Appendix A

Important canonical transformations

A.1 Lang-Firsov transformation

A.1.1 Model and task

We consider the Anderson-Holstein model [119,138] describing a spin-degenerate electronic level with on-site interaction ("molecule or dot"), coupled to two normal-conducting metallic electrodes, and interacting with a single mode of vibrations. The corresponding Hamiltonian is given by $H = H_{\mathrm{mol}} + H_{\mathrm{leads}} + H_{\mathrm{T}}$, where the dot is described by

$$H_{\mathrm{mol}} = \varepsilon_d n_d + U n_d(n_d - 1)/2 + \hbar\omega_0 b^\dagger b + \lambda\hbar\omega_0 n_d(b^\dagger + b), \tag{A.1}$$

the left and right electrode ($a = L, R$) by

$$H_{\mathrm{leads}} = \sum_{a\mathbf{p}\sigma} \epsilon_{a\mathbf{p}} c^\dagger_{a\mathbf{p}\sigma} c_{a\mathbf{p}\sigma}, \tag{A.2}$$

and the tunneling between dot and electrodes by

$$H_{\mathrm{T}} = \sum_{a\mathbf{p}\sigma} \left[t_{a\mathbf{p}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma + t^*_{a\mathbf{p}} d^\dagger_\sigma c_{a\mathbf{p}\sigma} \right]. \tag{A.3}$$

We wish to eliminate the coupling between electrons and phonons, which can be accomplished by the Lang-Firsov canonical transformation [71], also described in [41, 45, 139] This transformation results in a basis change to polaron-type quasi-particles – electrons surrounded by clouds of vibrations.

A.1.2 Preliminary remarks

Before carrying out the formal transformation, we first motivate its results with a few intuitive arguments. The harmonic oscillator potential in the presence of the electron-phonon coupling can be written as

$$\begin{aligned} V(x) &= \frac{1}{2} m\omega_0^2 x^2 + \lambda\hbar\omega_0 n_d(b^\dagger + b) = \frac{1}{2}\hbar\omega_0 \left(\frac{x}{\ell_{\mathrm{osc}}}\right)^2 + \sqrt{2}\lambda\hbar\omega_0 n_d \frac{x}{\ell_{\mathrm{osc}}} \\ &= \frac{1}{2}\hbar\omega_0 \left(\frac{x}{\ell_{\mathrm{osc}}} + \sqrt{2}\lambda n_d\right)^2 - \lambda^2\hbar\omega_0 n_d^2. \end{aligned} \tag{A.4}$$

Thus, we obtain a shifted harmonic-oscillator potential and an additional negative energy shift corresponding to the energy gain due to polaron-formation. By rewriting this polaron shift, we can anticipate the resulting renormalizations:

$$-\lambda^2\hbar\omega_0 n_d^2 = -2\lambda^2\hbar\omega_0 n_d(n_d-1)/2 - \lambda^2\hbar\omega_0 n_d. \tag{A.5}$$

Reabsorbing these terms into the original Hamiltonian, we expect the renormalizations $U \to U - 2\lambda^2\hbar\omega_0$, and $\varepsilon_d \to \varepsilon_d - \lambda^2\hbar\omega_0$. The fact that the potential minimum position now depends on the occupation number of the dot will lead to a modification of the tunneling Hamiltonian in the form of a shift operator.

A.1.3 Canonical transformation

After these remarks, we turn to the explicit canonical transformation $\bar{H} = e^S H e^{-S}$. As always, the transformation must be unitary to preserve the Hermiticity of the Hamilton operator. This implies that the transformation's generator S must be anti-Hermitian, $S^\dagger = -S$. The appropriate choice for S to eliminate the electron-phonon coupling is

$$S = \lambda(b^\dagger - b)n_d, \tag{A.6}$$

which was first suggested by Lang and Firsov [71]. In the following, we review how the transformation is carried out.

The essential building block of the calculation consists of exploiting the Baker-Campbell-Hausdorff formula,[1] which reads

$$e^A B e^{-A} = \sum_{n=0}^{\infty} \frac{1}{m!}[A,B]_m = B + [A,B] + \frac{1}{2}[A,[A,B]] + \frac{1}{6}[A,[A,[A,B]]] + \cdots \tag{A.7}$$

For the transformation of the relevant operators, we thus obtain

$$\bar{d}_\sigma = e^S d_\sigma e^{-S} = \sum_{n=0}^{\infty} \frac{\lambda^n (b^\dagger - b)^n}{n!}[n_d, d_\sigma]_n = d_\sigma\, e^{\lambda(b-b^\dagger)}, \tag{A.8}$$

$$\bar{d}_\sigma^\dagger = d_\sigma^\dagger e^{-\lambda(b-b^\dagger)}, \tag{A.9}$$

$$\bar{n}_d = n_d, \tag{A.10}$$

$$\bar{b} = e^S b e^{-S} = \sum_{n=0}^{\infty} \frac{\lambda^n n_d^n}{n!}[b^\dagger - b, b]_n = b - \lambda n_d, \tag{A.11}$$

$$\bar{b}^\dagger = b^\dagger - \lambda n_d, \tag{A.12}$$

$$\bar{c}_{a\mathbf{p}\sigma} = c_{a\mathbf{p}\sigma}, \quad \bar{c}_{a\mathbf{p}\sigma}^\dagger = c_{a\mathbf{p}\sigma}^\dagger \tag{A.13}$$

Here, we have used $[n_d, d_\sigma]_n = (-1)^n d_\sigma$, and $[b^\dagger - b, b] = -1$. Based on these relations, the

[1] The Baker-Campbell-Hausdorff formula can easily be proved by defining $B(\tau) = e^{\tau A} B e^{-\tau A}$ and formally integrating its equation of motion $dB/d\tau = [A, B(\tau)]$.

transformed Hamiltonian takes the form $\bar{H} = \bar{H}_{\mathrm{mol}} + \bar{H}_{\mathrm{leads}} + \bar{H}_{\mathrm{T}}$ with

$$\bar{H}_{\mathrm{mol}} = (\varepsilon_d - \lambda^2\hbar\omega_0)n_d + (U - 2\lambda^2\hbar\omega_0)/2\, n_d(n_d - 1) + \hbar\omega_0 b^\dagger b \tag{A.14}$$

$$\bar{H}_{\mathrm{leads}} = \sum_{a\mathbf{p}\sigma} \epsilon_{a\mathbf{p}} c^\dagger_{a\mathbf{p}\sigma} c_{a\mathbf{p}\sigma}, \tag{A.15}$$

$$\bar{H}_{\mathrm{T}} = \sum_{a\mathbf{p}\sigma} \left[t_{a\mathbf{p}} e^{-\lambda(b^\dagger - b)} c^\dagger_{a\mathbf{p}\sigma} d_\sigma + t^*_{a\mathbf{p}} e^{\lambda(b^\dagger - b)} d^\dagger_\sigma c_{a\mathbf{p}\sigma} \right]. \tag{A.16}$$

The transformation indeed leads to the renormalizations discussed in the previous section, and it introduces a shift operator

$$e^{\lambda(b - b^\dagger)} = e^{\sqrt{2}\lambda\ell_{\mathrm{osc}} d/dx} \tag{A.17}$$

into the tunneling matrix elements.

A.2 Schrieffer-Wolff transformation

Here, we review the basics of the Schrieffer-Wolff transformation [126]. In situations where sequential tunneling of single electrons between the leads and the dot is irrelevant, tunneling proceeds only via higher-order processes, and changes of the charge state of the dot by one only occur virtually. In such a scenario, the tunneling Hamiltonian H_{T} can be eliminated to lowest order, leaving only terms $\sim H_{\mathrm{T}}^2$ (and, in principle, higher-order terms). This is what is accomplished by the Schrieffer-Wolff transformation, which can either be carried out along the lines of Schrieffer and Wolff's original paper by means of an approximate canonical transformation [126], or using the projection-operator technique as presented, e.g., in Ref. [140].

Our starting point is the Anderson model $H = H_0 + H_{\mathrm{T}}$, where

$$H_0 = \varepsilon_d \sum_\sigma d^\dagger_\sigma d_\sigma + U n_{d\uparrow} n_{d\downarrow} + \sum_{ak\sigma} \epsilon_{ak} c^\dagger_{a\mathbf{p}\sigma} c_{a\mathbf{p}\sigma} \tag{A.18}$$

describes the dot as well as the left and right lead, and

$$H_{\mathrm{T}} = \sum_{a\mathbf{p}\sigma} \left[t_{a\mathbf{p}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma + t^*_{a\mathbf{p}} d^\dagger_\sigma c_{a\mathbf{p}\sigma} \right] \tag{A.19}$$

promotes the tunneling of electrons between the leads and the dot.

The first step consists of a canonical transformation $\bar{H} = e^S H e^{-S}$ such that in the resulting Hamiltonian $\bar{H}$ no terms linear in the tunneling appear. Using the Baker-Campbell-Hausdorff formula, the transformed Hamiltonian can be rewritten as an expansion

$$\bar{H} = \sum_{n=0}^{\infty} \frac{1}{m!} [S, H]_m = H + [S, H] + \frac{1}{2}[S, [S, H]] + \frac{1}{6}[S, [S, [S, H]]] + \cdots \tag{A.20}$$

The anti-Hermitian generator S of the canonical transformation turns out to be linear in H_{T} so that the latter equation is indeed an expansion in powers of H_{T}. The absence of linear-order terms of H_{T} in $\bar{H}$ then leads to the requirement

$$[S, H_0] = -H_{\mathrm{T}}. \tag{A.21}$$

Successive exploitation of this relation reduces the transformation to the expression

$$\bar{H} = H_0 + \frac{1}{2}[S, H_\mathrm{T}] + \frac{1}{3}[S,[S,H_\mathrm{T}]] + \frac{1}{8}[S,[S,[S,H_\mathrm{T}]]] + \cdots , \tag{A.22}$$

where the tunneling appears only in second (and higher) order. The generator $S = S_1 - S_1^\dagger$ meeting the condition (A.21) is given by

$$S_1 \equiv \sum_{a\mathbf{p}\sigma} \left[\frac{t_{a\mathbf{p}}}{\epsilon_{ak} - \varepsilon_d - U} n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma + \frac{t_{a\mathbf{p}}}{\epsilon_{a\mathbf{p}} - \varepsilon_d} (1 - n_{d\bar{\sigma}}) c^\dagger_{a\mathbf{p}\sigma} d_\sigma \right], \tag{A.23}$$

where $\bar{\sigma} = -\sigma$. We verify this claim in detail by calculating the relevant commutators. First, we split H_0 into $H_0 = H_\epsilon + H_U + H_l$ with the separate parts standing for the one-particle dot contribution, the Coulomb term, and the leads contribution. The basic commutators needed for the evaluations are

$$\begin{aligned}
\left[c^\dagger_{a\mathbf{p}\sigma} c_{a\mathbf{p}\sigma}, n_{d\bar{\sigma}'} c^\dagger_{a'\mathbf{p}'\sigma'} d_{\sigma'} \right] &= \delta_{aa'} \delta_{\mathbf{p}\mathbf{p}'} \delta_{\sigma\sigma'} n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma \\
\left[c^\dagger_{a\mathbf{p}\sigma} c_{a\mathbf{p}\sigma}, (1 - n_{d\bar{\sigma}'}) c^\dagger_{a'\mathbf{p}'\sigma'} d_{\sigma'} \right] &= \delta_{aa'} \delta_{\mathbf{p}\mathbf{p}'} \delta_{\sigma\sigma'} (1 - n_{d\bar{\sigma}}) c^\dagger_{a\mathbf{p}\sigma} d_\sigma \\
\left[d^\dagger_\sigma d_\sigma, n_{d\bar{\sigma}'} c^\dagger_{a\mathbf{p}\sigma'} d_{\sigma'} \right] &= -\delta_{\sigma\sigma'} n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma \\
\left[d^\dagger_\sigma d_\sigma, (1 - n_{d\bar{\sigma}}) c^\dagger_{a\mathbf{p}\sigma'} d_{\sigma'} \right] &= -\delta_{\sigma\sigma'} (1 - n_{d\bar{\sigma}}) c^\dagger_{a\mathbf{p}\sigma} d_\sigma \\
\left[n_{d\uparrow} n_{d\downarrow}, n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma \right] &= -n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma \\
\left[n_{d\uparrow} n_{d\downarrow}, (1 - n_{d\bar{\sigma}'}) c^\dagger_{a\mathbf{p}\sigma} d_\sigma \right] &= 0
\end{aligned}$$

Using these relations, we obtain

$$[H_l, S_1] = \sum_{a\mathbf{p}\sigma} \epsilon_{a\mathbf{p}} \left[\frac{t_{a\mathbf{p}}}{\epsilon_{a\mathbf{p}} - \varepsilon_d - U} n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma + \frac{t_{a\mathbf{p}}}{\epsilon_{a\mathbf{p}} - \varepsilon_d} (1 - n_{d\bar{\sigma}}) c^\dagger_{a\mathbf{p}\sigma} d_\sigma \right] \tag{A.24}$$

$$[H_\epsilon, S_1] = -\epsilon_d \sum_{a\mathbf{p}\sigma} \left[\frac{t_{a\mathbf{p}}}{\epsilon_{a\mathbf{p}} - \varepsilon_d - U} n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma + \frac{t_{a\mathbf{p}}}{\epsilon_{a\mathbf{p}} - \varepsilon_d} (1 - n_{d\bar{\sigma}}) c^\dagger_{a\mathbf{p}\sigma} d_\sigma \right] \tag{A.25}$$

$$[H_U, S_1] = -U \sum_{a\mathbf{p}\sigma} \frac{t_{a\mathbf{p}}}{\epsilon_{a\mathbf{p}} - \varepsilon_d - U} n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma . \tag{A.26}$$

Collecting all terms together, one confirms that

$$[H_0, S] = [H_0, S_1] + [H_0, S_1]^\dagger = H_\mathrm{T}. \tag{A.27}$$

In order to account for second-order processes in H_T, we now evaluate the next-leading order contribution to $\bar{H}$, which is given by $[S, H_\mathrm{T}]/2$. This requires the calculation of four more commutators, namely

$$\begin{aligned}
\left[n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma, c^\dagger_{a'\mathbf{p}'\sigma'} d_{\sigma'} \right] &= \delta_{\sigma'\bar{\sigma}} c^\dagger_{a'\mathbf{p}'\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_{\bar{\sigma}} d_\sigma \\
\left[n_{d\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} d_\sigma, d^\dagger_{\sigma'} c_{a'\mathbf{p}'\sigma'} \right] &= \delta_{\sigma\sigma'} \left(c^\dagger_{a\mathbf{p}\sigma} c_{a'\mathbf{p}'\sigma} n_{d\bar{\sigma}} - \delta_{aa'} \delta_{\mathbf{p}\mathbf{p}'} n_{d\bar{\sigma}} n_{d\sigma} \right) - \delta_{\sigma'\bar{\sigma}} c^\dagger_{a\mathbf{p}\sigma} c_{a'\mathbf{p}'\bar{\sigma}} d^\dagger_{\bar{\sigma}} d_\sigma \\
\left[c^\dagger_{a\mathbf{p}\sigma} d_\sigma, d^\dagger_{\sigma'} c_{a'\mathbf{p}'\sigma'} \right] &= \delta_{\sigma\sigma'} \left(c^\dagger_{a\mathbf{p}\sigma} c_{a'k'\sigma} - \delta_{aa'} \delta_{\mathbf{p}\mathbf{p}'} n_{d\sigma} \right) \\
\left[c^\dagger_{a\mathbf{p}\sigma} d_\sigma, c^\dagger_{a'\mathbf{p}'\sigma'} d_{\sigma'} \right] &= 0
\end{aligned}$$

From the evaluation of the commutator, we obtain three new contributions,

$$\frac{1}{2}[S, H_{\mathrm{T}}] = H_{\mathrm{dir,ex}} + H_{\mathrm{pair}} + H_0'. \tag{A.28}$$

Here, the individual contributions correspond to direct and exchange coupling,

$$H_{\mathrm{dir,ex}} = \frac{1}{2}\sum_{aa'\mathbf{p}\mathbf{p}'\sigma}\left[\frac{t_{a\mathbf{p}}t^*_{a'\mathbf{p}'}}{\epsilon_{a\mathbf{p}}-\varepsilon_d}c^\dagger_{a\mathbf{p}\sigma}c_{a'\mathbf{p}'\sigma} + t_{a\mathbf{p}}t^*_{a'\mathbf{p}'}M_{a\mathbf{p}}\left(d^\dagger_{\bar\sigma}d_\sigma c^\dagger_{a\mathbf{p}\sigma}c_{a'\mathbf{p}'\bar\sigma} - c^\dagger_{a\mathbf{p}\sigma}c_{a'\mathbf{p}'\sigma}n_{d\bar\sigma}\right) + \mathrm{h.c.}\right], \tag{A.29}$$

to pair tunneling,

$$H_{\mathrm{pair}} = \sum_{aa'k\mathbf{p}'}\left[t_{a\mathbf{p}}t_{a'\mathbf{p}'}M_{a\mathbf{p}}c_{d\downarrow}c_{d\uparrow}c^\dagger_{a\mathbf{p}\downarrow}c^\dagger_{a'\mathbf{p}'\uparrow} + \mathrm{h.c.}\right], \tag{A.30}$$

and to a mere shift of the energy levels,

$$H_0' = -\sum_{a\mathbf{p}\sigma}\left[\frac{|t_{a\mathbf{p}}|^2}{\epsilon_{a\mathbf{p}}-\varepsilon_d}n_{d\sigma} - |t_{a\mathbf{p}}|^2 M_{a\mathbf{p}}n_{d\sigma}n_{d\bar\sigma}\right]. \tag{A.31}$$

As a shorthand, we have introduced $M_{a\mathbf{p}} = (\epsilon_{a\mathbf{p}}-\varepsilon_d)^{-1} - (\epsilon_{a\mathbf{p}}-\varepsilon_d-U)^{-1}$. Up to second order in the tunneling, the transformed Hamiltonian now reads

$$\bar H = H_0 + H_{\mathrm{dir,ex}} + H_{\mathrm{pair}} + H_0'. \tag{A.32}$$

For the positive-U case, the pair-tunneling term can generally be neglected [126], and the relevant contributions arise from the exchange interaction and potential scattering. We employ the usual definitions for the spin operator $\mathbf{S}$ on the dot, and $\mathbf{s}_{aa'\mathbf{p}\mathbf{p}'}$ for the conduction band electrons, namely

$$S^z = \frac{1}{2}(n_{d\uparrow}-n_{d\downarrow}) \qquad s^z_{aa'\mathbf{p}\mathbf{p}'} = \frac{1}{2}(c^\dagger_{a\mathbf{p}\uparrow}c_{a'\mathbf{p}'\uparrow} - c^\dagger_{a\mathbf{p}\downarrow}c_{a'\mathbf{p}'\downarrow}) \tag{A.33}$$

$$S^+ = d^\dagger_\uparrow d_\downarrow \qquad s^+_{aa'\mathbf{p}\mathbf{p}'} = c^\dagger_{a\mathbf{p}\uparrow}c_{a'\mathbf{p}'\downarrow} \tag{A.34}$$

$$S^- = d^\dagger_\downarrow d_\uparrow \qquad s^-_{aa'\mathbf{p}\mathbf{p}'} = c^\dagger_{a\mathbf{p}\downarrow}c_{a'\mathbf{p}'\uparrow}. \tag{A.35}$$

Then, the transformed Hamiltonian may be compactly rewritten as $\bar H = H_0 + H_{\mathrm{J}} + H_{\mathrm{pot}} + H_0'$, where

$$H_{\mathrm{J}} = \sum_{aa'\mathbf{p}\mathbf{p}'} J_{aa'\mathbf{p}\mathbf{p}'}\mathbf{s}_{aa'\mathbf{p}\mathbf{p}'}\cdot\mathbf{S}, \tag{A.36}$$

$$H_{\mathrm{pot}} = \sum_{aa'\mathbf{p}\mathbf{p}'\sigma} K_{aa'\mathbf{p}\mathbf{p}'}c^\dagger_{a\mathbf{p}\sigma}c_{a'\mathbf{p}'\sigma}. \tag{A.37}$$

The amplitudes J and K are defined as

$$J_{aa'\mathbf{p}\mathbf{p}'} = t_{a\mathbf{p}}t^*_{a'\mathbf{p}'}\left[\frac{1}{\epsilon_{a\mathbf{p}}-\varepsilon_d} + \frac{1}{\epsilon_{a'\mathbf{p}'}-\varepsilon_d} + \frac{1}{U+\varepsilon_d-\epsilon_{a\mathbf{p}}} + \frac{1}{U+\varepsilon_d-\epsilon_{a'\mathbf{p}'}}\right]$$

and

$$K_{aa'\mathbf{p}\mathbf{p}'} = \frac{t_{a\mathbf{p}}t^*_{a'\mathbf{p}'}}{4}\left[M_{a\mathbf{p}} + M_{a'\mathbf{p}'}\right].$$

A.3 Glazman-Raikh transformation

An important tool for studying transport within the linear-response regime consists of the Glazman-Raikh transformation [129]. Our starting point is a model including a left and a right electrode, as well as tunneling between both electrodes and the central system (e.g. a quantum dot). For *zero-bias*, the Glazman-Raikh transformation maps this problem to a model where the tunneling occurs only between the central system and *one* effective lead. For concreteness, let us consider the Anderson Hamiltonian

$$H = \sum_{\sigma} \varepsilon_d d_\sigma^\dagger d_\sigma + U n_{d\uparrow} n_{d\downarrow} + \sum_{a=L,R} \sum_{k,s} \xi_{ks} c_{aks}^\dagger c_{aks} + \sum_{a=L,R} \sum_{k,s} \left[t_a c_{aks}^\dagger d_s + \text{h.c.} \right]. \quad \text{(A.38)}$$

The basic idea is to perform a rotation in the space of lead annihilation operators,

$$\begin{pmatrix} \psi_{1ks} \\ \psi_{2ks} \end{pmatrix} = \begin{pmatrix} \cos\theta & e^{i\varphi}\sin\theta \\ -e^{-i\varphi}\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} c_{Rks} \\ c_{Lks} \end{pmatrix}, \quad \text{(A.39)}$$

where the rotation angles θ and φ will be fixed below by invoking the requirement that only one of the two channels ψ_{1ks}, ψ_{2ks} couples to the central system. It is straightforward to confirm that the new annihilation operators obey the necessary anticommutation rules

$$\{\psi_{iks}, \psi_{jk's'}\} = \{\psi_{iks}^\dagger, \psi_{jk's'}^\dagger\} = 0, \qquad \{\psi_{iks}^\dagger, \psi_{jk's'}\} = \delta_{ij}\delta_{kk'}\delta_{ss'} \quad \text{(A.40)}$$

Using the inverse of Eq. (A.39), one obtains

$$c_{Rks}^\dagger c_{Rks} = \cos^2\theta \psi_{1ks}^\dagger \psi_{1ks} + \sin^2\theta \psi_{2ks}^\dagger \psi_{2ks} - \sin(2\theta)(\psi_{1ks}^\dagger \psi_{2ks} e^{i\varphi} + \psi_{2ks}^\dagger \psi_{1ks} e^{-i\varphi}) \quad \text{(A.41)}$$

$$c_{Lks}^\dagger c_{Lks} = \sin^2\theta \psi_{1ks}^\dagger \psi_{1ks} + \cos^2\theta \psi_{2ks}^\dagger \psi_{2ks} + \sin(2\theta)(\psi_{1ks}^\dagger \psi_{2ks} e^{i\varphi} + \psi_{2ks}^\dagger \psi_{1ks} e^{-i\varphi}), \quad \text{(A.42)}$$

so that

$$\sum_{a=L,R} \sum_{k,s} \xi_{ks} c_{aks}^\dagger c_{aks} = \sum_{i=1,2} \sum_{k,s} \xi_{ks} \psi_{iks}^\dagger \psi_{iks}. \quad \text{(A.43)}$$

We now turn to the crucial point of transforming the tunneling Hamiltonian,

$$\sum_{a=L,R} [t_a c_{aks}^\dagger d_s + \text{h.c.}] = t_L(\sin\theta e^{i\varphi}\psi_{1ks}^\dagger - \cos\theta\psi_{2ks}^\dagger)d_s + t_R(\cos\theta\psi_{1ks}^\dagger - \sin\theta e^{-i\varphi}\psi_{2ks}^\dagger)d_s + \text{h.c.} \quad \text{(A.44)}$$

The angles θ and φ can now be fixed by requiring that the tunneling in channel $i = 2$ should vanish, i.e.

$$t_L \cos\theta - t_R e^{-i\varphi}\sin\theta = 0 \quad \Rightarrow \quad \varphi = \arg(t_R/t_L),\ \tan\theta = |t_L| \,/\, |t_R| \,. \quad \text{(A.45)}$$

For the coupling to channel $i = 1$ this yields

$$\left|\tilde{t}\right| = |t_L|\sin\theta + |t_R|\cos\theta = \sqrt{|t_L|^2 + |t_R|^2}. \quad \text{(A.46)}$$

As a result, the transformed Hamiltonian now reads

$$H = \sum_{\sigma} \varepsilon_d d_\sigma^\dagger d_\sigma + U n_{d\uparrow} n_{d\downarrow} + \sum_{i=1,2} \sum_{k,s} \xi_{ks} \psi_{iks}^\dagger \psi_{iks} + \sum_{k,s} \left[\tilde{t}\, \psi_{1ks}^\dagger d_s + \text{h.c.} \right], \quad \text{(A.47)}$$

whose advantage is that the tunneling coupling is reduced to one channel only. This reduction to a one-channel problem is particularly useful when studying the linear conductance. For reference, we specify the transformed current operators, which are required when evaluating the conductance via the Kubo formalism. Before the transformation, the current operators for the left and right junction are given by

$$I_a = \frac{dN_a}{dt} = \frac{i}{\hbar}\left[H, N_a\right] = -\frac{i}{\hbar}\sum_{k\sigma}\left[t_a c^\dagger_{ak\sigma} d_\sigma - \text{h.c.}\right]. \tag{A.48}$$

Up to an irrelevant phase factor, the Glazman-Raikh transformation maps these currents to

$$I_L = -\frac{i}{\hbar}\frac{1}{\sqrt{|t_L|^2 + |t_R|^2}}\sum_{ks}\left[\left(|t_L|^2\,\psi^\dagger_{1ks} + |t_L t_R|\,\psi^\dagger_{2ks}\right) d_s - \text{h.c.}\right] \tag{A.49}$$

$$I_R = -\frac{i}{\hbar}\frac{1}{\sqrt{|t_L|^2 + |t_R|^2}}\sum_{ks}\left[\left(|t_R|^2\,\psi^\dagger_{1ks} - |t_L t_R|\,\psi^\dagger_{2ks}\right) d_s - \text{h.c.}\right] \tag{A.50}$$

In the stationary case, the currents must be identical up to their sign, $\langle I_L\rangle = -\langle I_R\rangle$. Therefore the total current may be written as an arbitrary linear combination $I = \alpha I_L - (1-\alpha) I_R$. In the present case, the most convenient choice is

$$\alpha = \frac{|t_R|^2}{|t_L|^2 + |t_R|^2}, \tag{A.51}$$

see e.g. Ref. [141]. This remarkably cancels the channel $i = 1$ from the current operator, leaving only operators for the central system and the *decoupled* lead,

$$I = -\frac{i}{\hbar}\sum_{ks}\frac{|t_L|\,|t_R|}{\sqrt{|t_L|^2 + |t_R|^2}}\left[\psi^\dagger_{2ks} d_s - \text{h.c.}\right]. \tag{A.52}$$

Appendix B

Franck-Condon matrix elements

The FC matrix elements are a central consequence of the coupling between electronic and vibrational degrees of freedom in transport through single molecules. They reflect the displacement between molecular potential surfaces for different charge states. Accordingly, they can be represented as the overlap between spatially displaced vibrational states where the magnitude of the displacement is determined by the electron-phonon coupling strength λ. In the following, we derive expressions for the matrix elements for the relevant cases of (center-of-mass) oscillations and internal vibrations of the molecule [in the harmonic approximation], as well as for the anharmonic Morse potential.

B.1 FC matrix elements for vibrations and oscillations

Matrix elements for vibrations

In the harmonic approximation, the FC matrix elements for internal vibrations of the molecule read

$$M_{q_1 q_2} = \left\langle\, q_2 \,\middle|\, e^{-\lambda(b^\dagger - b)} \,\middle|\, q_1 \,\right\rangle = \int_{-\infty}^{\infty} dx\, \phi_{q_1}(x + \sqrt{2}\lambda\ell_{\mathrm{osc}})\phi^*_{q_2}(x) \tag{B.1}$$

Here, we have identified the exponential as a translation operator, $e^{-\lambda(b^\dagger - b)} = e^{\sqrt{2}\lambda\ell_{\mathrm{osc}} d/dx}$, and ϕ_q denotes the qth harmonic oscillator wavefunction,

$$\phi_q(x) = \left(\pi^{1/2} 2^q q!\, \ell_{\mathrm{osc}}\right)^{-1/2} e^{-x^2/(2\ell^2_{\mathrm{osc}})}\, \mathrm{H}_q(x/\ell_{\mathrm{osc}}). \tag{B.2}$$

The resulting integral is elementary and can be expressed in terms of generalized Laguerre polynomials,

$$\begin{aligned} M_{q_1 q_2} &= (2^{q+q'}\pi q! q'!)^{-1/2} e^{-\lambda^2/2} \int_{-\infty}^{+\infty} d\xi\, e^{-\xi^2}\, \mathrm{H}_{q'}(\xi - \lambda/\sqrt{2})\, \mathrm{H}_q(\xi + \lambda/\sqrt{2}) \qquad \text{(B.3)} \\ &= [\mathrm{sgn}(q_2 - q_1)]^{q_1 - q_2}\, \lambda^{Q-q} e^{-\lambda^2/2} \left(\frac{q!}{Q!}\right)^{1/2} \mathrm{L}_q^{Q-q}(\lambda^2), \end{aligned}$$

where we use $q = \min\{q_1, q_2\}$, $Q = \max\{q_1, q_2\}$. For sequential-tunneling transitions, only the square of the FC matrix elements is required and the actual sign in Eq. (B.3) is

irrelevant. However, for the interference terms in cotunneling rates [see Eqs. (2.5), (2.6), and (C.11)] the sign becomes important. The crucial point for a correct treatment of this sign is to notice that the tunneling Hamiltonian $H_{\rm T}$, Eq. (1.7), involves the exponential $e^{-\lambda(b^\dagger - b)}$ for a transition $n \to n-1$, but $e^{+\lambda(b^\dagger - b)}$ for transitions $n \to n+1$. Instead of assigning electronic indices to the FC matrix elements, we account for this sign change by noting that

$$M_{qq'}^{[n\to(n-1)]} = M_{q'q}^{[n\to(n+1)]}. \tag{B.4}$$

As a result, a transition $|\, n, q \,\rangle \to |\, n-1, q' \,\rangle$ is associated with the FC matrix element $M_{qq'}$. By contrast, the transition $|\, n, q \,\rangle \to |\, n+1, q' \,\rangle$ involves the FC matrix element $M_{q'q}$. This determines the order of M-indices in Eqs. (2.5), (2.6), and (C.11).

Matrix elements for oscillations

For center-of-mass (CM) oscillations of the molecule, the electron-phonon coupling arises from the exponential dependence of the tunneling matrix elements of the CM position of the molecule. The corresponding FC matrix elements are given by:

$$\begin{aligned} M_{q_1 q_2;\, L} &= \langle\, q_2 \,|\exp[-z/z_0]|\, q_1 \,\rangle = \left(2^{q+q'}\pi q! q'!\right)^{-1/2} \int_{-\infty}^{\infty} d\xi\, \exp\left[-\xi^2 - \xi/\xi_0\right] \mathrm{H}_q(\xi)\, \mathrm{H}_{q'}(\xi) \\ &= \left(\frac{2^{Q-q}\, q!}{Q!}\right)^{1/2} \left(-\frac{1}{2\xi_0}\right)^{Q-q} e^{\frac{1}{4\xi_0^2}}\, L_q^{Q-q}(-\tfrac{1}{2\xi_0^2}) \end{aligned} \tag{B.5}$$

$$M_{q_1 q_2;\, R} = \langle\, q_2 \,|\exp[+z/z_0]|\, q_1 \,\rangle = \left(\frac{2^{Q-q}\, q!}{Q!}\right)^{1/2} \left(+\frac{1}{2\xi_0}\right)^{Q-q} e^{\frac{1}{4\xi_0^2}}\, L_q^{Q-q}(-\tfrac{1}{2\xi_0^2}) \tag{B.6}$$

where $q = \min\{q_1, q_2\}$, $Q = \max\{q_1, q_2\}$, and $\xi_0 = z_0/\lambda_{\rm osc}$.

B.2 FC matrix elements for the Morse potential

The calculation of dissociation rates within the Morse-potential model requires not only the determination of FC matrix elements between bound states (see Chapter 5), but also matrix elements between bound and continuum states. Although analytical expressions for the continuum eigenfunctions of the Morse potential are known [142], their structure involves confluent hypergeometric functions with complex parameters, rendering a direct numerical evaluation of the FC matrix elements difficult.

Instead, we make use of the complete set of orthonormal functions introduced in Ref. [115],

$$\phi_n(x) = \sqrt{\frac{\beta_m n!}{\Gamma(2\sigma + n)}} L_n^{2\sigma-1}(y) y^\sigma e^{-y/2}. \tag{B.7}$$

Here, we denote $y = (2j+1)e^{-\beta_m x}$ and $\sigma = j - \lfloor j \rfloor$. j is fixed by the Morse potential parameters to

$$2j + 1 = \sqrt{8\mu D/\beta_m^2 \hbar^2}, \tag{B.8}$$

and $\lfloor j \rfloor$ [which is the integer closest to and smaller than j] gives the number of bound states. This set of functions has three appealing properties [115]:

(i) It forms a *discrete* complete orthonormal basis enumerated by $n = 0, 1, 2, \ldots$.

(ii) The first $\lfloor j \rfloor + 1$ functions form a basis for the bound eigenstates of the Morse potential, all remaining functions span the space of continuum eigenstates.

(iii) With respect to this basis, the Hamiltonian takes a particularly simple tridiagonal form.

Denoting the bound and continuum eigenstates of the Morse potential by $|\,\psi_q\,\rangle$ and $|\,\psi_E\,\rangle$, respectively, we can now calculate the relevant FC matrix element for a transition from a bound state $|\,\psi_q\,\rangle$ into a continuum state $|\,\psi_E\,\rangle$ by

$$M_{q\to E} = \left\langle\, \psi_E \,\middle|\, e^{\sqrt{2}\lambda\ell_{\mathrm{osc}}\frac{d}{dx}} \,\middle|\, \psi_q \,\right\rangle = \sum_{m=0}^{\lfloor j \rfloor} \sum_{n=\lfloor j \rfloor+1}^{\infty} \alpha^*_{En}\beta_{km} \left\langle\, \phi_n \,\middle|\, e^{\sqrt{2}\lambda\ell_{\mathrm{osc}}\frac{d}{dx}} \,\middle|\, \phi_m \,\right\rangle. \tag{B.9}$$

Here, the expansion coefficients α_{En} and β_{km} for continuum and bound eigenstates with respect to the $\{|\,\phi_n\,\rangle\}$ basis are obtained through numerical diagonalization of the Hamiltonian. Finally, the FC matrix for the $\{|\,\phi_n\,\rangle\}$ basis are given by

$$\begin{aligned}\left\langle\, \phi_n \,\middle|\, e^{\sqrt{2}\lambda\ell_{\mathrm{osc}}\frac{d}{dx}} \,\middle|\, \phi_{n'} \,\right\rangle =& \frac{(-1)^{n'}(4a)^{\sigma}\Gamma(n+n'+2\sigma)}{\sqrt{\Gamma(2\sigma+n)\Gamma(2\sigma+n')n!n'!}} \frac{(a-1)^{n+n'}}{(a+1)^{n+n'+2\sigma}} \\ & \times {}_2\mathrm{F}_1\left(-n', -n; -n-n'-2\sigma+1; \tfrac{(1+a)^2}{(1-a)^2}\right),\end{aligned} \tag{B.10}$$

where $a = \exp\left[-\frac{2\lambda}{\sqrt{\lambda+1}}\right]$ and ${}_2F_1$ denotes the (Gaussian) hypergeometric function. In practice, one introduces a cutoff for the basis $\{|\,\phi_n\,\rangle\}$, leading to a discretization of continuum eigenstates. In order to ensure a sufficiently dense spacing of the spectrum close to the dissociation limit, we take into account $\sim 10,000$ basis functions.

Appendix C

Regularization scheme for cotunneling rates

We have explained in Chapter 2 that the evaluation of cotunneling rates via Fermi's golden rule leads to the problem of divergences due to the lack of lifetime-broadening of the intermediate state within a purely perturbative approach. Here, we present the required regularization scheme that allows for the extraction of the correct rates.

For concreteness, we demonstrate the procedure for the example of cotunneling through the neutral molecule. The regularization of the rates for cotunneling through the singly and doubly occupied molecule proceed in a completely analogous fashion.[1] The naive expression for this cotunneling rate as obtained by Fermi's golden rule is given by

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

(The explicit factor of 2 accounts for the two incoherent contributions of a spin-up and a spin-down electron being transferred.) As motivated in Chapter 2, the first step in the regularization consists of introducing a finite level-width γ for the intermediate state. Defining the abbreviations $\epsilon_{q''} = \epsilon_d - (q-q'')\hbar\omega_0$, $E = (q'-q)\hbar\omega_0$, and $A_{q''} = M_{q'q''}M^*_{qq''}$, we may recast Eq. (C.1) into the form

$$\begin{aligned} W^{00}_{qq';ab} &= \frac{2\Gamma_a\Gamma_b}{2\pi\hbar}\sum_{q''}\int d\epsilon\,\frac{\left|A_{q''}\right|^2}{(\epsilon-\epsilon_{q''})^2+\gamma^2}f_a(\epsilon)\left[1-f_b(\epsilon-E)\right] \quad \text{(C.2)}\\ &+\frac{2\Gamma_a\Gamma_b}{2\pi\hbar}\cdot 2\,\mathrm{Re}\sum_{q''}\sum_{k''<q''}\int d\epsilon\,\frac{A_{q''}}{\epsilon-\epsilon_{q''}+i\gamma}\frac{A^*_{k''}}{\epsilon-\epsilon_{k''}-i\gamma}f_a(\epsilon)\left[1-f_b(\epsilon-E)\right]. \end{aligned}$$

Consequently, we obtain two types of integrals, which correspond to the term in the first and second line and which we denote J and I, respectively. The integrand of J has second-order poles at $\epsilon-\epsilon_{q''} = \pm i\gamma$, the I integrand has first-order poles at $\epsilon-\epsilon_{q''} = -i\gamma$ and $\epsilon-\epsilon_{k''} = i\gamma$. As described in Chapter 2, the regularization requires us to evaluate these integrals and expand them in γ, in the end only retaining the γ^0 terms.

[1] The only caveat concerns the question of coherent vs. incoherent contributions at finite U, see Appendix K.2.

C.1 The I integral

The I integral can be conveniently carried out by applying the Schwinger trick

$$\frac{1}{A} = \int_0^\infty d\alpha\, e^{-\alpha A} \tag{C.3}$$

to convert the energy denominators. Here, $\mathrm{Re}\, A > 0$ is required. This leads to

$$\begin{aligned} I(E_1, E_2, \epsilon_1, \epsilon_2) &= \lim_{\gamma\to 0} \mathrm{Re} \int d\epsilon\, f(\epsilon - E_1)\,[1 - f(\epsilon - E_2)]\, \frac{1}{\epsilon - \epsilon_1 - i\gamma} \frac{1}{\epsilon - \epsilon_2 + i\gamma} \qquad \text{(C.4)} \\ &= \lim_{\gamma\to 0} \mathrm{Re} \int d\epsilon\, f(\epsilon - E_1)\,[1 - f(\epsilon - E_2)]\, i \int_0^\infty dt_1\, e^{-i(\epsilon - \epsilon_1 - i\gamma)t_1} (-i) \int_0^\infty dt_2\, e^{i(\epsilon - \epsilon_2 + i\gamma)t_2} \\ &= \lim_{\gamma\to 0} \mathrm{Re} \int_{-\infty}^\infty d\tau \int_{|\tau|/2}^\infty dt\, e^{i(\epsilon_1 + \epsilon_2)\tau/2 - i(\epsilon_2 - \epsilon_1)t} e^{-2\gamma t} \int d\epsilon\, e^{-i\epsilon\tau} f(\epsilon - E_1)\,[1 - f(\epsilon - E_2)]\,, \end{aligned}$$

where in the last step we have introduced relative and "center-of-mass" coordinates $\tau = t_1 - t_2$ and $t = (t_1 + t_2)/2$. We proceed by evaluating the trivial t-integration and the Fourier transform of the Fermi function product,

$$\begin{aligned} i(E_1, E_2, t) &= \int dE\, e^{-\mathrm{i}\, Et} f(E - E_1)\,[1 - f(E - E_2)] \qquad \text{(C.5)} \\ &= \frac{i\pi}{\beta \sinh(\pi t/\beta)} \left[e^{-\mathrm{i}\, E_2 t} - e^{-\mathrm{i}\, E_1 t}\right] n_B(E_2 - E_1) \end{aligned}$$

This integration is performed easily by contour integration and using the residue theorem, and we have have expressed our result in terms of the Bose function $n_B(\epsilon) = (e^{\beta\epsilon} - 1)^{-1}$. As a result, the integral I now reads

$$I(E_1, E_2, \epsilon_1, \epsilon_2) = \lim_{\gamma\to 0} \mathrm{Re} \int_{-\infty}^\infty d\tau \frac{e^{i(\epsilon_1 + \epsilon_2)|\tau|/2}}{i(\epsilon_2 - \epsilon_1) + 2\gamma)} e^{i(\epsilon_1 + \epsilon_2)\tau/2} i(E_1, E_2, \tau). \tag{C.6}$$

At this point, we can carry out the $\gamma \to 0$ limit. The remaining integral can be solved in terms of digamma functions ψ, with the result

$$\begin{aligned} I(E_1, E_2, \epsilon_1, \epsilon_2) &= \lim_{\gamma\to 0} \mathrm{Re} \int d\epsilon\, f(\epsilon - E_1)\,[1 - f(\epsilon - E_2)]\, \frac{1}{\epsilon - \epsilon_1 - i\gamma} \frac{1}{\epsilon - \epsilon_2 + i\gamma} \qquad \text{(C.7)} \\ &= \frac{n_B(E_2 - E_1)}{\epsilon_1 - \epsilon_2} \mathrm{Re} \Big\{ \psi(1/2 + i\beta[E_2 - \epsilon_1]/2\pi) - \psi(1/2 - i\beta[E_2 - \epsilon_2]/2\pi) \\ &\qquad - \psi(1/2 + i\beta[E_1 - \epsilon_1]/2\pi) + \psi(1/2 - i\beta[E_1 - \epsilon_2]/2\pi) \Big\} \end{aligned}$$

C.2 The J integral

The J integral can be evaluated in an analogous way. First, we note that the energy denominator may be rewritten according to

$$\frac{1}{(\epsilon - \epsilon_1)^2 + \gamma^2} = \frac{1}{2\gamma} \int dt\, e^{-i(\epsilon - \epsilon_1)t - \gamma|t|}, \tag{C.8}$$

so that

$$\begin{aligned} J(E_1, E_2, \epsilon_1) &= \lim_{\gamma\to 0} \int d\epsilon\, f(\epsilon - E_1)\,[1 - f(\epsilon - E_2)]\,\frac{1}{(\epsilon-\epsilon_1)^2+\gamma^2} - \mathcal{O}(1/\gamma) \\ &= \lim_{\gamma\to 0} \frac{1}{2\gamma} \int dt\, e^{i\epsilon_1 t - \gamma|t|} \int d\epsilon\, e^{-i\epsilon t} f(\epsilon - E_1)\,[1 - f(\epsilon - E_2)] - \mathcal{O}(1/\gamma) \\ &= \lim_{\gamma\to 0} \frac{1}{2\gamma} \int dt\, e^{i\epsilon_1 t - \gamma|t|} i(E_1, E_2, t) - \mathcal{O}(1/\gamma) \end{aligned} \tag{C.9}$$

We expand the exponential for small γ, subtract the $1/\gamma$ term and carry out the $\gamma \to 0$ limit. This leads to

$$\begin{aligned} J(E_1, E_2, \epsilon_1) &= \frac{1}{2} \int dt\ |t|\, e^{i\epsilon t} i(E_1, E_2, t) \\ &= \frac{\beta}{2\pi} n_B(E_2 - E_1)\, \mathrm{Im}\left\{\psi'\left(1/2 + i\beta[E_2 - \epsilon_1]/2\pi\right) - \psi'\left(1/2 + i\beta[E_1 - \epsilon_1]/2\pi\right)\right\}. \end{aligned} \tag{C.10}$$

Altogether, the regularized expression for the cotunneling rate $W^{00}_{qq';ab}$ is given by

$$\begin{aligned} W^{0\to 0}_{q\to q';ab} =& \frac{2\Gamma_a\Gamma_b}{2\pi\hbar} \Bigg[\sum_r \left|M_{q'r} M_{qr}\right|^2 J\left(\mu_a, \mu_b - [q-q']\hbar\omega, \epsilon_d - [q-r]\hbar\omega\right) \\ &+ \sum_{r\neq s} M_{q'r} M^*_{qr} M^*_{q's} M_{qs} I\left(\mu_a, \mu_b - [q-q']\hbar\omega, \epsilon_d - [q-r]\hbar\omega, \epsilon_d - [q-s]\hbar\omega\right) \Bigg] \end{aligned} \tag{C.11}$$

Appendix D

Formalism for calculating current and shot noise

In this appendix, we describe the general rate-equations formalism and show how it is employed to calculate the stationary current, and we review Korotkov's technique for computing the current shot noise, Ref. [84]. In order to incorporate higher-order processes such as cotunneling, we slightly generalize his formalism. Throughout this section, we will keep wording and formalism as general as possible to stress the wide applicability of this approach.

We consider a system consisting of some central structure, such as a quantum dot or molecule, and source and drain electrodes coupled to the central structure. We assume that the state space of the center is discrete and finite, and we denote it by

$$\mathbb{S} \equiv \{1, 2, \ldots, N\}. \tag{D.1}$$

Then, the system's dynamics originates from transitions between pairs of these states, $|\, i \,\rangle \to |\, f \,\rangle$, which are associated with specific transition rates $W_{if} \geq 0$. Mathematically speaking, the dynamics can be classified as a time-dependent Markov process, and it is fully characterized by the Master equations

$$\frac{\partial}{\partial t} P(f, t|i) = \sum_{k \in \mathbb{S}} \left[P(k, t|i) W_{kf} - P(f, t|i) W_{fk} \right] \tag{D.2}$$

with initial condition $P(f, t = 0|i) = \delta_{if}$. Here, $P(f, t|i)$ denotes the conditional probability for the system to occupy the state $|\, f \,\rangle$ at time t, given that the initial state at time $t = 0$ was $|\, i \,\rangle$. Note that, due to our choice of labelling processes and corresponding rates with the center degrees of freedom only, rates W_{ii} with identical initial and final states exist and need to be taken into account. [A relevant example is given by elastic cotunneling processes.]

It is convenient to translate Eq. (D.2) into a compact matrix notation. This can be achieved by the definitions

$$\mathbf{p}_i(t) \equiv \left(P(1, t|i), P(2, t|i), \ldots, P(N, t|i) \right)^\top, \tag{D.3}$$

and

$$\mathsf{W} = \begin{pmatrix} -\sum_{k\neq 1} W_{1k} & W_{21} & W_{31} & \cdots \\ W_{12} & -\sum_{k\neq 2} W_{2k} & W_{32} & \cdots \\ W_{13} & W_{23} & -\sum_{k\neq 3} W_{3k} & \cdots \\ \vdots & & & \ddots \end{pmatrix}, \tag{D.4}$$

where all k-sums run over the state space $\mathbb{S}$. Now, the Master equation can be summarized into

$$\frac{\partial}{\partial t}\mathbf{p}_i(t) = \mathsf{W}\mathbf{p}_i(t) \tag{D.5}$$

with initial condition $\mathbf{p}_i(t=0) = \hat{\mathbf{e}}_i$, having the formal solution

$$\mathbf{p}_i(t) = e^{\mathsf{W}t}\hat{\mathbf{e}}_i. \tag{D.6}$$

In the following, the solution of the *stationary* rate equations will be denoted $\mathbf{P}$. Note that the sum over all components of the vector $\mathbf{P}$ is 1 (normalization), which we write as $\operatorname{tr}\mathbf{P} = 1$. It is important to note that the stationary rate equations $\mathsf{W}\mathbf{P} = 0$ cannot be solved by a direct inversion of the matrix W. Due to its structure, see Eq. (D.4), any rate-equations matrix satisfies the relations $\sum_i W_{ij} = 0$ for all j, i.e. the sum of its lines vanishes. Consequently, we have $\det\mathsf{W} = 0$ and W is not invertible. A convenient way for obtaining the stationary probabilities $\mathbf{P}$ consists of defining a matrix E with all entries set to 1. Then, one can show that $\mathsf{W}+\mathsf{E}$ is invertible. Applying its inverse to the vector $\mathbf{e} = (1, 1, \ldots, 1)^\top$,

$$\mathbf{P} = (\mathsf{W}+\mathsf{E})^{-1}\mathbf{e}, \tag{D.7}$$

yields the correct stationary probability distribution. We provide a proof of this statement at the the end of this appendix in Section D.3.

D.1 Current

Electron transfer between the electrodes and the central system gives rise to a current, whose time-average $\langle I\rangle$ (the stationary current) must be identical in the left and right junction, i.e. $\langle I\rangle = \langle I_L\rangle = \langle I_R\rangle$, due to charge conservation. [Here, and in the following, $\langle\cdot\rangle$ always denotes time averaging.] At this point, we may fix the sign of the current once and for all, defining the current to be positive for an electron transfer from the left to the right.

Some caution is now in place regarding the nature of the transitions $|\,i\,\rangle \to |\,f\,\rangle$. In general, there may be several different *processes* which cause a transition between the central system's states $|\,i\,\rangle$ and $|\,f\,\rangle$, and they differ from each other in the resulting leads' states. In order to elucidate this situation, we give one concrete example. Consider a system, whose central system is simply a single electronic level. Then, cotunneling will result in a transition $n \to n$, i.e. the electronic occupation of the center remains invariant. However, there are several incoherent contributions to this transition: The cotunneling transition can result in a transfer of one electron from the left to the right, or vice versa. In principle, the tunneling back and forth between only one lead and the center is possible as well.

This example reveals that, in general, each transition $|\,i\,\rangle \to |\,f\,\rangle$ may be made up of several elementary processes contributing to this transition. Accordingly, the rates W_{if} are

a sum of the rates of the corresponding elementary processes ν,

$$W_{if} = \sum_{\nu} W_{if}^{(\nu)}. \tag{D.8}$$

[Of course, the notion of "elementary processes" only comes about due to our choice of expressing all results in terms of the states of the central system alone.]

Generally, not all elementary processes contribute to the current, and each process which does, can transfer a number n of electrons either in the positive or negative direction. Taking this into account, we define the quantity $s_{if,\nu}^{a}$ as follows: If the elementary process ν belonging to the transition $|\, i \,\rangle \to |\, f \,\rangle$ gives a current contribution in junction a ($a = L, R$), then $s_{if,\nu}^{a}$ gives the number of electrons transferred across junction a within this process, and its sign reflects whether the transfer occurs in the positive or negative direction. For all processes without current contribution, $s_{if,\nu}^{a}$ vanishes. Now the stationary current in junction a can be written as

$$\langle I_a \rangle = e \sum_{i,f \in \mathbb{S}} \sum_{\nu} s_{if,\nu}^{a} P_i W_{if}^{(\nu)} = e \,\mathrm{tr}\, \mathsf{W}_I \mathbf{P}, \tag{D.9}$$

where the current coefficient matrix W_I is defined via

$$(\mathsf{W}_I)_{ij} = \sum_{\nu} s_{ji,\nu}^{a} W_{ji}^{(\nu)}. \tag{D.10}$$

For the analysis of the current shot noise, we are also interested in the explicit time-dependence of the current. Viewing the system dynamics as a Markov process consisting of quasi-instantaneous jumps between different states, we can define the times $t_n^{(if,\nu)}$ ($n = 1, 2, \ldots, \infty$) at which the process ν belonging to the transition $|\, i \,\rangle \to |\, f \,\rangle$ takes place. Then, the time-dependent current in junction a can formally be written as a sum of δ functions according to

$$I_a(t) = e \sum_{i,f \in \mathbb{S}} \sum_{\nu,n} s_{if,\nu}^{a} \delta(t - t_n^{(if,\nu)}). \tag{D.11}$$

Taking the time average of this expression and comparing with Eq. (D.9), we obtain the relation

$$\sum_{n} \langle \delta(t - t_n^{(if,\nu)}) \rangle = P_i W_{if}^{(\nu)}. \tag{D.12}$$

D.2 Noise

Our central goal consists of the derivation of a compact and general expression for the current noise defined by

$$S_{ab}(\omega) = 2 \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} \left[\langle I_a(\tau) I_b(0) \rangle - \langle I \rangle^2 \right]. \tag{D.13}$$

The starting point for our considerations is the current-current correlator $\langle I_a(t)I_b(t')\rangle$. When substituting Eq. (D.11) into the correlator, we obtain a multiple sum with each summand being proportional to the average of a product of two δ functions:

$$\langle I_a(t)I_b(t')\rangle = e^2 \sum_{i,f\in\mathbb{S}} \sum_{\nu,n} \sum_{i',f'\in\mathbb{S}} \sum_{\mu,m} s^a_{if,\nu} s^b_{i'f',\mu} \langle \delta(t - t_n^{(if,\nu)}) \delta(t' - t_m^{(i'f',\mu)}) \rangle. \tag{D.14}$$

As the set of all times $t_n^{(if,\nu)}$ forms the time lattice of the Markov process, the times are considered to be pairwise distinct. Thus, we have $t_n^{(if,\nu)} \neq t_m^{(i'f',\mu)}$ for $(n, if, \nu) \neq (m, i'f', \mu)$. Accordingly, the correlator can be separated into autocorrelation and cross-correlation contributions, $\langle I_a(t)I_b(t')\rangle_a = \langle I_a(t)I_b(t')\rangle_{\rm a} + \langle I_a(t)I_b(t')\rangle_{\rm x}$, where

$$\langle I_a(t)I_b(t')\rangle_{\rm a} = e^2 \sum_{i,f\in\mathbb{S}} \sum_{\nu,n} s^a_{if,\nu} s^b_{if,\nu} \times \langle \delta(t - t_n^{(if,\nu)}) \delta(t' - t_n^{(if,\nu)}) \rangle, \tag{D.15}$$

$$\langle I_a(t)I_b(t')\rangle_{\rm x} = \text{“non-diagonal terms”}. \tag{D.16}$$

We first turn to the evaluation of the autocorrelations. Using the fact that $\langle \delta(t - t_n^{(if,\nu)}) \delta(t' - t_n^{(if,\nu)}) \rangle = \delta(t - t') \langle \delta(t - t_n^{(if,\nu)})) \rangle$, and applying relation Eq. (D.12), we obtain

$$\langle I_a(t)I_b(t')\rangle_{\rm a} = e^2 \delta(t - t') \sum_{i,f\in\mathbb{S}} \sum_{\nu} s^a_{if,\nu} s^b_{if,\nu} P_i W^{(\nu)}_{if} \tag{D.17}$$

The cross-correlation terms now involve only distinct processes at different times. These contributions can be dealt with in the following way. Let us assume that $t \geq t'$. By using $I = dQ/dt$, we note that

$$\langle I_a(t)I_b(t')\rangle_{\rm x} = \frac{\langle dQ_a(t) dQ_b(t')\rangle}{dt\, dt'}, \tag{D.18}$$

and we only get a contribution to the time average, if there are current-contributing processes [causing charge variations dQ] in junction b during $[t', t' + dt']$, and in junction a during $[t, t + dt]$, which leads us to

$$\langle I_a(t)I_b(t')\rangle_{\rm x} = e^2 \sum_{i,j,k,f\in\mathbb{S}} \sum_{\mu,\nu} s^a_{ij,\nu} s^b_{kf,\mu} P_i W^{(\nu)}_{ij} p(k, t - t'|j) W^{(\mu)}_{kf}. \tag{D.19}$$

We are now in the position to give an intermediate result for the bracketed expression in Eq. (D.13). We find

$$\begin{aligned} \langle \delta I_a(\tau) \delta I_b(0)\rangle =& e^2 \delta(\tau) \sum_{i,f\in\mathbb{S}} \sum_{\nu} s^a_{if,\nu} s^b_{if,\nu} P_i W^{(\nu)}_{if} \\ &+ e^2 \sum_{i,j,k,f\in\mathbb{S}} \sum_{\mu,\nu} s^a_{ij,\nu} s^b_{kf,\mu} P_i W^{(\nu)}_{ij} \left[p(k, \tau|j) - P_k\right] W^{(\mu)}_{kf}. \end{aligned} \tag{D.20}$$

This expression is valid for $\tau \geq 0$. For $\tau < 0$ we exploit the symmetry

$$\langle \delta I_a(\tau) \delta I_b(0)\rangle = \langle \delta I_a(0) \delta I_b(-\tau)\rangle. \tag{D.21}$$

Now, the last missing piece for an evaluation of the noise consists of the determination of the Fourier transform of the term

$$G_{kj}(\tau) = \theta(\tau)\left[p(k,\tau|j) - P_k\right]. \tag{D.22}$$

Noting that $p(k,\tau|j) = (e^{\mathsf{W}\tau})_{kj}$ and defining the matrix V by $V_{kj} = P_k$, we can rewrite Eq. (D.22) in matrix form as $\mathsf{G}(\tau) = \theta(\tau)\left[e^{\mathsf{W}t} - \mathsf{V}\right]$, and its Fourier transform is found to be

$$\mathsf{G}(\omega) = \int_0^\infty dt\, e^{i\omega\tau}\left[e^{\mathsf{W}\tau} - \mathsf{V}\right] = -(\mathsf{W} + i\omega\mathbb{1})^{-1} + \frac{1}{i\omega}\mathsf{V}, \tag{D.23}$$

which can directly be evaluated at all finite frequencies. (The $\omega \to 0$ will be discussed below.) Thus, the noise can be expressed as

$$\begin{aligned} S_{ab}(\omega) =& 2e^2 \sum_{i,f\in\mathbb{S}} \sum_{\nu} s^a_{if,\nu} s^b_{if,\nu} P_i W^{(\nu)}_{if} \\ &+ 2e^2\Bigg[\sum_{i,j,k,f\in\mathbb{S}} \sum_{\mu,\nu} s^a_{ij,\nu} s^b_{kf,\mu} P_i W^{(\nu)}_{ij} G_{kj}(\omega) W^{(\mu)}_{kf} + (\text{same term with } a \leftrightarrow b)^*\Bigg] \\ =& 2e^2\left[\operatorname{tr}\mathbf{u}_{ab} + \mathbf{w}_b \mathsf{G}(\omega)\mathbf{y}_a + \mathbf{w}_a \mathsf{G}^*(\omega)\mathbf{y}_b\right]. \end{aligned} \tag{D.24}$$

Here we have defined the vectors $\mathbf{u}_{ab}$, $\mathbf{y}_a$ and $\mathbf{w}_b$ by

$$(u_{ab})_i = \sum_{f\in\mathbb{S}} \sum_{\nu} s^a_{if,\nu} s^b_{if,\nu} P_i W^{(\nu)}_{if} \tag{D.25}$$

$$(y_a)_j = \sum_{i\in\mathbb{S}} \sum_{\nu} s^a_{ij,\nu} P_i W^{(\nu)}_{ij} \tag{D.26}$$

$$(w_b)_k = \sum_{f\in\mathbb{S}} \sum_{\mu} s^b_{kf,\mu} W^{(\mu)}_{kf} \tag{D.27}$$

In order to evaluate the zero-frequency limit $\omega \to 0$, we make use of the following properties of the relevant matrices. First, we observe that $\mathsf{G}\mathbf{P} = 0$. Second, one easily confirms that $\mathsf{V}\mathbf{x} = 0$ for any traceless vector $\mathbf{x}$. Third, we note that any well-behaved rate-equations matrix W (which has a unique steady-state solution) is invertible in the subspace of traceless vectors. Thus, in Eq. (D.24) we may modify the vector $\mathbf{y}_a$ by adding some multiple of the stationary distribution $\mathbf{P}$, leaving the result invariant.

We choose

$$(\bar{y}_a)_j \equiv (y_a)_j - \langle I_a\rangle P_j/e, \tag{D.28}$$

which makes $\bar{\mathbf{y}}_a$ a traceless vector. Consequently, the zero-frequency noise can be evaluated via

$$S_{ab}(\omega = 0) = 2e^2\left[\operatorname{tr}\mathbf{u}_{ab} - \mathbf{w}_b\mathsf{W}^{-1}\bar{\mathbf{y}}_a - \mathbf{w}_a\mathsf{W}^{-1}\bar{\mathbf{y}}_b\right]. \tag{D.29}$$

D.3 Formula for the stationary probability distribution

Proposition.— Let $\mathsf{W} \in \mathrm{Mat}(\mathbb{R}, n)$ be a rate-equations matrix, i.e. $\sum_i W_{ij} = 0 \quad \forall j$, $\ker \mathsf{W} = \mathrm{span}\{\mathbf{P}\}$ with $P_n \geq 0$ and $\sum_n P_n = 1$. Define a matrix $\mathsf{E} \in \mathrm{Mat}(\mathbb{R}, n)$ with all entries set to 1, and a vector $\mathbf{e} \in \mathbb{R}^n$ with all entries set to 1. Then, the stationary probability distribution $\mathbf{P}$ (satisfying $\mathsf{W}\mathbf{P} = 0$ and $\mathsf{E}\mathbf{P} = \mathbf{e}$) is given by

$$\mathbf{P} = (\mathsf{W} + \mathsf{E})^{-1}\mathbf{e}. \tag{D.30}$$

Proof.— We need to show that $(\mathsf{W} + \mathsf{E})$ is invertible and that the vector $\mathbf{x} = (\mathsf{W} + \mathsf{E})^{-1}\mathbf{e}$ indeed satisfies $\mathsf{W}\mathbf{x} = 0$ and $\mathsf{E}\mathbf{x} = \mathbf{e}$ (and is thus identical with $\mathbf{P}$).

We choose a basis consisting of $\mathbf{a}_1 = (1, -1, 0, 0, \ldots, 0)$, $\mathbf{a}_2 = (0, 1, -1, 0, \ldots, 0)$, …, $\mathbf{a}_{n-1} = (0, 0, \ldots, 0, 1, -1)$, $\mathbf{P}$. Obviously, all $\mathbf{a}_i$ are linearly independent. They generate the subspace T of traceless vectors, i.e.

$$\mathbf{x} \in \mathrm{span}\{\mathbf{a}_1, \ldots \mathbf{a}_{n-1}\} =: T \quad \Rightarrow \quad \mathrm{tr}\,\mathbf{x} = \sum_n x_n = 0. \tag{D.31}$$

Since $\mathbf{P}$ is not traceless, it is linearly independent, and one concludes that the choice above indeed forms a basis of the vector space.

In the next step, we verify that W is invertible in the subspace T. Since W is a rate-equations matrix, we have $\sum_i W_{ij} = 0 \quad \forall j$. This immediately leads to $\mathrm{Im}\,\mathsf{W} \subset T$. W is a linear operator, hence it is sufficient to show that $\mathsf{W}|_T$ is injective. Let $\mathbf{t_1}, \mathbf{t_2} \in T$ with $\mathsf{W}\mathbf{t}_1 = \mathsf{W}\mathbf{t}_2$. This gives $\mathsf{W}(\mathbf{t}_1 - \mathbf{t}_2) = 0$, and consequently $(\mathbf{t}_1 - \mathbf{t}_2)$ is a traceless vector with $(\mathbf{t}_1 - \mathbf{t}_2) \in \ker \mathsf{W}$. This is only possible for $(\mathbf{t}_1 - \mathbf{t}_2) = 0$, therefore $\mathsf{W}|_T$ is injective (and hence bijective).

Now we prove that $(\mathsf{W}+\mathsf{E})$ is invertible by showing that $\ker(\mathsf{W}+\mathsf{E}) = \{0\}$. Let $\mathbf{x} \in \mathbb{R}^n$ with $(\mathsf{W} + \mathsf{E})\mathbf{x} = 0$. We decompose $\mathbf{x}$ using the basis above, $\mathbf{x} = \sum_i \alpha_i \mathbf{a}_i + \beta\mathbf{P} = \mathbf{y} + \beta\mathbf{P}$. Then,

$$(\mathsf{W} + \mathsf{E})\mathbf{x} = 0 \quad \Leftrightarrow \quad \mathsf{W}\mathbf{y} = -\beta\mathbf{e}. \tag{D.32}$$

While the vector on the left-hand side is traceless, $\mathsf{W}\mathbf{y} \in T$, the vector on the right-hand side has nonzero trace for $\beta \neq 0$, $-\beta\mathbf{e} \notin T$. It follows that $\beta = 0$, from which one concludes $\mathsf{W}\mathbf{y} = 0$. Since W is invertible in T, this leads to $\mathbf{y} = 0$, so that $\mathbf{x} = 0$, overall resulting in $\ker(\mathsf{W} + \mathsf{E}) = \{0\}$.

Now let $\mathbf{x} = (\mathsf{W} + \mathsf{E})^{-1}\mathbf{e}$. This is equivalent to (*) $(\mathsf{W} + \mathsf{E})\mathbf{x} = \mathbf{e}$, and again we decompose $\mathbf{x} = \sum_i \alpha_i \mathbf{a}_i + \beta\mathbf{p}$. Then, (*) gives

$$\mathsf{W}\sum_i \alpha_i \mathbf{a}_i + \beta\mathsf{E}\mathbf{p} = \mathsf{W}\sum_i \alpha_i \mathbf{a}_i + \beta\mathbf{e} = \mathbf{e} \tag{D.33}$$

from which one infers $\beta = 1$, $\alpha_i = 0$ and therefore $\mathbf{x} = \mathbf{p}$. □

Appendix E

Details: Analytical treatment of avalanche transport

In Chapter 3 we have presented an analytical treatment of avalanche transport relevant in the Franck-Condon blockade regime. For better legibility, we have focused on the main line of thought, leaving out some of the calculational details. These intermediate steps in the derivation are provided in this Appendix.

E.1 Derivation of the full counting statistics

Determination of $\tilde{\mathcal{P}}_q(\alpha)$

For the Fourier transform $\tilde{\mathcal{P}}_q(\alpha)$ of the distribution function for the number N of electrons per generation–q avalanche, we derived the recursion relation

$$\tilde{\mathcal{P}}_q(\alpha) = \frac{1}{1 - \overline{n}_q \ln[\tilde{\mathcal{P}}_{q+1}(\alpha)]}, \tag{E.1}$$

see Eq. (3.7). Since the Fourier transform $\tilde{\mathcal{P}}_q(\alpha)$ must vanish sufficiently rapidly for $\alpha \to \infty$, it is convenient to expand its inverse in powers of α, and we choose the form

$$\tilde{\mathcal{P}}_q(\alpha) = \frac{1}{\sum_{k=0}^{\infty} c_{q,k} \left(\alpha \overline{N}^{(q)}\right)^k}. \tag{E.2}$$

We can now exploit the self-similarity of avalanches to show that the coefficients $c_{q,k}$ in fact do *not* depend on the hierarchy index q. To see this, we note that the self-similarity implies a scaling form for the distribution of the number of electrons per generation–q avalanche. Specifically, we expect

$$\mathcal{P}_q(N) = \frac{1}{\overline{N}^{(q)}} g\left(N/\overline{N}^{(q)}\right), \tag{E.3}$$

where $g(x)$ is a scaling function *independent* of q. For the Fourier transform of the distribution function, we therefore obtain

$$\tilde{\mathcal{P}}_q(\alpha) = \int dx\, g(x) e^{i\alpha \overline{N}^{(q)} x} = \tilde{g}\left(\alpha \overline{N}^{(q)}\right). \tag{E.4}$$

From a comparison with the expansion in Eq. (E.2), we conclude that the coefficients $c_{q,k}$ must be independent of the hierarchy index q, and we will drop it henceforth.

With the normalization condition for $\mathcal{P}_q(N)$ and the definition of its first moment as $\overline{N}^{(q)}$, the coefficients c_k for $k = 0$ and 1 are fixed, and we obtain

$$\tilde{\mathcal{P}}_q(\alpha) = \frac{1}{1 + i\alpha\overline{N}^{(q)} + c_2(\alpha\overline{N}^{(q)})^2 + \cdots}. \tag{E.5}$$

Substituting this expression on the right-hand side of Eq. (E.1) and expanding the logarithm, we obtain the equation

$$1 + i\alpha\overline{N}^{(q)} + c_2(\alpha\overline{N}^{(q)})^2 + \cdots = 1 + i\alpha\overline{n}_q\overline{N}^{(q+1)} + c_2(\alpha\overline{N}^{(q+1)})^2 + \frac{1}{2}(\alpha\overline{N}^{(q+1)})^2 + \cdots \tag{E.6}$$

Employing the relation $\overline{N}^{(q)} = \overline{n}_q\overline{N}^{(q+1)}$, and performing a coefficients comparison in powers of α, we can extract the recursion relation for the coefficient c_2, namely

$$c_2 = (c_2 + 1/2)/\overline{n}_q. \tag{E.7}$$

With $1/\overline{n}_q \ll 1$ being a small parameter, we find the asymptotic solution $c_2 = 0$. Extending this analysis to higher orders in α, we find relations similar to Eq. (E.7) with $c_k \sim (1/\overline{n}_q)^{k-1}$. Consequently, the fix-point solution corresponds to $c_k = 0$ for $k \geq 2$ so that

$$\tilde{\mathcal{P}}_q(\alpha) = \frac{1}{1 + i\alpha\overline{N}_{(q)}}. \tag{E.8}$$

Performing the integral for obtaining $P_t(Q)$

With the input $\tilde{\mathcal{P}}_0(\alpha) = (1 + i\alpha\overline{N}^{(0)})^{-1}$, we may use Eq. (3.3) to calculate the full counting statistics $P_t(Q)$. Substituting the expression for $\tilde{\mathcal{P}}_0(\alpha)$ and the Poisson distribution $\varphi_t(n)$, we obtain

$$\begin{aligned} P_t(Q) &= \sum_{n=0}^{\infty} \frac{e^{-\overline{n}_t}(\overline{n}_t)^n}{n!} \int \frac{d\alpha}{2\pi} \frac{e^{i\alpha Q}}{\left(1 + i\alpha\overline{N}^{(0)}\right)^n} \\ &= e^{-\overline{n}_t}\delta(Q) + \sum_{n=1}^{\infty} \frac{e^{-\overline{n}_t}(\overline{n}_t)^n}{n!} \int \frac{d\alpha}{2\pi} \frac{e^{i\alpha Q}}{\left(i\overline{N}^{(0)}\right)^n \left(\alpha - i/\overline{N}^{(0)}\right)^n} \end{aligned} \tag{E.9}$$

The remaining α integrals may be carried out using the residue theorem, which leads to

$$\begin{aligned} P_t(Q) &= e^{-\overline{n}_t}\delta(Q) + \sum_{n=1}^{\infty} \frac{e^{-\overline{n}_t}(\overline{n}_t)^n}{n!} \frac{i}{(n-1)!\left(i\overline{N}^{(0)}\right)^n} \frac{\partial^{n-1}}{\partial\alpha^{n-1}} e^{i\alpha Q}\Big|_{\alpha = i/\overline{N}^{(0)}} \\ &= e^{-\overline{n}_t}\delta(Q) + e^{-\overline{n}_t - Q/\overline{N}^{(0)}} \frac{1}{Q} \frac{\overline{n}_t Q}{\overline{N}^{(0)}} \sum_{n=0}^{\infty} \frac{1}{n!(n+1)!} \left[\frac{\overline{n}_t Q}{\overline{N}^{(0)}}\right]^n \end{aligned} \tag{E.10}$$

Comparing the last term with the series expansion for the modified Bessel function I_ν,

$$\mathrm{I}_\nu(z) = (z/2)^\nu \sum_{k=0}^{\infty} \frac{(z^2/4)^k}{k!\,\Gamma(\nu+k+1)}, \tag{E.11}$$

we obtain our final expression for the full counting statistics,

$$P_t(Q) = e^{-\overline{n}_t}\delta(Q) + e^{-\frac{Q}{\overline{N}^{(0)}}-\overline{n}_t}\sqrt{\frac{\overline{n}_t}{\overline{N}^{(0)}Q}}\,\mathrm{I}_1\left(\sqrt{\frac{4\overline{n}_t Q}{\overline{N}^{(0)}}}\right). \tag{E.12}$$

E.2 Derivation of the stationary current and the noise spectrum

Our starting point for the analytical calculation of the stationary current and the noise spectrum is the representation of the current as

$$I(t) = \sum_{i=1}^{\infty} N_i\,\delta\left(t - \sum_{k=1}^{i} t_k\right), \tag{E.13}$$

valid for frequencies smaller than $1/\tau^{(0)}$. For the evaluation of the stationary current, it is convenient to perform the averaging over the electron numbers N_i and the waiting times t_i in the Fourier representation of the current,

$$\langle I(t)\rangle = \left\langle \int \frac{d\alpha}{2\pi} e^{i\alpha t}\tilde{I}(\alpha)\right\rangle. \tag{E.14}$$

The "naive" Fourier transform of the current is given by

$$\tilde{I}(\alpha) = \int dt\, e^{-i\alpha t} I(t) = \sum_{i=1}^{\infty} N_i \exp\left[-i\alpha \sum_{k=1}^{i} t_i\right].$$

The evident problem of this expression is a divergence for $\alpha \to 0$, which corresponds to the fact that an infinite amount of charge is transferred for $t \to \infty$. A direct substitution into Eq. (E.14) and the attempt of averaging immediately leads to further divergences. This difficulty may be circumvented by the following regularization. We introduce a switch-off parameter $\eta > 0$ so that the current reads

$$I(t) = e^{-\eta t} \sum_{i=1}^{\infty} N_i\,\delta\left(t - \sum_{k=1}^{i} t_k\right). \tag{E.15}$$

Its Fourier transform now acquires the regularized form

$$\tilde{I}(\alpha) = \sum_{i=1}^{\infty} N_i \exp\left[-i(\alpha - i\eta) \sum_{k=1}^{i} t_i\right]. \tag{E.16}$$

This expression is suitable for the evaluation of the stationary current. Its substitution into Eq. (E.14) results in

$$\begin{aligned}\langle I(t)\rangle &= \left\langle \int \frac{d\alpha}{2\pi} e^{i\alpha t} \sum_{i=1}^{\infty} N_i e^{-i(\alpha - i\eta)\sum_{k=1}^{i} t_k} \right\rangle = \langle N_i\rangle \sum_{i=1}^{\infty} \int \frac{d\alpha}{2\pi} e^{i\alpha t} \left\langle e^{-i(\alpha-i\eta)t_k} \right\rangle^i \\ &= \langle N_i\rangle \int \frac{d\alpha}{2\pi} e^{i\alpha t} \frac{\tilde{W}(\alpha - i\eta)}{1 - \tilde{W}(\alpha - i\eta)} \end{aligned} \tag{E.17}$$

As explained in Chapter 3, the relevant contribution from the integrand in the long-time limit stems from small α, so that we may substitute the expansion $\tilde{W}(\alpha) = 1 - i\alpha\langle t_i\rangle - (1/2)\alpha^2\langle t_i^2\rangle + \ldots$. Keeping the leading-order term we find

$$\langle I(t)\rangle = \frac{\langle N_i\rangle}{\langle t_i\rangle} \int \frac{d\alpha}{2\pi i} \frac{e^{i\alpha t}}{(\alpha - i\eta)} = \frac{\langle N_i\rangle}{\langle t_i\rangle} e^{-\eta t} \overset{\eta\to 0}{\to} \frac{\langle N_i\rangle}{\langle t_i\rangle}. \tag{E.18}$$

Based on this regularization, the current-current correlator and noise spectrum may be derived in a completely analogous fashion.

Appendix F

Sketch of Monte-Carlo simulations for Markov processes

The dynamics of tunneling events and the resulting current and noise characteristics can be simulated by Monte Carlo methods. The mathematical justification for this statement is given by the intimate relation between the rate equations and time-dependent Markov processes [93, 94]. The physical idea is to track the system's state and to generate random tunneling events in time, obeying the statistics induced by the transition rates.

In particular, assume that the system is in an initial state $|\, i \,\rangle$, and that tunneling induces a transition to the final state $|\, f \,\rangle$ with average rate W_{if}. In complete analogy to the decay of excited atoms or radioactive nuclei, the time dependence of the "decay" of the initial state follows an exponential law. The arguments leading to this result are reviewed here briefly; more extensive discussions can be found in any good textbook about nuclear or atomic physics. Consider the decay of an ensemble of N_0 systems, all in the initial state at the time $t = 0$. The number of systems in the initial state decreases due to decay according to $dN = -W_{if} N\, dt$, from which one infers that the number of systems remaining in the initial state at time t is given by $N(t) = N_0 e^{-W_{if} t}$. Hence, the probability that a single system has not decayed in the time interval $[0, t]$ is given by $P(t) = N(t)/N_0 = e^{-W_{if} t}$. As a result, the probability for a decay of the system in the time interval $[t, t + dt]$ is obtained as

$$p(t)dt = 1 - P(t + dt) - [1 - P(t)] = -\frac{dP(t)}{dt} dt = W_{if} e^{-W_{if} t} dt. \tag{F.1}$$

The probability distribution $p(t)$ describes the transition (or decay) dynamics.

Analogous to the case of nuclear decay with several decay channels, one can now consider the more general case of multiple final states, which we denote by $|\, f_1 \,\rangle$, $|\, f_2 \,\rangle$, etc. The corresponding transition rates are written as W_{if_n}. The total decay rate is given by the sum of all decay rates for the possible channels: $W_i^{(\mathrm{tot})} = \sum_n W_{if_n}$. The relative probability for a decay into channel f_k is given by the ratio of its partial rate and the total rate, i.e.

$$P_{f_k}^{(\mathrm{ch})} = W_{if_n} / W_i^{(\mathrm{tot})} \tag{F.2}$$

Accordingly, the probability for a decay of the system in the time interval $[t, t + dt]$ via the

channel f_k is given by the following generalization of Eq. (F.1):

$$p_k(t)dt = P_{f_k}^{(\mathrm{ch})} W_i^{(\mathrm{tot})} e^{-W_i^{(\mathrm{tot})} t} dt. \tag{F.3}$$

The MC simulation of tunneling events can now be accomplished by the generation of two random numbers per event: The first random number determines the decay channel for the event, the second random number gives the time at which the event occurs. The random number for the decay channel can be chosen as a uniform deviate within the range $[0, 1]$. For the decay time, the random numbers have to obey the statistics given by Eq. (F.1). This is achieved by applying the transformation method for uniform deviates, see e.g. [143].

F.0.1 Relaxation in Monte Carlo simulations

In order to take into account relaxation, the additional term

$$-\frac{1}{\tau}\left[P_q^n - P_q^{\mathrm{eq}} \sum_{q'} P_{q'}^n\right] \tag{F.4}$$

in the rate equations should be translated into the language of Markov processes. This can be achieved by rewriting this term in a form resembling the other transition terms, namely

$$-\frac{1}{\tau}\left[P_q^n - P_q^{\mathrm{eq}} \sum_{q'} P_{q'}^n\right] = \sum_{q'}\left[P_{q'}^n \frac{1}{\tau} P_q^{\mathrm{eq}} - P_q^n \frac{1}{\tau} P_{q'}^{\mathrm{eq}}\right] = \sum_{n',q'}\left[P_{q'}^{n'} R_{q'q}^{n'n} - P_q^n R_{qq'}^{nn'}\right], \tag{F.5}$$

where the phonon relaxation rates $R_{qq'}^{nn'} \equiv \delta_{n,n'} \frac{1}{\tau} P_{q'}^{\mathrm{eq}}$ have been introduced. Accordingly, relaxation processes can be treated on the same basis as tunneling processes.

Appendix G

Exactly solvable case: the resonant-level model

We consider the simple case of a single spin-degenerate, noninteracting level coupled to two leads, the resonant-level model. Due to the absence of interaction in this model, spin only results in trivial factors of 2 and may be neglected. We have picked this trivial model, since it is exactly solvable, e.g. using a one-particle scattering approach.

G.1 Current

The current is given by

$$I = \frac{e}{h} \int dE \, \frac{\Gamma_L(E)\Gamma_R(E)}{\Gamma_L(E) + \Gamma_R(E)} A_d(E)[f_L(E) - f_R(E)], \tag{G.1}$$

where A_d denotes the spectral function of the dot,

$$A_d(E) = -2 \operatorname{Im} G_d^R(E) = \frac{\Gamma(E)}{[E - \epsilon_d]^2 + [\Gamma(E)/2]^2}, \tag{G.2}$$

and the energy broadening of the level is $\Gamma(E) = \Gamma_L(E) + \Gamma_R(E)$ with $\Gamma_a(E) = 2\pi\rho_a(E)\,|t_a|^2$. (Note that any possible energy shift due to the tunnel coupling has been absorbed into ϵ_d.) In the wide-band limit and for symmetric voltage splitting, the solution reads

$$\begin{aligned} I &= \frac{e}{h} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \int dE \frac{\Gamma}{[E - \epsilon_d]^2 + [\Gamma/2]^2} \, [f_L(E) - f_R(E)] \\ &= \frac{e}{\hbar} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{1}{\pi} \operatorname{Im} \sum_a a\psi \left(\frac{1}{2} + \frac{\Gamma\beta}{4\pi} + i \frac{\beta}{2\pi} [\epsilon_d + aeV/2] \right). \end{aligned} \tag{G.3}$$

Here, ψ denotes the digamma function. The exact result can be expanded in orders of Γ, which gives

$$\begin{aligned} I &= \frac{e}{\hbar} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \, [f_L(\epsilon_d) - f_R(\epsilon_d)] \\ &+ \frac{e}{h} \frac{\beta}{2\pi} \Gamma_L \Gamma_R \operatorname{Im} \sum_a a\psi' \left(\frac{1}{2} + i \frac{\beta}{2\pi} [\epsilon_d + aeV/2] \right) + \mathcal{O}(\Gamma^3) \end{aligned} \tag{G.4}$$

For the weak-coupling case we can alternatively apply the rate-equations approach. In this case, the stationary current is calculated via $I = I_L = -I_R$ with

$$\begin{aligned} I_L &= I_L^{(\mathrm{seq})} + I_L^{(\mathrm{cot})} \\ &= e[P_0 W_L^+ - P_1 W_L^-] + e[P_0(W_{LR}^{00} - W_{RL}^{00}) + P_1(W_{LR}^{11} - W_{RL}^{11})]. \end{aligned} \tag{G.5}$$

Here, W_a^+ (W_a^-) gives the rate for a sequential-tunneling process in junction a where one electron enters (leaves) the dot. Similarly, W_{LR}^{nn} (W_{RL}^{nn}) denotes the rate for a cotunneling process with initial and final charge state n where one electron is coherently transferred from the left to the right lead (or vice versa). The stationary probabilities for the empty and occupied dot P_0 and P_1 are obtained from the rate equations

$$0 = \frac{dP_0}{dt} = P_1 W^- - P_0 W^+, \qquad P_0 + P_1 = 1, \tag{G.6}$$

where $W^\pm \equiv W_L^\pm + W_R^\pm$. It is important to note that in this case, there are no cotunneling contributions to the rate equations: Elastic cotunneling does not change the charge state of the dot, and hence does not affect the probability distribution.

Sequential-tunneling contributions

In the first step, we calculate the stationary probabilities and the sequential-tunneling current. The transition rates obtained from Fermi's golden rule are

$$W_a^+ = \frac{1}{\hbar}\Gamma_a f_a(\epsilon_d), \qquad W_a^- = \frac{1}{\hbar}\Gamma_a[1 - f_a(\epsilon_d)]. \tag{G.7}$$

From substituting this into Eq. (G.6) one obtains

$$P_0 = \frac{W^-}{W^- + W^+} = \frac{\sum_a \Gamma_a[1 - f_a(\epsilon_d)]}{\Gamma_L + \Gamma_R} \tag{G.8}$$

$$P_1 = \frac{W^+}{W^- + W^+} = \frac{\sum_a \Gamma_a f_a(\epsilon_d)}{\Gamma_L + \Gamma_R}, \tag{G.9}$$

and upon substituting into Eq. (G.5), the sequential-tunneling current is found to be

$$I^{(\mathrm{seq})} = \frac{e}{\hbar}\frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R}\left[f_L(\epsilon_d) - f_R(\epsilon_d)\right] \tag{G.10}$$

Indeed, this expression is identical with the leading-order current contribution from the expansion of the exact solution, see Eq. (G.4).

Cotunneling contributions

In the second step, we calculate the cotunneling current by evaluating the cotunneling rates

$$W_{ab}^{nn} = \frac{\Gamma_a \Gamma_b}{2\pi\hbar}\int d\epsilon \left|\frac{1}{\epsilon - \epsilon_d}\right|^2 f_a(\epsilon)[1 - f_b(\epsilon)]. \tag{G.11}$$

After regularization, we find

$$W_{ab}^{nn} = \frac{\beta}{4\pi^2}\frac{\Gamma_a\Gamma_b}{\hbar} n_B(\mu_b-\mu_a)\,\mathrm{Im}\left\{\psi'\left(\tfrac{1}{2}+i\tfrac{\beta}{2\pi}[\mu_b-\epsilon_d]\right)-\psi'\left(\tfrac{1}{2}+i\tfrac{\beta}{2\pi}[\mu_a-\epsilon_d]\right)\right\}. \quad \text{(G.12)}$$

Substituting this together with Eqs. (G.8), (G.9) into the expression for the cotunneling current from Eq. (G.5), and using $n_B(x)+n_B(-x)=-1$ leads to

$$I^{(\mathrm{cot})} = \frac{e}{h}\Gamma_L\Gamma_R\frac{\beta}{2\pi}\,\mathrm{Im}\sum_a a\,\psi'\left(\frac{1}{2}+i\frac{\beta}{2\pi}[\epsilon_d+aeV/2]\right). \quad \text{(G.13)}$$

By comparison with Eq. (G.4) one verifies that this is identical with the next-to-leading order term of the expansion of the exact solution.

G.2 Zero-frequency noise

Our starting point for the exact noise calculation is the two-terminal formula for the zero-frequency noise,

$$S = \frac{2e^2}{h}\int dE\left\{\sum_a T(E)f_a(E)\left[1-f_a(E)\right]+T(E)\left[1-T(E)\right]\left[f_L(E)-f_R(E)\right]^2\right\}, \quad \text{(G.14)}$$

see, e.g., Ref. [96]. The transmission coefficient $T(E)$ is known to be proportional to the spectral function $A_d(E)$. The exact relation between them can be extracted easily by comparing Eq. (G.1) to the Landauer formula

$$\langle I\rangle = \frac{e}{h}\int dE\,T(E)\left[f_L(E)-f_R(E)\right]. \quad \text{(G.15)}$$

This leads to $T(E)=A_d(E)\Gamma_L\Gamma_R/\Gamma$.

The integrations can be carried out by invoking the Fourier transform for the Lorentzian. The energy-integration then turns into a Fourier transform of the Fermi factors, which may be carried out by contour integration. The remaining time-integration leads to polygamma functions. The exact result for the zero-frequency noise is given by

$$\begin{aligned} S = \frac{2e^2}{h}\Bigg\{ & \frac{2\Gamma_L\Gamma_R(\Gamma_L^2+\Gamma_R^2)}{\Gamma^3}\coth(\beta eV/2)\,\mathrm{Im}\sum_a a\,\psi\left(\frac{1}{2}+i\frac{\beta}{2\pi}[\epsilon_d+aeV/2]+\frac{\beta\Gamma}{4\pi}\right) \\ & +\frac{2(\Gamma_L\Gamma_R)^2}{\Gamma^2}\frac{\beta}{2\pi}\coth(\alpha\beta)\,\mathrm{Im}\sum_a a\,\psi'\left(\frac{1}{2}+i\frac{\beta}{2\pi}[\epsilon_d+aeV/2]+\frac{\beta\Gamma}{4\pi}\right) \\ & +\frac{2(\Gamma_L\Gamma_R)^2}{\pi\Gamma^3}\,\mathrm{Re}\sum_a \psi'\left(\frac{1}{2}+i\frac{\beta}{2\pi}[\epsilon_d+aeV/2]+\frac{\beta\Gamma}{4\pi}\right) \\ & -\frac{(\Gamma_L\Gamma_R)^2}{\pi\Gamma^2}\frac{\beta}{2\pi}\,\mathrm{Re}\sum_a \psi''\left(\frac{1}{2}+i\frac{\beta}{2\pi}[\epsilon_d+aeV/2]+\frac{\beta\Gamma}{4\pi}\right)\Bigg\} \end{aligned} \quad \text{(G.16)}$$

Expanding this expression in Γ, we find in leading and next-to-leading order

$$S^{(1)} = \frac{2e^2}{h}\Bigg\{\frac{2\pi\Gamma_L\Gamma_R(\Gamma_L^2+\Gamma_R^2)}{\Gamma^3}\left[f_R(\epsilon_d)+f_L(\epsilon_d)-2f_L(\epsilon_d)f_R(\epsilon_d)\right] + \frac{4\pi(\Gamma_L\Gamma_R)^2}{\Gamma^3}\left[f_L(\epsilon_d)[1-f_L(\epsilon_d)]+f_L(\epsilon_d)[1-f_L(\epsilon_d)]\right]\Bigg\} \tag{G.17}$$

$$S^{(2)} = \frac{2e^2\Gamma_L\Gamma_R}{h}\frac{\beta}{2\pi}\coth(\alpha\beta)\,\mathrm{Im}\sum_a a\psi'\left(\frac{1}{2}+i\frac{\beta}{2\pi}[\epsilon_d+aeV/2]\right) \tag{G.18}$$

Again, we can compare this expansion with the results from the rate-equations approach. Employing the formalism described in Appendix D, we obtain the occupation probabilities

$$P_0 = \frac{\sum_a \Gamma_a[1-f_a]}{\Gamma_L+\Gamma_R}, \qquad P_1 = \frac{\sum_a \Gamma_a f_a}{\Gamma_L+\Gamma_R}, \tag{G.19}$$

the steady-state current

$$\langle I\rangle e\left[\frac{\Gamma_L\Gamma_R}{\Gamma_L+\Gamma_R}(f_L-f_R)+w_{LR}-w_{RL}\right], \tag{G.20}$$

and the vectors

$$\mathbf{u}_{LL} = \begin{pmatrix} P_0(\Gamma_L f_L/\hbar + w_{LR}+w_{RL}) \\ P_1(\Gamma_L[1-f_L]/\hbar + w_{LR}+w_{RL}) \end{pmatrix}, \tag{G.21}$$

$$\mathbf{u}_{RR} = \begin{pmatrix} P_0(\Gamma_R f_R/\hbar + w_{LR}+w_{RL}) \\ P_1(\Gamma_R[1-f_R]/\hbar + w_{LR}+w_{RL}) \end{pmatrix}, \tag{G.22}$$

$$\mathbf{u}_{RL} = \mathbf{u}_{LR} = \begin{pmatrix} P_0(w_{LR}+w_{RL}) \\ P_1(w_{LR}+w_{RL}) \end{pmatrix}, \tag{G.23}$$

$$\mathbf{y}_L = \begin{pmatrix} -P_1\Gamma_L[1-f_L]/\hbar + P_0(w_{LR}-w_{RL}) \\ P_0\Gamma_L f_L/\hbar + P_1(w_{LR}-w_{RL}) \end{pmatrix}, \tag{G.24}$$

$$\mathbf{y}_R = \begin{pmatrix} P_1\Gamma_R[1-f_R]/\hbar + P_0(w_{LR}-w_{RL}) \\ P_0\Gamma_R f_R/\hbar + P_1(w_{LR}-w_{RL}) \end{pmatrix}, \tag{G.25}$$

$$\mathbf{w}_L = \begin{pmatrix} \Gamma_L f_L/\hbar + w_{LR}-w_{RL} \\ -\Gamma_L[1-f_L]/\hbar + w_{LR}-w_{RL} \end{pmatrix}, \tag{G.26}$$

$$\mathbf{w}_R = \begin{pmatrix} -\Gamma_R f_R/\hbar + w_{LR}-w_{RL} \\ \Gamma_R[1-f_R]/\hbar + w_{LR}-w_{RL} \end{pmatrix}. \tag{G.27}$$

A lengthy but straightforward calculation shows that the rate-equations results for the zero-frequency noise in leading and next-to-leading order are identical with Eqs. (G.17) and (G.18).

Appendix H

Approximate evaluation of cotunneling rates

We derive an approximate expression for the elastic cotunneling rate $W^{00}_{00;ab}$, valid for strong electron-phonon coupling $\lambda \gg 1$. Our starting point is the (unregularized) rate as obtained by Fermi's golden rule, see Eq. (2.5). This expression can be greatly simplified by noting that only a few terms in the q'' sum give significant contributions, which is due to the behavior of Franck-Condon matrix elements for strong electron-phonon coupling. Specifically, the relevant matrix elements read

$$|M_{0q}|^2 = \frac{\lambda^{2q} e^{-\lambda^2}}{q!} \simeq \frac{1}{\sqrt{2\pi}} \exp\left[-\lambda^2 + 2q \ln\lambda + q - q\ln q - \tfrac{1}{2}\ln q\right], \tag{H.1}$$

where we have used Sterling's approximation for the factorial in the last step. By inspection for $\lambda \gg 1$, we find that the argument of the exponenial function is strictly negative and exhibits a single maximum at $q \approx \lambda^2$. We obtain a reasonable approximation for the strong-coupling FC matrix elements by expanding the argument to second order in q around the maximum $q = \lambda^2$, which leads to the Gaussian

$$|M_{0q}|^2 \approx \frac{1}{\sqrt{2\pi}\lambda} \exp\left[-\frac{(q-\lambda^2)^2}{2\lambda^2}\right]. \tag{H.2}$$

Consequently, as a function of q the (squared) FC matrix element $|M_{0q}|^2$ exhibits a single peak of width $\sim \lambda$ centered at $q = \lambda^2$. Accordingly, in Eq. (2.5) we only need to account for contributions from these summands. To leading order in $1/\lambda$, we can then neglect the variation of $1/q''$ within the Gaussian peak, i.e. setting $q'' = \lambda^2$ in the energy denominator, and noting that $|\epsilon| \ll (\epsilon_d - \lambda^2\hbar\omega)$ for bias and gate voltages small compared to the polaron shift, we obtain the approximation

$$\begin{aligned} W^{00}_{00;ab} &\approx \frac{\Gamma_a\Gamma_b}{\pi\hbar} \frac{k_BT + eV}{(\varepsilon_d + \lambda^2\hbar\omega_0)^2} \left(\sum_{q''} \left|M_{0q''}\right|^2\right)^2 \qquad \text{(H.3)} \\ &\approx \frac{\Gamma_a\Gamma_b}{\pi\hbar} \frac{k_BT + eV}{(\varepsilon_d + \lambda^2\hbar\omega_0)^2} \left(\int_{-\infty}^{\infty} dq\, \frac{1}{\sqrt{2\pi}\lambda} \exp\left[-\frac{(q-\lambda^2)^2}{2\lambda^2}\right]\right)^2 \approx \frac{\Gamma_a\Gamma_b}{\pi\hbar} \frac{k_BT + eV}{(\varepsilon_d + \lambda^2\hbar\omega_0)^2}. \end{aligned}$$

Appendix I

Details: Noise calculations

I.1 Zero-frequency noise and Fano factor for the telegraph regime

According to the simplest situation where telegraph noise occurs, we take into account the transitions (1) $|\,0,0\,\rangle \to |\,1,0\,\rangle$ and $|\,1,0\,\rangle \to |\,0,0\,\rangle$ due to sequential tunneling, and (2) $|\,0,0\,\rangle \to |\,0,0\,\rangle$ and $|\,1,1\,\rangle \to |\,1,1\,\rangle$ due to cotunneling. At finite bias the transport is essentially unidirectional, so that we restrict to LR cotunneling, as well as sequential tunneling $|\,0,0\,\rangle \to |\,1,0\,\rangle$ via the left junction and $|\,1,0\,\rangle \to |\,0,0\,\rangle$ via the right junction. In order to avoid irrelevant indices, we will here denote the rates as W^+, W^- for sequential tunneling, and W^0, W^1 for cotunneling. The rate-equation matrix then reads

$$\mathsf{W} = \begin{pmatrix} -W^+ & W^- \\ W^- & -W^+ \end{pmatrix}, \tag{I.1}$$

and the resulting steady-state occupation probabilities for the empty and singly-occupied molecule are

$$P_0 = \frac{W^-}{W^+ + W^-}, \quad P_1 = \frac{W^+}{W^+ + W^-}. \tag{I.2}$$

Note that due to the spin-degeneracy of the singly-occupied state, the sequential rates obey $W^+ = 2W^-$, leading to $P_0 = 1/3$ and $P_1 = 2/3$. Neglecting sequential rates as compared to cotunneling rates where appropriate, we find that the vectors $\mathbf{u}_{aa'}$, $\mathbf{y}_a$, and $\mathbf{w}_a$ are given by

$$\mathbf{u}_{aa'} = \begin{pmatrix} P_0 W^0 \\ P_1 W^1 \end{pmatrix} = \mathbf{y}_a, \tag{I.3}$$

$$\mathbf{w}_a = \begin{pmatrix} W^0 \\ W^1 \end{pmatrix}. \tag{I.4}$$

The steady-state current is

$$\langle I \rangle = P_0 W^0 + P_1 W^1 = \frac{1}{3} W^0 + \frac{2}{3} W^1, \tag{I.5}$$

so that $\bar{\mathbf{y}}_a$ is obtained as

$$\bar{\mathbf{y}}_L = \bar{\mathbf{y}}_R = \frac{W^+ W^- (W^0 - W^1)}{(W^+ + W^-)^2} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{I.6}$$

Finally, we have

$$\mathsf{W}^{-1}\bar{\mathbf{y}}_a = -\frac{W^+W^-(W^0-W^1)}{(W^++W^-)^3}\begin{pmatrix}1\\-1\end{pmatrix}. \tag{I.7}$$

For the noise, we therefore find $S_{LL} = S_{RR} = S_{LR} = S_{RL}$, and the final results are

$$S(\omega=0) \approx 4e^2\frac{W^+W^-(W^0-W^1)^2}{(W^++W^-)^3}, \tag{I.8}$$

$$F \approx 6\frac{W^+W^-(W^0-W^1)^2}{(W^0+2W^1)(W^++W^-)^3}. \tag{I.9}$$

I.2 Zero-frequency noise in the pair-tunneling regime

The calculation of the zero-frequency noise for the pair-tunneling regime can be carried out along the lines of Appendix D. Here, we list the relevant processes and the charges transferred by them, see Figure I.1 and Table I.1.

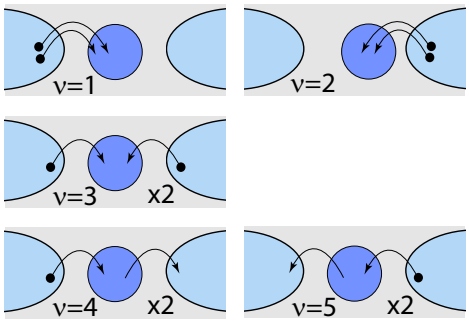


Figure I.1: Elementary processes for the transitions $|\,0\,\rangle \to |\,2\,\rangle$ and $|\,0\,\rangle \to |\,0\,\rangle$. The label "×2" signals an additional factor of 2 due to two incoherent spin contributions. The diagrams for the processes corresponding to the transitions $|\,2\,\rangle \to |\,0\,\rangle$ and $|\,2\,\rangle \to |\,2\,\rangle$ are obtained by reversing the direction of all arrows.

$s^a_{02,\nu}$	$a=L$	$a=R$	$s^a_{20,\nu}$	$a=L$	$a=R$
$\nu=1$	2	0	$\nu=1$	-2	0
2	0	-2	2	0	2
3	1	-1	3	-1	1
$s^a_{00,\nu}$	$a=L$	$a=R$	$s^a_{22,\nu}$	$a=L$	$a=R$
4	1	1	4	1	1
5	-1	-1	5	-1	-1

Table I.1: All nonvanishing coefficients $s^a_{if,\nu}$ characterizing the current contributions of individual processes.

Appendix J

Quantum mechanics of the Morse potential

The Morse potential [109]

$$V(x) = D\left[e^{-2\beta x} - 2e^{-\beta x}\right] \tag{J.1}$$

is one of the few exactly solvable problems in quantum mechanics. Beyond this fact, it has two other appealing properties: (i) It allows the investigation of *anharmonicities*, and (ii) it describes not only bound states but also continuum states, opening up the possibility to study the dissociation of molecules. Here, we briefly highlight the basics of its quantum mechanical treatment.

The Morse parameters D and β determine the depth and inverse width of the Morse potential. For a sufficiently deep Morse potential, it is evident that the vicinity of the potential minimum at $x = 0$ is well approximated by a parabola. An expansion of the potential around $x = 0$ yields

$$V(x) = -D + D\beta^2 x^2 - D\beta^3 x^3 + \mathcal{O}(x^4). \tag{J.2}$$

In the harmonic approximation, this allows us to identify $\mu\omega_e^2/2 = D\beta^2$, i.e.

$$\hbar\omega_e = \hbar\beta^2\sqrt{2D/\mu}, \tag{J.3}$$

where μ is the reduced mass. The corresponding oscillator length is given by $\ell_e = \sqrt{\frac{\hbar}{\mu\omega_e}}$, and we can immediately define a dimensionless parameter χ describing the anharmonicity strength by comparing the quadratic and cubic term,

$$\chi = \frac{1}{2}\left(\frac{D\beta^3\ell_e}{D\beta^2}\right)^2 = \beta^2\ell_e^2/2 = \frac{\hbar\beta}{2\sqrt{2D\mu}}. \tag{J.4}$$

Here, the additional factor 1/2 and our choice to square the ratio are not essential, and are merely motivated by making contact with the definitions conventionally used in the literature.

For energies $E < 0$, the stationary Schrödinger equation can be solved exactly by substituting $z = e^{-\beta x}$. The resulting eigenenergies and eigenfunctions (see e.g. Ref. [144])

are given by[1]

$$E_q = -D + \hbar\omega_e(q + 1/2) - \hbar\omega_e\chi(q + 1/2)^2, \tag{J.5}$$

$$\psi_q(\xi) = N_q e^{-\xi/2}\xi^{j-q}\,\mathrm{L}_q^{2(j-q)}(\xi). \tag{J.6}$$

Here, we have used the transformed coordinate $\xi = (2j + 1)e^{-\beta x}$, and we have introduced the parameter j related to the asymmetry parameter χ through $2j + 1 = 1/\chi$. This parameter is useful, since $\lfloor j \rfloor + 1$ represents the total number of bound states of the Morse potential. Hence, the quantum number q takes the values $q = 0, 1, \ldots, \lfloor j \rfloor$. Finally, N_q is a normalization constant fixed by

$$N_q = \sqrt{\frac{\beta\, q!\, 2(j - q)}{\Gamma(2j - q + 1)}}. \tag{J.7}$$

The treatment of the continuum state requires some more care. We refer the reader to Ref. [115] (and references therein) for a discussion of the scattering states solution.

[1] We caution the reader about the fact that expressions in Morse's original paper [109] must be addressed with some care due to an unconventional definition of the generalized Laguerre polynomials in his work.

Appendix K

Thermopower: Linearized rate equations and expansion coefficients

K.1 Linearized rate equations

The rate equations for the deviations Θ_q^n and Φ_q^n from the equilibrium probability have the following form:

$$
\begin{aligned}
0 = \quad & \sum_{q'} \Big[\overline{P_{q'}^{n-1}} (\Delta T\, t_{q'q}^{n-1,n} + V\, v_{q'q}^{n-1,n}) + \overline{P_{q'}^{n+1}} (\Delta T\, t_{q',q}^{n+1,n} + V\, v_{q'q}^{n+1,n}) \\
& - \overline{P_q^n} (\Delta T\, t_{qq'}^{n,n+1} + V\, v_{qq'}^{n,n+1} + \Delta T\, t_{qq'}^{n,n-1} + V\, v_{qq'}^{n,n-1}) + (\Delta T\, \Theta_{q'}^{n-1} + V\, \Phi_{q'}^{n-1}) w_{q'q}^{n-1,n} \\
& + (\Delta T\, \Theta_{q'}^{n+1} + V\, \Phi_{q'}^{n+1}) w_{q'q}^{n+1n} - (\Delta T\, \Theta_q^n + V\, \Phi_q^n)(w_{qq'}^{n,n+1} + w_{qq'}^{n,n-1}) \Big] \\
& + \sum_{q' \neq q} \Big[\overline{P_{q'}^n} (\Delta T\, t_{q'q}^{nn} + V\, v_{q'q}^{nn}) - \overline{P_q^n} (\Delta T\, t_{qq'}^{nn} + V\, v_{qq'}^{nn}) + (\Delta T\, \Theta_{q'}^n + V\, \Phi_{q'}^n) w_{q'q}^{nn} \\
& - (\Delta T\, \Theta_q^n + V\, \Phi_q^n) w_{qq'}^{nn} \Big] - \frac{1}{\tau} \Big[\Delta T\, \Theta_q^n + V\, \Phi_q^n - P_q^{\mathrm{eq}} \sum_{q'} (\Delta T \Theta_{q'}^n + V\, \Phi_{q'}^n) \Big]
\end{aligned}
\tag{K.1}
$$

K.2 Expansion coefficients

By expanding (2.2) and (2.4) one obtains the following expressions for the expansion coefficients of the sequential-tunneling rates $W_{qq'}^{n,n\pm1} = \sum_a W_{qq';\,a}^{n,n\pm1}$:

$$
w_{qq';\,a}^{n,n+1} = \Gamma_a/\hbar \left| M_{qq'} \right|^2 s(n, n+1) f(E_{q'}^{n+1} - E_q^n), \tag{K.2}
$$

$$
w_{qq';\,a}^{n,n-1} = \Gamma_a/\hbar \left| M_{qq'} \right|^2 s(n, n-1) \left[1 - f(E_q^n - E_{q'}^{n-1}) \right], \tag{K.3}
$$

$$
t_{qq';\,L}^{n,n+1} = \Gamma_L/\hbar \left| M_{qq'} \right|^2 s(n, n+1)(E_q^n - E_{q'}^{n+1})/T\, f'(E_{q'}^{n+1} - E_q^n), \qquad t_{qq';\,R}^{n,n+1} = 0, \tag{K.4}
$$

$$
t_{qq';\,L}^{n,n-1} = \Gamma_L/\hbar \left| M_{qq'} \right|^2 s(n, n-1)(E_q^n - E_{q'}^{n-1})/T\, f'(E_q^n - E_{q'}^{n-1}), \qquad t_{qq';\,R}^{n,n-1} = 0, \tag{K.5}
$$

$$v^{n,n+1}_{qq';\,L} = \Gamma_L/\hbar \left|M_{qq'}\right|^2 s(n,n+1)e\, f'(E^{n+1}_{q'} - E^n_q), \qquad v^{n,n+1}_{qq';\,R} = 0, \quad \text{(K.6)}$$

$$v^{n,n-1}_{qq';\,L} = \Gamma_L/\hbar \left|M_{qq'}\right|^2 s(n,n-1)(-e) f'(E^n_q - E^{n-1}_{q'}), \qquad v^{n,n-1}_{qq';\,R} = 0. \quad \text{(K.7)}$$

Similarly, the expansion of the cotunneling rates Eqs. (2.5) and (2.6) is carried out. Defining the abbreviations

$$A_{qq'q''}(\epsilon) = \frac{M_{qq''}M^*_{q'q''}}{\epsilon + E^0_q - E^1_{q''}}, \qquad B_{qq'q''}(\epsilon) = \frac{M_{qq''}M^*_{q'q''}}{\epsilon + E^1_{q''} - E^2_{q'}}, \quad \text{(K.8)}$$

$$C_{qq'q''}(\epsilon) = \frac{M_{qq''}M^*_{q'q''}}{\epsilon + E^1_q - E^2_{q''}}, \qquad D_{qq'q''}(\epsilon) = \frac{M_{qq''}M^*_{q'q''}}{\epsilon + E^0_{q''} - E^1_{q'}} \quad \text{(K.9)}$$

we obtain for the relevant expansion coefficients

$$w^{00}_{qq';\,ab} = 2\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon \left|\sum_{q''} A_{qq'q''}(\epsilon)\right|^2 f(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \quad \text{(K.10)}$$

$$w^{22}_{qq';\,ab} = 2\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon \left|\sum_{q''} B_{qq'q''}(\epsilon)\right|^2 f(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \quad \text{(K.11)}$$

$$\begin{aligned} w^{11}_{qq';\,ab} = {} & \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon \left|\sum_{q''} C_{qq'q''}(\epsilon)\right|^2 f(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \\ & + \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon \left|\sum_{q''} D_{qq'q''}(\epsilon)\right|^2 f(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \\ & + \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon \left|\sum_{q''} \left[C_{qq'q''}(\epsilon) - D_{qq'q''}(\epsilon)\right]\right|^2 f(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \end{aligned} \quad \text{(K.12)}$$

$$t^{00}_{qq';\,LR} = -2\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\, \frac{\epsilon}{T} \left|\sum_{q''} A_{qq'q''}(\epsilon)\right|^2 f'(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \quad \text{(K.13)}$$

$$t^{22}_{qq';\,LR} = -2\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\, \frac{\epsilon}{T} \left|\sum_{q''} B_{qq'q''}(\epsilon)\right|^2 f'(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \quad \text{(K.14)}$$

$$\begin{aligned} t^{11}_{qq';\,ab} = {} & -\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\, \frac{\epsilon}{T} \left|\sum_{q''} C_{qq'q''}(\epsilon)\right|^2 f'(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \\ & - \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\, \frac{\epsilon}{T} \left|\sum_{q''} D_{qq'q''}(\epsilon)\right|^2 f'(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \\ & - \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\, \frac{\epsilon}{T} \left|\sum_{q''} \left[C_{qq'q''}(\epsilon) - D_{qq'q''}(\epsilon)\right]\right|^2 f'(\epsilon)\left[1 - f(\epsilon + \hbar\omega_0[q-q'])\right] \end{aligned} \quad \text{(K.15)}$$

$$t^{00}_{qq';\,RL} = 2\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\,\frac{\epsilon+\hbar\omega_0[q-q']}{T}\left|\sum_{q''}A_{qq'q''}(\epsilon)\right|^2 f(\epsilon)f'(\epsilon+\hbar\omega_0[q-q']) \tag{K.16}$$

$$t^{22}_{qq';\,RL} = 2\frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\,\frac{\epsilon+\hbar\omega_0[q-q']}{T}\left|\sum_{q''}B_{qq'q''}(\epsilon)\right|^2 f(\epsilon)f'(\epsilon+\hbar\omega_0[q-q']) \tag{K.17}$$

$$\begin{aligned} t^{11}_{qq';\,RL} &= \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\,\frac{\epsilon+\hbar\omega_0[q-q']}{T}\left|\sum_{q''}C_{qq'q''}(\epsilon)\right|^2 f(\epsilon)f'(\epsilon+\hbar\omega_0[q-q']) \\ &+ \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\,\frac{\epsilon+\hbar\omega_0[q-q']}{T}\left|\sum_{q''}D_{qq'q''}(\epsilon)\right|^2 f(\epsilon)f'(\epsilon+\hbar\omega_0[q-q']) \\ &+ \frac{\Gamma_a\Gamma_b}{2\pi\hbar}\int d\epsilon\,\frac{\epsilon+\hbar\omega_0[q-q']}{T}\left|\sum_{q''}\left[C_{qq'q''}(\epsilon)-D_{qq'q''}(\epsilon)\right]\right|^2 f(\epsilon)f'(\epsilon+\hbar\omega_0[q-q']) \end{aligned} \tag{K.18}$$

(K.19)

The expressions for $v^{nn}_{qq';ab}$ are obtained from the $t^{nn}_{qq';ab}$ expressions by substituting ϵ/T, $(\epsilon+\hbar\omega_0[q-q'])/T \to e$. We point out that Eqs. (K.10)–(K.18) correct an erroneous statement about spin factors in Ref. [145]. For the case of finite charging energies, a careful consideration of incoherent vs. coherent contributions is crucial and leads to the above cotunneling expressions.

The calculation of the regularized expansion coefficients proceeds in analogy to our treatment in Appendix C. It is important to note that the coefficients for elastic cotunneling t^{nn}_{qq} etc. remain divergent in the zero-bias limit. However, the evaluation of G and G_T always requires the subtraction of two such coefficients and the divergences cancel out exactly. Here, we list the additional types of integrals required for the computation.

$$\begin{aligned} I_1(E_1,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\, f(E-E_1)\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\ &= \frac{1}{\epsilon_1-\epsilon_2}\Big\{\mathrm{i}\,\pi+\psi(1/2+\mathrm{i}\,\beta[E_1-\epsilon_1]/2\pi)-\psi(1/2-\mathrm{i}\,\beta[E_1-\epsilon_2]/2\pi)\Big\} \\ I_2(E_1,E_2,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\, f(E-E_1)f(E-E_2)\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\ &= \frac{1}{\epsilon_1-\epsilon_2}\Big\{\mathrm{i}\,\pi+n_B(E_1-E_2)\left[-\psi(1/2+\mathrm{i}\,\beta[E_1-\epsilon_1]/2\pi)+\psi(1/2-\mathrm{i}\,\beta[E_1-\epsilon_2]/2\pi)\right] \\ &\qquad + n_B(E_2-E_1)\left[-\psi(1/2+\mathrm{i}\,\beta[E_2-\epsilon_1]/2\pi)+\psi(1/2-\mathrm{i}\,\beta[E_2-\epsilon_2]/2\pi)\right]\Big\} \\ I(E_1,E_2,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\, f(E-E_1)\left[1-f(E-E_2)\right]\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\ &= \frac{1}{\epsilon_1-\epsilon_2}\Big\{\left[1+n_B(E_1-E_2)\right]\left[\psi(1/2+\mathrm{i}\,\beta[E_1-\epsilon_1]/2\pi)-\psi(1/2-\mathrm{i}\,\beta[E_1-\epsilon_2]/2\pi)\right] \\ &\qquad + n_B(E_2-E_1)\left[\psi(1/2+\mathrm{i}\,\beta[E_2-\epsilon_1]/2\pi)-\psi(1/2-\mathrm{i}\,\beta[E_2-\epsilon_2]/2\pi)\right]\Big\} \end{aligned}$$

$$
\begin{aligned}
J_1(E_1,\epsilon) &= \lim_{\Gamma\to 0}\left[\int dE\, f(E-E_1)\frac{1}{(E-\epsilon)^2+\Gamma^2} - \mathcal{O}(1/\Gamma)\right] \\
&= \frac{\beta}{2\pi}\,\mathrm{Im}\,\psi^{(1)}\left(1/2+\mathrm{i}\,\beta(E_1-\epsilon)/2\pi\right) \\
J_2(E_1,E_2,\epsilon) &= \lim_{\Gamma\to 0}\left[\int dE\, f(E-E_1)f(E-E_2)\frac{1}{(E-\epsilon)^2+\Gamma^2} - \mathcal{O}(1/\Gamma)\right] \\
&= \frac{\beta}{2\pi}\Big[n_B(E_1-E_2)\,\mathrm{Im}\,\psi^{(1)}\left(1/2+\mathrm{i}\,\beta[\epsilon-E_1]/2\pi\right) \\
&\qquad + n_B(E_2-E_1)\,\mathrm{Im}\,\psi^{(1)}\left(1/2+\mathrm{i}\,\beta[\epsilon-E_2]/2\pi\right)\Big] \\
J(E_1,E_2,\epsilon) &= \lim_{\Gamma\to 0}\left[\int dE\, f(E-E_1)\left[1-f(E-E_2)\right]\frac{1}{(E-\epsilon)^2+\Gamma^2} - \mathcal{O}(1/\Gamma)\right] \\
&= \frac{\beta}{2\pi}\Big[\left(1+n_B(E_1-E_2)\right)\mathrm{Im}\,\psi^{(1)}\left(1/2+\mathrm{i}\,\beta[E_1-\epsilon]/2\pi\right) \\
&\qquad + n_B(E_2-E_1)\,\mathrm{Im}\,\psi^{(1)}\left(1/2+\mathrm{i}\,\beta[E_2-\epsilon]/2\pi\right)\Big]
\end{aligned}
$$

$$
\begin{aligned}
K_2(E_1,E_2,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\, f'(E-E_1)f(E-E_2)\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\
&= -\partial I_2/\partial E_1 \\
K_1(E_1,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\, f'(E-E_1)\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\
&= -\partial I_1/\partial E_1 \\
K(E_1,E_2,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\, f'(E-E_1)\left[1-f(E-E_2)\right]\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\
&= -\partial I/\partial E_1
\end{aligned}
$$

$$
\begin{aligned}
L_2(E_1,E_2,\epsilon) &= \lim_{\Gamma\to 0}\left[\int dE\, f'(E-E_1)f(E-E_2)\frac{1}{(E-\epsilon)^2+\Gamma^2} - \mathcal{O}(1/\Gamma)\right] \\
&= -\partial J_2/\partial E_1 \\
L_1(E_1,\epsilon) &= \lim_{\Gamma\to 0}\left[\int dE\, f'(E-E_1)\frac{1}{(E-\epsilon)^2+\Gamma^2} - \mathcal{O}(1/\Gamma)\right] \\
&= -\partial J_1/\partial E_1 \\
L(E_1,E_2,\epsilon) &= \lim_{\Gamma\to\infty}\left[\int dE\, f'(E-E_1)\left[1-f(E-E_2)\right]\frac{1}{(E-\epsilon)^2+\Gamma^2} - \mathcal{O}(1/\Gamma)\right] \\
&= -\partial J/\partial E_1
\end{aligned}
$$

$$
\begin{aligned}
M_2(E_1,E_2,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\,(E-E_1)f'(E-E_1)f(E-E_2)\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2} \\
&= G_2(E_1,E_2,\epsilon_1) + (\epsilon_2-E_1)K_2(E_1,E_2,\epsilon_1,\epsilon_2)
\end{aligned}
$$

$$
\begin{aligned}
M_1(E_1,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\,(E-E_1)f'(E-E_1)\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2}\\
&= \beta\,\partial/\partial\beta\, I_1(E_1,\epsilon_1,\epsilon_2)\\
M(E_1,E_2,\epsilon_1,\epsilon_2) &= \lim_{\Gamma_i\to 0}\int dE\,(E-E_1)f'(E-E_1)\,[1-f(E-E_2)]\,\frac{1}{E-\epsilon_1-\mathrm{i}\,\Gamma_1}\frac{1}{E-\epsilon_2+\mathrm{i}\,\Gamma_2}\\
&= M_1(E_1,\epsilon_1,\epsilon_2)-M_2(E_1,E_2,\epsilon_1,\epsilon_2)
\end{aligned}
$$

$$
\begin{aligned}
N_2(E_1,E_2,\epsilon) &= \lim_{\Gamma\to 0}\left[\int dE\,(E-E_1)f'(E-E_1)f(E-E_2)\frac{1}{(E-\epsilon)^2+\Gamma^2}-\mathcal{O}(1/\Gamma)\right]\\
&= \mathrm{Re}\,G_2(E_1,E_2,\epsilon)+(\epsilon-E_1)L_2(E_1,E_2,\epsilon)\\
N_1(E_1,\epsilon) &= \lim_{\Gamma\to 0}\int dE\,(E-E_1)f'(E-E_1)\frac{1}{(E-\epsilon)^2+\Gamma^2}-\mathcal{O}(1/\Gamma)\\
&= \beta\,\partial/\partial\beta\, J_1(E_1,\epsilon)\\
N(E_1,E_2,\epsilon) &= \lim_{\Gamma\to 0}\int dE\,(E-E_1)f'(E-E_1)\,[1-f(E-E_2)]\,\frac{1}{(E-\epsilon)^2+\Gamma^2}-\mathcal{O}(1/\Gamma)\\
&= N_1(E_1,\epsilon)-N_2(E_1,E_2,\epsilon)
\end{aligned}
$$

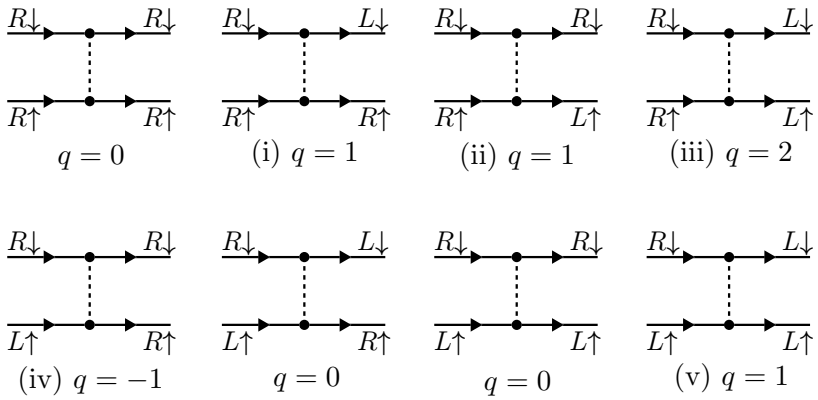
Appendix L

Kondo regime – Inelastic backscattering contributions

In this appendix, we detail the analysis of inelatic contributions to the backscattering current in the Kondo regime, see Chapter 8. Upon decomposing the quasiparticles into left- and right-movers, the relevant part of the effective Hamiltonian reads

$$H_{\text{in}} = \frac{\beta}{4\pi\rho^2 T_K} \sum_{k_1,k_2,k_3,k_4} \sum_{a,b,c,d=L,R} a^\dagger_{k_1\uparrow} b_{k_2\uparrow} c^\dagger_{k_3\downarrow} d_{k_4\downarrow}. \tag{L.1}$$

This gives rise to 2^4 different processes. Here, we depict the 8 processes with an incoming spin-down right-mover (i.e. $d = R$):



The remaining eight processes are obtained from these diagrams by interchanging $L \leftrightarrow R$ and inverting the sign of q. Again, only diagrams with nonvanishing q can contribute to the backscattering current. Furthermore, one easily confirms that $q < 0$ processes have zero phase space and lead to vanishing rates. Altogether, the five processes (i)–(v) remain for consideration. (By process (iv) we denote the inverted diagram from now on.)

In the following, we evaluate the separate contributions to the backscattering current one by one. We start with the two-particle process (iii), for which we obtain by Fermi's

golden rule

$$
\begin{aligned}
I_\beta^{(\mathrm{iii})} =& 2\frac{2\pi e}{\hbar}\sum_{k_1,k_2,k_3,k_4}\left|\langle \mathrm{gs}|R^\dagger_{k_4\downarrow}L_{k_3\downarrow}R^\dagger_{k_2\uparrow}L_{k_1\uparrow}H_{\mathrm{in}}|\mathrm{gs}\rangle\right|^2 \\
&\times f_L(\xi_{k_4})f_L(\xi_{k_2})[1-f_R(\xi_{k_3})][1-f_R(\xi_{k_1})]\delta(\xi_{k_1}+\xi_{k_3}-\xi_{k_2}-\xi_{k_4}) \\
=& 2\frac{2\pi e}{\hbar}\left(\frac{\beta}{4\pi\rho^2 T_K}\right)^2\rho^4\int d\epsilon_1\, d\epsilon_2\, d\epsilon_3\, d\epsilon_4\,\theta(eV/2-\epsilon_2)\theta(eV/2-\epsilon_4) \\
&\times\theta(eV/2+\epsilon_1)\theta(eV/2+\epsilon_3)\delta(\epsilon_1+\epsilon_3-\epsilon_2-\epsilon_4) \\
=& 2\frac{2e}{h}\frac{\beta^2}{T_K^2}\frac{1}{8}\int_{-\infty}^{eV/2}d\epsilon_2\int_{-eV/2}^{\infty}d\epsilon_3\int_{-\infty}^{eV/2}d\epsilon_4\,\theta(eV/2+\epsilon_3-\epsilon_2-\epsilon_4) \\
=& \frac{2e^2}{h}V\frac{\beta^2}{3}\left(\frac{eV}{T_K}\right)^2
\end{aligned}
\tag{L.2}
$$

The explicit factor of 2 describes the backscattering of a particle *pair*. The remaining four integrals are found to be indentical, and give (explicitly shown for the example of $I_\beta^{(\mathrm{i})}$)

$$
\begin{aligned}
I_\beta^{(\mathrm{i})} =& I_\beta^{(\mathrm{ii})} = I_\beta^{(\mathrm{iv})} = I_\beta^{(\mathrm{v})} \\
=& \frac{2\pi e}{\hbar}\sum_{k_1,k_2,k_3,k_4}\left|\langle \mathrm{gs}|R^\dagger_{k_4\downarrow}L_{k_3\downarrow}R^\dagger_{k_2\uparrow}R_{k_1\uparrow}H_{\mathrm{in}}|\mathrm{gs}\rangle\right|^2 \\
&\times f_L(\xi_{k_4})f_L(\xi_{k_2})[1-f_L(\xi_{k_3})][1-f_R(\xi_{k_1})]\delta(\xi_{k_1}+\xi_{k_3}-\xi_{k_2}-\xi_{k_4}) \\
=& \frac{2\pi e}{\hbar}\left(\frac{\beta}{4\pi\rho^2 T_K}\right)^2\rho^4\int d\epsilon_1\, d\epsilon_2\, d\epsilon_3\, d\epsilon_4\,\theta(eV/2+\epsilon_1)\theta(-eV/2+\epsilon_3) \\
&\times\theta(eV/2-\epsilon_2)\theta(eV/2-\epsilon_4)\delta(\epsilon_1+\epsilon_3-\epsilon_2-\epsilon_4) \\
=& \frac{2e}{h}\frac{\beta^2}{T_K^2}\frac{1}{8}\int_{-\infty}^{eV/2}d\epsilon_2\int_{eV/2}^{\infty}d\epsilon_3\int_{-\infty}^{eV/2}d\epsilon_4\,\theta(eV/2-\epsilon_3+\epsilon_2+\epsilon_4) \\
=& \frac{2e^2}{h}V\frac{\beta^2}{48}\left(\frac{eV}{T_K}\right)^2
\end{aligned}
\tag{L.3}
$$

As a result, the total inelastic contribution to the backscattering current is given by

$$
I_\beta = \frac{2e^2}{h}V\frac{5\beta^2}{12}\left(\frac{eV}{T_K}\right)^2. \tag{L.4}
$$