Chapter 2
Transport Theory

2.1 Retarded and Advanced Green's Functions for Electrons Traveling Through a MMM Junction

We start our theoretical analysis of MMM junctions transport properties by briefly introducing the concept of Green's functions which are necessary for the development of the transport theory. A very thorough treatment of the Green's functions properties and their quantum mechanical applications is given in numerous works on the subject. Here, we minimize mathematical intricacies by considering a system whose Hamiltonian H is independent of time. In this case the time evolution of a Schrodinger state vector $\{\psi(t)\}$ may be described by means of the time evolution operator $U(t,t')$:

$$\{\psi(t)\} = U(t,t')\{\psi(t')\} \tag{2.1}$$

which satisfies the equation of motion:

$$i\hbar\frac{\partial U(t,t')}{\partial t} - HU(t,t') = 0. \tag{2.2}$$

The time evolution operator must satisfy the condition $U(t,t) = [1]$ where $[1]$ is the unit operator. Keeping this in mind one can find the appropriate solution of Eq. (2.2), namely,

$$U(t,t') = \exp\left[\frac{1}{i\hbar}H(t-t')\right]. \tag{2.3}$$

The retarded and advanced Green's functions for the considered system are closely related to the time evolution operator. These operators are defined as

$$G^{(r)}(t,t') = \tfrac{1}{i}\theta(t-t')U(t,t'), \tag{2.4}$$

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$$G^{(a)}(t,t') = -\tfrac{1}{i}\theta(t'-t)U(t,t'), \tag{2.5}$$

where

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x \leq 0 \end{cases} \tag{2.6}$$

is the Heaviside step function. As follows from definitions (2.4) and (2.5), the retarded Green's function $G^{(r)}(t,t')$ only propagates forward in time (and hence effects caused by sources are always "retarded" for they occur later in time, as follows from the causality principle). The advanced Green's function $G^{(a)}(t,t')$ propagates backward. The time evolution operator obeys the rule $U^{\dagger}(t,t') = U(t',t)$, so the retarded and advanced Green's functions are Hermitian conjugates of each other:

$$\left[G^{(r)}(t,t')\right]^{\dagger} = G^{(a)}(t',t). \tag{2.7}$$

Using definitions (2.4) and (2.5), the equation of motion for the time evolution operator (2.2) and the relation between the step function and the delta function ($d\theta/dx = \delta(x)$), one may show that the operators $G^{(r,a)}(t,t')$ satisfy the equation with the delta function source term:

$$i\hbar\frac{\partial}{\partial t}G^{(r,a)}(t,t') - HG^{(r,a)}(t,t') = \hbar\delta(t-t') \tag{2.8}$$

which justifies the commonly accepted recognition of these operators as Green's functions.

For the considered case of the time-independent Hamiltonian H, the time evolution operator depends on the difference between the time coordinates t and t', and the same is valid for the Green's functions. So we may write

$$G^{(r,a)}(t,t') = G^{(r.a)}(t-t',0). \tag{2.9}$$

Now, Eq. (2.8) may be solved by applying the Fourier transformation. In general case, the relations between an arbitrary function $f(t)$ and its Fourier transform $F(E)$ are given by

$$F(E) = \int_{-\infty}^{\infty}\frac{dt}{\hbar}e^{iEt/\hbar}f(t), \tag{2.10}$$

$$f(t) = \int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{-iEt/\hbar}F(E). \tag{2.11}$$

While computing Fourier transforms for the Green's functions, one meets a technical difficulty arising because the corresponding integrals diverge. To circumvent this difficulty, one must introduce damping factors $\exp[\mp\eta(t-t')]$ assuming that η

is a positive infinitesimal quantity ($\eta \to 0^+$). Then one may set $t - t' \to t$ and write out the following expressions for the Fourier transforms:

$$G^{(r,a)}(E) = \int_{-\infty}^{\infty} \frac{dt}{\hbar} e^{i(E \pm i\eta)t/\hbar} G^{(r,a)}(t, 0). \tag{2.12}$$

Here, the sign before $i\eta$ corresponds to the retarded $(+)$ and advanced $(-)$ Green's functions, respectively. In agreement with Eq. (2.11), these functions are expressed in terms of their Fourier transforms as follows:

$$e^{\mp \eta t} G^{(r,a)}(t, 0) = \int_{-\infty}^{\infty} \frac{dE}{2\pi} e^{-iEt/\hbar} G^{(r,a)}(E). \tag{2.13}$$

Substituting expressions of the form (2.13) into Eq. (2.8), one may reduce these differential equations for the original Green's functions to the algebraic equations for their Fourier transforms. As a result, one obtains the Green's functions in the energy representation:

$$G^{(r)}(E) = \left[(E - i\eta)[1] - H\right]^{-1}, \tag{2.14}$$

$$G^{(a)}(E) = \left[G^{(r)}(E)\right]^{\dagger} = \left[(E + i\eta)[1] - H\right]^{-1}. \tag{2.15}$$

Here, as before, $[1]$ stands for the unit operator, and H is Hamiltonian of the considered system. Due to the simple symmetry relation between the retarded and advanced Green's functions one may choose one of them to analyze its properties and then apply the obtained results to describe the properties of the remaining Green's operator. In further analysis we choose the retarded Green's function $G^{(r)}(E)$ for this purpose.

The Green's functions are often employed to theoretically analyze various properties of mesoscopic systems, including their transport properties. The important advantage of Green's function-based formalisms is that they allow to include into consideration various interaction effects. Now, we illustrate this by considering the Green's function of a system consisting of two electron reservoirs (source and drain) linked by a channel. Obviously the obtained results could be applied to study transport properties of metal–molecular junctions. In the analysis presented below we follow the method suggested and described by Datta in his book [4]. This method allows to bypass numerous computational difficulties arising when one follows more formal and rigorous methods described in several books and research articles (see, e.g., [202–210] and the last section of this chapter). The price which one pays for this simplification is that one must treat interactions perturbatively.

We start from partitioning of the system Hamiltonian H in such a way that the terms corresponding to the source (H_L) and drain (H_R) are separated from the part corresponding to the channel (H_C):

$$H = \begin{pmatrix} H_L - i\eta & \tau_L^\dagger & 0 \\ \tau_L & H_C & \tau_R \\ 0 & \tau_R^\dagger & H_R - i\eta \end{pmatrix}. \tag{2.16}$$

Here, the operators τ_β ($\beta \in L, R$) describe the coupling of the source and drain to the channel. We consider the system in the stationary state with the energy E, so the Schrodinger equation has the form $H\Psi = E\Psi$ where the Hamiltonian H is given by Eq. (2.16) and the state vector (wave function) may be presented as follows:

$$\Psi = \begin{pmatrix} \Phi_L + \chi_L \\ \psi \\ \Phi_R + \chi_R \end{pmatrix} \tag{2.17}$$

where $\{\Phi_\beta\}$ ($\beta \in L, R$) are the incident waves functions in the contact reservoirs, $\{\psi\}$ is the wave function transmitted into the channel, and $\{\chi_\beta\}$ correspond to the parts reflected back into the reservoirs. Implying that the functions $\{\Phi_\beta\}$ are the solutions of the equations $(H_\beta - i\eta)\{\Phi_\beta\} = E\{\Phi_\beta\}$, one may obtain the following expressions for $\{\chi_\beta\}$:

$$\{\chi_\beta\} = g_\beta^r(E)\tau_\beta\{\psi\}. \tag{2.18}$$

Here

$$g_\beta^r(E) = \big((E - i\eta)[1] - H_\beta\big)^{-1} \tag{2.19}$$

are retarded Green's functions for the contacts (reservoirs).

Substituting these expressions into the original Schrodinger equation, one gets

$$\big(E[1] - H_C - \Sigma_L^r - \Sigma_R^r\big)\{\psi\} = \{S\} \tag{2.20}$$

where $\Sigma_\beta^r = \tau_\beta^\dagger g_\beta^r \tau_\beta$ are self-energy terms originating from the interactions between the channel and the contacts and $\{S\} = \tau_L\{\Phi_L\} + \tau_R\{\Phi_R\}$. As mentioned above, $\{\Phi_\beta\}$ are the wave functions of the contacts in the absence of the coupling between them and the channel, so the term $\{S\}$ on the right side of Eq. (2.20) describes the electrons flow into the channel (inflow). At the same time, the term $(\Sigma_L^r + \Sigma_R^r)\{\psi\}$ is associated with the electrons flow from the channel to the contacts (outflow).

As follows from Eq. (2.20) and the definitions of the Green's functions, the retarded Green's function of the considered system (in the energy representation) has the form

$$G^r(E) = \big(E[1] - H_C - \Sigma_L^r - \Sigma_R^r\big)^{-1} \tag{2.21}$$

and it is related to the corresponding Green's function for the isolated channel

$$G_0^r(E) = \big((E - i\eta)[1] - H_C\big)^{-1} \tag{2.22}$$

by means of the Dyson equation:

$$G^r(E)^{-1} = G_0^r(E)^{-1} - \Sigma^r(E) \tag{2.23}$$

where $\Sigma^r(E) = \Sigma_L^r(E) + \Sigma_R^r(E)$. The Dyson equation separates out the response G_0^r of an isolated channel grouping the corrections due to interactions in the self-energy term Σ^r. In deriving Eq. (2.23), we took into account only interactions of the channel with the contacts, and this has determined the particular form of self-energy term. In general case, the self-energy terms may include contributions from other kinds of interactions such as electron–phonon interactions.

Equation (2.23) may be converted to the commonly used form:

$$G^r(E) = G_0^r(E) + G^r(E)\Sigma^r(E)G_0^r(E) \tag{2.24}$$

which can be rewritten as a series:

$$\begin{aligned} G^r(E) =& G_0^r(E) + G_0^r(E)\Sigma^r(E)G_0^r(E) \\ &+ G_0^r(E)\Sigma^r(E)G_0^r(E)\Sigma^r(E)G_0^r(E) + \cdots \end{aligned} \tag{2.25}$$

that schematically represents the role of various interactions.

The retarded and advanced Green's functions determine the spectral function $A(E)$ defined by the expression

$$A(E) = i\big[G^r(E) - G^a(E)\big] \equiv i\big[G^r(E) - G^r(E)^\dagger\big]. \tag{2.26}$$

The physical meaning of this operator is that its trace gives the electron density of states at a certain energy, namely,

$$D(E) = \frac{1}{2\pi}\mathrm{Trace}[A(E)] \equiv \sum_\alpha \delta(E - E_\alpha) \tag{2.27}$$

where the summation is carried over all eigenstates of the considered system. So, the spectral function $A(E)$ represents the matrix version of the electron density of states, and it is closely related to the density matrix of the considered system. Actually, when the electron system described by the Hamiltonian H is in the equilibrium state, the corresponding density matrix may be presented as

$$\rho \equiv \{\Psi\}\{\Psi\}^\dagger = \int \frac{dE}{2\pi} f(E - \mu)A(E) \tag{2.28}$$

where $f(E - \mu)$ is the Fermi distribution function with the chemical potential μ. When the system departs from the equilibrium state, its density matrix is given by

$$\rho = \int \frac{dE}{2\pi i} G^{<}(E) \tag{2.29}$$

where the lesser Green's function $G^{<}(E)$ is introduced. It could be expressed in terms of the retarded and advanced Green's functions. Now, we find the expression for $G^{<}(E)$ for our system including the channel coupled to the two contacts. In such a system, before the contact is established between the source and drain electron reservoirs and the channel, the electrons on the contacts remain in equilibrium states described by the density matrices

$$\rho_\beta = \{\Phi_\beta\}\{\Phi_\beta\}^\dagger = \int \frac{dE}{2\pi} f_\beta(E-\mu_\beta) A_\beta(E); \qquad \beta \in L, R. \tag{2.30}$$

Here, μ_β are the chemical potentials for the reservoirs and spectral functions $A_\beta(E)$ are equal:

$$A_\beta(E) = i\big[g^r_\beta(E) - g^a_\beta(E)\big] \tag{2.31}$$

where the retarded Green's functions for the reservoirs are determined by Eq. (2.19). Assuming that the contact between the source and drain reservoirs and the channel is established and using Eq. (2.19), one obtains

$$\begin{aligned} \rho &= \{\psi\}\{\psi^\dagger\} = G^r\{S\}\{S\}^\dagger G^a \\ &= G^r\big(\tau_L\{\Phi_L\}\{\Phi_L\}^\dagger\tau_L^\dagger + \tau_R\{\Phi_R\}\{\Phi_R\}^\dagger\tau_R^\dagger\big)G^a. \end{aligned} \tag{2.32}$$

The cross terms which appear when one calculates the product $\{S\}\{S\}^\dagger$ are zero because the wave functions $\{\Phi_L\}$ and $\{\Phi_R\}$ are related to different electron reservoirs which are connected only by the channel. Using the expressions for the density matrices on the contacts (2.30) and introducing denotations

$$\Gamma_\beta \equiv i\big(\Sigma^r_\beta - \Sigma^a_\beta\big) = \tau_\beta A_\beta \tau^\dagger_\beta \tag{2.33}$$

we may write down the following expression for the electron density matrix of the channel:

$$\rho = \int \frac{dE}{2\pi} G^r(E)\big[f_L(E-\mu_L)\Gamma_L + f_R(E-\mu_R)\Gamma_R\big]G^a(E). \tag{2.34}$$

Comparing Eqs. (2.29) and (2.34), one concludes that the lesser Green's function satisfies the Keldysh equation:

$$G^{<}(E) = G^r(E)\Sigma^{<}(E)G^a(E) \tag{2.35}$$

where the self-energy term has the form

$$\frac{1}{i}\Sigma^{<}(E) = f_L(E-\mu_L)\Gamma_L + f_R(E-\mu_R)\Gamma_R. \tag{2.36}$$

As follows from the general theory, the relation (2.35) remains valid when other interactions apart from the interactions between the channel and the contacts are taken into account. However, the form of the self-energy term $\Sigma^{<}$ varies depending on the considered interactions.

The lesser Green's function including the self-energy term of the form (2.36) may be presented as the sum of two terms associated with the contacts:

$$G^{<}(E) = \sum_{\beta} f_\beta G^r \Gamma_\beta G^a. \tag{2.37}$$

This means that the nonequilibrium density matrix for the channel retains the form similar to that given by Eq. (2.28). Now, however, the spectral function $A(E)$ consists of two parts, each part associated with the certain (left/right) contact. It is natural to think that the part $A_L(E) = G^r(E)\Gamma_L G^a(E)$ appears due spilling-over states belonging to the left contact which is filled according to the Fermi function f_L. Similarly, the contribution $A_R(E) = G^r(E)\Gamma_R G^a(E)$ arises from the spillover of the states from the right contact filled according to the Fermi function f_R. We remark that in the case when the channel is characterized by a single energy level E_0 (a single-site bridge), Eq. (2.35) becomes reduced to expression (1.9) for the electron density on the bridge which was obtained using the simplified model for a MMM junction.

Introducing a suitable set of basis functions, one may compute matrix elements of the Green's functions. Thus, the retarded Green's function $G^r(E)$ given by Eq. (2.21) may be presented in the form

$$G^r(E) = \left(ES - F - \Sigma_L^r - \Sigma_R^r\right)^{-1} \tag{2.38}$$

where S and F are the corresponding overlap and Fock matrices. If the basis functions are orthonormalized, $S_{ij} = \delta_{ij}$, δ_{ij} being the Kronecker symbol. As for the self-energy matrices Σ_β, they need to be carefully computed taking into account the chemical coupling of individual lead orbitals (for the corresponding lead) with the bridge orbitals, as well as the band structure of the leads. Also, one must accurately describe the dependencies of self-energy terms of energy E.

To elucidate the crucial importance of a proper modeling of the self-energy term, we cite an example considered by Datta in his book [4]. The energy eigenvalues of a two-site system with the site energies E_1 and E_2 and site-to-site coupling τ_0 may be found by solving the quadratic equation:

$$(E-E_1)(E-E_2) - \tau_0^2 = 0. \tag{2.39}$$

However, one could treat this system as a combination of a contact and a channel coupled to the latter. For certainty, we assume that the site with the energy E_1 takes

on the part of the contact, and the remaining site corresponds to the channel. For such a simple system both the Green's function given by Eq. (2.38) and the self-energy term Σ are scalar quantities. We have

$$G^r(E) = \left(E - E_2 - \Sigma^r(E)\right)^{-1}. \tag{2.40}$$

The eigenenergies of the considered system coincide with the poles of this Green's function. Comparing Eqs. (2.39) and (2.40), one may see that the agreement in the results for the eigenenergies is achieved provided that the self-energy term has the form

$$\Sigma^r(E) = \frac{\tau_0^2}{E - E_1 + i\eta} \tag{2.41}$$

where, as before, η is a small positive quantity which is introduced to describe the broadening of energy levels.

Also, one may treat the site with the energy E_1 as a channel and that with the energy E_2 as a contact. Then the energy E_2 is to be replaced by E_1 in expression (2.40) for the Green's function, and E_2 takes the place of E_1 in expression (2.41) for the self-energy term. Nevertheless, the poles of the Green's function remain undisturbed. It is worthwhile to remark that the real and imaginary parts of the self-energy given by (2.41) obey Kramers–Kronig relation:

$$\mathrm{Re}\left[\Sigma^r(E)\right] = \frac{1}{\pi}\int \frac{dE'[\mathrm{Im}\Sigma^r(E')]}{E - E'}. \tag{2.42}$$

Formally, this constraint maintains the causality of the retarded response functions by shifting their poles to the lower part of the complex energy plane. Physical meaning of this relation is that it guarantees the conservation of states upon establishing contacts between atoms. The considered example illustrates that it is possible to formally treat a system in several ways separating out a certain part as a channel (bridge) and identifying the remaining parts with the contacts (leads). However, after choosing the way to subdivide the original system, one must properly and accurately compute the self-energy terms taking into account the detailed interfacial chemistry and the eigenenergies associated with the possible states on the contacts. Moreover, in subdividing the system, one must bear in mind that an arbitrarily chosen contact may not act as a good one, that is, the one whose properties are nearly independent of the dynamics of the bridge.

Another important property of a good contact is manifested as an absence of correlations between the states on the left and right contact included into the system. Also, a good contact must remain in equilibrium while electrons travel through the system. These inherent properties of the good contacts provide justification for the expression (2.36) which presents the self-energy term $\Sigma^<(E)$ as the sum of independent contributions from the left and right leads. Realistic contacts may

possess the described properties only when there is a profusion of scattering in their bodies. The scattering processes should include dephasing scattering eliminating coherences between the contacts as well as inelastic scattering which helps to keep the contacts in the state of thermal equilibrium. It is worthwhile to emphasize that as the leads shrink in size, the above requirements may cease to be valid, and the expression (2.36) may become unjustified.

2.2 The Green's Function for the Atomic Wire; an Analytical Example

Now, we apply relations presented in the previous section to compute the retarded Green's function G^r for a periodical chain of identical atoms which can be parametrized as hydrogens. We assume that N atoms are included in the chain. The chain ends are put in contact with the source and drain reservoirs which are also imitated by semi-infinite atomic chains. Obviously, this model imitates a MMM junction, and the results described in this section could be used to qualitatively analyze transport properties of such systems.

In the following calculations we start from a tight-binding Hamiltonian for the chain

$$H = H_0 + H_1 \tag{2.43}$$

whose matrix elements between states $|k>$ and $|l>$ corresponding to the kth and lth sites of the chain (the states are supposed to be orthogonal) are given by

$$\begin{aligned} (H_0)_{kl} &= \alpha_k \delta_{kl}, \\ (H_1)_{kl} &= \mathcal{V}_{kl}, \end{aligned} \tag{2.44}$$

where $\mathcal{V}_{kl}$= 0 when $k = l$. The diagonal matrix elements α_k are ionization energies of electrons at sites k, while $\mathcal{V}_{kl} = \mathcal{V}_{lk}$ describes the coupling between kth and lth sites and includes both direct and exchange energy contributions. Also, we assume that the contacts are coupled only to the end atoms of the chain. Then the nonzero matrix elements of the self-energy matrices $\Sigma^r_\beta(E)$ accept the form

$$\left(\Sigma^r_\beta\right)_{ii} = \sum_m \frac{|\tau_{im}|^2}{E - \epsilon_{m\beta} - \sigma_{m\beta}}. \tag{2.45}$$

Here, the index i takes on the values 1 and N for the left and right contacts, respectively. Summation over "m" in Eq. (2.45) is carried out over the contact states with the energies $\epsilon_{m\beta}$, and $\sigma_{m\beta} = \frac{1}{2}\left\{\theta_{m\beta} - i\sqrt{4\gamma^2_{m\beta} - \theta^2_{m\beta}}\right\}$ are the self-energy corrections of the semi-infinite chains attached to the bridge ends [67].

In the expression for $\sigma_{m\beta}$, $\theta_{m\beta} = E - \epsilon_{m\beta}$ and $\gamma_{m\beta}$ are the nearest-neighbor hopping integrals for the contacts. When $E - \epsilon_{m\beta}$ is smaller than $\gamma_{m\beta}$, we have $\sigma_{m\beta} \approx -i\gamma_{m\beta}$. In the opposite limit $\mid E - \epsilon_{m\beta} \mid \gg \gamma_{m\beta}$, this quantity takes on values close to zero.

Due to the presence of self-energy corrections Σ^r_β, the eigenvalues of the effective Hamiltonian (for the atomic wire bridge) include imaginary parts Γ_i which represent broadening of the bridge energy-level E_i originating from the coupling of the bridge to the leads. Assuming that basis functions are orthogonal, we may calculate matrix elements for the retarded Green's function solving the system of linear equations which follows from the expression (2.38):

$$\begin{aligned} &\left\{E - \alpha_k - \left(\Sigma^r_L\right)_{kk}\delta_{k1}\delta_{l1} - \left(\Sigma^r_R\right)_{kk}\delta_{kN}\delta_{lN}\right\}G^r_{kl} \\ &- \sum_{n\neq k} \mathcal{V}_{kn}G^r_{nl} = \delta_{kl} \end{aligned} \tag{2.46}$$

where the indexes k, l take on values corresponding to the chain sites.

We obtain the solution of equations (2.46) by using a graphic technique similar to that described in detail for the nearest neighbors (NN) approximation in an earlier work [211]. However, this technique may be generalized to include also next nearest neighbors (NNN) couplings [51]. This generalization may be useful for it is known that even modest fluctuations of the bridge geometry arising due to its flexibility or some other reasons can result in noticeable changes of transport characteristics of the chain. The NNN couplings are very sensitive to any changes in the geometry of the bridge, and in many practical molecules, they are rather strong, though weaker than NN couplings. Further generalization is also possible, but it significantly enlarges the whole body of calculations. Besides, NNNN and succeeding couplings are mostly very weak and could be neglected without noticeable changes in the results.

First, we present our chain of sites as a graph Δ_{1N}, using the following rules:

1. Any site included in the chain corresponds to a graph vertex.
2. A term $E - \alpha_k$ corresponds to a loop attached to the vertex "k" when $k \neq 1, N$.
3. For $k = 1, N$ the terms attached to the corresponding vertices equal $E - \alpha_1 - \Sigma^r_L$ and $E - \alpha_N - \Sigma^r_R$, respectively.
4. A hopping integral $\mathcal{V}_{kl}$ corresponds to an edge originating at the vertex "k" and ending at the vertex "l".

Taking into account only nearest neighbors (NN) and next nearest neighbor (NNN) couplings, we can introduce a new notation for the nonzero hopping integrals, i.e., $\mathcal{V}_{k,k+1} = \mathcal{V}_{k-1,k} = \beta_k$ and $\mathcal{V}_{k,k+2} = \mathcal{V}_{k-2,k} = \gamma_k$. Within this approximation, Δ_{ij} has the form shown in Fig. 2.1.

Now, we define a cycle as a sequence of graph edges without self-intersections where a successive edge originates at the point where the previous edge ends and the last edge ends where the first one starts. Then we also define the value of the cycle **O** as the product of values of the edges included into the cycle multiplied by the

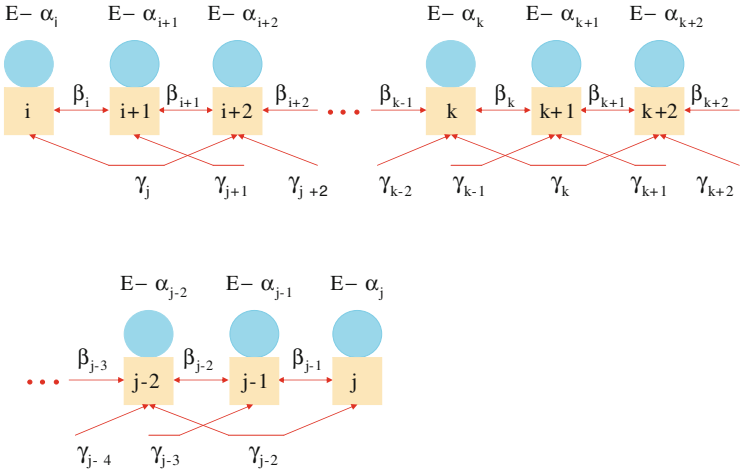


Fig. 2.1 Graph Δ_{ij} representing the chain segment starting at "i"th site and ending at "j"th site

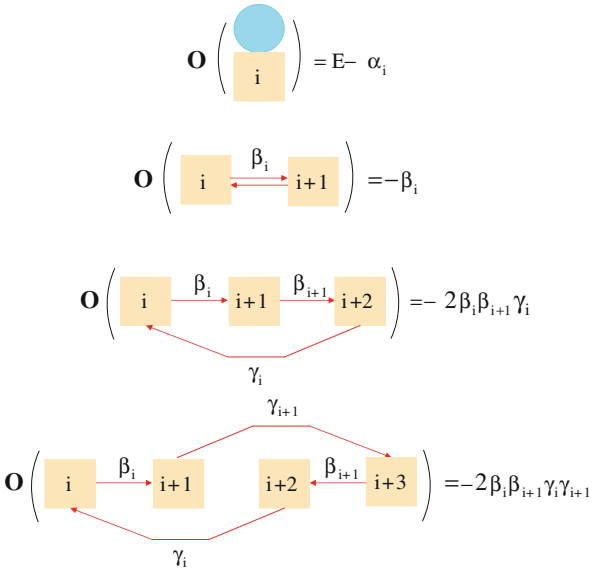


Fig. 2.2 Schematics of cycles taken into account in computation of the Green's function matrix elements within the NNN approximation

number of the edges connecting the first and last sites with a negative sign. When the numbers of the edges associated with the paths from the first site to the last one and back differ, we have to multiply by the maximum number of edges. The values of some simple cycles are given in Fig. 2.2.

We also introduce the definition of a cyclic term which is a set of cycles including all sites of the system. The value of the cyclic term is equal to the product of cyclic

values of these cycles. According to [211], the sum of all possible cyclic terms $\mathbf{O}_r$ gives us the cyclic value $\Theta(\Delta_{ij})$ of the graph Δ_{ij} for our system, namely,

$$\Theta(\Delta_{ij}) = \sum_r (\mathbf{O}_r)_{ij}. \tag{2.47}$$

This quantity $\Theta(\Delta_{ij})$ is the determinant of the system of Dyson equations (2.46), and it is included in the expression for the matrix element G^r_{ij} which can be obtained in the form

$$G^r_{ij} = \sum_\sigma \frac{P^\sigma_{ij}}{\Theta(\Delta_{ij})}. \tag{2.48}$$

Here, the summation over σ is carried out over all possible pathways along the chosen chain, and the value of a pathway P^σ_{ij} has to be calculated as the product of all edges along the pathway. When the pathway includes all vertices of the graph Δ_{ij}, we have

$$\begin{aligned} &P_{ij}(i \longrightarrow i+1 \longrightarrow \cdots \longrightarrow k \\ &\longrightarrow k+1 \cdots \longrightarrow j-1 \longrightarrow j) = \prod_{k=i}^{j-1} \beta_k. \end{aligned} \tag{2.49}$$

When the pathway does not include some vertices, this produces different values for the corresponding P_{ij}. For example, when the electron is being transferred from the site l to the site $l+2$, passing the intermediate site $l+1$, the corresponding factor is equal to $(E-\alpha_{l+1})\gamma_l$. Consequently, we obtain for the pathway which excludes this vertex

$$\begin{aligned} &P_{ij}(i \longrightarrow i+1 \longrightarrow \cdots \longrightarrow l-1 \longrightarrow l \longrightarrow l+2 \\ &\longrightarrow \cdots \longrightarrow j-1 \longrightarrow j) = (E-\alpha_{l+1})\gamma_l \prod_{k=i,k\neq l,l+1}^{j-1} \beta_k. \end{aligned} \tag{2.50}$$

We can easily write the expressions for P_{ij} when the pathway passes more than one vertex. To obtain the corresponding result, we must bear in mind that, within the NNN approximation, omitted vertices cannot be adjacent ones. Suppose that we pass the sites $l+1$ and $m+1$, then

$$\begin{aligned} &P_{ij}(i \longrightarrow i+1 \longrightarrow \cdots \longrightarrow l-1 \longrightarrow l \longrightarrow l+2 \longrightarrow \cdots \\ &\longrightarrow m-1 \longrightarrow m \longrightarrow m+2 \longrightarrow \cdots \longrightarrow j-1 \longrightarrow j) \\ &=(E-\alpha_{l+1})(E-\alpha_{m+1})\gamma_l\gamma_m \prod_{k=i,k\neq l,l+1,k\neq m,m+1}^{j-1} \beta_k. \end{aligned} \tag{2.51}$$

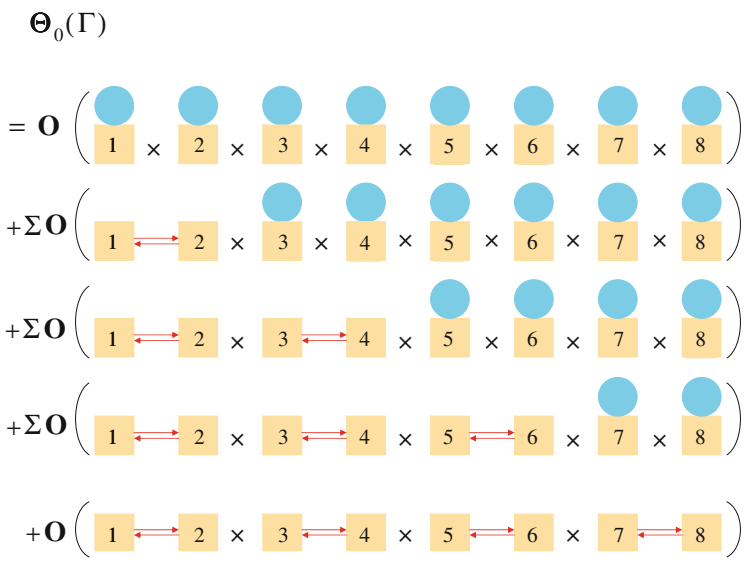


Fig. 2.3 Schematics of computation of $\Theta_0(\Delta)$ within NN approximation for the chain including eight sites

Within the NN approximation, the numerator in the expression for the Green's function G^r_{ij} is factorized as:

$$G^r_{ij} = \frac{1}{\Theta_0(\Delta_{ij})} \prod_{k=i}^{j-1} \beta_k. \tag{2.52}$$

Here, $\Theta_0(\Delta_{ij})$ is the cycle value of the graph calculated within the NN approximation. The method of computing of $\Theta_0(\Delta_{ij})$ is schematically shown in Fig. 2.3.

One may further simplify this result assuming that all hopping parameters β_i and ionization energies for all sites α_i take on the same values ($\beta_i = \beta$, $\alpha_i = E_0$, respectively) and omitting the real parts of the self-energy terms. Then, assuming that the chain includes an odd number of atoms ($N = 2m - 1$), one arrives at the following expression for the matrix element $G^r_{1,2m-1}$:

$$G^r_{1,2m-1}(E) = \frac{4^m \beta^{2(m-1)} \zeta}{(\lambda+\zeta)^{2(m-1)}(\lambda+\zeta+i\Gamma)^2 - (\lambda-\zeta)^{2(m-1)}(\lambda-\zeta+i\Gamma)^2}. \tag{2.53}$$

Here, $\lambda = E_0 - E$, $\zeta = \sqrt{\lambda^2 - 4\beta^2}$, $\Gamma = \Gamma_L + \Gamma_R$. This expression was first derived by Mujica et al. [45] using the method which differs from that described above.

2.3 Electron Transmission and Landauer Expression for the Current Through a MMM Junction

The standard approach to the elastic and phase-coherent transport through metal–molecular junctions is suggested by the Landauer–Buttiker formalism [1]. This formalism was developed in the context of mesoscopic physics. Within this approach, the expression for the current through a phase-coherent conductor connected to the electron reservoirs (source and drain) may be obtained if one calculates the total probability for an electron to travel between two electrodes at a certain tunnel energy E and then integrates the resulting probability over the whole energy range. Following this way one arrives at the well-known Landauer expression for the current:

$$I = \frac{e}{\pi\hbar}\int T(E)[f_L(E) - f_R(E)]dE \tag{2.54}$$

where

$$f_\beta(E) = \left\{1 + \exp\left[(E-\mu_\beta)/kT\right]\right\}^{-1} \tag{2.55}$$

are the Fermi distribution functions for the leads with the electrochemical potentials μ_β and $T(E)$ is the electron transmission function. To clarify the physical meaning of Eq. (2.54), one may rewrite it in the form

$$I = \frac{e}{\pi\hbar}\int T(E)\left\{f_L(E)[1 - f_R(E)] - f_R(E)[1 - f_L(E)]\right\}dE. \tag{2.56}$$

where the integrand is explicitly presented as the difference of two fluxes, one directed from the left to the right and another one flowing in the opposite direction.

The forms of these expressions coincides with Eqs. (1.11) and (1.13) which were derived within a simple model where the bridge was represented by a single orbital. This simplification resulted in the specific form of the electron transmission given by Eq. (1.12). Here, we derive the Landauer formula for the general case of a multilevel bridge. We use the formalism described in the first section. To obtain the expression for the current, one may compute the time rate of the probability density on the bridge. The latter is defined as $\psi^\dagger\psi$ where $\{\psi\}$ is the Schrodinger state vector for the bridge. For a system consisting of a sole electron reservoir and the attached channel, one may write down the following equation of motion [4]:

$$i\hbar\frac{d}{dt}\begin{Bmatrix}\psi\\ \Phi\end{Bmatrix} = \begin{pmatrix}H_C & \tau_R\\ \tau_R^\dagger & H_R - i\eta\end{pmatrix}\begin{Bmatrix}\psi\\ \Phi\end{Bmatrix}. \tag{2.57}$$

Here, we assume for certainty that the right end of the channel is put in contact with the reservoir. As before, the wave function $\{\Phi\}$ includes two terms ($\{\Phi\} =$

$\{\Phi_R + \chi_R\}$), where the second term is corresponding to the part which is reflected back to the channel. As follows from Eq. (2.57):

$$e\frac{d}{dt}(\psi^\dagger\psi) = \frac{e}{i\hbar}\mathrm{Trace}\{\psi^\dagger\tau_R\Phi_R - \Phi_R^\dagger\tau_R^\dagger\psi\} - \frac{e}{i\hbar}\mathrm{Trace}\{\chi_R^\dagger\tau_R^\dagger\psi - \psi^\dagger\tau_R\chi_R\} \equiv I_{\mathrm{in}} - I_{\mathrm{out}}. \tag{2.58}$$

In this expression, the first term gives the electron charge flow into the channel from the reservoir (inflow), whereas the second term corresponds to the charge flow back to the reservoir (outflow). The same expression remains valid if one is considering the current through the contact between the bridge and the right reservoir in a system where two electron reservoirs are linked by the channel (bridge). We remark that all terms on the right side of Eq. (2.58) are matrices and/or vectors, whereas the product $\psi^\dagger\psi$ on the left side of this expression is a scalar quantity. Treating the system with two reservoirs, the inflow term in Eq. (2.58) may be reorganized in the following way:

$$I_{\mathrm{in}} = \frac{e}{i\hbar}\mathrm{Trace}\{\psi^\dagger\tau_R\Phi_R - \Phi_R^\dagger\tau_R^\dagger\psi\} = \frac{e}{\hbar}\mathrm{Trace}\{S_R S_R^\dagger A\} \tag{2.59}$$

where $S_R = \tau_R\Phi_R$ and $A = i(G^r - G^a)$ is the spectral function.

Then one may use the expression (2.28) to obtain

$$I_{\mathrm{in}} = \frac{e}{\hbar}\int\frac{dE}{2\pi}f_R\mathrm{Trace}\{\Gamma_R A\}. \tag{2.60}$$

Similarity, the outflow term I_{out} may be rearranged as follows:

$$I_{\mathrm{out}} = \frac{e}{i\hbar}\mathrm{Trace}\{\psi^\dagger\tau_R g_R^\dagger\tau_R^\dagger\psi - \psi^\dagger\tau_R g_R\tau_R^\dagger\psi\} = \frac{e}{\hbar}\mathrm{Trace}\{\psi\psi^\dagger\Gamma_R\}. \tag{2.61}$$

Using the expression (2.29), one may present I_{out} in the form

$$I_{\mathrm{out}} = \frac{e}{\hbar}\int\frac{dE}{2\pi}\mathrm{Trace}[\Gamma_R G^<]. \tag{2.62}$$

Assuming that electrons flow from the left to the right and combining Eqs. (2.60) and (2.62), one gets

$$I = \frac{e}{\hbar}\int dE\big(\mathrm{Trace}[\Gamma_R G^<] - f_R\mathrm{Trace}[\Gamma_R A]\big). \tag{2.63}$$

Obviously, the electric charge flow through the considered system must remain the same at any part of the latter, so the expression may be treated as the general

expression for the electron current. In the considered case, the energy of the electrons in the channel remains the same (it is equal to the energy E corresponding to the stationary state of the junction introduced in the previous section). Therefore, the electron transport is to be treated as elastic and coherent, and we may employ the expression (2.36) for the self-energy term $\Sigma^<$ in the Keldysh equation which determines the lesser Green's function $G^<$. Also, using the definition (2.37) and the relation

$$(G^a)^{-1} - (G^r)^{-1} = -i\Gamma_L - i\Gamma_R \tag{2.64}$$

we may rewrite the expression for the spectral function as follows:

$$A = G^r \Gamma_L G^a + G^r \Gamma_R G^a. \tag{2.65}$$

Substituting these relations into the expression for electron tunnel current given by Eq. (2.60), we may convert it to the Landauer form (2.54) where the electron transmission $T(E)$ is given by [82]

$$T(E) = \mathrm{Trace}\left[\Gamma_L G^r \Gamma_R G^a\right]. \tag{2.66}$$

Imitating the MMM junction by a simple model where the bridge is represented by a single molecular orbital, one may significantly simplify the expression for the electron transmission. In this case it becomes reduced to the form given by Eq. (1.12).

The Landauer expression (2.54) confirms that a nonzero tunnel current may appear in the junction when the electrochemical potentials of the electrodes μ_L and μ_R differ due to the applied bias voltage and the bridge energy levels are situated between μ_L and μ_R. Otherwise, the difference of the Fermi functions becomes zero (assuming that the thermal broadening of the energy levels on the leads is neglected), and the current through the junction ceases to flow. As mentioned before, the Landauer expression for current (2.54), combined with the expression (2.66) for the electron transmission, correctly describes the coherent and elastic electron transport through MMM junctions. As an example, we present the results for the electron transmission and current calculated for the MMM including a porphyrin-nitrobenzene molecule as a linker (see Fig. 2.4). However, to adequately analyze the effects of electron–electron and electron–phonon interactions, one needs to go beyond the Landauer formula. A consistent approach to inelastic electron transport through molecular junctions and similar mesoscopic systems is provided by the nonequilibrium Green's function formalism [4, 202–204]. To compute the electron current through the junction within this approach, one must solve the system of interconnected equations for electron and phonon Green's functions, such as given in the works [26, 34]. To overcome extreme difficulties which one meets solving these equations, numerous approximate methods were developed. The validity of these approximations is determined by the relations between characteristic energies of the considered system, namely, the molecule-lead coupling parameters

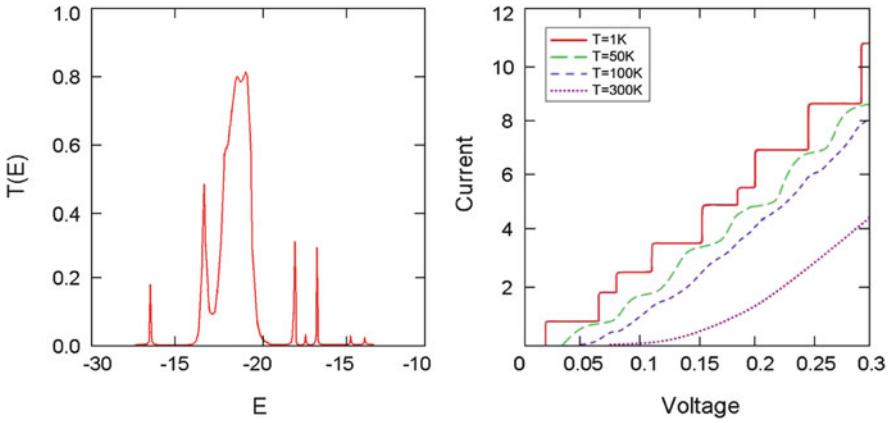


Fig. 2.4 *Left panel*: the calculated electron transmission function through the bridge $T(E)$ within a certain range of energies E (eV). *Right panel*: the calculated current (nA)–voltage (V) characteristic. Calculations are carried out for a porphyrin-nitrobenzene molecule using the Landauer formula [71]. Reprinted with the permission of the American Institute of Physics (AIP)

Γ_β, electron–phonon coupling strengths Λ_{km} and λ_{km} (see Eq. (1.41)), electron charging energy U_0, vibrational modes energies, and the thermal energy $k_{\mathrm{B}}T$ which characterizes the intensity of stochastic fluctuations in the environment. Commonly used approximate computational techniques are described and thoroughly analyzed in the review article [26] and references therein. Nevertheless, these approximations insufficiently simplify the basic NEGF equations for practical molecular junctions which limit the usefulness of the powerful NEGF formalism to relatively simple models for MMMs.

A simple and rather obvious way to generalize the Landauer formula and to make it appropriate for analysis of inelastic transport was suggested by Wingreen and coworkers [205, 206] and used in several later works [207–209]. The modified expression has the form

$$I = \frac{e}{\pi\hbar}\int dE_i dE_f T(E_i, E_f) \times \left\{ f_L(E_i)\left[1 - f_R(E_f)\right] - f_R(E_i)\left[1 - f_L(E_f)\right] \right\} \tag{2.67}$$

where E_i, E_f are the initial and final energies of the electron traveling through the junction and the factor $T(E_i, E_f)dE_f$ corresponds to the probability that an electron starting its travel with the energy E_i is transmitted through the system possessing the energy E_{F}. The expression (2.67) agrees with the Landauer formula (2.54), when the transport is elastic. In this case $T(E_i, E_f) = T(E_i)\delta(E_i - E_f)$ ($T(E_i)$ being the elastic electron transmission. Substituting this expression into Eq. (2.67), one easily converts it to the form given by Eq. (2.54).

There exist some difficulties with the justification of the approximation (2.67). Datta showed [210] that cancellation of some terms, which happens in the course of derivation of the Landauer formula for the elastic current, does not occur while considering inelastic transport. Also, employing the full NEGF formalism, it was demonstrated that approximation (2.67) could be derived if one disregards terms describing the effect of back reflection from the leads and assumes the phonon bath to remain in the state of thermal equilibrium [26]. However, the omission of the back reflection terms is impossible to validate basing on an expansion in powers of some small parameter, and Eq. (2.67) cannot be interpreted as a first term of such expansion. Therefore, it is hard to estimate the error in the transport calculations which appears when we employ approximation (2.67). Nevertheless, this approximation has some advantages for it can be used regardless of the electron–phonon interactions strength, as it was indicated in the works [207, 208] or up to high-order perturbation theory terms in the electron–phonon interactions [212, 213]. One may further improve approximation (2.67) by taking into account that the transmission function may depend on the applied bias voltage V. The effect of the bias voltage which is negligible at small values of V may become noticeable as V increases. The expression (2.67) is not the simplest approximation for the inelastic current. There exists an especially simple approximation, which preserves the Landauer form of expression for the current including inelastic effects into the expression for the electron transmission function. This approximation is based on the phenomenological Buttiker model for quantum transport. It will be considered in the next section.

2.4 Electron Transport Through a Junction as a Multichannel Scattering Problem

An important advantage of the phenomenological model for the incoherent/inelastic quantum transport proposed by Buttiker [72] is that this model could be easily adapted to analyze various inelastic effects in the electron transport through molecules (and some other mesoscopic systems) avoiding complicated and time-consuming advanced methods such as based on the nonequilibrium Green's functions formalism. First, we present the Buttiker model for a simple junction including two electrodes linked by a single-site molecular bridge. The bridge is attached to a dissipative electron reservoir, as shown in Fig. 2.5a. Electrons tunnel from the electrodes to the bridge and vice versa via the channels 1 and 2. While on the bridge, an electron could be scattered into the channels 3 and 4 with a certain probability ϵ. Such electron arrives at the reservoir where it undergoes inelastic scattering accompanied by phase breaking, and then, the reservoir reemits it back to the channels 3 and 4 with the same probability. So, within the Buttiker model, the electron transport through the junction is treated as the combination of tunnelings through the barriers separating the molecule from the electrodes and interaction

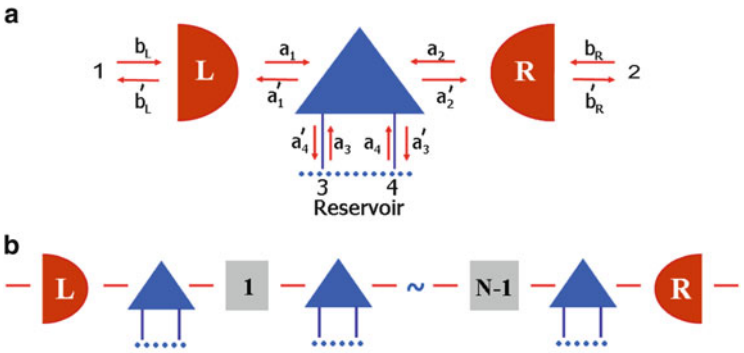


Fig. 2.5 Schematics of a junction including a single-site (**a**) and multisite (**b**) bridge linking the left and right electrodes. The triangles represent scatterers coupling the bridge sites with the electron reservoirs, and the squares indicate potential barriers separating the adjacent sites on the bridge

with the reservoir coupled to the bridge site. The key parameter of the model is the probability ϵ which is closely related to the coupling strength between the bridge site and the reservoir. When $\epsilon = 0$ the reservoir is detached from the bridge, and the electron transport is completely coherent and elastic. Within the opposite limit $(\epsilon = 1)$, electrons are necessarily scattered into the reservoir which results in the overall phase randomization and inelastic transport.

Within the Buttiker model, the particle fluxes outgoing from the junctions J_i' could be presented as linear combinations of the incoming fluxes J_k where the indexes i, k label the channels for the transport $1 \leq i \leq k \leq 4$.

$$J_i' = \sum_k T_{ik} J_k. \tag{2.68}$$

The coefficients T_{ik} in these linear equations are matrix elements of the transmission matrix which are related to the elements of the scattering matrix S, namely, $T_{ik} = |S_{ik}|^2$. The matrix S expresses outgoing wave amplitudes b_L', b_R', a_3', a_4' in terms of the incident ones b_L, b_R, a_3, a_4. To provide the charge conservation in the system, the net current in the channels 3 and 4 linking the system with the dephasing reservoir must be zero, so we may write

$$J_3 + J_4 - J_3' - J_4' = 0. \tag{2.69}$$

The transmission for the quantum transport could be defined as the ratio of the particle flux outgoing from the system and that one incoming to the latter. Solving Eqs. (2.68) and (2.69), we obtain

$$T(E) = \frac{J_2'}{J_1} = T_{21} + \frac{K_1 \cdot K_2}{2R} \tag{2.70}$$

where:

$$K_1 = T_{31} + T_{41};$$
$$K_2 = T_{23} + T_{24};$$
$$R = T_{33} + T_{44} + T_{43} + T_{34}. \tag{2.71}$$

The scatterer coupled to the bridge is described by the 4×4 scattering matrix s relating wave amplitudes $a_1',\ a_2',\ a_3',\ a_4'$ to the wave amplitudes $a_1,\ a_2,\ a_3,\ a_4$:

$$s = \begin{pmatrix} 0 & \sqrt{1-\epsilon} & \sqrt{\epsilon} & 0 \\ \sqrt{1-\epsilon} & 0 & 0 & \sqrt{\epsilon} \\ \sqrt{\epsilon} & 0 & 0 & -\sqrt{1-\epsilon} \\ 0 & \sqrt{\epsilon} & -\sqrt{1-\epsilon} & 0 \end{pmatrix}. \tag{2.72}$$

Also, the electron tunneling through a single barrier is described by the transmission and reflection amplitudes (t and r, respectively). These are the matrix elements of a 2×2 matrix:

$$s_{\mathrm{el}} = \begin{pmatrix} r & t \\ t & r \end{pmatrix}. \tag{2.73}$$

Combining Eqs. (2.72) and (2.73), we arrive at the expression for the scattering matrix S.

For the junction including the single-site bridge, the matrix S has the form [70, 72]

$$S = \frac{1}{Z} \begin{pmatrix} r_L + \alpha^2 r_R & \alpha t_L t_R & \beta t_L & \alpha\beta t_L r_R \\ \alpha t_L t_R & r_R + \alpha^2 r_L & \alpha\beta r_L t_R & \beta t_R \\ \beta t_L & \alpha\beta r_L t_R & \beta^2 r_L & \alpha r_L r_R - \alpha \\ \alpha\beta t_L r_R & \beta t_R & \alpha r_L r_R - \alpha & \beta^2 r_R \end{pmatrix}. \tag{2.74}$$

Here, $Z = 1 - \alpha^2 r_L r_R,\ \alpha = \sqrt{1-\epsilon},\ \beta = \sqrt{\epsilon}$ and $r_{L,R}$ and $t_{L,R}$ are the reflection and transmission coefficients for the barriers separating the bridge from the left and right electrode, respectively. The model may be generalized to include an arbitrary number of the bridge sites that is to describe a practical molecule presented as a set of energy levels. Here, however, we follow [45, 70, 109], and we mimic a molecular bridge linking two electrodes as a periodical chain of identical sites. The schematics of the adopted model is shown in Fig. 2.5b. The first and the last sites in the chain are attached to the leads and remain fixed. All sites are put in contact with electron reservoirs. We assume that the parameter ϵ may accept different values for scatterers attached to different bridge sites. So, we may characterize the system including N bridge sites with the set of parameters ϵ_j $(j = 1, \ldots, N)$.

To simplify the following calculations of the electron transmission we conjecture that an electron could be injected into the system shown in Fig. 2.5b and/or leave from there solely via $2N + 2$ channels indicated in the figure. Then the scattering matrix $S^{(N-1)}$ corresponding to the system including $N - 1$ $(N > 1)$ bridge sites has dimensions $2N \times 2N$. This matrix relates wave amplitudes outgoing from the system $b'_L,\ b'_R,\ a'_3,\ \ldots, a'_{2N-2}$ to the incoming amplitudes $b_L,\ b_R,\ a_3,\ \ldots, a_{2N-2}$. Here, the wave amplitudes $a_k,'\ a_k$ $(k = 3, 4, \ldots, 2N-2)$ are associated with the channels connecting the sites with the dissipative reservoirs.

Now, we may derive recursive expressions bringing into correlation matrix elements of the scattering matrices $S^{(N-1)}$ and $S^{(N)}$. For certainty, we put an extra site at the right end of the bridge chain. Then we split the whole system shown in Fig. 2.5b in two subsystems. The first subsystem consists of the left lead and the bridge including $N - 1$ sites, and the second one includes the extra site and the right lead. To proceed we introduce the matrix $\tilde{S}^{(N-1)}$ closely related to the matrix $S^{(N-1)}$. One may obtain expressions for matrix elements of $\tilde{S}^{(N-1)}$ replacing the reflection and transmission coefficients for the right lead r_R, t_R in the matrix elements of $S^{(N-1)}$ by the corresponding characteristics for the barrier separating $(N - 1)$th and Nth sites. The second subsystem could be considered as a junction with a single-site bridge and an absolutely transparent left lead $(t_L = 1,\ r_L = 0)$. So, the scattering matrix for this subsystem has the 4×4 dimensions, and it could be written in the form

$$\theta^{(N)} = \begin{pmatrix} \alpha_N^2 r_R & \alpha_N t_R & \beta_N & \alpha_N \beta_N r_R \\ \alpha_N t_R & r_R & 0 & \beta_N t_R \\ \beta_N & 0 & 0 & -\alpha_N \\ \alpha_N \beta_N r_R & \beta_N & -\alpha_N & \beta_N^2 r_R \end{pmatrix}. \tag{2.75}$$

Here, the parameters α_N, β_N characterize the coupling of the Nth site to the electron reservoir attached to the latter. The matrix $\tilde{S}^{(N-1)}$ relates the wave amplitudes $b'_L,\ b'_{N-1},\ a'_3, \ldots,\ a'_{2N-2}$ to the wave amplitudes $b_L,\ b_{N-1},\ a_3, \ldots,$ a_{2N-2} where the outgoing (b'_{N-1}) and incoming (b_{N-1}) wave amplitudes at the right end of the first subsystem appear. At the same time, b'_{N-1} corresponds to the wave entering the second subsystem from the left, whereas b_{N-1} is associated with the wave outgoing from there. Accordingly, the matrix $\theta^{(N)}$ relates $b_{N-1},\ b'_R,\ a'_{2N-1},\ a'_{2N}$ to $b'_{N-1},\ b_R,\ a_{2N-1},\ a_{2N}$. Excluding the wave amplitudes $b'_{N-1},\ b_{N-1}$ associated with the electron transport inside the system, we arrive at the desired recurrence formulas [109]

$$S_{\text{in}}^{(N)} = \theta_{\text{in}}^{(N)} + \theta_{i1}^{(N)} \tilde{S}_{22}^{(N-1)} \theta_{1n}^{(N)} / Z_N, \quad (i, n = 2,\ 2N + 1,\ 2N + 2), \tag{2.76}$$

$$S_{kl}^{(N)} = \tilde{S}_{kl}^{(N-1)} + \theta_{11}^{(N)} \tilde{S}_{k2}^{(N-1)} \tilde{S}_{2l}^{(N-1)} / Z_N, \quad (k, l = 1, 3, 4, \ldots, 2N - 1, 2N) \tag{2.77}$$

$$S_{ik}^{(N)} = \theta_{i1}^{(N)} \tilde{S}_{2k}^{(N-1)} / Z_N, \tag{2.78}$$

where $Z_N = 1 - \theta_{11}^{(N)} \tilde{S}_{22}^{(N-1)}$. Similar expressions were derived in the earlier work [70] to analyze long-range electron transfer reactions in macromolecules.

As before, the incoming particle fluxes are related to outgoing ones by the system of linear equations of the form (2.68), which now includes $2N + 2$ equations ($1 \leq i \leq k \leq 2N + 2$. Also, the charge conservation is required in the channels connecting every single site on the bridge with the corresponding dissipative reservoir. Solving this system we obtain the following result for the electron transmission [70]:

$$T(E) = T_{21} + \sum_{i,j=1}^{N-1} K_i^{(2)} (W^{-1})_{ij} K_j^{(1)} \tag{2.79}$$

where $1 \leq i, j \leq N - 1$;

$$\begin{aligned} K_i^{(1)} &= T_{2i+1,1} + T_{2i+2,1}; \\ K_i^{(2)} &= T_{2;2i+1} + T_{2,2i+2}; \end{aligned} \tag{2.80}$$

and W^{-1} is the matrix inversed with respect to the $(N - 1) \times (N - 1)$ matrix W, whose matrix elements are given by

$$W_{ij} = (2 - R_{ii})\delta_{ij} - \tilde{T}_{ij}(1 - \delta_{ij}), \tag{2.81}$$

In this expression we used the following denotations:

$$\begin{aligned} R_{ii} &= T_{2i+1,2i+1} + T_{2i+2,2i+2} + T_{2i+2,2i+1} + T_{2i+1,2i+2}, \\ \tilde{T}_{ij} &= T_{2i+1,2j+1} + T_{2i+1,2j+2} + T_{2i+2,2j+1} + T_{2i+2,2j+2}. \end{aligned} \tag{2.82}$$

Returning to the case of a single-site bridge and assuming for certainty that the charge flows from the left to the right, one may obtain

$$T(E) = \frac{t_L(E) t_R(E)(1 + \alpha^2)\big[1 - \alpha^2\big(1 - t_L(E) t_R(E)\big)\big]}{2\big[1 + \alpha^2\big(1 - t_L(E) t_R(E)\big)\big]^2}. \tag{2.83}$$

For elastic transport ($\alpha = 1$) the electron transmission accepts the form

$$T(E) = \frac{t_L^2 t_R^2}{(2 - t_L t_R)^2}. \tag{2.84}$$

At the same time, the elastic transmission is described by Eq. (1.12). Equating these two expressions, one finds

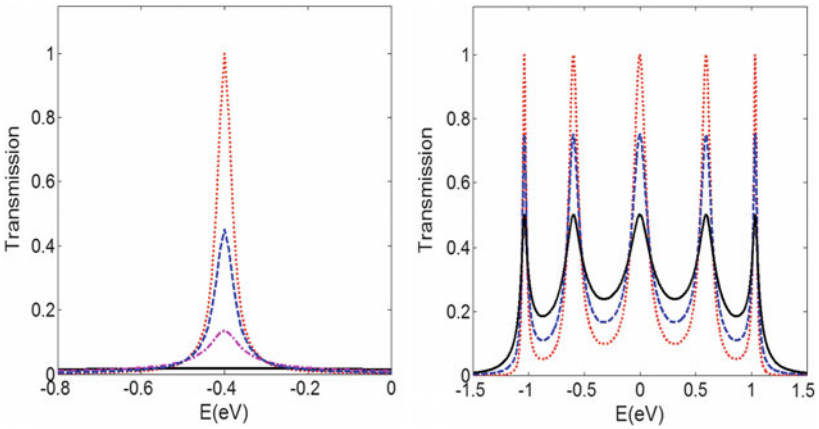


Fig. 2.6 Electron transmission through a junction including a single-site (*left panel*) and multisite (*right panel*) bridge. The curves are plotted assuming $\Gamma_L = \Gamma_R = 0.1\,\mathrm{eV}$, $T = 30\,\mathrm{K}$, $E_0 = -0.5\,\mathrm{eV}$, (*left panel*) and $E_0 = 0$ (*right panel*). The parameter ϵ takes on values $0.0,\ 0.1,\ 0.3,\ 0.7$ (*left panel*). In plotting the curves in the right panel it was assumed that there are five electronic states on the bridge, $\epsilon_i = 0$ $(i \neq 3)$, and $\epsilon_3 = 0$ (*dash-dotted line*) 0.5 (*dashed line*) and 1.0 (*solid line*) (after [52, 109]). Reprinted with the permission of the AIP

$$t_L t_R = \frac{2g}{1+g} \tag{2.85}$$

where

$$g = \sqrt{\frac{\Gamma_L \Gamma_R}{(E-E_0)^2 + (\Gamma/2)^2}}. \tag{2.86}$$

So, the expression (2.84) may be converted to the form [51]:

$$T(E) = \frac{g(E)(1+\alpha^2)\left[g(E)(1+\alpha^2)+1-\alpha^2\right]}{2\left[g(E)(1-\alpha^2)+1+\alpha^2\right]^2}. \tag{2.87}$$

Now, the electron transmission strongly depends on the scattering probability ϵ. As shown in Fig. 2.6, in the case of elastic transport $(\epsilon = 0)$, the transmission exhibits a sharp peak at $E = E_0$ which gives a step-like shape to the volt-ampere curve, as was discussed in the previous chapter. In the presence of dissipation the peak gets eroded. When the value ϵ approaches 1, the I–V curve becomes linear, corroborating the Ohmic law for the inelastic transport. For a multisite bridge, the electron transmission depends on the whole set of the dissipative parameters ϵ_j, as well as on the characteristics of the tunneling barriers separating the sites. For instance, within the model adopted in [109], the bridge chain included an odd number of sites $(N = 2m-1)$, and only the single site in the middle was assumed

to be attached to a dissipative reservoir ($\epsilon_j = 0$ for $j \neq m$). The energy dependence of the electron transmission calculated using this model is shown in the right panel of Fig. 2.6.

As expected, instead of a single maximum we now get a set of peaks. The number of peaks equals to the number of sites in the chain. These peaks correspond to the energy levels of the molecular bridge within the adopted model. The coupling of the chain ends to the leads affects the minimum values of transmission. As the coupling strengthens, the transmission minimum values increase. When the reservoir is attached to the middle site of the chain ($\epsilon_m > 0$), it causes a decrease in the range of the transmission variations. However, even within the strong dephasing/inelastic limit ($\epsilon_m = 1$), the transmission peaks remain well distinguishable for multisite molecular bridges, whereas the peak in the transmission through the single-site bridge appears to be completely washed out under such conditions. This discrepancy could be explained as an effect of elastic and coherent electron tunneling through the left and right halves of the bridge chain, which affects the transport characteristics even in the presence of a strong dissipation at the middle site. The single dissipative reservoir is not sufficient to completely suppress these effects. To fully wash out the peaks in the transmission one needs to attach dissipative reservoirs to all bridge sites and to assume $\epsilon_j = 1$ for $j = 1, \ldots, 2m - 1$.

Despite of its extreme simplicity, Eq. (2.87) for the electron transmission through a single-site molecular bridge may be of practical use. For example, it was successfully employed to explain some transport characteristics of conducting polymer (doped polyaniline–polyethylene (PANi) oxides) nanofibers, observed in experiments [214]. Starting from their discovery, conducting polymers have undergone intense research. These materials are significant mostly due to various possible applications in fabrication of nanodevices for polymer-based devices should have advantages of low cost and flexible, controlled chemistry [215]. Also, there are some unsolved problems concerning the physical nature of charge-transfer mechanisms in conducting polymers, making them interesting subjects for fundamental research [95, 96]. Conducting chemically doped polymers are known to be very inhomogeneous. In some regions polymer chains are disordered, forming an amorphous poorly conducting substance. In other regions the polymer chains are ordered and densely packed [216, 217]. These regions behave as metallic-like grains embedded in a disordered amorphous environment. This gives grounds to apply the model of a granular metal [218] to describe such materials. Prigodin and Epstein [219] suggested that the grain-to-grain transport in conducting polymers mostly occurs due to the resonance tunneling of electrons. The latter is provided by intermediate states on the chains connecting the grains. Applying this approach to the charge transport in conducting polymers, it was shown that the results are consistent with those obtained in transport experiments on individual PANi nanofibers.

The transmission coefficient for the electron resonance tunneling is determined with the probability of finding the resonance state. This probability T is estimated as $T \sim \exp(-L/\xi)$, where L is the average distance between the interacting grains

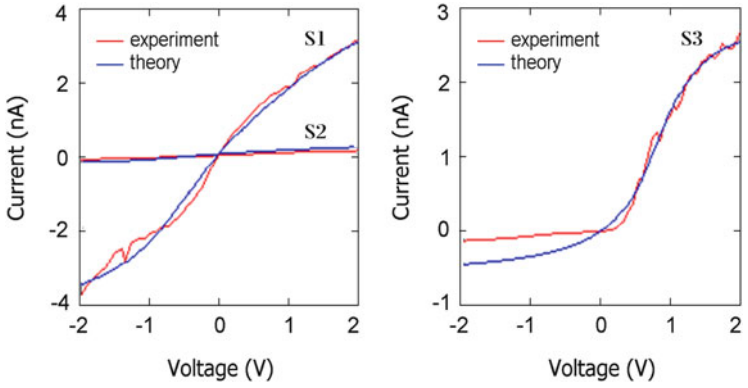


Fig. 2.7 Calculated and experimental current (nA)–voltage (V) characteristics for PANi-PEO nanofibers $T = 300\,\mathrm{K}$ (after [221]). Reprinted with the permission of the American Physical Society (APS)

and ξ is the localization length for electrons [219]. The tunneling probability takes on values which are small compared to unity but much greater than the transmission probability for sequential hoppings along the chains, $T_h \sim \exp(-2L/\xi)$ [220]. The probability for existence of a resonance state at a certain chain is rather low, so only a few out of the whole set of the chains connecting two grains are participating in the process of intergrain electron transport. Therefore, one could assume that any two adjacent metallic-like domains are connected by a single chain providing an intermediate state for the resonance tunneling. So, one may treat the adjacent islands as leads linked by single-site bridges. Realistic PANi nanofibers have diameters in the range ~ 20–$100\,\mathrm{nm}$ and lengths of the order of several micrometers. This is significantly greater than typical for conducting polymers sizes of metal-like grains and intergrain distances, which take on values $\sim 5\,\mathrm{nm}$ [215]. Therefore, one may treat a nanofiber as a set of parallel channels for the tunneling current, any channel being a sequence of metallic domains connected by resonance chains. The total current in the fiber is the sum of the contributions from all these channels. Also, the voltage V applied across the whole fiber is a sum of contributions δV from sequential pairs of grains along a single channel. One may assume as the first approximation that $\delta V \sim VL/L_f$, where L_f is the fiber length. Under these assumptions, the Landauer expression for the current (2.54) combined with the expression for the electron transmission (2.87) may be used to compute the current in the fibers. Such computations were carried out in [221], and a good agreement with the experiments [214] was obtained, as illustrated in Fig. 2.7.

Within the Buttiker's model, ϵ is introduced as a phenomenological parameter whose relation to the microscopic characteristics of dephasing/dissipative processes affecting electron transport through molecular junctions remains uncertain. To further advance this model one should find out how to express ϵ in terms of the relevant microscopic characteristics for various transport mechanisms. This should open the way to make a link between the phenomenological Buttiker model and

NEGF. Such attempt was carried out in [52, 222] where the effect of stochastic nuclear motion on the electron transport through molecules was analyzed.

2.5 Nonequilibrium Green's Functions Formalism

In the present section, a brief description of the nonequilibrium Green's function formalism is given which generalizes and extends the simplified approach presented in the previous sections of this chapter. The NEGF provides a powerful and systematic framework for computing optical and transport properties of various open many-body systems including metal–molecule junctions. Within the more frequently used NEGF version, the primary objects employed to describe and analyze transport properties of MMM junctions and other mesoscopic systems are Green's functions on the Keldysh contour [4, 93, 202–205], their projections to the real-time axis, and the corresponding self-energy parts. The Green's functions matrix elements may be expressed in terms of field operators. For instance, the electron Green's function matrix elements $G_{ij}(\tau, \tau')$ are defined as

$$G_{ij}(\tau, \tau') = -i\big\langle T_c c_i(\tau) c_j^\dagger(\tau')\big\rangle. \tag{2.88}$$

where $\big\langle \dots \big\rangle$ stands for averaging, τ is the Keldysh time starting and ending at $-\infty$, T_c is the contour time-ordering operator, and $c_i(\tau), c_j^\dagger(\tau)$ are the annihilation and creation operators for the electrons taken at the respective times τ and τ'. The crucial impact of electron–phonon interactions on the characteristics of electron transport makes it necessary to analyze the combined electron–phonon system coherently evolving according to the corresponding many-body Hamiltonian. The latter includes terms describing the electronic subsystem, the vibrational (phonon) subsystem, and the electron–phonon interactions. Consequently, one may introduce the phonon Green's functions of the form

$$D_{lk}^{(1)}(\tau, \tau') = -i\big\langle T_c A_l(\tau) A_k^\dagger(\tau')\big\rangle, \tag{2.89}$$

$$D_{mk}^{(2)}(\tau, \tau') = -i\big\langle T_c B_m(\tau) B_k^\dagger(\tau')\big\rangle, \tag{2.90}$$

which correspond to the vibrational and thermal phonons, respectively. Different versions of NEGF were developed basing on another time-ordering prescriptions known as "the single time" and the "physical" representations [223–225]. A Liouville space formulation of NEGF was presented in [226–228].

Now, we consider a metal–molecule junction assuming that the molecule is coupled to a set of vibrational phonons. For this system, the Green's functions defined by Eqs. (2.88) and (2.89) satisfy the integral equations given below [25]:

$$G_{ij}(\tau,\tau') = G^0_{ij}(\tau,\tau') + \sum_{k,l}\int d\tau_1 \int d\tau_2 G^0_{ik}(\tau,\tau_1)\Sigma_{kl}(\tau_1,\tau_2)G_{lj}(\tau_2,\tau'), \tag{2.91}$$

$$D^{(1)}_{lk}(\tau,\tau') = D^{(10)}_{lk}(\tau,\tau') + \sum_{m,n}\int d\tau_1 \int d\tau_2 D^{(10)}_{lm}(\tau,\tau_1)\Pi_{mn}(\tau_1,\tau_2)D^{(1)}_{nk}(\tau_2,\tau'). \tag{2.92}$$

In these equations, the integration over τ_1, τ_2 is carried out over the Keldysh contour; the Green's functions $G^0(\tau,\tau')$ and $D^{(10)}(\tau,\tau')$ are associated with the molecule detached from the leads and phonons and to the system of vibrational phonons decoupled from the electron system, respectively. The terms $\sum(\tau_1,\tau_2)$ and $\Pi(\tau_1,\tau_2)$ represent the electron and phonon self-energies. If necessary, a Dyson-type equation similar to Eqs. (2.91) and (2.92) may be written out for the Green's function $D^{(2)}(\tau,\tau')$ as well.

Restricting oneself with the consideration of steady-state processes, one may project the Green's functions onto the real-time axis. Then one may use the fact that under steady-state conditions, all two-time quantities actually depend only on differences in times, so one may turn to Fourier transformed functions in the energy space $(t - t' \to E)$. The relevant projections are retarded (r), advanced (a), less $(<)$, and greater $(>)$ Green's functions discussed in the first section of this chapter. Now, the retarded electron Green's function Fourier transform is introduced by the relation

$$G^r_{ij}(E) \equiv \left\langle\left\langle c_i, c_j^\dagger \right\rangle\right\rangle = -i\int_0^\infty \left\langle \left\{ c_i(t), c_j^\dagger \right\} \right\rangle \exp[i(E+i\eta)t]dt \tag{2.93}$$

where curly brackets denote the anticommutator and η is a positive infinitesimal parameter. The advanced electron Green's function is a Hermitian conjugate of the retarded one: $G^a(E) = [G^r(E)]^\dagger$. As for the functions $G^>, G^<$, they are determined by Keldysh equations. In matrix form the lesser electron Green's function $G^<$ satisfies equation (2.35). Similar equation could be written for the greater Green's function $G^>$, namely,

$$G^>(E) = G^r(E)\Sigma^>(E)G^a(E). \tag{2.94}$$

Also, Eq. (2.91) could be reduced to the standard Dyson equation for the retarded Green's function and the equivalent equation for its advanced counterpart. Similar equations may be written for the phonon Green's functions.

As discussed above, the significance of Green's functions and self-energies for the transport theory is based on the fact that they could be used to calculate important

observable transport characteristics. For example, the relaxation rates for electrons $\Gamma(E)$ and phonons $\gamma(E)$ have the form

$$\Gamma(E) = i[\Sigma^r(E) - \Sigma^a(E)];$$
$$\gamma(E) = i[\Pi^r(E) - \Pi^a(E)] \tag{2.95}$$

where $\Pi^{r,a}(E)$ are the retarded and advanced phonon self-energies. Also, the molecular spectral function describing the electron density of states is proportional to the difference of the retarded and advanced Green's functions, as given by Eq. (2.26), and the current flowing through the junction has the form [93, 229, 230]

$$I = \frac{e}{\hbar}\sum_{\beta}\int \frac{dE}{2\pi}\mathrm{Trace}\left[\Sigma^{<}_{\beta}(E)G^{>}(E) - \Sigma^{>}_{\beta}(E)G^{<}(E)\right]. \tag{2.96}$$

Here, as before, the relevant Green's functions and self-energy terms are matrices and must be treated as such. In general, the expressions for self-energies include contributions from all kinds of interactions occurring in the system. To simplify the forms of these terms the non-crossing approximation [231] is often used. Within this approximation, it is assumed that the molecule independently interacts with the leads and the environment (in the considered case with phonons). Correspondingly, the self-energies are presented as sums including terms associated with various kinds of interactions (see, e.g., [25, 26]). For instance, one may write

$$\Sigma^{r,a}(E) = \Sigma^{r,a}_{L}(E) + \Sigma^{r,a}_{R}(E) + \Sigma^{(1)r,a}_{\mathrm{ph}}(E) + \Sigma^{(2)r,a}_{\mathrm{ph}}(E) \tag{2.97}$$

where two first terms correspond to the couplings of the molecule to the leads and two last terms represent the effects of electron–phonon interactions.

The terms $\Sigma^{r,a}_{\beta}(E)$ may be obtained basing on the expressions (2.19) for the retarded Green's functions for the contacts. They have the form

$$\Sigma^{r}_{\beta} = \Sigma^{a}_{\beta} \equiv \Sigma_{0\beta}, \tag{2.98}$$

$$\Sigma^{ij}_{0\beta}(E) = \sum_{r,\sigma}\frac{\tau^{*}_{ir\beta\sigma}\tau_{jr\beta\sigma}}{E - \epsilon_{r\beta\sigma} + i\eta}. \tag{2.99}$$

Imaginary parts of the $\Sigma^{ij}_{0\beta}$ determine matrix elements of the matrices Γ_{β} which describe broadening of the molecular levels due to the coupling of the molecule to the leads:

$$\Gamma^{ij}_{\beta}(E) = \pi\sum_{r,\sigma}\tau^{*}_{ir\beta\sigma}\tau_{jr\beta\sigma}\delta(E - \epsilon_{r\beta\sigma}). \tag{2.100}$$

Also, assuming that electron–electron interactions on the molecule do not affect its coupling to the leads, we may write out the following expressions for the matrices $\Sigma^<$ and $\Sigma^>$ [4, 25]:

$$(\Sigma_\beta^<)^{ij} = i f_\beta(E)\Gamma_\beta^{ij}(E), \tag{2.101}$$

$$(\Sigma_\beta^>)^{ij} = -i\left\{1 - f_\beta(E)\right\}\Gamma_\beta^{ij}(E) \tag{2.102}$$

where $f_\beta(E)$ is the Fermi distribution function for the lead β and the matrix elements $\Gamma_\beta^{ij}(E)$ are given by Eq. (2.100). Within the often used wide-band approximation for the leads, Γ_β^{ij} become independent of energy E. We remark that the expression (2.99) for $\Sigma^<$ agrees with the previous result (2.36) which was obtained within the simplified approach.

Assuming that the transport through the junction is elastic and using Eqs. (2.35) and (2.96), one may rearrange the expression (2.96) for the current through the junction as follows:

$$I = \frac{e}{\pi\hbar}\int dE \mathrm{Trace}\left\{\Sigma_L^<(E)G^r(E)\left[\Sigma_L^>(E) + \Sigma_R^>(E)\right]G^a(E) - \Sigma_R^>(E)G^r(E)\left[\Sigma_L^<(E) + \Sigma_R^<(E)\right]G^a(E)\right\}. \tag{2.103}$$

Then, substituting into this formula the expressions (2.101) and (2.102) for the self-energy terms $\Sigma_\beta^<$ and $\Sigma_\beta^>$, one may reduce the expression (2.103) to the Landauer form given by Eqs. (2.54) and (2.66).

Putting aside the effect of electron–phonon interactions on the electron transport through molecular junctions (which is justified at low temperatures and in the absence of molecular vibrations), one may analytically calculate the electron Green's functions and then compute the current through the junction. This approach is often used in studies of diverse phenomena occurring due to electron–electron interactions on the molecular bridges such as the Coulomb blockade and/or the Kondo maximum in the conduction [34, 35, 86–90]. Here, we illustrate this by deriving the expression for the retarded electron Green's function by means of the commonly used technique based on the Heisenberg equations of motion for the electron creation and annihilation operators [86]. We mimic the molecular bridge in the considered junction by a single spin-degenerated level, so the bridge Hamiltonian H_M takes on the form given by Eq. (1.31), and the terms describing the molecule-lead couplings have the form

$$H_T = \sum_{r,\beta,\sigma}\tau_{r\beta\sigma}^* c_{r\beta\sigma}^\dagger c_\sigma + H.C. \tag{2.104}$$

The equation of motion for the retarded Green's function for the bridge $G_\sigma^r(E) \equiv \left\langle\left\langle c_\sigma; c_\sigma^\dagger\right\rangle\right\rangle$ reads

$$
\begin{aligned}
&(E - E_0 + i\eta)\langle\langle c_\sigma; c_\sigma^\dagger\rangle\rangle \\
&= 1 + \sum_{r,\beta} \tau_{r\beta,\sigma}\langle\langle c_{r\beta\sigma}; c_\sigma^\dagger\rangle\rangle \\
&\quad + U_0\langle\langle n_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle. \qquad (2.105)
\end{aligned}
$$

Here, $n_{-\sigma} \equiv c_{-\sigma}^\dagger c_{-\sigma}$, and $\langle\langle c_{r\beta\sigma}; c_\sigma^\dagger\rangle\rangle$ obeys the equation

$$
(E - \epsilon_{r\beta\sigma} + i\eta)\langle\langle c_{r\beta\sigma}; c_\sigma^\dagger\rangle\rangle = \tau_{r\beta\sigma}^*\langle\langle c_\sigma; c_\sigma^\dagger\rangle\rangle. \qquad (2.106)
$$

Substituting this expression into (2.105), we get

$$
(E - E_0 - \Sigma_{0\sigma})\langle\langle c_\sigma; c_\sigma^\dagger\rangle\rangle = 1 + U_0\langle\langle n_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle. \qquad (2.107)
$$

The self-energy part $\Sigma_{0\sigma}$ is given by Eq. (2.99) where the indices i, j are omitted in accordance with the chosen model for the bridge. The equation of motion for the four-operator function $\langle\langle n_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle$ includes higher-order averages. Omitting them we write out

$$
\begin{aligned}
&(E - E_0 - U_0 + i\eta)\langle\langle n_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle \\
&= \langle n_{-\sigma}\rangle \\
&\quad + \sum_{r,\beta} \big(\tau_{r\beta\sigma}\langle\langle c_{r\beta\sigma}n_{-\sigma}; c_\sigma^\dagger\rangle\rangle \\
&\quad + \tau_{r\beta;-\sigma}\langle\langle c_{-\sigma}^\dagger c_{r\beta;-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle \\
&\quad - \tau_{r\beta;-\sigma}^*\langle\langle c_{r\beta;-\sigma}c_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle\big). \qquad (2.108)
\end{aligned}
$$

To proceed we must write equations for the averages inserted in the right side of Eq. (2.108). We get

$$
\begin{aligned}
&(E - \epsilon_{r\beta\sigma} + i\eta)\langle\langle c_{r\beta\sigma}n_{-\sigma}; c_\sigma^\dagger\rangle\rangle \\
&= \tau_{r\beta\sigma}^*\langle\langle n_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle \\
&\quad + \sum_{r'\beta} \big(\tau_{r'\beta;-\sigma}\langle\langle c_{r\beta\sigma}c_{-\sigma}^\dagger c_{r'\beta;-\sigma}; c_\sigma^\dagger\rangle\rangle \\
&\quad - \tau_{r'\beta;-\sigma}^*\langle\langle c_{r'\beta-\sigma}c_{-\sigma}c_{r\beta;\sigma}; c_\sigma^\dagger\rangle\rangle\big), \qquad (2.109)
\end{aligned}
$$

$$
\begin{aligned}
&(E - \epsilon_{r\beta;-\sigma} + i\eta)\langle\langle c_{-\sigma}^\dagger c_{r\beta;-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle \\
&= \tau_{r\beta;-\sigma}^*\langle\langle n_{-\sigma}c_\sigma; c_\sigma^\dagger\rangle\rangle
\end{aligned}
$$

$$- \sum_{r'\beta} \left(\tau_{r'\beta-\sigma} \left\langle \left\langle c^{\dagger}_{r'\beta;-\sigma} c_{r\beta;-\sigma} c_{\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle \right.$$
$$\left. + \tau_{r'\beta\sigma} \left\langle \left\langle c^{\dagger}_{-\sigma} c_{r\beta;-\sigma} c_{r'\beta\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle \right), \tag{2.110}$$

$$\begin{aligned} &(E - 2E_0 - U_0 + \epsilon_{r\beta;-\sigma} + i\eta) \left\langle \left\langle c^{\dagger}_{r\beta;-\sigma} c_{-\sigma} c_{\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle \\ &= - \tau_{r\beta;-\sigma} \left\langle \left\langle n_{-\sigma} c_{\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle \\ &\quad + \sum_{r'\beta} \left(\tau_{r'\beta\sigma} \left\langle \left\langle c^{\dagger}_{r'\beta;-\sigma} c_{-\sigma} c_{r\beta\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle \right. \\ &\quad \left. - \tau_{r'\beta;-\sigma} \left\langle \left\langle c^{\dagger}_{r\beta;-\sigma} c_{\sigma} c_{r'\beta;-\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle \right). \end{aligned} \tag{2.111}$$

Writing out these equations (2.109)–(2.111), we neglected averages like $\left\langle c^{\dagger}_{\sigma} c_{r\beta\sigma} \right\rangle$ including a creation/annihilation operator for the molecule combined with the annihilation/creation operator for the left/right leads. Such averages are omitted in further calculations as well. Now, we decouple four-operator averages included in the sums over "r'" in these equations following the scheme [4, 91]:

$$\left\langle \left\langle A^{\dagger} BC; D^{\dagger} \right\rangle \right\rangle \approx \left\langle A^{\dagger} B \right\rangle \left\langle \left\langle C; D^{\dagger} \right\rangle \right\rangle - \left\langle A^{\dagger} C \right\rangle \left\langle \left\langle B; D^{\dagger} \right\rangle \right\rangle. \tag{2.112}$$

Also, we use the approximation

$$\left\langle c^{\dagger}_{r\beta\sigma} c_{r'\beta\sigma} \right\rangle = \left\langle c_{r'\beta\sigma} c^{\dagger}_{r\beta\sigma} \right\rangle = \delta_{rr'} f^{\beta}_{r\sigma} \tag{2.113}$$

where $f^{\beta}_{r\sigma}$ is the Fermi distribution function corresponding to the energy $\epsilon_{r\beta\sigma}$. As a result, the Green's functions included in the right-hand side of Eq. (2.108) get expressed in terms of $\left\langle \left\langle n_{-\sigma} c_{\sigma}; c^{+}_{\sigma} \right\rangle \right\rangle$ and $\left\langle \left\langle c_{\sigma}; c^{+}_{\sigma} \right\rangle \right\rangle$. Substituting these expressions into Eq. (2.108), we obtain

$$\left\langle \left\langle n_{-\sigma} c_{\sigma}; c^{+}_{\sigma} \right\rangle \right\rangle = \frac{\left\langle n_{-\sigma} \right\rangle + \Sigma_{1\sigma} \left\langle \left\langle c_{\sigma}; c^{\dagger}_{\sigma} \right\rangle \right\rangle}{E - E_0 - U_0 - \Sigma^{\sigma}_{02}}. \tag{2.114}$$

Here, self-energy parts $\Sigma_{1\sigma}, \Sigma_{2\sigma}, \Sigma^{\sigma}_{02}$ are given by

$$\begin{aligned} \Sigma_{1\sigma} &= \sum_{r\beta} |\tau_{r\beta,-\sigma}|^2 f^{\beta}_{r,-\sigma} \\ &\quad \times \left\{ \frac{1}{E - 2E_0 - U_0 + \epsilon_{r\beta,-\sigma} + i\eta} + \frac{1}{E - \epsilon_{r\beta,-\sigma} + i\eta} \right\}, \\ \Sigma_{2\sigma} &= \sum_{r\beta} |\tau_{r\beta,-\sigma}|^2 \end{aligned} \tag{2.115}$$

$$\times \left\{ \frac{1}{E - 2E_0 - U_0 + \epsilon_{r\beta,-\sigma} + i\eta} + \frac{1}{E - \epsilon_{r\beta,-\sigma} + i\eta} \right\}, \tag{2.116}$$

$$\Sigma_{02}^{\sigma} = \Sigma_{0\sigma} + \Sigma_{2\sigma}. \tag{2.117}$$

To arrive at the resulting expression for the electron Green's function $G_{\sigma}^{r} \equiv \left\langle\left\langle c_{\sigma}; c_{\sigma}^{\dagger} \right\rangle\right\rangle$, we substitute Eq. (2.114) into Eq. (2.107). We have

$$G_{\sigma}^{r}(E) = \frac{E - E_0 - \Sigma_{02}^{\sigma} - U_0(1 - \langle n_{-\sigma} \rangle)}{(E - E_0 - \Sigma_{0\sigma})(E - E_0 - U_0 - \Sigma_{02}^{\sigma}) + U_0\Sigma_{1\sigma}}. \tag{2.118}$$

This expression was first derived by Meir et al. [86], and it was repeatedly used in theoretical studies of the Coulomb blockade and Kondo peak ever since.

The above-mentioned non-crossing approximation does not provide the decoupling of the Keldysh and Dyson equations for the electron and phonon subsystems. The equations remain interconnected, which creates significant computational difficulties, calling for development of suitable approximate schemes for evaluating the relevant Green's functions. The commonly used computational techniques are described and analyzed in detail in the review paper [26], and we do not discuss them in the present work. Nevertheless, we consider it necessary to introduce a certain expression for the self-energy terms $\Sigma_{\mathrm{ph}}(E)$ which appear in the expressions for the electrons Green's functions due to electron–phonon interactions. Accordingly, we derive approximate expressions for these terms following [4, 5]. We start from the Hamiltonian describing the electron–phonon system which is written in the form

$$H = \sum_{k} E_k c_k^{\dagger} c_k + \sum_{l} \hbar\Omega_l a_l^{\dagger} a_l + \sum_{k,l} \Lambda_{kl} A_l c_k^{\dagger} c_k. \tag{2.119}$$

Here, as in the previous expressions (1.40) and (1.41), Ω_l and Λ_{kl} are the frequencies of the phonon modes and electron–phonon coupling constants, respectively, and E_k correspond to the eigenenergies of the electron system. We choose basis functions in a multiparticle electron–phonon Hilbert space as direct products of state vectors for the electron and phonon subsystems. Employing this basis we may write the Hamiltonian matrix in the following way:

$$\begin{bmatrix} \cdots & \epsilon_{N-1}^{k} & \Lambda_{kl}\sqrt{N_l} & \cdots & \cdots \\ \cdots & \Lambda_{kl}\sqrt{N_l} & \epsilon_{N}^{k} & \Lambda_{kl}\sqrt{N_l+1} & \cdots \\ \cdots & \cdots & \Lambda_{kl}\sqrt{N_l+1} & \epsilon_{N+1}^{k} & \cdots \end{bmatrix} \tag{2.120}$$

where $\epsilon_N^k = E_k + N_l\hbar\Omega_l$ and N_l is the number of phonons with such energy which is determined by the Bose–Einstein distribution function for the phonons with the energy $\hbar\Omega_l$: $N_l = \{\exp[\hbar\Omega_l/k_{\mathrm{B}}T] - 1\}^{-1}$. Comparing the explicitly presented part of the Hamiltonian matrix (2.119) with the Hamiltonian matrix (2.16), one may

conclude that the two resemble each other. On these grounds one may consider the subspace containing N_l phonons as an open system which is put in contact with the $(N_l - 1)$ and $(N_l + 1)$ phonon subspaces just like the channel is connected with the source and drain contacts [4]. As was discussed before, the effect of the source and/or drain contact is represented by the self-energy matrix of the form $\tau^\dagger g \tau$ (or its Hermitian conjugate) whose imaginary part represents the broadening of the energy levels in the channel (electron relaxation rates). As follows from comparison of matrices (2.16) and (2.120), the analogs of the matrices τ_β and $\tau_\beta^\dagger$ are expressed in terms of the sandwiching terms $\Lambda_{kl}\sqrt{N_l}$ and $\Lambda_{kl}\sqrt{N_l + 1}$. These terms could be identified with τ_β within a simplest model for a junction with a single-site bridge where both leads are represented by single sites as well. In general, one may treat Λ as a nondiagonal matrix with matrix elements Λ_{km}. Combining Λ terms in the expressions for τ matrices, one may generate the deformation potential L, which is a fourth-rank tensor [5]:

$$L_{ijkl} = \Lambda_{ij}\Lambda_{kl}^\dagger. \tag{2.121}$$

Assuming that the electron interacts with a sole vibrational mode with the frequency Ω, one could reduce the deformation potential to a second-rank tensor: $\Lambda_{ij} = \Lambda_i \Lambda_j^\dagger$. Holding on this assumption and following [5], one may write

$$G^<(E) = G^r(E)\Sigma_{\text{ph}}^<(E)G^a(E). \tag{2.122}$$

Here, the self-energy term $\Sigma_{\text{ph}}^<(E)G^a(E)$ satisfies the equation

$$\Sigma_{\text{ph}}^<(E) = L(\Omega) \otimes \big[N(\Omega)G^<(E - \hbar\Omega) + (N(\Omega) + 1)G^>(E + \hbar\Omega)\big]. \tag{2.123}$$

In Eq. (2.123), $N(\Omega)$ is the Bose–Einstein distribution function for the phonons with the energy $\hbar\Omega$, and the sign $\otimes$ indicates element by element multiplication as opposed to the ordinary matrix multiplication $[(A \otimes B)_{ij} = a_{ij}b_{ij}]$. As usual, Eqs. (2.122) and (2.123) may be complemented by the similar equations including the greater self-energy term $\Sigma_{\text{ph}}^>(E)$. In these equations the self-energy terms arising due to phonons $\Sigma_{\text{ph}}^<(E)$, $\Sigma_{\text{ph}}^>(E)$ are interconnected with the electrons Green's functions. Therefore, Eqs. (2.122) and (2.123) are to be solved together employing a self-consistent computational procedure. Also, these equations may be generalized to cover the case when the phonons with diverse energies participate in the interactions with electrons. This could be carried out by multiplying the right side of Eq. (2.122) by the phonon density of states and integrating the obtained expression over the phonon frequencies.

The broadening of the bridge energy levels originating from the electron–phonon interaction is given by

$$\Gamma_{\rm ph}(E) = i\big[\Sigma^r_{\rm ph}(E) - \Sigma^a_{\rm ph}(E)\big] \equiv \Sigma^<_{\rm ph}(E) + \Sigma^>_{\rm ph}(E). \tag{2.124}$$

Starting form this expression, one may find the imaginary part of $\Sigma^r_{\rm ph}(E)$ and then compute its real part using the Kramers–Kronig relations.

Electron-phonon interactions contribute to the current flowing through the junction. Here, we present the expression for the relevant contribution ΔI originating from the electron–phonon interactions. This expression was derived employing the model of a single-site bridge for the molecular linker in the junction [24, 25]. It has the form

$$\begin{aligned}\Delta I =& \frac{2e}{\hbar}\int dE \frac{\Gamma_L\Gamma_R}{\Gamma^2} D(E)\Gamma_{\rm ph}(E) \\ &\times \frac{(E-\tilde{E}_0)^2 - (\Gamma/2)^2}{(E-\tilde{E}_0)^2 + (\Gamma/2)^2}\left[f_L(E) - f_R(E)\right].\end{aligned} \tag{2.125}$$

Here, $\tilde{E}_0$ is the energy of the bridge level renormalized due to the electron–phonon interactions, $\Gamma = \Gamma_L + \Gamma_R + \Gamma_{\rm ph}(E)$; $D(E)$ is the electron density of states on the molecule, which (in the case of a single-level bridge) is given by Eq. (1.1), and the imaginary part of the phonon self-energy $\Sigma_{\rm ph}(E)$ is given by

$$\begin{aligned}\Gamma_{\rm ph}(E) = 2\pi\Lambda^2 \int_0^\infty & d\omega \rho_{\rm ph}(\omega) \\ &\times \Big\{\big[1+N(\omega)\big]D(E-\hbar\omega)\big[1-n(E-\hbar\omega)\big] \\ &+ N(\omega)D(E+\hbar\omega)\big[1-n(E+\hbar\omega)\big] \\ &+ N(\omega)D(E-\hbar\omega)n(E-\hbar\omega) \\ &+ \big[1+N(\omega)\big]D(E+\hbar\omega)n(E+\hbar\omega)\Big\}\end{aligned} \tag{2.126}$$

where the constant Λ describes the electron–phonon coupling strength, $\rho_{\rm ph}(\omega)$ is the phonon density of states,

$$n(E) = \frac{1}{2\pi}{\rm Im}G^<(E) \tag{2.127}$$

is the electron occupation number, and $N(\omega) = \big\{\exp[\hbar\omega/kT] - 1\big\}^{-1}$. The expressions (2.125) and (2.126) will be used in further analysis of the inelastic transport through molecular junctions.

2.6 Rate Equations

Presently, there exist numerous works where the electron transport through a MMM junction is analyzed using the system of kinetic equations for occupation probabilities of the molecular bridge. This approach was first suggested by Beenakker [74] and Averin and coworkers [75] to analyze the effects of electron–electron interactions on the electron transport through molecular junctions. The proposed approach is justified when the junction is weakly coupled, that is, the quantities Γ_β are significantly smaller than the electron charging energy U_0 and the spacings between the molecular orbitals involved in the transport. In general, the occupation probabilities for various states of the system determined by the relevant set of quantum numbers ν are given by diagonal elements of the density matrix of this system ρ. Time evolution of the density matrix is described by the Liouville equation:

$$i\hbar\frac{\partial\rho}{\partial t} = [H, \rho]. \tag{2.128}$$

Considering a weakly coupled junction, this equation may be transformed to a set of equations for the diagonal elements $\rho_{\nu\nu} \equiv P_\nu$:

$$\frac{dP_\nu}{dt} = -\sum_{\nu'}(W_{\nu\nu'}P_\nu - W_{\nu'\nu}P_{\nu'}). \tag{2.129}$$

Here, $W_{\nu\nu'}$ is the transition rate between the $|\nu\rangle$ and $|\nu'\rangle$ states of the system. The first term on the right-hand side of Eqs. (2.129), which are also known as "master equations," describes the transitions from the state $|\nu\rangle$ to other states of the system, whereas the second term corresponds to the transitions to the state $|\nu\rangle$ from the remaining states. The set of rate equations (2.129) is to be taken along with the normalization equation for the occupation probabilities

$$\sum_\nu P_\nu = 1. \tag{2.130}$$

In analyzing the electron transport through the molecular junctions, it is useful to consider the states $|\nu\rangle$ as many-body states $|N, i\rangle$ with N electrons on the molecule and the total energy $E_i(N)$. It is the commonly used assumption that the states involved in the transport process differ by a single electron. Then one may keep in Eq. (2.129) only those transition rates which correspond to the relevant transitions between the leads and the molecule. As a result, Eq. (2.129) accepts the form

$$\frac{dP_{N,i}}{dt} = -\sum_j \left(W_{N,i;N\pm1,j}P_{N,i} - W_{N\pm1,j;N,i}P_{N\pm1,j}\right) \tag{2.131}$$

where the rates $W_{N,i;N\pm1,j}$ and $W_{N\pm1,j;N,i}$ include contributions associated with the transport between the left/right lead and the molecule. For instance,

$$W_{N,i;N\pm1,j} = \sum_{\beta} W^{\beta}_{N,i;N\pm1,j} \qquad (\beta \in L, R). \tag{2.132}$$

Tunnel currents through both (left and right) barriers separating the leads from the molecular bridge must remain equal to provide the charge conservation. Therefore, the expression for the current through the junction may be written including only the transition rates associated with the chosen lead. Choosing the left lead, one obtains [83]

$$I_L = I = \pm e \sum_{ij} \left(W^{L}_{N,i;N\pm1,j} P_{N,i} - W^{L}_{N\pm1,j;N,i} P_{N\pm1,j} \right) \tag{2.133}$$

where the transitions corresponding to removing of an electron by the lead contribute with the negative sign. The transition rates included in Eq. (2.133) are usually presented as products of "unconditional" rates $\Gamma_{\beta}(N)$ determined by the coupling of the molecule to the leads and the occupancy factors for the electron states on the leads. We may write [81]

$$\begin{aligned} W^{\beta}_{N-1,i;N,j} &= \frac{1}{\hbar} \Gamma^{ij}_{\beta}(N) \left[1 - f\left(\epsilon_{ij}(N) - \mu_{\beta} \right) \right], \\ W^{\beta}_{N,i;N-1,j} &= \frac{1}{\hbar} \Gamma^{ij}_{\beta}(N) f\left(\epsilon_{ij}(N) - \mu_{\beta} \right). \end{aligned} \tag{2.134}$$

Here, $\epsilon_{ij}(N) = E_i(N) - E_j(N-1)$, and the leads occupancy factors are expressed in terms of the Fermi distribution functions $f(\epsilon - \mu_{\beta})$.

The sets of rate equations, similar to those presented above, were derived and used in numerous works where various aspects of the electron transport through molecular junctions were analyzed, setting aside the effects of electron–phonon interactions (see, e.g., [81, 83, 85, 147, 232]). For instance, such equations were successfully used to describe the effects of Coulomb and spin blockade observed in molecular junctions and some other similar systems. However, as already mentioned, these equations could be applied to analyze electron transport only in weakly coupled junctions. When the coupling of the molecule to the leads is strong, so that the coupling energies Γ_{β} have the same order of magnitude as some other relevant energies (e.g., the charging energy U_0), the rate equations fail to provide an adequate description of the junction transport characteristics. For instance, occurrence of the Kondo peak in the zero bias voltage conductance cannot be described following this way.

The rate ("master") equations were and still are employed to analyze the effects of the electron–vibron interactions on the electron transport through molecular junctions in the situations when these interactions are sufficiently strong [22, 103, 233–245]. Actually, the approach based on the kinetic equations is shown to be

justified when the typical time spent by the traveling electron on the molecule is significantly longer than characteristic times of the decoherence processes arising due to electron–electron interactions and/or stochastic nuclear fluctuations in the environment. Usually, these conditions are satisfied for weakly coupled junctions.

One of the early attempts to analyze the effect of the electron–vibron interactions on the electron transport basing on the rate equations was undertaken by Gorelik and coworkers [234]. They discussed a specific bridge-shuttle mechanism for the electron conduction through the molecular bridge considering the latter as a classical harmonic oscillator. It was assumed that the center of mass of the vibrating bridge is moving forth and back in between the leads. As a result, the widths of tunneling barriers separating the leads from the bridge vary in accordance with the variations of the bridge center of mass position x. The effect of the electronic transport on the bridge vibrations was expressed through the bridge charging, so that the bridge motion was described by the equation

$$m\frac{d^2x}{dt^2} = -kx - \gamma\frac{dx}{dt} + \alpha q \tag{2.135}$$

where m and k are the bridge mass and force constant, γ is the damping coefficient, and the parameter α characterizes the bridge charging. The charge q is determined by the probability $P_n(t)$ to have the excess of n electrons on the bridge at a certain instant t. Within this model, the rate equations accept the form

$$\begin{aligned}\frac{dP_n}{dt} =& e^{-x/\lambda}W(n-1,n)P_{n-1} + e^{x/\lambda}W(n+1,n)P_{n+1} \\ &- \left[e^{-x/\lambda}W(n,n+1) + e^{x/\lambda}W(n,n-1)\right]P_n.\end{aligned} \tag{2.136}$$

These equations were used to find the probabilities $P_n(t)$ which depend on the bridge position in the junction. Similar models were employed in several other works (see, e.g., [235–237]). However, in the majority of presently existing research articles, the molecular vibrations are treated within the quantum mechanical approach.

When electron–phonon interactions are taken into consideration, the transition rates in the kinetic equations are associated with the transitions between different states of the many-body electron–phonon system. These states are characterized by certain numbers of electrons and phonons. Assuming that the molecule is represented by a single spin-degenerated level coupled to a vibrational mode with the frequency Ω, one may write down the equations for probabilities P_m^N of the molecular bridge being in a state with N electrons and m phonons as follows [22]:

$$\frac{dP_m^N}{dt} = -\sum_{\beta,m'}\left(W^{\beta}_{N,m;N\pm1,m'}P_m^N + W^{\beta}_{N\pm1,m';N,m}P_{m'}^{N\pm1}\right) \tag{2.137}$$

where β denotes the left/right lead in the junction, and the expressions for the rates have the form

$$
\begin{aligned}
W^{\beta}_{N,m;N-1,m'} &= \frac{\Gamma_\beta}{\hbar}\,\gamma_{mm'} f\big[\hbar\Omega(m'-m)+U_0(N-1)-\mu_\beta\big],\\
W^{\beta}_{N,m;N+1,m'} &= \frac{\Gamma_\beta}{\hbar}\,\gamma_{mm'}\big\{1-f\big[\hbar\Omega(m'-m)+U_0N-\mu_\beta\big]\big\},\\
W^{\beta}_{N-1,m';N,m} &= \frac{\Gamma_\beta}{\hbar}\,\gamma_{m'm}\big\{1-f\big[\hbar\Omega(m-m')+U_0(N-1)-\mu_\beta\big]\big\},\\
W^{\beta}_{N+1,m';N,m} &= \frac{\Gamma_\beta}{\hbar}\,\gamma_{m'm} f\big[\hbar\Omega(m-m')+U_0N-\mu_\beta\big].
\end{aligned}
\tag{2.138}
$$

Here, $\dfrac{1}{\hbar}\Gamma_\beta\gamma_{mm'}$ represents the transition rate involving hopping an electron from the bridge to the lead β and changing the phonon occupancy from m (measured with respect to the ground state of the bridge with the electron occupancy N) to m' (measured relative to the bridge ground state with the electron occupancy $N-1$). In Eq. (2.138) the terms proportional to the charging energy U_0 appear due to electron–electron interactions on the bridge. The matrix elements $\gamma_{mm'}$ introduced in Eq. (2.138) are given by the expressions [22, 103]

$$
\gamma_{mm'} = \begin{cases}
\exp\left(-\dfrac{\tilde{\Lambda}^2}{2}\right)(-\tilde{\Lambda})^{m'-m}\sqrt{\dfrac{m'!}{m!}}\,L_m^{m'-m}(\tilde{\Lambda}^2) & \text{for} \quad m'>m\\[2ex]
\exp\left(-\dfrac{\tilde{\Lambda}^2}{2}\right)(-\tilde{\Lambda})^{m-m'}\sqrt{\dfrac{m!}{m'!}}\,L_{m'}^{m-m'}(\tilde{\Lambda}^2) & \text{for} \quad m'<m
\end{cases}
\tag{2.139}
$$

where $L_q^p(x)$ are the associated Laguerre polynomials and the dimensionless constant $\tilde{\Lambda}=\Lambda/\hbar\Omega$ determines the electron–phonon coupling strength. The model adopted in [22] may be generalized to describe a multilevel molecular bridge. Such generalization was carried out by Siddique and coworkers [103].

The rate equations (2.137) include the rates for transitions where the number of electrons on the bridge changes. The electrons enter or leave the molecular bridge by emitting and/or absorbing phonons associated with the vibrational mode. Also, the bridge vibrations produce electrostatic potential fluctuations in the environment, which result in the environment-mediated transitions between the vibrational states. These transitions are not accompanied with changes in the electron occupation. The relation between the transition rates corresponding to the phonon emission and absorption processes mediated by the thermal environment is given by the Boltzmann's ratio [103, 238]:

$$
\begin{aligned}
W^{\beta}_{N,m;N,m+1} &= \exp\left[-\frac{\hbar\Omega}{k_{\mathrm{B}}T}\right] W^{\beta}_{N,m+1;N,m}\\
&= K(m)\frac{\Omega}{\exp\left[\hbar\Omega/k_{\mathrm{B}}T\right]-1}.
\end{aligned}
\tag{2.140}
$$

Here, $K(m)$ is the dimensionless coefficient. As follows from this result, extra terms associated with nonzero transition rates described by Eq. (2.140) are to be included into the kinetic equations (2.137).

A different form of "master" equations invoking the transitions between the states of a many-body electron–phonon system was suggested and used in the works of Koch, von Oppen, and coworkers [239–242]. They presented the kinetic equations for the joint probabilities P_m^N as follows:

$$\frac{dP_m^N}{dt} = -\sum_{N'\neq N,m',\beta}\left(W^{\beta}_{N,m;N',m'}P_m^N - W^{\beta}_{N',m';N,m}P_{m'}^{N'}\right) - \frac{1}{\tau}\left(P_m^N - P_m^{\mathrm{eq}}\sum_{m'}P_{m'}^N\right). \tag{2.141}$$

Here, the last term on the right describes the direct vibrational relaxation towards the equilibrium phonon distribution P_m^{eq}. It is given by the Bose–Einstein distribution function $N(\Omega)$ where again Ω is the frequency of the vibrational mode coupled to electrons. The relaxation process is characterized by a single relaxation time τ.

To understand the effect of the direct vibrational relaxation on the phonon distribution, one must keep in mind that typical speeds of diffusion and drift processes in the phonon space strongly depend on the electron–phonon coupling strength. These processes slow down when the parameter $\tilde{\Lambda}$ characterizing the electron–phonon coupling strength decreases. It was shown [239] that as $\tilde{\Lambda}$ decreases, it reaches a crossover value $\tilde{\Lambda}_0$. When $\tilde{\Lambda} \gg \tilde{\Lambda}_0$, the vibrational diffusion is limited by the phonon drift which originates from the asymmetry between vibrational excitations and de-excitations. In the opposite limit $\tilde{\Lambda} \ll \tilde{\Lambda}_0$, the predominating limiting process is the direct vibrational relaxation leading to a decrease in the width of the phonon distribution. The crossover coupling parameter $\tilde{\Lambda}_0$ depends on the relaxation time τ but only moderately. The $\tilde{\Lambda}_0$ versus τ dependence is close to the power law with an exponent accepting values 1/4–1/3 [239]. When the electron–phonon coupling is strong ($\tilde{\Lambda} > 1$), this leads to exponentially small transition rates provided that the temperature is low ($k_{\mathrm{B}}T \ll \hbar\Omega$) and the bias voltage is small ($|e|V < \tilde{\Lambda}^2\hbar\Omega$). This results in the suppression of the current through the junction at low bias voltage arising due to electron–phonon interactions and termed Franck–Condon blockade [240]. We further discuss this issue in Chap. 4. Also, in the limit of strong electron–electron interactions ($U_0 \to \infty$) and at low temperatures, the expressions for the transition rates may be factorized as [239, 241]

$$W^{\beta}_{N,m;N',m'} = (1+\delta_{N',1})\,\delta_{|N-N'|,1}w_{mm'} \tag{2.142}$$

where $\delta_{nn'}$ is the Kronecker symbol and $w_{mm'}$ is the phonon factor. Using this result one may factorize the expressions for the occupational probabilities $P_m^N = P^N P_m$ and derive the rate equations for the phonons, as was shown in [239].

Finally, we note that the rate (master) equations were proven to be very useful, especially while analyzing transport through the molecular junctions with strong electron–electron and electron–phonon interactions and weak coupling of the linker to the leads. The general NEGF formalism should yield the rate equations as an appropriate limiting case thus establishing the agreement between these two approaches. Promising advances in this direction are offered (see, e.g., [229]), but the issue still needs further consideration.

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