Chapter 3

Theory

One of the ultimate goals in nanotechnology is the development of electronic devices whose main building blocks are individual conductive molecules contacted with two or more leads. To this aim it is certainly necessary to measure, control and understand electron transport phenomena occurring in such systems.

Transport is an inherently non-equilibrium phenomenon, where the role of dissipation and the coupling to the environment play a crucial role. The driving forces carrying the system out of equilibrium are usually electrical or magnetic, such as the electric field associated with an applied source-drain bias voltage, but also thermal and electrochemical potential gradients allow electronic transport to occur and its external manifestation in terms of macroscopic current.

The electrical conduction in macroscopic materials is described by first Ohm's law, which states that the current I is proportional to to the applied voltage V (for relatively small biases):

$$I = \frac{1}{R}V = GV \tag{3.1}$$

The constant of proportionality is known as conductance G (the inverse of the resistance R), which for a given conductor grows linearly with the transverse area S and it is inversely proportional to its length L (second Ohm's law):

$$G = \sigma \frac{S}{L} \tag{3.2}$$

where σ is a specific property of the material known as conductivity, a quantity independent on the geometry of the system.

The conductance is a key quantity in the description of the transport properties, but second Ohm's law is not applicable at the atomic scale, since the properties become
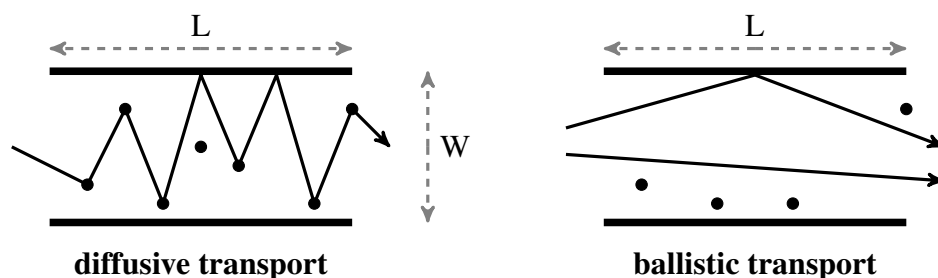
FIGURE 3.1: Schematic pictures of the diffusive and ballistic regimes

strongly geometry-dependent and quantum effects arise. Then different approaches are required when the dimensions of the system are scaled down to the mesoscale or to the nanoscale.

The nature of transport strongly depends on the characteristic dimensions of the active region of the device. Specifically, we can distinguish different transport regimes depending on how the width W and the length L of the conductor relate with the De Broglie wavelength of electrons near the Fermi energy (known as Fermi wavelength, λ_F). In fact, most of the properties of solids, involving electronic transport, are described by the dynamics of such electrons, thus one has to account for their scattering due, for instance, to a potential arising by phonons. If the variations in this potential are comparable to the Fermi wavelength then quantum effects become more prominent otherwise, *e. g.* if the potential is slowly varying, one can use the semi-classical description of the system.

Another important length scale is the elastic mean free path of the carriers l_c, which roughly measures the distance between elastic collisions with static impurities.

If both L and W are much larger than l_c the transport is purely diffusive and second Ohm's law hold. In a semi-classical picture the electron motion can be viewed as as a random walk of step size l_c among the impurities and the system properties obey the Boltzmann transport equation (see fig. 3.1-left).

Otherwise, if W is smaller than l_c, while L is still much longer, we deal with the case of a quantum confined system, in which the carrier motion is quantized in one (or two) dimension, but essentially behaves as a diffusive conductor in the others.

Finally, when both L and W are comparable with l_c, we reach the ballistic regime in which the electron momentum can be assumed to be constant and eventually only limited by the boundaries of the sample, then the motion of the carriers is governed by the wave-like behavior of the particle and its reflection and transmission properties through the structure. (see fig. 3.1-right)

One interesting aspect of transport in nanostructure systems is that the characteristic

length scales lie in transition range from classical to quantum transport. Hence transport may be semi-classical or purely quantum, or even more difficult, a mixture of the two in which the effects of decoherence and dissipation (inelastic scattering) play important roles, while at the same time, quantum effects are still dominant. Decoherence, in particular, introduces a further length scale which is decoherence length, fundamental for the definition of semiclassical transport, i.e. whereby interference can be neglected. Thus it appears clear that it becomes very cumbersome to describe the correct physics of such devices, since a single description (purely semi-classical or purely quantum) may not be sufficient.

Electronic transport at its most fundamental level requires a full many body quantum mechanical description. Clearly, a full many particle description of transport including the real number of particles of the device, its contact to the external environment, and the external environment itself, is beyond the ability of any computational platform. Hence, successive levels of approximation, neglecting some of such effect, are necessary in any sort of realistic description of transport.

The currently most popular method to compute electron transport in nanoscale systems is based on the use of Non-equilibrium Green's functions and on a mean-field approximation for the (coherent) electronic motion, necessary to transform the many-body problem into an effective one-electron problem. The central idea of this approach is that, if inelastic interactions can be ignored, transport in nanoscale devices can be treated as a quantum scattering problem. This means in practice that transport properties like the electrical conductance can be determined from the transmission probability for an electron to cross the conductor.

A full quantum, coherent approach bridging the gap between ballistic and (quantum) diffusive behavior is the Kubo-Greenwood approach, where conductivity is obtained by the velocity-velocity correlation function in a disordered system (treated at the one-electron level, eventually adjusted for many-body effects in an effective way).

Beyond these approximations, common methods are the quantum kinetic approaches in terms of the Liouville-von Neumann equation of motion for the density matrix or Wigner distribution approaches, both including quantum correlations but retaining the form of semi-classical approximation in terms of the distribution function.

In going from the quantum to the classical description, electronic transport start to be treated in terms of a classical particle system, in which informations concerning the phase of the electron and its non-local behavior are lost. The primary approximation for describing transport in semiconductors at the meso- and macroscale is the Bolzmann

transport equation (BTE). Within the relaxation time approximation, the BTE represents a kinetic equation describing the time evolution of the global non-equilibrium distribution function of the position and momentum of the particles in terms of local equilibrium distributions.

Finally further approximations to the BTE lead to the hydrodynamic and the drift-diffusion approaches to the transport. Specifically, the isothermal drift-diffusion model consists of carrier balance equations and current equations for electrons and holes, accounting for carrier drift induced by external driving forces. In the non-isothermal drift-diffusion approach, local thermal equilibrium is assumed, and an heat-flow equation has to be solved self-consistently with the carrier balance and flux equations, in order to describe thermal effects. If carriers are driven far from equilibrium, the hydrodynamic transport model is more appropriate, since it includes equations for the carrier energies and for the corresponding energy fluxes.

In this chapter we first summarize the concepts of Density Functional Theory (DFT)[78,79]. Next we introduce the basic concepts of electron transport in nanodevices considering the simple case of a single level conductor contacted with two electrodes[80,81]. Finally, we present the formalism allowing to compute the transport properties by means of Non-Equilibrium Green's Function (NEGF) approach[81,82]. In this respect the DFT mean-field potential can be considered to an approximation to the exact, non-local and energy-dependent self-energy governing the quasi-particle dynamics. An introduction to Green's functions[81–85] and their application in some relevant problems can be found in appendix A.

3.1 Density Functional Theory

The general expression for the electronic Hamiltonian for a system of N electron is

$$\hat{H}(\mathbf{r},t) = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + V_{ext}(\mathbf{r}_i,t) \right) + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{\mathbf{r}_{ij}} + V_{NN} \tag{3.3}$$

where the four terms are respectively the kinetic energy of electrons, the external potential, the repulsive potential energy between electrons and between nuclei. The latter is a constant and can be simply added to eigenvalues and in the following will be ignored. As well know, the Hartree-Fock theory cannot properly account for the electronic correlation, then a number of theoretical methods have been developed with the attempt to overcome this limit and recover the largest part of the correlation energy. On one hand

the possibility of building excited configurations from the Hartree-Fock determinant (configuration interaction (CI) methods) allows to radically improve the description of the electron-electron correlation, but at a very high computational costs. On the other hand, observing that the terms appearing in the Hamiltonian involve only one or two electronic coordinates, one can ask if it is necessary to deal with a complex wavefunction of 4N variables (3 spatial coordinates and one of spin for each electron) or if there is a simpler quantity allowing to calculate the properties of a system. Moreover, one can notice that for an N-electron system the external potential completely determines the Hamiltonian, because the kinetic and repulsion potential terms are fixed by N. Such a quantity exists, it is the electron density $\rho(\mathbf{r})$ and is the basic variable in the density functional theory (DFT) method.

The electron density $\rho(\mathbf{r})$ is defined as:

$$\rho(\mathbf{r}) = N \int ... \int |\Psi(\mathbf{x}_1, \mathbf{x}_2 ..., \mathbf{x}_N)|^2 d\sigma_1 d\mathbf{x}_2 ... d\mathbf{x}_N \qquad (3.4)$$

where N accounts for the indistinguibility of electrons. The electron density has the physical meaning of probability to find an electron in the infinitesimal volume $d\sigma_1 d\mathbf{x}_2 ... d\mathbf{x}_N$ and is a simple function of only three spatial variables. The integral on all space must give the total number of electrons:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \qquad (3.5)$$

3.1.1 Hohenberg-Kohn theorem and Levi constrained search

The first Hohemberg-Kohn theorem legitimizes the use of electron density as basic quantity to determine the ground-state wavefunction and the properties of the systems. Indeed it states that *the external potential V_{ext} is determined, within a trivial addictive constant, by the electron density*.

The proof of such theorem is remarkably simple and proceeds by *reductio ad absurdum*. Let there be two different external potentials, $V_{ext,1}(\mathbf{r})$ and $V_{ext,2}(\mathbf{r})$, that give rise to the same density $\rho_0(\mathbf{r})$. The associated Hamiltonians, $\hat{H}_1$ and $\hat{H}_2$, will therefore have different ground-state wavefunctions, Ψ_1 and Ψ_2, both yielding $\rho_0(\mathbf{r})$. Applying the variational principle and after some mathematical rearrangements, one obtains:

$$E_1^0 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle =$$
$$= E_2^0 + \int \rho_0(\mathbf{r}) [V_{ext,1}(\mathbf{r}) - V_{ext,2}(\mathbf{r})] dr \qquad (3.6)$$

where E_1^0 and E_2^0 are the ground-state energies corresponding to $\hat{H}_1$ and $\hat{H}_2$ respectively. It is at this point that the Hohenberg-Kohn theorems, and therefore DFT, apply rigorously to the ground-state only. An expression equivalent to 3.6 holds when the subscripts are interchanged:

$$E_2^0 < \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle + \langle \Psi_1 | \hat{H}_2 - \hat{H}_1 | \Psi_1 \rangle =$$
$$= E_1^0 + \int \rho_0(\mathbf{r})[V_{ext,2}(\mathbf{r}) - V_{ext,1}(\mathbf{r})]dr \qquad (3.7)$$

Therefore adding eq. 3.6 and 3.7 leads to the result:

$$E_1^0 + E_2^0 < E_2^0 + E_1^0 \qquad (3.8)$$

which is a contradiction, and as a result the ground-state density uniquely determines the external potential $V_{ext}(\mathbf{r})$, to within an additive constant.

The main consequence of this theorem is that the external potential is a functional of the electron density, implying that also the ground-state energy must be a functional of the same quantity:

$$V_{ext} = V_{ext}[\rho(\mathbf{r})] \quad \Rightarrow \quad E_0 = E_0[\rho(\mathbf{r})] \qquad (3.9)$$

Moreover, since $\rho(\mathbf{r})$ determines all properties of the ground-state system, all components of the energy must be functionals of the electron density. The ground-state energy is usually divided into different contributions as follows:

$$E_0[\rho] = T[\rho] + V_{ee}[\rho] + V_{ext}[\rho] = F_{HK}[\rho] + \int \rho(\mathbf{r})V_{ext}dr \qquad (3.10)$$

where $F_{HK}[\rho]$ includes the kinetic energy term $T[\rho]$ and electron-electron energy $V_{ee}[\rho]$. The latter is usually further split in two contributions:

$$V_{ee} = J[\rho] + nonclassical\ term \qquad (3.11)$$

$J[\rho]$ is the classical repulsion between two charge distributions, whereas the nonclassical term are usually referred as "exchange-correlation energy" and it will be defined later.

The second Hohemberg-Kohn theorem states that the ground-state energy can be obtained variationally: *for a trial density $\bar{\rho}(\mathbf{r})$ such that $\bar{\rho}(\mathbf{r}) \geqslant 0$ and integrating to N electrons, the condition $E_0[\rho(\mathbf{r})] \leqslant \bar{E}_0[\bar{\rho}(\mathbf{r})]$ holds, where $E_0[\rho(\mathbf{r})]$ and $\bar{E}_0[\bar{\rho}(\mathbf{r})]$ are the ground-state energies arising from the exact and the trial density, respectively.*

This is the analogous to the variational principle for wavefunctions. The proof of this theorem is also straightforward: as just shown, $\bar{\rho}(\mathbf{r})$ determines its own $\bar{V}_{ext}(\mathbf{r})$, and in turn $\hat{H}_{trial}$ and wavefunction $\bar{\Psi}$, which can be taken as a trial function for the problem of interest having external potential V_{ext}. Thus

$$\langle\bar{\Psi}|\hat{H}|\bar{\Psi}\rangle = \int \bar{\rho}(\mathbf{r})V_{ext}(\mathbf{r})dr + F_{HK}[\bar{\rho}(\mathbf{r})] = E_0[\bar{\rho}(\mathbf{r})] \geqslant \langle\Psi|\hat{H}|\Psi\rangle = E_0[\rho(\mathbf{r})] \quad (3.12)$$

Assuming differentiability of $E_0[\rho]$ the second Hohemberg-Kohn theorem requires that the ground state density satisfy the stationary principle:

$$\delta\left\{E[\rho] - \mu\left(\int \rho(\mathbf{r})dr - N\right)\right\} = 0 \quad (3.13)$$

where the Lagrange multiplier μ (which is the chemical potential) is introduced to ensure the conservation of the number of electrons. Solving, we obtain the Euler-Lagrange equation:

$$\mu = \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} = V_{ext}(\mathbf{r}) + \frac{\delta F_{HK}[\rho]}{\delta\rho(\mathbf{r})} \quad (3.14)$$

Notice that if we knew the exact $F_{HK}[\rho]$, the above equation would be an exact equation for the ground-state density. Moreover that F_{HK} is defined independently of the external potential, meaning that F_{HK} is a universal function of $\rho(\mathbf{r})$. Once we have an explicit form (approximate or accurate) for F_{HK} we can apply this method to any system. However, although the Hohemberg-Kohn theorems are extremely powerful, they do not offer a practical way of computing the ground-state density of a system.

Moreover, the Hohenberg-Kohn theorems, as defined above, require a one-to-one correspondence between ground-state wave function and the electronic density. It is through this unique mapping that a density determine the ground-state properties. A density which satisfy this condition is called *v*-representable, that is, it would be the density of an antisymmetric wavefunction for a given external potential. This condition is far to be achieved, since often many wavefunctions give rise to the same electron density. Fortunately it has been shown by Levi that a condition weaker than *v*-representability is sufficient: the *N*-representability. This condition is satisfied by every reasonable density, that is by every density derived from an antisymmetric wavefunction. This can be easily demonstrated by means of the Levi constrained search, schematized in fig. 3.2. From the variational principle we have:

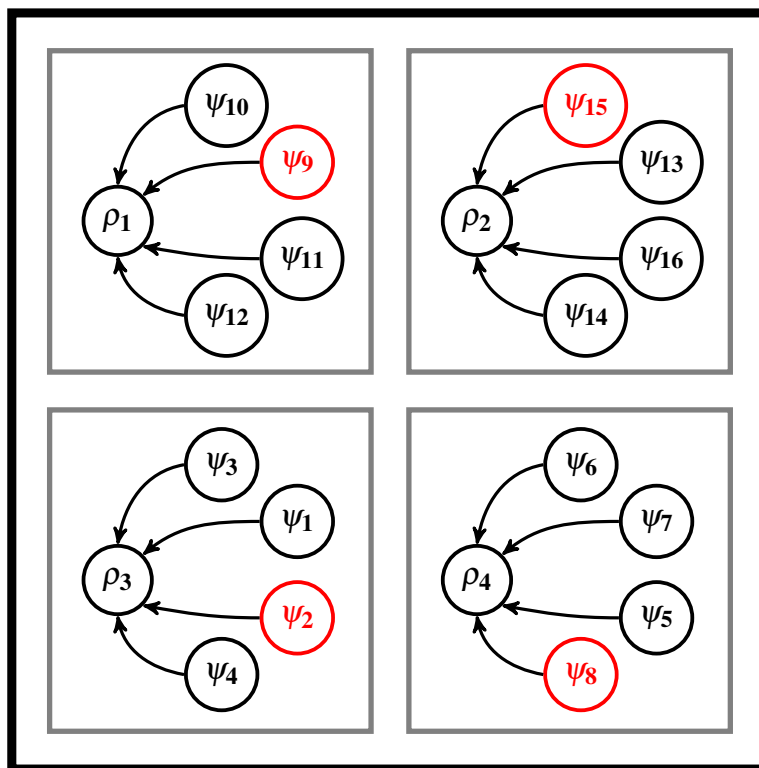$$E_0[\Psi] \leq \langle\Psi|\hat{H}|\Psi\rangle \quad (3.15)$$

FIGURE 3.2: Let be the black square the set of $\rho(\mathbf{r})$ integrating to N electrons. Each gray square is the set of all wavefunction integrating to a particular $\rho(\mathbf{r})$. The first step of the Levi method is the minimization of the ψ associated to each ρ, let's say we obtain ψ_9 for ρ_1, ψ_{15} for ρ_2... The second step of minimization will be over the such obtained subset $\{\psi_9, \psi_{15}, \psi_2, \psi_8\}$.

The procedure of minimization of energy can be divided in two steps. First we consider the wavefunctions giving by quadrature the same electron density $\rho(\mathbf{r})$ and constrain the search for the minimum energy in this subset only:

$$
\begin{aligned}
E_\rho[\rho] &= min_{\Psi \to \rho} \langle \Psi | \hat{H} | \Psi \rangle = min_{\Psi \to \rho} \langle \Psi | T + V_{ee} + V_{ext} | \Psi \rangle = \\
&= min_{\Psi \to \rho} \langle \Psi | T + V_{ee} | \Psi \rangle + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})dr = \\
&= F_{HK}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})dr
\end{aligned}
\tag{3.16}
$$

Once obtained the variational functional energy for a given density, in order to complete the search we minimize such functional with respect to the densities that integrate to N electrons:

$$
\begin{aligned}
E_0[\rho] &= min_{\rho \to N} E_\rho[\rho] = min_{\rho \to N} \left\{ F_{HK}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})dr \right\} = \\
&= min_{\rho \to N} \left\{ min_{\Psi \to \rho} \langle \Psi | \hat{H} | \Psi \rangle \right\} = min_\Psi \langle \Psi | \hat{H} | \Psi \rangle
\end{aligned}
\tag{3.17}
$$

In this form it is equivalent to the second theorem of Hohemberg-Kohn.

3.1.2   Kohn-Sham method

In the previous section we have seen that the ground-state energy of an atomic or molecular system can be written as

$$E_0[\rho] = T[\rho] + V_{ext}[\rho] + J[\rho] + V_{xc}[\rho] = F_{HK}[\rho] + V_{ext}[\rho] \tag{3.18}$$

where the functional $F_{HK}[\rho]$ contains the contributions of the kinetic energy $T[\rho]$, the classical Coulomb interaction $J[\rho]$ (called Hartree potential) and the non-classical part $V_{xc}[\rho]$ including all the other terms, specifically exchange and electron correlation effects. Of these, only $V_{ext}[\rho]$ and $J[\rho]$ are known:

$$V_{ext}[\rho] = \int V_{ext}[\rho]\rho(\mathbf{r})dr \tag{3.19}$$

$$J[\rho] = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\mathbf{r}_{12}} \tag{3.20}$$

while the explicit forms of the other two contributions remain a mystery. To understand how Kohn and Sham tackled this problem, we have to recall the Hartree-Fock scheme, in which the wave function was a single Slater determinant Φ_{HF} constructed from N spin orbitals χ_i. While the Slater determinant enters the HF method as the approximation to the true N-electron wave function, it can also be looked upon as the exact wave function of a fictitious system of N non-interacting electrons, moving in an effective potential due to the nuclei. For such system the kinetic energy can be exactly expressed as:

$$T_{KS} = -\frac{1}{2}\sum_i^N \langle \chi_i | \nabla^2 | \chi_i \rangle \tag{3.21}$$

The Hartree-Fock spin orbitals χ_i that appear in this expression are chosen such that the expectation value E_{HF} attains its minimum (under the usual constraint that the χ_i remain orthonormal).

$$E_0[\chi] = min_{\Phi_{HF}\to N} \langle \Phi_{HF} | T + V_{ee} + V_{ext} | \Phi_{HF} \rangle \tag{3.22}$$

The important connection to DFT is that we can use the above kinetic energy expression to compute the major fraction of the kinetic energy of our interacting system. We further ask if it is possible to built, also for DFT, a non-interacting reference system, introducing

an effective, local potential $V_{eff}(\mathbf{r})$ in the Hamiltonian:

$$H_{eff} = -\frac{1}{2}\sum_i^N \nabla_i^2 + \sum_i^N V_{eff}(\mathbf{r}_i) \qquad (3.23)$$

Accordingly, its ground-state wavefunction would be represented by a Slater determinant where the spin orbitals, in complete analogy to Hartree-Fock equations are determined by:

$$f_{KS}(i)\chi_i^{KS} = \varepsilon_i \chi_i^{KS} \qquad (3.24)$$

$$f_{KS}(i) = -\frac{1}{2}\nabla_i^2 + V_{eff}(\mathbf{r}_i) \qquad (3.25)$$

where the subscript KS indicates that those are the Kohn-Sham orbitals.

The connection of this artificial system to the interacting one is now established by choosing the effective potential V_{eff} such that the density of the non-interacting system $\rho(\mathbf{r}) = \sum_i |\chi_i(\mathbf{r})|^2$ exactly equals the ground state density of the real system.

At this point, we come back to the original problem: finding a better way for the determination of the kinetic energy. The very clever idea of Kohn and Sham was to realize that if we are not able to accurately determine the kinetic energy through an explicit functional we should be a bit less ambitious and concentrate on computing as much as we can of the exact kinetic energy, treating the other fraction in an approximate way. Hence, they suggested to calculate the exact kinetic energy of the non-interacting reference system T_{KS} with the same density as the interacting one using eq. 3.21 and including the remainder ($\Delta T[\rho]$) in the exchange-correlation functional:

$$T[\rho] = T_{KS}[\rho] + \Delta T[\rho] \qquad (3.26)$$

$$F_{KS}[\rho] = T_{KS}[\rho] + J[\rho] + E_{XC}[\rho] \qquad (3.27)$$

As a consequence of the first Hohemberg-Kohn theorem, T_{KS} is also necessarily a functional of the density but notice that we do not have a simple expression for T_{KS} where the density enters explicitly. So far so good, but before we are in business with this concept we need to find a prescription to uniquely determine the orbitals of the non-interacting reference system. In other words, we ask: how can we define V_{eff} such that it really provides us a Slater determinant which is characterized by exactly the same density as our real system? To solve this problem, we write down the expression for the energy of

our interacting, real system in terms of the separation described by equation 3.27:

$$E[\rho] = T_{KS}[\rho] + J[\rho] + E_{XC}[\rho] + V_{ext}[\rho]$$

$$= T_{KS}[\rho] + \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\mathbf{r}_{12}} + E_{XC}[\rho] + \int V_{ext}\rho(\mathbf{r})dr \qquad (3.28)$$

$$= -\frac{1}{2} \sum_{i}^{N} \langle \chi_i | \nabla^2 | \chi_i \rangle + \frac{1}{2} \sum_{i} \sum_{j} \int \int d\mathbf{r}_1 d\mathbf{r}_2 |\chi_i(\mathbf{r}_1)|^2 \frac{1}{\mathbf{r}_{12}} |\chi_j(\mathbf{r}_2)|^2 +$$

$$+ E_{XC}[\rho] - \sum_{i} \sum_{A} \int d\mathbf{r}_1 \frac{Z_A}{\mathbf{r}_{1A}} |\chi_i(\mathbf{r}_1)|^2 \qquad (3.29)$$

The only term for which no explicit form can be given is of course $E_{XC}[\rho]$. Applying the variational principle to eq. 3.28 in order to minimize the energy expression under the usual constraint of orthonormality we obtain the so-called Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + \left(\int \frac{\rho(\mathbf{r}_2)}{\mathbf{r}_{12}}d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) + V_{ext}(\mathbf{r}_1) \right) \right] \chi_i =$$

$$= \left[-\frac{1}{2}\nabla^2 + \left(\int \frac{|\chi_i(\mathbf{r}_2)|^2}{\mathbf{r}_{12}}d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) - \sum_{A} \frac{Z_A}{\mathbf{r}_{1A}} \right) \right] \chi_i =$$

$$= \left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}_1) \right] \chi_i = \varepsilon_i \chi_i \qquad (3.30)$$

If we compare this with the one-particle equation for the non-interacting reference system 3.25, we see immediately that V_{eff} reads as:

$$V_{eff}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}_2)}{\mathbf{r}_{12}}d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) + V_{ext}(\mathbf{r}_1) \qquad (3.31)$$

Thus, once we know the various contributions in the equation above we have a grip on the potential V_{eff} which we need to insert into the one-particle equations, which in turn determine the orbitals and hence the ground state density and energy. It should be noticed that $V_{eff}(\mathbf{r})$ already depends on the density (and thus on the orbitals) through the Coulomb term. Therefore, just like the Hartree-Fock equations, the Kohn-Sham equations also have to be solved iteratively. One term in the above equation needs some additional comments, V_{XC}, that is the potential due to the exchange-correlation energy E_{XC} (but also containing the kinetic energy correction) and is formally defined as its functional derivative:

$$V_{XC} = \frac{\delta E_{XC}[\rho]}{\delta \rho} \qquad (3.32)$$

Since we do not know how this energy should be expressed, we of course also have no clue on the explicit form of V_{XC}. Notice that, if we would knew V_{XC}, the Kohn-Sham

strategy would not contain any approximation, thus it would lead to the exact energy, i. e. the correct eigenvalue of the Hamilton operator of the Schroedinger equation. Then, unlike the Hartree-Fock model, where the approximation is introduced right at the beginning (the wave function is assumed to be a single Slater determinant), the Kohn-Sham approach is in principle exact. The approximation only enters when we have to introduce an explicit form of the unknown functional accounting for the exchange-correlation energy E_{XC} and the corresponding potential V_{XC}. The central goal of modern density functional theory is therefore to find better and better approximations to this quantity.

Here we briefly cite only the most common used exchange-correlation functionals:

- Local density approximation (LDA): is a class of local functionals, *i.e.* depending only on the value of the electronic density at each point in space. In general, for a spin-unpolarized system, a local-density approximation for the exchange-correlation energy[86,87] is written as

$$E_{xc}^{LDA}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho)dr \qquad (3.33)$$

where $\varepsilon_{XC} = \varepsilon_X + \varepsilon_C$ is the exchange-correlation energy per particle of an uniform electron gas, weighted with the probability $\rho(\mathbf{r})$ of finding the electron in this position of space. The exchange energy term ε_X is analytic, while the correlation term ε_C is a fit of the quantum montecarlo results of Ceperley and Alder[88].

- Generalized gradient approximation (GGA): is a class of local functional taking also into account the gradient of the electron density at the same point of space. This leads to an exchange-correlation functional approximation of the form:

$$E_{xc}^{GGA} = \int E_{xc}^{LDA}[\rho]F_{xc}(\rho,s)dr \qquad (3.34)$$

where s is the so-called reduced density gradient:

$$s = \frac{|\nabla\rho|}{\rho^{4/3}} \qquad (3.35)$$

and $F_{xc}(\rho,s)$ is a dumping function that accounts for the properly physical behavior of E_{xc}^{GGA} in the limit $r \to \infty$. For instance, in the Perdew, Burke and Ernzerhof (PBE) functional[89,90] the exchange component of such function takes the form:

$$E_x^{PBE} = \int E_x^{LDA}[\rho]F_x(\rho,s) = \int E_x^{LDA}[\rho]\left[1 + \frac{as^2}{1+bs^2}\right] \qquad (3.36)$$

where a and b are constants fitted by experimental data. The correlation term has a more complicated form, but also includes a dumping function to correctly describe the behavior of the correlation energy.

- Hybrid functionals: is a class of functionals in which a component of the Hartree-Fock exchange E_x^{HF} is included. For example, the popular B3LYP (Becke three-parameters[91] Lee-Yang-Parr) exchange-correlation functional is defined as:

$$E_{xc}^{B3LYP} = E_x^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + a_c(E_c^{GGA} - E_c^{LDA})$$

(3.37)

where a_0, a_x and a_c are three parameters, E_x^{GGA} and E_c^{GGA} are the exchange and correlation terms of a generalized gradient approximation, specifically the Becke 88 and the Lee, Yang and Parr (LYP)[92,93], respectively, while E_c^{LDA} is the local-density approximation to the correlation functional.

A long-range correction[94] can be applied to those functionals since the non-Coulomb part of exchange functionals typically decays too rapidly and usually becomes very inaccurate at long distances. This correction turns out to be particularly relevant in modeling processes such as electron excitations to high orbitals, considerably improving the description of charge transfer excitation energies and oscillator strengths in time-dependent Kohn-Sham calculations.

3.2 Single Level Model

Next, we move to the transport problem, starting from a simple model[80].
Consider a molecule (the channel) coupled with two electron reservoirs, which serve as a source and drain electrodes, as shown in fig. 3.3. For simplicity we assume metallic-like reservoirs characterized by chemical potentials μ_l and μ_r.
Of course, it is worth highlighting that the net separation of a nanodevice into ideal injecting and extracting contacts, and a channel region which limits the charge transport, has important limitations, since the contacts themselves are really part of the channel system, and are driven out of equilibrium due to current flow, as well as they strongly couple to the channels through the long range Coulomb interaction of charge carriers.
At the equilibrium the chemical potential must be the same throughout the system: $\mu_f = \mu_l = \mu_r$, as shown in fig. 3.3-left. The application of an external (positive) bias lowers the energy levels in the drain contact with respect to the source, driving the

channels into a non-equilibrium energy state (fig. 3.3-right). This gives rise to different Fermi functions for the two electrodes:

$$f_l(E) = \frac{1}{1 + e^{\frac{(E - \mu_l)}{K_B T}}} = f_0(E - \mu_l) \tag{3.38}$$

$$f_r(E) = \frac{1}{1 + e^{\frac{(E - \mu_r)}{K_B T}}} = f_0(E - \mu_r) \tag{3.39}$$

The difference $\Delta\mu$ between the electrochemical potentials μ_l and μ_r is proportional to the applied bias V_{SD}:

$$\Delta\mu = -|e|V_{SD} \tag{3.40}$$

where e is the electron charge. Each contact seeks to bring the channel in equilibrium with itself. The source keeps pumping electrons into it, while the drain keeps pulling electrons out in its bid, but equilibrium is never established since the bias ensures that $\Delta\mu$ being fixed. This generates an electrical current flowing from the source to the drain. The current thus depends on the electrochemical potential difference but also on the transmission properties of the channel region itself. Although it is straightforward that the conduction depends on the availability of molecular level with energy in between of μ_l and μ_r, it is less obvious that there is an upper limit to conductance value G_0 for each level:

$$G_0 = \frac{|e|^2}{h} = 38.7 \, \mu S \tag{3.41}$$

where h is the Plank constant. Actually, typical molecular channels have two degenerate levels (one for spin up and one for spin down), giving rise to a maximum conductance of $2G_0$.

Consider, for instance, the simple case in which a molecule with only one level at energy ε is coupled with a source and a drain contacts at different electrochemical potentials, as shown in fig. 3.3-right. Of course the source pumps electrons into the level, while the drain extracts electrons from it, both attempting to reach an equilibrium state. When this is achieved, the average occupation N of the level will be something intermediate between $f_l(\varepsilon)$ and $f_r(\varepsilon)$. Thus, a net flux of electrons I_l across the left junction, proportional to $f_l - N$ (the energy argument is dropped for clarity), is achieved:

$$I_l = -\frac{|e|\gamma_l}{\hbar}(f_l - N) \tag{3.42}$$

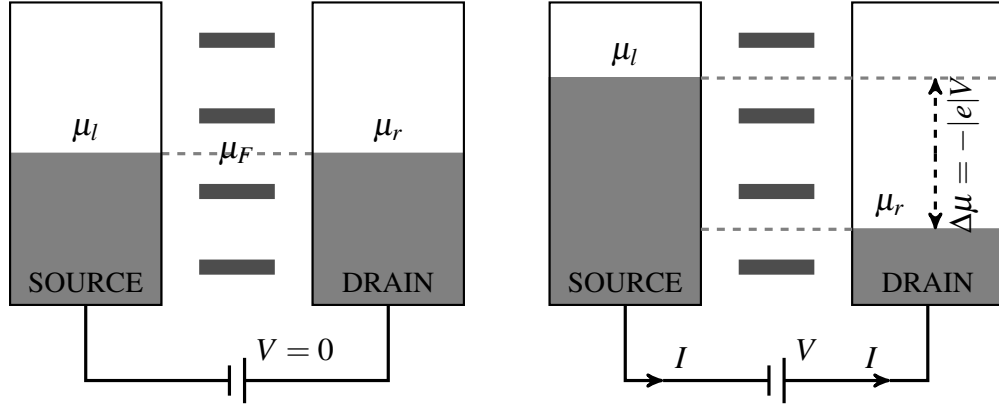With the same token, the net flux across the right junction reads as:

FIGURE 3.3: Energy level diagram of a two terminal device in equilibrium (left) and under forward bias (V>0) (right)
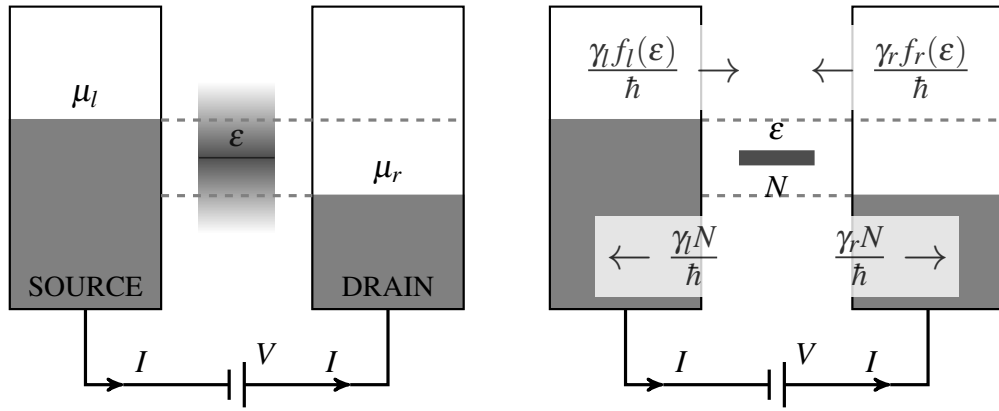

FIGURE 3.4: Energy level diagram taking into account level broadening (left) and flux of electrons into and out a one level channel (right)

$$I_r = -\frac{|e|\gamma_r}{\hbar}(f_r - N) \tag{3.43}$$

where $\gamma_l/\hbar$ and $\gamma_r/\hbar$ assume the meaning of rate constants, *i. e.* the rates at which one electron placed on level ε can escape into the source or drain, respectively (see fig. 3.4-right).

At steady state the net electron flux into or out of the channel must be zero, then

$$I_l + I_r = 0 \tag{3.44}$$

from which follows that the occupation N of the level is the weighted average of f_l and f_r:

$$N = \frac{\gamma_l f_l + \gamma_r f_r}{\gamma_l + \gamma_r} \tag{3.45}$$

Substituting this result into eq. 3.42 or 3.43, we get an expression for the steady-state current I (per spin):

$$I = I_l = -I_r = -\frac{e}{\hbar}\frac{\gamma_l\gamma_r}{\gamma l + \gamma_r}[f_l(\varepsilon) - f_r(\varepsilon)] \qquad (3.46)$$

It is evident from eq. 3.46 that no current flows if $f_l(\varepsilon) = f_r(\varepsilon)$. Thus, a level locate above ($f_l(\varepsilon) = f_r(\varepsilon) = 1$) or below ($f_l(\varepsilon) = f_r(\varepsilon) = 0$) both electrochemical potentials will not contribute to the current. Thus we arrive at the fundamental results that only levels in between of μ_l and μ_r take part in the conduction process.

Depending on whether the level ε is empty or filled (at steady state) we can distinguish two type of current:

- n-type: empty state at ε, electrons are first injected by the negative contact and subsequently collected by the positive contact.

- p-type: filled state at ε, electrons are first collected by the positive contact and then refilled by the negative contacts.

Let's assume that $\mu_l < \varepsilon < \mu_r$. If the temperature is low enough that $f_l(\varepsilon) \approx 1$ and $f_r(\varepsilon) \approx 0$ we can simplify the above expression for the current:

$$I = -\frac{e}{\hbar}\frac{\gamma_l\gamma_r}{\gamma_l + \gamma_r} \qquad (3.47)$$

Furthermore, for a symmetric device we have:

$$\gamma_l = \gamma_r = \gamma \qquad (3.48)$$

and eq. 3.47 reduces to:

$$I = -\frac{e\gamma}{\hbar} \qquad (3.49)$$

This would suggest that we can pump unlimited current through this one level device by increasing the coupling with the electrodes (γ). But this is in contrast with one of the main results stated above, that is the upper limit of conductance G_0 associated with a one-level device. What we have ignored is that the coupling causes the broadening of the level, the more the higher the coupling (see fig. 3.4-left). If the coupling is strong enough, part of the level is spread outside μ_l and μ_r, then the current is reduced by a factor:

$$\frac{\mu_l - \mu_r}{C\gamma} \qquad (3.50)$$

where C is a constant introduced in order to take into account the fraction of the level between μ_l and μ_r and $C\gamma$ represents the width of the level. Since $\mu_l - \mu_r = -|e|V_{SD}$, it follows that:

$$I = \frac{|e|^2 \gamma V_{SD}}{2\hbar C\gamma} \qquad (3.51)$$

$$G = \frac{I}{V_{SD}} = \frac{|e|^2}{2C\hbar} \qquad (3.52)$$

Then we arrive to the reasonable result that G approaches a constant value independent of the strength of the coupling to the contacts.

To make the result more general, one should introduce the density of states $D_\varepsilon(E)$ generated by the broadening of the level ε, then eq. 3.45 and 3.46 become:

$$N = \int_{-\infty}^{+\infty} dE\, D_\varepsilon(E) \frac{\gamma_l f_l(E) + \gamma_r f_r(E)}{\gamma_l + \gamma_r} \qquad (3.53)$$

$$I = -\frac{e}{\hbar} \int_{-\infty}^{+\infty} dE\, D_\varepsilon(E) \frac{\gamma_l \gamma_r}{\gamma_l + \gamma_r} [f_l(E) - f_r(E)] \qquad (3.54)$$

To further generalize the problem we introduce a gate potential $U = -|e|V_G$, where V_G is the gate bias, which is assumed to only raise in energy the level of the molecule and not to affect the density of states (*i.e.* the gate is capacitively coupled to the molecule). Thus the expression for N reads as:

$$N = \int_{-\infty}^{+\infty} dE\, D_\varepsilon(E - U) \frac{\gamma_l f_l(E) + \gamma_r f_r(E)}{\gamma_l + \gamma 2} = \int_{-\infty}^{+\infty} dE\, n(E) \qquad (3.55)$$

where

$$n(E) = D_\varepsilon(E - U) \frac{\gamma_l f_l(E) + \gamma_r f_r(E)}{\gamma_l + \gamma 2} \qquad (3.56)$$

assumes the meaning of the electron density per unit energy, while for I we get:

$$I = -\frac{|e|}{\hbar} \int_{-\infty}^{+\infty} dE\, D_\varepsilon(E - U) \frac{\gamma_l \gamma_r}{\gamma_l + \gamma 2} [f_l(E) - f_r(E)]$$

$$= -\frac{e}{h} \int_{-\infty}^{+\infty} dE\, T(E)[f_l(E) - f_r(E)] \qquad (3.57)$$

where we have introduced the transmission function $T(E)$:

$$T(E) = 2\pi D_\varepsilon (E - U) \frac{\gamma_l \gamma_r}{\gamma_l + \gamma_r} \tag{3.58}$$

This is a key quantity in the transport theory, describing the probability that an electron with energy E passes from one contact to the other through the level.

3.3 Dyson's equation for the single level model

Let's consider again the case of a single energy level coupled to two infinite electrodes. Such system is described by the Hamiltonian:

$$\hat{H} = \hat{H}_l + \hat{H}_r + \sum_\sigma \varepsilon_0 c_{0\sigma}^\dagger c_{0\sigma} +$$
$$+ \sum_\sigma t_l \left(c_{0\sigma}^\dagger c_{l\sigma} + c_{l\sigma}^\dagger c_{0\sigma} \right) + \sum_\sigma t_r \left(c_{0\sigma}^\dagger c_{r\sigma} + c_{r\sigma}^\dagger c_{0\sigma} \right) \tag{3.59}$$

where H_l and H_r describe the left and right leads, ε_0 is the energy of the level and the hopping elements t_l and t_r, assumed to be real, describes the coupling between the level and the electrode. c and $c^\dagger$ are the usual creation and annihilation operators for electrons. The subindex 0 refers to the level, while l and r refer to the outermost sites of the left and right electrode.

Specifically we want to understand how the level is modified by the coupling to the electrodes. For this reason it will not be necessary for the present discussion to specify anything about the shape or the electronic structure of the leads. To this aim we need to compute the local density of states projected onto the level. This requires the calculation of the Green's function matrix element $G_{00}(E)$ (no matter whether it is retarded or advanced) by means of the Dyson's equation*. Our choice for the unperturbed Hamiltonian H_0 is the sum of the Hamiltonians of the three uncoupled subsystems:

$$\hat{H}_0 = \hat{H}_l + \hat{H}_r + \sum_\sigma \varepsilon_0 c_{0\sigma}^\dagger c_{0\sigma} \tag{3.60}$$

Thus the perturbation V includes the terms describing the coupling between the localized level and the electrodes:

$$V = \sum_\sigma t_l \left(c_{0\sigma}^\dagger c_{l\sigma} + c_{l\sigma}^\dagger c_{0\sigma} \right) + \sum_\sigma t_r \left(c_{0\sigma}^\dagger c_{r\sigma} + c_{r\sigma}^\dagger c_{0\sigma} \right) \tag{3.61}$$

---

*The definition and the properties of Green's functions are reported in appendix A

Indicating with G the full Green's function and with g that of the unperturbed systems, the Dyson's equation in matrix form reads as:

$$
\begin{pmatrix} G_{ll} & G_{l0} & G_{lr} \\ G_{0l} & G_{00} & G_{0r} \\ G_{rl} & G_{r0} & G_{rr} \end{pmatrix} = \begin{pmatrix} g_{ll} & 0 & 0 \\ 0 & g_{00} & 0 \\ 0 & 0 & g_{rr} \end{pmatrix} +
$$
$$
+ \begin{pmatrix} g_{ll} & 0 & 0 \\ 0 & g_{00} & 0 \\ 0 & 0 & g_{rr} \end{pmatrix} \begin{pmatrix} 0 & V_{l0} & V_{lr} \\ V_{0l} & 0 & V_{0r} \\ V_{rl} & V_{r0} & 0 \end{pmatrix} \begin{pmatrix} G_{ll} & G_{l0} & G_{lr} \\ G_{0l} & G_{00} & G_{0r} \\ G_{rl} & G_{r0} & G_{rr} \end{pmatrix} \quad (3.62)
$$

Neglecting the interactions between the leads we have $V_{lr} = V_{rl} = 0$.
Specifically we are interest in the G_{00} element:

$$
G_{00}(E) = g_{00}(E) + g_{00}(E)V_{0l}G_{l0}(E) + g_{00}(E)V_{0r}G_{r0}(E) \quad (3.63)
$$

where $V_{0l} = t_l$, $V_{0r} = t_r$ and $g_{00}(E) = (E - \varepsilon_0)^{-1}$. To close this equation we need to determine the functions $G_{l0}(E)$ and $G_{r0}(E)$. This can be done by taking the corresponding elements in Dyson's equation:

$$
G_{l0}(E) = g_{ll}(E)V_{l0}G_{00}(E) \quad (3.64)
$$

$$
G_{r0}(E) = g_{rr}(E)V_{r0}G_{00}(E) \quad (3.65)
$$

where $V_{l0} = t_l$, $V_{r0} = t_r$ and $g_{ll}(E)$ and $g_{rr}(E)$ are the Green's functions of the two outermost sites of the left and right electrodes, respectively. Substituting into eq. 3.63 we obtain:

$$
G_{00}(E) = g_{00}(E) + g_{00}(E)V_{0l}g_{ll}(E)V_{l0}G_{00}(E) + g_{00}(E)V_{0r}g_{rr}(E)V_{r0}G_{00}(E) \quad (3.66)
$$

In this equation it is easy to identify the self-energy Σ_{00}:

$$
G_{00}(E) = g_{00}(E) + g_{00}(E)\left[V_{0l}g_{ll}(E)V_{l0} + V_{0r}g_{rr}(E)V_{r0}\right]G_{00}(E) \quad (3.67)
$$
$$
= g_{00}(E) + g_{00}(E)\left[g_{ll}(E)t_l^2 + g_{rr}(E)t_r^2\right]G_{00}(E) \quad (3.68)
$$
$$
= g_{00}(E) + g_{00}(E)\Sigma_{00}(E)G_{00}(E) \quad (3.69)
$$

In terms of the self-energy we can express $G_{00}(E)$ as:

$$
G_{00}(E) = \frac{1}{E - \varepsilon_0 - \Sigma_{00}(E)} \quad (3.70)
$$

where we have used the expression of $g_{00}(E)$. Here it appears evident that the self-energy describes how the resonant level is modified by the interaction with the leads. In particular its real part accounts for the renormalization of the level position, which becomes

$$\varepsilon_0 \ \rightarrow \ \bar{\varepsilon}_0 = \varepsilon_0 + Re\Sigma_{00}(E) \tag{3.71}$$

while its imaginary part describes the broadening in energy of the level due to the coupling with the electrodes. This latter point becomes more clear by using the following approximation. Let us assume that the Green's function of the (uncoupled) leads are imaginary for energy close to ε_0 and that they do not depend significantly on energy in this region. Hence g_{ll} and g_{rr} are related to the local density of states $\rho_{l,r}$ of the leads at the energy ε_0:

$$g_{ll}^{R,A} \approx \mp i\pi\rho_l(E = \varepsilon_0) \qquad g_{rr}^{R,A} \approx \mp i\pi\rho_r(E = \varepsilon_0) \tag{3.72}$$

Introducing the scattering rates $\Gamma_{l,r}$, *i.e.* the rates at which one electron on level ε can escape into the left or right electrodes:

$$\Gamma_l = t_l^2 \pi\rho_l(E = \varepsilon_0) \qquad \Gamma_r = t_r^2 \pi\rho_r(E = \varepsilon_0) \tag{3.73}$$

the self-energy becomes:

$$\Sigma_{00}^{r,a} = \mp i(\Gamma_l + \Gamma_r) \tag{3.74}$$

Finally, substituting the self-energy in eq. 3.70 the function $G_{00}(E)$ reads as:

$$G_{00}^{\pm}(E) = \frac{1}{E - \varepsilon_0 \pm i(\Gamma_l + \Gamma_r)} \tag{3.75}$$

The local density of states is related to the imaginary part of the Green's function, thus we arrive at the result:

$$\rho_0(E) = \mp\frac{1}{\pi}ImG_{00}^{\pm}(E) = \frac{1}{\pi}\frac{\Gamma_l + \Gamma_r}{(E - \varepsilon_0)^2 + (\Gamma_l + \Gamma_r)^2} \tag{3.76}$$

which is a lorentzian function where $\Gamma = \Gamma_l + \Gamma_r$ is the half-width at half-maximum. This result shows clearly that the resonant level, which originally had zero width, being an eigenstate of the isolated central region, acquires a finite width Γ as a consequence of the coupling to the leads. Of course this width depends both on the strength of the coupling, via the $t_{l,r}$ elements, and on the local electronic structure of the leads, through g_{ll} and g_{rr}. Furthermore, the inverse of the level width $\hbar/\Gamma$ assumes the meaning of the time spent by an electron in the resonant level. In other words, the stronger the coupling the quicker the electrons flow from the electrode into the level and viceversa.

3.4 Non-equilibrium Green's function method

In this section we will present a comprehensive description of the non-equilibrium Green function (NEGF) formalism applied to transport[†]. In particular our aim is to derive an equation for the current flowing between the leads when a bias voltage is applied. To this aim the Green functions can be used to calculate the steady-state charge density and a self-consistent procedure can be put in place provided the system's Hamiltonian is a functional of the charge density (or the density matrix). In order to simplify the problem we will further show that we can focus on an "extended molecule" region and add the effects of the electrodes in terms of self-energies which are only statically (non-self-consistently) affected by the external potential. The procedure presented here is very general. In principle, one could use any Hamiltonian to calculate the Green function. Specifically throughout this thesis the Hamiltonian will be computed at density functional theory (DFT) level, as implemented in the Siesta[95]/Transiesta[96] package.

3.4.1 Green's operator for the (coupled) scattering region

Let us consider a contact with an arbitrary geometry, that can be either an atomic contact or a molecular junction. The system can be divided intro three parts: the electron reservoirs L and R (the *electrodes*) and a central region C (the *scattering region*) that can have arbitrary shape and size (see fig. 4.1). In principle also the reservoirs could also have an arbitrary shape and we assume that an electron in these subsystems has a well defined temperature and chemical potential. The separation of the contact into these three subsystems is somewhat arbitrary, but we assume that the central part is large enough to avoid interactions between the reservoirs and to account for the screening effects (transferred charges). L and R are semi-infinite regions, but where electronic motion is non-interesting provided it does not interfere with the motion in C. We thus seek to express the relevant quantities in terms of operators pertaining to region C only. The Hamiltonian for the whole system, in matrix notation, reads as:

$$
\begin{bmatrix}
\hat{H}_{LL} & \hat{H}_{LC} & 0 \\
\hat{H}_{CL} & \hat{H}_{CC} & \hat{H}_{CR} \\
0 & \hat{H}_{RC} & \hat{H}_{RR}
\end{bmatrix}
\tag{3.77}
$$

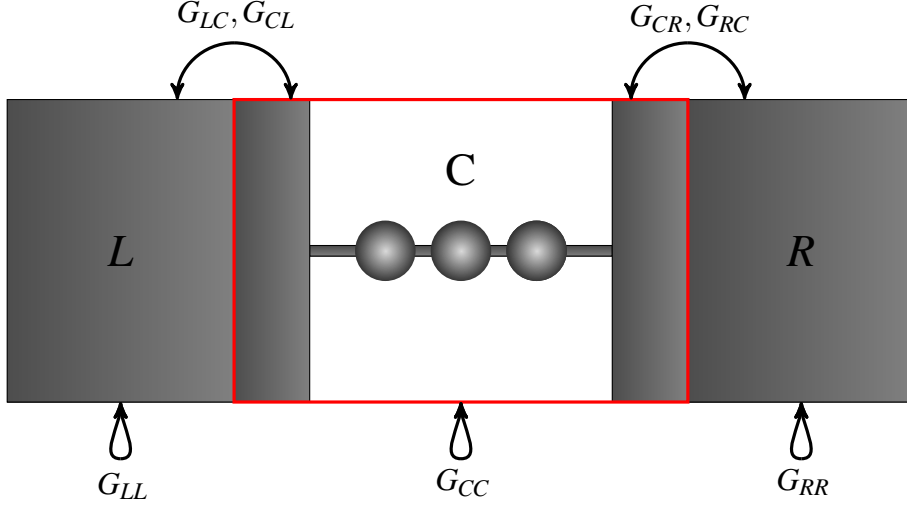[†]The content of this section is largely based on ref. [Martinazzo[82]], for courtesy of Prof. Martinazzo.

FIGURE 3.5: Schematic representation of an atomic scale contact with arbitrary geometry. The left and right electron reservoirs, in principle semi-infinite, are labeled L and R, respectively, the scattering region with C

where the diagonal elements are the Hamiltonians for the three subsystems and the remaining terms account for the coupling between them. In order to calculate the Green's function for the scattering region G_{CC}, we first introduce the projector operators for the three subsystems, which satisfy:

$$R^2 = R = R^\dagger \quad C^2 = C = C^\dagger \quad L^2 = L = L^\dagger$$

$$RL = LC = RC = 0 \quad LHR = RHL = 0 \quad R + L + C = 1 \tag{3.78}$$

The Green's function of the whole system obeys the equation:

$$(\lambda - \hat{H})G(\lambda) = \hat{I} \tag{3.79}$$

in terms of the components of the above spaces. In matrix notation we obtain:

$$\begin{bmatrix} \lambda - \hat{H}_{LL} & -\hat{H}_{LC} & 0 \\ -\hat{H}_{CL} & \lambda - \hat{H}_{CC} & -\hat{H}_{CR} \\ 0 & -\hat{H}_{RC} & \lambda - \hat{H}_{RR} \end{bmatrix} \begin{bmatrix} G_{LL}(\lambda) & G_{LC}(\lambda) & G_{LR}(\lambda) \\ G_{CL}(\lambda) & G_{CC}(\lambda) & G_{CR}(\lambda) \\ G_{RL}(\lambda) & G_{RC}(\lambda) & G_{RR}(\lambda) \end{bmatrix} = \begin{bmatrix} L & 0 & 0 \\ 0 & C & 0 \\ 0 & 0 & R \end{bmatrix} \tag{3.80}$$

Since we are interest only in G_{CC}, we focus on the middle-column equation only:

$$\begin{cases} (\lambda - \hat{H}_{LL})G_{LC}(\lambda) - \hat{H}_{LC}G_{CC}(\lambda) = 0 \\ (\lambda - \hat{H}_{CC})G_{CC}(\lambda) - \hat{H}_{CL}G_{LC}(\lambda) - \hat{H}_{CR}G_{RC}(\lambda) = 0 \\ (\lambda - \hat{H}_{RR})G_{RC}(\lambda) - \hat{H}_{RC}G_{CC}(\lambda) = 0 \end{cases} \tag{3.81}$$

Solving for G_{LC} and G_{RC} the first and third equations we get:

$$G_{LC}(\lambda) = g_L(\lambda)\hat{H}_{CL}G_{CC}(\lambda) \tag{3.82}$$

$$G_{RC}(\lambda) = g_R(\lambda)\hat{H}_{RC}G_{CC}(\lambda) \tag{3.83}$$

where $g_L(\lambda)$ and $g_R(\lambda)$ are the Green's functions for the uncoupled left and right electrodes, given by:

$$g_L(\lambda) = (\lambda - \hat{H}_{LL})^{-1} \tag{3.84}$$

$$g_R(\lambda) = (\lambda - \hat{H}_{RR})^{-1} \tag{3.85}$$

Substituting in eq. 3.81 we arrive at:

$$\left[(\lambda - \hat{H}_{CC}) - \hat{H}_{CL}g_L(\lambda)\hat{H}_{LC} - \hat{H}_{CR}g_R(\lambda)\hat{H}_{RC}\right]G_{CC}(\lambda) = C \tag{3.86}$$

Thus the scattering region projection of the exact Green's function is the Green's function of an effective Hamiltonian in C space:

$$(\lambda - \hat{H}_{eff}(\lambda))G_{CC}(\lambda) = C \tag{3.87}$$

i.e.

$$G_{CC}(\lambda) = \frac{C}{(\lambda - \hat{H}_{eff}(\lambda))} \tag{3.88}$$

where

$$\hat{H}_{eff}(\lambda) = \hat{H}_{CC} + \hat{H}_{CL}g_L(\lambda)\hat{H}_{LC} + \hat{H}_{CR}g_R(\lambda)\hat{H}_{RC} \tag{3.89}$$

In particular, considering $\lambda = \lim_{\eta \to 0^+}(E + i\eta)$ we can write:

$$\hat{H}_{eff}(E) = \hat{H}_{CC} + \Sigma_L^+(E) + \Sigma_R^+(E) \tag{3.90}$$

where

$$\Sigma_L^+(E) = \hat{H}_{CL}g_L^+(E)\hat{H}_{LC} \tag{3.91}$$

$$\Sigma_R^+(E) = \hat{H}_{CR}g_R^+(E)\hat{H}_{RC} \tag{3.92}$$

are the left and right self-energies of the electrodes, expressed in terms of the Green's functions of the semi-infinite leads. They have both a real and an imaginary part which readily follow from the real and imaginary part of g_L^+ and g_R^+:

$$Re\Sigma_L^+(E) = \hat{H}_{CL}g_L^p(E)\hat{H}_{LC} = \Delta_L(E) \tag{3.93}$$

$$Im\Sigma_L^+(E) = \hat{H}_{CL}(-\pi\delta(E - \hat{H}_{LL}))\hat{H}_{LC} = -\frac{\Gamma_L(E)}{2} \tag{3.94}$$

where $g_L^p(E)$ is the principal value of $g_L(E)$. In this way we can rewrite $\hat{H}_{eff}(E)$ as:

$$\hat{H}_{eff}(E) = \hat{H}_{CC} + \Delta(E) - i\frac{\Gamma(E)}{2} \tag{3.95}$$

where we have introduced the self-adjoint operators $\Delta(E)$ and $\Gamma(E)$ defined as:

$$\Delta(E) = \Delta_L(E) + \Delta_R(E) \tag{3.96}$$

$$\Gamma(E) = \Gamma_L(E) + \Gamma_R(E) \tag{3.97}$$

As anticipated in the single-level model section, the self-energy accounts for the modifications of the energy level of the scattering region. Specifically, $\Delta(E)$ describes their shift in energy while $\Gamma(E)$ their broadening as a consequence to the coupling with the electrodes. The problem of determining $G_{CC}^+(E)$ thus reduces to the problem of computing the electrodes self-energies and build up (and invert) the effective Hamiltonian. It is obvious that the self-energies account for the motion in the region L, R in which we are not interested. Note, however, that g_L (g_R) refers to $\hat{H}_{LL}$ ($\hat{H}_{RR}$) i.e. to the dynamics in electrode L (R) when it is not coupled to the scattering region (otherwise we would need of G_{LL} instead of g_L).

3.4.2 Green's operator for the uncoupled electrodes

The left (right) electrode regions are semi-infinite themselves, and no real simplification would occur if we could not compute the Green's operators $g_{L,R}^+(E)$. Fortunately, to compute the self-energy expression (here for the left electrode):

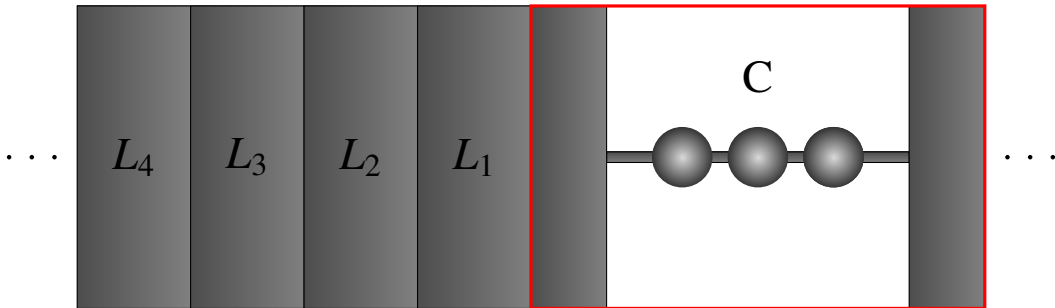$$\Sigma_L^+(e) = \hat{H}_{CL}g_L^+(E)\hat{H}_{LC} \tag{3.98}$$

FIGURE 3.6: Schematic representation of the partitioning of the left electrode

we only need those matrix elements $\langle E_i, L | \hat{H}_{LC} | E'_i, L \rangle$ involving electrode states $|E_i, L\rangle$, $|E'_i, L\rangle$ which are coupled to the scattering region states $|\phi_C\rangle$, i.e. for which $\langle E_i, L | \hat{H}_{LC} | \phi_C \rangle \neq 0$. This is the key observation, which considerably simplifies the problem. As before we could use the partitioning technique to divide the left electrode in infinite subregions, as shown in fig. 3.6. This allows to calculate the Green's function $g_{ii}(E)$ that accounts for the electron dynamics in the L_i region, *i.e.* the L_i projection of the exact Green's function of the uncoupled electrode.

Suppose that $\hat{H}_{LC}$ is of "short" range and consider the region L_1 which couples to C via $\hat{H}_{CL}$. If the subregions L_1, L_2 ... are large enough to interact with the nearest neighbors only we can write down the equation for $g_{11}(\lambda)$ (and for L_1):

$$
\begin{bmatrix}
\lambda - \hat{H}_{11} & -V_{12} & 0 & 0 & 0 \\
-V_{21} & \lambda - \hat{H}_{11} & -V_{23} & 0 & 0 \\
0 & -V_{32} & \lambda - \hat{H}_{11} & \ldots & 0 \\
0 & 0 & \ldots & \ldots & -V_{N-1,N} \\
0 & 0 & 0 & -V_{N,N-1} & \lambda - \hat{H}_{NN}
\end{bmatrix}
\begin{bmatrix}
g_{11}(\lambda) \\
g_{21}(\lambda) \\
g_{31}(\lambda) \\
\vdots \\
g_{N1}(\lambda)
\end{bmatrix}
=
\begin{bmatrix}
L_1 \\
0 \\
0 \\
\vdots \\
0
\end{bmatrix}
$$

$$(3.99)$$

Upon truncating at the N-th order, we solve for the N-th equation:

$$-V_{N,N-1} g_{N-1,1}(\lambda) + (E - \hat{H}_{NN}) g_{N1}(\lambda) = 0 \tag{3.100}$$

from which follows:

$$g_{N1}(\lambda) = (\lambda - \hat{H}_{NN})^{-1} V_{N,N-1} g_{N-1,1}(\lambda) \tag{3.101}$$

and inserting this expression in the $N-1$-th equation:

$$-V_{N-2,1} g_{N-2,1}(E) + \left[E - (\hat{H}_{N-1,N-1} - V_{N-1,N}(E - \hat{H}_{NN})^{-1} V_{N,N-1}) \right] g_{N-1,1} = 0 \tag{3.102}$$

we get the $g_{N-1,1}$ element:

$$g_{N-1,1}(\lambda) = \left[\lambda - (\hat{H}_{N-1,N-1} - V_{N-1,N}(\lambda - \hat{H}_{NN})^{-1} V_{N,N-1}) \right] V_{N-2,1} g_{N-2,1}(\lambda) \tag{3.103}$$

Keeping reasoning in this way, we arrive at the solution for g_{11}:

$$g_{11}(\lambda) = (\lambda - \hat{H}_1^{eff}(\lambda))^{-1} L_1 \tag{3.104}$$

where the N-th order electrode effective Hamiltonian and self-energy read as:

$$\begin{cases} \hat{H}_N^{eff}(\lambda) = \hat{H}_{NN} + \Sigma_N(\lambda) \\ \Sigma_N(\lambda) = V_{N,N+1}(\lambda - \hat{H}_{N+1}^{eff}(\lambda))^{-1} V_{N+1,N} \end{cases} \qquad \text{N=1,2...} \qquad (3.105)$$

Thus this procedure allows to compute the L_1 projection of g_L in terms of the self-energy $\Sigma_1^+(\lambda)$ of the remainder region $L_2 + L_3 + \dots$. In turn we would need the self-energies $\Sigma_2^+(\lambda)$, $\Sigma_3^+(\lambda)$, ... up to some high order N where we can reasonably truncate the procedure.

The alghoritm is completely general, considerable simplifications occur when L_n are periodic images of each other. Indeed in this case, upon introducing the matrices $\hat{\mathbf{H}}$ and $\hat{\mathbf{V}}$:

$$H_{nm} = \left\{ \langle \chi_n^{(1)} | \hat{H} | \chi_m^{(1)} \rangle \right\} \qquad (3.106)$$

$$V_{nm} = \left\{ \langle \chi_n^{(1)} | V | \chi_m^{(2)} \rangle \right\} \qquad (3.107)$$

where $|\chi_m^{(1)}\rangle$ and $|\chi_m^{(2)}\rangle$ are basis vectors in L_1 and L_2[‡], one obtains the matrix elements of the Green's functions of interest:

$$g_{nm}(\lambda) = \langle \chi_n^{(1)} | g_L(\lambda) | \chi_m^{(1)} \rangle \qquad (3.108)$$

which solves the matrix equation:

$$\left[\lambda - (\hat{\mathbf{H}} + \hat{\mathbf{V}} \mathbf{g}(\lambda) \hat{\mathbf{V}}^\dagger) \right] \mathbf{g}_L(\lambda) = 1 \qquad (3.109)$$

3.4.3   Scattering states

The Green's functions defined above provide a convenient way to calculate the current. Assuming that no energy relaxation processes occur in the scattering region, we can divide the electron in such region in two set of scattering-wave states, those coming from the left lead and those from the right. The left-lead states are, of course, filled up to the chemical potential in the left lead, μ_L, the right-lead states up to μ_R. The Green's function easily allows the determination of such scattering states, i. e. of those (improper) eigenvectors of the Hamiltonian which describe the evolution of a "free" propagating

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[‡]Of course the basis vectors in L_2 are the periodic images of the basis vectors in L_1

state into (and out) of the scattering region. According to the general scattering theory [§], the eigenstate $|\lambda_i, L+\rangle$ evolves from the freely propagating state $|\lambda_i, L\rangle$ in the left electrode according to Lippman-Schwinger equation:

$$(\lambda - \hat{H}) |\lambda_i, L+\rangle = (\lambda - \hat{H}_{LL}) |\lambda_i, L\rangle \tag{3.116}$$

Introducing $G(\lambda) = (\lambda - \hat{H})^{-1}$ and rearranging the above equation:

$$|\lambda_i, L+\rangle = G(\lambda)(\lambda - \hat{H} + \hat{H} - \hat{H}_{LL}) |\lambda_i, L\rangle = \left[1 + G(\lambda)(\hat{H} - \hat{H}_{LL})\right] |\lambda_i, L\rangle \tag{3.117}$$

[§] Typically, the scattering formalism is described in the following way: an incident particle in state $|\psi_0\rangle$ is scattered by the potential V, resulting in a scattered state $|\psi_s\rangle$. The incident state $|\psi_0\rangle$ is assumed to be an eigenstate of the free-particle Hamiltonian $\hat{H}_0$, with eigenvalue E. The goal of scattering theory is then to solve the full eigenstate problem:

$$(E - \hat{H}_0 - V) |\psi\rangle = 0 \tag{3.110}$$

where $|\psi\rangle$ is the eigenstate of the full Hamiltonian $\hat{H} = H_0 + V$ with energy E. It should be clear that there is a different $|\psi_0\rangle$ and correspondingly, a different $|\psi\rangle$ for each energy E, even though the notation does not indicate this explicitly. We first define the scattered state $|\psi_s\rangle$ as:

$$|\psi_s\rangle = |\psi\rangle - |\psi_0\rangle \tag{3.111}$$

Introducing this definition in eq. 3.110 and noticing that $(E - \hat{H}_0) |\psi\rangle = (E - \hat{H}_0) |\psi_0\rangle$ we get:

$$|\psi_s\rangle = (E - \hat{H}_0)^{-1} |\psi\rangle = G_0(E) |\psi\rangle \tag{3.112}$$

Where the unperturbed Green's function $G_0(E)$ has been introduced. Adding $|\psi_0\rangle$ to both sides:

$$|\psi\rangle = |\psi_0\rangle + G_0(E) V |\psi\rangle \tag{3.113}$$

This is known as the Lippman-Schwinger equation, and can be solved iteratively. After an infinite number of iterations, this procedure leads to:

$$|\psi\rangle = (1 + G_0(E)V + G_0(E)VG_0(E)V + G_0(E)VG_0(E)VG_0(E)V + ...) |\psi_0\rangle \tag{3.114}$$

which is known as the Born series. This is a perturbation expansion which is not guaranteed to converge, even though the above Lippman-Schwinger equation is always well defined (and the scattering states with it). Written as an integral equation, this reads as:

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int dr' G_0(r, r')V(r')\psi_0(r') + \int dr' \int dr'' G_0(r, r')V(r')G_0(r', r'')V(r'')\psi_0(r'') + ... \tag{3.115}$$

We can interpret this result as follows: if we put a detector at position r, the first term represents the probability amplitude that the particle arrive in r without scattering. The second terms describes the particle scattering once, at a point r', where its amplitude is increased/decreased by a factor $V(r')$, and then propagating as a free-spherical wave centered at r' to the detector. The integral over all r' then sums over all possible collision locations. The next terms describes the particle scattering twice, summing over both collision locations and so on. Thus we see that the total amplitude is the sum over all possible trajectories that the particle could travel to reach the detector, assuming straight-line propagation between point-contact collisions.

Specifically, considering $\lambda = \lim_{\eta \to 0^+}(E + i\eta)$, the above equations are well defined and have a single solution:

$$|E_i, L+\rangle = |E_i, L\rangle + G^+(E)(\hat{H} - \hat{H}_{LL})|E_i, L\rangle \tag{3.118}$$

The advantage of using the above formalism in defining the eigenstate $|E_i, L+\rangle$ is that one explicitly introduce in that way the desired boundary condition, i. e. $|E_i, L+\rangle \to |E_i, L\rangle$ when the interaction $\hat{H} - \hat{H}_{LL}$ is switched off.

The propagating states $|E_i, L\rangle$ satisfy the equations:

$$L|E_i, L\rangle = |E_i, L\rangle \tag{3.119}$$

$$(\hat{H} - \hat{H}_{LL})|E_i, L\rangle = \hat{H}_{CL}|E_i, L\rangle \tag{3.120}$$

since we have assumed no interactions between the leads ($\hat{H}_{RL} = 0$), hence:

$$|E_i, L+\rangle = |E_i, L\rangle + G^+(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.121}$$

from which the components of $|E_i, L+\rangle$ in the R, C, and L spaces, respectively, read as:

$$|\phi_R\rangle = R|E_i, L+\rangle = G^+_{RC}(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.122}$$

$$|\phi_C\rangle = C|E_i, L+\rangle = G^+_{CC}(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.123}$$

$$|\phi_L\rangle = |E_i, L\rangle + G^+_{LC}(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.124}$$

The latter in particular show both an "incident" contribution ($|E_i, L\rangle$) and a "scattered" term (second term on the r.h.s.). Introducing the previously obtained expressions for the Green's functions (eq. 3.82 and 3.83) in the scattering region we obtain:

$$|\phi_R\rangle = g^+_R \hat{H}_{RC} G^+_{CC}(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.125}$$

$$|\phi_C\rangle = G^+_{CC}(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.126}$$

$$|\phi_L\rangle = |E_i, L\rangle + g^+_L \hat{H}_{LC} G^+_{CC}(E)\hat{H}_{CL}|E_i, L\rangle \tag{3.127}$$

now in terms of the fundamental G^+_{CC} Green's function, defined, in according to eq. 3.88, as:

$$G^+_{CC}(E) = \lim_{\eta \to 0^+}(E + i\eta - \hat{H}_{eff}(E))^{-1}C \tag{3.128}$$

where, as previously defined, the effective Hamiltonian and the self-energies are defined by:

$$\hat{H}_{eff}(E) = \hat{H}_{CC} + \Sigma_R^+(E) + \Sigma_L^+(E) \tag{3.129}$$

$$\Sigma_L^+(E) = \hat{H}_{CL} g_L^+(E) \hat{H}_{LC} \tag{3.130}$$

$$\Sigma_R^+(E) = \hat{H}_{CR} g_R^+(E) \hat{H}_{RC} \tag{3.131}$$

It is obvious that, by construction, the vectors $|E_i, L+\rangle$ are eigenvectors of the full Hamiltonian with energy E, as it can be verified by an explicit calculation:

$$(E - \hat{H}) |E_i, L+\rangle = (E - \hat{H}) |E_i, L\rangle + (E - \hat{H}) G^+(E) |E_i, L\rangle =$$
$$= (E - \hat{H}_{CL} - \hat{H}_{LL}) |E_i, L\rangle = -\hat{H}_{CL} |E_i, L\rangle + \hat{H}_{CL} |E_i, L\rangle = 0 \tag{3.132}$$

where $\lim_{\eta \to 0^+} (E - \hat{H}) G^+(E) = 1$ and $(E - \hat{H}_{LL}) |E_i, L\rangle = 0$ have been used. The vectors $|E_i, L+\rangle$ contain the basic information we need to describe the scattering process and can be obtained through eq. 3.125-3.127 from $G_{CC}(E)$. In practice such equations determine the projection of the scattering states onto the R, C and L regions.

3.4.4 Self-consistency

So far we have assumed that the Hamiltonian is given and focused on how to express the quantities of interest in terms of the Green's function of the scattering region only. However $\hat{H}$ is at most a mean field Hamiltonian, i. e. an effective mono-electronic operator which has to be self-consistent with its solutions. For a system in equilibrium (i. e. $\mu_R = \mu_L = \mu_C$) this condition is easily established by looking at the density of states and populating them up to the Fermi level, namely introducing the density matrix of the electronic system, γ. Explicitly, in the interesting scattering region this reads as:

$$\gamma = \int dE \, f(E - \mu) \delta(E - \hat{H}_{eff}) \tag{3.133}$$

where $f(E - \mu)$ is the Fermi-Dirac distribution function:

$$f(E - \mu) = \frac{1}{1 + e^{\frac{(E - \mu)}{K_b T}}} \tag{3.134}$$

and $\delta(E - \hat{H}_{eff})$ is the density-of-states operator of the scattering region. Then, remembering that $ImG^+(E) = -\pi \delta(E - \hat{H})$, we can establish a connection between γ

and $G_{CC}^+(E)$:

$$\gamma = -\frac{1}{\pi} Im \int\limits_{-\infty}^{+\infty} G_{CC}^+(E) f(E-\mu) dE \tag{3.135}$$

which is usually evaluated by exploiting the analytic properties of $G_{CC}(E)$, namely replacing the path along the real axis with an equivalent path on the upper half plane, where $G_{CC}(\lambda)$ is free of singularities. Notice that the chemical potential is fixed by the normalization condition

$$Tr\gamma = N \tag{3.136}$$

where N is the number of electrons in the scattering region. We can explicitly write the density-of-states operator in terms of the effective Hamiltonian $\hat{H}_{eff}$ by using

$$ImG_{CC}(\lambda) = Im\left[G_{CC}(\lambda)(G_{CC}^+(\lambda))^{-1}G_{CC}^+(\lambda)\right] = Im\left[G_{CC}(\lambda)(\lambda^* - \hat{H}^{eff\dagger})G_{CC}^+(\lambda)\right] =$$

$$= G_{CC}(\lambda)\left[Im(\lambda^* - \hat{H}^{eff\dagger})\right]G_{CC}^+(\lambda) = G_{CC}(\lambda)\left[Im\lambda^* - \frac{\Gamma(\lambda)}{2})\right]G_{CC}^+(\lambda)$$

where eq. 3.88 and 3.94, along with the hermitian properties of Green's functions have been used. Considering $\lambda = \lim_{\eta \to 0^+}(E+i\eta)^{\P}$:

$$\delta(E-\hat{H}_{eff}) = \frac{1}{2\pi}G_{CC}^+(E)\Gamma(E)G_{CC}^-(E) \tag{3.137}$$

Taking into account that Γ has contribution from both the left and right electrodes (eq. 3.97), we end up with:

$$\gamma = \gamma_L + \gamma_R \tag{3.138}$$

where, recalling eq. 3.94, we define γ_L as:

$$\gamma_L = \frac{1}{2\pi} \int dE \, f(E-\mu)G_{CC}^+(E)\Gamma_L(E)G_{CC}^-(E) =$$

$$= \int dE \, f(E-\mu)G_{CC}^+(E)\hat{H}_{CL}\delta(E-\hat{H}_{LL})\hat{H}_{LC}G_{CC}^-(E) \tag{3.139}$$

and similarly for γ_R. In particular the charge density at the point x in the scattering region reads as:

$$\rho(x) = \rho_L(x) + \rho_R(x) = \langle x| \gamma_L |x\rangle + \langle x| \gamma_R |x\rangle \tag{3.140}$$

¶Notice that $Im\lambda^* \to 0^+$, but if Γ vanishes, *i.e.* in the presence of an isolated conductor, $Im\lambda^*$ cannot be neglected.

where

$$\rho_L(x) = \int dE \, f(E-\mu) \langle x| G_{CC}^+(E)\hat{H}_{CL}\delta(E-\hat{H}_{LL})\hat{H}_{LC}G_{CC}^-(E) |x\rangle \tag{3.141}$$

is the contribution of electrons from the left electrode and similarly for $\rho_R(x)$. More precisely with the help of the scattering states introduced above we can write down the contribution of the states which evolved from the left electrode:

$$\delta(E-\hat{H}_{eff}) = \sum_i C |E_i, L+\rangle \langle E_i, L+| C =$$

$$= \sum_i G_{CC}^+(E)\hat{H}_{CL} |E_i, L+\rangle \langle E_i, L+| \hat{H}_{LC}G_{CC}^-(E) =$$

$$= G_{CC}^+(E)\hat{H}_{CL}\delta(E-\hat{H}_{LL})\hat{H}_{LC}G_{CC}^-(E) \tag{3.142}$$

and similarly for the right electrode. This observation is crucial to investigate the case where the system is in a non-equilibrium state, i. e. $\mu_R - \mu_L = \Delta\mu \neq 0$. In this case, indeed it is reasonable to define the non-equilibrium density matrix as:

$$\gamma = \gamma_L + \gamma_R \tag{3.143}$$

$$\gamma_L = \int dE \, f(E-\mu_L)\delta_L(E-\hat{H}_{eff}) \tag{3.144}$$

$$\gamma_R = \int dE \, f(E-\mu_R)\delta_R(E-\hat{H}_{eff}) \tag{3.145}$$

where μ_R and μ_L are now external parameters, typically expressed as:

$$\mu_L = \mu + \frac{\Delta\mu}{2} \tag{3.146}$$

$$\mu_R = \mu - \frac{\Delta\mu}{2} \tag{3.147}$$

where $\mu = \frac{\mu_L + \mu_R}{2}$ is the equilibrium chemical potential and $\Delta\mu$ is related to the "macroscopic" bias:

$$\Delta\mu = -|e|V_{bias} \tag{3.148}$$

Thus the non-equilibrium charge $\rho(x)$ in the scattering region used to built the effective Hamiltonian has to be consistent with the density matrix defined above, namely:

$$\rho(x) = \langle x| \gamma |x\rangle = \langle x| \gamma_L |x\rangle + \langle x| \gamma_R |x\rangle \tag{3.149}$$

This define a self-consistent procedure which is of paramount importance to correctly describe screening effects within the scattering region; at self-consistency, $\hat{H}_{eff}$ (for a given $\Delta\mu$) is the effective Hamiltonian whose eigenvectors contain the scattering information needed to describe transport across the scattering region.

3.4.5   Transmission probability and current

Having defined an effective Hamiltonian for a given non-equilibrium condition, we are in a position of computing the relevant scattering information. We are interested in the probability that an electron coming from the left electrode ends up in the right electrode, that can be called the *transmission probability*. According to general scattering theory this probability is the expectation value of a *product-region flux operator F_R* which, in our case, reads as:

$$F_R = i\left[\hat{H}, R\right] = i(\hat{H}R - R\hat{H}) = i(\hat{H}_{CR} - \hat{H}_{RC}) = -2Im H_{CR} \tag{3.150}$$

on account of the property $\hat{H}_{LR} = \hat{H}_{RL} = 0$. The probability that an electron in the state $|E_i, L\rangle$ "evolves" into the right electrode is then given by:

$$P_i = 2\pi \langle E_i, L+| F_R |E_i, L+\rangle \tag{3.151}$$

The total (or cumulative) transmission probability from left to right is obtained upon summing over $|E_i, L+\rangle$:

$$T_{R\leftarrow L}(E) = 2\pi \sum_i \langle E_i, L+| F_R |E_i, L+\rangle = -4\pi \sum_i Im \langle E_i, L+| H_{CR} |E_i, L+\rangle \tag{3.152}$$

and takes a simple form once

$$R|E_i, L+\rangle = g_R^+(E)\hat{H}_{RC}G_{CC}^+(E)\hat{H}_{CL}|E_i, L+\rangle \tag{3.153}$$

$$C|E_i, L+\rangle = G_{CC}^+\hat{H}_{CL}|E_i, L+\rangle \tag{3.154}$$

are introduced in eq. 3.152 and the sum is replaced by an appropriate trace operation, the trace being conveniently taken over states in the scattering region. To this end, we introduce a basis $|\chi_k\rangle$ in C:

$$T_{R\leftarrow L}(E) = -4\pi \sum_{i,k} Im \left[\langle E_i, L+|\chi_k\rangle \langle \chi_k| \hat{H}_{CR} |E_i, L+\rangle\right] \tag{3.155}$$

After some mathematical rearrangements and introducing $\Gamma_L(E)$ (defined in eq. 3.94) we arrive at:

$$T_{R \leftarrow L}(E) = -2Im \left[Tr(\hat{H}_{CR} g_R^+(E) \hat{H}_{RC} G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E)) \right] \tag{3.156}$$

The imaginary part is easily computed after noticing that:

$$Tr(\hat{H}_{CR} g_R^+(E) \hat{H}_{RC} G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E))^\dagger =$$
$$= Tr(G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E) \hat{H}_{CR} g_R^-(E) \hat{H}_{RC}) =$$
$$= Tr(\hat{H}_{CR} g_R^-(E) \hat{H}_{RC} G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E)) \tag{3.157}$$

thanks to the invariance under cyclic permutation of the traced operator and we found that:

$$T_{R \leftarrow L}(E) = Tr \left[\hat{H}_{CR}(-2Im g_R^-(E)) \hat{H}_{RC} G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E) \right] \tag{3.158}$$

where $-2Im g_R^-(E) = 2\pi\delta(E - \hat{H}_{RR})$ and thus:

$$T_{R \leftarrow L}(E) = Tr \left[\Gamma_R(E) G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E) \right] \tag{3.159}$$

once $\Gamma_R(E) = 2\pi \hat{H}_{CR}\delta(E - \hat{H}_{RR})\hat{H}_{RC}$ has been introduced. From this expression it is not hard to show that, if $\hat{H}$ is invariant under time-reversal operation,[‖] we have for the reverse process:

$$T_{L \leftarrow R}(E) = T_{R \leftarrow L}(E) = Tr \left[\Gamma_L(E) G_{CC}^+(E) \Gamma_R(E) G_{CC}^-(E) \right] \tag{3.161}$$

Thus, under such circumstances, we can unambiguously refer to the *cumulative transmission probability* as:

$$T(E) = Tr(\Gamma_R(E) G_{CC}^+(E) \Gamma_L(E) G_{CC}^-(E)) \tag{3.162}$$

[‖]The anti-linear time-reversal operator $\hat{T}_{tr}$, acts on the position and momentum operators as follows:

$$\hat{T}_{tr}^\dagger \hat{x} \hat{T}_{tr} = \hat{x} \qquad \hat{T}_{tr}^\dagger \hat{p} \hat{T}_{tr} = -\hat{p} \tag{3.160}$$

If no linear terms in $\hat{p}$ appear in the Hamiltonian *e.g.*, this results invariant under time-reversal operations

The current can be computed with the help of the above results. The current $L \to R$ carried by the states $|E_i, L\rangle$ is given by:

$$dI_{i,L} = -|e|n_L(E)P_i(E)v_i(E)\frac{dk}{2\pi} \tag{3.163}$$

where n_L is the occupation probability of the state, $P_i(E)$ is the above transmission probability, $v_i(E) = \partial E / \partial k$ is electron velocity in the state and $dK/2\pi$ accounts for the discretization of states in k-space:

$$\frac{dk}{2\pi} = number\ of\ states\ for\ unit\ length\ \times\ number\ of\ states\ for\ unit\ k \tag{3.164}$$

The number of states for unit length times $n_L(E)P_i(E)$ defines the linear density of current-carrying electrons. Upon summing over i and noticing that $v_i(E)dk = dE$, irrespective of the dispersion relation (along the transport direction):

$$dI_L = -\frac{|e|}{h}n_L(E)T_{R\leftarrow L}(E)dE \tag{3.165}$$

Thus the total current from left to right reads as:

$$I = -\frac{|e|}{h}\int\limits_{-\infty}^{+\infty} dE\ [n_L(E)T_{R\leftarrow L}(E) - n_R(E)T_{L\leftarrow R}(E)] \tag{3.166}$$

on accounts of those electrons that starting from the right electrode ends up to the left one. Under time-reversal invariance the above expression simplifies to:

$$I = -\frac{|e|}{h}\int\limits_{-\infty}^{+\infty} dE\ T(E)(n_L(E) - n_R(E)) \tag{3.167}$$

The zero-temperature case is schematically shown if fig. 3.7. Here, for small bias $\delta\mu$ and at ordinary temperatures, which are well below the fermi temperature of the metals,

$$n_L(E) - n_R(E) \approx \frac{\partial n}{\partial\mu}(E, \overline{\mu})\delta\mu \approx \delta(E - \overline{\mu})\delta\mu \tag{3.168}$$

where $\overline{\mu} = \frac{\mu_L + \mu_R}{2}$ is the average chemical potential, hence:

$$\delta I = \frac{|e|^2}{h}T(\overline{\mu})\delta V = G(\overline{\mu})\delta V \tag{3.169}$$
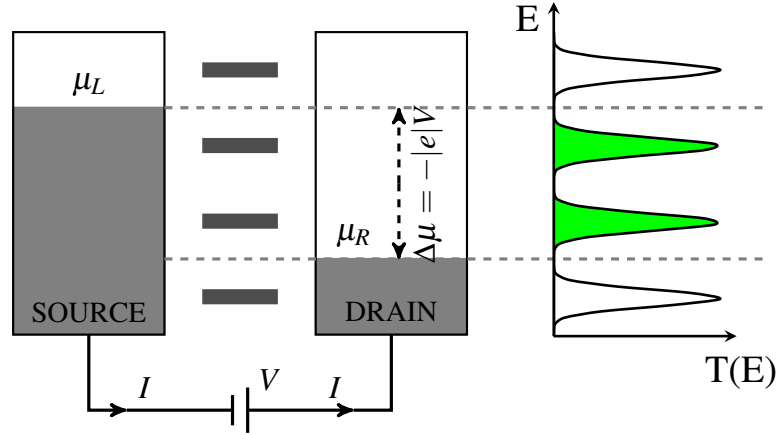
FIGURE 3.7: Energy level diagram of a two terminal device under applied bias. Notice that the maxima of the transmission function correspond to the energy levels of the molecule. The current flowing between the leads is proportional to the green area of the transmission plot.

where $\delta\mu = -|e|\delta V$ has been used and

$$G(\overline{\mu}) = \frac{|e|^2}{h}T(\overline{\mu}) \qquad (3.170)$$

is the conductance (at zero bias), when the Fermi level is positioned at $\overline{\mu}$. Thus we can interpret $T(E)$ as the zero-bias conductance (in units of the quantum of conductance $|e|^2/h$) when the fermi level is located at energy E, provided we disregard the effect that any gate potential has on the effective Hamiltonian used to compute $T(E)$. Alternatively, but always assuming that $T(E)$ does not essentially depend on the bias we can consider the *differential conductance*:

$$\frac{dI}{dV} = -|e|\frac{dI}{d(\Delta\mu)} = \frac{|e|^2}{2}\int\limits_{-\infty}^{+\infty} dE\, T(E)\frac{d}{d(\Delta\mu)}\left[n(E,\overline{\mu}+\frac{\Delta\mu}{2}) - n(E,\overline{\mu}-\frac{\Delta\mu}{2}) \right]$$

$$(3.171)$$

$$= \frac{|e|^2}{2}\int\limits_{-\infty}^{+\infty} dE\, T(E)\frac{1}{2}\left[\frac{\partial n}{\partial\mu}(E,\mu_L) - \frac{\partial n}{\partial\mu}(E,\mu_R) \right] \qquad (3.172)$$

where $\frac{\partial n}{\partial\mu}(E,\mu) \approx \delta(E-\mu)$ and thus:

$$\frac{dI}{dV} \cong \frac{|e|^2}{2}\frac{T(\mu_L)+T(\mu_R)}{2} \qquad (3.173)$$

which obviously reduces to the previous result when the conductance is taken at zero bias ($\mu_L = \mu_R = \overline{\mu}$). The above result also show that under the above hypothesis $dI/dV > 0$, thus the negative differential resistance which is observed in some instances

can only be due to the dependence of $T(E)$ on the applied bias.

3.4.6 Combining DFT with NEGF

The junction considered above are neither finite nor periodic, making difficult the application of DFT. Moreover we are interest in situations in which the system is driven out of equilibrium, for instance by the application of a bias voltage. Although these situations are out of the scope of the standard ground-state DFT, we can combine this technique with NEGF in order to describe transport properties of nanoscale devices. Essentially two issues need to be answered, specifically (i) how to compute the charge density and (ii) how to make finite the dimension of the problem. To this aim we first divide the junction into three parts, the left and right electrodes and the central scattering region, as already explained in the previous sections.

In this division one assumes that the electrodes are not perturbed by the central part and thus their Hamiltonians and charge densities can be obtained from a separated DFT bulk-like calculation. This is based on the assumption that deep inside a solid the Kohn-Sham potential approaches the bulk potential. This approximation is often referred as the screening approximation and in practice defines the size of the scattering region.

Second, within the LCAO approach, the charge density can be computed in terms of the density matrix, which in turn can be calculated from the Green's functions. These, in terms of the local basis functions $|\chi\rangle$, admit spectral representation:

$$G_{\mu\nu}^{\pm}(E) = \sum_i \frac{|\chi_{\mu i}\rangle \langle \chi_{i\nu}|}{E - E_i \pm i\eta} \tag{3.174}$$

As shown in the previous section, the retarded or advanced Green's function of the central part allows to calculate the density matrix of this part of the system:

$$\gamma = \mp \frac{1}{\pi} \int_{\infty}^{\infty} dE \, ImG_{CC}^{\pm} f(E - \mu) \tag{3.175}$$

Now these Green's function can be computed via their Dyson's equation:

$$\mathbf{G}^{\pm} = \left[(E \pm i\eta)\mathbf{S} - \mathbf{H} - \Sigma_L^{\pm} - \Sigma_R^{\pm} \right]^{-1} \tag{3.176}$$

where $S = \langle \chi_i | \chi_j \rangle$ is the overlap matrix, H the one-electron Kohn-Sham hamiltonian of the central part and $\Sigma_{L,R}^{\pm}$ are the self-energies of the left and right electrodes. The calculation of these self-energies requires the computation of the Hamiltonian and Green's
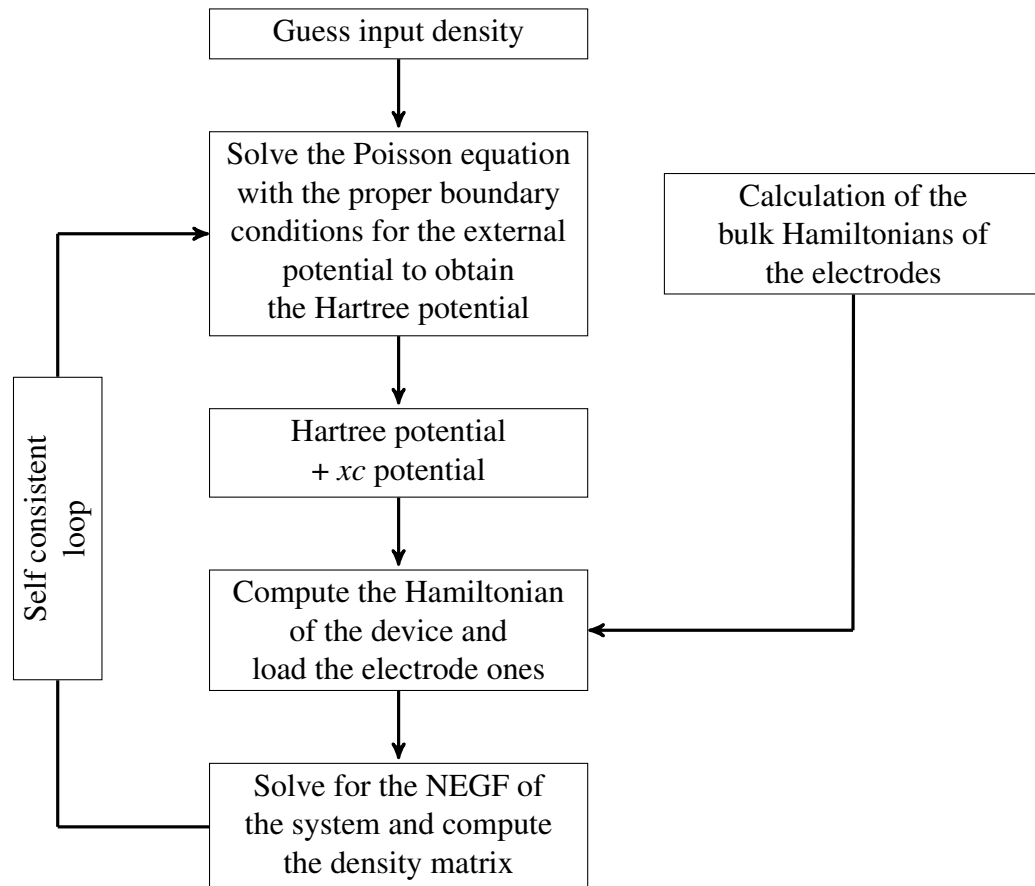
FIGURE 3.8: Flowchart of the self-consistent loop for the solution of the non-equilibrium transport problem. Adapted from ref. [Cuevas and Scheer[81]]

function of the electrodes.

In this case DFT is used to compute the density matrix rather than solving the Kohn-Sham equations. Such evaluation requires the calculations of the Green's functions via eq. 3.176 from the Kohn-Sham Hamiltonian of the central part. Since this in turn depends on the charge density (and thus on the density matrix), eq. 3.175 and 3.176 are coupled and need to be solved self-consistently. In this way we obtain an effective one-electron description of the system and we can calculate the transmission probabilities. One of the practical difficulties in the implementation of this method is the efficient and accurate integration of the density matrix because of the poles of the Green's function on the real axis. However this problem is usually overcome using the fact that Green's functions are analytical functions in the upper and lower parts of the complex plane. This means in practice that the integral in eq. 3.175 can be done by integrating along a contour in the complex plane, where these functions are very smooth. Moreover, for negative energy values, the integral in eq. 3.175 only requires the inclusion of all occupied states of the scattering region and of the electrodes. Hence we can chose a finite value for the lower limit of integration providing all the available states below the Fermi

level being counted.

The practical implementation of the DFT-NEGF method in general follows the general scheme shown in fig. 3.8, and differentiates mainly in the way in which the electrodes Green's functions are determined and how the potential and the Hamiltonian of the central part are forced to match the corresponding ones of the electrodes.