# Time-convolutionless master equation for quantum dots: Perturbative expansion to arbitrary order

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The master equation describing the nonequilibrium dynamics of a quantum dot coupled to metallic leads is considered. Employing a superoperator approach, we derive an exact time-convolutionless master equation for the probabilities of dot states, i.e., a time-convolutionless Pauli master equation. The generator of this master equation is derived order by order in the hybridization between dot and leads. Although the generator turns out to be closely related to the $T$-matrix expressions for the transition rates, which are plagued by divergences, in the time-convolutionless generator all divergences cancel order by order. The time-convolutionless and $T$-matrix master equations are contrasted to the Nakajima-Zwanzig version. The absence of divergences in the Nakajima-Zwanzig master equation due to the nonexistence of secular reducible contributions becomes rather transparent in our approach, which explicitly projects out these contributions. We also show that the time-convolutionless generator contains the generator of the Nakajima-Zwanzig master equation in the Markov approximation plus corrections, which we make explicit. Furthermore, it is shown that the stationary solutions of the time-convolutionless and the Nakajima-Zwanzig master equations are identical. However, this identity neither extends to perturbative expansions truncated at finite order nor to dynamical solutions. We discuss the conditions under which the Nakajima-Zwanzig-Markov master equation nevertheless yields good results.

## I. INTRODUCTION

Electronic transport through small quantum systems, such as quantum dots or single molecules, has been intensively studied in recent years.[1–3] Apart from the envisioned applications, such devices address fundamental questions of nonequilibrium quantum statistics. Quantum dots coupled to electronic leads under a bias voltage generically relax toward a stationary state. Unless the number of relevant degrees of freedom of the quantum dot is very small, the relaxational dynamics is complex, including broadly distributed time scales and damped oscillatory behavior. The stationary state that is eventually approached typically depends on the physical parameters in a complicated way and can, in particular, be very different from the equilibrium state of the isolated dot.

The descriptions of transport through quantum dots or molecules far from equilibrium have so far followed three broad approaches. In the first, the focus is on an electron tunneling through the device. Its dynamics is described by a nonequilibrium Green's function (NEGF). The current through the dot can be expressed in terms of the local NEGF on the dot, which contains self-energies due to the tunneling or hybridization between dot and leads.[4] This hybridization, which is described by a bilinear component $H_{hyb}$ of the Hamiltonian, can, in principle, be incorporated exactly. On the other hand, interactions with other electrons, with vibrational modes, or with local spins, which all are particularly important for small dots or single molecules, require approximations.[5–15]

The second approach revolves around the nonequilibrium Keldysh generating function.[16,17] It is most naturally expressed as a functional integral and, with suitable source terms, contains the full information on the system. This formulation is particularly suitable for numerical calculations. When errors due to Trotter discretization and a cutoff time for the memory kernel are properly controlled, the results are numerically exact.

The third approach focuses on the dynamics of the small system. An equation of motion for the reduced density operator

in the Fock subspace of the small system is derived by integrating out the lead degrees of freedom. The result is a *master equation* (ME).[9,18–26] If the small system is sufficiently simple, the interactions within this system can be treated exactly. However, integrating out the lead states naturally leads to a perturbative series in the hybridization $H_{hyb}$.

Master equations can be either nonlocal or local in time. A nonlocal ME, for example, of Nakajima-Zwanzig (NZ) type,[27,28] contains a memory kernel, which relates the rate of change of the reduced density operator at a time $t$ to the reduced density operator at all previous times $t' < t$. On the other hand, a local ["time-convolutionless," (TCL)] ME (Refs. 29–31) expresses the rate of change of the reduced density operator at time $t$ in terms of the reduced density operator at time $t$ only.

If one has a practical method for generating all terms in the perturbation series for the transition rates or memory kernel in orders of $H_{hyb}$, one can hope to resum the series or at least a subseries. This idea has been very fruitful for many-particle physics, from the Dyson equation to the theory of the Kondo effect. For the nonlocal ME of NZ type, Schoeller, Schön, and König have developed a real-time diagrammatic scheme that generates all terms.[18–20,25] For a large class of systems, including a quite general coupling Hamiltonian $H_{hyb}$, Schoeller[25] has presented a compact superoperator formulation in Laplace space. This formulation is particularly suitable for a nonequilibrium renormalization-group approach, which, in principle, includes all orders in $H_{hyb}$.[25]

Apart from the NZ ME, the $T$-matrix approach from time-dependent perturbation theory has been used to calculate the transition rates in the ME.[22,32–37] It has the advantage of being relatively straightforward but is known to produce divergences beyond second order in $H_{hyb}$, the nature of which has recently been clarified.[23,26,38] The superoperator derivation of the $T$-matrix ME will make their origin transparent.

The TCL ME has the obvious advantage of being an *exact* ME describing the full dynamics that is nevertheless local in time. However, so far a method for generating all terms in the

perturbation series for the TCL ME has been lacking, which has limited its usefulness.

The main purpose of this paper is to derive an iterative scheme for constructing all orders in the perturbative expansion of the generator of the TCL ME. The results are valid for the exact ME describing the full dynamics. Only at the end will we discuss the implications for the stationary state. Furthermore, a surprising connection between the TCL generator and the $T$-matrix transition rates is uncovered. This connection introduces the divergences of the $T$-matrix rates into the expansion terms of the TCL generator. We will show that these divergences cancel order by order. In this paper, we concentrate on master equations for the diagonal components of the reduced density matrix, i.e., for the probabilities. We will call these the *Pauli* master equations or rate equations.

In the remainder of this paper, the theoretical development is presented in Sec. II. After a brief review of the super-operator formalism and the TCL ME, we derive the Pauli version thereof, i.e., the TCL rate equations. Then, we derive the $T$-matrix formula for the transition rates within the same formalism and exhibit the relation between the rates derived within the two approaches. After that, we organize the perturbative expansion of the rates derived within both approaches in a way that makes all divergent terms explicit, and then show that all the divergences cancel in the TCL rates. Finally, additional insight is gained by a discussion of the Nakajima-Zwanzig ME and of the stationary state. The results are summarized in Sec. III, where we also draw a number of conclusions. Several proofs are relegated to appendices.

## II. THEORY

### A. Superoperators and the TCL master equation

Since we will make extensive use of the superoperator formalism, we briefly review the superoperator derivation of the TCL ME.[23,29–31,39] To make contact with the $T$-matrix approach and to allow for the analysis of divergences, we consider a time-dependent hybridization between dot and leads. The Hamiltonian reads as

$$H(t) = H_0 + H_{\text{hyb}}\, e^{\eta t}, \tag{1}$$

where $\eta$ is small and positive. $H_0 = H_{\text{dot}} + H_{\text{leads}}$ describes the decoupled dot and leads. For convenience, we assume that the eigenstates $|m\rangle$ of $H_{\text{dot}}$ are nondegenerate.[40] As usual, the leads are represented by noninteracting Fermi seas.

The density operator $\rho$ of the full system satisfies the von Neumann equation

$$\dot{\rho} = -i[H(t), \rho] =: -i\mathcal{L}(t)\,\rho, \tag{2}$$

where we have defined the Liouvillian $\mathcal{L}$. The resulting unitary time evolution of $\rho$ can be expressed as

$$\rho(t) = T_{\leftarrow} \exp\left(-i\int_{t_0}^{t} dt'\,\mathcal{L}(t')\right)\rho(t_0), \tag{3}$$

where $T_{\leftarrow}$ is the time-ordering directive.

Projection superoperators $\mathcal{P}$ and $\mathcal{Q}$ are defined by

$$\mathcal{P}\rho(t) := [\text{tr}_{\text{leads}}\,\rho(t)] \otimes \rho_{\text{leads}}^0 \tag{4}$$

and $\mathcal{Q} := 1 - \mathcal{P}$. Here, $\rho_{\text{leads}}^0$ describes the leads in generally separate equilibrium—each lead is in equilibrium at its own chemical potential and possibly temperature. We write $\mathcal{L}(t) = \mathcal{L}_0 + \mathcal{L}_{\text{hyb}}e^{\eta t}$ with obvious definitions and note the identities[23]

$$\mathcal{P}\mathcal{L}_0 = \mathcal{L}_0\mathcal{P}, \tag{5}$$

$$\mathcal{P}\mathcal{L}_{\text{hyb}}\mathcal{P} = 0. \tag{6}$$

We assume that the system was in a product state at time $t_0$ with the leads in equilibrium, i.e., $\mathcal{Q}\rho(t_0) = 0$. Dropping this assumption would lead to additional terms describing the propagation of $\mathcal{Q}\rho(t_0)$ from time $t_0$ to $t$. Since we are interested in the case $t_0 \to -\infty$, we do not expect the initial state to be relevant. We then obtain

$$\mathcal{P}\rho(t) = \mathcal{P}\,T_{\leftarrow} \exp\left(-i\int_{t_0}^{t} dt'\,[\mathcal{L}_0 + \mathcal{L}_{\text{hyb}}\,e^{\eta t'}]\right)\mathcal{P}\rho(t_0). \tag{7}$$

The time-ordered exponential is expanded as

$$
\begin{aligned}
\mathcal{P}\rho(t) = \mathcal{P}\sum_{\nu=0}^{\infty}(-i)^{\nu}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{\nu-1}} dt_\nu \\
\times\, e^{-i\mathcal{L}_0(t-t_1)}\mathcal{L}_{\text{hyb}}e^{\eta t_1}e^{-i\mathcal{L}_0(t_1-t_2)}\mathcal{L}_{\text{hyb}}e^{\eta t_2}\cdots \\
\times\, \mathcal{L}_{\text{hyb}}e^{\eta t_\nu}e^{-i\mathcal{L}_0(t_\nu-t_0)}\mathcal{P}\rho(t_0).
\end{aligned}
\tag{8}
$$

Equations (7) and (8) simply represent the time evolution of the density operator, projected with $\mathcal{P}$ at time $t$.

The TCL ME is derived by splitting the von Neumann equation (2) into two parts:

$$d\mathcal{P}\rho(t)/dt = -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) - i\mathcal{P}\mathcal{L}(t)\mathcal{Q}\rho(t), \tag{9}$$

$$d\mathcal{Q}\rho(t)/dt = -i\mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho(t) - i\mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho(t). \tag{10}$$

The second equation is solved by

$$
\begin{aligned}
\mathcal{Q}\rho(t) = T_{\leftarrow}\exp\left(-i\mathcal{Q}\int_{t_0}^{t} dt'\mathcal{L}(t')\right)\mathcal{Q}\rho(t_0) - i\int_{t_0}^{t} dt'\,T_{\leftarrow} \\
\times \exp\left(-i\mathcal{Q}\int_{t'}^{t} dt''\mathcal{L}(t'')\right)\mathcal{Q}\mathcal{L}(t')\mathcal{P}\rho(t'),
\end{aligned}
\tag{11}
$$

where the first term vanishes under our assumption of $\mathcal{Q}\rho(t_0) = 0$. The main idea of the TCL approach[29,30] is to express $\rho(t')$ by propagating the full density operator backward in time:

$$\rho(t') = T_{\rightarrow}\exp\left(i\int_{t'}^{t} dt''\,\mathcal{L}(t'')\right)\rho(t), \tag{12}$$

where $T_{\rightarrow}$ is the anti-time-ordering directive. Insertion into Eq. (11) gives

$$
\begin{aligned}
\mathcal{Q}\rho(t) = -i\int_{t_0}^{t} dt'\,T_{\leftarrow}\exp\left(-i\mathcal{Q}\int_{t'}^{t} dt''\mathcal{L}(t'')\right)\mathcal{Q}\mathcal{L}(t')\mathcal{P} \\
\times\, T_{\rightarrow}\exp\left(i\int_{t'}^{t} dt''\mathcal{L}(t'')\right)[\mathcal{P}\rho(t) + \mathcal{Q}\rho(t)]. \tag{13}
\end{aligned}
$$

Solving for $\mathcal{Q}\rho(t)$ yields

$$\mathcal{Q}\rho(t) = [1 - \Sigma(t, t_0)]^{-1}\Sigma(t, t_0)\,\mathcal{P}\rho(t) \tag{14}$$

with

$$\Sigma(t,t_0) := -i \int_{t_0}^{t} dt' T_{\leftarrow} \exp\left(-i\mathcal{Q} \int_{t'}^{t} dt'' \mathcal{L}(t'')\right)$$

$$\times \mathcal{Q}\mathcal{L}(t')\mathcal{P}T_{\rightarrow} \exp\left(i \int_{t'}^{t} dt'' \mathcal{L}(t'')\right). \quad (15)$$

Inserting $\mathcal{Q}\rho(t)$ into Eq. (9) results in an equation of motion for $\mathcal{P}\rho$ alone,

$$d\mathcal{P}\rho(t)/dt = -i\mathcal{P}\mathcal{L}(t)\left[1 - \Sigma(t,t_0)\right]^{-1} \mathcal{P}\rho(t). \quad (16)$$

This is the TCL ME for the case $\mathcal{Q}\rho(t_0) = 0$. Using Eq. (5) and noting that $\Sigma(t,t_0)$ contains a projection $\mathcal{Q}$ to the left, we can rewrite this more specifically as

$$d\mathcal{P}\rho(t)/dt$$
$$= -i\mathcal{P}\mathcal{L}_0\mathcal{P}\rho(t) - i\mathcal{P}\mathcal{L}_{\mathrm{hyb}}e^{\eta t}\left[1 - \Sigma(t,t_0)\right]^{-1} \mathcal{P}\rho(t) \quad (17)$$

with

$$\Sigma(t,t_0)$$
$$= -i\mathcal{Q} \int_{t_0}^{t} dt' T_{\leftarrow} \exp\left(-i \int_{t'}^{t} dt''[\mathcal{L}_0 + \mathcal{Q}\mathcal{L}_{\mathrm{hyb}}e^{\eta t''}\mathcal{Q}]\right)$$
$$\times \mathcal{L}_{\mathrm{hyb}}e^{\eta t'}\mathcal{P}T_{\rightarrow} \exp\left(i \int_{t'}^{t} dt''[\mathcal{L}_0 + \mathcal{L}_{\mathrm{hyb}}e^{\eta t''}]\right). \quad (18)$$

The first term in Eq. (17) describes the unperturbed time evolution, while the second stems from the hybridization.

### B. The TCL Pauli master equation

We here derive an exact TCL ME for the diagonal components of the reduced density operator. Since we are assuming nondegenerate dot states, this is equivalent to an equation for the secular part of the reduced density operator.[26] A ME for the diagonal components of the density operator, albeit nonlocal in time, has been derived by Zwanzig[28] and rediscovered, in the context of transport, by Leijnse and Wegewijs.[24]

We introduce new projection operators by

$$\tilde{\mathcal{P}}\rho(t) := \left[\sum_{m} |m\rangle\langle m| \mathrm{tr}_{\mathrm{leads}} \rho(t)|m\rangle\langle m|\right] \otimes \rho_{\mathrm{leads}}^{0}, \quad (19)$$

where the $|m\rangle$ are the unperturbed dot eigenstates, and $\tilde{\mathcal{Q}} := 1 - \tilde{\mathcal{P}}$. $\tilde{\mathcal{P}}$ evidently projects the density operator onto a product form with *diagonal* reduced density operator.[28] We will call $\tilde{\mathcal{P}}\rho$ the *diagonally projected* density operator. It is easy to show that

$$\tilde{\mathcal{P}}\mathcal{L}_0 = \mathcal{L}_0\tilde{\mathcal{P}} = 0, \quad (20)$$

which goes beyond Eq. (5) for $\mathcal{P}$. Since $H_{\mathrm{hyb}}$ changes the electron number in the leads by $\pm 1$, we have

$$\tilde{\mathcal{P}}\mathcal{L}_{\mathrm{hyb}}\tilde{\mathcal{P}} = 0. \quad (21)$$

We now assume that the system was in a product state at time $t_0$ with the leads in generally separate equilibrium and *diagonal* reduced density operator $\tilde{\mathcal{Q}}\rho(t_0) = 0$.

Repeating the derivation in Sec. II A with the new projections $\tilde{\mathcal{P}}$, $\tilde{\mathcal{Q}}$, we obtain

$$d\tilde{\mathcal{P}}\rho(t)/dt = -i\tilde{\mathcal{P}}\mathcal{L}_{\mathrm{hyb}}e^{\eta t}\left[1 - \tilde{\Sigma}(t,t_0)\right]^{-1} \tilde{\mathcal{P}}\rho(t) \quad (22)$$

with

$$\tilde{\Sigma}(t,t_0)$$
$$:= -i\tilde{\mathcal{Q}} \int_{t_0}^{t} dt' T_{\leftarrow} \exp\left(-i \int_{t'}^{t} dt''[\mathcal{L}_0 + \tilde{\mathcal{Q}}\mathcal{L}_{\mathrm{hyb}}e^{\eta t''}\tilde{\mathcal{Q}}]\right)$$
$$\times \mathcal{L}_{\mathrm{hyb}}e^{\eta t'}\tilde{\mathcal{P}}T_{\rightarrow} \exp\left(i \int_{t'}^{t} dt''[\mathcal{L}_0 + \mathcal{L}_{\mathrm{hyb}}e^{\eta t''}]\right). \quad (23)$$

Due to Eq. (20), the unperturbed time evolution has dropped out of Eq. (22). We can now write

$$d\tilde{\mathcal{P}}\rho(t)/dt = \tilde{\mathcal{S}}(t,t_0) \tilde{\mathcal{P}}\rho(t) \quad (24)$$

with the generator

$$\tilde{\mathcal{S}}(t,t_0) = -i\tilde{\mathcal{P}}\mathcal{L}_{\mathrm{hyb}}e^{\eta t}\left[1 - \tilde{\Sigma}(t,t_0)\right]^{-1}\tilde{\mathcal{P}}. \quad (25)$$

Equation (24) is an exact ME for the diagonally projected density operator under the condition $\tilde{\mathcal{Q}}\rho(t_0) = 0$. It is evidently local in time. Since it only involves the diagonal components, we call it the TCL *Pauli* ME. A Pauli ME in the reduced Fock space of the dot is, of course, obtained by taking the trace over the lead degrees of freedom:

$$d\rho_{\mathrm{dot}}/dt = \mathrm{tr}_{\mathrm{leads}}\tilde{\mathcal{S}}(t,t_0)\rho_{\mathrm{dot}}(t) \otimes \rho_{\mathrm{leads}}^{0} =: \tilde{\mathcal{S}}_{\mathrm{dot}}\rho_{\mathrm{dot}}(t). \quad (26)$$

The reduced generator $\tilde{\mathcal{S}}_{\mathrm{dot}}$ written in the dot eigenbasis is the transition-rate matrix. Ensembles of such matrices are studied in Ref. 41 within random matrix theory.

We have now eliminated the off-diagonal components of the reduced density matrix $\rho_{\mathrm{dot}}$ from the equations of motion, similar in spirit to Zwanzig's work[28] and also to Refs. 24 and 26. We are therefore able to determine the dynamics of the probabilities of dot states exclusively from the knowledge of these probabilities at a given time. This does not mean that we assume the off-diagonal components to be small, which is not generally true.

The knowledge of the probabilities is sufficient for the calculations of dot observables that commute with the dot Hamiltonian $H_{\mathrm{dot}}$. To see this, we denote the operator for such an observable by $A$ in the Fock space of the dot. Then, the operator in the Fock space of the whole system is $A \otimes 1_{\mathrm{leads}}$ in an obvious notation. The average of the observable is

$$\langle A\rangle(t) = \mathrm{Tr}\,\rho(t)A \otimes 1_{\mathrm{leads}} = \mathrm{tr}_{\mathrm{dot}}\rho_{\mathrm{dot}}(t)\,A$$
$$= \sum_{mn} \rho_{mn}^{\mathrm{dot}}(t)\,A_{nm}, \quad (27)$$

writing matrix elements of dot states $|m\rangle$, $|n\rangle$ as $\rho_{mn}^{\mathrm{dot}} = \langle m|\rho_{\mathrm{dot}}|n\rangle$, etc. If $A$ commutes with the dot Hamiltonian, we can choose $A$ to be diagonal in the dot eigenbasis $\{|m\rangle\}$ so that

$$\langle A\rangle(t) = \sum_{m} \rho_{mm}^{\mathrm{dot}}(t)\,A_{mm} = \mathrm{Tr}\,\tilde{\mathcal{P}}\rho(t)\,A. \quad (28)$$

Thus, the knowledge of $\tilde{\mathcal{P}}\rho(t)$ is sufficient to calculate the average. Examples are the charge on the dot, the vibrational

energy of a molecule, or the component of its spin parallel to an applied magnetic field, assuming vanishing transverse anisotropy. On the other hand, the current does not commute with $H_{dot}$ and thus does depend on the off-diagonal components.[42] However, it is possible to reconstruct the full density operator from $\tilde{\mathcal{P}}\rho(t)$,

$$\rho(t) = \tilde{\mathcal{P}}\rho(t) + \tilde{\mathcal{Q}}\rho(t) = [1 - \tilde{\Sigma}(t, t_0)]^{-1} \tilde{\mathcal{P}}\rho(t) \quad (29)$$

[compare Eq. (14)].

### C. Superoperator derivation of the *T*-matrix formula

In the following, the *T*-matrix formula for the transition rates is rederived within the superoperator formalism to allow a direct comparison with the exact TCL ME. Moreover, we show that this derivation relies on a single straightforward, but generally unjustified, approximation.

To start with, note that the exponential time dependence of the perturbation in Eq. (1) is exactly the case considered by Bruus and Flensberg[22] in their derivation of the *T*-matrix formula. The analog of Eqs. (7) and (8) for diagonal projection reads as

$$\tilde{\mathcal{P}}\rho(t) = \tilde{\mathcal{P}}T_{\leftarrow} \exp\left(-i\int_{t_0}^{t} dt'[\mathcal{L}_0 + \mathcal{L}_{hyb}\,e^{\eta t'}]\right)\tilde{\mathcal{P}}\rho(t_0)$$

$$= \tilde{\mathcal{P}}\sum_{\nu=0}^{\infty}(-i)^{\nu}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{\nu-1}}dt_\nu \mathcal{L}_{hyb}e^{\eta t_1}$$

$$\times e^{-i\mathcal{L}_0(t_1-t_2)}\mathcal{L}_{hyb}e^{\eta t_2}\cdots\mathcal{L}_{hyb}e^{\eta t_\nu}\tilde{\mathcal{P}}\rho(t_0), \quad (30)$$

where we have used Eq. (20). This is the time evolution of the full density operator under the condition $\tilde{\mathcal{Q}}\rho(t_0) = 0$, projected with $\tilde{\mathcal{P}}$ at time $t$.

Taking the time derivative of Eq. (30), we obtain

$$d\tilde{\mathcal{P}}\rho(t)/dt = \tilde{\mathcal{R}}(t, t_0)\tilde{\mathcal{P}}\rho(t_0) \quad (31)$$

with

$$\tilde{\mathcal{R}}(t, t_0) := -i\tilde{\mathcal{P}}\mathcal{L}_{hyb}e^{\eta t}\sum_{\mu=0}^{\infty}(-i)^{\mu}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots$$

$$\times \int_{t_0}^{t_{\mu-1}}dt_\mu e^{-i\mathcal{L}_0(t-t_1)}\mathcal{L}_{hyb}e^{\eta t_1}e^{-i\mathcal{L}_0(t_1-t_2)}$$

$$\times\mathcal{L}_{hyb}e^{\eta t_2}\cdots\mathcal{L}_{hyb}e^{\eta t_\mu}\tilde{\mathcal{P}}, \quad (32)$$

where the new summation index is $\mu = \nu - 1$ and the integration variables are now counted by $\mu$. The terms in this series are of order $\mu + 1$ in $\mathcal{L}_{hyb}$. In the limit $t_0 \to -\infty$, it is straightforward to evaluate the time integrals at nonzero $\eta$,

$$\tilde{\mathcal{R}}(t, -\infty) = -i\sum_{\nu=1}^{\infty}e^{\nu\eta t}\tilde{\mathcal{P}}\mathcal{L}_{hyb}\left[-\mathcal{L}_0 + (\nu-1)i\eta\right]^{-1}\mathcal{L}_{hyb}$$

$$\times\left[-\mathcal{L}_0 + (\nu-2)i\eta\right]^{-1}\mathcal{L}_{hyb}\cdots$$

$$\times\mathcal{L}_{hyb}\left(-\mathcal{L}_0 + i\eta\right)^{-1}\mathcal{L}_{hyb}\tilde{\mathcal{P}}. \quad (33)$$

The terms are of order $\nu$ in $\mathcal{L}_{hyb}$. Due to the trace over lead states coming from the leftmost $\tilde{\mathcal{P}}$ and the equilibrium lead density operator $\rho_{leads}^0$ contained in the rightmost $\tilde{\mathcal{P}}$, this expression contains *equilibrium* averages of products of lead electron creation operators $a_{\alpha\mathbf{k}\sigma}^\dagger$ and annihilation operators $a_{\alpha\mathbf{k}\sigma}$. To obtain a nonzero contribution, these operators must be paired. Since the hybridization Hamiltonian $H_{hyb}$ is linear in these operators, only terms of even order $\nu$ contribute to $\tilde{\mathcal{R}}(t, -\infty)$.

We will now show that the central approximation of the *T*-matrix approach consists of taking $\tilde{\mathcal{R}}(t, t_0)$ to be the generator of a Pauli ME that is local in time,

$$d\tilde{\mathcal{P}}\rho(t)/dt \approx \tilde{\mathcal{R}}(t, t_0)\tilde{\mathcal{P}}\rho(t). \quad (34)$$

To that end, we show that this ME indeed leads to the usual *T*-matrix formula.[22]

Expressing the Liouvillians in Eq. (32) in terms of the corresponding Hamiltonians, we obtain

$$\tilde{\mathcal{R}}(t, t_0)\bullet = -i\tilde{\mathcal{P}}\left\{\sum_{\mu=0}^{\infty}(-i)^{\mu}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{\mu-1}}dt_\mu[H_{hyb}e^{\eta t}, e^{-iH_0(t-t_1)}[H_{hyb}e^{\eta t_1}, e^{-iH_0(t_1-t_2)}\right.$$

$$\left.\times[H_{hyb}e^{\eta t_2}, \ldots[H_{hyb}e^{\eta t_\mu}, e^{-iH_0(t_\mu-t_0)}\tilde{\mathcal{P}}\bullet e^{iH_0(t_\mu-t_0)}]\cdots]e^{iH_0(t_1-t_2)}]e^{iH_0(t-t_1)}]\right\}. \quad (35)$$

We now consider unequal initial and final eigenstates, $|i\rangle$ and $|f\rangle$, respectively, of $H_0$. Pure initial and final states are described by the density operators $|i\rangle\langle i|$ and $|f\rangle\langle f|$, respectively. Expanding the nested commutators, except for the outermost one, we obtain, for the matrix element of $\tilde{\mathcal{R}}(t, t_0)$ between these pure states,

$$\Gamma_{fi} := \langle f|\{\tilde{\mathcal{R}}(t, t_0)|i\rangle\langle i|\}|f\rangle = -i\langle f|\sum_{\mu, \nu=0}^{\infty}(-i)^{\mu}i^{\nu}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{\mu-1}}dt_\mu\int_{t_0}^{t}dt_1'\int_{t_0}^{t_1'}dt_2'\cdots\int_{t_0}^{t_{\nu-1}'}dt_\nu'$$

$$\times\{H_{hyb}e^{\eta t}, e^{-iH_0(t-t_1)}H_{hyb}e^{\eta t_1}e^{-iH_0(t_1-t_2)}H_{hyb}e^{\eta t_2}\cdots H_{hyb}e^{\eta t_\mu}e^{-iH_0(t_\mu-t_0)}|i\rangle\langle i|e^{iH_0(t_\nu'-t_0)}H_{hyb}e^{\eta t_\nu'}\cdots$$

$$\times H_{hyb}e^{\eta t_2'}e^{iH_0(t_1'-t_2')}H_{hyb}e^{\eta t_1'}e^{iH_0(t-t_1')}\}|f\rangle. \quad (36)$$

It is helpful to rewrite this expression as a derivative

$$\Gamma_{fi} = \frac{d}{dt}\left|\langle f|\sum_{\mu=0}^{\infty}(-i)^{\mu}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\cdots\int_{t_0}^{t_{\mu-1}}dt_\mu e^{iH_0 t_1}H_{hyb}e^{\eta t_1}e^{-iH_0(t_1-t_2)}H_{hyb}e^{\eta t_2}\cdots H_{hyb}e^{\eta t_\mu}e^{-iH_0 t_\mu}|i\rangle\right|^2. \quad (37)$$

Next, the initial time $t_0$ is sent to $-\infty$ at finite $\eta$. With $\tau_1 = t - t_1$ and $\tau_\mu = t_{\mu-1} - t_\mu$ for $\mu > 1$, we obtain

$$
\begin{aligned}
\Gamma_{fi} = \frac{d}{dt}\bigg| &\langle f| e^{iH_0 t} \sum_{\mu=1}^{\infty} (-i)^\mu \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \cdots \int_0^\infty d\tau_\mu e^{-iH_0\tau_1} H_{\text{hyb}} e^{-iH_0\tau_2} H_{\text{hyb}} e^{-iH_0\tau_3} \cdots e^{-iH_0\tau_\mu} H_{\text{hyb}} \\
&\times e^{-iH_0(t-\tau_1-\cdots-\tau_\mu)} e^{\eta[\mu t - \mu\tau_1 - (\mu-1)\tau_2 - \cdots - \tau_\mu]} |i\rangle \bigg|^2 \\
= \frac{d}{dt}\bigg| &\langle f| \sum_{\mu=1}^{\infty} e^{\mu\eta t} \frac{1}{E_i - E_f + i\mu\eta} H_{\text{hyb}} \frac{1}{E_i - H_0 + i(\mu-1)\eta} H_{\text{hyb}} \cdots \frac{1}{E_i - H_0 + i\eta} H_{\text{hyb}} |i\rangle \bigg|^2.
\end{aligned}
\tag{38}
$$

We have used that the $\mu = 0$ term vanishes for $|f\rangle \neq |i\rangle$. The fractions are to be understood as inverse ordinary operators. The time derivative can now be evaluated:

$$
\begin{aligned}
\Gamma_{fi} = \sum_{\mu=1}^{\infty} \sum_{\nu=1}^{\infty} &\frac{(\mu+\nu)\,\eta\, e^{\mu\eta t} e^{\nu\eta t}}{(E_i - E_f - i\mu\eta)(E_i - E_f + i\nu\eta)} \langle i| H_{\text{hyb}} \frac{1}{E_i - H_0 - i\eta} \cdots H_{\text{hyb}} \frac{1}{E_i - H_0 - i(\mu-1)\eta} H_{\text{hyb}} |f\rangle \\
&\times \langle f| H_{\text{hyb}} \frac{1}{E_i - H_0 + i(\nu-1)\eta} H_{\text{hyb}} \cdots \frac{1}{E_i - H_0 + i\eta} H_{\text{hyb}} |i\rangle.
\end{aligned}
\tag{39}
$$

We notice that the limit $\eta \to 0^+$ can be taken in the factors $(E_i - H_0 \pm i\kappa\eta)^{-1}$ independently from the first factor under the sum. In the former, $\eta > 0$ indicates in which complex half-plane the poles are located. In the latter, the limit $\eta \to 0^+$ leads to a $\delta$ function implementing energy conservation,

$$
\begin{aligned}
\Gamma_{fi} = \sum_{\mu=1}^{\infty} \sum_{\nu=1}^{\infty} &2\pi\,\delta(E_i - E_f)\langle i| \left( H_{\text{hyb}} \frac{1}{E_i - H_0 - i0^+} \right)^{\mu-1} \\
&\times H_{\text{hyb}} |f\rangle \langle f| H_{\text{hyb}} \left( \frac{1}{E_i - H_0 + i0^+} H_{\text{hyb}} \right)^{\nu-1} |i\rangle.
\end{aligned}
\tag{40}
$$

Since $H_{\text{hyb}}$ changes the electron number in the leads by $\pm 1$, $\Gamma_{fi}$ can only be nonzero if $\mu$ and $\nu$ are both even or both odd.

Defining the $T$-matrix as

$$
T := \sum_{\mu=1}^{\infty} H_{\text{hyb}} \left( \frac{1}{E_i - H_0 + i0^+} H_{\text{hyb}} \right)^{\mu-1},
\tag{41}
$$

we obtain the well-known result[22]

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

Note that we have obtained this result explicitly for the exponential time dependence of the hybridization. It was not necessary to consider a different time dependence at intermediate steps, as in Ref. 22.

We now use a product basis of unperturbed eigenstates $|m\rangle$, $|n\rangle$ of the dot and $|i\rangle\!\rangle$, $|f\rangle\!\rangle$ of the leads. Summing over all initial lead states $|i\rangle\!\rangle$ and final lead states $|f\rangle\!\rangle$, we obtain the $T$-matrix expression for the transition rate from dot state $|n\rangle$ to dot state $|m\rangle \neq |n\rangle$:

$$
\tilde{R}_{n \to m} = 2\pi \sum_{i,f} W_i |\langle\!\langle f|(m|T|n)|i\rangle\!\rangle|^2 \delta(E_n + \epsilon_i - E_m - \epsilon_f).
\tag{43}
$$

Here, $E_m$ ($\epsilon_i$) are eigenenergies of dot (lead) states and $W_i$ is the equilibrium probability to find the leads in state $|i\rangle\!\rangle$.

The sums over lead states are understood as integrals if their spectrum is continuous.

We have shown that the $T$-matrix formula (43) for the transition rates is what one gets if one takes the exact time evolution of the density operator, projects onto diagonal density operators of product form with the leads in equilibrium, and then *by hand* replaces the projected density operator at the initial time $\tilde{\mathcal{P}}\rho(t_0)$ by the projected density operator at the present time $\tilde{\mathcal{P}}\rho(t)$. This confirms the statement made in Ref. 23 that the $T$-matrix approach to transport misinterprets the transition rates between dot states $|n\rangle$ at time $t_0 \to -\infty$ and $|m\rangle$ at time $t$ as transition rates between $|n\rangle$ and $|m\rangle$ both at time $t$.

### D. Relation between TCL Pauli and *T*-matrix generators

We derive two simple relations between the generators $\tilde{\mathcal{S}}$ and $\tilde{\mathcal{R}}$. The defining equations (24) and (31) read as

$$
\begin{aligned}
d\tilde{\mathcal{P}}\rho(t)/dt &= \tilde{\mathcal{S}}(t,t_0)\,\tilde{\mathcal{P}}\rho(t), \\
d\tilde{\mathcal{P}}\rho(t)/dt &= \tilde{\mathcal{R}}(t,t_0)\,\tilde{\mathcal{P}}\rho(t_0).
\end{aligned}
$$

The first equation is solved by

$$
\tilde{\mathcal{P}}\rho(t_1) = T_\leftarrow \exp\left( \int_{t_2}^{t_1} dt'\,\tilde{\mathcal{S}}(t',t_0) \right) \tilde{\mathcal{P}}\rho(t_2),
\tag{44}
$$

where $t_1 \geqslant t_2$. Choosing $t_1 = t$ and $t_2 = t_0$ and taking the time derivative we obtain

$$
\frac{d}{dt}\tilde{\mathcal{P}}\rho(t) = \tilde{\mathcal{S}}(t,t_0)\, T_\leftarrow \exp\left( \int_{t_0}^{t} dt'\,\tilde{\mathcal{S}}(t',t_0) \right) \tilde{\mathcal{P}}\rho(t_0).
\tag{45}
$$

Comparison with Eq. (31) yields the identity

$$
\tilde{\mathcal{R}}(t,t_0) = \tilde{\mathcal{S}}(t,t_0)\, T_\leftarrow \exp\left( \int_{t_0}^{t} dt'\,\tilde{\mathcal{S}}(t',t_0) \right).
\tag{46}
$$

Conversely, to represent $\tilde{\mathcal{S}}$ in terms of $\tilde{\mathcal{R}}$, we integrate Eq. (31) from time $t_0$ to $t$:

$$\tilde{\mathcal{P}}\rho(t) = \tilde{\mathcal{P}}\rho(t_0) + \int_{t_0}^{t} dt'\, \tilde{\mathcal{R}}(t',t_0)\, \tilde{\mathcal{P}}\rho(t_0). \quad (47)$$

Comparison with Eq. (44) yields

$$T_{\leftarrow} \exp\left(\int_{t_0}^{t} dt'\, \tilde{\mathcal{S}}(t',t_0)\right) = 1 + \int_{t_0}^{t} dt'\, \tilde{\mathcal{R}}(t',t_0). \quad (48)$$

Inserting this equation into Eq. (46), we finally obtain

$$\tilde{\mathcal{S}}(t,t_0) = \tilde{\mathcal{R}}(t,t_0)\left[1 + \int_{t_0}^{t} dt'\, \tilde{\mathcal{R}}(t',t_0)\right]^{-1}. \quad (49)$$

This remarkable expression allows us to obtain the generator of the TCL Pauli ME from the $T$-matrix generator, in principle. This result is potentially useful since we have an explicit expression for the transition rates in the $T$-matrix approach in terms of ordinary operators. It will also allow us to derive the perturbative expansion of $\tilde{\mathcal{S}}(t,t_0)$ in the following.

The derivation also goes through for the full nondiagonal ME. The corresponding expressions can be obtained by removing the tilde from all symbols. The result is equivalent to an identity found by Bužek.[43]

### E. Perturbative expansion in the hybridization

In this section, we derive expansions of the TCL Pauli and $T$-matrix generators in powers of $H_{\text{hyb}}$ or $\mathcal{L}_{\text{hyb}}$. In the following, we send $t_0 \to -\infty$ and suppress the arguments $(t,-\infty)$. The expansion of the $T$-matrix generator is obtained from Eq. (33), i.e., $\tilde{\mathcal{R}} = \sum_{\mu=1}^{\infty} \tilde{\mathcal{R}}^{(2\mu)}$ with

$$\tilde{\mathcal{R}}^{(2\mu)} = -i e^{2\mu\eta t} \tilde{\mathcal{P}}\mathcal{L}_{\text{hyb}}[-\mathcal{L}_0 + (2\mu-1)i\eta]^{-1}\mathcal{L}_{\text{hyb}}$$
$$\times [-\mathcal{L}_0 + (2\mu-2)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\cdots$$
$$\times \mathcal{L}_{\text{hyb}}(-\mathcal{L}_0 + i\eta)^{-1}\mathcal{L}_{\text{hyb}}\tilde{\mathcal{P}}. \quad (50)$$

We have used that all odd orders vanish.

The TCL generator is obtained from $\tilde{\mathcal{R}}$ using Eq. (49). The time integral is easily performed,

$$\tilde{\mathcal{S}} \equiv \sum_{\mu=1}^{\infty} \tilde{\mathcal{S}}^{(2\mu)} = \sum_{\mu=1}^{\infty} \tilde{\mathcal{R}}^{(2\mu)}\left[1 + \sum_{\mu=1}^{\infty} \frac{\tilde{\mathcal{R}}^{(2\mu)}}{2\mu\eta}\right]^{-1}. \quad (51)$$

Expanding the inverse and comparing the two sides order by order, we obtain

$$\tilde{\mathcal{S}}^{(2\mu)} = \sum_{q=0}^{\mu-1}(-1)^q \sum_{\mu_0+\mu_1+\cdots+\mu_q=\mu} \tilde{\mathcal{R}}^{(2\mu_0)}\frac{\tilde{\mathcal{R}}^{(2\mu_1)}}{2\mu_1\eta}\cdots\frac{\tilde{\mathcal{R}}^{(2\mu_q)}}{2\mu_q\eta}, \quad (52)$$

where the second sum is over $q+1$ positive integers $\mu_i$ adding up to $\mu$. We note in passing that Eq. (52) can also be obtained from the expansion of the TCL generator in terms of ordered cumulants, following van Kampen.[39,44] The first few terms read explicitly as

$$\tilde{\mathcal{S}}^{(2)} = \tilde{\mathcal{R}}^{(2)}, \quad (53)$$

$$\tilde{\mathcal{S}}^{(4)} = \tilde{\mathcal{R}}^{(4)} - \tilde{\mathcal{R}}^{(2)}\frac{\tilde{\mathcal{R}}^{(2)}}{2\eta}, \quad (54)$$

$$\tilde{\mathcal{S}}^{(6)} = \tilde{\mathcal{R}}^{(6)} - \tilde{\mathcal{R}}^{(4)}\frac{\tilde{\mathcal{R}}^{(2)}}{2\eta} - \tilde{\mathcal{R}}^{(2)}\frac{\tilde{\mathcal{R}}^{(4)}}{4\eta} + \tilde{\mathcal{R}}^{(2)}\frac{\tilde{\mathcal{R}}^{(2)}}{2\eta}\frac{\tilde{\mathcal{R}}^{(2)}}{2\eta}. \quad (55)$$

The first equation shows that, in the sequential-tunneling approximation, the TCL and $T$-matrix expressions for the transition rates agree.[23]

The problem in exploiting the expansion (52) is that the $\tilde{\mathcal{R}}^{(2\mu)}$ diverge for $\eta \to 0^+$ for all $2\mu \geqslant 4$. This is in addition to the explicit divergences due to negative powers of $\eta$ in Eq. (52). We would much prefer a representation of $\tilde{\mathcal{S}}^{(2\mu)}$ in terms of expressions that remain finite. To obtain one, we first simplify the notation by setting $t = 0$ since, in the limit $\eta \to 0^+$, the value of $t$ does not matter. We then define

$$\tilde{\mathcal{R}}^{(2\mu,2\mu')} = -i\tilde{\mathcal{P}}\mathcal{L}_{\text{hyb}}[-\mathcal{L}_0 + (2\mu-1)i\eta]^{-1}\mathcal{L}_{\text{hyb}}$$
$$\times [-\mathcal{L}_0 + (2\mu-2)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\cdots\mathcal{L}_{\text{hyb}}$$
$$\times [-\mathcal{L}_0 + (2\mu'+1)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\tilde{\mathcal{P}}, \quad (56)$$

where $\mu > \mu'$. Note the identity $\tilde{\mathcal{R}}^{(2\mu,0)} = \tilde{\mathcal{R}}^{(2\mu)}$.

Divergences of the type of negative powers of $\eta$ arise whenever $\mathcal{L}_0$ in the inverse superoperators $(-\mathcal{L}_0 + i\kappa\eta)^{-1}$ can be replaced by zero. These divergences are singled out by inserting $1 = \tilde{\mathcal{P}} + \tilde{\mathcal{Q}}$ between each pair of $\mathcal{L}_{\text{hyb}}$. We note that, under the assumption of nondegenerate dot states, the projection $\tilde{\mathcal{P}}$ projects out the *secular reducible contributions*.[26] These are thus removed by $\tilde{\mathcal{Q}}$. Since the lead-electron creation and annihilation operators must be paired between any two $\tilde{\mathcal{P}}$, all expressions with an odd number of $\mathcal{L}_{\text{hyb}}$ superoperators between two $\tilde{\mathcal{P}}$ projections vanish. Thus, at the odd-numbered positions between the $\mathcal{L}_{\text{hyb}}$, $\tilde{\mathcal{Q}} = 1 - \tilde{\mathcal{P}}$ does not do anything and $\tilde{\mathcal{Q}}$ is redundant. This also means that divergences can not arise from the inverse superoperators at odd-numbered positions. We therefore only insert $1 = \tilde{\mathcal{P}} + \tilde{\mathcal{Q}}$ at the even-numbered positions

$$\tilde{\mathcal{R}}^{(2\mu)} = -i\tilde{\mathcal{P}}\mathcal{L}_{\text{hyb}}[-\mathcal{L}_0 + (2\mu-1)i\eta]^{-1}\mathcal{L}_{\text{hyb}}(\tilde{\mathcal{P}} + \tilde{\mathcal{Q}})$$
$$\times [-\mathcal{L}_0 + (2\mu-2)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\cdots(\tilde{\mathcal{P}} + \tilde{\mathcal{Q}})$$
$$\times \mathcal{L}_{\text{hyb}}(-\mathcal{L}_0 + i\eta)^{-1}\mathcal{L}_{\text{hyb}}\tilde{\mathcal{P}}. \quad (57)$$

We denote the regular parts of $\tilde{\mathcal{R}}^{(2\mu,2\mu')}$ by

$$\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')} := -i\tilde{\mathcal{P}}\,\mathcal{L}_{\text{hyb}}[-\mathcal{L}_0 + (2\mu-1)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\,\tilde{\mathcal{Q}}$$
$$\times [-\mathcal{L}_0 + (2\mu-2)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\cdots\tilde{\mathcal{Q}}\,\mathcal{L}_{\text{hyb}}$$
$$\times [-\mathcal{L}_0 + (2\mu'+1)i\eta]^{-1}\mathcal{L}_{\text{hyb}}\,\tilde{\mathcal{P}}, \quad (58)$$

where a projection $\tilde{\mathcal{Q}}$ is inserted at every even-numbered position between the $\mathcal{L}_{\text{hyb}}$. We also define $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,0)} := \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)}$. The finiteness of $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')}$ for $\eta \to 0^+$ is shown in a more general context in Appendix C. Note that $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu-2)} = \tilde{\mathcal{R}}^{(2\mu,2\mu-2)}$ and, in particular, $\tilde{\mathcal{R}}_{\text{reg}}^{(2)} = \tilde{\mathcal{R}}^{(2)}$, since there is no position to

insert $\tilde{\mathcal{Q}}$. This reproduces the well-known observation that the second-order rates in the $T$-matrix formalism do not show divergences.

From Eq. (57) we now obtain, using Eq. (20),

$$
\begin{aligned}
\tilde{\mathcal{R}}^{(2\mu)} = {} & \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,0)} + \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} + \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,4)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,0)}}{4\eta} \\
& + \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,4)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,2)}}{4\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} + \cdots + \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu-2)} \\
& \times \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu-2,2\mu-4)}}{(2\mu-2)\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu-4,2\mu-6)}}{(2\mu-4)\eta} \cdots \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta}. \quad (59)
\end{aligned}
$$

Since we have inserted $\tilde{\mathcal{P}} + \tilde{\mathcal{Q}}$ in $\mu - 1$ positions, there are $2^{\mu-1}$ terms in this sum. In particular, we find

$$
\tilde{\mathcal{R}}^{(2)} = \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}, \quad (60)
$$

$$
\tilde{\mathcal{R}}^{(4)} = \tilde{\mathcal{R}}_{\text{reg}}^{(4,0)} + \tilde{\mathcal{R}}_{\text{reg}}^{(4,2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta}, \quad (61)
$$

$$
\begin{aligned}
\tilde{\mathcal{R}}^{(6)} = {} & \tilde{\mathcal{R}}_{\text{reg}}^{(6,0)} + \tilde{\mathcal{R}}_{\text{reg}}^{(6,2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} + \tilde{\mathcal{R}}_{\text{reg}}^{(6,4)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,0)}}{4\eta} \\
& + \tilde{\mathcal{R}}_{\text{reg}}^{(6,4)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,2)}}{4\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta}. \quad (62)
\end{aligned}
$$

As an intermediate result, we have thus written the $T$-matrix generator $\tilde{\mathcal{R}}$ order by order in terms of expressions that remain finite for $\eta \to 0^+$ and explicit negative powers of $\eta$. Since each insertion of $\tilde{\mathcal{P}}$ generates a factor of $1/\eta$, the most strongly diverging term in $\tilde{\mathcal{R}}^{(2\mu)}$ scales as $1/\eta^{\mu-1}$.

Inserting Eq. (59) into Eq. (52), we obtain $\tilde{\mathcal{S}}^{(2\mu)}$ in terms of $\tilde{\mathcal{R}}_{\text{reg}}^{(2\nu,2\nu')}$ with $0 \leqslant \nu' < \nu \leqslant \mu$ for all $\mu$. The leading terms read as

$$
\tilde{\mathcal{S}}^{(2)} = \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}, \quad (63)
$$

$$
\tilde{\mathcal{S}}^{(4)} = \tilde{\mathcal{R}}_{\text{reg}}^{(4,0)} + \tilde{\mathcal{R}}_{\text{reg}}^{(4,2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} - \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta}, \quad (64)
$$

$$
\begin{aligned}
\tilde{\mathcal{S}}^{(6)} = {} & \tilde{\mathcal{R}}_{\text{reg}}^{(6,0)} + \tilde{\mathcal{R}}_{\text{reg}}^{(6,2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} + \tilde{\mathcal{R}}_{\text{reg}}^{(6,4)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,0)}}{4\eta} + \tilde{\mathcal{R}}_{\text{reg}}^{(6,4)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,2)}}{4\eta} \\
& \times \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} - \tilde{\mathcal{R}}_{\text{reg}}^{(4,0)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} - \tilde{\mathcal{R}}_{\text{reg}}^{(4,2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} \\
& - \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,0)}}{4\eta} - \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(4,2)}}{4\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} \\
& + \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}}{2\eta}. \quad (65)
\end{aligned}
$$

In this expansion of the exact TCL Pauli generator, all singular contributions in the limit $\eta \to 0^+$ have been made explicit. The maximum power is $1/\eta^{\mu-1}$.

To conclude this section, we illustrate the results by considering the terms of fourth order. The corresponding term

in the $T$-matrix generator reads as

$$
\begin{aligned}
\tilde{\mathcal{R}}^{(4)} = {} & -i\, \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + 3i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} (-\mathcal{L}_0 + 2i\eta)^{-1} \\
& \times \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}}. \quad (66)
\end{aligned}
$$

Let $\tilde{\mathcal{R}}^{(4)}$ act upon some density operator $\rho$. Then, $\mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}} \rho$ contains contributions for which the second (from the right) superoperator $\mathcal{L}_{\text{hyb}}$ undoes the changes introduced by the first $\mathcal{L}_{\text{hyb}}$. Hence, $\mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}} \rho$ is an operator with nonvanishing *diagonal* components in the product basis of unperturbed eigenstates. But, for diagonal components $|j\rangle\langle j|$, we have $\mathcal{L}_0 |j\rangle\langle j| = 0$ so that $\mathcal{L}_0$ in the next superoperator to the left, $(-\mathcal{L}_0 + 2i\eta)^{-1}$, can be replaced by zero. We thus obtain a singular contribution proportional to $1/2i\eta$. More formally, we single out the divergent contributions by introducing $1 = \tilde{\mathcal{Q}} + \tilde{\mathcal{P}}$:

$$
\begin{aligned}
\tilde{\mathcal{R}}^{(4)} = {} & -i\, \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + 3i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + 2i\eta \right)^{-1} \tilde{\mathcal{Q}} \mathcal{L}_{\text{hyb}} \\
& \times \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}} - i\, \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + 3i\eta \right)^{-1} \\
& \times \mathcal{L}_{\text{hyb}} \frac{-i}{2\eta} \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} (-\mathcal{L}_0 + i\eta)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}} \\
=: {} & \tilde{\mathcal{R}}_{\text{reg}}^{(4)} + \tilde{\mathcal{R}}_{\text{div}}^{(4)}. \quad (67)
\end{aligned}
$$

The divergent part $\tilde{\mathcal{R}}_{\text{div}}^{(4)}$ is identical to $\tilde{\mathcal{R}}_{\text{reg}}^{(4,2)} \tilde{\mathcal{R}}_{\text{reg}}^{(2,0)}/2\eta$, according to the definition (58).

The fourth-order term $\tilde{\mathcal{S}}^{(4)}$ of the TCL generator contains a correction term beyond $\tilde{\mathcal{R}}^{(4)}$ [cf. Eq. (54)], namely,

$$
\begin{aligned}
-\tilde{\mathcal{R}}^{(2)} \frac{\tilde{\mathcal{R}}^{(2)}}{2\eta} \equiv {} & -\tilde{\mathcal{R}}_{\text{reg}}^{(2)} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2)}}{2\eta} \\
= {} & +i\, \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \frac{-i}{2\eta} \\
& \times \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}}. \quad (68)
\end{aligned}
$$

This looks very similar to the divergent part $\tilde{\mathcal{R}}_{\text{div}}^{(4)}$. The differences are the opposite sign and a different prefactor of $i\eta$ in the leftmost inverse superoperator. If this factor were the same, the correction term would exactly cancel the divergent part. As it is, the correction term does remove the divergence for $\eta \to 0^+$ but leaves a nonzero difference behind:

$$
\begin{aligned}
\tilde{\mathcal{R}}_{\text{div}}^{(4)} - \tilde{\mathcal{R}}^{(2)} \frac{\tilde{\mathcal{R}}^{(2)}}{2\eta} = {} & i\, \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} (-\mathcal{L}_0 + 3i\eta)^{-1} \\
& \times \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} \left( -\mathcal{L}_0 + i\eta \right)^{-1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}}. \quad (69)
\end{aligned}
$$

We will show that this difference indeed remains finite.

### F. Cancelation of divergences

Our next goal is to show that the divergences described by negative powers of $\eta$ all cancel in the limit $\eta \to 0^+$. It is useful to resum the terms in Eq. (52), i.e.,

$$
\tilde{\mathcal{S}} = \sum_{q=0}^{\infty} (-1)^q \sum_{\mu_0, \mu_1, \ldots, \mu_q = 1}^{\infty} \tilde{\mathcal{R}}^{(2\mu_0)} \frac{\tilde{\mathcal{R}}^{(2\mu_1)}}{2\mu_1 \eta} \cdots \frac{\tilde{\mathcal{R}}^{(2\mu_q)}}{2\mu_q \eta}. \quad (70)
$$

Inserting Eq. (59), we obtain

$$\tilde{S} = \sum_{p=0}^{\infty} \sum_{\mu_0,\mu_0',\mu_1,\mu_1',\mu_2,\mu_2',\ldots,\mu_p} (-1)^{n'} \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu_0,2\mu_0')} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu_1,2\mu_1')}}{2\mu_1\eta} \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu_2,2\mu_2')}}{2\mu_2\eta} \cdots \frac{\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu_p,2\mu_p'=0)}}{2\mu_p\eta}, \tag{71}$$

where $n'+1$ is the number of $\mu_i'$ being zero. The second sum is over $p+1$ pairs $(\mu_i,\mu_i')$, $i=0,1,\ldots,p$, with $\mu_i = 1,2,\ldots$, $\mu_i' = 0,1,\ldots$, and $\mu_i > \mu_i'$, satisfying either $\mu_i' = \mu_{i+1}$ or $\mu_i' = 0$ for any two consecutive pairs. The last $\mu_i' = \mu_p'$ must equal zero.

In Eq. (71), $p$ represents the explicit order in $1/\eta$. However, the superoperators $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')}$ also depend on $\eta$. To find the limit $\eta \to 0^+$, we thus have to expand them up to the order $\eta^p$. Their Taylor series in $\eta$ reads as

$$\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')} = -i \sum_{m_{2\mu-1},m_{2\mu-2}\cdots m_{2\mu'+1}=0}^{\infty} (-i\,\eta)^{m_{2\mu-1}+m_{2\mu-2}+\cdots+m_{2\mu'+1}}(2\mu-1)^{m_{2\mu-1}}(2\mu-2)^{m_{2\mu-2}}\cdots(2\mu'+1)^{m_{2\mu'+1}}$$

$$\times [m_{2\mu-1},m_{2\mu-2},\ldots,m_{2\mu'+1}]^{(2\mu,2\mu')}, \tag{72}$$

where we have defined the notation

$$[m_{2\mu-1},m_{2\mu-2},\ldots,m_{2\mu'+1}]^{(2\mu,2\mu')} := \lim_{\eta\to0^+} \tilde{\mathcal{P}}\,\mathcal{L}_{\text{hyb}}[-\mathcal{L}_0+(2\mu-1)i\eta]^{-1-m_{2\mu-1}}\,\mathcal{L}_{\text{hyb}}\,\tilde{\mathcal{Q}}[-\mathcal{L}_0+(2\mu-2)i\eta]^{-1-m_{2\mu-2}}$$

$$\times \mathcal{L}_{\text{hyb}}\cdots\mathcal{L}_{\text{hyb}}[-\mathcal{L}_0+(2\mu'+1)i\eta]^{-1-m_{2\mu'+1}}\,\mathcal{L}_{\text{hyb}}\,\tilde{\mathcal{P}} \tag{73}$$

with $\tilde{\mathcal{Q}}$ inserted at all even-numbered positions. In particular, Eq. (72) implies that

$$\lim_{\eta\to0^+} \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)} = -i\,[0,0,\ldots,0]^{(2\mu,0)}. \tag{74}$$

It is shown in Appendix C that the limit $\eta \to 0^+$ in Eq. (73) converges for all $m_{2\mu-1},m_{2\mu-2},\ldots,m_{2\mu'+1} \geqslant 0$. Moreover,

we show in Appendix B that the superoperator defined in Eq. (73) does not depend on the values of the prefactors of $i\eta$, as long as they are all positive. Thus, it does not depend on $\mu$ and $\mu'$ except in so far as $2\mu - 2\mu' - 1$ is the number of its arguments $m_\nu$. We therefore drop the superscript $(2\mu,2\mu')$ from now on.

Insertion of Eq. (72) into Eq. (71) leads to an expansion of the TCL generator $\tilde{S}$,

$$\tilde{S} = \sum_{p=0}^{\infty} (-i)^{p+1} \sum_{\mu_0,\mu_0',\mu_1,\mu_1',\mu_2,\mu_2',\ldots\mu_p} (-1)^{n'} \sum_{m_{0,2\mu_0-1},\ldots,m_{0,2\mu_0'+1},\ldots,m_{p,2\mu_p-1},\ldots,m_{p,1}=0}^{\infty} \frac{(-i)^{\Sigma_m}}{2\mu_1\,2\mu_2\cdots2\mu_p}(2\mu_0-1)^{m_{0,2\mu_0-1}}\cdots$$

$$\times (2\mu_0'+1)^{m_{0,2\mu_0'+1}}\cdots(2\mu_p-1)^{m_{p,2\mu_p-1}}\ldots[m_{0,2\mu_0-1},\ldots,m_{0,2\mu_0'+1}]\cdots[m_{p,2\mu_p-1},\ldots,m_{p,1}]\eta^{\Sigma_m-p}, \tag{75}$$

where $\Sigma_m := m_{0,2\mu_0-1} + \cdots + m_{p,1}$ is the sum of all $m_{i,\nu}$. The two indices of $m_{i,\nu}$ enumerate the factors of $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')}$ in Eq. (71) and the inverse superoperators in $[m_{2\mu-1},m_{2\mu-2},\ldots,m_{2\mu'+1}]$, respectively.

Terms containing positive powers $\Sigma_m - p > 0$ of $\eta$ vanish in the limit $\eta \to 0^+$ and can thus be disregarded. On the other hand, to obtain a finite limit, the prefactors in all terms involving negative powers $\Sigma_m - p < 0$ must cancel. The cancellations can only involve terms with the same superoperator factor $[m_{0,2\mu_0-1},\ldots,m_{0,2\mu_0'+1}]\cdots[m_{p,2\mu_p-1},\ldots,m_{p,1}]$. These terms have the same values of $p$, of the orders $2n_i = 2\mu_i - 2\mu_i'$, and of all $m_{i,\nu}$. We thus write

$$\tilde{S} = \sum_{p=0}^{\infty} (-i)^{p+1} \sum_{n_0,n_1,\ldots,n_p=1}^{\infty} \sum_{m_{0,2\mu_0-1},\ldots,m_{0,2\mu_0'+1},\ldots,m_{p,2\mu_p-1},\ldots,m_{p,1}=0}^{\infty} (-i)^{\Sigma_m} f(n_0,n_1,\ldots,n_p;m_{0,2\mu_0-1},\ldots,m_{p,1})$$

$$\times [m_{0,2\mu_0-1},\ldots,m_{0,2\mu_0'+1}]\cdots[m_{p,2\mu_p-1},\ldots,m_{p,1}]\eta^{\Sigma_m-p} \tag{76}$$

with the prefactors

$$f(n_0,n_1,\ldots,n_p;m_{0,2\mu_0-1},\ldots,m_{p,1})$$

$$:= \sum_{\mu_0,\mu_0',\mu_1,\mu_1',\mu_2,\mu_2',\ldots,\mu_p} \frac{(-1)^{n'}}{2\mu_1\,2\mu_2\cdots2\mu_p}(2\mu_0-1)^{m_{0,2\mu_0-1}}\cdots(2\mu_0'+1)^{m_{0,2\mu_0'+1}}\cdots(2\mu_p-1)^{m_{p,2\mu_p-1}}\cdots, \tag{77}$$

where the sum in Eq. (77) is now constrained by $2\mu_i - 2\mu_i' = 2n_i$ being given. With this constraint, the only freedom left in the sum is the choice of which $\mu_i'$ are zero; recall that the nonzero $\mu_i'$ equal $\mu_{i+1}$. The numbers $\mu_0, \mu_0', \mu_1, \mu_1', \mu_2, \mu_2', \ldots, \mu_p$ can be reconstructed from the orders $n_0, n_1, n_2, \ldots, n_p$ and the indices $i$ of the $\mu_i'$ that equal zero. Defining the set

$$Z := \{i \,|\, \mu_i' = 0\}, \qquad (78)$$

we have $p \in Z$ and $n' = |Z| - 1$, where $|Z|$ is the cardinality of $Z$. Defining the "nonmember function"

$$\pi_i^Z := \begin{cases} 0 & \text{if } i \in Z, \\ 1 & \text{if } i \notin Z, \end{cases} \qquad (79)$$

we have $\pi_p^Z = 0$ and $n' = p - \sum_{i=0}^{p-1} \pi_i^Z$. Replacing $\mu_i'$ by $\mu_i - n_i$ in Eq. (77), we obtain

$$f(n_0, n_1, \ldots, n_p; m_{0,2\mu_0-1}, \ldots, m_{p,1}) = (-1)^p \sum_{\pi_0^Z, \pi_1^Z, \ldots, \pi_{p-1}^Z = 0}^{1} \frac{\prod_{i=0}^{p-1} (-1)^{\pi_i^Z}}{2\mu_1 2\mu_2 \cdots 2\mu_p} (2\mu_0 - 1)^{m_{0,2\mu_0-1}} (2\mu_0 - 2)^{m_{0,2\mu_0-2}} \cdots$$

$$\times (2\mu_0 - 2n_0 + 1)^{m_{0,2\mu_0-2n_0+1}} \cdots (2\mu_p - 1)^{m_{p,2\mu_p-1}} (2\mu_p - 2)^{m_{p,2\mu_p-2}} \cdots 1^{m_{p,1}}, \qquad (80)$$

where $\mu_i = n_i + \pi_i^Z n_{i+1} + \pi_i^Z \pi_{i+1}^Z n_{i+2} + \cdots$ and $\mu_p = n_p$, and products are understood to equal unity if they do not contain any factors. For convenience, we define

$$M_i := m_{i,2\mu_i-1} + m_{i,2\mu_i-2} + \cdots + m_{i,2\mu_i-2n_i+1}. \qquad (81)$$

Note that $\Sigma_m = \sum_{i=0}^{p} M_i$.

The evaluation of Eq. (80), which is presented in Appendix C, is rather lengthy but has a remarkably simple result: For all $\Sigma_m \leqslant p$,

$$f(n_0, n_1, \ldots, n_p; m_{0,2\mu_0-1}, \ldots, m_{p,1}) = 1 \qquad (82)$$

if and only if

$$\Sigma_m - p = M_0 + M_1 + \cdots + M_p - p = 0 \qquad (83)$$

and there does not exist any integer $i < p$ such that

$$M_0 + M_1 + \cdots + M_i - i = 0. \qquad (84)$$

Otherwise, $f = 0$. Recall that $f$ is not of interest if $\Sigma_m > p$. Furthermore, we also show in Appendix C that the condition for nonzero $f$ can only be satisfied if $m_{p,2\mu_p-1} = \cdots = m_{p,1} = 0$.

Inserting these results into Eq. (76), taking the limit $\eta \to 0^+$, and renumbering the $m_{i,\nu}$, we obtain

$$\lim_{\eta \to 0^+} \tilde{\mathcal{S}} = -i \sum_{p=0}^{\infty} (-1)^p \sum_{n_0, n_1, \ldots, n_p = 1}^{\infty}$$

$$\times \sum_{m_{0,1}, \ldots, m_{0,2n_0-1}, \ldots, m_{p-1,1}, \ldots, m_{p-1,2n_{p-1}-1}}$$

$$\times \Theta(M_0 - 1)\Theta(M_0 + M_1 - 2) \cdots$$

$$\times \Theta(M_0 + M_1 + \cdots + M_{p-1} - p)$$

$$\times [m_{0,1}, \ldots, m_{0,2n_0-1}] \cdots [m_{p-1,1}, \ldots, m_{p-1,2n_{p-1}-1}]$$

$$\times [0, \ldots, 0], \qquad (85)$$

where the sum over the $m_{i,\nu}$ is constrained by $m_{0,1} + \cdots + m_{p-1,2n_{p-1}-1} = p$ and we have defined

$$\Theta(n) := \begin{cases} 0 & \text{for } n < 0, \\ 1 & \text{for } n \geqslant 0. \end{cases} \qquad (86)$$

Note that the factor $\Theta(M_0 + M_1 + \cdots + M_{p-1} - p)$ is redundant.

The $p = 0$ contribution in Eq. (85) does not contain any sums over $m_{i,\nu}$ since $\Sigma_m = p = 0$. There just remains a sum over $n_0$, the order in $H_{\text{hyb}}$, i.e., the $p = 0$ contribution reads $-i\,[0] - i\,[0,0,0] - \ldots$. According to Eq. (74), this equals $\lim_{\eta \to 0^+} \sum_\mu \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)}$. Thus, in the expansion in $H_{\text{hyb}}$, the expansion term $\tilde{\mathcal{S}}^{(2\mu)}$ of the TCL generator contains the properly regularized $T$-matrix term $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)}$ plus corrections. Furthermore, all these corrections contain $[0, \ldots, 0]$, i.e., an expansion term of $\tilde{\mathcal{R}}_{\text{reg}}$, as the rightmost superoperator factor.

Suppressing the limit directive from now on, we find that $i\tilde{\mathcal{S}}$ in Eq. (85) is the sum of all terms that can be constructed according to the following rules:

(i) Each term is a product of $p + 1 = 1, 2, \ldots$ superoperators of the form $[m_{j,1}, \ldots, m_{j,2n_j-1}]$ with $j = 0, \ldots, p$, $n_j = 1, 2, \ldots$, and $m_{j,\nu} = 0, 1, \ldots$.

(ii) Defining $M_j := m_{j,1} + \cdots m_{j,2n_j-1}$, only terms with $M_0 + M_1 + \cdots + M_j > j$ for all $j < p$ are allowed.

(iii) Only terms with $M_0 + M_1 + \cdots + M_p = p$ are allowed.

(iv) Each term obtains a factor $(-1)^p$.

We draw a number of conclusions: If an allowed term contains a factor $[m_{j,1}, \ldots, m_{j,2n_j-1}]$, then any term with this factor replaced by $[m_{j,1}', \ldots, m_{j,2n_j'-1}']$ with $m_{j,1}' + \cdots + m_{j,2n_j'-1}' = m_{j,1} + \cdots + m_{j,2n_j-1}$ is also allowed. If we denote the sum of all such terms by

$$[[M]] := \sum_{n=1}^{\infty} \sum_{m_1 + \cdots + m_{2n-1} = M} [m_1, \ldots, m_{2n-1}], \qquad (87)$$

we obtain

$$i\tilde{\mathcal{S}} = \sum_{p=0}^{\infty} (-1)^p \sum_{M_0=1}^{\infty}$$

$$\times \sum_{M_1=\max(0,2-M_0)}^{\infty} \sum_{M_2=\max(0,3-M_0-M_1)}^{\infty} \cdots \sum_{M_{p-1}=\max(0,p-M_0-\cdots-M_{p-2})}^{p-M_0-M_1-\cdots-M_{p-2}}$$

$$\times [[M_0]]\,[[M_1]] \cdots [[M_{p-1}]]\,[[0]]. \qquad (88)$$

The last sum is understood to equal zero if the upper limit is smaller than the lower one. In order to obtain an expansion of $i\tilde{\mathcal{S}}$ in powers of $H_{\text{hyb}}$, we note that $[m_1, \ldots, m_{2n-1}]$ is of order $H_{\text{hyb}}^{2n}$ with $2n \geqslant 2$. Thus $[[M]]$ contains contributions of second and higher orders. To obtain the expansion term $i\tilde{\mathcal{S}}^{(2\mu)}$ of order $2\mu$, we thus only have to consider terms with $p+1 \leqslant \mu$ factors $[[M_j]]$ in Eq. (88). The first few terms read as

$$\tilde{\mathcal{S}}^{(2)} = -i\,[0], \tag{89}$$

$$\tilde{\mathcal{S}}^{(4)} = -i\,[0,0,0] + i\,[1][0], \tag{90}$$

$$\tilde{\mathcal{S}}^{(6)} = -i\,[0,0,0,0,0] + i\,[0,0,1][0] + i\,[0,1,0][0]$$
$$+ i\,[1,0,0][0] + i\,[1][0,0,0] - i\,[1][1][0] - i\,[2][0][0]. \tag{91}$$

Higher-order terms are easily generated using computer algebra. They become increasingly lengthy; $\tilde{\mathcal{S}}^{(8)}$ contains 30 terms and $\tilde{\mathcal{S}}^{(10)}$ already has 143. Simplification is possible by realizing that some of the terms in $\tilde{\mathcal{S}}^{(2\mu)}$ contain factors of $\tilde{\mathcal{S}}^{(2\mu')}$ with $\mu' < \mu$, as we show now.

Equation (88) is equivalent to the surprising identity

$$i\,\tilde{\mathcal{S}} = \sum_{M=0}^{\infty} [[M]]\,(-i\,\tilde{\mathcal{S}})^M. \tag{92}$$

The usefulness of this equation rests on the observation that $[[M]]$ is of at least second order in $H_{\text{hyb}}$. Therefore, we can express $\tilde{\mathcal{S}}^{(2\mu)}$ by *lower-order* terms $\tilde{\mathcal{S}}^{(2\mu')}$, $\mu' < \mu$. Together with the starting value $\tilde{\mathcal{S}}^{(2)} = -i\,[0] = \tilde{\mathcal{R}}_{\text{reg}}^{(2)}$, we obtain a recursive scheme for determining $\tilde{\mathcal{S}}^{(2\mu)}$.

To prove that Eq. (92) has the solution given in Eq. (88), we iterate Eq. (92):

$$i\,\tilde{\mathcal{S}} = [[0]] + \sum_{M_0=1}^{\infty} [[M_0]]\,(-i\,\tilde{\mathcal{S}})^{M_0}$$

$$= [[0]] - \sum_{M_0=1}^{\infty} \sum_{M_1=0}^{\infty} [[M_0]]\,[[M_1]]\,(-i\,\tilde{\mathcal{S}})^{M_0+M_1-1}$$

$$= [[0]] - [[1]]\,[[0]] + \sum_{M_0=1}^{\infty} \sum_{M_1=\max(0,2-M_0)}^{\infty} \sum_{M_2=0}^{\infty} [[M_0]]$$
$$\times [[M_1]]\,[[M_2]]\,(-i\tilde{\mathcal{S}})^{M_0+M_1+M_2-2}$$

$$= [[0]] - [[1]]\,[[0]] + \sum_{M_0=1}^{2} [[M_0]]\,[[2-M_0]]\,[[0]] \mp \cdots. \tag{93}$$

It is clear how this continues. The terms no longer containing $\tilde{\mathcal{S}}$ are the ones satisfying the conditions in the multiple sum in Eq. (88). Thus, Eq. (88) is a solution of Eq. (92). To show that it is the only solution, i.e., that Eq. (88) implies Eq. (92), we note that the iteration shows that any solution $\tilde{\mathcal{S}}'$ of Eq. (92) agrees with Eq. (88) order by order in the number $p+1$ of superoperator factors. Thus, we find $\tilde{\mathcal{S}}' = \tilde{\mathcal{S}}$ to any order $p+1$.

### G. Relation to the Nakajima-Zwanzig master equation

The Nakajima-Zwanzig ME (Refs. 27 and 28) and equivalent formulations are commonly used in the field of transport through nanostructures. The real-time diagrammatic technique[18–20] and the suitably generalized Wangsness-Bloch-Redfield theory[45–47] are such equivalent formulations.[23,26] We again only consider the initial condition $\mathcal{Q}\rho(t_0) = 0$. The derivation starts in the same way as the one of the TCL ME, leading to Eq. (11). Inserting this equation into Eq. (9) and using the identities (5) and (6), we obtain the NZ ME (Ref. 39)

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{L}_0\mathcal{P}\rho(t) - \mathcal{P}\mathcal{L}_{\text{hyb}}e^{\eta t}\int_{t_0}^{t} dt'\,T_{\leftarrow}\exp\left[-i\int_{t'}^{t} dt''(\mathcal{L}_0 + \mathcal{Q}\mathcal{L}_{\text{hyb}}e^{\eta t''})\right]\mathcal{Q}\mathcal{L}_{\text{hyb}}e^{\eta t'}\mathcal{P}\rho(t'). \tag{94}$$

Expansion in powers of $\mathcal{L}_{\text{hyb}}$ yields

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{L}_0\mathcal{P}\rho(t) - \mathcal{P}\mathcal{L}_{\text{hyb}}e^{\eta t}\sum_{\nu=0}^{\infty}(-i)^{\nu}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{\nu-1}} dt_{\nu} \int_{t_0}^{t_{\nu}} dt_{\nu+1}\,e^{-i\mathcal{L}_0(t-t_1)}\mathcal{Q}\mathcal{L}_{\text{hyb}}e^{\eta t_1}\,e^{-i\mathcal{L}_0(t_1-t_2)}$$

$$\times \mathcal{Q}\mathcal{L}_{\text{hyb}}e^{\eta t_2}\cdots \mathcal{Q}\mathcal{L}_{\text{hyb}}e^{\eta t_{\nu}}e^{-i\mathcal{L}_0(t_{\nu}-t_{\nu+1})}\mathcal{Q}\mathcal{L}_{\text{hyb}}e^{\eta t_{\nu+1}}\mathcal{P}\rho(t_{\nu+1}). \tag{95}$$

As above, the projections $\mathcal{Q}$ at odd-numbered positions are redundant, while at even-numbered positions they remove divergent reducible contributions.[23,26,38]

The derivation goes through if we replace $\mathcal{P}$ and $\mathcal{Q}$ by $\tilde{\mathcal{P}}$ and $\tilde{\mathcal{Q}}$, respectively. We end up with a Nakajima-Zwanzig-Pauli ME for the diagonally projected density operator,

$$\frac{d}{dt}\tilde{\mathcal{P}}\rho(t) = -\tilde{\mathcal{P}}\mathcal{L}_{\text{hyb}}e^{\eta t}\int_{t_0}^{t} dt'\,T_{\leftarrow}\exp\left[-i\int_{t'}^{t} dt''(\mathcal{L}_0 + \tilde{\mathcal{Q}}\mathcal{L}_{\text{hyb}}e^{\eta t''})\right]\tilde{\mathcal{Q}}\mathcal{L}_{\text{hyb}}e^{\eta t'}\tilde{\mathcal{P}}\rho(t'). \tag{96}$$

The bare time evolution has dropped out because of Eq. (20). It is this ME that is expanded up to fourth order in Refs. 24 and 26. The projections $\tilde{\mathcal{Q}}$ now remove only the *diagonal* reducible contributions, but not all of them. They thus implement the regularization discussed by Koller *et al.*[26] As in Ref. 26, the regularization is automatically included. Our result shows that it can be formulated compactly using suitable projection operators $\tilde{\mathcal{P}}$ and $\tilde{\mathcal{Q}}$. It has been noted in Ref. 38 and shown explicitly in Ref. 26 that the Turek-Matveev scheme[34,48] differs from this built-in regularization already at fourth order.

If one is only interested in the stationary solution of the ME, $\tilde{\mathcal{P}}\rho(t')$ on the right-hand side of Eq. (96) can be taken to be time independent. It is then possible to evaluate the time integrals explicitly. The resulting equation for the stationary state reads as $0 = \tilde{\mathcal{G}}\tilde{\mathcal{P}}\rho$ with the generator, for $t_0 \to -\infty$,

$$\tilde{\mathcal{G}} \equiv \sum_{\mu=1}^{\infty} \tilde{\mathcal{G}}^{(2\mu)} := -i\tilde{\mathcal{P}}\mathcal{L}_{\text{hyb}} \sum_{\mu=1}^{\infty} e^{2\mu\eta t}$$

$$\times [-\mathcal{L}_0 + (2\mu-1)i\eta]^{-1} \mathcal{L}_{\text{hyb}}\tilde{\mathcal{Q}} [-\mathcal{L}_0 + (2\mu-2)i\eta]^{-1}$$

$$\times \mathcal{L}_{\text{hyb}} \cdots \tilde{\mathcal{Q}}\mathcal{L}_{\text{hyb}} (-\mathcal{L}_0 + i\eta)^{-1} \mathcal{L}_{\text{hyb}}\tilde{\mathcal{P}}. \quad (97)$$

The redundant projections $\tilde{\mathcal{Q}}$ at odd-numbered positions have been omitted. Since this is an exact result for the stationary state, it should agree with what the exact TCL ME predicts. We will return to this point shortly.

If one is interested in the dynamics, one can still obtain a local ME from the NZ approach. This requires the Markov approximation, which is based on the assumption that the memory kernel in Eq. (96) decays rapidly in time. This assumption is often justified since relaxation in the leads is rapid but also follows directly from the condition of a nearly closed conduction channel $I/V \ll e^2/h$.[23] With the Markov approximation, $\tilde{\mathcal{P}}\rho(t')$ is replaced by $\tilde{\mathcal{P}}\rho(t)$. Taking $t_0 \to -\infty$, one obtains the approximate "Nakajima-Zwanzig-Markov-Pauli" ME

$$d\tilde{\mathcal{P}}\rho(t)/dt = \tilde{\mathcal{G}}\tilde{\mathcal{P}}\rho(t) \quad (98)$$

with the generator $\tilde{\mathcal{G}}$ defined in Eq. (97).

Comparison of Eqs. (97) and (58) shows that the expansion terms are identical to the *properly regularized* expansion terms of the $T$-matrix generator (we suppress the limit $\eta \to 0^+$),

$$\tilde{\mathcal{G}}^{(2\mu)} = \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)}. \quad (99)$$

Hence, the Nakajima-Zwanzig-Markov-Pauli ME is identical, order by order in $H_{\text{hyb}}$, to the ME with rates obtained from the $T$-matrix approach and regularized by dropping secular reducible contributions. Up to fourth order, this has been shown by Koller *et al.*[26]

We can now gain additional insight into the failure[26] of the Turek-Matveev regularization scheme.[48] The proper regularization of the $T$-matrix expressions can be understood as omitting all terms in Eq. (59) except for the first one or, in other words, as omitting all terms containing *explicit* negative powers of $\eta$. The Turek-Matveev scheme, applied to the calculation of the fourth-order rates,[34] corresponds to expanding the rates into powers of $\eta$ and omitting the diverging part proportional to $1/\eta$ and then letting $\eta$ go to zero. The

obvious generalization to all orders is to omit all negative powers of $\eta$. The two regularization procedures thus look quite similar. They are not identical, though, since the superoperators $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')}$ appearing in the proper expansion (59) contain positive powers of $\eta$. The positive powers from $\tilde{\mathcal{R}}_{\text{reg}}^{(2\mu,2\mu')}$ together with the explicit negative powers lead to terms of order $\eta^0$, which are retained by the Turek-Matveev scheme but are absent in the proper regularization. We reiterate that both the Nakajima-Zwanzig-Markov-Pauli ME and the TCL Pauli ME are automatically regularized—for the TCL case, this is one of our central results. The discussion of the proper regularization scheme is only relevant if one wants to construct the NZ transition rates from the $T$-matrix expressions.

The exact TCL ME is not equivalent to the approximate Nakajima-Zwanzig-Markov-Pauli ME: As noted in the discussion of Eq. (85), the $p = 0$ term in this expansion is $\sum_\mu \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)}$, which we have now identified as the Nakajima-Zwanzig-Markov-Pauli generator $\tilde{\mathcal{G}}$. Using Eqs. (74) and (87), we can also write this generator as

$$\tilde{\mathcal{G}} \equiv \sum_\mu \tilde{\mathcal{R}}_{\text{reg}}^{(2\mu)} \equiv -i\, [[0]]. \quad (100)$$

The expansion (88) of the TCL generator $\tilde{\mathcal{S}}$ contains $\tilde{\mathcal{G}}$ as the first term, but it is followed by an infinite series of additional terms.

## H. The stationary state

Global conservation of probability implies that a stationary solution of any well-formed Pauli ME exists. Equation (24) then shows that the TCL generator $\tilde{\mathcal{S}}$ must have a right eigenoperator $\rho_{\text{stat}}$ to the eigenvalue zero. Due to the $\tilde{\mathcal{P}}$ projections in $\tilde{\mathcal{S}}$, this right eigenoperator must be of the form

$$\rho_{\text{stat}} = \rho_{\text{dot}}^{\text{stat}} \otimes \rho_{\text{leads}}^0, \quad (101)$$

where $\rho_{\text{dot}}^{\text{stat}}$ is diagonal.

Applying Eq. (92) to $\rho_{\text{stat}}$, only the $M = 0$ term in the sum survives and we obtain $0 = [[0]]\,\rho_{\text{stat}}$, which together with Eq. (100) implies

$$\tilde{\mathcal{G}}\,\rho_{\text{stat}} = 0. \quad (102)$$

The reverse is also true: If $\tilde{\mathcal{G}}\rho'_{\text{stat}} = [[0]]\,\rho'_{\text{stat}} = 0$, then Eq. (88) shows that $\tilde{\mathcal{S}}\rho'_{\text{stat}} = 0$.

Thus, $\rho_{\text{stat}}$ is an exact stationary state *if and only if* $\rho_{\text{stat}}$ is a right eigenoperator of $\tilde{\mathcal{G}}$ to the eigenvalue zero. The exact stationary state can thus be obtained from the regularized $T$ matrix or Nakajima-Zwanzig-Markov-Pauli generator $\tilde{\mathcal{G}}$ alone, in principle. The formal origin of this result is that all corrections to $\tilde{\mathcal{G}}$ in $\tilde{\mathcal{S}}$ contain $\tilde{\mathcal{G}}$ as the rightmost factor [cf. Eq. (88)].

There are two caveats, though: (i) The result does not apply to approximations obtained by truncating the perturbative expansion in $H_{\text{hyb}}$. It does work trivially at second order since $\tilde{\mathcal{G}}^{(2)} = \tilde{\mathcal{S}}^{(2)}$. But, already at fourth order, the TCL Pauli ME for the stationary state reads as

$$-i\, ([0] + [0,0,0] - [1][0])\, \rho_{\text{stat}} = 0, \quad (103)$$

whereas the Nakajima-Zwanzig-Markov-Pauli ME is

$$-i \left([0] + [0,0,0]\right) \rho_{\text{stat}} = 0, \tag{104}$$

which is not equivalent. (ii) The result does not carry over to time-dependent solutions. Indeed, if $\rho$ is any eigenoperator of $\tilde{\mathcal{S}}$ to the eigenvalue $\lambda$, Eq. (92) gives

$$i\lambda\rho = \sum_{M=0}^{\infty} (-i\lambda)^M \left[[M]\right] \rho. \tag{105}$$

For $\lambda \neq 0$, this does not imply anything for the eigenoperators of $\tilde{\mathcal{G}} = -i \left[[0]\right]$. Conversely, knowing an eigenoperator of $\tilde{\mathcal{G}}$ to a nonzero eigenvalue does not help in finding an eigenoperator of the TCL generator. For the dynamics, the regularized $T$ matrix or Nakajima-Zwanzig-Markov-Pauli generator $\tilde{\mathcal{G}}$ is not sufficient.

### III. SUMMARY AND CONCLUSIONS

The dynamics of a quantum dot coupled to electronic leads can be described in the master-equation formalism. To use this formalism beyond the regime of weak hybridization between dot and leads, further insight into the structure of higher-order terms is required. With this motivation, we have derived Pauli master equations (rate equations) for the probabilites of dot states, to all orders in the hybridization, and both in time-convolutionless and time-nonlocal (Nakajima-Zwanzig) form. Our approach uses a projection superoperator $\tilde{\mathcal{P}}$ onto product states with diagonal reduced density matrix. To fourth order, the reduction to the probabilities has been implemented in Refs. 24 and 26 by explicitly eliminating the off-diagonal components from a Nakajima-Zwanzig–type ME. Our approach leads to more compact superoperator expressions and is easily generalized to all orders.

Furthermore, we have presented a superoperator derivation of the $T$-matrix expression for the Pauli ME and showed that it fails to take into account the propagation of the density operator from the present time $t$ back to an initial time $t_0$. This answers the question posed in Ref. 23 as to whether it is possible to derive the Pauli master equation within the $T$-matrix formalism instead of using it *ad hoc* to calculate the transition rates. The superoperator formalism has allowed us to establish relationships between the TCL Pauli generator $\tilde{\mathcal{S}}$, the NZ generator in the Markov approximation (exact for the stationary state), $\tilde{\mathcal{G}}$, and the $T$-matrix generator $\tilde{\mathcal{R}}$. The off-diagonal components of these generators are the transition rates in the respective pictures. Relations between the expansion terms of order $2\mu$, $\tilde{\mathcal{S}}^{(2\mu)}$, $\tilde{\mathcal{G}}^{(2\mu)}$, and $\tilde{\mathcal{R}}^{(2\mu)}$, respectively, have been given. In particular, the expansion terms $\tilde{\mathcal{S}}^{(2\mu)}$ of the TCL Pauli generator are the sum of the corresponding terms $\tilde{\mathcal{G}}^{(2\mu)}$ order by order, plus corrections, which come from propagating the density operator backward in time in Eq. (12). Only at the second (lowest) order are the expressions identical. We have shown that both the Nakajima-Zwanzig-Markov-Pauli and the TCL Pauli generators converge in the limit $\eta \to 0^+$, order by order. Here, $\eta$ is the rate with which the hybridization is switched on. In the NZ case, the absence of divergences readily emerges from the superoperator expressions, in which the secular reducible terms are

explicitly projected out, whereas for the TCL Pauli generator it relies on a sweeping cancellation of negative powers of $\eta$.

It is crucial for the derivation that the averages of lead operators satisfy Wick's theorem, i.e., that they can be decomposed into averages of pairs. Aside from reservoirs consisting of free fermions as considered here, an analogous derivation should be possible for free bosons.

As is well known, the $T$-matrix rates diverge for $\eta \to 0^+$. Specifically, the term $\tilde{\mathcal{R}}^{(2\mu)}$ diverges as $1/\eta^{\mu-1}$. The divergence noted for the fourth-order term by Averin[49] thus becomes even stronger at higher orders. We have shown that the Nakajima-Zwanzig-Markov-Pauli rates $\tilde{\mathcal{G}}^{(2\mu)}$ are identical, order by order, to the $T$-matrix rates with proper regularization. This might lead to an advantage in practical calculations, as the $T$-matrix method formulated using ordinary operators instead of superoperators is expected to be easier to implement. This regularization differs from the one proposed by Turek and Matveev.[26,38,48]

As a consistency check, we have shown that the stationary state obtained from the Nakajima-Zwanzig-Markov-Pauli ME is the exact one, i.e., it is identical to the stationary solution of the TCL ME. It is quite interesting how this result comes about: $\tilde{\mathcal{S}}$ can be written as $\tilde{\mathcal{G}}$ plus corrections that all have $\tilde{\mathcal{S}}$ as the rightmost factor again [cf. Eqs. (92) and (100)]. The result does not carry over to expansions truncated at finite order or to time-dependent solutions, though.

Another relation between the expansion terms, Eq. (88), is also important: all correction terms in $\tilde{\mathcal{S}}^{(2\mu)}$ beyond $\tilde{\mathcal{G}}^{(2\mu)}$ have factors $\tilde{\mathcal{G}}^{(2\mu')}$ of lower order $\mu' < \mu$ at their right end. Consider the case that all $\tilde{\mathcal{G}}^{(2\mu')}$ for $\mu' < \mu_c$ are suppressed but $\tilde{\mathcal{G}}^{(2\mu_c)}$ is not. Then, all corrections in $\tilde{\mathcal{S}}^{(2\mu_c)}$ beyond the Nakajima-Zwanzig-Markov-Pauli term $\tilde{\mathcal{G}}^{(2\mu_c)}$ are also small. For example, in the Coulomb-blockade regime, $\tilde{\mathcal{G}}^{(2)}$ is suppressed, but $\tilde{\mathcal{G}}^{(4)}$ is not. Then, the corrections to the co-tunneling rates are small in the Coulomb-blockade regime since they involve sequential-tunneling rates. On the other hand, deep in the sequential-tunneling regime, all fourth-order terms are small compared to the sequential-tunneling rates if hybridization is weak. However, close to a threshold where some $\tilde{\mathcal{G}}^{(2\mu')}$ crosses over from small to large, for example, at the Coulomb-blockade threshold, the corrections can be comparable to the NZ rates.

Of course, outside of the perturbative regime, there is no *a priori* reason for any term to be small. It is in this intermediate coupling regime[50] that we expect the TCL Pauli ME to all orders to show its power. Since the TCL ME describes the dynamics exactly, not just the stationary state, and is local in time, it is promising for resummation schemes addressing for example the dynamical nonequilibrium Kondo effect.

## APPENDIX A: PROOF OF THE CONVERGENCE OF CERTAIN SUPEROPERATORS FOR $\eta \to 0^+$

We want to show that the limit for $\eta \to 0^+$ in Eq. (73) exists and is finite for all non-negative integers $m_{2\mu-1}, m_{2\mu-2}, \ldots, m_{2\mu'+1}$, where $\mu > \mu' \geqslant 0$. It is useful to prove a more general statement: For $\mu = 1, 2, \ldots$, the limit for $\eta \to 0^+$ of the superoperator

$$\tilde{\mathcal{P}} \mathcal{L}_{\text{hyb}} (-\mathcal{L}_0 + c_{2\mu-1} i\eta)^{-1-m_{2\mu-1}} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{Q}}$$
$$\times (-\mathcal{L}_0 + c_{2\mu-2} i\eta)^{-1-m_{2\mu-2}} \mathcal{L}_{\text{hyb}} \cdots$$
$$\times \mathcal{L}_{\text{hyb}} (-\mathcal{L}_0 + c_1 i\eta)^{-1-m_1} \mathcal{L}_{\text{hyb}} \tilde{\mathcal{P}}, \quad \text{(A1)}$$

where $\tilde{\mathcal{Q}}$ is inserted at all even-numbered positions, exists and is finite for all non-negative integers $m_{2\mu-1}, m_{2\mu-2}, \ldots, m_1$ and all positive real numbers $c_{2\mu-1}, c_{2\mu-2}, \ldots, c_1$. By a finite limit of a superoperator, we mean a finite limit of all its matrix elements.[51]

By inserting the completeness relation

$$\bullet = \sum_{ij} |i\rangle\langle i| \bullet |j\rangle\langle j| = \sum_{ij} \langle i| \bullet |j\rangle \, |i\rangle\langle j| \quad \text{(A2)}$$

in suitable places, the matrix elements of Eq. (A1) can be expressed in terms of matrix elements of $\mathcal{L}_0$, $\mathcal{L}_{\text{hyb}}$, and $\tilde{\mathcal{Q}}$ alone. The matrix elements of $\mathcal{L}_0$ are

$$\text{Tr} \, |i\rangle\langle j| \mathcal{L}_0 |k\rangle\langle l| = \delta_{jk}\delta_{il} (E_k - E_l). \quad \text{(A3)}$$

Here, $E_k$ and $E_l$ are eigenenergies of $H_0$, including dot and lead contributions. The former are discrete and, by assumption, nondegenerate, whereas the latter have a continuous spectrum. The proposition could fail if a zero matrix element of $\mathcal{L}_0$ occurred in Eq. (A1).

At this point, it is useful to go over to a single-particle description of the leads. As noted in Sec. II C, the projections $\tilde{\mathcal{P}}$ in Eq. (A1) introduce equilibrium averages, $\text{tr}_{\text{leads}} \cdots \rho_{\text{leads}}^0$, over lead-electron creation and annihilation operators. These averages are nonzero only if all lead operators are paired. In the expression (A1), which is of order $2\mu$ in $\mathcal{L}_{\text{hyb}}$, there are $\mu$ such pairs.

Consider a certain inverse superoperator $(-\mathcal{L}_0 + c_\nu i\eta)^{-1-m_\nu}$ in Eq. (A1). Some of the paired lead operators may straddle its position, which is numbered by $\nu$. For two paired lead operators that are both to the right of this position, the superoperator $(-\mathcal{L}_0 + c_\nu i\eta)^{-1-m_\nu}$ acts on an operator that is diagonal in the single-electron state associated with the paired operators. Its energy thus does not appear in the difference $E_k - E_l$ in Eq. (A3). Consequently, only lead-operator pairs that straddle the position $\nu$ contribute to the energy difference. Let us denote the number of such pairs by $\zeta_\nu \geqslant 0$. Then, the difference $E_k - E_l$ has the form $E_n - E_{n'} + \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p\nu i}$, where $E_n$, $E_{n'}$ now denote the energies of the *dot* many-particle eigenstates $|n\rangle$ and $|n'\rangle$, respectively, and the $\Delta\epsilon_p$, $p = 1, 2, \ldots, \mu$ are lead single-electron energies. There are $\mu$ such energies, which are independently integrated over from $-\infty$ to $\infty$. The ordering of the two $\mathcal{L}_{\text{hyb}}$ insertions where the corresponding lead electron is created and annihilated determines whether this energy enters with a plus or minus sign in the energy differences coming from the $\mathcal{L}_0$ sandwiched between these two $\mathcal{L}_{\text{hyb}}$. The single-particle energy enters with the same sign in all these factors. It is thus possible to absorb all minus signs into the definitions of $\Delta\epsilon_p$.

The integrand in the integrals over $\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu$ assumes the general form

$$\frac{F(\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu)}{\prod_{\nu=1}^{2\mu-1} \left( E_{n_\nu} - E_{n'_\nu} + \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p\nu i} + c_\nu i\eta \right)^{1+m_\nu}}, \quad \text{(A4)}$$

where the function $F$ contains the remaining dependence on the single-electron energies due to Fermi functions and possibly energy-dependent densities of states and tunneling amplitudes. $F$ is assumed to be a real analytic and bounded function of its arguments. Note that, for perfect crystals, this does not hold due to the appearance of van Hove singularities in the density of states. Any disorder will remove these, though.

We rewrite the expression (A4) by introducing two sets of auxiliary variables $x_\nu$ and $\lambda_\nu$,

$$F(\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu) \int dx_1 \cdots dx_{2\mu-1} \prod_{\nu=1}^{2\mu-1} \frac{\delta\left(x_\nu - \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p\nu i}\right)}{(E_{n_\nu} - E_{n'_\nu} + x_\nu + c_\nu i\eta)^{1+m_\nu}}$$

$$= F(\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu) \int dx_1 \cdots dx_{2\mu-1} \int \frac{d\lambda_1}{2\pi} \cdots \frac{d\lambda_{2\mu-1}}{2\pi} \prod_{\nu=1}^{2\mu-1} \frac{\exp\left[i\lambda_\nu\left(x_\nu - \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p\nu i}\right)\right]}{(E_{n_\nu} - E_{n'_\nu} + x_\nu + c_\nu i\eta)^{1+m_\nu}}. \quad \text{(A5)}$$

The integrand as a function of $x_\nu$ has a pole of order $1 + m_\nu$ in the negative half-plane. Furthermore, it vanishes rapidly for $x_\nu \to +i\infty$ ($x_\nu \to -i\infty$) if $\lambda_\nu \geqslant 0$ ($\lambda_\nu \leqslant 0$). The only possible exception is the case of $m_\nu = 0$ and $\lambda_\nu = 0$, which we exclude now and treat separately later. Hence, we can close the integration contour in the upper (lower) half-plane and obtain

$$\int dx_\nu \frac{\exp\left[i\lambda_\nu\left(x_\nu - \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p\nu i}\right)\right]}{(E_{n_\nu} - E_{n'_\nu} + x_\nu + c_\nu i\eta)^{1+m_\nu}} = \begin{cases} 0 & \text{for } \lambda_\nu \geqslant 0, \\ -\frac{2\pi i}{m_\nu!} (i\lambda_\nu)^{m_\nu} \exp\left[-i\lambda_\nu\left(E_{n_\nu} - E_{n'_\nu} + \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p\nu i} + c_\nu i\eta\right)\right] & \text{for } \lambda_\nu \leqslant 0. \end{cases} \quad \text{(A6)}$$

Note that, for $m_\nu \geqslant 1$, the case $\lambda_\nu = 0$, which is included in both lines, is consistent. On the other hand, for $m_\nu = 0$ this case was excluded. We find that Eq. (A6) shows a step discontinuity at $\lambda_\nu = 0$ for $m_\nu = 0$. The result after performing the integral over $\lambda_\nu$ does not depend on the value at a single point, though. The expression in Eqs. (A4) and (A5) now becomes

$$F(\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu) \int_{-\infty}^0 d\lambda_1 \frac{-i^{1+m_1}\lambda_1^{m_1}}{m_1!} \cdots \int_{-\infty}^0 d\lambda_{2\mu-1} \frac{-i^{1+m_{2\mu-1}}\lambda_{2\mu-1}^{m_{2\mu-1}}}{m_{2\mu-1}!} \exp\left[-i \sum_{\nu=1}^{2\mu-1} \lambda_\nu \left(E_{n_\nu} - E_{n'_\nu} + \sum_{i=1}^{\zeta_\nu} \Delta\epsilon_{p_{\nu i}} + c_\nu i\eta\right)\right]$$

$$= F(\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu) \int_{-\infty}^0 d\lambda_1 \frac{-i^{1+m_1}\lambda_1^{m_1} e^{c_1\eta\lambda_1}}{m_1!} \exp\left[-i\lambda_1\left(E_{n_1} - E_{n'_1}\right)\right] \cdots \int_{-\infty}^0 d\lambda_{2\mu-1}$$

$$\times \frac{-i^{1+m_{2\mu-1}}\lambda_{2\mu-1}^{m_{2\mu-1}} e^{c_{2\mu-1}\eta\lambda_{2\mu-1}}}{m_{2\mu-1}!} \exp\left[-i\lambda_{2\mu-1}\left(E_{n_{2\mu-1}} - E_{n'_{2\mu-1}}\right)\right] \exp\left[-i\sum_{p=1}^\mu \left(\lambda_{\nu_p^-} + \cdots + \lambda_{\nu_p^+}\right)\Delta\epsilon_p\right], \tag{A7}$$

where $\nu_p^-$ ($\nu_p^+$) is the first (last) position for which the single-electron energy $\Delta\epsilon_p$ appears in the energy denominators in Eq. (A4).

Integrating Eq. (A7) over all $\Delta\epsilon_p$, we obtain

$$\int_{-\infty}^0 d\lambda_1 \frac{-i^{1+m_1}\lambda_1^{m_1} e^{c_1\eta\lambda_1}}{m_1!} \exp\left[-i\lambda_1\left(E_{n_1} - E_{n'_1}\right)\right] \cdots \int_{-\infty}^0 d\lambda_{2\mu-1} \frac{-i^{1+m_{2\mu-1}}\lambda_{2\mu-1}^{m_{2\mu-1}} e^{c_{2\mu-1}\eta\lambda_{2\mu-1}}}{m_{2\mu-1}!}$$

$$\times \exp\left[-i\lambda_{2\mu-1}\left(E_{n_{2\mu-1}} - E_{n'_{2\mu-1}}\right)\right] \hat{F}\left(\lambda_{\nu_1^-} + \cdots + \lambda_{\nu_1^+}, \ldots, \lambda_{\nu_\mu^-} + \cdots + \lambda_{\nu_\mu^+}\right) \tag{A8}$$

with the Fourier transform

$$\hat{F}(\kappa_1, \ldots, \kappa_\mu) := \int d\Delta\epsilon_1 \, e^{-i\kappa_1\Delta\epsilon_1} \cdots \int d\Delta\epsilon_\mu \, e^{-i\kappa_\mu\Delta\epsilon_\mu}$$
$$\times F(\Delta\epsilon_1, \ldots, \Delta\epsilon_\mu). \tag{A9}$$

If there are no lead-operator pairs straddling the position $\nu$, i.e., $\zeta_\nu = 0$, the variable $\lambda_\nu$ does not occur in $\hat{F}$ in Eq. (A8). The integral over $\lambda_\nu$ can then be evaluated and is proportional to $[c_\nu\eta - i(E_{n_\nu} - E_{n'_\nu})]^{-1-m_\nu}$. If, in addition, $E_{n_\nu} - E_{n'_\nu}$ vanishes, we obtain a divergence for $\eta \to 0^+$. But, by our assumption of nondegenerate dot states, $E_{n_\nu} = E_{n'_\nu}$ implies $|n_\nu\rangle = |n'_\nu\rangle$. Thus, for this contribution, the dot density matrix is diagonal at position $\nu$. Because of $\zeta_\nu = 0$, we can then insert a projection $\tilde{\mathcal{P}}$ without changing the result. But there is already a projection $\tilde{\mathcal{Q}}$ at this (even-numbered) position and we obtain $\tilde{\mathcal{P}}\tilde{\mathcal{Q}} = 0$. The divergent term is thus removed. On the other hand, for $E_{n_\nu} \neq E_{n'_\nu}$ there is no divergence.

It remains to consider the case of at least one lead-operator pair straddling position $\nu$. Then, $\lambda_\nu$ does occur in $\hat{F}$. We now consider the properties of the functions $F$ and $\hat{F}$. The behavior of $F$ at large $|\Delta\epsilon_p|$ should not affect the transport and we can therefore assume that $F$ vanishes sufficiently rapidly and sufficiently smoothly for $\Delta\epsilon_p \to \pm\infty$. We thus assume that all derivatives $\partial^n F/\partial\Delta\epsilon_p^n$, $n = 0, 1, 2, \ldots$, vanish for $\Delta\epsilon_p \to \pm\infty$ and that all these derivatives are absolutely integrable in $\Delta\epsilon_p$ over the real axis. These assumptions require the previously discussed analyticity property. Under these conditions, we have $\lim_{\kappa_p \to \pm\infty} \kappa_p^n \hat{F} = 0$ for all $n = 0, 1, 2, \ldots$ and all $p = 1, \ldots, \mu$. Thus, the Fourier transform $\hat{F}$ falls off faster than any power for $\kappa_p \to \pm\infty$ for all $p$.

It follows that $\hat{F}$ falls off faster than any power for $\lambda_\nu \to -\infty$. Thus, the integral over $\lambda_\nu$ in Eq. (A8) converges for any $m_\nu$, $E_{n_\nu} - E_{n'_\nu}$, and $\eta \geqslant 0$. It thus converges pointwise for $\eta \to 0^+$. The convergence is also uniform since the integrand

in Eq. (A8) is bounded in absolute value by the integrand in the expression

$$\int_{-\infty}^0 d\lambda_1 \frac{\lambda_1^{m_1}}{m_1!} \cdots \int_{-\infty}^0 d\lambda_{2\mu-1} \frac{\lambda_{2\mu-1}^{m_{2\mu-1}}}{m_{2\mu-1}!}$$

$$\times \left|\hat{F}\left(\lambda_{\nu_1^-} + \cdots + \lambda_{\nu_1^+}, \ldots, \lambda_{\nu_\mu^-} + \cdots + \lambda_{\nu_\mu^+}\right)\right| \tag{A10}$$

and this integral converges.

In summary, all terms generated by taking the relevant matrix elements of Eq. (A1) and introducing the completeness relation (A2) remain finite for $\eta \to 0^+$. Since the number of these terms is finite, the whole quantity remains finite. The convergence is uniform.

## APPENDIX B: PROOF OF THE IDENTITY OF CERTAIN SUPEROPERATORS

To prove the cancellation of divergences in Sec. II F, we also need to show that the superoperators $[m_{2\mu-1}, m_{2\mu-2}, \ldots, m_{2\mu'+1}]^{(2\mu, 2\mu')}$ defined in Eq. (73) do not depend on the values of the prefactors of $i\eta$, as long as these are all positive. Therefore, we now prove the following statement: In the limit $\eta \to 0^+$, the superoperator in Eq. (A1) is independent of $c_{2\mu-1}, c_{2\mu-2}, \ldots, c_1$ for all non-negative integers $m_{2\mu-1}, m_{2\mu-2}, \ldots, m_1$ and all positive real numbers $c_{2\mu-1}, c_{2\mu-2}, \ldots, c_1$.

As shown in Appendix C, this limit is finite. The derivative of (A1) with respect to $c_\nu$ is

$$-i(1 + m_\nu)\eta \, \tilde{\mathcal{P}} \, \mathcal{L}_{\text{hyb}} \left(-\mathcal{L}_0 + c_{2\mu-1} i\eta\right)^{-1-m_{2\mu-1}}$$

$$\times \mathcal{L}_{\text{hyb}} \, \tilde{\mathcal{Q}} \cdots \left(-\mathcal{L}_0 + c - \nu i\eta\right)^{-2-m_\nu} \cdots \mathcal{L}_{\text{hyb}} \, \tilde{\mathcal{P}}. \tag{B1}$$

The derivative and the limit $\eta \to 0^+$ commute because (i) the expression (A1) is differentiable with respect to $c_\nu$ for all $\eta > 0$, (ii) it converges pointwise for $\eta \to 0^+$ as shown in Appendix C, and (iii) its derivative with respect to $c_\nu$ converges uniformly for $\eta \to 0^+$ (this is shown by a trivial modification of the proof in Appendix C noting that the factor $\eta$ is bounded by unity for $0 < \eta \leqslant 1$).

In Eq. (B1), the part $\tilde{\mathcal{P}} \cdots \tilde{\mathcal{P}}$ has a finite limit for $\eta \to 0^+$, as shown in Appendix C. Including the extra factor of $\eta$, the limit vanishes. Consequently, the expression (A1) is a constant function of $c_{2\mu-1}, c_{2\mu-2}, \ldots, c_1$.

## APPENDIX C: EVALUATION OF PREFACTORS IN THE SUPEROPERATOR EXPANSION

In this appendix, we evaluate the functions $f$ defined in Eq. (80), which appear as prefactors in the expansion of the TCL generator in powers of $\eta$. We first consider the case $p = 0$, which is more easily done for the original expression in Eq. (77). This expression does not contain any sum since $n_p = n_0$ is fixed, $n'$ equals zero because of $\mu'_p = \mu'_0 = 0$, and we obtain

$$f(n_0; m_{0,2n_0-1}, \ldots, m_{0,1})$$
$$= (2\mu_0 - 1)^{m_{0,2n_0-1}}(2n_0 - 2)^{m_{0,2n_0-2}} \cdots 1^{m_{0,1}}. \quad \text{(C1)}$$

Since we are only interested in the case $\Sigma_m = M_0 \leqslant p = 0$, the only possibility is $M_0 = 0$ and, thus, $m_{0,\nu} = 0$ for all $\nu$, giving $f(n_0; 0, \ldots, 0) = 1$.

For $p \geqslant 1$, we evaluate Eq. (80) by iteration. We first perform the sum over $\pi_0^Z$. The term under the sum is a polynomial in $2\pi_0^Z \mu_1$ of order $M_0$. The zero-order term in this polynomial vanishes when the sum is performed due to the factor $(-1)^{\pi_0^Z}$. In particular, for $M_0 = 0$, this is the only term and the whole expression vanishes, $f(n_0, n_1, \ldots, n_p; 0, \ldots, 0, m_{1,2\mu_1-1}, \ldots, m_{p,1}) = 0$. For $M_0 \geqslant 1$, in all remaining terms of orders $1, \ldots, M_0$ in $2\pi_0^Z \mu_1$, only the $\pi_0^Z = 1$ contribution survives. We thus obtain a polynomial of order $M_0$ in $2\mu_1$ with the zero-order term missing. It is thus possible to cancel a factor of $2\mu_1$ with the same factor in the denominator. What remains is a polynomial in $2\mu_1$ of order $M_0 - 1 \geqslant 0$.

Now we combine this polynomial with the factors $(2\mu_1 - 1)^{m_{1,2\mu_1-1}}(2\mu_1 - 2)^{m_{1,2\mu_1-2}} \cdots (2\mu_1 - 2n_1 + 1)^{m_{1,2\mu_1-2n_1+1}}$ in Eq. (80). These represent a polynomial in $2\mu_1$ of order $M_1 \geqslant 0$. The product is thus a polynomial of order $M_0 + M_1 - 1 \geqslant 0$. Using $\mu_1 = n_1 + \pi_1^Z \mu_2$, we obtain polynomials in $2\pi_1^Z \mu_2$ of order $M_0 + M_1 - 1$. If $M_0 + M_1 - 1 = 0$ and $p = 1$, $\pi_1^Z = 0$

is fixed and we obtain a nonzero result. If $M_0 + M_1 - 1 = 0$ and $p \geqslant 2$, we can perform the sum over $\pi_1^Z$. However, only the factor $(-1)^{\pi_1^Z}$ depends on $\pi_1^Z$ and $f$ vanishes.

If $M_0 + M_1 - 1 \geqslant 1$, we necessarily have $\Sigma_m \geqslant 2$. Then, we only have to consider $p \geqslant 2$ and there exists a sum over $\pi_1^Z \mu_2$. As before, the zero-order term in the polynomial in $2\pi_1^Z \mu_2$ cancels and the other terms only survive for $\pi_1^Z = 1$. The result is a polynomial in $2\mu_2$ of order $M_0 + M_1 - 1 \geqslant 1$ with the zero-order term missing. Canceling a factor $2\mu_2$ with the denominator, we obtain a polynomial in $2\mu_2$ of order $M_0 + M_1 - 2 \geqslant 0$, which we combine with the following term to give a polynomial of order $M_0 + M_1 + M_2 - 2 \geqslant 0$. Analogously to the above, if $M_0 + M_1 + M_2 - 2 \geqslant 0$ and $p = 2$, we obtain a nonzero result, whereas for $M_0 + M_1 + M_2 - 2 \geqslant 0$ and $p \geqslant 3$ we get $f = 0$. If $M_0 + M_1 + M_2 - 2 \geqslant 1$, which requires $\Sigma_m \geqslant 3$, we iterate these steps.

We obtain $f = 0$ if there exists an integer $i < p$ with

$$M_0 + M_1 + \cdots + M_i - i = 0. \quad \text{(C2)}$$

We obtain $f \neq 0$ if this condition is not satisfied and

$$M_0 + M_1 + \cdots + M_p - p \equiv \Sigma_m - p = 0. \quad \text{(C3)}$$

This implies that $M_0 \geqslant 1$, $M_0 + M_1 - 1 \geqslant 1$, $M_0 + M_1 - 1 + M_2 - 1 \geqslant 1$, etc., and thus

$$M_0 + M_1 + \cdots + M_i - i \geqslant 1 \quad \text{(C4)}$$

for all $i < p$. Finally, if $M_0 + M_1 + \cdots + M_p - p \equiv \Sigma_m - p < 0$, there must exist an $i < p$ such that condition (C2) is satisfied and we obtain $f = 0$.

We draw some conclusions for the case of nonzero $f$ with $\Sigma_m = p$. Since $M_0 + M_1 - 1 + \cdots + M_{p-1} - 1 \geqslant 1$ and $M_0 + M_1 - 1 + \cdots + M_p - 1 = 0$, we find $M_p = 0$. This implies that $M_0 + M_1 - 1 + \cdots + M_{p-1} - 1 = 1$. Since further $M_0 + M_1 - 1 + \cdots + M_{p-2} - 1 \geqslant 1$, we conclude that $M_{p-1} \leqslant 1$. By iteration we find that $M_i \leqslant p - i$.

The next goal is to find the nonzero values of $f$ for all cases with $\Sigma_m = p$. For $p = 0$, we have found $f(n_0; 0, \ldots, 0) = 1$. For $p \geqslant 1$, we already know that $m_{p,2\mu_p-1} = m_{p,2\mu_p-2} = \cdots = m_{p,1} = 0$ is required for a nonzero result. Equation (80) then assumes the form

$$f(n_0, n_1, \ldots, n_p; m_{0,2\mu_0-1}, \ldots, m_{p-1,2\mu_{p-1}-2n_{p-1}+1}, 0, \ldots, 0)$$

$$= (-1)^p \sum_{\pi_0^Z, \pi_1^Z, \ldots, \pi_{p-1}^Z = 0}^{1} \frac{\prod_{i=0}^{p-1}(-1)^{\pi_i^Z}}{2\mu_1 2\mu_2 \cdots 2\mu_p} (2\mu_0 - 1)^{m_{0,2\mu_0-1}}(2\mu_0 - 2)^{m_{0,2\mu_0-2}} \cdots$$

$$\times (2\mu_0 - 2n_0 + 1)^{m_{0,2\mu_0-2n_0+1}} \cdots (2\mu_{p-1} - 1)^{m_{p-1,2\mu_{p-1}-1}}(2\mu_{p-1} - 2)^{m_{p-1,2\mu_{p-1}-2}} \cdots 1^{m_{p-1,2\mu_{p-1}-2n_{p-1}+1}}. \quad \text{(C5)}$$

The factors following the fraction contain exactly $p$ factors of the form $2\mu_i - \nu = 2(n_i + \pi_i^Z n_{i+1} + \pi_i^Z \pi_{i+1}^Z n_{i+2} + \cdots) - \nu$ with $i \in \{0, \ldots, p-1\}$ and $\nu \in \{1, \ldots, 2n_i - 1\}$, where for $m_{i\nu} \geqslant 2$ we count $m_{i\nu}$ factors. We rewrite this product as $\prod_{k=0}^{p-1}(2\mu_{i_k} - \nu_k)$, where we assume, without loss of generality, $0 \leqslant i_0 \leqslant i_1 \leqslant \cdots \leqslant i_{p-1} \leqslant p - 1$ and $\nu_k \leqslant \nu_{k'}$ if $i_k = i_{k'}$ and $k < k'$. Then the condition $M_0 + M_1 + \cdots + M_i - i \geqslant 1$ for $i < p$ implies $i_k \leqslant k$ for all $k$. Thus, we have

$$f(n_0, n_1, \ldots, n_p; m_{0,2\mu_0-1}, \ldots, 0) = (-1)^p \sum_{\pi_0^Z, \pi_1^Z, \ldots, \pi_{p-1}^Z = 0}^{1} \prod_{i=0}^{p-1}(-1)^{\pi_i^Z} \frac{\prod_{k=0}^{p-1}(2\mu_{i_k} - \nu_k)}{\prod_{i=1}^{p} 2\mu_i}$$

$$=: \tilde{f}_p(n_0, n_1, \ldots, n_p; i_0, i_1, \ldots, i_{p-1}; \nu_0, \nu_1, \ldots, \nu_{p-1}), \quad \text{(C6)}$$

where the subscript in $\tilde{f}_p$ refers to the number of factors $2\mu_{i_k} - \nu_k$ in the numerator.

By adding and subtracting a constant, we can write for any $j \in \{0, \ldots, p-1\}$ and any real number $c$,

$$\tilde{f}_p(n_0,n_1,\ldots,n_p;i_0,i_1,\ldots,i_{p-1};v_0,v_1,\ldots,v_{p-1}) = \tilde{f}_p(n_0,\ldots,n_p;i_0,\ldots,i_{p-1};v_0,\ldots,v_{j-1},c,v_{j+1},\ldots,v_{p-1})$$
$$- (v_j - c)\,\tilde{f}_{p-1}(n_0,\ldots,n_p;i_0,\ldots,i_{j-1},i_{j+1},\ldots,i_{p-1};v_0,\ldots,v_{j-1},v_{j+1},\ldots,v_{p-1}). \tag{C7}$$

The second term on the right-hand side contains $\tilde{f}_{p-1}$, which has $\Sigma_m = p - 1$ factors $2\mu_{i_k} - v_k$ in the numerator. We have shown above that, for $\Sigma_m < p$, the term $f$ vanishes. Thus, only the first term remains and we find that $f = \tilde{f}_p$ does not depend on $v_j$ for any $j$. Thus, we can replace $v_j$ by $2(n_{i_j} + n_{i_{j+1}} + \cdots + n_j)$ (recall that $i_j \leqslant j$ for all $j$) without changing the value of $f$. We obtain

$$\tilde{f}_p(n_0,n_1,\ldots,n_p;i_0,i_1,\ldots,i_{p-1};v_0,v_1,\ldots,v_{p-1})$$
$$= (-1)^p \sum_{\pi_0^Z,\pi_1^Z,\ldots,\pi_{p-1}^Z=0}^{1} \prod_{i=0}^{p-1} (-1)^{\pi_i^Z}$$
$$\times \frac{\prod_{k=0}^{p-1} 2\big(n_{i_k} + \pi_{i_k}^Z \mu_{i_k+1} - n_{i_k} - n_{i_k+1} - \cdots - n_k\big)}{\prod_{i=1}^{p} 2\mu_i}. \tag{C8}$$

The factor for $k = 0$ in the numerator contains $i_k = i_0 = 0$ and thus reads $2(n_0 + \pi_0^Z \mu_1 - n_0) = 2\pi_0^Z \mu_1$. In the factor for $k = 1$ we have to distinguish the two cases $i_1 = 0, 1$. For $i_1 = 0$, the corresponding factor in the numerator reads as $2(n_0 + \pi_0^Z \mu_1 - n_0 - n_1) = 2(\pi_0^Z n_1 + \pi_0^Z \pi_1^Z \mu_2 - n_1)$. This factor is

multiplied by $\pi_0^Z$ from the $k = 0$ factor. Since $(\pi_i^Z)^2 = \pi_i^Z$, we can drop the $\pi_0^Z$ in the $k = 1$ factor and write it as $2(n_1 + \pi_1^Z \mu_2 - n_1) = 2\pi_1^Z \mu_2$. If instead $i_1 = 1$, the $k = 1$ factor reads $2(n_1 + \pi_1^Z \mu_2 - n_1) = 2\pi_1^Z \mu_2$. We thus obtain the same result in both cases.

For larger $k$, the factor in the numerator reads as

$$2(n_{i_k} + \pi_{i_k}^Z n_{i_k+1} + \cdots + \pi_{i_k}^Z \pi_{i_k+1}^Z \cdots \pi_k^Z \mu_{k+1}$$
$$-n_{i_k} - n_{i_k+1} - \cdots - n_k). \tag{C9}$$

Since this factor is multiplied by $\pi_0^Z, \ldots, \pi_{k-1}^Z$ from the factors for $j < k$, we can drop all $\pi_j^Z$ with $j < k$ and obtain simply $2\pi_k^Z \mu_{k+1}$. We finally find

$$\tilde{f}_p(n_0,n_1,\ldots,n_p;i_0,i_1,\ldots,i_{p-1};v_0,v_1,\ldots,v_{p-1})$$
$$= (-1)^p \sum_{\pi_0^Z,\pi_1^Z,\ldots,\pi_{p-1}^Z=0}^{1} \prod_{i=0}^{p-1} (-1)^{\pi_i^Z} \frac{\prod_{k=0}^{p-1} 2\pi_k^Z \mu_{k+1}}{\prod_{i=1}^{p} 2\mu_i}$$
$$= (-1)^p (-1)^p = 1. \tag{C10}$$

We have shown that the coefficients $f$ for $\Sigma_m = p$ vanish if condition (C2) is satisfied and equal unity otherwise.

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[1] L. Bogani and W. Wernsdorfer, Nature Mater. **7**, 179 (2008).

[2] E. A. Osorio, T. Bjørnholm, J.-M. Lehn, M. Ruben, and H. S. J. van der Zant, J. Phys. Condens. Matter **20**, 374121 (2008).

[3] S. Andergassen, V. Meden, H. Schoeller, J. Splettstoesser, and M. R. Wegewijs, Nanotechnology **21**, 272001 (2010).

[4] Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).

[5] N. S. Wingreen and Y. Meir, Phys. Rev. B **49**, 11040 (1994).

[6] M. H. Hettler, J. Kroha, and S. Hershfield, Phys. Rev. B **58**, 5649 (1998).

[7] H. Schoeller and J. König, Phys. Rev. Lett. **84**, 3686 (2000).

[8] A. Rosch, J. Kroha, and P. Wölfle, Phys. Rev. Lett. **87**, 156802 (2001); A. Rosch, J. Paaske, J. Kroha, and P. Wölfle, ibid. **90**, 076804 (2003).

[9] A. Mitra, I. Aleiner, and A. J. Millis, Phys. Rev. B **69**, 245302 (2004).

[10] M. Plihal, D. C. Langreth, and P. Nordlander, Phys. Rev. B **71**, 165321 (2005).

[11] R. Gezzi, T. Pruschke, and V. Meden, Phys. Rev. B **75**, 045324 (2007).

[12] A. Mitra and A. J. Millis, Phys. Rev. B **76**, 085342 (2007).

[13] T. Korb, F. Reininghaus, H. Schoeller, and J. König, Phys. Rev. B **76**, 165316 (2007).

[14] S. G. Jakobs, V. Meden, and H. Schoeller, Phys. Rev. Lett. **99**, 150603 (2007).

[15] F. Elste and C. Timm, Phys. Rev. B **81**, 024421 (2010).

[16] S. Weiss, J. Eckel, M. Thorwart, and R. Egger, Phys. Rev. B **77**, 195316 (2008).

[17] D. Segal, A. J. Millis, and D. R. Reichman, Phys. Rev. B **82**, 205323 (2010).

[18] H. Schoeller and G. Schön, Phys. Rev. B **50**, 18436 (1994); Phys. B (Amsterdam) **203**, 423 (1994).

[19] J. König, H. Schoeller, and G. Schön, Europhys. Lett. **31**, 31 (1995); Phys. Rev. Lett. **76**, 1715 (1996).

[20] J. König, J. Schmid, H. Schoeller, and G. Schön, Phys. Rev. B **54**, 16820 (1996).

[21] S. Braig and K. Flensberg, Phys. Rev. B **68**, 205324 (2003).

[22] H. Bruus and K. Flensberg, Many-Body Quantum Theory in Condensed Matter Physics (Oxford University Press, Oxford, 2004).

[23] C. Timm, Phys. Rev. B **77**, 195416 (2008).

[24] M. Leijnse and M. R. Wegewijs, Phys. Rev. B **78**, 235424 (2008).

[25] H. Schoeller, Eur. Phys. J. Spec. Topics **168**, 179 (2009).

[26] S. Koller, M. Grifoni, M. Leijnse, and M. R. Wegewijs, Phys. Rev. B **82**, 235307 (2010).

[27] S. Nakajima, Prog. Theor. Phys. **20**, 948 (1958).

[28] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); Physica (Amsterdam) **30**, 1109 (1964).

[29] M. Tokuyama and H. Mori, Prog. Theor. Phys. **55**, 411 (1976).

[30] N. Hashitsume, F. Shibata, and M. Shingū, J. Stat. Phys. **17**, 155 (1977); F. Shibata, Y. Takahashi, and N. Hashitsume, ibid. **17**, 171 (1977).

[31] D. Ahn, Phys. Rev. B **50**, 8310 (1994).

[32] H. Akera, Phys. Rev. B **60**, 10683 (1999).

[33] V. N. Golovach and D. Loss, Phys. Rev. B **69**, 245327 (2004).

[34] J. Koch, F. von Oppen, Y. Oreg, and E. Sela, Phys. Rev. B **70**, 195107 (2004); J. Koch, F. von Oppen, and A. V. Andreev, *ibid.* **74**, 205438 (2006).

[35] R. Jorn and T. Seideman, J. Chem. Phys. **124**, 084703 (2006).

[36] F. Elste and C. Timm, Phys. Rev. B **75**, 195341 (2007).

[37] M. C. Lüffe, J. Koch, and F. von Oppen, Phys. Rev. B **77**, 125306 (2008).

[38] G. Begemann, S. Koller, M. Grifoni, and J. Paaske, Phys. Rev. B **82**, 045316 (2010).

[39] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002).

[40] In order to describe a system with degenerate dot states, we could introduce a small *ad hoc* splitting that is sent to zero at the end of the calculation, after taking $\eta$ to zero.

[41] C. Timm, Phys. Rev. E **80**, 021140 (2009).

[42] M. G. Schultz and F. von Oppen, Phys. Rev. B **80**, 033302 (2009).

[43] V. Bužek, Phys. Rev. A **58**, 1723 (1998).

[44] N. G. van Kampen, Physica (Amsterdam) **74**, 215 (1974); **74**, 215 (1974); **74**, 239 (1974).

[45] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

[46] F. Bloch, Phys. Rev. **105**, 1206 (1957).

[47] A. G. Redfield, Adv. Magn. Reson. **1**, 1 (1965).

[48] M. Turek and K. A. Matveev, Phys. Rev. B **65**, 115332 (2002).

[49] D. V. Averin, Phys. B (Amsterdam) **194–196**, 979 (1994).

[50] N. Roch, R. Vincent, F. Elste, W. Harneit, W. Wernsdorfer, C. Timm, and F. Balestro, Phys. Rev. B **83**, 081407(R) (2011).

[51] Matrix elements of superoperators are here understood with reference to the scalar product of ordinary operators, $\langle A, B \rangle := \mathrm{Tr} A^{\dagger} B$. We do not consider problems arising from infinite-dimensional Fock spaces.