads does not undergo a level shift. If we take $U_R = 0$, equation 3.30 for $J_R(t)$ reduces to

$$J_R(t) = J_\alpha^S - 4e\gamma_R\gamma_L U_L e^{-\gamma t} \int \frac{d\omega}{2\pi} f(\omega) \frac{U_L e^{-\gamma t} + 2\omega \cos[(\omega + U_L)t] + 2\gamma \sin[(\omega + U_L)t]}{[\omega^2 + \gamma^2][(\omega + U_L)^2 + \gamma^2]}. \quad (3.39)$$

The time behaviour of the time-dependent current is not just a simple exponential decay towards the steady state current. In figure 3.1 the current is plotted versus t for different bias voltages which exactly matches the plot given in the paper of G. Stefanucci and C.-O. Almbladh [5]. For small applied bias voltages U_L , the current strongly depends on U_L . However, for high bias voltages there is some kind of saturation and it becomes independent of U_L . From the parameters in the graph one can say that the time-dependent current has the same shape for $U_L \gtrsim 8.0$.

The time-dependent behaviour of the current is also studied for the other parameters in the article [5]. Since I will not have them in the other models, I do not treat these effects here.

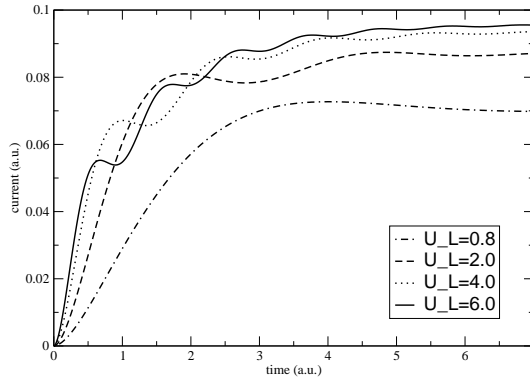


Figure 3.1: Time-dependent current $J_R(t)$ for different bias voltages $U_L = 0.8, 2.0, 4.0$ and 6.0 . The other parameters were set to $\gamma_R = \gamma_L = 0.2$, $\mu = 0$ and $\beta^{-1} = 0$. It exactly matches the plot in the article [5].

Chapter 4

Propagation of the Schrödinger equation

Instead of using the Green's function formalism to calculate the time-dependent current, one can also use the Schrödinger equation directly to propagate the wave function and calculate the observables of interest. The propagation of the wave function analytically can only be done for very simple systems, so a numerical approach will be mandatory from the beginning.

Numerical calculations will involve a diagonalization of the Hamiltonian matrix which is an expensive process ($\sim N^3$), so the basis set can not be too big. A calculation by diagonalization will only be possible for small systems. There are however other methods which can handle larger basis sets by approximating the evolution operator $\hat{U}(t, t')$. For example: polynomial expansions, projection in Krylov subspaces and split-operators. A nice overview can be found in [18]. In my work I have only investigated small systems, so I have only used diagonalization.

The Hamiltonian of a non-interacting N-particle system can be written as the sum of the Hamiltonians for the individual particles,

$$\hat{H} = \sum_i^N \hat{H}_i. \quad (4.1)$$

The N-particle wave function can be written as a product of N single particle wave functions

$$\Psi(\mathbf{r}, t) = \prod_{i=1}^N \psi_i(\mathbf{r}_i, t). \quad (4.2)$$

Putting this in the Schrödinger equation it is easily verified that the total energy can be written as the energies of the different occupied orbitals ψ_i , $E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^N E_i$. The same holds for every observable which makes it sufficient to treat the orbitals separately and Ψ does not have to be calculated.

To include the Pauli principle we make sure that in the calculation none of the occupied orbitals ψ_i are the same for different particles. Usually this is achieved by taking an anti-symmetrized combination of Ψ which is often done by taking the Slater determinant of the occupied orbitals.

4.1 Propagation for an orthonormal basis set

Usually the exact wave function is not known and the wave function $\psi_i(\mathbf{r}, t)$ is expanded in a basis set ϕ_i which is orthonormal, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. Putting the time-dependence in the coefficients is a convenient

way to propagate the system. Suppose we have the following expansion for $\psi_i(\mathbf{r}, t)$

$$\psi_i(\mathbf{r}, t) = \sum_j \phi_j(\mathbf{r})c_{ji}(t), \quad (4.3)$$

where $c_{ij}(t) = \langle \phi_i | \psi_j(t) \rangle$ which will be referred to as the ‘state matrix’. It is called the state matrix, since when a basis is chosen, the state of the system is completely described by the matrix $\mathbf{c}(t)$. Note that the index i refers to the orbital so it runs from 1 to N . The index j however runs over a complete set of states so it runs over infinite amount of numbers. Therefore the state matrix $\mathbf{c}(t)$ is in general not a square matrix.

Putting this in the Schrödinger equation we obtain the following equation for a time-independent hamiltonian

$$i \sum_k \phi_k(\mathbf{r}) \partial_t c_{kj}(t) = \sum_k \hat{H} \phi_k(\mathbf{r}) c_{kj}(t). \quad (4.4)$$

Multiplying from the left by $\phi_i(\mathbf{r})$, integrating over space and using the orthonormality of $\phi_i(\mathbf{r})$ we obtain an equation of motion for the coefficients

$$i \dot{c}_{ij}(t) = \sum_k H_{ik} c_{kj}(t), \quad (4.5)$$

The formal solution can be written as

$$c_{ij}(t) = \sum_k \left(e^{-i\mathbf{H}(t-t_0)} \right)_{ik} c_{kj}(t_0), \quad (4.6)$$

where the exponential is defined by its series. If the matrix \mathbf{H} is diagonalizable $(Q^{-1}\mathbf{H}Q)_{ij} = \epsilon_i \delta_{ij}$, the exponential can be calculated directly

$$\left(e^{-i\mathbf{H}\Delta t} \right)_{ij} = \sum_k Q_{ik} e^{-i\epsilon_k \Delta t} Q_{kj}^{-1}, \quad (4.7)$$

where $\Delta t = t - t_0$.

Formally every wave function can fully be described by such a set, but in practice it is not possible since the set has to be finite. However, often truncation is allowed if the remaining functions are the ones that have the largest overlap with the wave function.

The state matrix \mathbf{c} can be related directly to the density operator, which is useful for calculations since the trace of the product of the density operator and an observable gives the expectation value of that observable

$$\langle \hat{O} \rangle = \text{Tr} \left(\hat{\rho} \hat{O} \right) \quad (4.8)$$

The product of the state matrix with its complex conjugate will be equal to the density operator in that particular basis

$$\hat{\rho} = \sum_{i=1}^N |\psi_i\rangle \langle \psi_i| = \sum_{i=1}^N \sum_{kl} |k\rangle c_{ki} c_{il}^\dagger \langle l| = \sum_{kl} |k\rangle \rho_{kl} \langle l| \quad (4.9)$$

Every observable can be described in a basis since

$$\hat{O} = 1 \cdot \hat{O} \cdot 1 = \sum_{ij} |i\rangle \langle i| \hat{O} |j\rangle \langle j| = \sum_{ij} |i\rangle O_{ij} \langle j|, \quad (4.10)$$

where we defined $O_{ij} = \langle i | \hat{O} | j \rangle$.

So expectation value for an operator can be written as:

$$\langle \hat{O} \rangle = \text{Tr} \left(\hat{\rho} \hat{O} \right) = \sum_{nklmj} \langle n | k \rangle \rho_{kl} \langle l | m \rangle O_{mj} \langle j | n \rangle = \sum_{nklmj} \delta_{nk} \rho_{kl} \delta_{lm} O_{mj} \delta_{jn} = \sum_{ij} \rho_{ij} O_{ji} \quad (4.11)$$

4.2 Propagation for an non-orthonormal basis set

Although we have used an orthonormal basis in the previous section, one does not have to apply this restriction. However, the derivation for an equation for the time-dependence of $\mathbf{c}(t)$ is a bit more complicated. Assume a non-orthonormal set with the overlap matrix $S_{ij} = \int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r})$. The orbitals are still expanded in the usual way $\psi_i(\mathbf{r}, t) = \sum_j \phi_j(\mathbf{r}) c_{ji}(t)$. When this is put in the Schrödinger equation we get

$$i \sum_k \phi_k(\mathbf{r}) \partial_t c_{kj}(t) = \sum_k \hat{H}(t) \phi_k(\mathbf{r}) c_{kj}(t). \quad (4.12)$$

Multiplying with $\phi_i^*(\mathbf{r})$ and integrating over \mathbf{r} one gets

$$i \sum_k S_{ik} \dot{c}_{kj}(t) = \sum_k H_{ik}(t) c_{kj}(t), \quad (4.13)$$

where $H_{ij}(t) = \int d\mathbf{r} \phi_i^*(\mathbf{r}) \hat{H}(t) \phi_j(\mathbf{r})$. When the matrix $\mathbf{c}(t)$ is written as $\mathbf{c}(t) = \mathbf{T}\mathbf{b}(t)$ and the equation is multiplied by \mathbf{T}^\dagger from the left one gets

$$i \mathbf{T}^\dagger \mathbf{S} \mathbf{T} \dot{\mathbf{b}}(t) = \mathbf{T}^\dagger \mathbf{H}(t) \mathbf{T} \mathbf{b}(t) \quad (4.14)$$

When the matrix \mathbf{T} is defined to diagonalize \mathbf{S} , $(\mathbf{T}^\dagger \mathbf{S} \mathbf{T})_{ij} = \sigma_i \delta_{ij}$, the matrix equation can be written as

$$i \sigma_i \sum_k \delta_{ik} \dot{b}_{kj}(t) = \sum_k \check{H}_{ik}(t) b_{kj}(t), \quad (4.15)$$

where $\check{\mathbf{H}}(t) = \mathbf{T}^\dagger \mathbf{H}(t) \mathbf{T}$. Note that the hamiltonian $\check{\mathbf{H}}(t)$ is still hermitian. The coefficient $\mathbf{b}(t)$ can be replaced by $b_{ij} = d_{ij} / \sqrt{\sigma_i}$. When the equation is divided by $\sqrt{\sigma_i}$, one obtains

$$i \dot{\mathbf{d}}(t) = \tilde{\mathbf{H}}(t) \mathbf{d}(t), \quad (4.16)$$

where $\tilde{H}_{ij} = \frac{1}{\sqrt{\sigma_i}} \check{H}_{ij} \frac{1}{\sqrt{\sigma_j}}$. The matrix equation has now exact the same form as one started with an orthonormal base.

If the hamiltonian $\tilde{\mathbf{H}}$ is time-independent, one can calculate the eigenstates by diagonalization. If \mathbf{Q} is a matrix that diagonalizes the hamiltonian $\tilde{\mathbf{H}}$, $(\mathbf{Q}^\dagger \tilde{\mathbf{H}} \mathbf{Q})_{ij} = \epsilon_i \delta_{ij}$, the matrix equation results in the following eigen states

$$\psi_i = \sum_{kl} \phi_k T_{kl} \frac{1}{\sqrt{\sigma_l}} Q_{li} = \sum_j \phi_j c_{ji} \quad (4.17)$$

Chapter 5

Two level system

Very few time-dependent quantum systems can be solved analytically. One of them is the two level system which is treated in almost any self respecting introductory quantum mechanics course (see [19]). Since the answer is known it is a good starting point to get some experience solving the time-dependent Schrödinger equation numerically and test the core routines. Since it is a nice problem, I will repeat the analytical analysis here, followed by some numerical results.

5.1 Analytical solution

The two level systems has only two states $|\psi_a\rangle$ and $|\psi_b\rangle$ which are eigenstates of the hamiltonian \hat{H}_0 . The energies are then given by $\hat{H}_0|\psi_a\rangle = E_a|\psi_a\rangle$ and $\hat{H}_0|\psi_b\rangle = E_b|\psi_b\rangle$. For the sake of simplicity the states are assumed to be orthonormal $\langle\psi_a|\psi_b\rangle = \delta_{a,b}$. The wave function at $t = 0$ can be described by a linear combination of the two: $\Psi(0) = c_a\psi_a + c_b\psi_b$ with $|c_a|^2 + |c_b|^2 = 1$ for $\Psi(0)$ to be normalized. The time-dependent wave function will be

$$\Psi(t) = c_a\psi_a e^{-iE_a t} + c_b\psi_b e^{-iE_b t} \quad (5.1)$$

To describe a time-dependent perturbation $\hat{H}'(t)$, an additional time-dependence is required. Since it is convenient to leave the states $|\psi_a\rangle$ and $|\psi_b\rangle$ unchanged, the coefficients c_a and c_b are made time-dependent:

$$\Psi(t) = c_a(t)\psi_a e^{-iE_a t} + c_b(t)\psi_b e^{-iE_b t} \quad (5.2)$$

Putting $\Psi(t)$ into the Schrödinger equation $i\partial_t\Psi = \hat{H}\Psi$ with the new hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'(t)$ we obtain

$$\begin{aligned} & c_a\hat{H}_0\psi_a e^{-iE_a t} + c_b\hat{H}_0\psi_b e^{-iE_b t} + c_a\hat{H}'\psi_a e^{-iE_a t} + c_b\hat{H}'\psi_b e^{-iE_b t} \\ = & i \left[\dot{c}_a\psi_a e^{-iE_a t} + \dot{c}_b\psi_b e^{-iE_b t} + c_a(-iE_a)\psi_a e^{-iE_a t} + c_b(-iE_b)\psi_b e^{-iE_b t} \right]. \end{aligned} \quad (5.3)$$

Four of the terms cancel and we are left with an equation of four terms. By multiplying from the left by ψ_a or ψ_b and integrating we obtain two coupled first order differential equations for $c_a(t)$ and $c_b(t)$

$$\begin{cases} \dot{c}_a = -i \left[c_a H'_{aa} + c_b H'_{ab} e^{-i(\omega_b - \omega_a)t} \right] \\ \dot{c}_b = -i \left[c_b H'_{bb} + c_a H'_{ba} e^{-i(\omega_a - \omega_b)t} \right], \end{cases} \quad (5.4)$$

where we have defined $H'_{ij} = \langle i | H' | j \rangle$. Further assume that the perturbation has only off-diagonal elements $H'_{aa} = H'_{bb} = 0$ (it can always be chosen in this way)

$$\begin{cases} \dot{c}_a = -i c_b H'_{ab} e^{-i(\omega_b - \omega_a)t} \\ \dot{c}_b = -i c_a H'_{ba} e^{-i(\omega_a - \omega_b)t}. \end{cases} \quad (5.5)$$

The equations can be uncoupled by differentiating once to time. Further keep in mind that the hamiltonian is an hermitian operator, so $H'_{ab} = H'_{ba}^* = \omega_{ab}$. To keep the equations simple, the perturbation is assumed to be time-independent.

$$\begin{cases} \ddot{c}_a = -i\omega_{ab}\dot{c}_b e^{-i\omega_0 t} - \omega_0\omega_{ab}c_b e^{-i\omega_0 t} = -|\omega_{ab}|^2 c_a - i\omega_0\dot{c}_a \\ \ddot{c}_b = -i\omega_{ab}^*\dot{c}_a e^{+i\omega_0 t} + \omega_0\omega_{ab}c_a e^{+i\omega_0 t} = -|\omega_{ab}|^2 c_b + i\omega_0\dot{c}_b. \end{cases} \quad (5.6)$$

By substituting the general solution $c_{a(b)}(t) = Ae^{i\alpha(\beta)t}$ the two second order differential equations can be solved easily

$$\begin{aligned} -\alpha^2 Ae^{i\alpha(\beta)t} &= -|\omega_{ab}|^2 Ae^{i\alpha(\beta)t} + \omega_0\alpha Ae^{i\alpha(\beta)t} \quad \forall t \\ \Leftrightarrow \alpha^2 + \omega_0 - |\omega_{ab}|^2 &= 0 \Leftrightarrow \alpha = \frac{1}{2} \left(-\omega_0 \pm \sqrt{\omega_0^2 + 4|\omega_{ab}|^2} \right) = -\frac{1}{2}\omega_0 \pm \Omega \end{aligned} \quad (5.7)$$

$$\begin{aligned} -\beta^2 Ae^{i\beta(\beta)t} &= -|\omega_{ab}|^2 Ae^{i\beta(\beta)t} - \omega_0\beta Ae^{i\beta(\beta)t} \quad \forall t \\ \Leftrightarrow \beta^2 - \omega_0 - |\omega_{ab}|^2 &= 0 \Leftrightarrow \beta = \frac{1}{2} \left(\omega_0 \pm \sqrt{\omega_0^2 + 4|\omega_{ab}|^2} \right) = \frac{1}{2}\omega_0 \pm \Omega, \end{aligned} \quad (5.8)$$

where we defined $\Omega = \sqrt{\omega_0^2 + 4|\omega_{ab}|^2}$. So the solution for $c_a(t)$ and $c_b(t)$ can be written as

$$\begin{cases} c_a(t) = [A \sin(\Omega t) + B \cos(\Omega t)] e^{-\frac{i}{2}\omega_0 t} \\ c_b(t) = [C \sin(\Omega t) + D \cos(\Omega t)] e^{\frac{i}{2}\omega_0 t} \end{cases} \quad (5.9)$$

The problem is now basically solved. The four constants are determined by the boundary conditions. It is actually only necessary to give one condition, since there are already three boundary conditions. One comes from the normalization of the wave function $|c_a|^2 + |c_b|^2 = 1$. The other two come the connection between $c_a(t)$ and $c_b(t)$. By substituting the equation 5.9 in equation 5.5 the two additional relations are obtained

$$\begin{aligned} \dot{c}_b &= -ic_a\omega_{ab}e^{i\omega_0 t} \quad \forall t \\ \Leftrightarrow \left\{ \Omega [C \cos(\Omega t) - \sin(\Omega t)] + \frac{i}{2}\omega_0 [C \sin(\Omega t) + D \cos(\Omega t)] \right\} e^{\frac{i}{2}\omega_0 t} \\ &= -i\omega_{ab}^* [A \sin(\Omega t) + B \cos(\Omega t)] e^{\frac{i}{2}\omega_0 t} \quad \forall t \\ \Leftrightarrow C + \frac{i\omega_0}{2\Omega} D &= -\frac{i\omega_{ab}^*}{\Omega} B \wedge D - \frac{i\omega_0}{2\Omega} C = \frac{i\omega_{ab}^*}{\Omega} A \end{aligned} \quad (5.10)$$

Suppose we start at $t = 0$ with a fully occupied state $|\psi_a\rangle$. So $c_a(0) = 1$ and $c_b(0) = 0$. Putting this in equation 5.9, two of the constants are obtained

$$c_a(0) = B = 1 \quad (5.11)$$

$$c_b(0) = D = 0 \quad (5.12)$$

When we put this in equation 5.10 the other two constants are obtained

$$C = -\frac{i\omega_{ab}^*}{\Omega} B = -\frac{i\omega_{ab}^*}{\Omega} \quad (5.13)$$

$$A = -\frac{\omega_0}{2\omega_{ab}^*} C = \frac{i\omega_0}{2\Omega} \quad (5.14)$$

The equation for $c_a(t)$ and $c_b(t)$ has now been reduced to

$$\begin{cases} c_a(t) = \left(\cos(\Omega t) + \frac{i\omega_0}{2\Omega} \sin(\Omega t) \right) e^{-\frac{i}{2}\omega_0 t} \\ c_b(t) = -\frac{i\omega_{ab}^*}{\Omega} \sin(\Omega t) e^{\frac{i}{2}\omega_0 t} \end{cases} \quad (5.15)$$

The corresponding expectation values of the occupation of the levels becomes

$$|c_a(t)|^2 = \cos^2(\Omega t) + \frac{\omega_0^2}{4\Omega^2} \sin^2(\Omega t) \quad (5.16)$$

$$|c_b(t)|^2 = \frac{|\omega_{ab}|^2}{\Omega^2} \sin^2(\Omega t) \quad (5.17)$$

The expectation values of the levels of this analytical model will be compared to the ones obtained from the numerical calculation.

5.2 Results

The numerical treatment is done by propagating the orbitals as explained in section 4.1. The results show that the analytical and numerical treatment of the problem give exact the same results. the occupation number of the two levels are plotted in figure 5.1. For this plot both levels have the same energy. It is not possible to see the difference between the curves for the numerical and analytical calculations. Note the oscillations due to the disturbance. The system is not can not in an eigen state anymore and the occupation of the levels

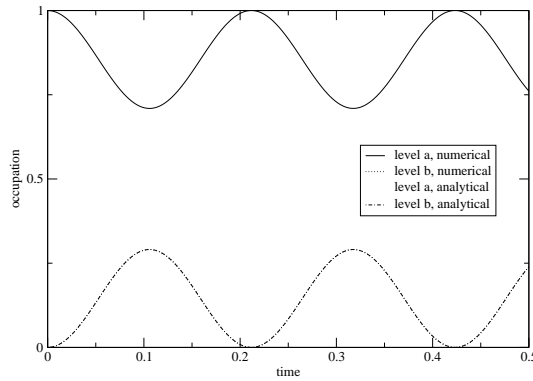


Figure 5.1: Plot of the occupation levels of a two level system after a perturbation is switched on. The time is plotted in atomic units. The energies of both levels are 25 and the off-diagonal elements are chosen to be 8.

Chapter 6

1D model

To get more experience with molecular transport systems, we will start with a small model system with non-interacting electrons. This has the advantage that we can easily solve the Schrödinger equation. As a model we will use a box with infinite walls and in the middle a potential to separate the electrons (see fig. 6.1). The two regions with electrons are identified with the leads of the original transport system. The barrier simulates the gap between the electrodes and the height of the barrier can be identified with the Fermi energy [20, 21]. However, since the barrier also will simulate the device between the leads, the barrier height is set independently from the Fermi energy. To keep things even more simple we start with a one dimensional system.

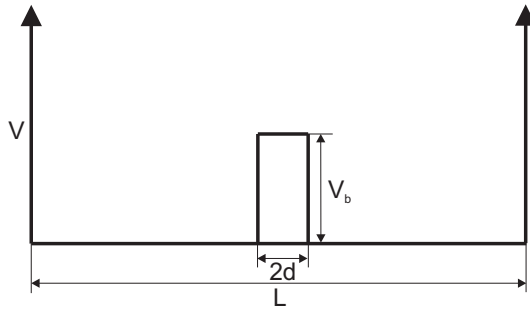


Figure 6.1: Schematical drawing of the 1D box. The total length of the box is L , the width of the barrier is $2d$ and the height of the barrier is V_b .

The system before $t = 0$ is described by the hamiltonian consisting of only the kinetic energy and the barrier

$$\hat{H} = -\frac{1}{2}\partial_x^2 + V_b\theta(d - |z|). \quad (6.1)$$

By calculating the ground state from this Hamiltonian we obtain an equilibrium state from which the system can evolve.

At $t = 0$ an additional potential is applied to one side of the box and the additional term to the Hamiltonian can be written as

$$\hat{H}'(t) = V\theta(-d - z)\theta(t). \quad (6.2)$$

As a basis we have chosen the eigen functions of the box. As explained in section 4.1, after all the matrix elements have been calculated, the system can be propagated. The propagation can be done to arbitrary times, since the perturbation is time-independent. At every time step, any observable can be calculated and its evolution can be plotted. In our case we will be interested in the number of particles at one side of the box and its derivative with respect to time which can be identified with a current.

6.1 Calculations

In this section we elaborate on the calculations. First the basis is introduced, then the matrices are calculated and some words are spend on the time-propagation of the system.

6.1.1 The basis set

Most people have seen how to solve the particle in a box. However, for completeness it is shown here again. The answers are given in two coordinate systems which will be useful when calculating the matrix elements. The coordinate system labeled by x (z) will have its origin at the left side (middle) of the box. The system has only the kinetic energy term for particles inside the box:

$$\hat{H} = -\frac{1}{2}\partial_x^2 \quad (6.3)$$

It is most convenient to do the calculation in x coordinate system and transform the results later to z by using the transformation $x = z + L/2$. Inserting the hamiltonian in the time-independent Schrödinger equation we obtain:

$$\hat{H}\Psi(x) = -\frac{1}{2}\partial_x^2\Psi(x) = -\frac{1}{2}\Psi''(x) = E\Psi(x) \quad (6.4)$$

Rewrite the equation as

$$\Psi''(x) = -k^2\Psi(x), \quad \text{where } k = \sqrt{2E}. \quad (6.5)$$

This is a simple homogeneous second order differential equation which has the following solution:

$$\Psi(x) = A \sin(kx) + B \cos(kx), \quad (6.6)$$

where A and B are constants that are determined by the boundary conditions. for the 1D box these are $\Psi(0) = \Psi(L) = 0$. This implies that $B = 0$ and $k = n\pi/L$:

$$\Psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right) \quad \text{and} \quad (6.7)$$

$$k = \frac{n\pi}{L} = \sqrt{2E} \Rightarrow E_n = \frac{1}{2}k^2 = \frac{n^2\pi^2}{2L^2}. \quad (6.8)$$

The only undetermined constant is A and it can be determined up to a phase factor by normalizing the wave function

$$\begin{aligned} \int_0^L dx |\Psi_n(x)|^2 &= |A|^2 \int_0^L dx \sin^2(kx) = \frac{|A|^2}{2} \int_0^L dx (1 - \cos(2kx)) = \frac{|A|^2}{2} \left[x - \frac{\sin(2kx)}{k} \right]_0^L \\ &= \frac{L}{2} |A|^2 = 1 \Rightarrow A = \sqrt{\frac{2}{L}} \end{aligned} \quad (6.9)$$

So we calculated as basis function:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \quad \text{and} \quad \Psi_n(z) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}\left(z + \frac{L}{2}\right)\right) \quad (6.10)$$

6.1.2 Matrix elements and time-propagation

Here we give all the answers to the matrix elements. For more details see appendix B.1. The most simple element is the kinetic energy since it is just equal to the energy in the 1D box. The rest has to be evaluated by integrals which can be done analytically.

$$\langle k|\hat{T}|q\rangle = \frac{k^2}{2}\delta_{k,q}, \quad (6.11)$$

$$\langle k|V_d\theta(d-|z|)|q\rangle = \frac{2V_d}{L} \left[\frac{\cos\left((k-q)\frac{L}{2}\right)\sin((k-q)d)}{k-q} - \frac{\cos\left((k+q)\frac{L}{2}\right)\sin((k+q)d)}{k+q} \right], \quad (6.12)$$

$$\langle k|V\theta(-d-z)|q\rangle = \frac{V}{L} \left[\frac{\sin((k-q)D)}{k-q} - \frac{\sin((k+q)D)}{k+q} \right], \quad (6.13)$$

where we have introduced the width of one lead $D = L/2 - d$.

To calculate the ground state of the system before $t = 0$, we just diagonalize the hamiltonian H . There are LAPACK routines [22] and routines from numerical recipes for C [24] available which can do this very fast for quite big matrices. Both routines are equally fast, but the LAPACK routine has the advantage that it orders the eigen values from the lowest to the highest, so I used the LAPACK routine. The orbitals that are obtained from the diagonalization are then filled up to a number of electrons one wants to have in the box. This is done by putting ones for increasing energies in the state matrix which was defined by equation 4.3. The highest occupied orbital (HOO) corresponds to the Fermi energy. Since the number of electrons is chosen, the Fermi energy does not the same as the barrier height.

To treat the perturbation, the perturbation is added to the hamiltonian. Since it is still a symmetric matrix, the exponential can be calculated exact. For every time-step the state matrix is multiplied by the exponential which gives a new state matrix which describes the system at that particular time. Then the density matrix can be calculated and with the density matrix every observable. In our case this will be the particle number in the left lead N^{left} . In our basis it will look just the same as the matrix for the perturbation, but without the V

$$N_{kq}^{\text{left}} = \langle k|\theta(D-x)|q\rangle = \frac{1}{L} \left[\frac{\sin((k-q)D)}{k-q} - \frac{\sin((k+q)D)}{k+q} \right]. \quad (6.14)$$

From the number of particles it is easy to calculate the current by using the definition of differentiation applied on a final grid. Just take the difference of the particle number divided by the time-step.

The density is calculated as well. The density $\hat{n}(x)$ is easily expressed in every basis as

$$n_{ij}(x) = \phi_i^*(x)\phi_j(x), \quad (6.15)$$

from which the density at any point x can be calculated.

6.2 Results

In this section some results are shown for a chosen set of parameters which show the interesting features of the 1D model. The parameters used for this calculation are listed in table 6.1. The energies are obtained from the calculations.

From the calculations it has become clear that for a good description of the box, the orbital with the maximum energy that the set can describe has to be $E_{MAX} \geq V_d/2$. Most of the calculations were done for E_{MAX} well above the barrier height V_d to avoid any doubt if the basis set was large enough. The size of the box determines the energy spectrum and therefore the number of wave functions required for a good description is also related to the length of the box. For a 1D box the energy goes as $E \sim k^2 \sim n^2/L^2$. Therefore, the size of the basis set will grow linear with the size of the box.

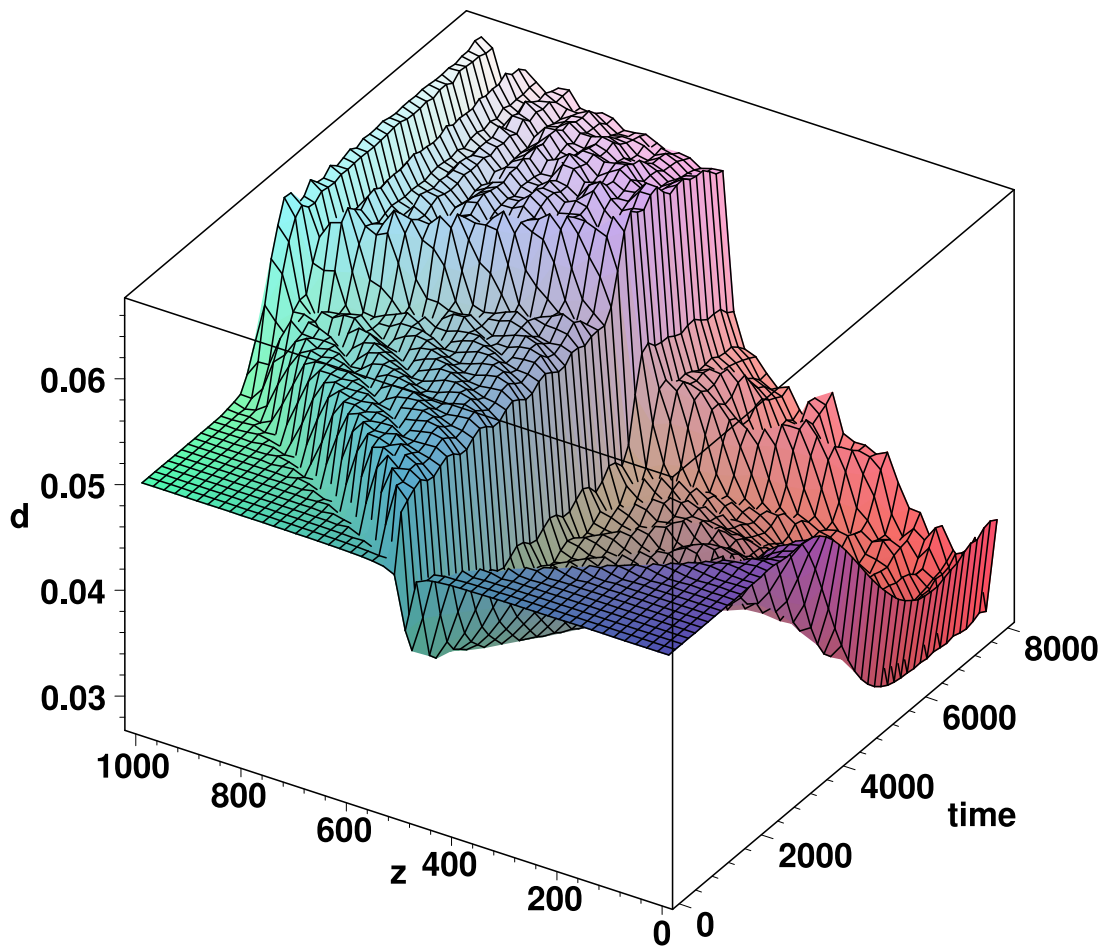


Figure 6.2: The density in the 1D box evolving in time. The density, d , the position, z , and time are in atomic units. One can see the electrons travel to the other side of the box, hitting the wall at $t \approx 3000$ and even returning to the other side of the box at $t \approx 6000$.

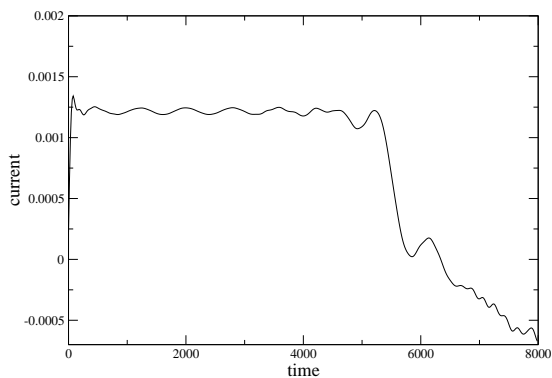


Figure 6.3: The current in the same 1D box plotted against time. Everything is in atomic units. The current becomes negative at $t \approx 6000$. This is caused by the back scattered electrons.

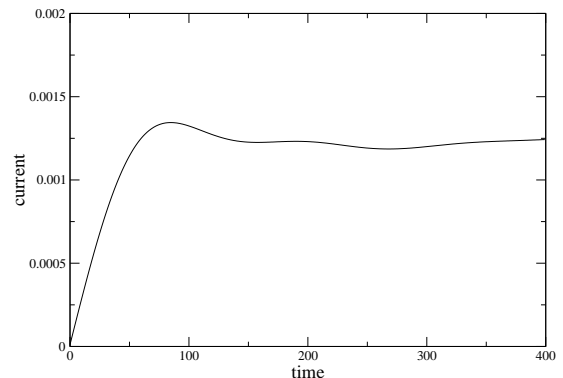


Figure 6.4: The current in the same box again, but for a smaller time scale. No electrons are reflected from the walls at these times yet, so it should be comparable to infinite leads. One can also see some switch on effects, before the current reaches a steady state.

size of one lead = D	500
width of the barrier = $2d$	0.5
total size of the box = L	1000.5
height of the barrier = V_d	0.04
number of electrons	50
density in the leads	0.05
number of basis functions	100
applied potential = V	0.008
groundstate energy = E_0	$1.65 \cdot 10^{-5}$
highest occupied energy = E_{HOO}	0.0123
highest energy E_{MAX}	0.0493

Table 6.1: The parameters used for calculations on a 1D box. The energies are obtained from the calculation.

size of one lead = D	500
width of the barrier = $2d$	0.5
total size of the box = L	1000.5
height of the barrier = V_d	0.04
number of electrons	25/50
density in the leads	0.025/0.05
number of basis functions	100
groundstate energy = E_0	$1.65 \cdot 10^{-5}$
highest occupied energy = E_{HOO}	0.00312/0.0123
highest energy E_{MAX}	0.0493

Table 6.2: The parameters used for calculations on a 1D box. The energies are obtained from the calculation.

In figure 6.2 a three dimensional plot is shown of the density evolving in time. This gives a good view of the effect of the perturbation on the electrons. The applied potential is pushing away the electrons from one side of the box to the other. After some time ($t \approx 3000$) the electrons hit the wall and bounce back which raises the density even more. Then at $t \approx 6000$ the electrons move back into the other lead which causes the current to become negative.

To give more quantitative proof, the current is plotted in figure 6.3. At $t \approx 6000$ the current becomes negative due to the back scattered electrons. The traveling electrons will be the ones that have energies close to the Fermi energy. For this calculation the highest occupied energy is $E_{HOO} = 0.012$. The velocity of these electrons will be $v_{HOO} = \sqrt{2E_{HOO}} = 0.16$. At $t \approx 6000$ they have traveled a distance $l_{HOO}(6000) = 942$, which is very close to twice the size of one lead $2D = 1000$.

Before the electrons reach the wall at the other side, one can argue that the current is the same as for a system with semi-infinite leads. The electrons have not had enough time to interact with the wall, so for short time scales one can use this as a model system for the transport problem. The current is plotted in figure 6.4, which looks exactly the same as the switch on current that is expected for semi-infinite leads. One clearly sees a rise of the current including switch on effects. After some time the current saturates to some finite value.

It has also been investigated how much current the system can handle. Therefore some calculations have been done where only the applied bias voltage has been changed. For these calculations parameters are used listed in table 6.2.

The time-dependent currents for different applied bias voltages for the box with 50 electrons are shown in figure 6.5 and for the box with 25 electrons in figure 6.6. One can see that the current saturates for some value of the applied bias. So only for values of the applied bias voltage below a certain threshold, the current increases with the applied voltage. To get a better estimate of this point the conductance (I/V) of these systems has been plotted as well in the figures 6.7 and 6.8.

One can clearly see that the current increases linearly for sufficiently low bias. So for low voltages Ohms law will be valid. Notice that the saturation for the box with 25 electrons is achieved at much lower levels for the applied potential. When we look at the E_{HOO} , we see that the maximum for the applied bias voltage matches the Fermi energy. This is not very surprising. If the applied bias voltage is higher than the Fermi energy, it will not give more electrons an energy higher than the energy at the other side of the box. So there will not be extra electrons anymore that can travel to the other side of the box.

If one checks out figure 6.8 carefully, one observes another saturation level for higher voltages. This is due to the extra energy the electrons gain from the potential. The total energy of the electrons will

be $E \sim E_0 + V$. So the speed of the electrons will be $v \sim \sqrt{E + V} \sim I$. The conductance will have $\sigma = I/V \sim 1/\sqrt{V}$ as asymptotic value for high bias voltages.

The effect of the box size on the current is examined as well. As one can see from figure 6.9 the current will break down earlier for the smaller box as expected. One can also see that the modulations in the current are smaller for the larger box. This probably has to do with the finite number of electrons in the box. Since there is only a limited number of electrons, the density profile is not completely flat throughout the box. When a voltage is applied these modulations start to travel through the box, which is expressed in the time-dependent current as a wave. For larger boxes the density will be more flat like in a metal, so the modulations in the current will be smaller as well. Note that these modulations are so strong in the smaller box, that they are even visible in the switch on region (see fig. 6.10).

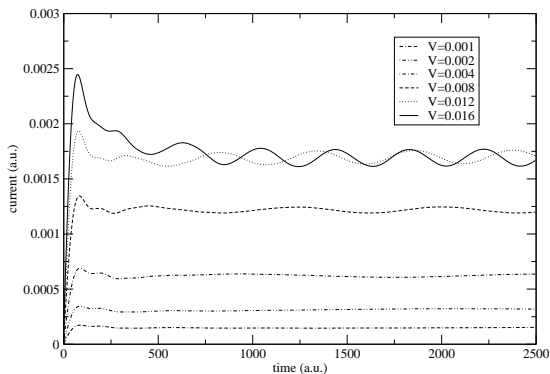


Figure 6.5: The current plotted for different values of the applied bias voltage. The number of electrons in the box is 50

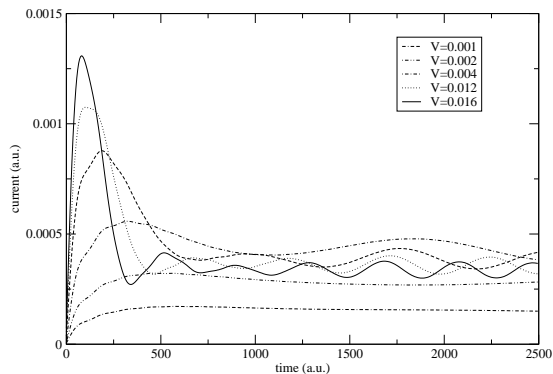


Figure 6.6: Same as the previous plot, but now for the same box with only 25 electrons.

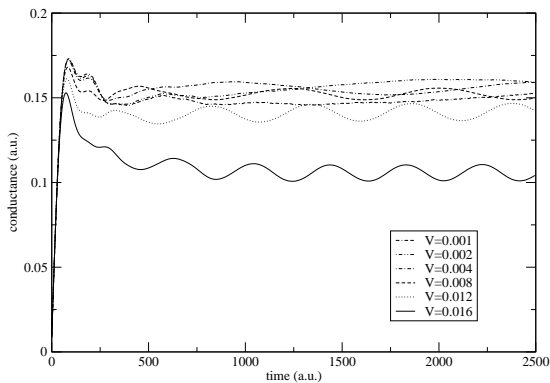


Figure 6.7: The conductance plotted for different values of the applied bias voltage. The number of electrons in the box is 50.

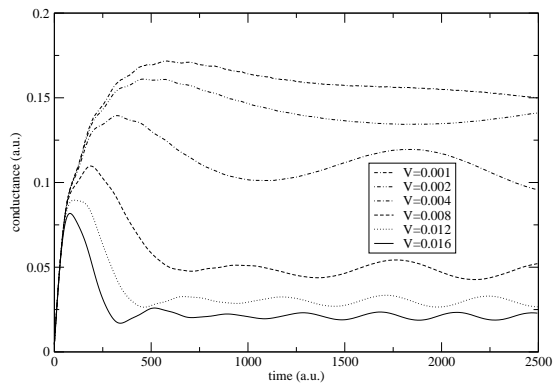


Figure 6.8: Same as the previous plot, but now for the same box with only 25 electrons.

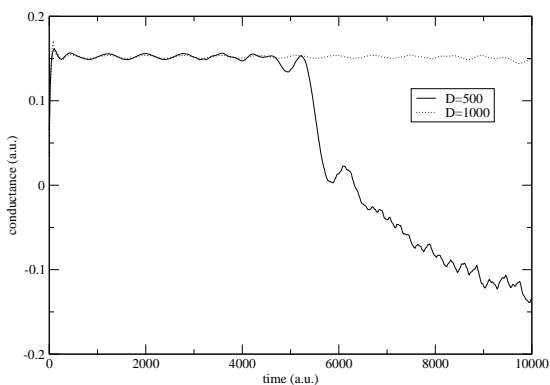


Figure 6.9: The current plotted for two boxes with different size. The number of electrons is doubled for the larger box to keep density the same in both boxes (0.05). All the other parameters in both boxes are equal as well.

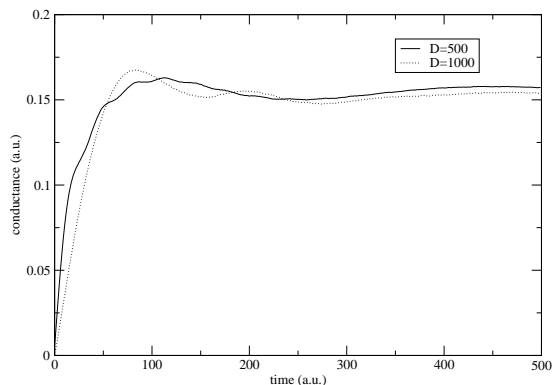


Figure 6.10: The same as in the previous figure, but now plotted on a shorter time scale.

Chapter 7

3D model

To go to a more realistic and interesting model we include the missing two dimensions. The 1D box is now extended in two directions and the barrier will become a slab. A nice feature of a three dimensional model is that it is now possible to include a local potential to simulate a molecule or another small object between two leads. The molecule can behave as a conduction channel through the barrier. This increases the parameters that can be examined drastically. Two extra dimensions and a local potential that in principle can be of any shape. The potential used here is the Yukawa or screened Coulomb potential

$$V(r) = V_{loc} \frac{e^{-\alpha r}}{r}. \quad (7.1)$$

This is a quite simple potential, but very realistic since it corresponds to the potential of an atom screened by electrons. Since the unscreened Coulomb potential has a Slater as the wave function with the lowest energy (better known as the 1s orbital of Hydrogen)

$$\phi(r) = \sqrt{\frac{b^3}{\pi}} e^{-br}, \quad (7.2)$$

it will be used as the local basis function.

It is ensured that the current goes only through the local potential. After electrons have travelled through the potential they will spread out through the leads. This will cause the current density to drop. For 3D leads it will go as $\sim 1/r^2$ (see fig. 7.2). This means that the current density far in the leads will go to zero.

The main challenge in the calculations is to control the number of basis functions required. A quick estimate calculation from the 1D model shows that one would need about $100^3 = 10^6$ basis functions. Everything stored in matrices and doing manipulations on them requires huge amounts of memory and calculation time. So a reduction of the basis is mandatory.

7.1 Calculations

As mentioned before the numerical analysis of this problem will mainly concern keeping the number of basis functions limited. There are a couple of tricks used: the use of only the occupied orbitals of the leads and the introduction of an extra localized wave function.

To create a small but adequate basis set, a first calculation is done where only the barrier is taken into account. Due to the mirror symmetry the total matrix can be divided in small submatrices which can be treated separately. Then only the orbitals are taken that have energies below a certain energy level. This will be a bit higher than the Fermi energy to ensure a good description of excited states.

Unlike the plane waves, the new basis set is localized in the leads, so an additional basis function is required on the device. The basis set localized on the leads, together with the basis function on the device, will form a new basis which is still adequate and can have a enormous reduction in size. However, the reduction is strongly dependent on the Fermi energy chosen and the excitation energies one wants to handle. It should at least be the Fermi energy plus the applied bias potential.

Additional the electric field between the two leads is taken into account. In the 1D box the applied potential was of the form $V\theta(-d-z)$. Now an extra term is included to count for the electric field between the leads $V_L = V_L\Theta(-z-d) + \frac{V_L}{2d}(d-z)\Theta(d-|z|)b$.

The numerical analysis involves a couple of different calculations. First there are the integrals that have to be evaluated. Unfortunately not all of them can be done analytically anymore. Then we have to choose a suitable value for the parameter b in the local wave function. But first some more aspects of the basis should be mentioned.

7.1.1 The basis set

The initial basis consists of the following functions

$$\phi_b = \sqrt{\frac{b^3}{\pi}} e^{-br} \quad (7.3)$$

$$\phi_{k_x, k_y, \pi_z, k_z} = \begin{cases} \sqrt{\frac{8}{\Omega}} \sin(k_x(x + \frac{a}{2})) \sin(k_y(y + \frac{a}{2})) \cos(k_z, g z) & \text{if } \pi_z = g \\ \sqrt{\frac{8}{\Omega}} \sin(k_x(x + \frac{a}{2})) \sin(k_y(y + \frac{a}{2})) \sin(k_z, u z) & \text{if } \pi_z = u \end{cases} \quad (7.4)$$

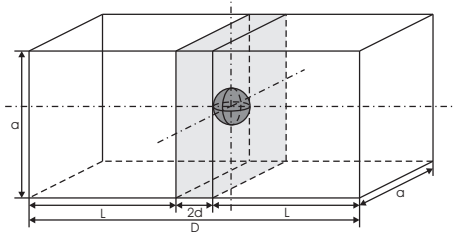


Figure 7.1: Draft of the 3D box. The gray shaded area indicates the barrier with a potential of V_d . In the middle is a sphere to indicate the atom, in our case a spherical potential. The middle of the box is at the crossing of the dash-dot lines which is the origin as well.

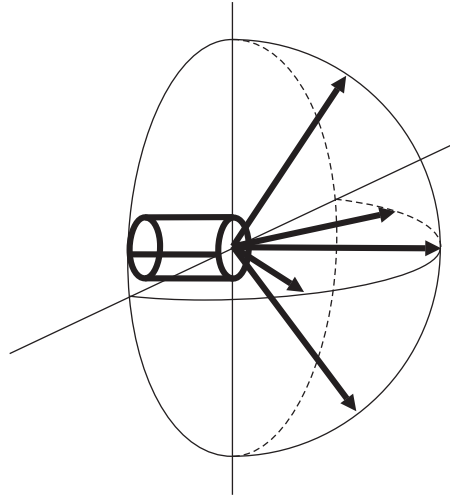


Figure 7.2: Impression of the current emerging from the conduction channel into the lead. The current will spread, so the current density will drop. In a three dimensional system the current has to be divided over a hemisphere, so the current density in the lead will behave as $1/r^2$.

where,

$$\begin{aligned}
k_x &= \frac{n_x \pi}{a}, \text{ with } n_x \in \mathbb{N}, \\
k_y &= \frac{n_y \pi}{a}, \text{ with } n_y \in \mathbb{N}, \\
\pi_z &= g(\text{erade}) / u(\text{ngerade}), \\
k_{z,g} &= \frac{(2n_z - 1)\pi}{D}, \text{ with } n_z \in \mathbb{N}, \\
k_{z,u} &= \frac{2\pi n_z}{D}, \text{ with } n_z \in \mathbb{N}, \\
\Omega &= a^2 D
\end{aligned}$$

The terms gerade and ungerade are with respect to the barrier. This is an extra symmetry that can be used to reduce the size of the matrices that describe the box with only the barrier. The extra label for the gerade / ungerade functions in fact is redundant, since they do not have their k_z in common. So π_z is actually determined by k_z .

Unfortunately the basis is not orthogonal anymore $\langle \phi_i | \phi_j \rangle \neq \delta_{i,j}$. The overlap element between the Slater function and the plane waves is

$$\langle \vec{k}, \pi_z | b \rangle = 16b^2 \sqrt{\frac{2\pi b}{\Omega}} \frac{\sin(k_x a/2) \sin(k_y a/2)}{(b^2 + k^2)^2} \delta_{\pi_z, g} \quad (7.5)$$

This non-orthonormality has to be taken into account. In section 4.2 it has been explained how to cope with non-orthonormal bases.

7.1.2 The matrix elements

A couple of matrix elements are just extensions what has been calculated for the 3D box. However, due to the extra wave function and extra potential there are many additional elements.

$$\langle b | \hat{T} | b \rangle = \frac{b^2}{2} \quad (7.6)$$

$$\langle b | V_d \Theta(d - |z|) | b \rangle = V_d (1 - e^{-2bd}(1 + bd)) \quad (7.7)$$

$$\langle b | V_{loc} \frac{e^{-\alpha r}}{r} | b \rangle = \frac{4b^3 V_{loc}}{(\alpha + 2b)^2} \quad (7.8)$$

$$\langle b | V_L | b \rangle = \frac{V_L}{2} \quad (7.9)$$

$$(7.10)$$

The elements for the plane waves are

$$\langle \vec{k}, \pi_z | \hat{T} | \vec{p}, \chi_z \rangle = \frac{k^2}{2} \delta_{k_x, p_x} \delta_{k_y, p_y} \delta_{\pi_z, \chi_z} \delta_{k_z, p_z} \quad (7.11)$$

$$\langle \vec{k}, g/u | V_d \Theta(d - |z|) | \vec{p}, \pi_z \rangle = \frac{2V_d}{D} \left[\frac{\sin((k_z - p_z)d)}{k_z - p_z} \pm \frac{\sin((k_z + p_z)d)}{k_z + p_z} \right] \delta_{k_x, p_x} \delta_{k_y, p_y} \delta_{g/u, \pi_z} \quad (7.12)$$

$$\langle \vec{k} | \frac{e^{-\alpha r}}{r} | \vec{q} \rangle = \sum_{\vec{p}} (-1)^{n_p} \frac{\cos((p_x)a/2) \cos((p_y)a/2)}{\alpha^2 + |p|^2} \delta_{g, \pi_z} \quad (7.13)$$

$$\langle \vec{k}, g/u | V_L | \vec{p}, \pi_z \rangle = \left[\frac{V_L}{2} \delta_{k_z, p_z} + \frac{V_L}{D} \left(\frac{\cos((k_z + p_z)\frac{D}{2})}{k_z + p_z} + \frac{\sin((k_z + p_z)d)}{d(k_z + p_z)^2} \mp \left(\frac{\cos((k_z - p_z)\frac{D}{2})}{k_z - p_z} + \frac{\sin((k_z - p_z)d)}{d(k_z - p_z)^2} \right) \right) (1 - \delta_{g/u, \pi_z}) \right] \delta_{k_x, p_x} \delta_{k_y, p_y} \quad (7.14)$$

Here we have introduced the sum over \vec{p} which means a summation over every possible combination of adding or subtracting the components of \vec{k} and \vec{q} . The number n_p refers to the number of additions to obtain the particular vector \vec{p} . The mixed matrix elements are

$$\langle \vec{k}, \pi_z | \hat{T} | b \rangle = \frac{k^2}{2} \langle \vec{k}, \pi_z | b \rangle = 8b^2 k^2 \sqrt{\frac{2\pi b}{\Omega}} \frac{\sin(k_x a/2) \sin(k_y a/2)}{(b^2 + k^2)^2} \delta_{\pi_z, g} \quad (7.15)$$

$$\langle \vec{k}, \pi_z | V_d \Theta(d - |z|) | b \rangle = 4bV_d \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \times \int_{-d}^d dz \int_0^\infty d\rho \rho J_0(k\rho) e^{-b\sqrt{\rho^2 + z^2}} \cos(k_z z) \delta_{\pi_z, g} \quad (7.16)$$

$$\langle \vec{k}, \pi_z | V_{loc} \frac{e^{-\alpha r}}{r} | b \rangle = \sqrt{\frac{2\pi b}{\Omega}} \frac{8bV_{loc}}{(\alpha + b)^2 + k^2} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \delta_{\pi_z, g} \quad (7.17)$$

$$\langle \vec{k}, \pi_z | V_L | b \rangle = 4bV_L \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \left\{ \frac{2b}{(b^2 + k^2)^2} \delta_{\pi_z, g} - \int_0^\infty d\rho \left(\int_d^\infty dz + \int_{-d}^d dz \frac{z}{2d} \right) \rho J_0(k\rho) e^{-b\sqrt{\rho^2 + z^2}} \sin(k_z z) \delta_{\pi_z, u} \right\} \quad (7.18)$$

For more details on the calculations of these integrals, see appendix C.1. Some of the integrals could not be solved analytically, so they were done numerically. For more details about the numerical integration see appendix C.2

7.1.3 Choosing a suitable value for b

For an unscreened local potential, which is the potential of a hydrogen atom, the optimal choice for b is just $b = V$. For a screened potential this is not true anymore and one has to recalculate it by using the variational principle ($\langle \psi | \hat{H} | \psi \rangle \geq E_{groundstate}$). The hamiltonian looks like:

$$\hat{H} = -\frac{1}{2} \nabla^2 - V \frac{e^{-\alpha r}}{r}. \quad (7.19)$$

The energy then becomes:

$$E_b = \langle b | \hat{H} | b \rangle = \frac{b^2}{2} - \frac{4b^3 V}{(\alpha + 2b)^2}. \quad (7.20)$$

First we look for points where the energy becomes zero:

$$E_b = \frac{b^2}{2} \left(1 - \frac{8bV}{(\alpha + 2b)^2} \right) = 0$$

$$\Leftrightarrow b^2 = 0 \vee b = V - \frac{\alpha}{2} \pm \sqrt{(V - \alpha)V} \quad (7.21)$$

The parameter b has to be positive and real. This gives an extra condition on the choice of α and V :

$$V \geq \alpha. \quad (7.22)$$

Differentiating gives:

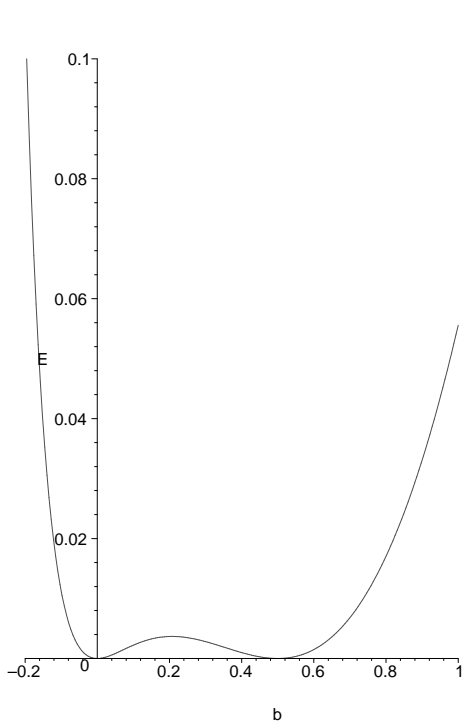


Figure 7.3: Plot of the energy $E(b)$ as function of b with $V = 1$ and $\alpha = 1$.

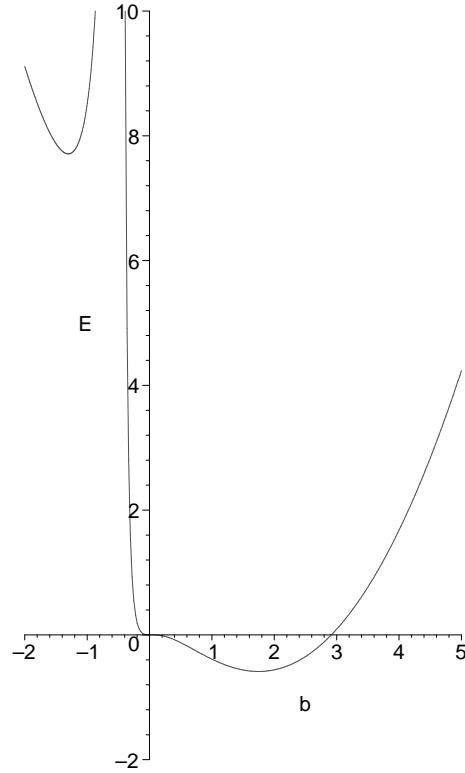


Figure 7.4: Plot of the energy $E(b)$ as function of b with the following parameters: $V = 2$ and $\alpha = 1$.

$$\partial_b E_b = \frac{b(8b^3 + 4(3\alpha - 2V)b^2 + 6\alpha(\alpha - 2V)b + \alpha^3)}{(\alpha + 2b)^3} = 0. \quad (7.23)$$

One solution is simple, but useless: $b = 0$. Solving the third order equation gives one real and two complex solutions:

$$b_1 = \frac{1}{6}K + 2B\frac{V}{K} + B - \alpha, \quad (7.24)$$

$$b_{2/3} = -\frac{1}{12}K + B\frac{V}{K} + B - \alpha \pm i\sqrt{3} \left(\frac{1}{12}K - B\frac{V}{K} \right) \quad (7.25)$$

where

$$K = \left[V \left(8V^2 + 18\alpha V - 54\alpha^2 + 6\sqrt{3}\alpha\sqrt{27\alpha^2 - 20\alpha V - 9V^2} \right) \right]^{1/3} \text{ and} \quad (7.26)$$

$$B = \frac{V}{3} + \frac{\alpha}{2} \quad (7.27)$$

Unfortunately K is real for $-3.17\alpha \lesssim V \lesssim 0.95\alpha$, so the answer will always be complex. This is not very strange, since we deal with a localized potential. So plane waves will mix in and an oscillation of the wave function is expected, which expresses itself as the imaginary part of b . It is similar to hard core potentials which have Hankel functions as their solution. Since the basis already contains plain waves, the imaginary part of b is neglected.

7.1.4 Numerical calculation

The main problem is the large number of basis functions required to describe the 3D box. The main part of the program is build to handle this problem. The plan of work is to start with a huge plane wave basis. The 3D box with only the barrier has a lot of symmetries which can be used to group the plane waves. The Hamiltonian matrix is divided in small submatrices which can be treated separately. From the matrix elements 7.11 and 7.12 it is clear that they can be separated by the quantum number k_x , k_y and π_z . This separation reduces the amount of memory required and calculation time enormously, without having a small basis.

After the matrices have been diagonalized, only the orbitals with energies lower than a certain energy E_{top} will be included in the new basis. This will be a bit higher than the Fermi energy E_F to allow for excitations. However, the local potential is badly described by the plane waves. Therefore a local wave function $|b\rangle$ is added to the basis. Unfortunately the basis is not orthonormal anymore. The system is now described by the equation

$$iS_{ik}\dot{c}_{kj}(t) = H_{ik}^0(t)c_{kj}(t), \quad (7.28)$$

where \mathbf{H}^0 now contains contributions from the kinetic energy, the barrier and the local potential. To determine the Hamiltonian \mathbf{H}^0 and the overlap matrix \mathbf{S} , they have to be calculated in the old basis and then transformed to the new one. By counting the number of states that have an energy $E \leq E_F$, the number of electrons is determined in the leads. The total number of electrons will be one more which comes from the bound state of the local potential.

It has been described in section 4.2 how to calculate the eigen states from such an equation. This will contain to additional transformations due to the ‘unifying’ of the overlap matrix \mathbf{S} and the diagonalization of the Hamiltonian matrix \mathbf{H}^0 . To describe the equilibrium of the system, the state matrix is now filled with ones for each electron.

To make a plot of the density, the density matrix in real space $\mathbf{n}(\mathbf{r})$ can be calculated

$$n_{ij}(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}) \quad (7.29)$$

Since we have an orthonormal basis now the expectation value can be written as

$$\langle \hat{n}(\mathbf{r}) \rangle = \text{Tr} \{ \hat{\rho} \hat{n}(\mathbf{r}) \} = \langle m || k \rangle c_{kn} c_{nl}^\dagger \langle l | i \rangle \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \langle j || m \rangle = c_{ni}^\dagger \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) c_{jn} \quad (7.30)$$

It is convenient to make a routine that given the matrix $\phi_j(\mathbf{r})c_{jn}$, calculates directly $\langle \hat{n}(\mathbf{r}) \rangle$, since it only needs to calculate the diagonal elements and sum them. Building this routine greatly pays off, since a typical grid on which $\langle \hat{n}(\mathbf{r}_i) \rangle$ is calculated contains $50^2 = 2500$ points. Note that is is only possible since the operator $n_{ij}(\mathbf{r})$ does not contain an integral. Otherwise the operator can not be split.

We have now an equilibrium state and can now apply a perturbation to it. Therefore, the term due to the applied voltage \mathbf{H}_L is calculated again in the old basis, transformed to the new basis and added to the

hamiltonian $\mathbf{H}_L + \mathbf{H}^0 = \mathbf{H}$. By diagonalizing the new hamiltonian, the exponential $\exp(-i\mathbf{H}t) = \mathbf{U}(t)$ can be calculated directly. Multiplying the matrix $\mathbf{U}(t)$ gives the state matrix evolved over the time t .

Since the perturbation is time-independent, the time steps can be made arbitrary large and it pays off to describe everything in the basis where the Hamiltonian is diagonal. The multiplication with a diagonal matrix is only a N^2 compared with a full matrix multiplication which is N^3 . Since a lot of time steps are made (typically ~ 200), it is certainly worth the trouble to transform everything one more time.

The number of particles in the left lead can be calculated by transforming the number operator for the left lead into the new basis and taking the trace with the density operator $\rho = \mathbf{c}\mathbf{c}^\dagger$ in that particular basis. Taking the difference between two neighbouring points in time and dividing by the time step, we obtain the time-dependent current for the system.

7.2 Results

The code for the 3 dimensional box is still at its testing stage. Some results will be shown in this section, but a complete analysis of the properties is not possible yet.

In figure 7.5 the initial density of the system is shown in the plane $x = 0$. The parameters used to make this plot are shown in table 7.1. To speed up the calculation, the density is not integrated over x . That is why the device shows a very large peak, which had to be cut off to make the density in the leads visible. Due to the finite number of electrons and the finite size of the box, the density is not a completely flat surface in the leads.

number of initial basis functions in x and y direction = n_{xy}	10
number of initial basis functions in z direction per parity = n_z	20
width of the box in x and y direction = a	50
length of one lead = L	50
width of the barrier = $2d$	2
Fermi energy = E_F	0.04
maximum energy included in the new basis = E_{top}	0.06
height of the barrier = V_d	E_F
the exponent in the local potential = α	1/d
the strength of the local potential = V_{loc}	1
the applied potential = V_L	0.01
the exponent in the local basis function = b	optimized
number of electrons	59

Table 7.1: The parameters used for the calculation for which the results are shown in figures 7.5 and 7.6. All the quantities are given in atomic units.

The current has been calculated as well and is shown in figure 7.6. One clearly sees some switch on effects which are damped. Something strange is that the current seems to saturate to a negative value before the break down. Making the same estimation as was done for the 1D box, we can estimate the time of break down of the current by calculating the Fermi velocity v_F . The Fermi velocity can be written as $v_F = \sqrt{2E_F} \approx 0.3$, from which the time of break down is calculated as $t_{bd} \approx 2L/v_F \approx 350$ which is reasonable compared to the current shown in figure 7.6.

However, this was a very small box, so it is difficult to separate all the effects we are interested in from the effects due to the finite size of the system (space and number of electrons). Larger boxes will have to be calculated to get better insight in the transport problem. For example the shortest length scale which might cause reflection is not the size of the lead in the z direction, L , but for this particular problem it

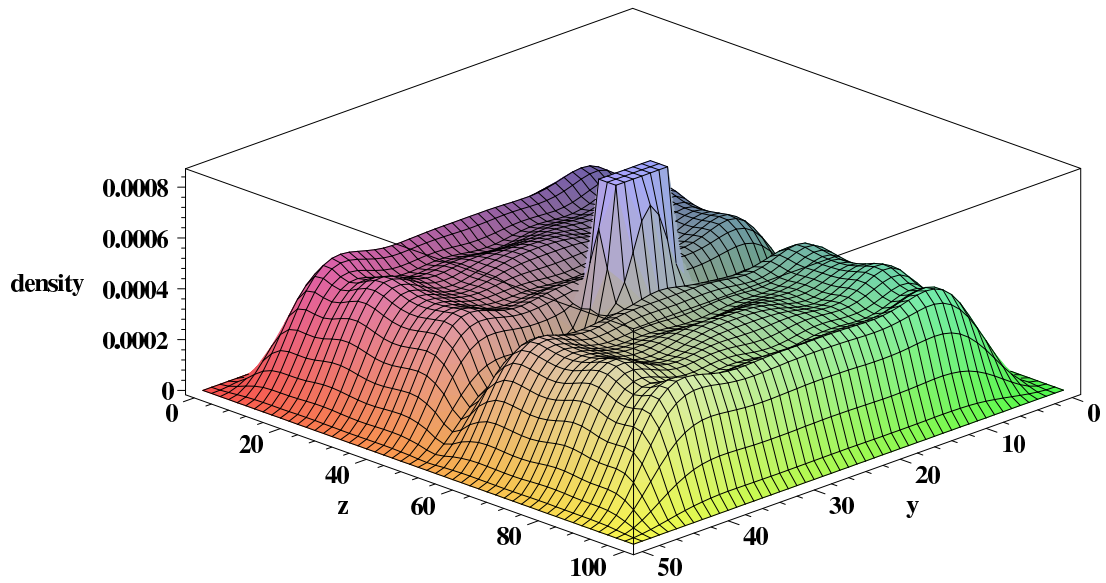


Figure 7.5: The density in a 3D box in the $x = 0$ plane. To make the density in the leads visible, the maximum density has been limited, which explains the cut off of the peak in the middle. All the quantities are given in atomic units.

is the size in the x and y direction, a . The electrons have to travel only half of the distance, but there is only little reflection expected from these sides. However it could explain the negative current saturation at $t \approx 200$. This would mean that the size of the leads in the x and y direction is also important for an adequate description of the transport problem.

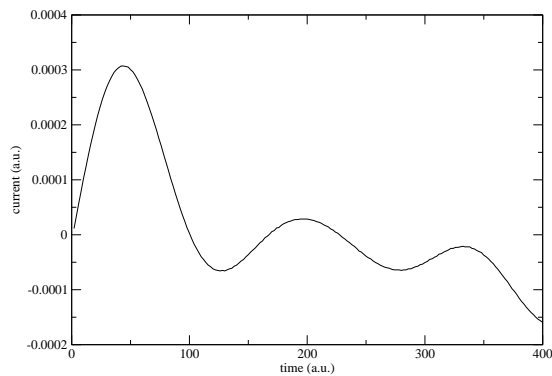


Figure 7.6: The time-dependent current in a 3D box. After some time the current breaks down due to the finite size of the system.

Chapter 8

Summary and Conclusions

We have studied the time-dependent current for molecular transport for non-interacting particles with two different approaches: non-equilibrium Green's functions and a wave function based approach. The model system used in both approaches consists of two leads with a device between them. At time $t = 0$ there is a sudden switch on of a bias voltage. The time-dependent current induced by this bias voltage is calculated in both approaches.

First non-equilibrium Green's functions were used to calculate the time-dependent current in a partition-free approach with infinite leads. The leads were taken into account through an effective self energy Σ . This builds on work of G. Stefanucci and C.-O. Almbladh [5]. It turned out that the steady state current is independent of the initial conditions. This implies that the steady state current in the partitioned approach is the same as in the partition-free approach. It has been shown that the behaviour of the time-dependent current is not just a simple exponential decay towards the steady state current and that the current for large bias voltages becomes independent of the applied bias voltage.

Next a wave function based approach was used to calculate the time-dependent current for finite sized leads. The time-dependent Schrödinger equation was used to propagate the wave function in time from which the current could be calculated directly.

First we limited the system to one dimension. The device was modeled as a simple barrier between the two leads. The time-dependent current showed first some switch-on effects and then saturates to a steady current which shows some small modulations due to the finite size of the system. Then after some time the current breaks down due to the reflection of the particles at the other side. The time of break down could be estimated as twice the size of one lead divided by the speed of the fastest particles. It has been shown that the time-dependent current during the switch-on and steady state was essentially the same for systems of different size. This shows that on this time scale the current is likely to be similar in an infinite sized system. In this system there was a saturation of the time dependent current as well which was due to the finite number of electrons that could participate in the current.

Next we increased the dimension of the system by two to a 3D system. Since the leads are three dimensional, the current density falls off as $\sim 1/r^2$. For infinite leads this would mean that the current density at infinity is zero! The device was modeled a screened Coulomb potential which is also known as a Yukawa potential. To keep the number of basis functions small, first basis functions localized in the leads were calculated from a huge plane wave basis. This could be done efficiently by using the mirror symmetries of the system. To describe the device a local basis function was added to the set.

As the code is still in its testing stage, only a few results were presented. For the ground state the density for the system in equilibrium was calculated. A plot of the time-dependent current could be made as well. Some switch-on effects are visible, some saturation and finally a break down of the current due to the finite size of the system.

Chapter 9

Prospects

To finish my report I would like to make some suggestions for further research on this topic. Of course the 3 dimensional model should be examined in much more detail. It has more parameters than the 1 dimensional model which should all be examined for their effects. Together with the decrease of the current density inside the leads ($\sim 1/r^2$), this could prove a very interesting model.

Both approaches are very different. The Green's function approach has infinite leads which are included by an effective self energy Σ . The self energy can be regarded as some spectral function of the leads, which was assumed to be constant to calculate the time-dependent current. However, the wave function approach uses finite leads which are taken into account explicitly. This makes it very difficult to quantitatively compare the results from both approaches.

It might be very interesting to get better resemblance between the two methods. This might be possible if a spectral function can be extracted from the wave function based approach. This could be used to calculate the self energy in the Green's function approach which makes a comparison between the two approaches much more justified.

Appendix A

Green's functions

A.1 The Fermi distribution function

We want to evaluate the expectation value

$$\langle \hat{c}_i^\dagger \hat{c}_j \rangle = \frac{\text{Tr} \left\{ e^{-\beta \hat{H}} \hat{c}_i^\dagger \hat{c}_j \right\}}{\text{Tr} \left\{ e^{-\beta \hat{H}} \right\}}, \quad (\text{A.1})$$

where the Hamiltonian $\hat{H} = \hat{H}(0)$ is of a form as given in equation 2.36. Let us introduce the operator

$$\hat{d}_i(\beta) \equiv e^{\beta \hat{H}} \hat{c}_i e^{-\beta \hat{H}} \quad (\text{A.2})$$

When we take the derivative with respect to β and use the expression for the commutator given by equation 2.39, we obtain

$$\partial_\beta \hat{d}_i(\beta) = -e^{\beta \hat{H}} [\hat{c}_i, \hat{H}] e^{-\beta \hat{H}} = - \sum_k h_{ik} e^{\beta \hat{H}} \hat{c}_k e^{-\beta \hat{H}} = - \sum_k h_{ik} \hat{d}_k(\beta) \quad (\text{A.3})$$

Since the hamiltonian is time-independent the solution of this differential equation can be written as $\hat{\mathbf{d}}(\beta) = e^{-\beta \mathbf{h}} \hat{\mathbf{d}}(0)$. When we use that $\hat{d}_i(0) = \hat{c}_i$ and use that the Hamiltonian commutes with itself, we can rewrite the equation in terms of \hat{c}_i

$$e^{\beta \hat{H}} \hat{c}_i e^{-\beta \hat{H}} = \sum_k (e^{-\beta \mathbf{h}})_{ik} \hat{c}_k \Rightarrow \hat{c}_i e^{-\beta \hat{H}} = \sum_k (e^{-\beta \mathbf{h}})_{ik} e^{-\beta \hat{H}} \hat{c}_k \quad (\text{A.4})$$

Together with the cyclic property of the trace and the anti-commutation relations, we can calculate

$$\begin{aligned} \text{Tr} \left\{ e^{-\beta \hat{H}} \hat{c}_i^\dagger \hat{c}_j \right\} &= \text{Tr} \left\{ \hat{c}_j e^{-\beta \hat{H}} \hat{c}_i^\dagger \right\} = \sum_k (e^{-\beta \mathbf{h}})_{jk} \text{Tr} \left\{ e^{-\beta \hat{H}} \hat{c}_k \hat{c}_i^\dagger \right\} \\ &= (e^{-\beta \mathbf{h}})_{ji} - \sum_k (e^{-\beta \mathbf{h}})_{jk} \text{Tr} \left\{ e^{-\beta \hat{H}} \hat{c}_i^\dagger \hat{c}_k \right\}. \end{aligned} \quad (\text{A.5})$$

Putting this in equation A.1, we obtain a solution for $\langle \hat{c}_i^\dagger \hat{c}_j \rangle$

$$\langle \hat{c}_i^\dagger \hat{c}_j \rangle = (e^{-\beta \mathbf{h}})_{ji} - \sum_k (e^{-\beta \mathbf{h}})_{jk} \langle \hat{c}_i^\dagger \hat{c}_k \rangle \quad (\text{A.6})$$

$$\Rightarrow \langle \hat{c}_i^\dagger \hat{c}_j \rangle = \left(\frac{1}{e^{\beta \mathbf{h}} + 1} \right)_{ji}, \quad (\text{A.7})$$

which is exactly the generalized Fermi distribution function $f(\mathbf{h})$. In the special case where the Hamiltonian matrix is diagonal, $h_{ij} = \epsilon_i \delta_{ij}$, the matrix has the simple form

$$\left(\frac{1}{e^{\beta \mathbf{h}} + 1} \right)_{ij} = \frac{\delta_{ij}}{e^{\beta \epsilon_i} + 1} = f(\epsilon_i) \quad (\text{A.8})$$

A.2 The Langreth theorem

Consider the Keldysh Green's function $\mathbf{G}(t_1, t_2)$ at a time t_2 later than t_1 on the time contour (see fig. 2.1). The Green's function is now given by $\mathbf{G}(t_1, t_2) = \mathbf{G}^<(t_1, t_2)$ and can be expressed in terms of \mathbf{g} by using equation 2.56

$$\mathbf{G}^<(t_1, t_2) = \mathbf{g}^<(t_1, t_2) + \int_C dt' \mathbf{g}(t_1, t') \mathbf{V}(t') \mathbf{G}(t', t_2) \quad (\text{A.9})$$

The integral over the contour can be split into four regions.

1. Starting from $t' = 0$ to $t' = t_1$, which is by definition earlier than t_2 . The Green's functions \mathbf{g} and \mathbf{G} can be written as $\mathbf{g} = \mathbf{g}^>$ and $\mathbf{G} = \mathbf{G}^<$.
2. From $t' = t_1$ to $t' = t_2$, the Green's functions can be written as $\mathbf{g} = \mathbf{g}^<$ and $\mathbf{G} = \mathbf{G}^<$.
3. From $t' = t_2$ to $t' = 0$, the Green's functions can be written as $\mathbf{g} = \mathbf{g}^<$ and $\mathbf{G} = \mathbf{G}^>$.
4. Finally from $t' = 0$ to $t' = -i\beta$, the Green's functions can be written as $\mathbf{g}(t, -i\tau) = \mathbf{g}^\parallel(t, \tau)$ and $\mathbf{G}(-i\tau, t) = \mathbf{G}^\parallel(\tau, t)$.

The equation can now be rewritten as

$$\begin{aligned} \mathbf{G}^<(t_1, t_2) &= \mathbf{g}^<(t_1, t_2) + \int_0^{t_1} dt' \mathbf{g}^>(t_1, t') \mathbf{V}(t') \mathbf{G}^<(t', t_2) + \int_{t_1}^{t_2} dt' \mathbf{g}^<(t_1, t') \mathbf{V}(t') \mathbf{G}^<(t', t_2) \\ &+ \int_{t_2}^0 dt' \mathbf{g}^<(t_1, t') \mathbf{V}(t') \mathbf{G}^>(t', t_2) - i \int_0^\beta d\tau \mathbf{g}^\parallel(t_1, \tau) \mathbf{V}(-i\tau) \mathbf{G}^\parallel(\tau, t_2). \end{aligned} \quad (\text{A.10})$$

Using that $\int_a^b dx f(x) + \int_b^a dx f(x) = 0$ and the definition of the retarded and advanced Green's function (eq. 2.37 and 2.38) the equation can be rewritten as

$$\begin{aligned} \mathbf{G}^<(t_1, t_2) &= \mathbf{g}^<(t_1, t_2) + \int_0^{t_1} dt' [\mathbf{g}^>(t_1, t') - \mathbf{g}^<(t_1, t')] \mathbf{V}(t') \mathbf{G}^<(t', t_2) \\ &- \int_0^{t_2} dt' \mathbf{g}^<(t_1, t') \mathbf{V}(t') [\mathbf{G}^>(t', t_2) - \mathbf{G}^<(t', t_2)] \\ &- i \int_0^\beta d\tau \mathbf{g}^\parallel(t_1, \tau) \mathbf{V}(-i\tau) \mathbf{G}^\parallel(\tau, t_2) \\ &= \mathbf{g}^<(t_1, t_2) + \int_0^\infty dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') \mathbf{G}^<(t', t_2) + \int_0^\infty dt' \mathbf{g}^<(t_1, t') \mathbf{V}(t') \mathbf{G}^A(t', t_2) \\ &- i \int_0^\beta d\tau \mathbf{g}^\parallel(t_1, \tau) \mathbf{V}(-i\tau) \mathbf{G}^\parallel(\tau, t_2), \end{aligned} \quad (\text{A.11})$$

where we used the definition of the retarded and advanced Green's function (eq. 2.37 and 2.38) to t_1 and t_2 with ∞ .

The exact same analysis for $\mathbf{G}^>$ results in a similar equation

$$\begin{aligned}\mathbf{G}^>(t_1, t_2) &= \mathbf{g}^>(t_1, t_2) + \int_0^\infty dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') \mathbf{G}^>(t', t_2) + \int_0^\infty dt' \mathbf{g}^>(t_1, t') \mathbf{V}(t') \mathbf{G}^A(t', t_2) \\ &\quad - i \int_0^\beta d\tau \mathbf{g}^\lceil(t_1, \tau) \mathbf{V}(-i\tau) \mathbf{G}^\lceil(\tau, t_2)\end{aligned}\quad (\text{A.12})$$

Subtracting equation A.11 from A.12 and then splitting the integral for $t_1 > t_2$ we obtain

$$\begin{aligned}\mathbf{G}^>(t_1, t_2) - \mathbf{G}^<(t_1, t_2) &= \mathbf{g}^>(t_1, t_2) - \mathbf{g}^<(t_1, t_2) + \int_0^{t_1} dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') [\mathbf{G}^>(t', t_2) - \mathbf{G}^<(t', t_2)] \\ &\quad + \int_0^{t_2} dt' [\mathbf{g}^>(t_1, t') - \mathbf{g}^<(t_1, t')] \mathbf{V}(t') \mathbf{G}^A(t', t_2) \\ &= \mathbf{g}^>(t_1, t_2) - \mathbf{g}^<(t_1, t_2) + \int_{t_2}^{t_1} dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') [\mathbf{G}^>(t', t_2) - \mathbf{G}^<(t', t_2)] \\ &\quad + \int_0^{t_2} dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') [\mathbf{G}^>(t', t_2) - \mathbf{G}^<(t', t_2)] \\ &\quad + \int_0^{t_2} dt' [\mathbf{g}^>(t_1, t') - \mathbf{g}^<(t_1, t')] \mathbf{V}(t') \mathbf{G}^A(t', t_2)\end{aligned}\quad (\text{A.13})$$

With the definition of the retarded Green's function \mathbf{G}^R the last two terms cancel and we are left with

$$\begin{aligned}\mathbf{G}^R(t_1, t_2) &= \mathbf{g}^R(t_1, t_2) + \int_0^\infty dt' \mathbf{g}^R(t_1, t') \mathbf{V}(t') \mathbf{G}^R(t', t_2) \\ &= \mathbf{g}^R(t_1, t_2) + [\mathbf{g}^R \cdot \mathbf{V} \cdot \mathbf{G}^R](t_1; t_2) = \mathbf{g}^R \cdot [\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^R](t_1; t_2),\end{aligned}\quad (\text{A.14})$$

where we used the convention from equations 2.60 and 2.61. The similar analysis for the advanced Green's function \mathbf{G}^A holds the equation

$$\begin{aligned}\mathbf{G}^A(t_1, t_2) &= \mathbf{g}^A(t_1, t_2) + \int_0^\infty dt' \mathbf{g}^A(t_1, t') \mathbf{V}(t') \mathbf{G}^A(t', t_2) \\ &= \mathbf{g}^A(t_1, t_2) + [\mathbf{g}^A \cdot \mathbf{V} \cdot \mathbf{G}^A](t_1; t_2) = \mathbf{g}^A \cdot [\mathbf{1} + \mathbf{V} \cdot \mathbf{G}^A](t_1; t_2).\end{aligned}\quad (\text{A.15})$$

A.3 Equilibrium Green's function

The noninteracting equilibrium Green's function $\mathbf{G}^<(0, 0)$ is

$$\mathbf{G}^<(0, 0) = \frac{i}{e^{\beta \mathbf{h}} + 1} \quad (\text{A.16})$$

where \mathbf{h} is the Hamiltonian matrix corresponding to some set of basis vectors $\{|\phi_i\rangle\}$. The matrix $\omega - \mathbf{h}$ is non-invertible, i.e. $\det(\omega - \mathbf{h}) = 0$, when ω is equal to an eigenvalue of \mathbf{h} . This is seen from the fact that the Hamiltonian matrix \mathbf{h} is hermitian, and can therefore be diagonalized by the transformation

$$\mathbf{h} = \mathbf{S}^\dagger \tilde{\mathbf{h}} \mathbf{S} \quad \text{where} \quad \tilde{h}_{ij} = \delta_{ij} \lambda_i. \quad (\text{A.17})$$

Here, the elements λ_i are the eigenvalues of the Hamiltonian, and the matrix \mathbf{S} consists of the inner products of the eigenvectors $\{|\lambda_i\rangle\}$ and the basis vectors,

$$S_{ij} = \langle \phi_i | \lambda_j \rangle. \quad (\text{A.18})$$

The inverse of the matrix $\omega - \mathbf{h}$ is therefore

$$[\omega - \mathbf{h}]^{-1} = [\omega - \mathbf{S}\tilde{\mathbf{h}}\mathbf{S}^\dagger]^{-1} = [\mathbf{S}(\omega - \tilde{\mathbf{h}})\mathbf{S}^\dagger]^{-1} = \mathbf{S}(\omega - \tilde{\mathbf{h}})^{-1}\mathbf{S}^\dagger. \quad (\text{A.19})$$

The matrix $\omega - \tilde{\mathbf{h}}$ is diagonal and obviously has a determinant equal to zero when ω is equal to one of the eigenvalues λ_i . This means that the matrix

$$(\omega - \mathbf{h})^{-1} \quad (\text{A.20})$$

has poles at these frequencies, and we can therefore write

$$\mathbf{G}^<(0, 0) = \frac{i}{e^{\beta\mathbf{h}} + 1} = \int_{\gamma} \frac{dz}{2\pi} \frac{1}{z - \mathbf{h}} \frac{e^{\eta z}}{e^{\beta z} + 1} \quad (\text{A.21})$$

where η is an infinitesimal number and the contour goes around the real frequency axis, as illustrated in Fig. A.1(a). The exponential $e^{\eta z}$ is added to ensure convergence. Notice that z is a complex number, while \mathbf{h} is a matrix. Under the assumption that the integrand vanishes faster than $1/|z|$ for $|z| \rightarrow \infty$, the contour γ can be deformed into the contour Γ , as illustrated in Fig. A.1(b). The integrand now has poles at those frequencies on the imaginary axis for which $e^{\beta z} + 1 = 0$. This happens at $z = i(2n + 1)\pi/\beta$, where n is an integer. These frequencies are called the Matsubara frequencies.

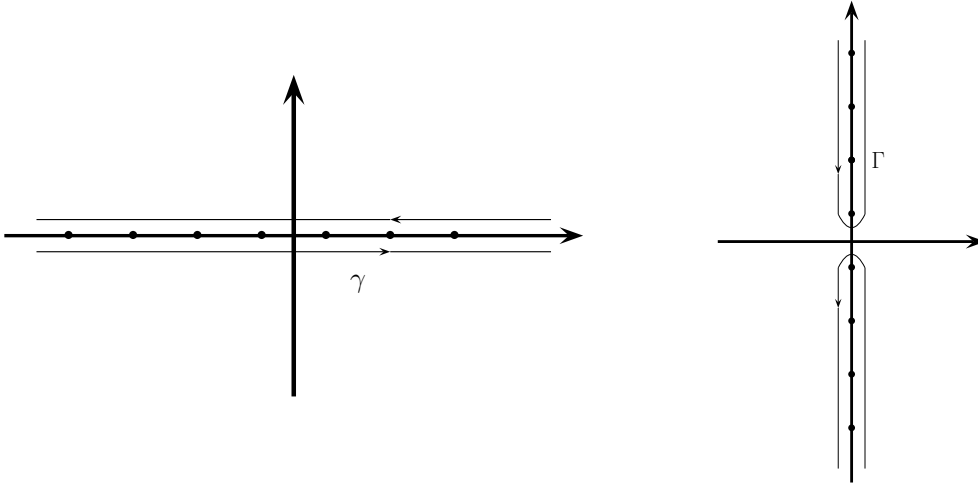


Figure A.1: Deforming the contour in frequency space.

A.4 Proof of equation 3.26

In this section the long time limit of $Q_\alpha(\zeta, t)$ is treated in more detail. Substituting equations 3.23, 3.24 and 3.25 into the definition of the kernel 3.6 one has

$$\begin{aligned}
\lim_{t \rightarrow \infty} Q_\alpha(\zeta, t) &= \sum_{k'} \frac{V_{k'\alpha}^2}{\zeta - \epsilon_{k'\alpha}} G_{0,0}^R(\tilde{\epsilon}_{k'\alpha}) + \sum_{k'\alpha'} \frac{V_{k'\alpha'}^2}{\zeta - \epsilon_{k'\alpha'}} G_{0,0}^R(\tilde{\epsilon}_{k'\alpha'}) G_{0,0}^A(\tilde{\epsilon}_{k'\alpha'}) \Sigma_\alpha^A(\tilde{\epsilon}_{k'\alpha'}) \\
&+ \lim_{t \rightarrow \infty} R_{0,0}(\zeta) \sum_{k'\alpha'} \frac{V_{k'\alpha'}^2}{\zeta - \epsilon_{k'\alpha'}} G_{0,0}^R(\tilde{\epsilon}_{k'\alpha'}) e^{-i\tilde{\epsilon}_{k'\alpha'} t} \sum_{k''} \frac{V_{k''\alpha}^2}{\zeta - \epsilon_{k''\alpha}} e^{i\tilde{\epsilon}_{k''\alpha} t} \\
&+ \lim_{t \rightarrow \infty} R_{0,0}(\zeta) \sum_{k'\alpha'} \frac{V_{k'\alpha'}^2}{\zeta - \epsilon_{k'\alpha'}} G_{0,0}^R(\tilde{\epsilon}_{k'\alpha'}) e^{-i\tilde{\epsilon}_{k'\alpha'} t} \\
&\times \sum_{k''\alpha''} \frac{V_{k''\alpha''}^2}{\zeta - \epsilon_{k''\alpha''}} G_{0,0}^A(\tilde{\epsilon}_{k''\alpha''}) \Sigma_\alpha^A(\tilde{\epsilon}_{k''\alpha''}) e^{i\tilde{\epsilon}_{k''\alpha''} t} \\
&= \int \frac{d\epsilon}{2\pi} \frac{\Gamma_\alpha(\epsilon)}{\zeta - \epsilon + U_\alpha} G_{0,0}^R(\epsilon) + \sum_{\alpha'} \int \frac{d\epsilon}{2\pi} \frac{\Gamma_{\alpha'}(\epsilon)}{\zeta - \epsilon + U_{\alpha'}} |G_{0,0}^R(\epsilon)|^2 \Sigma_\alpha^A(\epsilon) \\
&+ \lim_{t \rightarrow \infty} R_{0,0}(\zeta) \int \frac{d\epsilon}{2\pi} \Gamma_\alpha(\epsilon) \frac{e^{i\epsilon t}}{\zeta - \epsilon + U_\alpha} \sum_{\alpha'} \int \frac{d\epsilon'}{2\pi} \Gamma_{\alpha'}(\epsilon') \frac{e^{-i\epsilon' t}}{\zeta - \epsilon' + U_{\alpha'}} G_{0,0}^R(\epsilon') \\
&+ \lim_{t \rightarrow \infty} R_{0,0}(\zeta) \sum_{\alpha'} \int \frac{d\epsilon'}{2\pi} \Gamma_{\alpha'}(\epsilon') G_{0,0}^R(\epsilon') \frac{e^{-i\epsilon' t}}{\zeta - \epsilon' + U_{\alpha'}} \\
&\times \sum_{\alpha''} \int \frac{d\epsilon''}{2\pi} \Gamma_{\alpha''}(\epsilon'') G_{0,0}^A(\epsilon'') \Sigma_\alpha^A(\epsilon'') \frac{e^{i\epsilon'' t}}{\zeta - \epsilon'' + U_{\alpha''}}, \tag{A.22}
\end{aligned}$$

where equation 3.21 has been explicitly used. Since $\zeta \in \Gamma$, the term $[\zeta - \epsilon - U_\alpha]^{-1}$ will be a smooth function of ϵ for any real ϵ . So the last two terms will vanish in the limit $t \rightarrow \infty$ according to the Riemann-Lebesgue lemma and we obtain equation 3.26.

A.5 Proof of equation 3.30

We now approximate $\text{Re } \Sigma_\alpha^{R/A}(z) = 0$ and $\text{Im } \Sigma_\alpha^{R/A}(z) = \mp \gamma_\alpha = \mp \pi \sum_k \delta(\omega - \tilde{\epsilon}_{k\alpha}) V_{k\alpha}^2$. In this case,

$$G_{0,0}^{R/A}(z) = \frac{1}{z \pm i\gamma}, \tag{A.23}$$

$$G_{0,k\alpha}^{R/A}(z) = G_{0,0}^{R/A}(z) V_{k\alpha} g_{k\alpha}^{R/A}(z) = \frac{1}{z \pm i\gamma} V_{k\alpha} \frac{1}{z - \tilde{\epsilon}_{k\alpha} \pm i\eta}. \tag{A.24}$$

and

$$\begin{aligned}
G_{k\alpha, k'\alpha'}^{R/A}(z) &= \delta_{k\alpha, k'\alpha'} g_{k\alpha}^{R/A}(z) + g_{k\alpha}^{R/A}(z) V_{k\alpha} G_{0, k'\alpha'}^{R/A}(z) \\
&= \delta_{k\alpha, k'\alpha'} g_{k\alpha}^{R/A}(z) + g_{k\alpha}^{R/A}(z) V_{k\alpha} G_{0,0}^{R/A}(z) V_{k'\alpha'} g_{k'\alpha'}^{R/A}(z)
\end{aligned} \tag{A.25}$$

With our earlier established relation between $R(z)$ and $G^{R/A}(z)$ (eq. 3.5) we obtain

$$R(z) = \begin{cases} G^R(z) & \text{if } \text{Im } z > 0 \\ G^A(z) & \text{if } \text{Im } z < 0 \end{cases} \tag{A.26}$$

It is now easily seen that

$$G_{0,0}^R(t,0) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{e^{-i\omega t}}{\omega + i\gamma} = -ie^{-\gamma t} \quad (\text{A.27})$$

$$G_{0,k\alpha}^R(t,0) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} V_{k\alpha} e^{-i\omega t} \frac{1}{\omega + i\gamma} \frac{1}{\omega - \tilde{\epsilon}_{k\alpha} + i\eta} = -iV_{k\alpha} \frac{e^{-i\tilde{\epsilon}_{k\alpha} t} - e^{-\gamma t}}{\tilde{\epsilon}_{k\alpha} + i\gamma} \quad (\text{A.28})$$

$$\begin{aligned} \sum_{k\alpha} V_{k\alpha} G_{0,k\alpha}^A(0,t) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega t} \sum_{k\alpha} V_{k\alpha}^2 g_{k\alpha}^A(\omega) \frac{1}{\omega - \tilde{\epsilon}_{k\alpha} - i\eta} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega t} \frac{\Sigma_\alpha}{\omega - \tilde{\epsilon}_{k\alpha} - i\eta} \\ &= i\gamma_\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{e^{i\omega t}}{\omega - \tilde{\epsilon}_{k\alpha} - i\eta} = -\gamma_\alpha e^{-\gamma t} \end{aligned} \quad (\text{A.29})$$

$$\begin{aligned} \sum_{k'} V_{k'\alpha'} G_{k\alpha,k'\alpha'}^A(0,t) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega t} \sum_{k'} V_{k'\alpha'} \left\{ \delta_{k\alpha,k'\alpha'} \frac{1}{\omega - \tilde{\epsilon}_{k\alpha} - i\eta} + g_{k\alpha}^A(\omega) V_{k\alpha} G_{0,0}^A(\omega) V_{k'\alpha'}^2 g_{k'\alpha'}^A(\omega) \right\} \\ &= i\delta_{\alpha,\alpha'} V_{k\alpha} e^{-i\tilde{\epsilon}_{k\alpha} t} + \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega t} V_{k\alpha} \Sigma_{\alpha'} \frac{1}{\omega - \tilde{\epsilon}_{k\alpha} - i\eta} \frac{1}{\omega - i\gamma} \\ &= i\delta_{\alpha,\alpha'} V_{k\alpha} e^{-i\tilde{\epsilon}_{k\alpha} t} - \gamma_{\alpha'} V_{k\alpha} \frac{e^{i\tilde{\epsilon}_{k\alpha} t} - e^{-\gamma t}}{\tilde{\epsilon}_{k\alpha} - i\gamma}. \end{aligned} \quad (\text{A.30})$$

We can now calculate the expression

$$\begin{aligned} \sum_k [G^R(t,0)R(\zeta)G^A(0,t)]_{0,k\alpha} V_{k\alpha} &= G_{0,0}^R(t,0)R_{0,0}(\zeta) \sum_k G_{0,k\alpha}^A(0,t) V_{k\alpha} \\ &\quad + \sum_{k,k'\alpha'} G_{0,0}^R(t,0)R_{0,k'\alpha'}(\zeta) G_{k'\alpha',k\alpha}^A(0,t) V_{k\alpha} \\ &\quad + \sum_{k,k'\alpha'} G_{0,k'\alpha'}^R(t,0)R_{k'\alpha',0}(\zeta) G_{0,k\alpha}^A(0,t) V_{k\alpha} \\ &\quad + \sum_{\substack{k,k'\alpha' \\ k''\alpha''}} G_{0,k'\alpha'}^R(t,0)R_{k'\alpha',k''\alpha''}(\zeta) G_{k''\alpha'',k\alpha}^A(0,t) V_{k\alpha}. \end{aligned} \quad (\text{A.31})$$

The first term is

$$G_{0,0}^R(t,0)R_{0,0}(\zeta) \sum_k V_{k\alpha} G_{0,k\alpha}^A(0,t) = i\gamma_\alpha R_{0,0}(\zeta) e^{-2\gamma t} \quad (\text{A.32})$$

while the second term is

$$\begin{aligned} &\sum_{k'\alpha'} G_{0,0}^R(t,0)R_{0,k'\alpha'}(\zeta) \sum_k V_{k\alpha} G_{k'\alpha',k\alpha}^A(0,t) \\ &= G_{0,0}^R(t,0)R_{0,0}(\zeta) \sum_{k'\alpha'} V_{k'\alpha'} \frac{1}{\zeta - \epsilon_{k'\alpha'}} \left\{ i\delta_{\alpha,\alpha'} V_{k'\alpha'} e^{i\tilde{\epsilon}_{k'\alpha'} t} - \gamma_\alpha V_{k'\alpha'} \frac{e^{i\tilde{\epsilon}_{k'\alpha'} t} - e^{-\gamma t}}{\tilde{\epsilon}_{k\alpha} - i\gamma} \right\} \\ &= G_{0,0}^R(t,0)R_{0,0}(\zeta) \left\{ \sum_k iV_{k\alpha}^2 \frac{1}{\zeta - \epsilon_{k\alpha}} e^{i\tilde{\epsilon}_{k\alpha} t} - \gamma_\alpha \sum_{k'\alpha'} V_{k'\alpha'}^2 \frac{e^{i\tilde{\epsilon}_{k'\alpha'} t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} - i\gamma} \right\}. \end{aligned} \quad (\text{A.33})$$

The first term on the right hand side can be rewritten by using

$$i \sum_k V_{k\alpha}^2 \frac{e^{i\tilde{\epsilon}_{k\alpha} t}}{\zeta - \epsilon_{k\alpha}} = i \int d\omega \sum_k V_{k\alpha}^2 \frac{e^{i\omega t}}{\zeta + U_\alpha - \omega} \delta(\omega - \tilde{\epsilon}_{k\alpha}) = i2\gamma_\alpha \int \frac{d\omega}{2\pi} \frac{e^{i\omega t}}{\zeta + U_\alpha - \omega} \quad (\text{A.34})$$

while the second term is

$$\begin{aligned}
-\gamma_\alpha \sum_{k'\alpha'} V_{k'\alpha'}^2 \frac{1}{\zeta - \epsilon_{k'\alpha'}} \frac{e^{i\tilde{\epsilon}_{k'\alpha'} t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} - i\gamma} &= -\gamma_\alpha \int d\omega \sum_{k'\alpha'} \delta(\omega - \tilde{\epsilon}_{k'\alpha'}) V_{k'\alpha'}^2 \frac{e^{i\omega t} - e^{-\gamma t}}{(\zeta + U_{\alpha'} - \omega)(\omega - i\gamma)} \\
&= -2\gamma_\alpha \sum_{\alpha'} \gamma_{\alpha'} \int \frac{d\omega}{2\pi} \frac{e^{i\omega t} - e^{-\gamma t}}{(\zeta + U_{\alpha'} - \omega)(\omega - i\gamma)} \quad (\text{A.35})
\end{aligned}$$

In combination, we obtain

$$\begin{aligned}
&\sum_{k'\alpha'} G_{0,0}^R(t, 0) R_{0,k'\alpha'}(\zeta) \sum_k V_{k\alpha} G_{k'\alpha', k\alpha}^A(0, t) \\
&= 2\gamma_\alpha e^{-\gamma t} R_{0,0}(\zeta) \int \frac{d\omega}{2\pi} \frac{e^{i\omega t}}{\zeta + U_\alpha - \omega} + 2i\gamma_\alpha e^{-\gamma t} R_{0,0}(\zeta) \sum_{\alpha'} \gamma_{\alpha'} \int \frac{d\omega}{2\pi} \frac{e^{i\omega t} - e^{-\gamma t}}{(\zeta + U_{\alpha'} - \omega)(\omega - i\gamma)} \quad (\text{A.36})
\end{aligned}$$

The third term gives

$$\begin{aligned}
&\sum_{k'\alpha'} G^R(t, 0)_{0,k'\alpha'} R_{k'\alpha', 0}(\zeta) \sum_k V_{k\alpha} G_{0,k\alpha}^A \\
&= \sum_{k'\alpha'} (-iV_{k'\alpha'}) \frac{e^{-i\tilde{\epsilon}_{k'\alpha'} t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} + i\gamma} R_{0,0}(\zeta) V_{k'\alpha'} \frac{1}{\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'}} (-\gamma_\alpha) e^{-\gamma t} \\
&= i\gamma_\alpha e^{-\gamma t} R_{0,0}(\zeta) \sum_{k'\alpha'} V_{k'\alpha'}^2 \frac{e^{-i\tilde{\epsilon}_{k'\alpha'} t} - e^{-\gamma t}}{(\tilde{\epsilon}_{k'\alpha'} + i\gamma)(\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'})} \\
&= i\gamma_\alpha e^{-\gamma t} R_{0,0}(\zeta) \int d\omega \sum_{k'\alpha'} \delta(\omega - \tilde{\epsilon}_{k'\alpha'}) V_{k'\alpha'}^2 \frac{e^{-i\omega t} - e^{-\gamma t}}{(\omega + i\gamma)(\zeta + U_{\alpha'} - \omega)} \\
&= 2i\gamma_\alpha e^{-\gamma t} R_{0,0}(\zeta) \sum_{\alpha'} \gamma_{\alpha'} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega t} - e^{-\gamma t}}{(\omega + i\gamma)(\zeta + U_{\alpha'} - \omega)} \quad (\text{A.37})
\end{aligned}$$

The fourth term is

$$\begin{aligned}
& \sum_{\substack{k'\alpha' \\ k''\alpha''}} G_{0,k'\alpha'}^R(t,0) R_{k'\alpha',k''\alpha''}(\zeta) \sum_k G_{k''\alpha'',k\alpha}^A(0,t) V_{k\alpha} \\
&= \sum_{\substack{k'\alpha' \\ k''\alpha''}} (-iV_{k'\alpha'}) \frac{e^{-i\tilde{\epsilon}_{k'\alpha'}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} + i\gamma} \left[\frac{\delta_{k'\alpha',k''\alpha''}}{\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'}} + \frac{V_{k'\alpha'}}{\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'}} R_{0,0}(\zeta) \frac{V_{k''\alpha''}}{\zeta + U_{\alpha''} - \tilde{\epsilon}_{k''\alpha''}} \right] \\
&\quad \times \left[i\delta_{\alpha'',\alpha} V_{k''\alpha''} e^{i\tilde{\epsilon}_{k''\alpha''}t} - \gamma_{\alpha} V_{k''\alpha''} \frac{e^{i\tilde{\epsilon}_{k''\alpha''}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k''\alpha''} - i\gamma} \right] \\
&= \sum_{k'} V_{k'\alpha}^2 \frac{e^{-i\tilde{\epsilon}_{k'\alpha}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha} + i\gamma} \frac{1}{\zeta + U_{\alpha} - \tilde{\epsilon}_{k'\alpha}} e^{i\tilde{\epsilon}_{k'\alpha}t} \\
&\quad + i \sum_{k'\alpha'} V_{k'\alpha'}^2 \frac{e^{-i\tilde{\epsilon}_{k'\alpha'}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} + i\gamma} \frac{1}{\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'}} \gamma_{\alpha} \frac{e^{i\tilde{\epsilon}_{k'\alpha'}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} - i\gamma} \\
&\quad + \sum_{\substack{k'\alpha' \\ k''\alpha''}} V_{k'\alpha'}^2 \frac{e^{-i\tilde{\epsilon}_{k'\alpha'}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} + i\gamma} \frac{1}{\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'}} R_{0,0}(\zeta) \frac{1}{\zeta + U_{\alpha} - \tilde{\epsilon}_{k''\alpha}} V_{k''\alpha}^2 e^{i\tilde{\epsilon}_{k''\alpha}t} \\
&\quad + i \sum_{\substack{k'\alpha' \\ k''\alpha''}} V_{k'\alpha'}^2 \frac{e^{-i\tilde{\epsilon}_{k'\alpha'}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k'\alpha'} + i\gamma} \frac{1}{\zeta + U_{\alpha'} - \tilde{\epsilon}_{k'\alpha'}} R_{0,0}(\zeta) \frac{1}{\zeta + U_{\alpha''} - \tilde{\epsilon}_{k''\alpha''}} \gamma_{\alpha} V_{k''\alpha''}^2 \frac{e^{i\tilde{\epsilon}_{k''\alpha''}t} - e^{-\gamma t}}{\tilde{\epsilon}_{k''\alpha''} - i\gamma} \\
&= \int d\omega \sum_{k'} \delta(\omega - \tilde{\epsilon}_{k'\alpha}) V_{k'\alpha}^2 \frac{e^{-i\omega t} - e^{-\gamma t}}{\omega + i\gamma} \frac{1}{\zeta + U_{\alpha} - \omega} e^{i\omega t} \\
&\quad + i\gamma_{\alpha} \int d\omega \sum_{k'\alpha'} \delta(\omega - \tilde{\epsilon}_{k'\alpha'}) V_{k'\alpha'}^2 \frac{e^{-i\omega} - e^{-\gamma t}}{\omega + i\gamma} \frac{1}{\zeta + U_{\alpha'} - \omega} \frac{e^{i\omega t} - e^{-\gamma t}}{\omega - i\gamma} \\
&\quad + R_{0,0}(\zeta) \int d\omega \int d\omega' \sum_{\substack{k'\alpha' \\ k''\alpha''}} \delta(\omega - \tilde{\epsilon}_{k'\alpha'}) \delta(\omega - \tilde{\epsilon}_{k''\alpha}) \frac{e^{-i\omega} - e^{-\gamma t}}{\omega + i\gamma} \frac{V_{k'\alpha'}^2}{\zeta + U_{\alpha'} - \omega} \frac{V_{k''\alpha}^2 e^{i\omega' t}}{\zeta + U_{\alpha} - \omega'} \\
&\quad + iR_{0,0}(\zeta) \gamma_{\alpha} \int d\omega \int d\omega' \sum_{\substack{k'\alpha' \\ k''\alpha''}} V_{k'\alpha'}^2 V_{k''\alpha''}^2 \delta(\omega - \tilde{\epsilon}_{k'\alpha'}) \delta(\omega - \tilde{\epsilon}_{k''\alpha''}) \\
&\quad \times \frac{e^{-i\omega} - e^{-\gamma t}}{\omega + i\gamma} \frac{1}{\zeta + U_{\alpha'} - \omega} \frac{1}{\zeta + U_{\alpha''} - \omega'} \frac{e^{i\omega' t} - e^{-\gamma t}}{\omega' - i\gamma} \\
&= 2\gamma_{\alpha} \int \frac{d\omega}{2\pi} \frac{1 - e^{i\omega t - \gamma t}}{(\omega + i\gamma)(\zeta + U_{\alpha} - \omega)} \\
&\quad + 2i\gamma_{\alpha} \sum_{\alpha'} \gamma_{\alpha'} \int \frac{d\omega}{2\pi} \left| \frac{e^{i\omega} - e^{-\gamma t}}{\omega - i\gamma} \right|^2 \frac{1}{\zeta + U_{\alpha'} - \omega} \\
&\quad + 4\gamma_{\alpha} R_{0,0}(\zeta) \sum_{\alpha'} \gamma_{\alpha'} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega} - e^{-\gamma t}}{(\omega + i\gamma)(\zeta + U_{\alpha'} - \omega)} \\
&\quad \times \int \frac{d\omega'}{2\pi} \frac{e^{i\omega' t}}{\zeta + U_{\alpha} - \omega'} + i \sum_{\alpha''} \gamma_{\alpha''} \frac{e^{i\omega' t} - e^{-\gamma t}}{(\omega' - i\gamma)(\zeta + U_{\alpha''} - \omega')}. \tag{A.38}
\end{aligned}$$

The equations above have now to be multiplied by $f(\zeta)e^{\eta\zeta}$ and integrated over the contour Γ . Transforming the contour back to the real axis (we get the contour γ back) the first term (eq. A.32) contributes to

the current as

$$4e\gamma_\alpha e^{-2\gamma t} \text{Im} \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) \frac{1}{\omega + i\gamma} \right\}. \quad (\text{A.39})$$

The contribution from the first term of equation A.36 can be calculated by closing the contour in the complex upper half plane. Therefore there is a contribution only if $\text{Im}\{\zeta\} > 0$, so only the upper branch of Γ contributes. Transforming the contour again to the real axis one has

$$-4e\gamma_\alpha e^{-\gamma t} \text{Im} \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) \frac{e^{i(\omega+U_\alpha)t}}{\omega + i\gamma} \right\}. \quad (\text{A.40})$$

The second term can be evaluated by the same procedure by closing the contour in the upper half plane. The pole $\epsilon = i\gamma$ has no contribution since its residue is zero. The other pole is at $\epsilon = \zeta + U_\alpha$, so we get

$$-4e\gamma_\alpha e^{-\gamma t} \text{Re} \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{f(\omega)}{\omega + i\gamma} \sum_{\alpha'} \gamma_{\alpha'} \frac{e^{i(\omega+U_{\alpha'})t} - e^{-\gamma t}}{\omega + U_{\alpha'} - i\gamma} \right\}. \quad (\text{A.41})$$

By the same analysis it can be calculated that the contribution from the third term (eq. A.36) as the same as in equation A.41. The first two terms in the right hand side of equation A.38 do not have $R_{0,0}(\zeta)$ in the integrand, so the integral over ζ can be performed

$$-4e\gamma_\alpha \text{Im} \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega - U_\alpha) \frac{1 - e^{i\omega t} e^{-\gamma t}}{\omega + i\gamma} \right\} \quad (\text{A.42})$$

$$-4e\gamma_\alpha \text{Re} \left\{ \sum_{\alpha'} \gamma_{\alpha'} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega - U_{\alpha'}) \left| \frac{e^{i\omega t} - e^{-\gamma t}}{\omega + i\gamma} \right|^2 \right\}. \quad (\text{A.43})$$

The last two terms of the fourth term vanishes. The integral over ϵ has poles at $\epsilon = -i\gamma$, which has residue equal to zero, and $\epsilon = \zeta + U_{\alpha'}$, which only contributes for $\text{Im}\{\zeta\} < 0$. One readily sees that the integral over ϵ' only contributes is $\text{Im}\{\zeta\} > 0$. So the contribution for this term is zero. The terms can now be grouped in terms that contribute to the stationary current, terms that are proportional to $e^{-\gamma t}$ and terms that are proportional to $e^{-2\gamma t}$. The summation of the last ones gives

$$-4e\gamma_\alpha e^{-2\gamma t} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) \sum_{\alpha'} \frac{\gamma_{\alpha'} U_{\alpha'}^2}{[\omega^2 + \gamma^2][(\omega + U_{\alpha'})^2 + \gamma^2]}. \quad (\text{A.44})$$

Consider now the terms proportional to $e^{-\gamma t}$. The contribution from equations A.40 and A.42 sum up to

$$-4e\gamma_\alpha U_\alpha e^{-\gamma t} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) \text{Im} \left\{ \frac{e^{i(\omega+U_\alpha)t}}{(\omega + i\gamma)(\omega + U_\alpha + i\gamma)} \right\}. \quad (\text{A.45})$$

The other two contributions come from equations A.41 and A.43 which sum up to

$$-8e\gamma_\alpha e^{-\gamma t} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) \sum_{\alpha'} \gamma_{\alpha'} U_{\alpha'} \frac{\omega \cos[(\omega + U_{\alpha'})t] + \gamma \sin[(\omega + U_{\alpha'})t]}{[\omega^2 + \gamma^2][(\omega + U_{\alpha'})^2 + \gamma^2]}. \quad (\text{A.46})$$

Summing the equations A.44–A.46 gives exactly the quantity $J_\alpha(t) - J_\alpha^S$ of equation 3.30

Appendix B

1Dbox

B.1 Matrix elements of 1D model

Here we put the integrals that are used in the 1D model in a more extensive form. First the overlap of the plane waves with the barrier

$$\begin{aligned}
\langle k|V_d\theta(d-|z|)|k\rangle &= V_d \frac{2}{L} \int_{-d}^d dz \sin^2 \left(k \left(z + \frac{L}{2} \right) \right) = \frac{V_d}{L} \int_{-d}^d dz \left(1 - \cos \left(2k \left(z + \frac{L}{2} \right) \right) \right) \\
&= \frac{V_d}{L} \left[1 - \frac{1}{2k} \sin \left(2k \left(z + \frac{L}{2} \right) \right) \right]_{-d}^d = \frac{V_d}{L} \left[1 - \cos(n\pi) \frac{\sin(2kz)}{2k} \right]_{-d}^d \\
&= \frac{V_d}{L} \left[2d - \cos(n\pi) \frac{\sin(2kd)}{k} \right] \tag{B.1}
\end{aligned}$$

$$\begin{aligned}
\langle k|V_d\theta(d-|z|)|q\rangle &= V_d \frac{2}{L} \int_{-d}^d dz \sin \left(k \left(z + \frac{L}{2} \right) \right) \sin \left(q \left(z + \frac{L}{2} \right) \right) \\
&= \frac{V_d}{L} \int_{-d}^d dz \cos \left((k-q) \left(z + \frac{L}{2} \right) \right) - \cos \left((k+q) \left(z + \frac{L}{2} \right) \right) \\
&= \frac{V_d}{L} \left[\frac{\sin \left((k-q) \left(z + \frac{L}{2} \right) \right)}{k-q} - \frac{\sin \left((k+q) \left(z + \frac{L}{2} \right) \right)}{k+q} \right]_{-d}^d \\
&= \frac{V_d}{L} \left[\frac{\sin \left((k-q) \frac{L}{2} \right) \cos \left((k-q)z \right) + \cos \left((k-q) \frac{L}{2} \right) \sin \left((k-q)z \right)}{k-q} - \right. \\
&\quad \left. \frac{\sin \left((k+q) \frac{L}{2} \right) \cos \left((k+q)z \right) + \cos \left((k+q) \frac{L}{2} \right) \sin \left((k+q)z \right)}{k+q} \right]_{-d}^d \\
&= \frac{2V_d}{L} \left[\frac{\cos \left((k-q) \frac{L}{2} \right) \sin \left((k-q)d \right)}{k-q} - \frac{\cos \left((k+q) \frac{L}{2} \right) \sin \left((k+q)d \right)}{k+q} \right] \tag{B.2}
\end{aligned}$$

As an extra check one can take the limit $k = q$ which is exactly the same as $\langle k|V_d\theta(d-|z|)|k\rangle$ as it should.

Now continue with the elements from $H'(t)$. It is convenient to introduce the variable $D = L/2 - d$.

$$\begin{aligned}
\langle k|V\theta(-d-z)|k\rangle &= \langle k|V\theta(D-x)|k\rangle = V\frac{2}{L}\int_0^D dx \sin^2(kx) = \frac{V}{L}\int_0^D dx(1 - \cos(2kx)) \\
&= \frac{V}{L}\left[x - \frac{\sin(2kx)}{2k}\right]_0^D = \frac{V}{L}\left[D - \frac{\sin(2kD)}{2k}\right]
\end{aligned} \tag{B.3}$$

$$\begin{aligned}
\langle k|V\theta(-d-z)|q\rangle &= \langle k|V\theta(D-x)|q\rangle = V\frac{2}{L}\int_0^D dx \sin(kx)\sin(qx) \\
&= \frac{V}{L}\int_0^D dx \cos((k-q)x) - \cos((k+q)x) = \frac{V}{L}\left[\frac{\sin((k-q)x)}{k-q} - \frac{\sin((k+q)x)}{k+q}\right]_0^D \\
&= \frac{V}{L}\left[\frac{\sin((k-q)D)}{k-q} - \frac{\sin((k+q)D)}{k+q}\right]
\end{aligned} \tag{B.4}$$

Again the limit $k = q$ gives the same answer as calculating $\langle k|V\theta(-d-z)|k\rangle$ directly.

Appendix C

3Dbox

C.1 Matrix elements of 3D model

The overlap matrix with the Slater function, $\langle \phi_{k_x, k_y, \pi_z, k_z} | \phi_0 \rangle$ is comparable to $\langle \vec{k} | e^{-\alpha r} / r | \vec{q} \rangle$, but now the following integrals are used:

$$\int d^3r \sin(\vec{k} \cdot \vec{r}) e^{-br} = \frac{4\pi}{k} \int_0^\infty dr \cos(kr) r e^{-br} = 0, \quad (\text{C.1})$$

$$\int d^3r \cos(\vec{k} \cdot \vec{r}) e^{-br} = \frac{4\pi}{k} \int_0^\infty dr \sin(kr) r e^{-br} = \frac{8\pi b}{(b^2 + k^2)^2}. \quad (\text{C.2})$$

Keeping in mind that only the gerade terms contribute one readily finds:

$$\langle \vec{k}, \pi_z | b \rangle = 16b^2 \sqrt{\frac{2\pi b}{\Omega}} \frac{\sin(k_x a/2) \sin(k_y a/2)}{(b^2 + k^2)^2} \delta_{\pi_z, g} \quad (\text{C.3})$$

The matrix elements for the local wave function are:

$$\begin{aligned} \langle b | \hat{T} | b \rangle &= -\frac{1}{2} \frac{b^3}{\pi} \int d^3r e^{-br} \nabla^2 e^{-br} = -2b^3 \int_0^\infty dr e^{-br} \partial_r r^2 \partial_r e^{-br} \\ &= 2b^4 \int_0^\infty dr e^{-br} \partial_r r^2 e^{-br} = 2b^4 \int_0^\infty dr e^{-2br} (2r - br^2) \\ &= -\frac{b^4}{2} (4\partial_b + b\partial_b^2) \int_0^\infty dr e^{-2br} = -\frac{b^4}{2} (4\partial_b + b\partial_b^2) \frac{1}{2b} = \frac{b^2}{2} \end{aligned} \quad (\text{C.4})$$

$$\begin{aligned}
\langle b|V_d\Theta(d-|z|)|b\rangle &= \frac{b^3}{\pi}V_d \int_{-d}^d dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx e^{-2b\sqrt{x^2+y^2+z^2}} \\
&= \frac{b^3V_d}{\pi} \int_{-d}^d dz \underbrace{2\pi \int_0^{\infty} d\rho \rho e^{-2b\sqrt{\rho^2+z^2}}}_{I(z)} \\
&= -2b^3V_d \int_{-d}^d dz \left. \frac{e^{-2b\sqrt{\rho^2+z^2}} (1+2b\sqrt{\rho^2+z^2})}{4b^2} \right|_{\rho=0}^{\infty} \\
&= \frac{bV_b}{2} \int_{-d}^d dz e^{-2b|z|} (1+2b|z|) = bV_b (1-b\partial_b) \int_0^d dz e^{-2bz} \\
&= bV_b (1-b\partial_b) \frac{1-e^{-2bd}}{2b} = V_d (1-e^{-2bd}(1+bd)) \tag{C.5}
\end{aligned}$$

$$\begin{aligned}
I(z) &= \int_0^{\infty} d\rho \rho e^{-2b\sqrt{\rho^2+z^2}} = \int_{|z|}^{\infty} y e^{-2by} dy = -\frac{1}{2}\partial_b \int_{|z|}^{\infty} e^{-2by} dy \\
&= \frac{1}{2}\partial_b \left. \frac{e^{-2by}}{2b} \right|_{|z|}^{\infty} = -\frac{1}{4}\partial_b \frac{e^{-2b|z|}}{b} = \frac{e^{-2b|z|}}{4b^2} (1+2b|z|) \tag{C.6}
\end{aligned}$$

$$\langle b|V_{loc} \frac{e^{-\alpha r}}{r} |b\rangle = \frac{b^3V_{loc}}{\pi} \int d^3r e^{-2br} \frac{e^{-\alpha r}}{r} = 4b^3V_{loc} \int_0^{\infty} r e^{-(\alpha+2b)r} dr = \frac{4b^3V_{loc}}{(\alpha+2b)^2} \tag{C.7}$$

The matrix elements for the bias voltage are very similar to the matrix element for the barrier, but just with other boundaries for the integral in the z -direction:

$$\begin{aligned}
\langle b|V_L\Theta(-z-d)|b\rangle &= \frac{b^3}{\pi}V_L \int_{-\infty}^{-d} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx e^{-2b\sqrt{x^2+y^2+z^2}} \\
&= \frac{bV_L}{2} \int_{-\infty}^{-d} dz e^{-2b|z|} (1+2b|z|) = \frac{bV_L}{2} (1-b\partial_b) \int_d^{\infty} dz e^{-2bz} \\
&= \frac{bV_L}{2} (1-b\partial_b) \frac{e^{-2bd}}{b} = \frac{V_L}{2} e^{-2bd} (1+bd) \tag{C.8}
\end{aligned}$$

$$\begin{aligned}
\langle b|\frac{V_L}{2d}(d-z)\Theta(d-|z|)|b\rangle &= \frac{b^3}{\pi} \frac{V_L}{2d} \int_{-d}^d dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx e^{-2b\sqrt{x^2+y^2+z^2}} (d-z) \\
&= \frac{bV_L}{4d} \int_{-d}^d dz e^{-2b|z|} (1+2b|z|) (d-z) = \frac{bV_L}{2} (1-b\partial_b) \int_0^d dz e^{-2bz} \\
&= \frac{1}{2} \langle b|V_L\Theta(d-|z|)|b\rangle = \frac{V_L}{2} (1-e^{-2bd}(1+bd)) \tag{C.9}
\end{aligned}$$

So the matrix element due to an applied bias voltage V_L becomes:

$$\langle b|V_L|b\rangle = \frac{V_L}{2}, \tag{C.10}$$

which is not surprising.

The matrix elements for the plane waves are:

$$\begin{aligned}
\langle \vec{k}, \pi_z | \hat{T} | \vec{p}, \chi_z \rangle &= -\frac{1}{2} \frac{8}{\Omega} \int_0^a dx \int_0^a dy \int_0^D dz \sin(k_x x) \sin(k_y y) \sin(k_z z) \nabla^2 \sin(k_x x) \sin(k_y y) \sin(k_z z) \\
&= \frac{k^2}{2} \langle k_x, k_y, \pi_z, k_z | p_x, p_y, \chi_z, p_z \rangle = \frac{k^2}{2} \delta_{k_x, p_x} \delta_{k_y, p_y} \delta_{\pi_z, \chi_z} \delta_{k_z, p_z} \tag{C.11}
\end{aligned}$$

$$\begin{aligned}
\langle \vec{k}, g/u | V_d \Theta(d - |z|) | \vec{k}, g/u \rangle &= \frac{8V_d}{\Omega} \int_0^a dx \int_0^a dy \sin^2(k_x x) \sin^2(k_y y) \int_{-d}^d dz \left[\begin{array}{c} \cos^2(k_z z) \\ \sin^2(k_z z) \end{array} \right] \\
&= \frac{V_d}{D} \int_{-d}^d dz (1 \pm \cos(2k_z z)) = \frac{V_d}{D} \left[2d \pm \frac{\sin(2k_z d)}{k_z} \right] \quad (C.12)
\end{aligned}$$

$$\begin{aligned}
\langle \vec{k}, g/u | V_d \Theta(d - |z|) | \vec{p}, \pi_z \rangle &= \frac{2V_d}{D} \int_{-d}^d dz \left[\begin{array}{c} \cos(k_z z) \cos(p_z z) \\ \sin(k_z z) \sin(p_z z) \\ \sin(k_z z) \cos(p_z z) \\ \cos(k_z z) \sin(p_z z) \end{array} \right] \delta_{k_x, p_x} \delta_{k_y, p_y} \\
&= \frac{V_d}{D} \int_{-d}^d dz \left[\begin{array}{c} \cos((k_z - p_z)z) \pm \cos((k_z + p_z)z) \\ \sin((k_z + p_z)z) \pm \sin((k_z - p_z)z) \end{array} \right] \delta_{k_x, p_x} \delta_{k_y, p_y} \\
&= \frac{V_d}{D} \left[\frac{\sin((k_z - p_z)z)}{k_z - p_z} \pm \frac{\sin((k_z + p_z)z)}{k_z + p_z} \right]_{-d}^d \delta_{k_x, p_x} \delta_{k_y, p_y} \delta_{g/u, \pi_z} \\
&= \frac{2V_d}{D} \left[\frac{\sin((k_z - p_z)d)}{k_z - p_z} \pm \frac{\sin((k_z + p_z)d)}{k_z + p_z} \right] \delta_{k_x, p_x} \delta_{k_y, p_y} \delta_{g/u, \pi_z} \quad (C.13)
\end{aligned}$$

Calculating the matrix element $\langle \vec{k} | e^{-\alpha r} / r | \vec{q} \rangle$ is not very difficult, but involves a lot of terms which make it a laborious integral. The product of sine terms will reduce to integrals of the following form:

$$\int d^3 r \sin(\vec{k} \cdot \vec{r}) \frac{e^{-\alpha r}}{r} = \frac{1}{2i} \int d^3 r \left(e^{i\vec{k} \cdot \vec{r}} - e^{-i\vec{k} \cdot \vec{r}} \right) \frac{e^{-\alpha r}}{r} = \frac{1}{2i} \left[\frac{4\pi}{\alpha^2 + k^2} - \frac{4\pi}{\alpha^2 + k^2} \right] = 0, \quad (C.14)$$

$$\int d^3 r \cos(\vec{k} \cdot \vec{r}) \frac{e^{-\alpha r}}{r} = \frac{1}{2} \int d^3 r \left(e^{i\vec{k} \cdot \vec{r}} + e^{-i\vec{k} \cdot \vec{r}} \right) \frac{e^{-\alpha r}}{r} = \frac{1}{2} \left[\frac{2\pi}{\alpha^2 + k^2} + \frac{2\pi}{\alpha^2 + k^2} \right] = \frac{4\pi}{\alpha^2 + k^2} \quad (C.15)$$

With these integrals in mind, the integral can be evaluated quite easily:

$$\begin{aligned}
\langle \vec{k}, g/u | \frac{e^{-\alpha r}}{r} | \vec{q}, \pi_z \rangle &= \frac{8}{\Omega} \int d^3 r \sin\left(k_x \left(x + \frac{a}{2}\right)\right) \sin\left(k_y \left(y + \frac{a}{2}\right)\right) \left[\begin{array}{c} \cos(k_z z) \\ \sin(k_z z) \end{array} \right] \frac{e^{-\alpha r}}{r} \\
&\quad \sin\left(q_x \left(x + \frac{a}{2}\right)\right) \sin\left(q_y \left(y + \frac{a}{2}\right)\right) \left[\begin{array}{c} \cos(q_z z) \\ \sin(q_z z) \end{array} \right] \\
&= \frac{1}{\Omega} \int d^3 r \frac{e^{-\alpha r}}{r} \left(\cos((k_x - q_x)x) \cos\left((k_x - q_x)\frac{a}{2}\right) - \right. \\
&\quad \sin((k_x - q_x)x) \sin\left((k_x - q_x)\frac{a}{2}\right) - \cos((k_x + q_x)x) \cos\left((k_x + q_x)\frac{a}{2}\right) + \\
&\quad \left. \sin((k_x + q_x)x) \sin\left((k_x + q_x)\frac{a}{2}\right) \right) \cdot \left(\cos((k_y - q_y)y) \cos\left((k_y - q_y)\frac{a}{2}\right) - \right. \\
&\quad \sin((k_y - q_y)y) \sin\left((k_y - q_y)\frac{a}{2}\right) - \cos((k_y + q_y)y) \cos\left((k_y + q_y)\frac{a}{2}\right) + \\
&\quad \left. \sin((k_y + q_y)y) \sin\left((k_y + q_y)\frac{a}{2}\right) \right) \left[\begin{array}{c} \cos((k_z - p_z)z) \pm \cos((k_z + p_z)z) \\ \sin((k_z + p_z)z) \pm \sin((k_z - p_z)z) \end{array} \right] \quad (C.16)
\end{aligned}$$

where the ordering is gg , uu , ug and gu .

A lot of terms from the products will cancel in the integration. Therefore it is convenient to consider the

terms separately with general terms:

$$\begin{aligned} \cos(k_x x) \cos(k_y y) \cos(k_z z) &= \frac{1}{4} [\cos(k_x x + k_y y + k_z z) + \cos(k_x x + k_y y - k_z z) + \\ &\quad \cos(k_x x - k_y y + k_z z) + \cos(k_x x - k_y y - k_z z)] \Rightarrow \frac{4\pi}{\alpha^2 + k^2} \end{aligned} \quad (\text{C.17})$$

$$\begin{aligned} \cos(k_x x) \cos(k_y y) \sin(k_z z) &= \frac{1}{4} [\sin(k_x x + k_y y + k_z z) - \sin(k_x x + k_y y - k_z z) + \\ &\quad \sin(k_x x - k_y y + k_z z) - \sin(k_x x - k_y y - k_z z)] \Rightarrow 0, \end{aligned} \quad (\text{C.18})$$

$$\begin{aligned} \cos(k_x x) \sin(k_y y) \sin(k_z z) &= \frac{1}{4} [\cos(k_x x + k_y y - k_z z) - \cos(k_x x + k_y y + k_z z) - \\ &\quad \cos(k_x x - k_y y - k_z z) + \cos(k_x x - k_y y + k_z z)] \Rightarrow 0, \end{aligned} \quad (\text{C.19})$$

$$\begin{aligned} \sin(k_x x) \sin(k_y y) \sin(k_z z) &= \frac{1}{4} [\sin(k_x x - k_y y + k_z z) - \sin(k_x x - k_y y - k_z z) - \\ &\quad \sin(k_x x + k_y y + k_z z) + \sin(k_x x + k_y y - k_z z)] \Rightarrow 0. \end{aligned} \quad (\text{C.20})$$

As one can see, only the terms consisting of cosines will survive. So the integral gives:

$$\begin{aligned} \langle \vec{k} | \frac{e^{-\alpha r}}{r} | \vec{q} \rangle &= \frac{4\pi}{\Omega} \left[\frac{\cos((k_x - q_x)a/2) \cos((k_y - q_y)a/2)}{\alpha^2 + (k_x - q_x)^2 + (k_y - q_y)^2 + (k_z - q_z)^2} - \right. \\ &\quad \frac{\cos((k_x - q_x)a/2) \cos((k_y - q_y)a/2)}{\alpha^2 + (k_x - q_x)^2 + (k_y - q_y)^2 + (k_z + q_z)^2} - \\ &\quad \frac{\cos((k_x - q_x)a/2) \cos((k_y + q_y)a/2)}{\alpha^2 + (k_x - q_x)^2 + (k_y + q_y)^2 + (k_z - q_z)^2} - \\ &\quad \frac{\cos((k_x + q_x)a/2) \cos((k_y - q_y)a/2)}{\alpha^2 + (k_x + q_x)^2 + (k_y - q_y)^2 + (k_z - q_z)^2} + \\ &\quad \frac{\cos((k_x - q_x)a/2) \cos((k_y + q_y)a/2)}{\alpha^2 + (k_x - q_x)^2 + (k_y + q_y)^2 + (k_z + q_z)^2} + \\ &\quad \frac{\cos((k_x + q_x)a/2) \cos((k_y - q_y)a/2)}{\alpha^2 + (k_x + q_x)^2 + (k_y - q_y)^2 + (k_z + q_z)^2} + \\ &\quad \left. \frac{\cos((k_x + q_x)a/2) \cos((k_y + q_y)a/2)}{\alpha^2 + (k_x + q_x)^2 + (k_y + q_y)^2 + (k_z - q_z)^2} - \right. \\ &\quad \left. \frac{\cos((k_x + q_x)a/2) \cos((k_y + q_y)a/2)}{\alpha^2 + (k_x + q_x)^2 + (k_y + q_y)^2 + (k_z + q_z)^2} \right] \delta_{g, \pi_z} \\ &= \sum_{\vec{p}} (-1)^{n_p} \frac{\cos((p_x)a/2) \cos((p_y)a/2)}{\alpha^2 + |p|^2} \delta_{g, \pi_z}. \end{aligned} \quad (\text{C.21})$$

Here we have introduced the sum over \vec{p} which means a summation over every possible combination of adding or subtracting the elements of \vec{k} and \vec{q} . The number n_p refers to the number of additions to obtain the particular vector \vec{p} .

We will now calculate the matrix elements for the applied bias voltage.

$$\begin{aligned}
\langle \vec{k}, g/u | V_L \Theta(-z-d) | \vec{k}, g/u \rangle &= \frac{8V_L}{\Omega} \int_0^a dx \int_0^a dy \sin^2(k_x x) \sin^2(k_y y) \int_{-D/2}^{-d} dz \begin{bmatrix} \cos^2(k_z z) \\ \sin^2(k_z z) \end{bmatrix} \\
&= \frac{V_L}{D} \int_{-D/2}^{-d} dz (1 \pm \cos(2k_z z)) = \frac{V_L}{D} \left[L \pm \left(\frac{\sin(Dk_z)}{2k_z} - \frac{\sin(2k_z d)}{2k_z} \right) \right] \\
&= \frac{V_L}{D} \left[L \mp \frac{\sin(2k_z d)}{2k_z} \right] \tag{C.22}
\end{aligned}$$

$$\begin{aligned}
\langle \vec{k}, g/u | V_L \Theta(-z-d) | \vec{p}, \pi_z \rangle &= \frac{2V_L}{D} \int_{-D/2}^{-d} dz \begin{bmatrix} \cos(k_z z) \cos(p_z z) \\ \sin(k_z z) \sin(p_z z) \\ \sin(k_z z) \cos(p_z z) \\ \cos(k_z z) \sin(p_z z) \end{bmatrix} \delta_{k_x, p_x} \delta_{k_y, p_y} \\
&= \frac{V_L}{D} \int_{-D/2}^{-d} dz \begin{bmatrix} \cos((k_z - p_z)z) \pm \cos((k_z + p_z)z) \\ \sin((k_z + p_z)z) \pm \sin((k_z - p_z)z) \end{bmatrix} \delta_{k_x, p_x} \delta_{k_y, p_y} \\
&= \frac{V_L}{D} \begin{bmatrix} S_1(k_z - p_z) \pm S_1(k_z + p_z) \\ C_1(k_z + p_z) \pm C_1(k_z - p_z) \end{bmatrix} \delta_{k_x, p_x} \delta_{k_y, p_y}, \tag{C.23}
\end{aligned}$$

where

$$S_1(\Delta) = \left. \frac{\sin(\Delta z)}{\Delta} \right|_{-D/2}^{-d} = \frac{\sin(\Delta(L+d)) - \sin(\Delta d)}{\Delta} = \frac{D}{2} \delta_{\Delta,0} - \frac{\sin(\Delta d)}{\Delta}, \text{ and} \tag{C.24}$$

$$C_1(\Delta) = \left. -\frac{\cos(\Delta z)}{\Delta} \right|_{-D/2}^{-d} = \frac{\cos(\Delta(L+d)) - \cos(\Delta d)}{\Delta} \tag{C.25}$$

$$\begin{aligned}
\langle \vec{k}, g/u | \frac{V_L}{2d} (d-z) \Theta(d-|z|) | \vec{k}, g/u \rangle &= \frac{V_L}{2d} \frac{2}{D} \int_{-d}^d dz \begin{bmatrix} \cos^2(k_z z) \\ \sin^2(k_z z) \end{bmatrix} (d-z) \\
&= \frac{V_L}{2dD} \int_{-d}^d dz (1 \pm \cos(2k_z z)) (d-z) \\
&= \frac{V_L}{D} \left[d \pm \frac{\sin(2k_z d)}{k_z} \right] \tag{C.26}
\end{aligned}$$

$$\begin{aligned}
\langle \vec{k}, g/u | \frac{V_L}{2d} (d-z) \Theta(d-|z|) | \vec{p}, \pi_z \rangle &= \frac{V_L}{2d} \frac{2}{D} \int_{-d}^d dz \begin{bmatrix} \cos(k_z z) \cos(p_z z) \\ \sin(k_z z) \sin(p_z z) \\ \sin(k_z z) \cos(p_z z) \\ \cos(k_z z) \sin(p_z z) \end{bmatrix} (d-z) \delta_{k_x, p_x} \delta_{k_y, p_y} \\
&= \frac{V_L}{2dD} \int_{-d}^d dz \begin{bmatrix} \cos((k_z - p_z)z) \pm \cos((k_z + p_z)z) \\ \sin((k_z + p_z)z) \pm \sin((k_z - p_z)z) \end{bmatrix} (d-z) \delta_{k_x, p_x} \delta_{k_y, p_y} \\
&= \frac{V_L}{D} \begin{bmatrix} S_2(k_z - p_z) \pm S_2(k_z + p_z) \\ C_2(k_z + p_z) + \frac{S_2(k_z + p_z)}{d(k_z + p_z)} \pm \left(C_2(k_z - p_z) + \frac{S_2(k_z - p_z)}{d(k_z - p_z)} \right) \end{bmatrix} \delta_{k_x, p_x} \delta_{k_y, p_y}, \tag{C.27}
\end{aligned}$$

where

$$S_2(\Delta) = \left. \frac{\sin(\Delta)}{\Delta} \right|_0^d = \frac{\sin(\Delta d)}{\Delta}, \text{ and} \tag{C.28}$$

$$C_2(\Delta) = \left. \frac{\cos(\Delta)}{\Delta} \right|_0^d = \frac{\cos(\Delta d)}{\Delta} \tag{C.29}$$

Adding the two terms the following equation is obtained for the matrix element due to the applied bias voltage:

$$\begin{aligned} \langle \vec{k}, g/u | V_L | \vec{p}, \pi_z \rangle &= \left[\frac{V_L}{2} \delta_{k_z, p_z} + \frac{V_L}{D} \left(\frac{\cos\left(\frac{(k_z + p_z)D}{2}\right)}{k_z + p_z} + \frac{\sin\left(\frac{(k_z + p_z)d}{d(k_z + p_z)^2}\right)}{d(k_z + p_z)^2} \mp \right. \right. \\ &\quad \left. \left. \left(\frac{\cos\left(\frac{(k_z - p_z)D}{2}\right)}{k_z - p_z} + \frac{\sin\left(\frac{(k_z - p_z)d}{d(k_z - p_z)^2}\right)}{d(k_z - p_z)^2} \right) (1 - \delta_{g/u, \pi_z}) \right] \delta_{k_x, p_x} \delta_{k_y, p_y} \quad (\text{C.30}) \end{aligned}$$

The mixed matrix elements are:

$$\begin{aligned} \langle \vec{k}, \pi_z | \hat{T} | b \rangle &= -\frac{1}{2} \sqrt{\frac{8b^3}{\pi\Omega}} \int d^3r e^{-br} \nabla^2 \sin\left(k_x \left(x + \frac{a}{2}\right)\right) \sin\left(k_y \left(y + \frac{a}{2}\right)\right) \begin{bmatrix} \cos(k_z z) \\ \sin(k_z z) \end{bmatrix} \\ &= \frac{k^2}{2} \langle \vec{k}, \pi_z | b \rangle = 8b^2 k^2 \sqrt{\frac{2\pi b}{\Omega}} \frac{\sin(k_x a/2) \sin(k_y a/2)}{(b^2 + k^2)^2} \delta_{\pi_z, g} \quad (\text{C.31}) \end{aligned}$$

$\langle \vec{k}, \pi_z | V_d \Theta(d - |z|) | b \rangle$ Is probably the nastiest matrix element. For easier calculations, consider first the overlap element with an imaginary plane wave, $\frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}}$:

$$\begin{aligned} \langle \vec{k} | V_d \Theta(d - |z|) | b \rangle &= \sqrt{\frac{b^3}{\pi\Omega}} \int d^3r V_d \Theta(d - |z|) e^{-b|r|} e^{i\vec{k}\cdot\vec{r}} \\ &= \sqrt{\frac{b^3}{\pi\Omega}} V_d \int_0^{2\pi} d\phi \int_0^\infty \rho d\rho \int_{-d}^d dz e^{-b\sqrt{\rho^2 + z^2}} e^{i(k_\rho \rho \cos\phi + k_z z)}, \quad (\text{C.32}) \end{aligned}$$

where $k_\rho^2 = k_x^2 + k_y^2$.

This is not a trivial integral. However, it can be solved for $k_\rho = 0$:

$$\begin{aligned} \langle \vec{k} | V_d \Theta(d - |z|) | b \rangle_{k_\rho=0} &= 2bV_d \sqrt{\frac{b\pi}{\Omega}} \int_{-d}^d dz \int_0^\infty d\rho e^{ik_z z} \rho e^{-b\sqrt{\rho^2 + z^2}} \\ &= 2bV_d \sqrt{\frac{b\pi}{\Omega}} \int_{-d}^d dz e^{ik_z z} \left[-\frac{e^{-b\sqrt{\rho^2 + z^2}} (1 + b\sqrt{\rho^2 + z^2})}{b^2} \right]_0^\infty \\ &= 2V_d \sqrt{\frac{\pi}{b\Omega}} \int_{-d}^d dz e^{ik_z z} e^{-b|z|} (1 + b|z|) \\ &= 2V_d \sqrt{\frac{\pi}{b\Omega}} \left(\int_{-d}^0 dz e^{ik_z z} e^{bz} (1 - bz) + \int_0^d dz e^{ik_z z} e^{-bz} (1 + bz) \right) \\ &= 4V_d \sqrt{\frac{\pi}{b\Omega}} \int_0^d dz \cos(k_z z) e^{-bz} (1 + bz) = \sqrt{\frac{\pi}{b\Omega}} \frac{4V_d}{(b^2 + k_z^2)^2} \left[2b^3 - e^{-bd} \right. \\ &\quad \left. (b^2(2b + (b^2 + k_z^2)d) \cos(k_z d) + k_z(3b^2 + k_z + bd(b^2 + k_z^2)) \sin(k_z d)) \right] \quad (\text{C.33}) \end{aligned}$$

The limits for this result give correct answers:

$$\lim_{d \rightarrow \infty} \langle \vec{k} | V_d \Theta(d - |z|) | b \rangle_{k_\rho=0} = V_d \sqrt{\frac{b\pi}{\Omega}} \frac{8b^2}{(b^2 + k^2)^2} = V_d \langle \vec{k} | b \rangle \quad (\text{C.34})$$

$$\lim_{d \rightarrow 0} \langle \vec{k} | V_d \Theta(d - |z|) | b \rangle_{k_\rho=0} = \sqrt{\frac{\pi}{b\Omega}} \frac{4V_d}{(b^2 + k_z^2)^2} [2b^3 - 2b^3] = 0 \quad (\text{C.35})$$

But how to cope with $k_\rho \neq 0$? First the integral over ϕ can be evaluated:

$$\int_0^{2\pi} d\phi e^{ik_\rho \rho \cos \phi} = \int_0^{2\pi} d\phi Q(\cos \phi) = \int_0^{2\pi} d\phi e^{ia \cos \phi}, \text{ with } a = k_\rho \rho \quad (\text{C.36})$$

The variable ϕ can be redefined to a variable, z , in the complex plane that runs over the unit circle, so $Q(\cos \phi) = Q(\frac{1}{2}(z + 1/z))$, where $z = e^{i\phi}$. Next one can construct $f(z) = \frac{1}{iz}Q(\frac{1}{2}(z + 1/z))$, such that:

$$\int_0^{2\pi} d\phi Q(\cos \phi) = 2\pi i \sum \text{residues of } f \text{ inside the unit circle} \quad (\text{C.37})$$

For proof for even more general $Q(\cos \phi, \sin \phi)$ see [23]. The function $f(z)$ has only a pole at $z = 0$. To determine the residue an expansion can be made:

$$\begin{aligned} e^{\frac{1}{2}(z+1/z)} &= \left(1 + \frac{ia}{2}z - \frac{a^2}{8}z^2 + \dots\right) \left(1 + \frac{ia}{2}\frac{1}{z} - \frac{a^2}{8}\frac{1}{z^2} + \dots\right) \\ &\stackrel{x=a/2}{=} \left(1 + ixz - \frac{1}{2}x^2z^2 + \dots\right) \left(1 + \frac{x}{z} - \frac{1}{2}\frac{x^2}{z^2} + \dots\right) \end{aligned} \quad (\text{C.38})$$

So the residue at $z = 0$ of $f(z)$ can be easily determined to be:

$$\text{Res}_{z=0}f(z) = -i \left(1 - x^2 + \frac{1}{4}x^4 - \frac{1}{36} + \dots\right) = -i \sum_{n=0}^{\infty} (-1)^n \left(\frac{x^n}{n!}\right)^2 = -iJ_0(2x), \quad (\text{C.39})$$

where $J_n(z)$ is a Bessel function of the first kind. Plugging this in, the result is:

$$\int_0^{2\pi} d\phi e^{ik_\rho \rho \cos \phi} = 2\pi J_0(k_\rho \rho) \quad (\text{C.40})$$

So the matrix element has been reduced to:

$$\langle \vec{k} | V_d \Theta(d - |z|) | b \rangle = 2bV_d \sqrt{\frac{b\pi}{\Omega}} \int_{-d}^d dz \int_0^\infty d\rho \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} e^{ik_z z} \quad (\text{C.41})$$

Going back to our original wave functions one has to add two additional sines and an extra $\sqrt{8}$ due to the different normalization. Since the integral will be zero for odd values of n_z , a Kronecker delta is also be included and $e^{ik_z z}$ is replaced by $\cos(k_z z)$:

$$\begin{aligned} \langle \vec{k}, \pi_z | V_d \Theta(d - |z|) | b \rangle &= 4bV_d \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \times \\ &\int_{-d}^d dz \int_0^\infty d\rho \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \cos(k_z z) \delta_{\pi_z, g} \end{aligned} \quad (\text{C.42})$$

$$\begin{aligned} \langle \vec{k}, \pi_z | V_{loc} \frac{e^{-\alpha r}}{r} | b \rangle &= V_{loc} \sqrt{\frac{8b^3}{\pi\Omega}} \int d^3 r \sin\left(k_x \left(x + \frac{a}{2}\right)\right) \sin\left(k_y \left(y + \frac{a}{2}\right)\right) \left[\frac{\cos(k_z z)}{\sin(k_z z)} \right] \frac{e^{-\alpha r}}{r} e^{-br} \\ &= 2bV_{loc} \sqrt{\frac{2b}{\pi\Omega}} \int d^3 r \left(\sin(k_x x) \cos\left(\frac{k_x a}{2}\right) + \cos(k_x x) \sin\left(\frac{k_x a}{2}\right) \right) \cdot \\ &\quad \left(\sin(k_y y) \cos\left(\frac{k_y a}{2}\right) + \cos(k_y y) \sin\left(\frac{k_y a}{2}\right) \right) \left[\frac{\cos(k_z z)}{\sin(k_z z)} \right] \frac{e^{-(\alpha+b)r}}{r} \\ &= \sqrt{\frac{2\pi b}{\Omega}} \frac{8bV_{loc}}{(\alpha + b)^2 + k^2} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \delta_{\pi_z, g} \end{aligned} \quad (\text{C.43})$$

The matrix element from the applied potential is very similar and the result is basically the same as for the barrier:

$$\begin{aligned} \langle \vec{k}, \pi_z | V_L \Theta(-z-d) | b \rangle &= 4bV_L \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \times \\ &\int_{-\infty}^{-d} dz \int_0^{\infty} d\rho \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \begin{bmatrix} \cos(k_z z) \\ \sin(k_z z) \end{bmatrix} \end{aligned} \quad (\text{C.44})$$

Then the other part due to the applied bias voltage is calculated:

$$\begin{aligned} \langle \vec{k}, \pi_z | \frac{V_L}{2d} (d-z) \Theta(d-|z|) | b \rangle &= 2bV_L \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \times \\ &\int_{-d}^d dz \int_0^{\infty} d\rho \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \left(\cos(k_z z) \delta_{\pi_z, g} - \frac{z}{d} \sin(k_z z) \delta_{\pi_z, u} \right) \end{aligned} \quad (\text{C.45})$$

So the total matrix element becomes:

$$\begin{aligned} \langle \vec{k}, \pi_z | V_L | b \rangle &= 4bV_L \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \left\{ \int_0^{\infty} dz \cos(k_z z) \delta_{\pi_z, g} - \right. \\ &\left. \left(\int_d^{\infty} dz + \int_{-d}^d dz \frac{z}{2d} \right) \sin(k_z z) \delta_{\pi_z, u} \right\} \int_0^{\infty} d\rho \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \end{aligned} \quad (\text{C.46})$$

The first integral over z is nothing else than half the overlap element between the localized function and the plane waves. Taking care of all the pre-factors we obtain the following equation

$$\begin{aligned} \langle \vec{k}, \pi_z | V_L | b \rangle &= 4bV_L \sqrt{\frac{2b\pi}{\Omega}} \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \left\{ \frac{2b}{(b^2+k^2)^2} \delta_{\pi_z, g} - \right. \\ &\left. \int_0^{\infty} d\rho \left(\int_d^{\infty} dz + \int_{-d}^d dz \frac{z}{2d} \right) \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \sin(k_z z) \delta_{\pi_z, u} \right\} \end{aligned} \quad (\text{C.47})$$

C.2 Numerical integrations

A number of integrals couldn't be solved analytically, so they were done numerically using Gaussian quadratures. For more information about numerical integration using Gaussian quadratures see section 4.5 of [24]. In this appendix the transformations are showed to perform the numerical analysis. We start with the integral in equation C.42.

$$\begin{aligned} \int_{-d}^d dz \int_0^{\infty} d\rho \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \cos(k_z z) &= d \int_{-1}^1 du \int_0^{\infty} d\rho \rho J_0(k_\rho \rho) e^{-b(\sqrt{\rho^2+d^2 u^2}-\rho)} e^{-b\rho} \cos(dk_z u) \\ &= \frac{d}{b} \int_{-1}^1 du \int_0^{\infty} dr \frac{r}{b} J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+b^2 d^2 u^2}+r} e^{-r} \cos(dk_z u) \\ &= \frac{d}{b^2} \int_{-1}^1 du \int_0^{\infty} dr r e^{-r} f_{b,d}(r, u), \end{aligned} \quad (\text{C.48})$$

where we used the following transformations

$$\begin{aligned} u &= z/d, \\ r &= b\rho \end{aligned}$$

and the defined the function

$$f_{b,d}(r, u) = J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+b^2d^2u^2+r}} \cos(dk_z u). \quad (\text{C.49})$$

We are now left with two integrals over the function $f_{b,d}(r, u)$. The integral over u can be evaluated by using Legendre polynomials and the integral over r can be evaluated by using Laguerre polynomials.

Next there are two integrals in equation C.47. The first one is:

$$\begin{aligned} \int_0^\infty d\rho \int_d^\infty dz \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \sin(k_z z) &= \int_0^\infty d\rho \int_0^\infty dx \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+(x+d)^2}} \sin(k_z(x+d)) \\ &= \int_0^\infty d\rho \int_0^\infty dx \rho J_0(k_\rho \rho) e^{-b(\sqrt{\rho^2+(x+d)^2}-\rho-x)} e^{-b\rho} e^{-bx} \sin(k_z(x+d)) \\ &= \frac{1}{b^2} \int_0^\infty dr \int_0^\infty du \frac{r}{b} J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+(u+bd)^2+r+u}} e^{-r} e^{-u} \sin\left(k_z\left(\frac{u}{b}+d\right)\right) \\ &= \frac{1}{b^3} \int_0^\infty dr r e^{-r} \int_0^\infty du e^{-u} f_{b,d}(r, u), \end{aligned} \quad (\text{C.50})$$

where we have used the transformations

$$\begin{aligned} x &= z - d, \\ r &= b\rho, \\ u &= bx \end{aligned}$$

and the defined the function

$$f_{b,d}(r, u) = J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+(u+bd)^2+r+u}} \sin\left(k_z\left(\frac{u}{b}+d\right)\right). \quad (\text{C.51})$$

We are now left with two integrals over the function $f_{b,d}(r, u)$. Both integrals can be evaluated by using Laguerre polynomials. Unfortunately this approach converges very bad. This is due to the wild oscillations at the beginning of the function, see C.1. It can be questioned why this is not a problem in the r -direction. The Bessel function in the r -direction is decaying, but the sine in the z -direction not at all. It seems that the decay of the Bessel function is sufficient to ensure convergence in the r -direction.

To map the beginning of the function better, the integral is split into two parts. One from d to c and the other from c to ∞ . The parameter c is chosen in such a way that the exponential is less than 1%: so $c < -\log(0.01)/b \simeq 5.0/b$. The integral over finite interval is rewritten as

$$\begin{aligned} \int_0^\infty d\rho \int_d^c dz \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \sin(k_z z) &= \int_0^\infty d\rho \int_d^c dz \rho e^{-b\rho} J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}-\rho} \sin(k_z z) \\ &= \frac{1}{b^2} \int_0^\infty dr r e^{-br} \int_d^c dz f_b(r, z), \end{aligned} \quad (\text{C.52})$$

where the the transformation $r = b\rho$ is used and the following function is defined

$$f_b(r, z) = J_0(k_\rho \rho) e^{r-\sqrt{r^2+b^2z^2}} \sin(k_z z) \quad (\text{C.53})$$

The other integral is basically the same as the integral we started (eq. C.50). Only the lower boundary d is interchanged by c .

$$\int_0^\infty d\rho \int_c^\infty dz \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \sin(k_z z) = \frac{1}{b^3} \int_0^\infty dr r e^{-r} \int_0^\infty du e^{-u} f_{b,c}(r, u), \quad (\text{C.54})$$

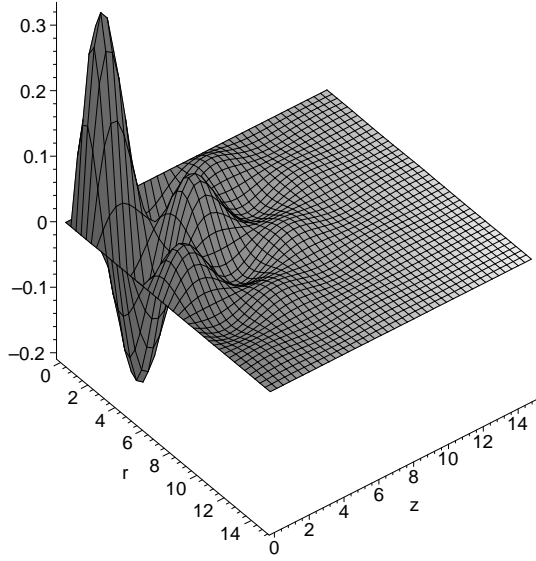


Figure C.1: Plot of the function $\rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \sin(k_z z)$, with $b = 0.5$. One clearly sees the wild oscillations near the origin.

with

$$f_{b,d}(r, u) = J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+(u+bc)^2+r+u}} \sin\left(k_z \left(\frac{u}{b} + c\right)\right). \quad (\text{C.55})$$

However, the contribution of the last integral is basically zero, so it could be neglected as well.

The next integrals is:

$$\begin{aligned} & \int_0^\infty d\rho \int_{-d}^d dz \frac{z}{2d} \rho J_0(k_\rho \rho) e^{-b\sqrt{\rho^2+z^2}} \sin(k_z z) \\ &= \frac{d}{2} \int_0^\infty d\rho \int_{-1}^1 dx x \rho J_0(k_\rho \rho) e^{-b(\sqrt{\rho^2+d^2 x^2}-\rho)} e^{-b\rho} \sin(dk_z x) \\ &= \frac{d}{2b} \int_0^\infty dr \int_{-1}^1 dx x \frac{r}{b} J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+b^2 d^2 x^2}+r} e^{-r} \sin(dk_z x) \\ &= \frac{d}{2b^2} \int_0^\infty dr r e^{-r} \int_{-1}^1 dx f_{b,d}(r, x), \end{aligned} \quad (\text{C.56})$$

where we have used the transformations

$$\begin{aligned} x &= z/d, \\ r &= b\rho \end{aligned}$$

and the defined the function

$$f_{b,d}(r, x) = x J_0\left(k_\rho \frac{r}{b}\right) e^{-\sqrt{r^2+b^2 d^2 x^2}+r} \sin(dk_z x) \quad (\text{C.57})$$

We are now left with two integrals over the function $f_{b,d}(r, u)$. The integral over x can be evaluated by using Legendre polynomials and the integral over r can be evaluated by using Laguerre polynomials.

Appendix D

Unused stuff

D.1 Diagonalization of a bordered unit matrix

Consider the matrix S where $s_{ii} = 1$, $s_{1i} = s_{i1} \neq 0$ and all the other elements are 0. The following eigen problem $\mathbf{Q}\mathbf{S}\mathbf{Q}^T = \mathbf{D}$ can be written as:

$$\begin{pmatrix} q_{11} & \cdots & q_{1n} \\ \vdots & \ddots & \vdots \\ q_{n1} & \cdots & q_{nn} \end{pmatrix} \begin{pmatrix} s_{11} & \cdots & s_{1n} \\ \vdots & \ddots & 0 \\ s_{n1} & 0 & s_{nn} \end{pmatrix} = \begin{pmatrix} d_1 & & 0 \\ & \ddots & \\ 0 & & d_1 \end{pmatrix} \begin{pmatrix} q_{11} & \cdots & q_{1n} \\ \vdots & \ddots & \vdots \\ q_{n1} & \cdots & q_{nn} \end{pmatrix} \quad (\text{D.1})$$

One can extract the following equations from this:

$$\sum_i q_{ki} s_{i1} = d_k q_{k1} \quad (\text{D.2})$$

$$\text{for } i > 1 \quad q_{k1} s_{1i} + q_{ki} s_{ii} = d_k q_{ki} \rightarrow q_{ki} = q_{k1} \frac{s_{1i}}{d_k - s_{ii}} \quad (\text{D.3})$$

Keeping in mind that the diagonal elements of \mathbf{S} are 1, we can solve for d_k

$$\begin{aligned} \sum_i q_{ki} s_{i1} &= q_{k1} s_{11} + \sum_{i>1} q_{k1} \frac{s_{1i}}{d_k - s_{ii}} s_{i1} \\ \Leftrightarrow \sum_{i>1} \frac{s_{1i}^2}{d_k - 1} &= d_k - 1 \quad \vee \quad q_{k1} = 0 \\ \Leftrightarrow d_k &= 1 \pm \sqrt{\sum_{i>1} s_{1i}^2} \equiv 1 \pm \sqrt{S} \quad \vee \quad (d_k = 1 \wedge q_{k1} = 0) \end{aligned} \quad (\text{D.4})$$

There is still some freedom of choosing the elements of \mathbf{Q} , but we can restrict them by the additional condition $\mathbf{Q}\mathbf{Q}^T = \mathbf{1}$:

$$\sum_k q_{ki} q_{kj} = \delta_{ij} \quad (\text{D.5})$$

$$\begin{aligned} \sum_k q_{ki}^2 &= q_{k1}^2 \left(1 + \sum_{i>1} \frac{s_{1i}^2}{(d_k - 1)^2} \right) = q_{k1}^2 \left(1 + \frac{S}{(d_k - 1)^2} \right) = 1 \Rightarrow \\ q_{k1} &= \frac{1}{\sqrt{1 + \frac{S}{(d_k - 1)^2}}} = \frac{1}{\sqrt{2}} \end{aligned} \quad (\text{D.6})$$

If $q_{k1} = 0$ and $d_k = 1$ this result makes no sense, and for these eigenvectors it is tricky to solve.

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