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Optical field control of charge transmission through a molecular wire.
I. Generalized master equation description

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A generalized master equation description of charge transmission through a single molecule that goes beyond a perturbative treatment of electron-vibrational coupling and accounts for nonequilibrium vibrational distributions is presented. By utilizing a projection superoperator formalism, exact expressions for the generalized master equation kernels that include intramolecular vibrational energy redistribution, excited electronic levels, as well as their optical excitation and de-excitation are derived. This enables one to study optical current switching in the case of weak electron-lead coupling and large reorganization energy upon charging. Additionally, it is possible to quantify the influence of intramolecular vibrational energy redistribution and excited state de-excitation on the current switching.

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I. INTRODUCTION

A frequent motif in molecular electronic devices is that of a single molecule attached to two nanoelectrodes.[1] Often, the molecule-lead coupling energy is smaller than the energy of molecular vibrational excitation and nuclear rearrangement (NR) upon charging or discharging of the molecule. This necessitates the inclusion of the coupling of transmitted electrons to intramolecular vibrations when computing, for example, *IV* characteristics.[1] A powerful concept to account for electron-vibrational coupling is represented by Born–Oppenheimer potential energy surfaces (PESs) which determine the nuclear motion in the various electronic levels as well as the NR effects upon changing the electronic state.[2]

While electron-vibrational coupling attracted less interest in the early days of theoretical studies on single electron transmission, there is a number of different approaches as reviewed in Ref. 3. In order to underline the specific aspects of the present treatment, we briefly comment on previous routes tackling electron-vibrational coupling (for a more complete list of references, see Ref. 3). They include (i) the nonequilibrium Green function (NGF) technique,[4–7] (ii) the use of density matrix equations[8–16] or (iii) rate (master) as well as generalized rate equations,[17–27] and (iv) scattering theory.[28–31]

The widely used NGF approach has the advantage that it can be efficiently combined with electronic structure calculations (see Ref. 1). However, electron-vibrational coupling is usually considered as a perturbation, i.e., by computing respective self-energies up to second order only. Thus, NR is accounted for approximately, although, upon combining the NGF approach with standard polaron canonical transformation, vibrational sidebands could be described as in Ref. 7.

The use of the density matrix approach traces back to the study of charge transmission through semiconducting quantum dots and is based on a diagrammatic computation of a self-energy-type superoperator[8] (see also Ref. 32). Electron-phonon coupling was also described in a renormalization group approach.[10,11] Other treatments use a density matrix theory which rests on a second-order approximation of the electron-vibrational interaction.[12,14,15] While the renormalization group approach has not been confronted with the results obtained by direct use of the molecular PES, any second-order approximation is, of course, only reliable for weak coupling situations.

There are several approaches considering populations only, i.e., diagonal density matrix elements, which are based on ordinary or generalized rate equations. Two routes can be identified, the first one uses the overall electronic distribution function, often derived systematically from the respective rate equations (see, e.g., Refs. 17–20). The other more sophisticated route rests on electron-vibrational distribution functions also accounting for a vibrational nonequilibrium situation.[21–27] Here, rate equations governing electron-vibrational distribution functions are frequently given without detailed derivations. This has to be considered as being a clear drawback which gives the motivation for the present systematic derivation of such generalized rate equations and respective rate expressions.

Our derivation features the following five key points: (i) The charge transmission through a molecular wire attached to nanoleads is described in a multielectron picture. The different molecular charging states are characterized by the number N of excess electrons. (ii) A many-electron description of the electrons of the metal lead is undertaken. (iii) An important aspect of the present description is that electron-vibrational coupling is fully accounted for via PES. Thus, from the very beginning, one avoids any perturbational treatment of electron-vibrational coupling or, in other words, NR upon changing the electronic state of the molecule is considered nonperturbatively. (iv) Vibrational relaxation is introduced via intramolecular vibrational energy redistribution (IVR). (v) Finally, we incorporate excited electronic states of the molecule. Hence, it is possible to model the effects of optical excitation of the molecule during charge transmission as well as electronic de-excitation via electron-hole pair generation in the leads.

To our knowledge, a generalized master equation approach that combines excited electronic states with vibrational nonequilibrium states of the neutral and charged molecules including possible excitation and de-excitation of the molecule has not be considered so far. It enables us to suggest optical current switching in the case of weak electron-lead coupling and large reorganization energy upon charging. Furthermore, it becomes possible to quantify the influence of IVR and excited state de-excitation on the current switching. Both issues will be investigated in an accompanying numerical study.[33]

Underlying the present approach is a formulation in terms of molecular adiabatic electronic states, ϕ_{Na}, which describe the presence of $N(=\ldots,-1,0,1,\ldots)$ excess electrons and which refer to the ground state, $a=g$, or some excited state, $a=e$, both referring to the actual charging state. These states are understood to account for the applied voltage V in the stationary current regime and polarization effects of the leads, i.e., we assume that a self-consistent determination of the molecular states has been carried out. In principle, the charged molecular states would require a correct classification with respect to their spin states. This problem, however, is of less importance for the present general study.

In the following, the emphasis lies on the incorporation of particular molecular vibrations which couple strongly to the charge transmission process (so-called reaction coordinates). Electronic states and reaction coordinates form the *active* electron-vibrational degrees of freedom. They will be described by vibrational wave functions $\chi_{Na\nu}$ referring to the particular electronic state, ϕ_{Na}, and being characterized by vibrational quantum numbers ν. The resulting electron-vibrational states, $\Psi_{Na\nu}=\chi_{Na\nu}\phi_{Na}$, form the basis for all considerations hereafter. In particular, the generalized rate equations will be formulated for the respective state populations $P_{Na\nu}(t)$. The approach is based on a projection operator method used already in Ref. 35 and later in Refs. 18 and 36. Moreover, we will also demonstrate how to obtain a current formula within this framework.

The projection operator formalism for the derivation of the generalized rate equation for the populations $P_{Na\nu}(t)$ yields formally exact expressions in terms of integral kernels of the form

$$K_{Ma\mu\to Nb\nu}(t,\bar{t})=\mathrm{tr}\{|\Psi_{Nb\nu}\rangle\langle\Psi_{Nb\nu}|\mathcal{M}(t,\bar{t})\hat{W}^{(\mathrm{eq})}_{Ma\mu}\}. \tag{1}$$

They describe the transfer from the initial state $\Psi_{Ma\mu}$ of the molecule (at time $\bar{t}$) into the final state $\Psi_{Nb\nu}$ (at time t). The initial state is characterized by the equilibrium statistical operator $\hat{W}^{(\mathrm{eq})}_{Ma\mu}$ referring to the equilibrium state of the electrons in the leads as well as to the vibrational equilibrium of all inactive coordinates in the initial state formed by the active degrees of freedom. The transfer to the final state is caused by the transfer superoperator $\mathcal{M}(t,\bar{t})$. It covers all orders with respect to the relevant interactions (molecule-lead coupling, IVR, time-dependent external fields). If $\mathcal{M}$ is considered in second order with respect to the various couplings, standard second-order rate expressions can be obtained straightforwardly.

Although the following formulation is general in principle, and thus also illustrates how to go beyond a low order description, concrete expression will be given for the case of a second-order approximation. Section II introduces the model Hamiltonian. Then, Sec. III briefly demonstrates the construction of a generalized master equation and the derivation of a current formula. Second-order rates for all types of couplings are derived in Sec. IV. The paper concludes with some final remarks in Sec. V.

II. MODEL

The Hamiltonian to be introduced in the following subsections reads as

$$H=H_{\mathrm{mol}}+H_{\mathrm{lead}}+H_{\mathrm{mol\text{-}lead}}. \tag{2}$$

Here, H_{mol} represents the single molecule attached to the two nanoelectrodes. Furthermore, there is a coupling part to the leads, denoted by $H_{\mathrm{mol\text{-}lead}}$, and the metal leads are described by H_{lead}. Again, we stress that the model is based on the introduction of electronic states of the molecule and the leads, which have been self-consistently determined in the presence of an applied voltage (see, for example, Ref. 1).

A. Molecular Hamiltonian

The molecular Hamiltonian H_{mol} is expressed in terms of the adiabatic electronic states ϕ_{Na}, where $N=\ldots,-1,0,1,\ldots$ counts the number of excess electrons (or holes) and a is the specific label for the actual electronic level (recall that we do not touch here the issue of molecular spin states). To each electronic state ϕ_{Na} belongs a PES $U_{Na}(R)$ which depends on the set R of all nuclear coordinates of the molecule. Together with the respective kinetic energy operator T_{nuc}, they define the vibrational Hamiltonians

$$H_{Na}(R)=T_{\mathrm{nuc}}+U_{Na}(R)\equiv\hbar\varepsilon_{Na}+\mathcal{H}_{Na}(R). \tag{3}$$

Here, $\hbar\varepsilon_{Na}$ are the relaxed electronic energies corresponding to the minima of the PES plus the vibrational zero-point energy, that is, the spectrum of the $\mathcal{H}_{Na}$ counts from zero energy. Notice that nonadiabatic couplings among different electronic states will not be considered here.

However, in many applications, it is impossible to account for the complete set of nuclear coordinates, and the whole set of coordinates does not contribute to the electronic transitions in the same manner. There are reaction coordinates which strongly couple to the electronic transitions (giving rise to a pronounced shift of the respective equilibrium configurations). The remaining set of coordinates, being inactive with respect to the electronic transitions, however, can couple to the reaction coordinates, and hence cause IVR. To model IVR, we separate the whole set R of nuclear coordinates into reaction coordinates Q and thermal bath (reservoir) coordinates Z and write the Hamiltonian [Eq. (3)] as

$$\mathcal{H}_{Na}=\mathcal{H}^{(\mathrm{vib})}_{Na}+\mathcal{H}^{(\mathrm{int})}_{Na}+\mathcal{H}^{(\mathrm{R})}_{Na}, \tag{4}$$

with the reaction coordinate Hamiltonian $\mathcal{H}^{(\mathrm{vib})}_{Na}$, the system-reservoir coupling $\mathcal{H}^{(\mathrm{int})}_{Na}$, and the reservoir Hamiltonian $\mathcal{H}^{(\mathrm{R})}_{Na}$.

With $\chi_{Na\nu}$ being the vibrational eigenstates of the reaction coordinates at energy $\hbar\varepsilon_{Na\nu}$, the state vector of the active electron-vibrational system is written as

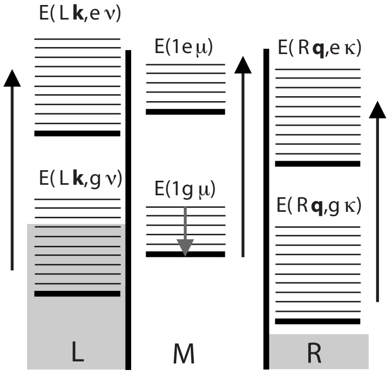

FIG. 1. Electron-vibrational energy level scheme for electron exchange between a left electrode (L, chemical potential in the presence of an applied voltage: μ_L, Fermi sea of electrons drawn in gray), a right electrode (R, chemical potential: $\mu_R \neq \mu_L$), and a molecule (M). Its energy levels $E(1a\mu)=\hbar\varepsilon_{1a\mu}$ belonging to the singly charged state are shown in the center and include the electronic ground state ($a=g$) as well as the excited electronic state ($a=e$) together with vibrational levels (labeled by μ). To draw the energy levels of the neutral molecule in the same scheme, they are combined with a possible electron energy of the left electrode to arrive at $E(L\mathbf{k},a\nu)=\hbar\varepsilon_{L\mathbf{k}}+\hbar\varepsilon_{0a\nu}$ and of the right electrode to arrive at $E(R\mathbf{q},a\kappa)=\hbar\varepsilon_{R\mathbf{q}}+\hbar\varepsilon_{0a\kappa}$. Optical excitation of the molecule is indicated by the black vertical arrows. The single gray arrow indicates IVR. Sequential charging and discharge of the molecule can be visualized in the scheme by horizontal transitions.

$$|\Psi_{Na\nu}\rangle \equiv |\Psi_\alpha\rangle = |\chi_{Na\nu}\rangle|\phi_{Na}\rangle, \tag{5}$$

where the index α comprises electronic and vibrational quantum numbers. Related energies are denoted as (see Fig. 1)

$$\hbar\varepsilon_\alpha \equiv \hbar\varepsilon_{Na\nu} = \hbar\varepsilon_{Na} + \hbar\omega_{Na\nu}. \tag{6}$$

For further use, we introduce the projection operator

$$\hat{\Pi}_\alpha = |\Psi_\alpha\rangle\langle\Psi_\alpha|, \tag{7}$$

and point out that when carrying out a summation with respect to α, it should include a summation with respect to N, too.

An expansion of $\mathcal{H}_{Na}$ with respect to the states $\chi_{Na\nu}$ yields

$$\mathcal{H}_{Na} = \sum_{\mu,\nu} \{\delta_{\mu,\nu}[\hbar\omega_{Na\nu} + \mathcal{H}_{Na}^{(\mathrm{R})}] + \hbar\hat{h}(Na,\mu\nu;Z)\}|\chi_{Na\mu}\rangle\langle\chi_{Na\nu}|, \tag{8}$$

with the matrix elements

$$\hbar\hat{h}(Na,\mu\nu;Z) = \langle\chi_{Na\mu}|\mathcal{H}_{Na}^{(\mathrm{int})}|\chi_{Na\nu}\rangle. \tag{9}$$

Besides the static electric field strength related to the applied voltage, time-dependent external fields may trigger vibrational or electronic molecular transitions. In most applications, the following dipole coupling is sufficient to treat the optical and infrared regime:

$$H_{\mathrm{field}}(t) = -\mathbf{E}(t)\hat{\boldsymbol{\mu}}. \tag{10}$$

Here, $\mathbf{E}(t)$ is the electric field strength and $\hat{\boldsymbol{\mu}}$ the molecular dipole operator. When considering electronic transitions, i.e., optical excitations, we have to deal with electronic off-diagonal matrix elements in the expansion

$$\hat{\boldsymbol{\mu}} = \sum_{N,a,b} \mathbf{d}_{Na,Nb}|\phi_{Na}\rangle\langle\phi_{Nb}|. \tag{11}$$

Of course, states with a different number of excess electrons are not connected by optical transitions. It becomes possible only if charge transfer states between the lead and the excited molecule are formed (see, e.g., Ref. 34). This effect will be neglected as well as the possibility of direct excitation of the leads and infrared excitations of vibrational states.

According to the separations given above, the molecular Hamiltonian H_{mol} can be written as (see Fig. 1)

$$H_{\mathrm{mol}}(t) = H_{\mathrm{el+vib}} + H_{\mathrm{R}} + H_{\mathrm{int}} + H_{\mathrm{field}}(t). \tag{12}$$

The active system comprising the electronic states together with the reaction coordinate are included in

$$H_{\mathrm{el+vib}} = \sum_\alpha \hbar\varepsilon_\alpha|\Psi_\alpha\rangle\langle\Psi_\alpha|. \tag{13}$$

The reservoir coordinates are contained in

$$H_{\mathrm{R}} = \sum_\alpha \mathcal{H}_{Na}^{(\mathrm{R})}|\Psi_\alpha\rangle\langle\Psi_\alpha|, \tag{14}$$

and their coupling to the active vibrational coordinates is given by

$$H_{\mathrm{int}} = \sum_{\alpha,\beta} \delta_{Ma,Nb}\hbar\hat{h}(Ma,\mu\nu;Z)|\Psi_\alpha\rangle\langle\Psi_\beta|. \tag{15}$$

B. Description of the leads and molecule-lead coupling

The lead Hamiltonian is written in the standard second-quantized form as

$$H_{\mathrm{lead}} = \sum_X H_X^{(\mathrm{lead})} \equiv \sum_X \sum_{\mathbf{k},s} \hbar\varepsilon_{X\mathbf{k}s}a_{X\mathbf{k}s}^+a_{X\mathbf{k}s}, \tag{16}$$

where X counts the different leads the molecule has been attached to. Moreover, we have the respective electron wave vector $\mathbf{k}$ of the Bloch state and the electron spin s for the conduction band denoted as $\hbar\varepsilon_{X\mathbf{k}s}$. Since the leads are considered as macroscopic systems, they have to be characterized by a grand-canonical equilibrium statistical operator:

$$\hat{W}_{\mathrm{lead}} = \prod_X \hat{W}_X = \prod_X \frac{1}{Z_X}\exp([H_X^{(\mathrm{lead})} - \mu_X\hat{N}_X]/k_BT). \tag{17}$$

Here, Z_X is the partition function referring to lead X and, μ_X denotes the chemical potential of the electrons. The associated number operator reads

$$\hat{N}_X = \sum_{\mathbf{k},s} a_{X\mathbf{k}s}^+a_{X\mathbf{k}s}. \tag{18}$$

Equation (17) indicates that the electrons of each lead are in a separate equilibrium state characterized by a particular chemical potential.

Concerning the Coulomb coupling between the leads and the molecule, we will consider two types, i.e., a direct charge transfer coupling and a case without charge transfer. The first one takes the following form:

$$H^{(1)}_{\text{mol-lead}} = \sum_{N,a,b} \sum_{X,\mathbf{k},s} V_X(N+1a,Nb,\mathbf{k}s) a_{X\mathbf{k}s} |\phi_{N+1a}\rangle\langle\phi_{Nb}| + \sum_{N,a,b} \sum_{X,\mathbf{k},s} V_X(N-1a,Nb,\mathbf{k}s) a^{+}_{X\mathbf{k}s} |\phi_{N-1a}\rangle\langle\phi_{Nb}|, \tag{19}$$

where the first term describes the transition of a single electron from lead X into the molecule, changing the state of the latter from ϕ_{Nb} to ϕ_{N+1a}. In contrast, the second term corresponds to charge injection from the molecule to the lead with changing the molecular state from ϕ_{Nb} to ϕ_{N-1a}. Long-range Coulomb interactions causing lead polarization upon charging of the molecule are not connected to charge transmission processes. In part, they have been already accounted for in the definition of the electronic states of the molecule. We additionally include Coulombic coupling which may transform molecular excitation into an electron-hole pair excitation of the leads.[34] It is written as

$$H^{(2)}_{\text{mol-lead}} = \sum_{N,a,b} \sum_{X,\mathbf{k},\mathbf{q},s} V_X(Na,Nb,\mathbf{kq}s) a^{+}_{X\mathbf{k}s} a_{X\mathbf{q}s} |\phi_{Na}\rangle\langle\phi_{Nb}|. \tag{20}$$

In Eqs. (19) and (20), the coupling matrix elements V_X account for the concrete molecular transitions.

C. Current

To characterize the charge transmission process in terms of IV characteristics, we will use the following expression specifying the (nonstationary) current through lead X as

$$I_X(t) = -|e| \frac{\partial}{\partial t} \text{tr}\{\hat{W}(t)\hat{N}_X\}. \tag{21}$$

The nonequilibrium statistical operator of the whole system is denoted by $\hat{W}(t)$ and the operator $\hat{N}_X$ of the electron number in lead X has been introduced in Eq. (18). The trace includes the trace with respect to the lead electron states (lead), the active electron-vibrational states of the molecule (el+vib) in the neutral, as well as the various charged states, and the trace with respect to the thermal reservoir of bath vibrational coordinates (R):

$$\text{tr}\{\cdots\} = \text{tr}_{\text{lead+el+vib+R}}\{\cdots\}. \tag{22}$$

Often, Eq. (21) is rewritten by carrying out the time derivative of $\hat{W}(t)$, finally resulting in a commutator of $\hat{N}_X$ with the system Hamiltonian. This strategy is not followed here and the current will be calculated directly using the projection operator formalisms which leads to generalized rate equations for the molecular electron-vibrational states. This approach is explained in the next section.

III. GENERALIZED RATE EQUATIONS

The technique used in the following to derive generalized rate equations is well established.[2,35] Recently, it has been applied to compute IV characteristics of a molecule in the framework of a single electron approach.[18] Here, we utilize the respective projection superoperator methodology for a more general model (for a preliminary account, see also Ref. 25). Therefore, in order to compute the current, it is of advantage to use a description based on the populations $P_{Na\nu}(t) \equiv P_\alpha(t)$ of the molecular electron-vibrational states [Eq. (5)]:

$$P_\alpha(t) = \langle\Psi_\alpha|\text{tr}_{\text{lead+R}}\{\hat{W}(t)\}|\Psi_\alpha\rangle \equiv \text{tr}\{\hat{W}(t)\hat{\Pi}_\alpha\}. \tag{23}$$

The expression includes the total nonequilibrium statistical operator $\hat{W}(t)$ of the electron-vibrational system under consideration, already introduced in Eq. (21). Using the projector [Eq. (7)], the more compact form of $P_\alpha(t)$ on the right-hand side can be defined where the trace covers all states of the molecule-lead system [cf. Eq. (22)].

As already indicated, we will choose a description where we assume individual equilibrium of the electrons within each lead. This can be accounted for in the definition of a particular projection superoperator. We introduce

$$\mathcal{P}\cdots = \sum_\alpha \hat{W}^{(\text{eq})}_\alpha \text{tr}\{\hat{\Pi}_\alpha \ldots\}, \tag{24}$$

with

$$\hat{W}^{(\text{eq})}_\alpha = \hat{W}_{\text{lead}}\hat{R}_{\text{R}}\hat{\Pi}_\alpha. \tag{25}$$

This density operator characterizes electronic equilibrium in the leads [cf. Eq. (17)] and vibrational equilibrium with respect to the reservoir coordinates of the molecule (described by the equilibrium density operator $\hat{R}_R$). One easily verifies that $\mathcal{P}$ is indeed a projector. Once $\mathcal{P}$ has been applied to $\hat{W}(t)$, the population is obtained as

$$P_\alpha(t) = \text{tr}\{\hat{\Pi}_\alpha \mathcal{P}\hat{W}(t)\}. \tag{26}$$

There are different ways to derive rate equations governing the time evolution of populations. Here, we start with the Nakjima–Zwanzig equation for $\mathcal{P}\hat{W}(t)$:

$$\frac{\partial}{\partial t}\mathcal{P}\hat{W}(t) = -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\hat{W}(t) - \int_{t_0}^{t} d\bar{t}\,\mathcal{P}\mathcal{L}(t)\mathcal{U}_{\mathcal{Q}}(t,\bar{t})\mathcal{Q}\mathcal{L}(\bar{t})\mathcal{P}\hat{W}(\bar{t}). \tag{27}$$

In deriving this equation, it has been assumed that the term $\mathcal{U}_{\mathcal{Q}}(t,t_0)\mathcal{Q}\hat{W}(t_0)$ vanishes (absence of initial correlations). $\mathcal{L}(t)$ is the time-dependent Liouvillian referring to the total Hamiltonian [Eq. (2)]. Moreover, the time evolution superoperator introduced above reads ($\mathcal{T}$ indicates the respective time ordering)

$$\mathcal{U}_{\mathcal{Q}}(t,t_0) = \mathcal{T}\exp\left(-i\int_{t_0}^{t} d\tau\,\mathcal{Q}\mathcal{L}(\tau)\right). \tag{28}$$

We note that so far, we have not yet separated the full Hamiltonian into a zero-order part and a perturbation. Strictly speaking, however, this separation has already been fixed implicitly by the specific structure of the projection superoperator [Eq. (25)] because it holds that

$$[\hat{\Pi}_\alpha, H(t)]_- = [\hat{\Pi}_\alpha, \hat{V}(t)]_-, \tag{29}$$

with the interaction Hamiltonian

$$\hat{V}(t) = H_{\mathrm{int}} + H_{\mathrm{field}}(t) + H_{\mathrm{mol\text{-}lead}}. \tag{30}$$

Applying the procedure introduced in Eq. (26) to the Nakjima–Zwanzig identity [Eq. (27)], one arrives at an equation of motion for the state populations (generalized rate equation). It contains two trace expressions both of the type $\mathrm{tr}\{\hat{\Pi}_\alpha \mathcal{P}\mathcal{L}(t)\hat{O}\} = \mathrm{tr}\{\hat{\Pi}_\alpha \mathcal{L}(t)\hat{O}\}$ with the operator $\hat{O}$ given either by $\mathcal{P}\hat{W}(t)$ or by $\mathcal{U}_Q(t,\bar{t})\mathcal{Q}\mathcal{L}(\bar{t})\mathcal{P}\hat{W}(\bar{t})$. The first trace vanishes since $\hat{\Pi}_\alpha$ commutes with $\hat{W}_\alpha^{(\mathrm{eq})}$. The second one which will be written in the form $\mathrm{tr}\{[\hat{\Pi}_\alpha, H(t)]_- \hat{O}\}$ defines the kernel of the generalized rate equation which follows as

$$\frac{\partial}{\partial t} P_\alpha(t) = \sum_\beta \int_{t_0}^{\infty} d\bar{t} K_{\alpha\beta}(t,\bar{t}) P_\beta(\bar{t}). \tag{31}$$

The kernel takes the form

$$K_{\alpha\beta}(t,\bar{t}) = -\frac{1}{\hbar^2}\Theta(t-\bar{t})\mathrm{tr}\{[\hat{\Pi}_\alpha, H(t)]_- \mathcal{U}_Q(t,\bar{t})[H(\bar{t}), \hat{W}_\beta^{(\mathrm{eq})}]_-\}. \tag{32}$$

Here, we have used for the kernel that $\mathcal{Q}\mathcal{L}(\bar{t})\mathcal{P}\hat{W}(\bar{t})$ leads to the expression $\mathcal{Q}\mathcal{L}(\bar{t})\hat{W}_\beta^{(\mathrm{eq})}$ where the $\mathcal{P}\mathcal{L}(\bar{t})\hat{W}_\beta^{(\mathrm{eq})}$ part does not contribute.

The two commutators in the kernel [Eq. (32)] specify the perturbation part of the Hamiltonian, see Eqs. (29) and (30). The second commutator reads

$$[H(\bar{t}), \hat{W}_\beta^{(\mathrm{eq})}]_- = [\hat{V}(\bar{t}), \hat{W}_\beta^{(\mathrm{eq})}]_-. \tag{33}$$

Introducing the interaction Liouvillian $\mathcal{V}(t)$ referring to $\hat{V}(t)$ [Eq. (30)], the kernel [Eq. (32)] is written as

$$K_{\alpha\beta}(t,\bar{t}) = -\Theta(t-\bar{t})\mathrm{tr}\{\hat{\Pi}_\alpha \mathcal{V}(t)\mathcal{U}_Q(t,\bar{t})\mathcal{V}(\bar{t})\hat{W}_\beta^{(\mathrm{eq})}\}. \tag{34}$$

This expression fulfills the sum rule

$$\sum_\alpha K_{\alpha\beta}(t,\bar{t}) = 0, \tag{35}$$

which directly follows from the completeness relation $\Sigma_\alpha \hat{\Pi}_\alpha = 1$ and the fact that the remaining expression vanishes (trace of a commutator equals zero). The result guarantees probability conservation and we can further introduce transition kernels according to

$$K_{\alpha\beta}(t,\bar{t}) = \delta_{\alpha,\beta} K_\alpha(t,\bar{t}) + (1-\delta_{\alpha,\beta})K_{\beta\to\alpha}(t,\bar{t}). \tag{36}$$

Noting the sum rule, we may deduce that

$$K_\beta(t,\bar{t}) = -\sum_{\alpha\neq\beta} K_{\beta\to\alpha}(t,\bar{t}). \tag{37}$$

This enables us to rewrite the generalized rate equation (31) in the more suggestive form

$$\frac{\partial}{\partial t} P_\alpha(t) = -\sum_\beta \int_{t_0}^{\infty} d\bar{t} [K_{\alpha\to\beta}(t,\bar{t})P_\alpha(\bar{t}) - K_{\beta\to\alpha}(t,\bar{t})P_\beta(\bar{t})]. \tag{38}$$

In the limit $t\to\infty$ (and for a quasistationary action of external fields), the generalized rate equation should result in stationary populations $P_\alpha^{(\mathrm{stat})}$:

$$0 = \sum_\beta (k_{\alpha\to\beta}P_\alpha^{(\mathrm{stat})} - k_{\beta\to\alpha}P_\beta^{(\mathrm{stat})}). \tag{39}$$

Here, Fourier-transformed transition kernels [Eq. (34)] at zero-frequency enter (note also the limit $t_0 \to -\infty$)

$$k_{\alpha\to\beta} = K_{\alpha\to\beta}(\omega = 0). \tag{40}$$

A. Current formula

We relate Eq. (21) for the current to the projection superoperator approach presented in the preceding section and set

$$\mathrm{tr}\{\hat{W}(t)\hat{N}_X\} = \mathrm{tr}\{\hat{N}_X(\mathcal{P}+\mathcal{Q})\hat{W}(t)\}. \tag{41}$$

The term including $\mathcal{P}$ is easily computed, whereas that with $\mathcal{Q}\hat{W}(t)$ is obtained by the second term on the right-hand side of Eq. (27) without the prefactor $-i\mathcal{P}\mathcal{L}(t)$. As a result, we may write

$$\mathrm{tr}\{\hat{W}(t)\hat{N}_X\} = \sum_\alpha \Bigg(\langle \hat{N}_X \rangle P_\alpha(t) - i\int_{t_0}^{t} d\bar{t}\,\mathrm{tr}\{\hat{N}_X \mathcal{U}_Q(t,\bar{t})\mathcal{V}(\bar{t})\hat{W}_\alpha^{(\mathrm{eq})}\} P_\alpha(\bar{t}) \Bigg). \tag{42}$$

The first term on the right-hand side includes the mean electron number in lead X:

$$\langle \hat{N}_X \rangle = \mathrm{tr}\{\hat{N}_X \hat{W}_\alpha^{(\mathrm{eq})}\}, \tag{43}$$

and the second term stemming from $\mathcal{Q}\hat{W}(t)$ has been rewritten according to the results of the foregoing section. Both expressions are inserted into Eq. (21), where a time derivative gives the current according to

$$I_X(t) = -|e|\sum_\alpha \Bigg(\langle \hat{N}_X \rangle \frac{\partial}{\partial t} P_\alpha(t) - i\,\mathrm{tr}\{\hat{N}_X \mathcal{V}(t)\hat{W}_\alpha^{(\mathrm{eq})}\} P_\alpha(t) - \int_{t_0}^{t} d\bar{t}\,\mathrm{tr}\{\hat{N}_X \mathcal{Q}\mathcal{L}(t)\mathcal{U}_Q(t,\bar{t})\mathcal{V}(\bar{t})\hat{W}_\alpha^{(\mathrm{eq})}\} P_\alpha(\bar{t}) \Bigg). \tag{44}$$

The second term on the right-hand side vanishes, which can be shown by using the same reasoning as in the foregoing section [$\mathcal{V}(t)$ is incorporated in a trace expression which contains two operators which are diagonal with respect to lead and molecular states]. Using $\mathcal{Q} = 1 - \mathcal{P}$, the third term on the right-hand side of Eq. (44) is separated into two terms, giving the current as

$$I_X(t) = -|e|\sum_\alpha \Bigg(\langle \hat{N}_X \rangle \frac{\partial}{\partial t} P_\alpha(t) - \int_{t_0}^{t} d\bar{t}\, \mathrm{tr}\{\hat{N}_X \mathcal{L}(t) \mathcal{U}_Q(t,\bar{t}) \mathcal{V}(\bar{t}) \hat{W}_\alpha^{(\mathrm{eq})}\} P_\alpha(\bar{t}) - \sum_\beta \int_{t_0}^{t} d\bar{t} \langle \hat{N}_X \rangle K_{\beta\alpha}(t,\bar{t}) P_\alpha(\bar{t}) \Bigg). \tag{45}$$

The first and third terms on the right-hand side cancel each other because of the generalized rate equation (31). Thus, the current reads [note the rearrangement of $\hat{N}_X\mathcal{L}(t)$ in the remaining term]

$$I_X(t) = |e|\sum_\alpha \int_{t_0}^{t} d\bar{t}\, \mathrm{tr}\{[\mathcal{L}(t)\hat{N}_X][\mathcal{U}_Q(t,\bar{t})\mathcal{V}(\bar{t})\hat{W}_\alpha^{(\mathrm{eq})}]\} P_\alpha(\bar{t}). \tag{46}$$

Obviously, the expression contributes to the current only by those terms where $\mathcal{L}(t)\hat{N}_X \neq 0$. Within the present description, this is the case for the molecule-lead coupling, i.e., $\mathcal{L}(t)\hat{N}_X$ can be replaced by $(H_{\text{mol-lead}}, \hat{N}_X)_-/\hbar$.

To have a more compact notation, we introduce a kernel which describes the transition from molecular state α into lead X:

$$K_{\alpha\to X}(t,\bar{t}) = -\Theta(t-\bar{t})\mathrm{tr}\{[\mathcal{L}(t)\hat{N}_X][\mathcal{U}_Q(t,\bar{t})\mathcal{V}(\bar{t})\hat{W}_\alpha^{(\mathrm{eq})}]\}, \tag{47}$$

and write

$$I_X(t) = -|e|\sum_\alpha \int_{t_0}^{\infty} d\bar{t} K_{\alpha\to X}(t,\bar{t}) P_\alpha(\bar{t}). \tag{48}$$

If the kernel $K_{\alpha\to X}(t,\bar{t})$ only depends on the time difference $t-\bar{t}$ as discussed in the next section, one obtains a stationary current at $t\to\infty$:

$$I^{(\mathrm{stat})}(t) = -|e|\sum_\alpha K_{\alpha\to X}(\omega=0) P_\alpha^{(\mathrm{stat})}. \tag{49}$$

Here, we again assumed $t_0\to-\infty$, which results in the zero-frequency Fourier-transformed kernel.

IV. SECOND-ORDER TRANSITION RATES

The following considerations focus on the determination of second-order rates in the case of weak molecule-lead coupling. In the Appendix, we outline how to go beyond a second-order theory in the case of a memory kernel without a time-dependent external field. The kernels account for the molecule-lead coupling of type 1 ($K^{(\text{mol-lead})}$), of type 2 ($K^{(\mathrm{dec})}$), of IVR ($K^{(\mathrm{IVR})}$), and of optical excitation ($K^{(\mathrm{opt})}$):

$$K_{\alpha\to\beta} = K_{\alpha\to\beta}^{(\text{mol-lead})} + K_{\alpha\to\beta}^{(\mathrm{dec})} + K_{\alpha\to\beta}^{(\mathrm{IVR})} + K_{\alpha\to\beta}^{(\mathrm{opt})}. \tag{50}$$

The current is also calculated at the same order of perturbation theory.

To arrive at second-order kernels, the time-evolution superoperator $\mathcal{U}_Q(t,\bar{t})$ appearing in Eq. (34) has to be replaced by a zero-order expression $\mathcal{U}_0$ with respect to the coupling Liouvillian $\mathcal{V}$ defined via Eq. (30). We note that $\mathcal{Q}[\mathcal{L}(t) - \mathcal{V}(t)] = \mathcal{L}_0$, where the latter zero-order Liouvillian is defined by $H_0 = H(t) - \hat{V}(t)$, i.e., by the Hamiltonian of the unperturbed lead molecule electron-vibrational system ($H_0 = H_{\mathrm{el+vib}} + H_{\mathrm{R}} + H_{\mathrm{lead}}$). The zero-order time-evolution superoperator simply reads

$$\mathcal{U}_0(t)\cdots = U_{\mathrm{lead}}(t)U_{\mathrm{R}}(t)U_{\mathrm{el+vib}}(t)\cdots U_{\mathrm{el+vib}}^+(t)U_{\mathrm{R}}^+(t)U_{\mathrm{lead}}^+(t). \tag{51}$$

This expression includes the electron-vibrational contribution $U_{\mathrm{el+vib}}$, the reservoir coordinate contribution U_{R}, and the contribution U_{lead} referring to the various leads.

The respective transition kernel follows as (note the introduction of $\tau = t-\bar{t}$, the interchange of α and β, and $\alpha\neq\beta$)

$$\begin{aligned} K_{\alpha\to\beta}^{(2)}(t,t-\tau) &= -\Theta(\tau)\mathrm{tr}\{\hat{\Pi}_\beta \mathcal{V}(t)\mathcal{U}_0(\tau)\mathcal{V}(t-\tau)\hat{W}_\alpha^{(\mathrm{eq})}\} \\ &\equiv -\frac{\Theta(\tau)}{\hbar^2}\mathrm{tr}\{\hat{\Pi}_\beta[\hat{V}(t), U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau)U_{\mathrm{el+vib}}(\tau) \\ &\quad\times[\hat{V}(t-\tau), \hat{W}_\alpha^{(\mathrm{eq})}]_- U_{\mathrm{el+vib}}^+(\tau) \\ &\quad\times U_{\mathrm{R}}^+(\tau)U_{\mathrm{lead}}^+(\tau)]_-\}. \end{aligned} \tag{52}$$

This expression can be cast into a more explicit form by introducing matrix elements with respect to the molecule electron-vibrational states Ψ_α [Eq. (5)]. Since $\alpha\neq\beta$, there remain two terms:

$$\begin{aligned} K_{\alpha\to\beta}^{(2)}(t,t-\tau) = \frac{\Theta(\tau)}{\hbar^2}\mathrm{tr}_{\mathrm{lead+R}}\{&\langle\Psi_\beta|\hat{V}(t)U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau)U_{\mathrm{el+vib}}(\tau) \\ &\times\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}|\Psi_\alpha\rangle\langle\Psi_\alpha|\hat{V}(t-\tau)U_{\mathrm{el+vib}}^+(\tau) \\ &\times U_{\mathrm{R}}^+(\tau)U_{\mathrm{lead}}^+(\tau)|\Psi_\beta\rangle + \langle\Psi_\beta|U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau) \\ &\times U_{\mathrm{el+vib}}(\tau)\hat{V}(t-\tau)\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}|\Psi_\alpha\rangle \\ &\times\langle\Psi_\alpha|U_{\mathrm{el+vib}}^+(\tau)U_{\mathrm{R}}^+(\tau)U_{\mathrm{lead}}^+(\tau)\hat{V}(t)|\Psi_\beta\rangle\}. \end{aligned} \tag{53}$$

We take into account that $U_{\mathrm{el+vib}}(\tau)|\Psi_\alpha\rangle = \exp(-i\varepsilon_\alpha\tau)|\Psi_\alpha\rangle$ [cf. Eq. (13)] and obtain ($\varepsilon_{\alpha\beta} = \varepsilon_\alpha - \varepsilon_\beta$)

$$\begin{aligned} K_{\alpha\to\beta}^{(2)}(t,t-\tau) = \frac{\Theta(\tau)}{\hbar^2}\mathrm{tr}_{\mathrm{lead+R}}\{&e^{-i\varepsilon_{\alpha\beta}\tau}\langle\Psi_\beta|\hat{V}(t) \\ &\times|\Psi_\alpha\rangle U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau)\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}\langle\Psi_\alpha|\hat{V}(t-\tau) \\ &\times|\Psi_\beta\rangle U_{\mathrm{R}}^+(\tau)U_{\mathrm{lead}}^+(\tau) + e^{i\varepsilon_{\alpha\beta}\tau}U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau) \\ &\times\langle\Psi_\beta|\hat{V}(t-\tau)|\Psi_\alpha\rangle\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}U_{\mathrm{R}}^+(\tau)U_{\mathrm{lead}}^+(\tau) \\ &\times\langle\Psi_\alpha|\hat{V}(t)|\Psi_\beta\rangle\}. \end{aligned} \tag{54}$$

This can be put into the following form:

$$\begin{aligned} K^{(2)}_{\alpha\to\beta}(t,t-\tau) = {} & \frac{\Theta(\tau)}{\hbar^2} e^{-i\varepsilon_{\alpha\beta}\tau} \mathrm{tr}_{\mathrm{lead+R}}\{\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}\langle\Psi_\alpha|\hat{V}(t-\tau) \\ & \times|\Psi_\beta\rangle U^{+}_{\mathrm{R}}(\tau)U^{+}_{\mathrm{lead}}(\tau)\langle\Psi_\beta|\hat{V}(t)|\Psi_\alpha\rangle \\ & \times U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau)\} + \frac{\Theta(\tau)}{\hbar^2} e^{i\varepsilon_{\alpha\beta}\tau} \\ & \times \mathrm{tr}_{\mathrm{lead+R}}\{\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}U^{+}_{\mathrm{R}}(\tau)U^{+}_{\mathrm{lead}}(\tau)\langle\Psi_\alpha|\hat{V}(t)|\Psi_\beta\rangle \\ & \times U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau)\langle\Psi_\beta|\hat{V}(t-\tau)|\Psi_\alpha\rangle\}. \end{aligned} \tag{55}$$

If the coupling Hamiltonian becomes time independent, the second matrix element product in the trace represents the Hermitian conjugate of the first one.

The remainder of this section is devoted to a computation of $K^{(2)}_{\alpha\beta}$ for the different parts entering $\hat{V}$. According to Eqs. (30) and (50), there are four different contributions, two related to the molecule-lead coupling (with and without Coulomb coupling causing electron exchange between the molecule and the leads). The other two contributions are related to the mechanism of IVR and describe the action of time-dependent external fields (mixed contributions do not exist in the second-order theory).

A. Kernel of molecule-lead coupling causing electron transfer

For completeness, we briefly indicate how to compute the rate (for a discussion, see also Refs. 5, 22, and 25) but also indicate how to go beyond a second-order expression. To get the second-order rate $K^{(\mathrm{mol\text{-}lead})}$, we have to replace $\hat{V}$ in Eq. (55) by $H^{(1)}_{\mathrm{mol\text{-}lead}}$ [Eq. (19)]. Moreover, we notice that the trace with respect to the reservoir coordinates gives unity and only matrix elements of $H_{\mathrm{mol\text{-}lead}}$ with electronic states appear. The vibrational states simply result in vibrational overlap integrals (Franck–Condon factors).

The electronic matrix elements of $H_{\mathrm{mol\text{-}lead}}$ (entering the rate expressions) are obtained as (note the use of the new indices K and L for excess electrons in the molecule)

$$\begin{aligned} & \langle\phi_{Ma}|H_{\mathrm{mol\text{-}lead}}|\phi_{Nb}\rangle \\ & \quad = \sum_{X,\mathbf{k},s}\sum_{K,c}\sum_{L,d}\langle\phi_{Ma}|[\delta_{K,L+1}V_X(L+1c,Ld,\mathbf{k}s)|\phi_{L+1c}\rangle \\ & \qquad \times\langle\phi_{Ld}|a_{X\mathbf{k}s} + \delta_{K,L-1}V_X(L-1c,Ld,\mathbf{k}s) \\ & \qquad \times a^{+}_{X\mathbf{k}s}|\phi_{L-1c}\rangle\langle\phi_{Ld}|]|\phi_{Nb}\rangle \\ & \quad = \sum_{X,\mathbf{k},s}[\delta_{M,N+1}V_X(N+1a,Nb,\mathbf{k}s)a_{X\mathbf{k}s} \\ & \qquad + \delta_{M,N-1}V_X(N-1a,Nb,\mathbf{k}s)a^{+}_{X\mathbf{k}s}]. \end{aligned} \tag{56}$$

Consequently, the trace in Eq. (55) takes the form

$$\begin{aligned} & \mathrm{tr}_{\mathrm{lead}}\{\hat{W}_{\mathrm{lead}}\langle\phi_{Ma}|H_{\mathrm{mol\text{-}lead}}|\phi_{Nb}\rangle U^{+}_{\mathrm{lead}}(t) \\ & \quad \times\langle\phi_{Nb}|H_{\mathrm{mol\text{-}lead}}|\phi_{Ma}\rangle U_{\mathrm{lead}}(t)\} \\ & \quad = \sum_{X,\mathbf{k},s}\sum_{Y,\mathbf{q},s'}\{\delta_{N,M-1}V_X(Ma,M-1b,\mathbf{k}s) \\ & \qquad \times V_X(M-1b,Ma,\mathbf{q}s') \\ & \qquad \times\mathrm{tr}_{\mathrm{lead}}\{\hat{W}_{\mathrm{lead}}a_{X\mathbf{k}s}U^{+}_{\mathrm{lead}}(t)a^{+}_{Y\mathbf{q}s'}U_{\mathrm{lead}}(t)\} \\ & \qquad + \delta_{N,M+1}V_X(Ma,M+1b,\mathbf{k}s) \\ & \qquad \times V_Y(M+1b,Ma,\mathbf{q}s') \\ & \qquad \times\mathrm{tr}_{\mathrm{lead}}\{\hat{W}_{\mathrm{lead}}a^{+}_{X\mathbf{k}s}U^{+}_{\mathrm{lead}}(t)a_{Y\mathbf{q}s'}U_{\mathrm{lead}}(t)\}\}. \end{aligned} \tag{57}$$

The remaining trace expressions follow as (any electron-electron interaction within the electrodes has been neglected)

$$\begin{aligned} & \mathrm{tr}_{\mathrm{lead}}\{\hat{W}_{\mathrm{lead}}a_{X\mathbf{k}s}U^{+}_{\mathrm{lead}}(t)a^{+}_{Y\mathbf{q}s'}U_{\mathrm{lead}}(t)\} \\ & \quad = \delta_{X\mathbf{k}s,Y\mathbf{q}s'}[1-f_F(\hbar\varepsilon_{X\mathbf{k}s}-\mu_X)]\exp(i\varepsilon_{X\mathbf{k}s}t) \end{aligned} \tag{58}$$

and

$$\begin{aligned} & \mathrm{tr}_{\mathrm{lead}}\{\hat{W}_{\mathrm{lead}}a^{+}_{X\mathbf{k}s}U^{+}_{\mathrm{lead}}(t)a_{Y\mathbf{q}s'}U_{\mathrm{lead}}(t)\} \\ & \quad = \delta_{X\mathbf{k}s,Y\mathbf{q}s'}f_F(\hbar\varepsilon_{X\mathbf{k}s}-\mu_X)\exp(-i\varepsilon_{X\mathbf{k}s}t). \end{aligned} \tag{59}$$

Since the different electrodes are independent of each other, the expressions are diagonal with respect to the electrode index. The used model for the lead electrons results in the Fermi distribution f_F and the electronic energies $E_{X\mathbf{k}s}$.

We insert all into the general expression [Eq. (55)] for the second-order kernel and get

$$\begin{aligned} K^{(\mathrm{mol\text{-}lead})}_{Ma\mu\to Nb\nu}(\tau) = {} & \frac{\Theta(\tau)}{\hbar^2}|\langle\chi_{Ma\mu}|\chi_{Nb\nu}\rangle|^2 e^{-i\varepsilon(Ma\mu,Nb\nu)t} \\ & \times\sum_{X,\mathbf{k},s}\{\delta_{N,M-1}|V_X(Ma,M-1b,\mathbf{k}s)|^2 \\ & \times[1-f_F(\hbar\varepsilon_{X\mathbf{k}s}-\mu_X)]e^{i\varepsilon_{X\mathbf{k}s}t} \\ & + \delta_{N,M+1}|V_X(Ma,M+1b,\mathbf{k}s)|^2 \\ & \times f_F(\hbar\varepsilon_{X\mathbf{k}s}-\mu_X)e^{-i\varepsilon_{X\mathbf{k}s}t}\} + \mathrm{c.c.}, \end{aligned} \tag{60}$$

with $\varepsilon(Ma\mu,Nb\nu)=\varepsilon_{Ma\mu}-\varepsilon_{Nb\nu}$. This can be rewritten as

$$\begin{aligned} K^{(\mathrm{mol\text{-}lead})}_{Ma\mu\to Nb\nu}(\tau) = {} & \delta_{N,M-1}K^{(\mathrm{mol\text{-}lead})}_{Ma\mu\to M-1b\nu}(\tau) \\ & + \delta_{N,M+1}K^{(\mathrm{mol\text{-}lead})}_{Ma\mu\to M+1b\nu}(\tau), \end{aligned} \tag{61}$$

covering the rate describing discharge of the molecule and charging, respectively. Ordinary rates are obtained from zero-frequency Fourier-transformed kernels. The discharge rate reads

$$\begin{aligned} k^{(\mathrm{mol\text{-}lead})}_{Ma\mu\to M-1b\nu} = {} & \frac{2\pi}{\hbar^2}|\langle\chi_{Ma\mu}|\chi_{M-1b\nu}\rangle|^2\sum_{X,\mathbf{k},s}|V_X(Ma,M-1b,\mathbf{k}s)|^2 \\ & \times[1-f_F(\hbar\varepsilon_{X\mathbf{k}}-\mu_X)] \\ & \times\delta[\varepsilon(Ma\mu,M-1b\nu)-\varepsilon_{X\mathbf{k}}] \\ \equiv {} & \frac{4\pi}{\hbar^2}|\langle\chi_{Ma\mu}|\chi_{M-1b\nu}\rangle|^2\sum_X\mathcal{N}_X[\varepsilon(Ma\mu,M-1b\nu)] \\ & \times|V_X[Ma,M-1b,\varepsilon(Ma\mu,M-1b\nu)]|^2 \\ & \times\{1-f_F[\hbar\varepsilon(Ma\mu,M-1b\nu)-\mu_X]\} \\ \equiv {} & \sum_X k^{(\mathrm{mol\text{-}lead})}_{X,Ma\mu\to M-1b\nu}, \end{aligned} \tag{62}$$

and the charging rate is

$$
\begin{aligned}
k^{(\text{mol-lead})}_{Ma\mu\to M+1b\nu} &= \frac{2\pi}{\hbar^2}|\langle\chi_{Ma\mu}|\chi_{M+1b\nu}\rangle|^2\sum_{X,\mathbf{k},s}|V_X(Ma,M+1b,\mathbf{k}s)|^2\\
&\quad\times f_F(\hbar\varepsilon_{X\mathbf{k}}-\mu_X)\delta[\varepsilon(Ma\mu,M+1b\nu)+\varepsilon_{X\mathbf{k}}]\\
&\equiv \frac{4\pi}{\hbar^2}|\langle\chi_{Ma\mu}|\chi_{M+1b\nu}\rangle|^2\sum_X\mathcal{N}_X[\varepsilon(M+1b\nu,Ma\mu)]\\
&\quad\times|V_X(Ma,M+1b,\varepsilon(M+1b\nu,Ma\mu))|^2\\
&\quad\times f_F[\hbar\varepsilon(M+1b\nu,Ma\mu)-\mu_X]\\
&\equiv\sum_X k^{(\text{mol-lead})}_{X,Ma\mu\to M+1b\nu}. \qquad (63)
\end{aligned}
$$

Here, an additional factor of 2 appears since coupling potentials are assumed to be spin independent. Moreover, we introduced the density of states $\mathcal{N}_X(\Omega)$ of electrode X and the frequency dependent transfer couplings V_X. Since the $\mathbf{k}$ summation has been replaced by an Ω integral, the δ function disappears. For later use, we also introduced rates which describe charging and discharge of the molecule via the coupling to a specific electrode X.

B. Kernel related to molecular de-excitation by electron-hole pair formation

To calculate the second-order rate $K^{(\text{dec})}$ for the decay of excited molecular states (molecular de-excitation by electron-hole pair formation in the leads), we proceed in analogy to the foregoing section and, first, replace $\hat{V}$ in Eq. (55) by $H^{(2)}_{\text{mol-lead}}$ [Eq. (20)]. Again, we notice that the trace with respect to the reservoir coordinates is unity. Only matrix elements of $H_{\text{mol-lead}}$ with electronic states appear and the vibrational states result in respective Franck–Condon factors.

First, the electronic matrix elements of $H^{(2)}_{\text{mol-lead}}$ are obtained as (note the use of the new index K for the number of excess electrons in the molecule)

$$
\begin{aligned}
\langle\phi_{Ma}|H_{\text{mol-lead}}|\phi_{Nb}\rangle &= \sum_{X,\mathbf{k},\mathbf{q},s}\sum_{K,c,d}\langle\phi_{Ma}|V_X(Kc,Kd,\mathbf{kq}s)|\phi_{Kc}\rangle\\
&\quad\times\langle\phi_{Kd}|a^+_{X\mathbf{k}s}a_{X\mathbf{q}s}|\phi_{Nb}\rangle\\
&=\delta_{M,N}\sum_{X,\mathbf{k},\mathbf{q},s}V_X(Na,Nb,\mathbf{kq}s)a^+_{X\mathbf{k}s}a_{X\mathbf{q}s}. \qquad (64)
\end{aligned}
$$

The trace in Eq. (55) takes the form

$$
\begin{aligned}
&\text{tr}_{\text{lead}}\{\hat{W}_{\text{lead}}\langle\phi_{Ma}|H_{\text{mol-lead}}|\phi_{Nb}\rangle U^+_{\text{lead}}(t)\\
&\quad\times\langle\phi_{Nb}|H_{\text{mol-lead}}|\phi_{Ma}\rangle U_{\text{lead}}(t)\}\\
&\quad=\sum_{X,\mathbf{k},\mathbf{q},s}\sum_{\mathbf{k}',\mathbf{q}',s'}\delta_{N,M}V_X(Ma,Mb,\mathbf{kq}s)V_X(Mb,Ma,\mathbf{k}'\mathbf{q}'s')\\
&\qquad\times\text{tr}_{\text{lead}}\{\hat{W}_{\text{lead}}a^+_{X\mathbf{k}s}a_{X\mathbf{q}s}U^+_{\text{lead}}(t)a^+_{X\mathbf{k}'s'}a_{X\mathbf{q}'s'}U_{\text{lead}}(t)\}. \qquad (65)
\end{aligned}
$$

The formula makes use of the assumption that exclusively electrons of the same lead are correlated one to another. We insert these expressions into Eq. (55) for the second–order kernel and obtain

$$
\begin{aligned}
K^{(\text{mol-lead})}_{Ma\mu\to Nb\nu}(\tau) &= \delta_{M,N}\frac{\Theta(\tau)}{\hbar^2}|\langle\chi_{Ma\mu}|\chi_{Mb\nu}\rangle|^2 e^{-i\varepsilon(Ma\mu,Mb\nu)t}\\
&\quad\times\sum_{X,\mathbf{k},\mathbf{q},s}\sum_{\mathbf{k}',\mathbf{q}',s'}V_X(Ma,Mb,\mathbf{kq}s)\\
&\quad\times V_X(Mb,Ma,\mathbf{k}'\mathbf{q}'s')\text{tr}_{\text{lead}}\{\hat{W}_{\text{lead}}a^+_{X\mathbf{k}s}a_{X\mathbf{q}s}\\
&\quad\times U^+_{\text{lead}}(t)a^+_{X\mathbf{k}'s'}a_{X\mathbf{q}'s'}U_{\text{lead}}(t)\}+\text{c.c.} \qquad (66)
\end{aligned}
$$

Ordinary rates are recovered from zero-frequency Fourier-transformed kernels

$$
\begin{aligned}
k^{(\text{mol-lead})}_{Ma\mu\to Nb\nu} &= \delta_{M,N}|\langle\chi_{Ma\mu}|\chi_{Mb\nu}\rangle|^2\\
&\quad\times 2\,\text{Re}\sum_{X,\mathbf{k},\mathbf{q},s}\sum_{\mathbf{k}',\mathbf{q}',s'}V_X(Ma,Mb,\mathbf{kq}s)\\
&\quad\times V_X(Mb,Ma,\mathbf{k}'\mathbf{q}'s')\\
&\quad\times\int_0^\infty dt e^{-i\varepsilon(Ma\mu,Mb\nu)t}\text{tr}_{\text{lead}}\{\hat{W}_{\text{lead}}a^+_{X\mathbf{k}s}a_{X\mathbf{q}s}\\
&\quad\times U^+_{\text{lead}}(t)a^+_{X\mathbf{k}'s'}a_{X\mathbf{q}'s'}U_{\text{lead}}(t)\}. \qquad (67)
\end{aligned}
$$

The obtained expressions contain an electron-hole pair correlation function and can be related to the dielectric function of the leads (see, for example, Ref. 37, and references therein).

C. Kernel related to intramolecular vibrational energy redistribution

To compute $K^{(\text{IVR})}$, we have to replace $\hat{V}$ in Eq. (55) by H_{int}. The respective electron-vibrational state matrix elements follow as

$$
\langle\Psi_{Nb\nu}|H_{\text{int}}|\Psi_{Ma\mu}\rangle=\delta_{Nb,Ma}\hbar\hat{h}(Nb,\nu\mu;Z) \qquad (68)
$$

and the other one by interchanging the quantum numbers. Both expressions result in ($\omega_{Ma,\mu\nu}=\omega_{Ma\mu}-\omega_{Ma\nu}$)

$$
\begin{aligned}
K^{(\text{IVR})}_{Ma\mu\to Nb\nu;\omega}(\tau) &= \delta_{Ma,Nb}\Theta(\tau)\\
&\quad\times(e^{-i\omega_{Ma,\mu\nu}\tau}\text{tr}_{\text{R}}\{\hat{h}(Ma,\nu\mu;Z)U_{\text{R}}(\tau)\\
&\quad\times\hat{R}\hat{h}(Ma,\mu\nu;Z)U^+_{\text{R}}(\tau)\}+e^{i\omega_{Ma,\mu\nu}\tau}\\
&\quad\times\text{tr}_{\text{R}}\{U_{\text{R}}(\tau)\hat{h}(Ma,\nu\mu;Z)\hat{R}U^+_{\text{R}}(\tau)\\
&\quad\times\hat{h}(Ma,\mu\nu;Z)\}). \qquad (69)
\end{aligned}
$$

The obtained expression suggests the notation

$$
K^{(\text{IVR})}_{Ma\mu\to Nb\nu}(\tau)=\delta_{Ma,Nb}K^{(\text{IVR})}_{Ma,\mu\to\nu}(\tau). \qquad (70)
$$

1. Bilinear single-mode reservoir coupling

As a specific case, we consider the bilinear coupling of a single active molecular coordinate Q (with equilibrium value Q_{Ma}) to a reservoir of uncoupled harmonic oscillators with coordinates Z_ξ (normal-mode description of secondary molecular coordinates as well as environmental coordinates). Therefore, we set

$$\mathcal{H}_{Ma}^{(\mathrm{int})} = \hbar \sum_{\xi} k_{\xi}(Ma)(Q - Q_{Ma})Z_{\xi}, \tag{71}$$

and

$$m_{Ma}(\mu\nu) = \langle \chi_{Ma\mu} | Q - Q_{Ma} | \chi_{Ma\nu} \rangle = \delta_{\mu,\nu-1}\sqrt{\nu} + \delta_{\mu,\nu+1}\sqrt{\nu+1}, \tag{72}$$

which results in

$$\hat{h}(Ma,\mu\nu;Z) = m_{Ma}(\mu\nu) \sum_{\xi} k_{\xi}(Ma) Z_{\xi}. \tag{73}$$

The kernel caused by IVR follows as

$$K_{Ma,\mu\to\nu}^{(\mathrm{IVR})}(\tau) = \Theta(\tau) e^{-i\omega_{Ma,\mu\nu}\tau} \mathrm{tr}_{\mathrm{R}}\{\hat{R}\hat{h}(Ma,\mu\nu;Z)U_{\mathrm{R}}^{+}(\tau) \times \hat{h}(Ma,\nu\mu;Z)U_{\mathrm{R}}(\tau)\}. \tag{74}$$

The calculation of the reservoir correlation function is standard and yields

$$\mathrm{tr}_{\mathrm{R}}\{\hat{R}\hat{h}(Ma,\mu\nu;Z)U_{\mathrm{R}}^{+}(t)\hat{h}(Ma,\nu\mu;Z)U_{\mathrm{R}}(t)\} = |m_{a}(\mu\nu)|^{2} \sum_{\xi} k_{\xi}^{2}(Ma)\{[1+n(\omega_{\xi})]e^{i\omega_{\xi}t} + n(\omega_{\xi})e^{-i\omega_{\xi}t}\}. \tag{75}$$

We introduce the spectral density

$$J_{Ma}(\omega) = \sum_{\xi} k_{\xi}^{2}(Ma)\,\delta(\omega - \omega_{\xi}) \tag{76}$$

and obtain for the related rate

$$\begin{aligned} k_{Ma,\mu\to\nu}^{(\mathrm{IVR})} &= \delta_{\nu,\mu+1} 2\pi(\mu+1) n(\omega_{\mathrm{vib}}) J_{Ma}(\omega_{\mathrm{vib}}) \\ &\quad + \delta_{\nu,\mu-1} 2\pi\mu[1+n(\omega_{\mathrm{vib}})] J_{Ma}(\omega_{\mathrm{vib}}) \\ &\equiv \delta_{\nu,\mu+1} k_{Ma,\mu\to\mu+1}^{(\mathrm{IVR})} + \delta_{\nu,\mu-1} k_{Ma,\mu\to\mu-1}^{(\mathrm{IVR})}. \end{aligned} \tag{77}$$

D. Kernel related to the action of external fields

In the following, we use the coupling Hamiltonian [Eq. (10)], which should induce exclusively electronic transitions. This yields a second-order kernel as

$$\begin{aligned} K_{\alpha\to\beta}^{(\mathrm{field})}(t,t-\tau) &= \frac{\Theta(\tau)}{\hbar^{2}} \mathrm{tr}_{\mathrm{lead+R}}\{e^{-i\varepsilon_{\alpha\beta}\tau}\langle\Psi_{\beta}|\hat{\boldsymbol{\mu}}U_{\mathrm{lead}}(\tau) \\ &\quad \times U_{\mathrm{R}}(\tau)\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}|\Psi_{\alpha}\rangle \\ &\quad \times \langle\Psi_{\alpha}|\hat{\boldsymbol{\mu}}U_{\mathrm{R}}^{+}(\tau)U_{\mathrm{lead}}^{+}(\tau)|\Psi_{\beta}\rangle \\ &\quad + e^{i\varepsilon_{\alpha\beta}\tau}\langle\Psi_{\beta}|U_{\mathrm{lead}}(\tau)U_{\mathrm{R}}(\tau)\hat{\boldsymbol{\mu}}\hat{W}_{\mathrm{lead}}\hat{R}_{\mathrm{R}}|\Psi_{\alpha}\rangle \\ &\quad \times \langle\Psi_{\alpha}|U_{\mathrm{R}}^{+}(\tau)U_{\mathrm{lead}}^{+}(\tau)\hat{\boldsymbol{\mu}}|\Psi_{\beta}\rangle\}\mathbf{E}(t)\mathbf{E}(t-\tau). \end{aligned} \tag{78}$$

This expression results in a rather simple formula:

$$\begin{aligned} K_{\alpha\to\beta}^{(\mathrm{field})}(t,t-\tau) &= \frac{\Theta(\tau)}{\hbar^{2}}[e^{-i\varepsilon_{\alpha\beta}\tau}\mathbf{d}_{\beta\alpha}\mathbf{E}(t)\mathbf{d}_{\alpha\beta}\mathbf{E}(t-\tau) \\ &\quad + e^{i\varepsilon_{\alpha\beta}\tau}\mathbf{d}_{\alpha\beta}\mathbf{E}(t)\mathbf{d}_{\beta\alpha}\mathbf{E}(t-\tau)], \end{aligned} \tag{79}$$

with the transition matrix elements $\mathbf{d}_{\alpha\beta} = \langle\Psi_{\alpha}|\hat{\boldsymbol{\mu}}|\Psi_{\beta}\rangle$. Focusing on optical transitions and applying the Condon approximation, one obtains

$$\mathbf{d}_{\alpha\beta} = \delta_{M,N}\langle\chi_{Ma\mu}|\chi_{Mb\nu}\rangle\mathbf{d}_{Ma,Mb}. \tag{80}$$

The electronic transition matrix element (at a given charging state of the molecule) is denoted here by $\mathbf{d}_{Ma,Mb}$, and the field is written as

$$\mathbf{E}(t) = \mathbf{n}E(t)e^{-i\omega_{0}t} + \mathrm{c.c.}, \tag{81}$$

where $\mathbf{n}$ is the polarization unit vector, ω_0 the excitation frequency, and $E(t)$ the field envelope which is assumed to vary rather weakly with time such as to approach a (quasi) stationary regime. Applying the rotating wave approximation, we get ($d_{\alpha\beta} = \mathbf{n}\mathbf{d}_{\alpha\beta}$)

$$\begin{aligned} K_{\alpha\to\beta}^{(\mathrm{field})}(t,t-\tau) &= \frac{\Theta(\tau)|d_{\alpha\beta}|^{2}}{\hbar^{2}}[e^{-i(\varepsilon_{\alpha\beta}+\omega_{0})\tau}E(t)E^{*}(t-\tau) \\ &\quad + e^{-i(\varepsilon_{\alpha\beta}-\omega_{0})\tau}E^{*}(t)E(t-\tau)] + \mathrm{c.c.} \end{aligned} \tag{82}$$

If the time dependence of the field envelope gives rise to an adiabatic switch on and switch off of the field, the kernel exclusively depends on τ and the related rate reads

$$k_{\alpha\to\beta}^{(\mathrm{field})} = \delta_{M,N} k_{Ma\mu\to Mb\nu}^{(\mathrm{field})}, \tag{83}$$

with

$$\begin{aligned} k_{Ma\mu\to Mb\nu}^{(\mathrm{field})} &= \frac{2\pi}{\hbar^{2}}(E_{Ma,Mb}^{(\mathrm{R})})^{2}|\langle\chi_{Ma\mu}|\chi_{Mb\nu}\rangle|[\delta(\varepsilon_{Ma\mu,Mb\nu}+\omega_{0}) \\ &\quad + \delta(\varepsilon_{Ma\mu,Mb\nu}-\omega_{0})]. \end{aligned} \tag{84}$$

Here, we introduced the so-called Rabi energy $E_{Ma,Mb}^{(\mathrm{R})} = d_{Ma,Mb}E_{0}$, where E_0 is the field amplitude. For concrete computations, one may broaden the δ function by introducing electronic dephasing times to arrive at a Lorentzian line shape $[\pi\delta(\omega) \to \gamma/(\omega^{2}+\gamma^{2})]$.

E. Second-order stationary current

As indicated above for the particular chosen external field, the respective kernel depends only on τ and we can expect the formation of a stationary current at a finite applied voltage. According to Eq. (49), it is determined by $K_{\alpha\to X}(\omega=0)$, which has to be calculated here with respect to the second order in the molecule-lead coupling:

$$\begin{aligned} K_{\alpha\to X}^{(2)}(\tau) &= -\frac{1}{\hbar^{2}}\Theta(\tau)\mathrm{tr}\{(H_{\mathrm{mol\text{-}lead}}^{(1)},\hat{N}_{X})_{-}\mathcal{U}_{0}(\tau) \\ &\quad \times (H_{\mathrm{mol\text{-}lead}}^{(1)},\hat{W}_{\alpha}^{(\mathrm{eq})})_{-}\}. \end{aligned} \tag{85}$$

The zero-order time-evolution superoperator $\mathcal{U}_{0}(\tau)$ has been defined in Eq. (51). One immediately realizes that it only contributes via U_{lead} and $U_{\mathrm{el+vib}}$. In the following, we briefly demonstrate the computation of $K_{\alpha\to X}^{(2)}$ which is similar to that of the molecule-lead coupling rates due to electron transfer (Sec. IV A). First, we note that

$$(H^{(1)}_{\text{mol-lead}},\hat{N}_X)_- = \sum_{\mathbf{k},s}\sum_{N,a,b}[V_X(N+1a,Nb;\mathbf{k}s)|\phi_{N+1a}\rangle\langle\phi_{Nb}|a_{X\mathbf{k}s} - V_X(N-1a,Nb;\mathbf{k}s)|\phi_{N-1a}\rangle\langle\phi_{Nb}|a^+_{X\mathbf{k}s}] \quad (86)$$

and

$$(H^{(1)}_{\text{mol-lead}},\hat{W}^{(\text{eq})}_\alpha)_- = \sum_{X,\mathbf{k},s}\sum_b \hat{R}_{\text{R}}|\chi_{Na\mu}\rangle\langle\chi_{Na\mu}|[V_X(N+1b,Na;\mathbf{k}s)|\phi_{N+1b}\rangle \times\langle\phi_{Na}|a_{X\mathbf{k}s}\hat{W}_{\text{lead}} + V_X(N-1b,Na;\mathbf{k}s)|\phi_{N-1b}\rangle \times\langle\phi_{Na}|a^+_{X\mathbf{k}s}\hat{W}_{\text{lead}} - V_X(Na,N-1b;\mathbf{k}s)|\phi_{Na}\rangle \times\langle\phi_{N-1b}|\hat{W}_{\text{lead}}a_{X\mathbf{k}s} - V_X(Na,N+1b;\mathbf{k}s)|\phi_{Na}\rangle \times\langle\phi_{N+1b}|\hat{W}_{\text{lead}}a^+_{X\mathbf{k}s}]. \quad (87)$$

If both commutators are inserted into $K^{(2)}_{\alpha\to X}(\tau)$ [Eq. (85)], we obtain expectation values of lead operators resulting in Fermi distributions and expressions containing the trace with respect to the molecular electron-vibrational states. The vibrational part results in

$$\text{tr}_{\text{vib}}\{U^+_{aN}(\tau)|\chi_{a\mu}\rangle\langle\chi_{a\mu}|U_{N\pm1b}(\tau)\} = \sum_\nu |\langle\chi_{Na\mu}|\chi_{N\pm1b\nu}\rangle|^2 e^{i\varepsilon(Na\mu,N\pm1b\nu)\tau}. \quad (88)$$

Correspondingly, we get ($\alpha=Na\mu$)

$$K^{(2)}_{Na\mu\to X}(\tau) = -\frac{1}{\hbar^2}\Theta(\tau)\sum_{\mathbf{k},s}\sum_{b,\nu}[|\langle\chi_{Na\mu}|\chi_{N-1b\nu}\rangle \times V_X(Na,N-1b;\mathbf{k}s)|^2 e^{i\varepsilon(Na\mu,N-1b\nu)\tau} \times[1-f_F(\hbar\varepsilon_{X\mathbf{k}s}-\mu_X)]e^{-i\varepsilon_{X\mathbf{k}s}\tau} - |\langle\chi_{Na\mu}|\chi_{N+1b\nu}\rangle V_X(Na,N+1b;\mathbf{k}s)|^2 \times e^{i\varepsilon(Na\mu,N+1b\nu)\tau}f_F(\hbar\varepsilon_{X\mathbf{k}s}-\mu_X)e^{i\varepsilon_{X\mathbf{k}s}\tau}] + \text{c.c.} \quad (89)$$

After Fourier transformation at $\omega\to0$ and an interchange of both terms, we may write

$$K^{(2)}_{Na\mu\to X}(\omega=0) = -\sum_{b,\nu}(k^{(\text{mol-lead})}_{X,Na\mu\to N+1b\nu} - k^{(\text{mol-lead})}_{X,Na\mu\to N-1b\nu}). \quad (90)$$

The molecule–single-lead coupling rates $k^{(\text{mol-lead})}_X(Na\mu \to N\pm1b\nu)$ have been introduced in Eqs. (62) and (63), respectively. The result indicates the consistency of the present generalized master equation description. Together with the current, it is determined by the same rate expressions (based on the same level of approximation).

V. CONCLUSIONS

A generalized master equation description of charge transmission through a single molecule has been presented. It goes beyond any perturbative treatment of electron-vibrational coupling and accounts for nonequilibrium vibrational distributions. Based on a projection superoperator formalism, exact expressions for the generalized master equation kernels could be derived. Our approach accounts for intramolecular vibrational energy redistribution, excited electronic levels, as well as their optical excitation and deexcitation. Respective second-order transition rates have been derived for all mentioned processes:

$$k_{Ma\mu\to Nb\nu} = k^{(\text{mol-lead})}_{Ma\mu\to Nb\nu} + k^{(\text{IVR})}_{Ma\mu\to Nb\nu} + k^{(\text{opt})}_{Ma\mu\to Nb\nu} + k^{(\text{dec})}_{Ma\mu\to Nb\nu}, \quad (91)$$

with the molecule-lead coupling rate $k^{(\text{mol-lead})}$ responsible for charge transfer, and the rates $k^{(\text{IVR})}$, $k^{(\text{opt})}$, and $k^{(\text{dec})}$ of IVR, optical excitation, and non-radiative de-excitation, respectively. They describe transitions from a charging state M of the molecule into the charging state N with a possible change of the electronic level from a to b and a change of the vibrational state from μ to ν. Related numerical results for a model with a singly charged state ($M,N=0,1$), an electronic ground and a single excited state, and the vibrational levels belonging to a single reaction coordinate will be given in an accompanying publication.[33] In particular, an optical current switching is suggested for the case of weak electron-lead coupling and large reorganization energy upon charging. Further, a quantitative account will be given on how intramolecular vibrational energy redistribution and excited state deexcitation influence the current switching.

Although the approach has been explicitly outlined for the case of second-order rate expression, the calculation of fourth-order rates is straightforward. Future extensions of the model therefore may account for cotunneling in a similar fashion as it has been already done in the single-electron description of Ref. 18. Furthermore, it would be interesting to account for a direct rate of photoassisted charging or discharging of the molecule in the relation to optical current switching.

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APPENDIX: MEMORY KERNEL IN THE ABSENCE OF TIME-DEPENDENT EXTERNAL FIELDS

In the following, some formal relations which are useful when going beyond second-order rates in the case of no external field coupling will be presented. Here, the kernel [Eq. (34)] depends on the time difference only. This makes it convenient to introduce the Fourier-transformed kernel

$$K_{\alpha\beta}(\omega) = -i\,\text{tr}\{\hat{\Pi}_\alpha\mathcal{V}\tilde{\mathcal{G}}(\omega)\mathcal{V}\hat{W}^{(\text{eq})}_\beta\} = \delta_{\alpha,\beta}K_\alpha(\omega) + (1+\delta_{\alpha,\beta})K_{\beta\to\alpha}(\omega). \quad (A1)$$

The expression includes the Green's superoperator

$$\tilde{\mathcal{G}}(\omega) = -i\int_0^\infty dt e^{i\omega t}\mathcal{U}_{\mathcal{Q}}(t) = (\omega - \mathcal{Q}\mathcal{L} + i\epsilon)^{-1} \qquad \text{(A2)}$$

and the frequency dependent transition rates $K_{\beta\to\alpha}(\omega)$ (ordinary rates are met in the limit $\omega\to 0$ and we introduced $\mathcal{L} = \mathcal{L}_0 + \mathcal{V}$ with $\mathcal{L}_0 \ldots = [H_{\mathrm{mol}} + H_{\mathrm{lead}}, \ldots]_-/\hbar$). Next, but in a more general frame, we again demonstrate the existence of a particular sum rule already used in Sec. III.

1. Sum rule

First we note the general property of the kernel [Eq. (A1)]:

$$\sum_\alpha K_{\alpha\beta} = -i\,\mathrm{tr}\{\mathcal{V}\tilde{\mathcal{G}}(\omega)\mathcal{V}\hat{W}_\beta^{(\mathrm{eq})}\} = 0. \qquad \text{(A3)}$$

This result follows from the completeness relation $\Sigma_\alpha \hat{\Pi}_\alpha = 1$. Further, the obtained expression vanishes identically because it is the trace of a commutator. Since $\tilde{\mathcal{G}}$ has not been affected, the relation, which can be understood as a certain type of sum rule, is also valid for other types of Green superoperators and their possible approximations. In the limit $\omega = 0$ Eq. (A3) reflects probability conservation of the ordinary rate equations (without memory effects). In particular, we may deduce

$$K_\beta(0) = -\sum_\alpha K_{\beta\to\alpha}(0), \qquad \text{(A4)}$$

where $-K_\beta(0)$ can be interpreted as the inverse lifetime of state β.

2. Removal of the projection superoperator $\mathcal{P}$

Next, we remove the Green superoperator $\tilde{\mathcal{G}}(\omega)$ from the kernel Eq. (A1) by introducing the Green' superoperator

$$\mathcal{G}(\omega) = (\omega - \mathcal{L} + i\epsilon)^{-1}. \qquad \text{(A5)}$$

It is independent of the projector $\mathcal{P}$. Taking into account

$$[\mathcal{G}^{-1}(\omega) + \mathcal{P}\mathcal{V}]\tilde{\mathcal{G}}(\omega) = 1, \qquad \text{(A6)}$$

we may simply derive

$$\tilde{\mathcal{G}}(\omega) = \mathcal{G}(\omega) - \mathcal{G}(\omega)\mathcal{P}\mathcal{V}\tilde{\mathcal{G}}(\omega). \qquad \text{(A7)}$$

If inserted into Eq. (A1), one obtains

$$\begin{aligned} K_{\alpha\beta}(\omega) &= -i\,\mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\hat{W}_\beta^{(\mathrm{eq})}\} \\ &\quad + i\,\mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\mathcal{P}\mathcal{V}\tilde{\mathcal{G}}(\omega)\mathcal{V}\hat{W}_\beta^{(\mathrm{eq})}\} \\ &= -i\,\mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\hat{W}_\beta^{(\mathrm{eq})}\} \\ &\quad + i\sum_\gamma \mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\hat{W}_\gamma^{(\mathrm{eq})}\}\mathrm{tr}\{\hat{\Pi}_\gamma\mathcal{V}\tilde{\mathcal{G}}(\omega)\mathcal{V}\hat{W}_\beta^{(\mathrm{eq})}\}. \end{aligned} \qquad \text{(A8)}$$

Here, the second trace in the γ sum reproduces the kernel $K_{\gamma\beta}(\omega)$. To rewrite the first trace in the γ sum, we deduce from Eq. (A5)

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}(\omega) \qquad \text{(A9)}$$

and

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}(\omega)\mathcal{V}\mathcal{G}_0(\omega). \qquad \text{(A10)}$$

Then, we may set

$$\begin{aligned} \mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\hat{W}_\gamma^{(\mathrm{eq})}\} &= \mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}_0(\omega)\hat{W}_\gamma^{(\mathrm{lead})}\} \\ &\quad + \mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\mathcal{G}_0(\omega)\hat{W}_\gamma^{(\mathrm{eq})}\} \\ &= \frac{1}{\omega + i\epsilon}\mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\hat{W}_\gamma^{(\mathrm{eq})}\}. \end{aligned} \qquad \text{(A11)}$$

The last line follows from the fact that trace expressions of first order in $\mathcal{V}$ vanish and that $\mathcal{G}_0(\omega)$ applied to $\hat{W}_\gamma^{(\mathrm{eq})}$ simply produces a frequency denominator.

We denote the rate expressions which do not contain the projector $\mathcal{P}$ as

$$L_{\alpha\beta}(\omega) = -i\,\mathrm{tr}\{\hat{\Pi}_\alpha\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\hat{W}_\beta^{(\mathrm{eq})}\}. \qquad \text{(A12)}$$

Moreover, the notation

$$L_{\alpha\beta}(\omega) = \delta_{\alpha,\beta}L_\alpha(\omega) + (1 - \delta_{\alpha,\beta})L_{\beta\to\alpha}(\omega) \qquad \text{(A13)}$$

is introduced. Then, $K_{\alpha\beta}$ and $L_{\alpha\beta}$ are related to each other by the following equation:

$$K_{\alpha\beta}(\omega) = L_{\alpha\beta}(\omega) - \frac{i}{\omega + i\epsilon}\sum_\gamma L_{\alpha\gamma}K_{\gamma\beta}. \qquad \text{(A14)}$$

Introducing the matrix notation $\hat{K}$ and $\hat{L}$ for both sets $K_{\alpha\beta}$ and $L_{\alpha\beta}$, respectively, a closed expression for $\hat{K}$ simply follows from Eq. (A14) as

$$\hat{K}(\omega) = \left(1 + i\frac{\hat{L}(\omega)}{\omega + i\epsilon}\right)^{-1}\hat{L}(\omega). \qquad \text{(A15)}$$

This expression guarantees that the $K_{\beta\to\alpha}$ entering the rate equations do not lead to a double counting of lower-order rates. If, for example, $K_{\alpha\beta}$ has been calculated in a certain order with respect to the transfer coupling $H_{\text{mol-lead}}$, any lower-order rate has been removed. Moreover, if $\hat{K}(\omega)$ becomes divergent for $\omega\to 0$, Eq. (A16) indicates the way to make the expression regular. A power expansion of Eq. (A15) takes the form

$$\hat{K}(\omega) = \hat{L}(\omega) + \sum_{n=1}^\infty\left(\frac{-i\hat{L}(\omega)}{\omega + i\epsilon}\right)^n\hat{L}(\omega). \qquad \text{(A16)}$$

3. Some approximations

We rewrite $L_{\alpha\beta}$ in such a way to let the lowest-order contribution appear explicitly. Therefore, $\mathcal{G}(\omega)$ in Eq. (A12) is replaced according to

$$\mathcal{G}(\omega) = \mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}_0(\omega) + \mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\mathcal{G}_0(\omega). \tag{A17}$$

If inserted into Eq. (A12), the first term produces the second-order rate

$$L^{(2)}_{\alpha\beta}(\omega) = -i\,\mathrm{tr}\{\hat{\Pi}_\alpha \mathcal{V}\mathcal{G}_0(\omega)\mathcal{V}\hat{W}^{(\mathrm{eq})}_\beta\}. \tag{A18}$$

Here, we note that $L^{(2)} = K^{(2)}$ [cf. Eq. (A14)]. Moreover, the second term on the right-hand side of Eq. (A17) does not contribute, and the third one gives higher-order contributions in $H_{\text{mol-lead}}$. It is written as

$$\tilde{L}_{\alpha\beta}(\omega) = -i\,\mathrm{tr}\{\hat{\Pi}_\alpha \mathcal{V}\mathcal{G}_0(\omega)\mathcal{V}\mathcal{G}(\omega)\mathcal{V}\mathcal{G}_0(\omega)\mathcal{V}\hat{W}^{(\mathrm{eq})}_\beta\}. \tag{A19}$$

First, notice that this expression, at least in principle, accounts for charge transmission processes leading directly from one lead to another (cotunneling). An ordinary fourth-order approximation for $\tilde{L}_{\alpha\beta}$ follows immediately by replacing $\mathcal{G}$ by $\mathcal{G}_0$. To get $K^{(4)}_{\alpha\beta}$, we utilize Eq. (A16) and directly obtain

$$K^{(4)}_{\beta\to\alpha}(\omega) = L^{(4)}_{\beta\to\alpha}(\omega) - \frac{i}{\omega + i\epsilon}\sum_\gamma L^{(2)}_{\beta\gamma}L^{(2)}_{\gamma\alpha}. \tag{A20}$$

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