Tunneling through molecules and quantum dots: Master-equation approaches

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An important class of approaches to the description of electronic transport through molecules and quantum dots is based on the master equation. We discuss various formalisms for deriving a master equation and their interrelations. It is shown that the master equation derived by König *et al.* [Phys. Rev. Lett. **76**, 1715 (1996); Phys. Rev. B **54**, 16820 (1996)] is equivalent to the Wangsness-Bloch-Redfield master equation. The roles of the large-reservoir and Markov approximations are clarified. At low temperatures, when the quasiparticle lifetime becomes large, the Markov approximation can be derived from the assumption of weak tunneling under certain conditions. Interactions in the leads are shown to be irrelevant for the transport in the case of momentum-independent tunneling. It is explained why the T-matrix formalism gives incomplete results except for diagonal density operators to second order in the tunneling amplitudes. The time-convolutionless master equation is adapted to tunneling problems and a diagrammatic scheme for generating arbitrary orders in the tunneling amplitudes is developed.

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I. INTRODUCTION

Most approaches employed for the description of tunneling through molecules and quantum dots fall into one of two conceptual classes: in the first, one focuses on the dynamics of individual *electrons* tunneling through the system. Their dynamics is often described with the help of single-particle nonequilibrium Green functions.[1,2] This approach is sometimes combined with *ab initio* methods[3,4] or perturbation theory for the interactions on the dot. In the second, one focuses on the time evolution of the *many-particle state* of the dot and integrates out the effect of the leads. This allows one to exactly treat the strong interactions on the dot. Typically, the reduced density operator of the dot is considered. Its equation of motion is the master equation (ME). The two approaches become equivalent in the absence of interactions.

The ME approach involves two steps. First, one derives the ME from the von Neumann equation for the full system. It tells one how the reduced density operator changes based on its present and often its past values. It is clear that this requires additional assumptions since the dot is coupled to the leads, which can be in any state. It is, of course, desirable to get by with only weak assumptions.

Second, one solves the ME to find the time evolution or the stationary state. Finding the time evolution is more complicated if the ME contains the history of the dot. It is thus desirable to obtain a ME that is local in time. There exist both approximate and exact methods for achieving this.

The ME approach comes in a number of flavors, among them the original Wangsness-Bloch-Redfield (WBR) approach,[5–7] the superoperator formalism, the T-matrix formalism, the Keldysh-contour formulation of König *et al.*,[8–11] and the so-called time-convolutionless (TCL) ME.[12] The purpose of this paper is to clarify the interrelations between these pictures and to analyze some of their problems. It is hoped that this will facilitate the comparison between results obtained with different methods. In addition, the TCL formalism is generalized to the tunneling case and is argued to provide a powerful tool for studying the dynamics of a dot under bias.

II. WANGSNESS-BLOCH-REDFIELD MASTER EQUATION

A. Conventional derivation

This approach[5–7] is commonly described in textbooks,[13–16] though not in relation to particle transport. Several groups have recently applied it to tunneling through molecules.[17–23] We start from a Hamiltonian, $H=H_{\rm dot}+H_{\rm leads}+H_{\rm hyb}$, where the terms describe the dot, the leads, and hybridization between them, respectively. $H_{\rm dot}$ may contain vibrational or spin degrees of freedom and their coupling to the electrons. The time evolution of the density operator ρ of the *full* system is described by the von Neumann equation $\dot{\rho}=-i[H,\rho]$, where $\hbar=1$. We wish to find the ME for the reduced density operator $\rho_{\rm dot}(t)\equiv \mathrm{tr}_{\rm leads}\,\rho(t)$, where the trace is over many-particle states of the leads.

We take $H_{\rm hyb}$ to be a sum of bilinear terms that each create an electron in the dot and annihilate one in the leads or vice versa. A typical form is

$$H_{\rm hyb}=-\frac{1}{\sqrt{N}}\sum_{\alpha\mathbf{k}\sigma\nu}(t_{\alpha\mathbf{k}\sigma\nu}a^{\dagger}_{\alpha\mathbf{k}\sigma}c_{\nu\sigma}+\mathrm{H.c.}), \quad (1)$$

where N is the number of sites in each lead. $a^{\dagger}_{\alpha\mathbf{k}\sigma}$ ($c^{\dagger}_{\nu\sigma}$) creates an electron in lead $\alpha=L, R$ with wave vector $\mathbf{k}$ and spin σ (in molecular orbital ν with spin σ). We assume that crystal momentum, spin, and lead index are conserved in the leads. The central assumption is that $H_{\rm hyb}$ can be treated perturbatively.

Operators A are transformed into the interaction picture with respect to $H_{\rm hyb}$,

$$A_I(t)=e^{i(H_{\rm dot}+H_{\rm leads})t}A(t)e^{-i(H_{\rm dot}+H_{\rm leads})t}. \quad (2)$$

The density operator in the interaction picture satisfies

$$\dot{\rho}_I=-i[H_{{\rm hyb},I},\rho_I]. \quad (3)$$

Integrating this equation from t_0 to t yields

$$\rho_I(t) = \rho_I(t_0) - i\int_{t_0}^{t} dt' \, [H_{\mathrm{hyb},I}(t'),\rho_I(t')]. \tag{4}$$

By inserting this again into Eq. (3), one obtains

$$\dot{\rho}_I(t) = - i[H_{\mathrm{hyb},I}(t),\rho_I(t_0)] - \int_{t_0}^{t} dt' [H_{\mathrm{hyb},I}(t),[H_{\mathrm{hyb},I}(t'),\rho_I(t')]]. \tag{5}$$

By continuing the iteration, one generates equations containing arbitrary powers of H_{hyb}. However, in all of them, all terms except for the one with the highest power contain ρ_I only at time t_0. This is problematic when we introduce approximations. For example, if we describe cotunneling (fourth order), sequential tunneling (second order) would only appear in the dependence on the initial conditions. Section II B explains how to avoid this.

We now consider the initial condition that the system was in a product state at an early time t_0,

$$\rho(t_0) = \rho_{\mathrm{dot}}(t_0) \otimes \rho^0_{\mathrm{leads}}, \tag{6}$$

with ρ^0_{leads} describing separate thermal equilibria of the two leads; their chemical potentials and temperatures can be different. A product state is equivalent to dot and leads being statistically independent at time t_0, which is natural if H_{hyb} is switched on at time t_0. The initial condition [Eq. (6)] implies that

$$\mathrm{tr}_{\mathrm{leads}}\, H_{\mathrm{hyb},I}(t)\rho_I(t_0) = 0, \tag{7}$$

since ρ^0_{leads} only contains states with sharp electron number, whereas each term in H_{hyb} changes the lead-electron number and thus gives zero under the trace.

The trace over lead states of Eq. (5) is

$$\dot{\rho}_{\mathrm{dot},I}(t) = - \int_{t_0}^{t} dt' \; \mathrm{tr}_{\mathrm{leads}}[H_{\mathrm{hyb},I}(t),[H_{\mathrm{hyb},I}(t'),\rho_I(t')]]. \tag{8}$$

The first term in Eq. (5) drops out due to Eq. (7). Up to this point, the results are exact.

The integral in every term in Eq. (8) is of the form

$$\pm \prod A_{\mathrm{dot},I}\Big(\mathrm{tr}_{\mathrm{leads}} \prod B_{\mathrm{leads},I}\rho_I\Big)\prod{}' A_{\mathrm{dot},I}, \tag{9}$$

where the first and last factors are products of zero or more dot electron operators and $\Pi B_{\mathrm{leads},I}$ is a product of two lead-electron operators. The operators may have different time arguments. We have already made the assumption of weak tunneling. At this point, it is assumed in addition that the leads form large reservoirs so that the tunneling has negligible effect on the leads.[24] Therefore, in any term, one makes the replacement[5,6,14,16]

$$\mathrm{tr}_{\mathrm{leads}} \prod B_{\mathrm{leads},I}\rho_I \approx \mathrm{tr}_{\mathrm{leads}} \prod B_{\mathrm{leads},I}\rho_{\mathrm{dot},I} \otimes \rho^0_{\mathrm{leads}} = \rho_{\mathrm{dot},I} \otimes \mathrm{tr}_{\mathrm{leads}} \prod B_{\mathrm{leads},I}\rho^0_{\mathrm{leads}}. \tag{10}$$

Here, one replaces any two-time correlation function of the leads by the correlation function in equilibrium. Gardiner and Zoller[16] point out that one only has to make this assumption in the second-order terms.

In fact, we *must* only make it in the second-order terms: if we were to argue that since tunneling should have negligible effect on the leads, we can replace $\rho(t)$ by $\rho_{\mathrm{dot}}(t)\otimes\rho^0_{\mathrm{leads}}$ globally in the von Neumann equation, and we obtain $\dot{\rho}_{\mathrm{dot}} = -i\,\mathrm{tr}_{\mathrm{leads}}[H,\rho_{\mathrm{dot}}\otimes\rho^0_{\mathrm{leads}}] = -i\,\mathrm{tr}_{\mathrm{leads}}[H_{\mathrm{dot}},\rho_{\mathrm{dot}}]\otimes\rho^0_{\mathrm{leads}}$, which is just the unperturbed time evolution. This is exact if $\rho(t) = \rho_{\mathrm{dot}}(t)\otimes\rho^0_{\mathrm{leads}}$ holds, but this is not very useful since the condition is generally not satisfied at any other time. We will see that in the superoperator approach, we do not have to worry about this since we only assume a product state at an initial time t_0, as in Eq. (6). Furthermore, in the TCL approach, we can avoid even this assumption.

If approximation (10) holds, Eq. (8) becomes

$$\dot{\rho}_{\mathrm{dot},I}(t) = - \int_{t_0}^{t} dt' \; \mathrm{tr}_{\mathrm{leads}}[H_{\mathrm{hyb},I}(t),[H_{\mathrm{hyb},I}(t'),\rho_{\mathrm{dot},I}(t') \otimes \rho^0_{\mathrm{leads}}]]. \tag{11}$$

This ME is nonlocal in time.

To make it local, one usually introduces the Markov approximation, which replaces $\rho_{\mathrm{dot},I}(t')$ by $\rho_{\mathrm{dot},I}(t)$. This means that the rate of change of $\rho_{\mathrm{dot},I}$ at time t is determined by $\rho_{\mathrm{dot},I}$ at the same time t only. The approximation is usually motivated by an argument of the following type[14,16]: Eq. (11) contains two-time correlation functions for the leads of the form (10). These correlation functions rapidly decay on the time scale of the dot dynamics so that they can be replaced by δ functions. We come back to this point in Sec. II B.

The same assumption also implies that as long as $t-t_0$ is large compared to the lead correlation time, one can replace t_0 by $-\infty$. With $t'=t-\tau$, one obtains

$$\dot{\rho}_{\mathrm{dot},I}(t) = - \int_{0}^{\infty} d\tau \, \mathrm{tr}_{\mathrm{leads}}[H_{\mathrm{hyb},I}(t),[H_{\mathrm{hyb},I}(t-\tau),\rho_{\mathrm{dot},I}(t) \otimes \rho^0_{\mathrm{leads}}]]. \tag{12}$$

Transforming back into the Schrödinger picture using $\rho_{\mathrm{dot},I}(t) = e^{iH_{\mathrm{dot}}t}\rho_{\mathrm{dot}}(t)e^{-iH_{\mathrm{dot}}t}$, one finds the WBR ME,

$$\dot{\rho}_{\mathrm{dot}}(t) = - i[H_{\mathrm{dot}},\rho_{\mathrm{dot}}(t)] - \int_{0}^{\infty} d\tau \, \mathrm{tr}_{\mathrm{leads}}[H_{\mathrm{hyb}},[e^{-i(H_{\mathrm{dot}}+H_{\mathrm{leads}})\tau}H_{\mathrm{hyb}} \times e^{i(H_{\mathrm{dot}}+H_{\mathrm{leads}})\tau},\rho_{\mathrm{dot}}(t) \otimes \rho^0_{\mathrm{leads}}]], \tag{13}$$

which is local in time. The first term describes the unperturbed time evolution of ρ_{dot} and the second is a correction of second order in H_{hyb}. The restriction to second order entered when we made the large-reservoir approximation after iterating the equation of motion to second order. Explicit expressions are given in Appendix A. They show that within this approximation and if the tunneling amplitudes do not depend on wave vector, the leads only enter through their density of states, temperature, and chemical potentials, regardless of interactions in the leads.

At this point, it is often assumed that the off-diagonal components of ρ_{dot} rapidly decay and can be neglected. For some components, this can be motivated by superselection rules[25–27]: if two dot states $|m)$, $|n)$ differ in an observable that strongly couples to the environment, unavoidable interactions lead to rapid decay of superpositions of these states and thus of ρ^{dot}_{mn}.[26] The standard example is the charge.[22,27] Due to Gauss' law, the charge on the dot interacts with charge fluctuations at all distances.[27] Therefore, superpositions of dot states with different charges are not observed. On the other hand, the description of spin precession[28] requires the off-diagonal components. Different spin states also differ in their long-range (dipole) fields, but these fall off more rapidly than the Coulomb field.

If all off-diagonal components rapidly decay, one is left with the diagonal components $P_m \equiv \rho^{\text{dot}}_{mm}$, i.e., the probabilities of dot many-particle states $|m)$. The principal-value terms in Eq. (A1) then cancel and one obtains

$$\dot{P}_m = -2\pi \sum_{ij} \sum_{p} |\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle|^2 \times (W_i P_m - W_j P_p)\, \delta(E_p + \epsilon_j - E_m - \epsilon_i). \tag{14}$$

Here, $W_i \equiv \langle\langle i|\rho^0_{\text{leads}}|i\rangle\rangle$ is the probability to find the leads in state $|i\rangle\rangle$. By defining the transition rates,

$$R_{n\to m} \equiv 2\pi \sum_{ij} W_j |\langle\langle i|(m|H_{\text{hyb}}|n)|j\rangle\rangle|^2 \delta(E_p + \epsilon_j - E_m - \epsilon_i), \tag{15}$$

we obtain the well-known *rate equations*,

$$\dot{P}_m = \sum_n R_{n\to m} P_n - \sum_n R_{m\to n} P_m. \tag{16}$$

The first term describes transitions from other states $|n)$ to state $|m)$, whereas the second describes transition out of state $|m)$. The rate equations imply *local* conservation of probability—P_m only changes due to the probability flowing into or out of state $|m)$. This conservation law can be implemented in a gauge theory.[29]

B. Discussion of the Markov approximation

The Markov approximation is usually motivated by the rapid decay of the lead correlation functions.[14,16,30] We assume that the hybridization is described by H_{hyb} in Eq. (1). In the second-order approximation, each nonvanishing term contains one lead-electron creation operator $a^\dagger$ and one annihilation operator a. The result is nonzero only if both belong to the same single-particle state characterized by α, $\mathbf{k}$, and σ. The trace tr_{leads} over lead many-particle states is replaced by a sum over single-particle states. As discussed in Appendix A, the correlation functions are Green functions $G^<$, $G^>$. If the leads are normal metals, these decay on the time scale of the quasiparticle lifetime. (The nonquasiparticle background in the spectral function is broader than the quasiparticle peak, corresponding to *faster* processes, which are less critical for the validity of the Markov approximation.) However, the quasiparticle lifetime becomes long at low temperatures. Does the Markov approximation break down in the experimental temperature range?

We now show why this is usually not the case, while in some situation it might be. There are, in fact, two time scales that govern the decay of the relevant lead correlation functions. The first is the quasiparticle lifetime. In normal metals at not too low temperatures, it is usually sufficiently short to justify the Markov assumption. At low temperatures, the quasiparticle lifetime is proportional to $1/T^2$.[32] Assuming an infinite lifetime (like in calculations with noninteracting H_{leads}), the $G^<$, $G^>$ for specific $\mathbf{k}$ do not decay. However, their sum over $\mathbf{k}$ does: we replace the sum by an integral over energy, including the density of states. At low temperatures, we can restrict the integral to the energy window between the two chemical potentials $\mu_<$, $\mu_>$. By assuming a constant density of states and $\mathbf{k}$-independent tunneling amplitudes, we end up with integrals of the type

$$\int_{\mu_<}^{\mu_>} dE e^{\pm iE\tau} = \pm \frac{e^{\pm i\mu_> \tau} - e^{\pm i\mu_< \tau}}{i\tau}. \tag{17}$$

This expression contains a typical time scale, $h/(\mu_> - \mu_<) = h/eV \equiv \tau_{\text{leads}}$, for the decay of correlations, restoring Planck's constant for the moment. Thus, the relevant correlation function also decays on a time scale set by the bias voltage. The same energy scale determines dephasing, i.e., the decay of superpositions due to different chemical potentials in the leads.[31] For arbitrary temperatures, the limits of integration are roughly $\mu_< - k_B T$ and $\mu_> + k_B T$ and the characteristic time is the smaller of h/eV and $h/k_B T$. The contribution from the quasiparticle lifetime is proportional to $1/T^2$ and thus irrelevant at low temperatures.

For weak tunneling or, specifically, if the conductance is small compared to the quantum conductance,

$$I/V \ll e^2/h, \tag{18}$$

the typical time between two tunneling events is $\tau_0 = e/I \gg h/eV = \tau_{\text{leads}}$. Then, the dot dynamics is indeed much slower than the decay of lead correlations and the Markov approximation is justified regardless of the quasiparticle lifetime. It follows from the weak-tunneling approximation, which we have to make in any case to work in low-order perturbation theory.

This argument may fail if tunneling events are strongly correlated.[33–36] In this case, two or more tunneling events often take place during a time much shorter than $\tau_0 = e/I$ and the relation (18) does not guarantee the validity of the Markov approximation.

A related point is seen if we proceed slightly differently in the derivation. By starting from Eq. (5) and inserting Eq. (4) with renamed variables,

$$\rho_I(t') = \rho_I(t) - i \int_t^{t'} dt'' \, [H_{\text{hyb},I}(t''), \rho_I(t'')], \tag{19}$$

we obtain

$$\begin{aligned}\dot{\rho}_I(t) = &-i[H_{\text{hyb},I}(t), \rho_I(t_0)] \\ &- \int_{t_0}^{t} dt' [H_{\text{hyb},I}(t), [H_{\text{hyb},I}(t'), \rho_I(t)]] + i \int_{t_0}^{t} dt' \\ &\times \int_t^{t'} dt'' [H_{\text{hyb},I}(t), [H_{\text{hyb},I}(t'), [H_{\text{hyb},I}(t''), \rho_I(t'')]]],\end{aligned} \tag{20}$$

which is still exact. If we now restrict ourselves to the second order in H_{hyb}, we can drop the last term. We have obtained an equation that is local in time without invoking the Markov approximation.

We have pushed nonlocal terms into higher orders in H_{hyb}. By iterating the procedure, we can achieve this to any order. All relevant terms contain $\rho_I(t)$ instead of $\rho_I(t_0)$, which appears in the naive expansion in Sec. II A. Thus, we can, for example, derive a ME containing sequential and cotunneling contributions.

Now, we can make the additional large-reservoir approximation and replace $\rho_I(t)$ by $\rho_{\text{dot},I}(t)\otimes\rho^0_{\text{leads}}$, as above. However, here, we perform this replacement *only* at time t. We then obtain, by tracing over the leads,

$$\dot{\rho}_{\text{dot},I}(t) = -\int_{t_0}^{t} dt'\, \text{tr}_{\text{leads}}[H_{\text{hyb},I}(t),[H_{\text{hyb},I}(t'),\rho_{\text{dot},I}(t) \otimes \rho^0_{\text{leads}}]]. \tag{21}$$

We finally replace t_0 by $-\infty$. The choice of t_0 can be viewed as a part of our model, as opposed to the approximations employed to solve it. Equation (21) can also be obtained from a variational principle, again only expanding in H_{hyb} without explicit Markov assumption.[37]

We have obtained the same local ME in seemingly different ways. The explanation is that we have not made independent approximations. The rapid decay of the lead correlation functions follows from the assumption of weak tunneling, which also allows us to use perturbation theory in H_{hyb}. On the other hand, the large-reservoir approximation, which is also required to justify the replacement $\rho_I(t)\cong\rho_{\text{dot},I}(t)\otimes\rho^0_{\text{leads}}$, is logically independent.[24]

III. SUPEROPERATOR FORMALISM

The WBR ME can also be derived in the superoperator formalism,[15,16,38,39] which facilitates expansion to higher orders in H_{hyb}. Here, we define a superoperator as an operator acting on the space of linear operators on the Hilbert space. The von Neumann equation is written as $\dot{\rho}=-i\mathcal{L}\rho$, where

$$\mathcal{L} = \mathcal{L}_{\text{dot}} + \mathcal{L}_{\text{leads}} + \mathcal{L}_{\text{hyb}} \tag{22}$$

is the Liouvillian defined by $\mathcal{L}_{\text{dot}}\rho\equiv[H_{\text{dot}},\rho]$, etc. The solution reads $\rho(t)=e^{-i\mathcal{L}(t-t_0)}\rho(t_0)$. We define projection (super) operators[40,41] $\mathcal{P}$, $\mathcal{Q}$ by $\mathcal{P}\rho(t)\equiv[\text{tr}_{\text{leads}}\,\rho(t)]\otimes\rho^0_{\text{leads}}$ and $\mathcal{Q}\equiv 1-\mathcal{P}$. Note that $\mathcal{P}$ maps a density operator onto one in product form with the leads in equilibrium, while retaining the information on the dot state. Conversely, $\mathcal{Q}\rho$ contains the information on the leads and the dot-lead correlations. Since H_{hyb} is a sum of bilinear terms of dot and lead-electron operators, it is easy to prove the identities,

$$\mathcal{P}\mathcal{L}_{\text{dot}} = \mathcal{L}_{\text{dot}}\mathcal{P}, \tag{23}$$

$$\mathcal{P}\mathcal{L}_{\text{leads}} = \mathcal{L}_{\text{leads}}\mathcal{P} = 0, \tag{24}$$

$$\mathcal{P}\mathcal{L}_{\text{hyb}}\mathcal{P} = 0. \tag{25}$$

The last relation is essentially equivalent to Eq. (7).

The von Neumann equation can be split into two equations,[15,16,38,39]

$$\frac{d}{dt}\mathcal{P}\rho = -i\mathcal{P}\mathcal{L}\mathcal{P}\rho - i\mathcal{P}\mathcal{L}\mathcal{Q}\rho, \tag{26}$$

$$\frac{d}{dt}\mathcal{Q}\rho = -i\mathcal{Q}\mathcal{L}\mathcal{Q}\rho - i\mathcal{Q}\mathcal{L}\mathcal{P}\rho, \tag{27}$$

which can be solved by a Laplace transformation,

$$\tilde{F}(s) \equiv \int_0^\infty dt e^{-st}F(t), \tag{28}$$

where we have set $t_0=0$. We find

$$s\mathcal{P}\tilde{\rho} - \mathcal{P}\rho(0) = -i\mathcal{P}\mathcal{L}\mathcal{P}\tilde{\rho} - i\mathcal{P}\mathcal{L}\mathcal{Q}\tilde{\rho}, \tag{29}$$

$$s\mathcal{Q}\tilde{\rho} - \mathcal{Q}\rho(0) = -i\mathcal{Q}\mathcal{L}\mathcal{Q}\tilde{\rho} - i\mathcal{Q}\mathcal{L}\mathcal{P}\tilde{\rho}. \tag{30}$$

By inserting the solution of the second equation,

$$\mathcal{Q}\tilde{\rho} = (s+i\mathcal{Q}\mathcal{L})^{-1}\mathcal{Q}\rho(0) - i(s+i\mathcal{Q}\mathcal{L})^{-1}\mathcal{Q}\mathcal{L}\mathcal{P}\rho, \tag{31}$$

into the first, we obtain

$$s\mathcal{P}\tilde{\rho} = \mathcal{P}\rho(0) - i\mathcal{P}\mathcal{L}(s+i\mathcal{Q}\mathcal{L})^{-1}\mathcal{Q}\rho(0) - i\mathcal{P}\mathcal{L}\mathcal{P}\tilde{\rho} - \mathcal{P}\mathcal{L}(s+i\mathcal{Q}\mathcal{L})^{-1}\mathcal{Q}\mathcal{L}\mathcal{P}\tilde{\rho}. \tag{32}$$

By using Eqs. (22)–(25), we find

$$s\mathcal{P}\tilde{\rho} = \mathcal{P}\rho(0) - i\mathcal{P}\mathcal{L}_{\text{hyb}}(s+i\mathcal{L}_{\text{dot}}+i\mathcal{L}_{\text{leads}}+i\mathcal{Q}\mathcal{L}_{\text{hyb}})^{-1}\mathcal{Q}\rho(0) - i\mathcal{P}\mathcal{L}_{\text{dot}}\mathcal{P}\tilde{\rho} - \mathcal{P}\mathcal{L}_{\text{hyb}}(s+i\mathcal{L}_{\text{dot}}+i\mathcal{L}_{\text{leads}} + i\mathcal{Q}\mathcal{L}_{\text{hyb}})^{-1}\mathcal{Q}\mathcal{L}_{\text{hyb}}\mathcal{P}\tilde{\rho}. \tag{33}$$

We could insert a $\mathcal{Q}$ following $\mathcal{Q}\mathcal{L}_{\text{hyb}}$ since $\mathcal{Q}=\mathcal{Q}\mathcal{Q}$.

By transforming back into the time domain and shifting the initial time back to t_0, we find

$$\frac{d}{dt}\mathcal{P}\rho = -i\mathcal{P}\mathcal{L}_{\text{hyb}}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{Q}\mathcal{L}_{\text{hyb}}\mathcal{Q})(t-t_0)}\mathcal{Q}\rho(t_0) - i\mathcal{P}\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - \mathcal{P}\mathcal{L}_{\text{hyb}}\int_{t_0}^{t} dt'\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{Q}\mathcal{L}_{\text{hyb}}\mathcal{Q})(t-t')}\mathcal{L}_{\text{hyb}}\mathcal{P}\rho(t'). \tag{34}$$

(We will show later that the projections $\mathcal{Q}$ in the exponentials remove all reducible terms from the expansion in powers of $\mathcal{L}_{\text{hyb}}$.) Equation (34) is an exact ME, which is nonlocal in time.

Starting from Eq. (34), the weak-coupling limit as discussed in Ref. 16 now consists of (a) neglecting all powers of $\mathcal{L}_{\text{hyb}}$ beyond the second and (b) dropping the dependence on the initial condition for $\mathcal{Q}\rho(t_0)$. (a) is just the weak-tunneling approximation of Sec. II A. (b) neglects a term of *linear* order in $\mathcal{L}_{\text{hyb}}$ and has to be shown to be consistent. The rationale given in Ref. 16 is twofold: first, the term in $\mathcal{Q}\rho(t_0)$ is a small (of order H_{hyb}) correction to $\mathcal{P}\rho(t_0)$, and second, it is not accumulated over time, being a correction to the initial conditions. These arguments appear to be weak: $\mathcal{Q}\rho(t_0)$ and $\mathcal{P}\rho(t_0)$ lie in orthogonal subspaces and it is not obvious that their magnitudes can be meaningfully compared. Furthermore, Eq. (34) shows that $\mathcal{Q}\rho(t_0)$ does affect $\mathcal{P}\rho(t)$ for all $t > t_0$, even to first order.

Dropping the dependence on $\mathcal{Q}\rho(t_0)$ is trivial if $\mathcal{Q}\rho(t_0) = 0$. This is not an approximation but an initial condition, see Sec. II A.

With approximations (a) and (b), Eq. (34) becomes

$$\frac{d}{dt}\mathcal{P}\rho \cong -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - \mathcal{P}\mathcal{L}_{\text{hyb}}\int_{t_0}^{t} dt'\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')}\mathcal{L}_{\text{hyb}}\mathcal{P}\rho(t'). \tag{35}$$

By inserting the definition of $\mathcal{P}$ and writing the Liouvillians as commutators, we obtain

$$\frac{d}{dt}\rho_{\text{dot}} \cong -i[H_{\text{dot}},\rho_{\text{dot}}(t)] - \int_{t_0}^{t} dt'\, \text{tr}_{\text{leads}}[H_{\text{hyb}}, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')}[H_{\text{hyb}},\rho_{\text{dot}}(t') \otimes \rho^0_{\text{leads}}]]. \tag{36}$$

Now, for any Hamiltonian H with associated Liouvillian $\mathcal{L}$ and any operator (not superoperator) A, the identity $e^{-i\mathcal{L}\tau}A = e^{-iH\tau}Ae^{iH\tau}$ implies

$$\frac{d}{dt}\rho_{\text{dot}} \cong -i[H_{\text{dot}},\rho_{\text{dot}}(t)] - \int_{t_0}^{t} dt'\, \text{tr}_{\text{leads}}[H_{\text{hyb}},[e^{-i(H_{\text{dot}}+H_{\text{leads}})(t-t')}H_{\text{hyb}} \times e^{i(H_{\text{dot}}+H_{\text{leads}})(t-t')}, e^{-iH_{\text{dot}}(t-t')}\rho_{\text{dot}}(t')e^{iH_{\text{dot}}(t-t')} \otimes \rho^0_{\text{leads}}]]. \tag{37}$$

Compare this to the WBR result [Eq. (13)]. To get there, we have to replace $e^{-iH_{\text{dot}}(t-t')}\rho_{\text{dot}}(t')e^{iH_{\text{dot}}(t-t')}$ by $\rho_{\text{dot}}(t)$. This is *nearly* the same: $\rho_{\text{dot}}(t)$ is described by the full Hamiltonian H, while Eq. (37) only contains the unperturbed time evolution due to H_{dot}. This is consistent with the second-order approximation since any correction to the unperturbed time evolution adds more powers of H_{hyb}. Thus, the Markov property again follows. We can extend the range of integration to $t_0 \to -\infty$ arguing as in Sec. II B.

Note that we did not need the assumption $\rho(t) \cong \rho_{\text{dot}}(t) \otimes \rho^0_{\text{leads}}$ in this approach. We have only assumed the density operator to be of this product form at an early time t_0—a much weaker assumption.

IV. *T*-MATRIX APPROACH AND FERMI'S GOLDEN RULE

The *T*-matrix approach[32,34–36,42–44] and its leading-order approximation, Fermi's golden rule,[45–47] are used by several groups to describe tunneling processes since they provide a straightforward derivation of the transition rates in the *diagonal* rate equations. The approach is presented in many textbooks. Bruus and Flensberg[32] discussed it in relation to the tunneling problem.

The derivation starts out by writing

$$H(t) = \underbrace{H_{\text{dot}} + H_{\text{leads}}}_{=H_0} + \underbrace{H_{\text{hyb}}e^{\eta t}}_{=V(t)}, \tag{38}$$

where η is small and positive. Thus, the hybridization is switched on very slowly. We assume that the system was in an eigenstate $|i\rangle$ of H_0 at time t_0. The probability that it is in another eigenstate $|f\rangle$ at time t reads

$$|\langle f|i(t)\rangle|^2 \equiv \left|\langle f|\mathcal{T}\exp\left[-i\int_{t_0}^{t} dt'\, V_I(t')\right]|i\rangle\right|^2, \tag{39}$$

where $\mathcal{T}$ is the time-ordering operator. The transition rate between states $|i\rangle$ and $|f\rangle$ is then defined as

$$\Gamma_{fi} \equiv \frac{d}{dt}|\langle f|i(t)\rangle|^2. \tag{40}$$

By taking the limit $\eta \to 0^+$ and defining the T matrix,

$$T(E_i) \equiv H_{\text{hyb}} + H_{\text{hyb}}\frac{1}{E_i - H_0 + i0^+}H_{\text{hyb}} + H_{\text{hyb}}\frac{1}{E_i - H_0 + i0^+}H_{\text{hyb}}\frac{1}{E_i - H_0 + i0^+}H_{\text{hyb}} + \cdots, \tag{41}$$

one obtains

$$\Gamma_{fi} = 2\pi\delta(E_i - E_f)|\langle f|T|i\rangle|^2, \tag{42}$$

where E_i and E_f are the eigenenergies of states $|i\rangle$ and $|f\rangle$, respectively. The leading order is obtained by replacing T by H_{hyb},

$$\Gamma_{fi} = 2\pi\delta(E_i - E_f)|\langle f|H_{\text{hyb}}|i\rangle|^2, \tag{43}$$

which is Fermi's golden rule.

To draw the connection with the rate equations, we choose the states $|i\rangle$, $|f\rangle$ as product states of many-particle states of the dot, $|m)$, and of the leads, $|i\rangle\rangle$. Summing Γ_{fi} over the lead states, we obtain the transition rates,

$$\tilde{R}_{n\to m} = 2\pi\sum_{if} W_i|\langle\langle f|(m|T|n)|i\rangle\rangle|^2\delta(E_n + \epsilon_i - E_m - \epsilon_f), \tag{44}$$

from state $|n)$ to $|m)$. Here, E_m (ϵ_i) are eigenenergies of dot (lead) states and W_i is the probability to find the leads in initial state $|i\rangle$ at time $t_0 \to -\infty$. To write down Eq. (44), one has to make the assumption that the probability W_i is independent of the state of the dot. This means that the system is in a product state $\rho=\rho_{\mathrm{dot}}\otimes\rho_{\mathrm{leads}}$ at time t_0. This is the same assumption usually made in density-operator approaches. If the leads are in equilibrium at time t_0, one can express W_i in terms of Fermi functions.

In the next step, $\tilde{R}_{n\to m}$ is identified with the transition rate $R_{n\to m}$ appearing in the rate equations. However, what is actually calculated is the rate of change of the probability of state $|m)$ under the condition that the dot was in state $|n)$ at time $t_0\to-\infty$ [cf. Eqs. (40) and (44)]. On the other hand, in the density-operator approach, one calculates the rate of change of the probability of state $|m)$ under the condition that it is in state $|n)$ at the *same* time t, immediately before a possible transition. The two are the same only if the dot remains in state $|n)$ from time t_0 through t. This is, of course, not usually the case.

In the sequential-tunneling approximation, one evaluates the rates to second order in H_{hyb}. Since two powers of H_{hyb} are required for the final transition to state $|m)$, no transitions can occur between t_0 and t. Therefore, to second order, where the T-matrix approach reduces to Fermi's golden rule, it gives the same transition rates $R_{n\to m}$ as the WBR approach. Beyond leading order, $\tilde{R}_{n\to m}$ and $R_{n\to m}$ describe different quantities.

To leading order, $T\cong H_{\mathrm{hyb}}$, the rates $\tilde{R}_{n\to m}$ in Eq. (44) are indeed identical to the the WBR result [Eq. (15)]. The latter has been obtained under the Markov assumption. One might wonder where the Markov assumption entered in the T-matrix formalism. It is implied in the derivation since to second order ρ does not change between times t_0 and t anyway.

The rate equations [Eq. (16)] appear to be obvious. However, can they be *derived* in the T-matrix framework? Certainly not without further assumptions, since they omit the off-diagonal components of ρ_{dot} necessary for a complete description.

V. KELDYSH-CONTOUR APPROACH OF KÖNIG *ET AL.*

König *et al.*[8–11] have developed a diagrammatic technique to generate a perturbative expansion in the tunneling amplitudes. This approach has also been applied to tunneling through molecules.[11,48] In the present section, we show how it is related to the WBR theory. Reference 9 concerns a quantum dot with electron-electron and electron-vibration interactions. A unitary transformation replaces the latter with an exponential operator in the tunneling Hamiltonian.[49] We do not consider this transformation here. This does not restrict the models covered by our discussion—we include any bosonic modes and electron-boson interactions into H_{dot}.

As usual, the system is assumed to be in a product state at an early time t_0 with the leads in separate equilibria. The propagator Π of ρ_{dot} from time t_0 to $t\geqslant t_0$ is defined by

$$\rho_{\mathrm{dot}}(t)=\Pi(t,t_0)\rho_{\mathrm{dot}}(t_0). \tag{45}$$

(We use the same notation and time ordering as elsewhere in this paper.) $\Pi(t,t_0)$ is represented by a diagram on the Keldysh contour between times t_0 and t (Fig. 3 in Ref. 9). König *et al.* then identified the irreducible part Σ_K of Π (a subscript is added to distinguish Σ_K from Σ introduced above), which is defined as the sum of all diagrams that cannot be cut at an intermediate time without cutting a lead line representing the pairing of $a^\dagger_{\alpha\mathbf{k}\sigma}$ and $a_{\alpha\mathbf{k}\sigma}$. Π is expressed in terms of Σ_K by a Dyson-type equation,

$$\Pi(t,t_0)=\Pi^{(0)}(t,t_0)+\int_{t_0}^{t}dt_2\int_{t_0}^{t_2}dt_1\,\Pi^{(0)}(t,t_2)\Sigma_K(t_2,t_1)\Pi(t_1,t_0), \tag{46}$$

containing the bare propagator,

$$[\Pi^{(0)}(t,t_0)]^{nn'}_{mm'}=\delta_{mm'}\delta_{nn'}e^{-i(E_n-E_m)(t-t_0)}. \tag{47}$$

In Ref. 9, Eqs. (45)–(47) are presented for arbitrary initial time $t'\geqslant t_0$. Equation (45) would then imply $\Pi(t,t'')=\Pi(t,t')\Pi(t',t'')$, which contradicts Eq. (46).[50] This is not a problem since the equations with initial time t_0 are sufficient for the derivation of the ME.

We want to explicitly find the propagator Π. Clearly, we have $\mathcal{P}\rho(t)=\mathcal{P}e^{-i\mathcal{L}(t-t_0)}\rho(t_0)$. Since the initial condition $\mathcal{Q}\rho(t_0)=0$ is assumed, we find

$$\mathcal{P}\rho(t)=[\mathcal{P}e^{-i\mathcal{L}(t-t_0)}\mathcal{P}]\mathcal{P}\rho(t_0)\equiv\Pi(t,t_0)\mathcal{P}\rho(t_0). \tag{48}$$

This defines the propagator Π for initial time t_0. The last factor $\mathcal{P}$ in Π is expendable.

Can we find Σ_K to satisfy Eq. (46)? We expand the exponential in Eq. (48), noting that all lead creation and annihilation operators must be paired for the result to be nonzero since $\mathcal{P}\mathcal{L}_{\mathrm{hyb}}\mathcal{P}=0$. Diagrammatically, this is represented by a lead-fermion line connecting two H_{hyb} insertions.[9] The lead trace then gives a Fermi factor for each pair of insertions. With regard to this pairing, we can identify the irreducible part Σ_K and write

$$\begin{aligned}\mathcal{P}e^{-i\mathcal{L}(t-t_0)}\mathcal{P}&=\mathcal{P}e^{-i(\mathcal{L}_{\mathrm{dot}}+\mathcal{L}_{\mathrm{leads}})(t-t_0)}+\mathcal{P}\int_{t_0}^{t}dt_2\int_{t_0}^{t_2}dt_1\,e^{-i(\mathcal{L}_{\mathrm{dot}}+\mathcal{L}_{\mathrm{leads}})(t-t_2)}\Sigma_K(t_2,t_1)e^{-i(\mathcal{L}_{\mathrm{dot}}+\mathcal{L}_{\mathrm{leads}})(t_1-t_0)}\mathcal{P}+\cdots\\&=\mathcal{P}e^{-i(\mathcal{L}_{\mathrm{dot}}+\mathcal{L}_{\mathrm{leads}})(t-t_0)}+\mathcal{P}\int_{t_0}^{t}dt_2\int_{t_0}^{t_2}dt_1\,e^{-i(\mathcal{L}_{\mathrm{dot}}+\mathcal{L}_{\mathrm{leads}})(t-t_2)}\Sigma_K(t_2,t_1)e^{-i\mathcal{L}(t_1-t_0)}\mathcal{P}.\end{aligned} \tag{49}$$

If we insert $\mathcal{P}$ at some intermediate time t_n in Eq. (49), this forces all lead-fermion operators to be separately paired for times $t<t_n$ and $t>t_n$. This is equivalent to the diagram being reducible at time t_n. Conversely, if a diagram is reducible at time t_n, inserting $\mathcal{P}$ there does not change the result. Consequently,

$$\mathcal{P}e^{-i\mathcal{L}(t-t_0)}\mathcal{P} = \mathcal{P}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t_0)} + \mathcal{P}\int_{t_0}^{t} dt_2 \times \int_{t_0}^{t_2} dt_1\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t_2)}\Sigma_K(t_2,t_1)\mathcal{P}e^{-i\mathcal{L}(t_1-t_0)}\mathcal{P}. \tag{50}$$

Here, we can identify the bare propagator,

$$\Pi^{(0)}(t,t') \equiv \mathcal{P}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')}. \tag{51}$$

These two equations correspond to Eqs. (46) and (47) except that we had to introduce another projection $\mathcal{P}$ at the final time. Apart from this, we recover the Dyson-type equation of Ref. 9 for initial time t_0.

By inserting the Dyson-type equation [Eq. (50)] for the propagator into Eq. (48) and taking the time derivative, one obtains a ME,[9]

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) + \mathcal{P}\int_{t_0}^{t} dt'\, \Sigma_K(t,t')\mathcal{P}\rho(t'). \tag{52}$$

This corresponds to Eq. (25) in Ref. 9 (a factor of $\mathcal{P}$ on the left can be included into the definition of Σ_K).

We can gain further insight by returning to Eq. (34), restricted to the case $\mathcal{Q}\rho(t_0)=0$,

$$\frac{d}{dt}\mathcal{P}\rho = -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - \mathcal{P}\mathcal{L}_{\text{hyb}}\int_{t_0}^{t} dt'\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{Q}\mathcal{L}_{\text{hyb}}\mathcal{Q})(t-t')}\mathcal{L}_{\text{hyb}}\mathcal{P}\rho(t'). \tag{53}$$

By comparing to Eq. (52), we find

$$\mathcal{P}\Sigma_K(t,t')\mathcal{P} = \mathcal{P}\mathcal{L}_{\text{hyb}}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{Q}\mathcal{L}_{\text{hyb}}\mathcal{Q})(t-t')}\mathcal{L}_{\text{hyb}}\mathcal{P}. \tag{54}$$

Thus, the ME of Ref. 9 is equivalent to the WBR ME to all orders in H_{hyb} and we have derived an explicit expression for the irreducible part. For later, we introduce in Fig. 1 a diagrammatic representation for the second term in Eq. (53).

Now, the factors of $\mathcal{Q}$ in the exponential find a natural interpretation: they remove all reducible terms from the expansion of Eq. (54) in powers of $\mathcal{L}_{\text{hyb}}$. This is because at a point where a diagram is reducible, one can insert a $\mathcal{P}$. However, if a $\mathcal{Q}$ is present at this point, we obtain $\mathcal{P}\mathcal{Q}=\mathcal{Q}\mathcal{P}=0$.

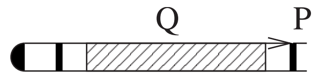

FIG. 1. Diagram for the second term in the ME [Eq. (53)]. Time is increasing to the right. The bare propagator $e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')}$ for the density operator (not occurring here) would be represented by just two lines. The full propagator $e^{-i\mathcal{L}(t-t')}$ is shown as a hatched box. Its irreducible part $e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t')}$ is distinguished by writing "Q" beside it. All additional projection operators are likewise indicated by "P" or "Q." An insertion of $-i\mathcal{L}_{\text{hyb}}$ is denoted by a heavy bar connecting the two lines. The projected density operator $\mathcal{P}\rho(t')$ at time t' is shown as a filled semicircle.

Thus, all diagrams in the expansion that are reducible to the left or to the right of an insertion of $\mathcal{L}_{\text{hyb}}$ vanish.

VI. TIME-CONVOLUTIONLESS MASTER EQUATION

This approach leads to a ME that is local in time and exact and thus avoids the Markov assumption. The Markov assumption is valid for weak tunneling and not strongly correlated tunneling events, as discussed above, but becomes increasingly dubious at higher orders in H_{hyb} or in resummation or nonperturbative schemes. The approach was developed by Tokuyama and Mori[12] and others[51–53] and is discussed in Ref. 15. This section adapts it to the tunneling problem.

We again start from Eqs. (26) and (27) and express $\mathcal{Q}\rho(t)$ in the first equation in terms of $\mathcal{P}\rho(t)$ and $\mathcal{Q}\rho(t_0)$ with the help of the second. We do not make any assumptions on $\mathcal{Q}\rho(t_0)$. The solution of Eq. (27) reads

$$\mathcal{Q}\rho(t) = e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t_0)}\mathcal{Q}\rho(t_0) - i\int_{t_0}^{t} dt'\, e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t')}\mathcal{Q}\mathcal{L}\mathcal{P}\rho(t'). \tag{55}$$

Next, we express $\rho(t')$ by propagating the full density operator backward in time,

$$\mathcal{Q}\rho(t) = e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t_0)}\mathcal{Q}\rho(t_0) - i\int_{t_0}^{t} dt'\, e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t')}\mathcal{Q}\mathcal{L}\mathcal{P}e^{-i\mathcal{L}(t'-t)} \times[\mathcal{P}\rho(t)+\mathcal{Q}\rho(t)]. \tag{56}$$

By moving all terms in $\mathcal{Q}\rho(t)$ to the left, we obtain

$$(1-\Sigma)\mathcal{Q}\rho(t) = e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t_0)}\mathcal{Q}\rho(t_0) + \Sigma\mathcal{P}\rho(t), \tag{57}$$

with the superoperator,

$$\Sigma(t-t_0) \equiv -i\int_{t_0}^{t} dt'\, e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t')}\mathcal{Q}\mathcal{L}\mathcal{P}e^{-i\mathcal{L}(t'-t)}. \tag{58}$$

The time argument $t-t_0$ will be suppressed if confusion is unlikely. The integral can be performed, giving

$$\Sigma(t-t_0) = \int_{t_0}^{t} dt' \left(e^{-i\mathcal{QLQ}(t-t')}\mathcal{Q}\frac{\partial}{\partial t'}e^{-i\mathcal{L}(t'-t)} + \left[\frac{\partial}{\partial t'}e^{-i\mathcal{QLQ}(t-t')}\right]\mathcal{Q}e^{-i\mathcal{L}(t'-t)}\right) = \mathcal{Q} - e^{-i\mathcal{QLQ}(t-t_0)}\mathcal{Q}e^{-i\mathcal{L}(t_0-t)}. \quad (59)$$

The integral form [Eq. (58)] is more suitable for the expansion in $\mathcal{L}_{\text{hyb}}$, though.

By applying the inverse $(1-\Sigma)^{-1}$ to Eq. (57), we obtain

$$\mathcal{Q}\rho(t) = (1-\Sigma)^{-1}e^{-i\mathcal{QLQ}(t-t_0)}\mathcal{Q}\rho(t_0) + (1-\Sigma)^{-1}\Sigma\mathcal{P}\rho(t). \quad (60)$$

This remarkable equation asserts that we can reconstruct $\mathcal{Q}\rho$ and, thus, $\rho=\mathcal{P}\rho+\mathcal{Q}\rho$ at time t from $\mathcal{P}\rho$ at time t and $\mathcal{Q}\rho$ at some arbitrarily early time t_0, even though $\mathcal{P}\rho$ only contains information on the dot state.

By inserting Eq. (60) into Eq. (26), we obtain an equation of motion for $\mathcal{P}\rho$ alone,

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{PL}(1-\Sigma)^{-1}\mathcal{P}\rho(t) - i\mathcal{PL}(1-\Sigma)^{-1}e^{-i\mathcal{QLQ}(t-t_0)}\mathcal{Q}\rho(t_0), \quad (61)$$

which, together with Eq. (58) or (59), constitutes the TCL ME. Equations (61) and (58) can be generalized for time-dependent Hamiltonians[51,53] by replacing the multiplication with $t-t_0$ by a time integral.

The TCL ME is exact but relies on the condition that the inverse of $1-\Sigma$ exists. For a different system not involving transport, one can find cases when $1-\Sigma$ is singular.[54] Since Σ vanishes at $t=t_0$ [cf. Eq. (59)], Breuer *et al.*[15,54] conclude that $1-\Sigma$ is not singular for sufficiently small $t-t_0$. This does not directly apply to our case since the time dependence is governed by the dynamics of the full system, which permits arbitarily large excitation energies. In other words, the eigenvalues of $\mathcal{L}$ and $\mathcal{QLQ}$ in Eq. (59) are not bounded.

By using Eqs. (22)–(25), we obtain a more explicit form,

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - i\mathcal{PL}_{\text{hyb}}(1-\Sigma)^{-1}\mathcal{P}\rho(t) - i\mathcal{PL}_{\text{hyb}}(1-\Sigma)^{-1}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{QL}_{\text{hyb}}\mathcal{Q})(t-t_0)}\mathcal{Q}\rho(t_0), \quad (62)$$

with

$$\Sigma(t-t_0) = -i\mathcal{Q}\int_{t_0}^{t} dt'\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{QL}_{\text{hyb}}\mathcal{Q})(t-t')}\mathcal{L}_{\text{hyb}}\mathcal{P}e^{-i\mathcal{L}(t'-t)}. \quad (63)$$

We have used that $\mathcal{P}(1-\Sigma)^{-1}=\mathcal{P}$, as can be seen by expanding in powers of Σ. Equation (62) should be compared to the nonlocal ME [Eq. (34)].

For the case $\mathcal{Q}\rho(t_0)=0$, the equation simplifies to

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - i\mathcal{PL}_{\text{hyb}}[1-\Sigma(t-t_0)]^{-1}\mathcal{P}\rho(t). \quad (64)$$

It is then tempting to take the limit $t_0\to-\infty$. One has to check whether this limit exists for $\Sigma(t-t_0)$.

As advertised, the TCL ME [Eq.(62)] is local in time, although the dynamics is generally not Markovian. The memory effects have been shifted into the time dependence of the coefficients of $\mathcal{P}\rho$.[55–57] This works because the integrodifferential WBR ME is linear. One can then show that a purely differential equation with the same solution exists.[55] Maniscalco *et al.*[56] use the exact solution for the damped harmonic oscillator to illustrate that non-Markovian dynamics is indeed compatible with a TCL formulation. This and related results[57,58] do not involve transport.

We briefly comment on the question of positivity of the reduced density operator, i.e., the requirement that all its eigenvalues are non-negative. As in Ref. 57, the coefficients in the TCL ME are time dependent. Thus, Lindblad's[59] criterion for (complete[15,60]) positivity does not apply. However, the TCL ME is exact so that its solution for $\mathcal{P}\rho$ satisfies $\mathcal{P}\rho=[\text{tr}_{\text{leads}}\,\rho]\otimes\rho^0_{\text{leads}}$ at all times. Thus, $\rho_{\text{dot}}=\text{tr}_{\text{leads}}\rho=\text{tr}_{\text{leads}}\,\mathcal{P}\rho$ is certainly positive. It is important to check under what conditions an approximation scheme respects positivity.

To obtain the sequential-tunneling approximation to Eq. (62), we expand to second order in $\mathcal{L}_{\text{hyb}}$,

$$\frac{d}{dt}\mathcal{P}\rho(t) \cong -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - \mathcal{PL}_{\text{hyb}}\int_{t_0}^{t} dt'\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')}\mathcal{L}_{\text{hyb}}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t'-t)}\mathcal{P}\rho(t) - i\mathcal{PL}_{\text{hyb}}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t_0)}\mathcal{Q}\rho(t_0) - \mathcal{PL}_{\text{hyb}}\int_{t_0}^{t} dt'\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')}\mathcal{L}_{\text{hyb}}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t'-t_0)}\mathcal{Q}\rho(t_0). \quad (65)$$

The first term describes the unperturbed time evolution. The two inhomogeneous terms describe the effect of a deviation of the state at time t_0 from a product state with leads in equilibrium. The third term is the only one of first order in the tunneling amplitudes; thus, for $\mathcal{Q}\rho(t_0)=0$, there are no first-order terms. For readers familiar with optical response theory, this may seem surprising. We briefly discuss first-order terms in Appendix B.

A. Perturbative expansion

Since expansions beyond second order are clearly cumbersome to write down, a diagrammatic representation is helpful. Here, we assume the simplifying initial condition, $\mathcal{Q}\rho(t_0)=0$. We first expand Eq. (64) in powers of Σ,

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{L}_{\text{dot}}\mathcal{P}\rho(t) - i\mathcal{P}\mathcal{L}_{\text{hyb}}(\Sigma + \Sigma\Sigma + \Sigma\Sigma\Sigma + \cdots)\mathcal{P}\rho(t). \tag{66}$$

The first-order term vanishes since $\mathcal{P}\mathcal{L}_{\text{hyb}}\mathcal{P}=0$. Note that the series $1+\Sigma+\Sigma^2+\cdots$ might not converge even if the inverse of $1-\Sigma$ exists.

The superoperator Σ [Eq. (63)] first propagates the density operator backward in time, projects it, inserts a perturbation $\mathcal{L}_{\text{hyb}}$, and then propagates it forward again. Its diagrammatic representation is shown in Fig. 2. The contributions to Eq. (66) with one and two powers of Σ are represented by the diagrams in Fig. 3. It is obvious how the series continues.

This is a good place to compare to the approach of WBR and König *et al.* The contribution from the tunneling is in this case given by the last term in Eq. (53) or the diagram in Fig. 1. To show its consistency with the TCL equation, we note that all tunneling contributions in the TCL approach are of the form shown in Fig. 4. This is indeed just a deformation of Fig. 1 (the "Q" adjacent to the final $\mathcal{L}_{\text{hyb}}$ is expendable). The upper part of Σ is thus identical to the irreducible part Σ_K without the final $\mathcal{L}_{\text{hyb}}$. This is also seen by comparing the algebraic expressions (54) and (63).

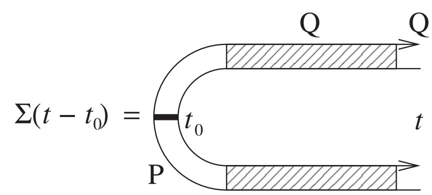

FIG. 2. Diagram for the superoperator $\Sigma(t-t_0)$. The interpretation of symbols is given in the caption of Fig. 1. The rightmost superoperator in Eq. (63) corresponds to the lower right corner of the diagram.

In order to expand the ME in powers of $\mathcal{L}_{\text{hyb}}$, we next expand the exponentials as

$$e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{Q}\mathcal{L}_{\text{hyb}}\mathcal{Q})(t-t')} = e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t')} - i\mathcal{Q}\int_{t'}^{t} dt_1\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t_1)}\mathcal{L}_{\text{hyb}}\mathcal{Q}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t_1-t')}$$
$$- \mathcal{Q}\int_{t'}^{t} dt_2 \int_{t'}^{t_2} dt_1\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t-t_2)}\mathcal{L}_{\text{hyb}}\mathcal{Q}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t_2-t_1)}\mathcal{L}_{\text{hyb}}\mathcal{Q}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t_1-t')} + \cdots \tag{67}$$

and

$$e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}}+\mathcal{L}_{\text{hyb}})(t'-t)} = e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t'-t)} + i\int_{t'}^{t} dt_1\, e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t'-t_1)}\mathcal{L}_{\text{hyb}}e^{-i(\mathcal{L}_{\text{dot}}+\mathcal{L}_{\text{leads}})(t_1-t)} + \cdots . \tag{68}$$

The odd terms in Eq. (68) obtain an additional minus sign since the reversed time order gives an additional minus sign for each integral.

As discussed earlier, any insertion of $\mathcal{P}$ forces an expression to be reducible at that point and any insertion of $\mathcal{Q}$ means that the diagram must not be reducible at that point. $\mathcal{P}$ and $\mathcal{Q}$ thus govern the construction of nonvanishing diagrams but do not affect their values. For the case of a single factor of Σ, the only diagrams up to fourth order in $\mathcal{L}_{\text{hyb}}$ are the ones shown in Figs. 5(a)–5(d). The only fourth-order contribution from the term with two Σ is shown in Fig. 5(e). The second insertion of $\mathcal{L}_{\text{hyb}}$ counting from the lower right comes from the upper factor of Σ due to the rightmost Q in Fig. 3(b).

The diagrams in Figs. 5(d) and 5(e) are topologically equivalent but differ in the time ordering. Diagram (d) has $t\equiv t_4>t_1>t_2>t_3$, whereas (e) has $t_4>t_1$ and $t_4>t_2>t_3$. In addition, (e) has an odd number of $\mathcal{L}_{\text{hyb}}$ on the lower branch of the upper Σ, leading to an additional minus sign from Eq. (68). If we add (d) and (e), contributions with $t_1>t_2$ cancel and we obtain $t_4>t_2>t_1$ and $t_2>t_3$ and an overall minus sign. Higher-order diagrams are constructed in the same manner.

VII. SUMMARY

In this paper, various approaches to the ME for tunneling through molecules and quantum dots have been discussed and compared. The standard derivation of the WBR ME relies on two assumptions: (1) weak tunneling, which allows one to use low-order perturbation theory in the tunneling amplitude; (2) the leads form large energy and particle reservoirs, which, together with the first assumption and a density operator of product form with the leads in equilibrium at an early time t_0, allows one to write the density operator as a product at all times. Assumption (2) must only be made when calculating expressions of the desired order in H_{hyb}. Making it globally leads to trivial dynamics.

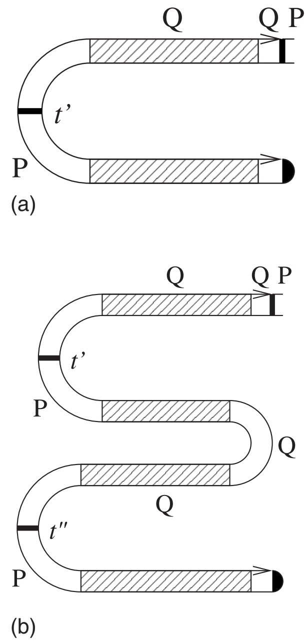

FIG. 3. Contributions to the TCL ME [Eq. (66)] containing (a) one and (b) two powers of the superoperator Σ. The filled semicircle denotes the density operator $\mathcal{P}\rho(t)$. In (b), no time ordering of t' and t'' is implied.

At low temperatures, the Markov approximation is not governed by the quasiparticle lifetime, which becomes long in this regime, but by a time scale given by the inverse bias or the inverse thermal energy, whichever is smaller. The Markov property then usually follows from the weak-tunneling assumption. Furthermore, in the sequential-tunneling approximation, the finite quasiparticle lifetime and the corresponding broadening of the spectral function are irrelevant for the tunneling if the tunneling matrix elements do not depend on the wave vector. The Markov assumption can fail, however, if tunneling events are highly correlated in time.

The superoperator derivation of the WBR ME clarifies the role of the Markov approximation. No assumptions beyond weak tunneling and an initial density operator of product form are made. The large-reservoir assumption (2) is not required, beyond this initial condition. The resulting WBR ME is nonlocal in time. An explicit Markov approximation is required to make it local.

The ME of König *et al.*[9] is equivalent to the WBR ME to all orders in tunneling. Its memory kernel, given as a diagrammatic perturbation series in Ref. 9, has been written down in superoperator form.

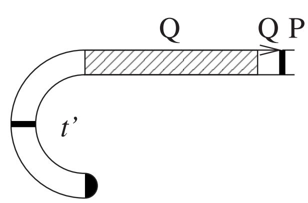

FIG. 4. General form of all terms involving tunneling in the TCL ME [Eq. (66)]. Here, the filled semicircle denotes the projected density operator $\mathcal{P}\rho$ at time t'.

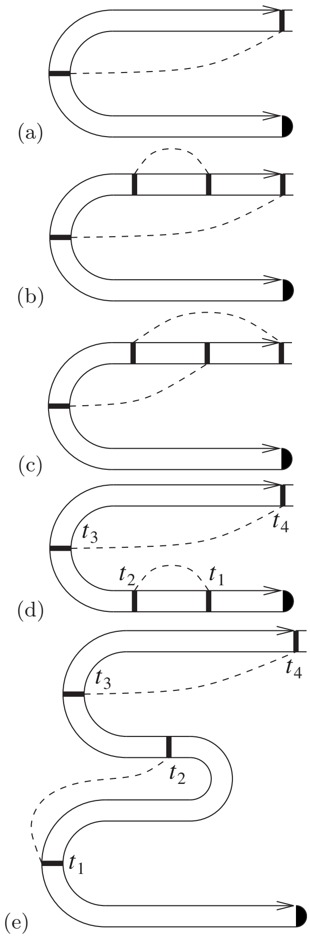

FIG. 5. Diagrams for all terms in the TCL ME up to fourth order in the tunneling amplitudes. The dashed lines denote the pairing of lead-electron operators a, $a^{\dagger}$ with the same quantum numbers.

The T-matrix approach only gives rates for the *diagonal* components of the reduced density operator. The large-reservoir assumption of a product state enters in the guise of statistical independence of dot and lead states. The T-matrix approach gives the same expression for these rates as WBR theory with the Markov assumption only to leading (second) order in H_{hyb}, corresponding to Fermi's golden rule. This is because in the T-matrix approach, one calculates a subtly different quantity than in the WBR approach.

The TCL ME[12] has been adapted to the transport problem. It is an exact equation for the dynamic reduced density operator that is local in time but does not require a Markov assumption. It thus works to arbitrary orders in perturbation theory. The superoperator $\Sigma(t-t_0)$ playing a pivotal role in the TCL ME has been given in an explicit form. The assumption of a product state with leads in equilibrium at time t_0 is not required in this approach but simplifies the results.

A number of open questions regarding the TCL formalism applied to transport have been uncovered. First, under what conditions does the inverse of the superoperator $1-\Sigma(t-t_0)$ exist, which appears in the ME? Second, if we assume the system to be in a product state with leads in equilibrium at time t_0, can the limit $t_0 \to -\infty$ be taken? Third, is positivity of probabilities satisfied in perturbative approximations to the

TCL ME? We leave these questions for future work.

A diagrammatic scheme for generating arbitrary orders in H_{hyb} in the TCL ME has been developed. The relation to the diagrams of König *et al.*[9] and thus to the WBR ME is easily seen. Our diagrams have an interesting additional structure since the projected density operator is propagated backward in time to make the equation local. The diagrammatic expansion to fourth order is explicitly shown.

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APPENDIX A: WANGSNESS-BLOCH-REDFIELD MASTER EQUATION TO SECOND ORDER

Equation (13) is the WBR ME to second order in H_{hyb}. Here, we give two more explicit forms. First, we derive a fully general expression useful for later comparisons. We introduce dot states $|m)$ and lead states $|i\rangle\rangle$ with eigenenergies E_m and ϵ_i, respectively, open the commutators, and perform the time integral,

$$\begin{aligned}\dot{\rho}^{\text{dot}}_{mn} = &-i(E_m-E_n)\rho^{\text{dot}}_{mn} - \pi\sum_{ij}\sum_{pq}\{W_i\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle\langle\langle j|(p|H_{\text{hyb}}|q)|i\rangle\rangle\rho^{\text{dot}}_{qn}\delta(E_p+\epsilon_j-E_q-\epsilon_i)\\
&- W_j\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle\rho^{\text{dot}}_{pq}\langle\langle j|(q|H_{\text{hyb}}|n)|i\rangle\rangle\delta(E_q+\epsilon_j-E_n-\epsilon_i)\\
&- W_j\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle\rho^{\text{dot}}_{pq}\langle\langle j|(q|H_{\text{hyb}}|n)|i\rangle\rangle\delta(E_m+\epsilon_i-E_p-\epsilon_j)\\
&+ W_i\rho^{\text{dot}}_{mp}\langle\langle i|(p|H_{\text{hyb}}|q)|j\rangle\rangle\langle\langle j|(q|H_{\text{hyb}}|n)|i\rangle\rangle\delta(E_m+\epsilon_i-E_q-\epsilon_j)\}\\
&+ i\sum_{ij}\sum_{pq}\left\{W_i\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle\langle\langle j|(p|H_{\text{hyb}}|q)|i\rangle\rangle\rho^{\text{dot}}_{qn}P\frac{1}{E_p+\epsilon_j-E_q-\epsilon_i}\right.\\
&- W_j\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle\rho^{\text{dot}}_{pq}\langle\langle j|(q|H_{\text{hyb}}|n)|i\rangle\rangle P\frac{1}{E_q+\epsilon_j-E_n-\epsilon_i}\\
&- W_j\langle\langle i|(m|H_{\text{hyb}}|p)|j\rangle\rangle\rho^{\text{dot}}_{pq}\langle\langle j|(q|H_{\text{hyb}}|n)|i\rangle\rangle P\frac{1}{E_m+\epsilon_i-E_p-\epsilon_j}\\
&\left.+ W_i\rho^{\text{dot}}_{mp}\langle\langle i|(p|H_{\text{hyb}}|q)|j\rangle\rangle\langle\langle j|(q|H_{\text{hyb}}|n)|i\rangle\rangle P\frac{1}{E_m+\epsilon_i-E_q-\epsilon_j}\right\}. \end{aligned} \tag{A1}$$

Here, $W_i\equiv\langle\langle i|\rho^0_{\text{leads}}|i\rangle\rangle$ is the probability to find the leads in state $|i\rangle\rangle$ and P denotes the principal value.

For the second expression, we make use of the specific form [Eq. (1)] of the hybridization Hamiltonian. If we insert H_{hyb} into Eq. (13), only a single sum over $\alpha,\mathbf{k},\sigma$ survives, due to the conservation of crystal momentum, spin, and lead indices. We introduce dot states $|m)$ with eigenenergies E_m and open the commutators. We only give the first of eight terms, the others are analogous,

$$\begin{aligned}\dot{\rho}^{\text{dot}}_{mn} = &-i(E_m-E_n)\rho^{\text{dot}}_{mn}\\
&-\int_0^\infty d\tau\, \text{tr}_{\text{leads}}\sum_{pq}\frac{1}{N}\sum_{\alpha\mathbf{k}\sigma}\sum_{\nu\nu'}[t_{\alpha\mathbf{k}\sigma\nu}a^\dagger_{\alpha\mathbf{k}\sigma}(m|c_{\nu\sigma}|p)\\
&\times e^{-iE_p\tau}e^{-iH_{\text{leads}}\tau}t^*_{\alpha\mathbf{k}\sigma\nu'}(p|c^\dagger_{\nu'\sigma}|q)a_{\alpha\mathbf{k}\sigma}e^{iE_q\tau}e^{iH_{\text{leads}}\tau}\\
&\times\rho^{\text{dot}}_{qn}\otimes\rho^0_{\text{leads}}+\cdots].\end{aligned} \tag{A2}$$

The second-order term contains the expression,

$$\text{tr}_{\text{leads}}\, a^\dagger_{\alpha\mathbf{k}\sigma}e^{-iH_{\text{leads}}\tau}a_{\alpha\mathbf{k}\sigma}e^{iH_{\text{leads}}\tau}\rho^0_{\text{leads}} = -iG^<_{\alpha\mathbf{k}\sigma}(-\tau). \tag{A3}$$

All terms contain equilibrium lesser or greater Green functions, $G^<$ or $G^>$, respectively, which describe the lead correlations discussed in Sec. II. Their Fourier transforms can be expressed in terms of the Fermi function n_F and the spectral function $A_{\alpha\mathbf{k}\sigma}(\omega)$ of the leads as[61]

$$G^<_{\alpha\mathbf{k}\sigma}(\omega) = in_F(\omega-\mu_\alpha)A_{\alpha\mathbf{k}\sigma}(\omega-\mu_\alpha), \tag{A4}$$

$$G^>_{\alpha\mathbf{k}\sigma}(\omega) = -i[1-n_F(\omega-\mu_\alpha)]A_{\alpha\mathbf{k}\sigma}(\omega-\mu_\alpha), \tag{A5}$$

where μ_α is the chemical potential of lead α. By performing the integral over τ, we obtain

$$\dot{\rho}^{\text{dot}}_{mn} = -i(E_m - E_n)\rho^{\text{dot}}_{mn} + i\sum_{pq}\frac{1}{N}\sum_{\alpha\mathbf{k}\sigma}\sum_{\nu\nu'}\int\frac{d\omega}{2\pi}A_{\alpha\mathbf{k}\sigma}(\omega-\mu_\alpha) \times\left[\frac{n_F(\omega-\mu_\alpha)}{-\omega+E_p-E_q-i0^+}t_{\alpha\mathbf{k}\sigma\nu}t^*_{\alpha\mathbf{k}\sigma\nu'}(m|c_{\nu\sigma}|p) \times(p|c^\dagger_{\nu'\sigma}|q)\rho^{\text{dot}}_{qn} + \cdots\right]. \tag{A6}$$

If we assume that the tunneling amplitudes $t_{\alpha\mathbf{k}\sigma\nu} \equiv t_{\alpha\sigma\nu}$ do not depend on the wave vector $\mathbf{k}$, the sum over $\mathbf{k}$ can be performed, noting that the spin-resolved density of states is given by $D_{\alpha\sigma}(\omega) = (2\pi V)^{-1}\Sigma_{\mathbf{k}}A_{\alpha\mathbf{k}\sigma}(\omega)$. Here, V is the system volume. This leads to

$$\dot{\rho}^{\text{dot}}_{mn} = -i(E_m - E_n)\rho^{\text{dot}}_{mn} - \pi\frac{V}{N}\sum_{pq}\sum_{\alpha\sigma\nu\nu'}[D_{\alpha\sigma}(E_p-E_q-\mu_\alpha) \times n_F(E_p-E_q-\mu_\alpha)t_{\alpha\sigma\nu}t^*_{\alpha\sigma\nu'} \times(m|c_{\nu\sigma}|p)(p|c^\dagger_{\nu'\sigma}|q)\rho^{\text{dot}}_{qn} + \cdots] - i\frac{V}{N}\sum_{pq}\sum_{\alpha\sigma\nu\nu'}P\int d\omega\, D_{\alpha\sigma}(\omega-\mu_\alpha) \times\left[\frac{n_F(\omega-\mu_\alpha)}{\omega-E_p+E_q}t_{\alpha\sigma\nu}t^*_{\alpha\sigma\nu'}(m|c_{\nu\sigma}|p)(p|c^\dagger_{\nu'\sigma}|q)\rho^{\text{dot}}_{qn} + \cdots\right], \tag{A7}$$

where P indicates a principal-value integral.

We find that if the large-reservoir approximation is valid and if the tunneling amplitudes $t_{\alpha\mathbf{k}\sigma\nu}$ do not depend on $\mathbf{k}$, only the lead density of states enters.[62] Strong correlations in the leads, resulting in broad features in the spectral function, do no affect the tunneling. Under these conditions, all information on $\mathbf{k}$ is lost so that it is only important whether states at a given energy (and α, σ) exist. As discussed in Sec. II B, broad features in the spectral function do not invalidate the Markov assumption since they correspond to rapid processes.

APPENDIX B: FIRST-ORDER TERMS

We briefly discuss first-order terms in the ME. Equation (65) shows that the only first-order term comes from the initial condition for $\mathcal{Q}\rho(t_0)$. The origin of the vanishing of first-order terms is that they contain equilibrium averages of single lead-fermion operators [cf. Eqs. (7) and (25)].

The absence of first-order terms might be surprising. Let us consider ρ_{dot} with component $\rho^{\text{dot}}_{mn} \neq 0$, corresponding to the superposition of two states with electron number differing by 1. If $(n|H_{\text{hyb}}|m) \neq 0$, a single power of H_{hyb} is sufficient to lead to a change in ρ^{dot}_{mm} and ρ^{dot}_{nn}. This is analogous to the interaction of a superposition having an oscillating dipole moment with the light field. Superselection rules[25–27] suggest that superpositions of states with different charges dephase so rapidly that they are unobservable. However, this does not help us at a fundamental level since we would obtain the same equation if the tunneling fermions were neutral.

A first-order term is present if we expand the equation for the full density operator, $\rho(t) = e^{-i\mathcal{L}(t-t_0)}\rho(t_0)$, in powers of $\mathcal{L}_{\text{hyb}}$. Since first-order processes thus exist while $\mathcal{P}\rho$ does not describe them, the required information must be contained in $\mathcal{Q}\rho(t)$. If they happen to be relevant, we must appropriately choose $\mathcal{Q}\rho(t_0) \neq 0$.

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