Chapter 2

Theoretical framework in the weak-tunneling limit

In this Chapter, we develop the theoretical tools required for the study of transport in the Anderson-Holstein Hamiltonian in the limit of weak tunneling, $\Gamma \ll k_B T$, $\hbar\omega_0$. This regime allows for a perturbative treatment of the tunneling Hamiltonian H_{T}, and we start with a discussion of the systematic perturbation theory in H_{T}. The main input for the transport calculation consists of the transition rates induced by electron tunneling. In the following sections, we explain how to obtain these rates and how they enter the rate equations that determine the occupation probabilities of the system. Subsequently, we show how the rate-equations formalism can be employed for the computation of the stationary current and the current shot noise. This formalism forms the basis for most of the following Chapters, and in its development we closely follow pertinent references such as Refs. [45, 60, 84].

2.1 Transition rates

Regarding the tunneling Hamiltonian H_T as a perturbation, one can proceed to calculate rates for transitions $|\, i\,\rangle \to |\, f\,\rangle$ by an expansion of the T-matrix and applying Fermi's golden rule (see e.g. [85]),

$$\gamma_{if} = \frac{2\pi}{\hbar} \left|\langle\, f \,|\, T \,|\, i\,\rangle\right|^2 \delta(E_i - E_f) = \frac{2\pi}{\hbar} \left|\langle\, f \,|\, H_T + H_T G_0 H_T + \cdots |\, i\,\rangle\right|^2 \delta(E_i - E_f). \quad (2.1)$$

Here, E_i and E_f denote the energies of the initial and final states $|\, i\,\rangle$ and $|\, f\,\rangle$, and $G_0 = [E_i - H_{\mathrm{mol}} - H_{\mathrm{leads}} + i\eta]^{-1}$ is the free retarded Green's function. Generally, the initial and final states still involve degrees of freedom of the leads. These are eliminated by integrating over the energies of particles and holes generated in the Fermi seas during the process, taking into account thermal occupations by f or $1 - f$ factors, where $f(\epsilon) = (e^{\beta\epsilon} + 1)^{-1}$ is the Fermi function. Thus, one arrives at rates W which are labelled by molecular degrees of freedom only. [Of course, the rates will still include a label for the participating junction(s).]

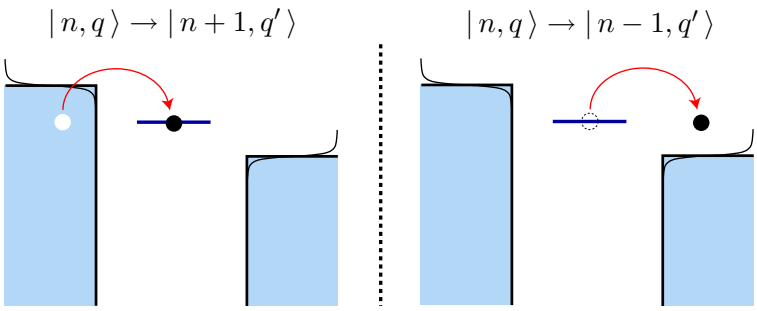

Figure 2.1: Sequential-tunneling processes, here schematically exemplified for tunneling onto and off of the molecule via the left and right junction, respectively. The "kets" $|\,n,q\,\rangle$ denote the state of the molecule, specifying the electronic occupation n and the number of vibrational excitations q.

2.1.1 Sequential tunneling and Franck-Condon matrix elements

To lowest order in H_T, one obtains *sequential tunneling* processes, which transfer one electron from a lead onto the molecule or vice versa, see Fig. 2.1. For example, the rate for a process changing the charge number of the molecule from $n = 0$ to $n = 1$ by tunneling across junction a, and simultaneously changing the number of excited phonons from q to q', is given by

$$W^{01}_{qq';\,a} = s(0,1)\frac{\Gamma_a}{\hbar}\left|M_{qq'}\right|^2 f_a(\varepsilon_d + [q'-q]\hbar\omega_0). \tag{2.2}$$

Here, $f_a(\epsilon) = f(\epsilon - \mu_a)$ denotes the Fermi function for lead a. Our choice of jointly treating the spin-up and the spin-down states as the singly-occupied state $n = 1$ requires the inclusion of a spin factor s. The spin factor definitions $s(0,1) \equiv 2$ and $s(1,0) \equiv 1$ reflect the fact that rates for processes $n = 0 \to 1$ are twice as large as rates for $n = 1 \to 0$ due to the spin-degeneracy of the state $n = 1$. The symbol $M_{qq'}$ denotes the Franck-Condon (FC) matrix element for a phonon transition $q \to q'$. This matrix element is given by the overlap of two harmonic oscillator wavefunctions ϕ_q and $\phi_{q'}$, spatially displaced by the distance $\Delta x = \sqrt{2}\lambda\ell_{\rm osc}$. Introducing $q = \min\{q_1, q_2\}$ and $Q = \max\{q_1, q_2\}$, the matrix elements read

$$M_{q_1q_2} = \int_{-\infty}^{\infty} dx\, \phi^*_{q_1}(x+\Delta x)\phi_{q_2}(x) = [\mathrm{sgn}(q_2-q_1)]^{q_1-q_2}\,\lambda^{Q-q}e^{-\lambda^2/2}\left(\frac{q!}{Q!}\right)^{1/2}\mathrm{L}_q^{Q-q}(\lambda^2), \tag{2.3}$$

where $\mathrm{L}^n_m(x)$ denotes the generalized Laguerre polynomial. As illustrated in Fig. 2.2, the behavior of the FC matrix elements crucially depends on the strength of the electron-phonon coupling (i.e., the magnitude of the wavefunction displacement), and detailed discussions of the cases of strong and weak coupling are provided in Chapters 3 and 6.

The rate for the analogous process $n = 0 \to 1$ can be obtained from Eq. (2.2) by swapping the spin factor and substituting f_a by $(1 - f_a)$, i.e.

$$W^{10}_{qq';a} = s(1,0)\frac{\Gamma_a}{\hbar}\left|M_{qq'}\right|^2 \left\{1 - f_a(\varepsilon_d - [q'-q]\hbar\omega_0)\right\}. \tag{2.4}$$

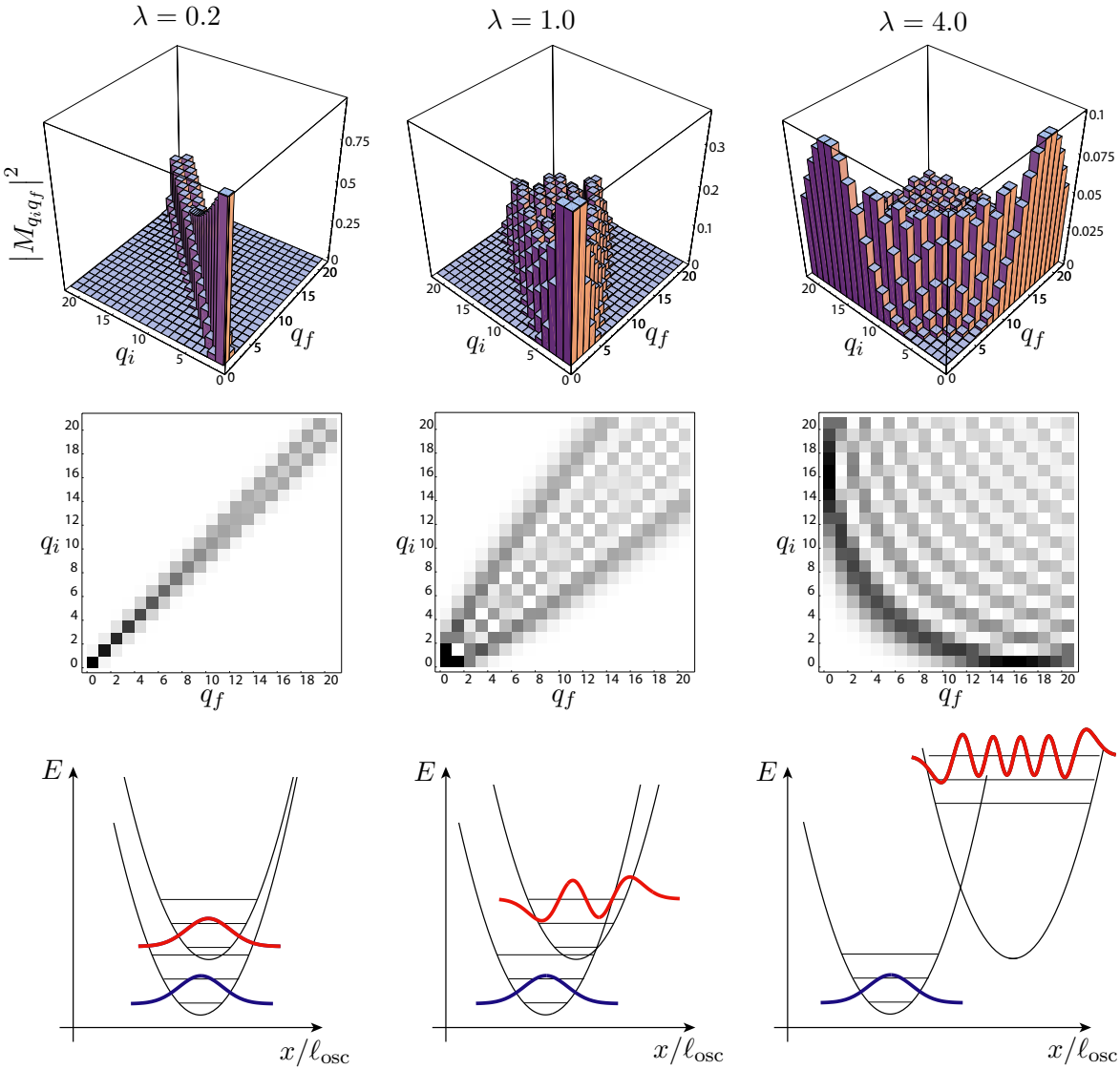

Figure 2.2: Franck-Condon matrix elements for weak ($\lambda = 0.2$), intermediate ($\lambda = 1$), and strong ($\lambda = 4$) electron-phonon coupling. Panels in the top and middle row show the square of the Franck-Condon matrix element as a function of initial and final phonon state q_i and q_f, respectively. The plots in the bottom row visualize the displacement of the molecular potential surfaces for the neutral and singly ionized molecule.

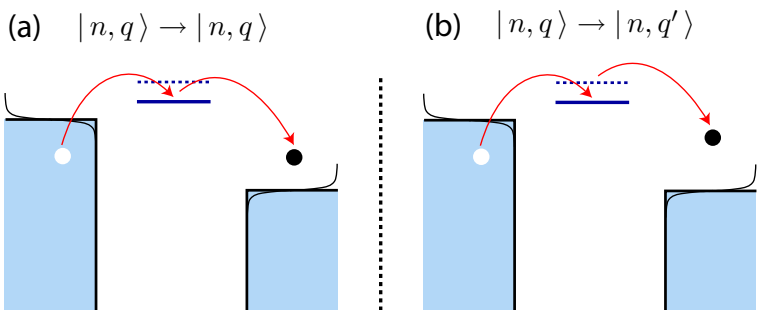

Figure 2.3: Cotunneling processes. (a) Elastic cotunneling, (b) inelastic cotunneling

2.1.2 Cotunneling

In next-to-leading order in H_T, *cotunneling* processes [11, 86] are generated, see Fig. 2.3. These transfer one electron from lead a to lead b, while the electronic occupation of the molecule changes only virtually in the intermediate state. Cotunneling transitions leaving the molecular state unchanged are referred to as *elastic cotunneling*. Transitions changing the molecular state, e.g. by a spin-flip or phonon excitation or deexcitation, are called *inelastic cotunneling*. For simplicity, let us consider the case of a large charging energy ($U \to \infty$) inhibiting double occupation of the molecule entirely. Then, based on Eq. (2.1), the corresponding rates are obtained as

$$W^{00}_{qq';ab} = \frac{s(0,0)}{2\pi\hbar}\Gamma_a\Gamma_b \int d\epsilon \left| \sum_{q''} \frac{M_{q'q''}M^*_{qq''}}{\epsilon - \varepsilon_d + (q-q'')\hbar\omega_0} \right|^2 f_a(\epsilon)\left[1 - f_b(\epsilon + [q-q']\hbar\omega_0)\right] \quad (2.5)$$

$$W^{11}_{qq';ab} = \frac{s(1,1)}{2\pi\hbar}\Gamma_a\Gamma_b \int d\epsilon \left| \sum_{q''} \frac{M_{q'q''}M^*_{qq''}}{\varepsilon_d - \epsilon + (q'-q'')\hbar\omega_0} \right|^2 f_a(\epsilon)\left[1 - f_b(\epsilon + [q-q']\hbar\omega_0)\right]. \quad (2.6)$$

Here, the spin factors are $s(0,0) = s(1,1) \equiv 2$, which follow from an analysis of the relevant contributions as illustrated in Fig. 2.4. For cotunneling through the empty molecule, $n = 0 \to 0$, there is an incoherent addition of the processes transferring a spin-up or a spin-down electron, respectively. For $n = 1 \to 1$ the cotunneling transition may either leave the molecule's spin state invariant or cause a spin flip, again resulting in two incoherent processes. In both cases $n = 0$ and 1, the rates of the two contributions are identical and hence can be absorbed into the spin factor. We stress that the *order* of indices associated with the FC matrix elements is *essential* here, since the sign of the FC matrix elements becomes relevant for the interference terms. This slightly subtle point is further elucidated in Appendix B.

It is crucial to note that, in general, the cotunneling rates cannot be directly evaluated from Eqs. (2.5) and (2.6). These expressions diverge due to second-order poles from the energy denominators. This divergence, related to the infinite lifetime of the virtual intermediate state within a purely perturbative approach, has been pointed out before [87, 88].

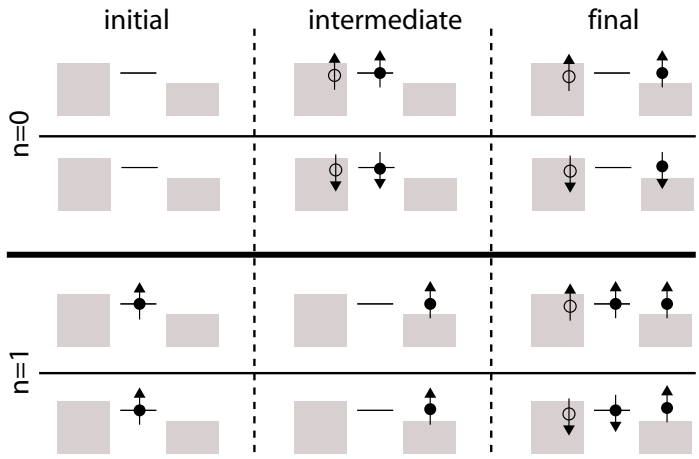

Figure 2.4: Relevant contributions to the cotunneling rates in the $U \to \infty$ limit. For both charge states $n = 0$ and 1 there are two incoherent contributions with either a spin-up or a spin-down electron being transferred across the molecule.

A regularization scheme has been developed in order to extract the correct cotunneling rates [87,88], which we summarize here, deferring the details to Appendix C. The basis for the regularization of cotunneling rates is given by two observations.

(i) Second-order perturbation theory clearly misses the fact that the intermediate state obtains a finite width $\sim \Gamma$ due to the tunneling. This width should enter the energy denominator as an imaginary part, shifting the pole away from the real axis.

(ii) For a specific cotunneling transition $|\, i \,\rangle \to |\, f \,\rangle$ at finite temperature, the final state $|\, f \,\rangle$ can also be reached from the initial state $|\, i \,\rangle$ by two sequential processes.

Specifically, the regularization proceeds as follows. First, a level width $\gamma \sim \Gamma$ is introduced in the energy denominators. With the poles shifted away from the real axis, the integral can now be carried out. The resulting expression is then expanded in powers of the level width γ. The leading order term is proportional to $1/\gamma$. When combining this with the prefactor $\Gamma_a \Gamma_b$ of the rates Eqs. (2.5) and (2.6) , the overall order of this term is found to be identical to a sequential-tunneling term. Following point (ii), this term must be disregarded to avoid double-counting of sequential processes. The next-to-leading order in the γ-expansion is a γ^0 term. It is this term which gives the regularized expression for the cotunneling rate. This procedure is carried out in detail in Appendix C.

It is interesting to note that these "cotunneling rates" may become *negative*. This result can in fact be expected by considering the simple case of a single-level resonant tunneling model without charging energy. For this model, the exact result for the current in the $T \to 0$ limit is

$$I = \mathrm{sgn}(eV) \frac{2e}{h} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \sum_{a=L,R} a \arctan \left[\frac{a\,|eV| - 2\varepsilon_d}{\Gamma} \right], \tag{2.7}$$

where we identify the index L (R) with $a = +1$ ($a = -1$). Expanding this in orders of Γ,

we find that the second-order term [corresponding to cotunneling] is given by

$$I_{\rm cot} = -\frac{e}{h}\Gamma_L\Gamma_R\frac{|eV|}{(eV/2)^2-\varepsilon_d^2}. \tag{2.8}$$

This expression indeed becomes negative, whenever the level is located inside the bias window, i.e. cotunneling *reduces* the sequential-tunneling current. Our regularization procedure combined with the rate-equations approach exactly reproduces these expressions, as shown in detail in Appendix G. It is worth noting that, alternatively, the formalism developed by König, Schoeller and Schön may be used to circumvent the necessity of regularization, see e.g. Ref. [89]. We find that additional corrections due to level shifts and broadening captured by their approach are irrelevant in the case $\Gamma \ll k_BT$ considered here. In this limit, both approaches are expected to give identical results.

2.2 Rate equations

The rates for transitions between different molecular states form the essential input for the *rate equations*, as introduced in the context of Coulomb blockade phenomena [90,91]. These determine the time-evolution of the probabilities P_q^n for the occupation of the molecular states $|\,n,q\,\rangle$, and they can be written in the intuitive form

$$\frac{dP_q^n}{dt} = \sum_{n',q'}\left[P_{q'}^{n'}W_{q'q}^{n'n} - P_q^nW_{qq'}^{nn'}\right] - \frac{1}{\tau}\left[P_q^n - P_q^{\rm eq}\textstyle\sum_{q'}P_{q'}^n\right]. \tag{2.9}$$

Here, the first sum describes the change of the occupation probability P_q^n due to probability flow into and out of this state, giving a corresponding positive (probability increase) and negative (probability decrease) contribution, respectively. The last term is added on a phenomenological basis, and describes relaxation of the vibrations towards the equilibrium distribution $P_q^{\rm eq} = e^{-q\hbar\omega_0/k_BT}(1-e^{-\hbar\omega_0/k_BT})$ on a time scale τ. In the course of this work, we will mainly investigate the two limiting cases of equilibrated phonons ($\tau\to 0$, distribution fixed to equilibrium), and unequilibrated phonons ($\tau\to\infty$, nonequilibrium distribution entirely determined through tunneling dynamics). However, we stress that the investigation of intermediate relaxation strengths according to Eq. (2.9) is straightforward, and will be studied in Chapter 3.

A rigorous derivation of the rate equations can be achieved through the density-matrix formalism [45,79,92]. Its starting point is the formulation of the von-Neumann equation for the reduced density matrix of the molecule. In general, this leads to a complicated integro-differential equation. The crucial simplification arises from the reasonable assumption that electronic relaxation in the leads is *fast* compared to the tunneling dynamics. In this case, the Born-Markov approximation can be employed, and the evolution equation becomes an ordinary differential equation – the *Master equation* for the reduced density matrix.[1] In the weak-tunneling limit $\Gamma \ll k_BT$, $\hbar\omega_0$, coherences between different molecular states $|\,n,q\,\rangle$ are negligible, and the Master equations reduce to rate equations. These represent the

[1] In the literature, the distinction between the terms "Master equation" and "rate equations" is slightly inconsistent. We suggest to refer to the equation of motion for the reduced density matrix as Master equation, and to its *diagonal* part as rate equations. We will follow this nomenclature throughout the text.

diagonal part of the reduced density matrix. Despite the somewhat disparate nomenclature and main focus, we find it useful to note that the theory of rate equations is well-known in mathematics under the name of "Continuous-Time Markov Chains", see e.g. the book by W. J. Anderson [93]. Another helpful introduction to Markov processes at the interface between physics and mathematics can be found in Ref. [94].

It is convenient to reexpress Eq. (2.9) in terms of a matrix equation of the form

$$\frac{d\mathbf{p}}{dt} = \mathsf{W}\mathbf{p}, \tag{2.10}$$

where W is a coefficient matrix containing all rates, and the vector $\mathbf{p}$ consists of all occupation probabilities, see Appendix D for further details. Given some initial condition $\mathbf{p}(t=0) = \mathbf{p}_0$, the rate equations are formally solved by

$$\mathbf{p}(t) = e^{\mathsf{W}t}\mathbf{p}_0. \tag{2.11}$$

Under rather general conditions, typically satisfied in physical applications, one can show that for long times the probability distribution converges to a unique stationary distribution $\mathbf{P}$ [93]. Instead of performing the limit

$$\mathbf{P} = \lim_{t\to\infty} \mathbf{p}(t) \qquad \text{(independent of the initial condition)}, \tag{2.12}$$

one can solve the stationary rate equations

$$\mathsf{W}\mathbf{P} = 0 \tag{2.13}$$

with the condition that the sum over all components of the vector $\mathbf{P}$ is 1 (normalization), which we write as $\operatorname{tr}\mathbf{P} = 1$.

For a systematic expansion in orders of the tunneling, we write $\mathsf{W} = \mathsf{W}^{(1)} + \mathsf{W}^{(2)} + \cdots$ as well as $\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} + \cdots$. Substituting this into the rate equation, we obtain up to second order the equations

$$\mathsf{W}^{(1)}\mathbf{P}^{(0)} = 0, \tag{2.14}$$

$$\mathsf{W}^{(1)}\mathbf{P}^{(1)} = -\mathsf{W}^{(2)}\mathbf{P}^{(0)}. \tag{2.15}$$

The normalization condition for $\mathbf{P}$ leads to $\operatorname{tr}\mathbf{P}^{(0)} = \sum_i P_i^{(0)} = 1$ and $\operatorname{tr}\mathbf{P}^{(1)} = 0$. Here and in the following, the "trace" of a vector always denotes the sum of its components.

2.3 Stationary current and shot noise

As shown, e.g., in Refs. [45] and [84], the steady-state current and the current noise can be computed via the rate-equations formalism. We first consider the steady-state current to leading order in H_T, i.e. sequential tunneling. Then, the expression for the current across the left junction, for instance, simply amounts to counting the electrons being transferred in the bias direction, and subtracting those which travel in the opposite direction. This leads to the intuitive expression

$$I_L = e\sum_n \sum_{q,q'} P_q^n \left[W^{n,n+1}_{qq';\,L} - W^{n,n-1}_{qq';\,L} \right]. \tag{2.16}$$

Due to charge conservation, the average current across the left and right junction must be identical in the stationary case, $I_L = I_R$.

When including processes beyond sequential tunneling, it is convenient to define a current coefficient matrix W_I, closely related to the coefficient matrix W of the rate equations; a detailed description is provided in Appendix D. Then, the current may be compactly written as

$$I = \operatorname{tr} \mathsf{W}_I \mathbf{P}, \tag{2.17}$$

which can be expanded order by order in the tunneling,

$$\begin{aligned} I &= I^{(1)} + I^{(2)} + \cdots \\ &= \operatorname{tr} \mathsf{W}_I^{(1)} \mathbf{P}^{(0)} + \operatorname{tr} \left[\mathsf{W}_I^{(1)} \mathbf{P}^{(1)} + \mathsf{W}_I^{(2)} \mathbf{P}^{(0)} \right] + \cdots \end{aligned} \tag{2.18}$$

The lowest-order current $I^{(1)}$ is the sequential-tunneling current. The second-order contribution $I^{(2)}$ contains the cotunneling current and corrections to the sequential current due to changes of the probability distribution by inelastic cotunneling.

A method for evaluating the current shot noise

$$S(\omega) = 2 \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} \left[\langle I(\tau + t) I(t) \rangle_t - \langle I(t) \rangle_t^2 \right] \tag{2.19}$$

within the rate-equations formalism has been developed by Korotkov in Ref. [84]. This formalism is based on the following two insights.

(i) In the regime of weak coupling between the molecule (dot) and the electrodes, the current is generated by discrete charge transfer processes at times τ_1, τ_2, ...

(ii) The waiting times $t_i = \tau_i - \tau_{i-1}$ between consecutive events is generally large compared to the duration of each charge transfer process.

Accordingly, the current in junction a may be approximated by the expression

$$I_a(t) = \sum_i N_i \, \delta(t - \tau_i), \tag{2.20}$$

where N_i denotes the number of electrons transferred across junction a in the event i. Substituting this expression into Eq. (2.19), it is possible to derive the noise power spectrum from the relevant transition rates. Korotkov's method can be generalized to include higher-order processes beyond sequential tunneling, as we show in detail in Appendix D.