Nonequilibrium steady state transport via the reduced density matrix operator

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We present a very simple model for numerically describing the steady state dynamics of a system interacting with continua of states representing a bath. Our model can be applied to equilibrium and nonequilibrium problems. For a one-state system coupled to two free electron reservoirs, our results match the Landauer formula for current traveling through a molecule. More significantly, we can also predict the nonequilibrium steady state population on a molecule between two out-of-equilibrium contacts. While the method presented here is for one-electron Hamiltonians, we outline how this model may be extended to include electron-electron interactions and correlations, an approach which suggests a connection between the conduction problem and the electronic structure problem. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3109898]

I. INTRODUCTION: STEADY STATE FORMALISMS, SCATTERING, AND TRANSPORT

There is a long history of using scattering theory as a steady state tool for doing quantum-mechanical calculations to capture the transport of charge from one side of a system to another. In basic three dimensional, time-independent scattering theory, one describes a single incoming electron impinging on an atomic target, and then scattering off toward infinity.[1] In one dimension, the Wentzel-Kramers-Brillouin (WKB) approximation is often used to describe the transmission and reflection of one electron incoming from the left which will ultimately scatter forward or backward.[2] In many physical applications, such scattering pictures have been successfully applied to model charge movement.

Over the past 20 years, Nitzan and others[3,4] showed that the time-independent scattering formalism can be generalized to a broad class of steady state nonequilibrium situations. In this framework, incoming waves become source or driving terms, while transmitted and reflected waves become drain terms. The drain term is usually cast in the form of a self-energy $\Sigma(E)$ that depends on the energy of an individual electron. The time-independent Schrodinger equation ($H\Psi = E\Psi$) which is used for time-independent scattering theory becomes a steady state equation. Using steady state equations, Nitzan and others showed that one can describe a variety of different nonequilibrium phenomena including energy transfer and charge transfer, especially within the context of a one-electron Hamiltonian.

When the physical model allows electrons to interact, however, and electrons exchange spin and energy with their environment, the steady state formulation becomes much more difficult to implement. One problem is that, when the incoming electron does not have a well-defined energy, there is no way to cleanly construct a sink ($\Sigma(E)$), and one must use absorbing boundary conditions, which both destroy the electron and distort the solution. For problems such as molecular conduction,[5,6] where there are different Fermi levels on both sides of the molecule, it is unclear how to impose boundary conditions on one electron if it is interacting with others. Ideally, we would prefer boundary conditions that are consistent with many electrons all together, rather than those that require us to know the individual energy of each electron. One appealing approach toward that goal is the stochastic surrogate Hamiltonian model of Katz *et al.*,[7] whereby one describes a bath of particles in layers of complexity, yielding a computational feasible method for describing relaxation for a system of many particles all together. There may well be an efficient algorithm combining the approach in Ref. 7 with the algorithm we present below.

In this paper, we will suggest a new steady state formalism that (i) treats many electrons at the same time, and that (ii) allows our system's boundaries to act as both sinks and sources at the same time and for all electrons. Our formalism will be based on the reduced density matrix of the system rather than the amplitudes of any wave function, and is summed up in Eqs. (9) and (26) below. We call these fundamental equations steady state reduced density matrix (SSRDM) equations. Although our present models for transport are limited to mean-field Hamiltonians, an obvious extension of our model toward understanding the role of electron-electron correlation in transport is discussed in Sec. V and is currently being investigated. Equation (54) shows that SSRDM equations for the two-particle RDM (2-RDM) are exactly the anti-Hermitian contracted Schrodinger equation (ACSE), which has been investigated by Mazziotti[8–13] and Valdemoro *et al.*,[15] plus damping terms that enforce open-boundary conditions and allow for nonequilibrium solutions.

The astute reader will notice that a model of transport similar to ours has been published recently and independently by Todorov and co-workers,[16,17] who investigated the time evolution of the one-electron reduced density matrix subject to a mean-field tight-binding Hamiltonian. Although

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Todorov and co-workers were focused more on the transient behavior of currents in capacitors, they came to similar conclusions regarding the usefulness of the damping parameter γ introduced in Eq. (9) in steady state. The results in this paper extend the work of those authors by further exploring the applicable conditions on γ, introducing bath reservoirs instead of tight-binding models, investigating the locality of correlations within those bath reservoirs, and suggesting extensions to account for electron-electron correlation in terms of the 2-RDM.

II. EQUILIBRIUM: A SINGLE STATE COUPLED TO A RESERVOIR

A. Theory

We first consider the simplest example in many-body physics: a single state coupled to a particle reservoir. The Hamiltonian is standard:

$$H = H_0 + H_1,$$

$$H_0 = \epsilon_s s^\dagger s + \sum_k \epsilon_k b_k^\dagger b_k, \tag{1}$$

$$H_1 = \sum_k V_k (s^\dagger b_k + b_k^\dagger s).$$

Here b_k destroys state k in the bath or reservoir and we use units in which $\hbar = 1$. We want to consider the case where there are an infinite number of single particle bath states (or k-states) spread continuously over an interval $[\epsilon_{\min}, \epsilon_{\max}]$, thus representing a metallic solid. In our numerical implementation, however, we discretize the continuum and include in our calculations only a finite number of k-states, spaced apart in energy by $\Delta\epsilon_k$. By including the appropriate broadening into our formalism (which requires the inclusion of imaginary terms), this finite number of k-states can, in fact, represent a continuum of states as has been shown many times before (e.g., see Ref. 18, and references therein).

Consider first the case of equilibrium, where we are interested in the population density on the system $\langle s^\dagger s \rangle$ given that the bath has Fermi energy μ_F. Although this problem can be solved in many ways,[19] including brute force (i.e., numerical diagonalization), this problem illustrates well our new numerical approach.

To begin with, we define the one-particle RDM (1-RDM) as

$$\rho_{uv} = \langle a_u^\dagger a_v \rangle, \tag{2}$$

where a is an annihilation operator representing either the bath (b) or the system (s). In this basis, we have

$$\rho = \begin{pmatrix} \rho_{ss} & \rho_{sb} \\ \rho_{bs} & \rho_{bb} \end{pmatrix} = \begin{pmatrix} \langle s^\dagger s \rangle & \langle s^\dagger b_k \rangle \\ \langle b_k^\dagger s \rangle & \langle b_k^\dagger b_{k'} \rangle \end{pmatrix}. \tag{3}$$

Note, that this definition of the 1-RDM is not universal. For a single electron in a pure state $|\Psi\rangle$, it is common to define the one-particle (full) density matrix as

$$\rho_{uv}^{\text{common}} = \langle u|\Psi\rangle\langle\Psi|v\rangle = \langle\Psi|a_v^\dagger a_u|\Psi\rangle = \langle a_v^\dagger a_u \rangle. \tag{4}$$

These two different definitions can lead to confusion when doing time dynamics, in particular, concerning the sign of the Liouville equation:

$$\frac{d}{dt}\rho_{uv}^{\text{common}} = -i(H\rho - \rho H)_{uv}, \tag{5}$$

$$\frac{d}{dt}\rho_{uv} = i(H^T\rho - \rho H^T)_{uv} \tag{6}$$

$$= i(H\rho - \rho H)_{uv}, \tag{7}$$

where we assume in Eq. (7) that the Hamiltonian H is real. We use the definition of the 1-RDM in Eq. (2) rather than Eq. (4) because it matches the definitions used in Ref. 20.

Now, in standard system-bath problems, the bath is taken to be strictly at equilibrium even during system relaxation. Physically, this reflects the fact that the bath is infinite and its state is not affected by processes in the system. This would imply that, for bath states labeled k and k', we have the following condition:

$$\rho_{kk'} \overset{\text{should}}{=} \rho_{kk'}^F \equiv \delta_{kk'} f(\epsilon_k) = \delta_{kk'} \frac{1}{1 + e^{\beta(\epsilon_k - \mu)}}. \tag{8}$$

In our numerical work, however, finite bath models are used. This makes it necessary to replace a requirement of strict equilibrium by the introduction of a relaxation term, similar to the addition of absorbing boundary conditions in numerical simulation. In the Appendix, we show that this bath relaxation is crucial in order to describe system broadening. The relaxation term is added to the bath-bath part of the Liouville equation. For a steady state solution, the entire Liouville expression is set to zero:

$$\dot{\rho} = i\left\{ \begin{pmatrix} H_{ss} & H_{sb} \\ H_{bs} & H_{bb} \end{pmatrix} \begin{pmatrix} \rho_{ss} & \rho_{sb} \\ \rho_{bs} & \rho_{bb} \end{pmatrix} - \begin{pmatrix} \rho_{ss} & \rho_{sb} \\ \rho_{bs} & \rho_{bb} \end{pmatrix} \begin{pmatrix} H_{ss} & H_{sb} \\ H_{bs} & H_{bb} \end{pmatrix} \right\}$$
$$- \gamma \left\{ \begin{pmatrix} 0 & 0 \\ 0 & \rho_{bb} \end{pmatrix} - \begin{pmatrix} 0 & 0 \\ 0 & \rho_{bb}^F \end{pmatrix} \right\} = 0. \tag{9}$$

Henceforward, Eq. (9) will be referred to as a SS-RDM equation.

For γ infinitesimal, Eq. (9) tries to satisfy two conditions which cannot be both be satisfied simultaneously (as the reader can easily verify):

(1) Steady state quantum dynamics ($[H, \rho] = 0$).
(2) The bath should look like a Fermi metal $\rho_{bb} = \rho_{bb}^F$.

In other words, Eq. (9) describes a steady state system where the bath is relaxed toward thermal equilibrium where Fermi statistics are obeyed. We will find empirically that Eq. (9) has a unique solution for the model Hamiltonian H in Eq. (1). Moreover, like numerical scattering calculations, the results obtained from Eq. (9) do not depend strongly on the damping parameter γ for γ chosen appropriately (as discussed below).

Equation (9) can be solved by propagating ρ forward in time with a simple differential equation propagator (like Runge–Kutta). For large enough γ, convergence is quick, but

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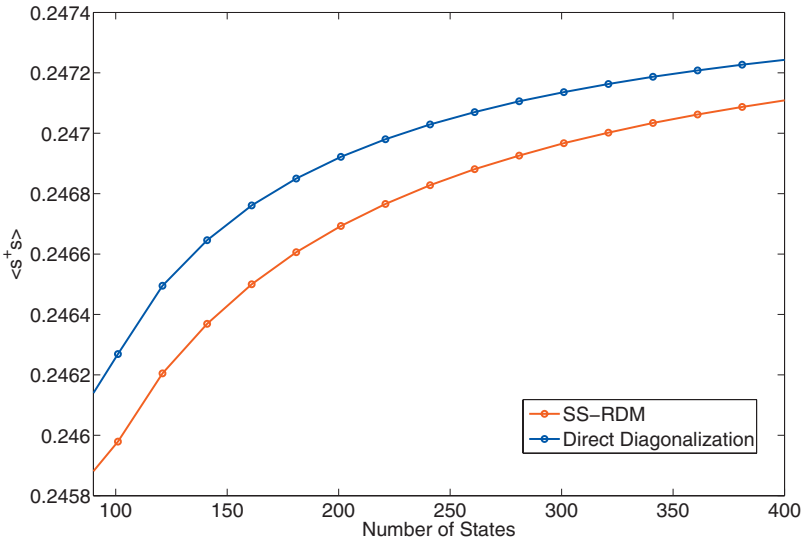


FIG. 1. (Color) Convergence of population with density of states. Here we choose the system energy to be $\epsilon_s=1$, the Fermi energy of the bath to be $\mu_F=0.5$, and the band edges of the continuum (in energy) to be $[-10,10]$. The energies of the single particle bath states have been spaced equally between the band edges of the continuum. Other parameters are the temperature ($T=0.1$) and the damping parameter γ in Eq. (9) ($\gamma=1\times10^{-4}$). The coupling of the system to the bath is fixed by $\Gamma=2\pi\eta V^2=1$. The direct diagonalization curve assumes the entire system is finite and points on this curve are obtained by diagonalizing the real, symmetric Hamiltonian in Eq. (1), filling up all eigenstates of H according to a Fermi distribution with a given Fermi level, and transforming all population information back to the original basis of separate, orthogonal, bath and systems states.

for small gamma, convergence is slow. A second approach which converges more quickly and gives us physical insight works by defining projection operators:

$$P=\begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix}, \tag{10}$$

$$Q=\begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix}. \tag{11}$$

P projects onto the state and Q projects onto the bath. In this language, the SS-RDM equation reads

$$\dot{\rho}=i(H\rho-\rho H)-\gamma Q\rho Q+\gamma Q\rho^F Q=0. \tag{12}$$

Equation (12) can be solved by rearranging the equation as

$$(iH-\gamma/2Q)\rho-\rho(iH+\gamma/2Q)+\gamma/2P\rho Q + \gamma/2Q\rho P+\gamma Q\rho^F Q=0 \tag{13}$$

and then iterating

$$R(\rho)=\frac{\gamma}{2}P\rho Q+\frac{\gamma}{2}Q\rho P+\gamma Q\rho^F Q, \tag{14}$$

$$(iH-\gamma/2Q)\rho-\rho(iH+\gamma/2Q)=-R(\rho). \tag{15}$$

If we regard $R(\rho)$ as a constant matrix in Eq. (15), then Eq. (15) is a Sylvester equation[21] and can be solved by standard techniques (e.g., in MATLAB). In particular, they can be solved rapidly by defining new operators H^+, H^- and their diagonal representations Ω, Λ:

$$H^+\equiv iH+\gamma/2Q=U^{-1}\Omega U, \tag{16}$$

$$H^-\equiv iH-\gamma/2Q=X^{-1}\Lambda X. \tag{17}$$

Even though the operators H^+, H^- are not Hermitian, and thus a complete set of eigenstates is not guaranteed, they are complex symmetric and not too far from Hermitian (for γ not too large). We therefore assume that they can be diagonalized, albeit in a nonorthogonal basis. This is equivalent to assuming the existence of a complete set of biorthogonal left and right eigenvectors for H^+ and H^-.

Using Eqs. (16) and (17), Eq. (15) becomes

$$\Lambda(X\rho U^{-1})-(X\rho U^{-1})\Omega=-XR(\rho)U^{-1}. \tag{18}$$

If we now change basis, Eqs. (14) and (15) become very simple to solve

$$\Lambda\tilde{\rho}-\tilde{\rho}\Omega=-\tilde{R}(\tilde{\rho}), \tag{19}$$

$$\tilde{R}(\tilde{\rho})=\frac{\gamma}{2}\tilde{P}\tilde{\rho}\tilde{Q}+\frac{\gamma}{2}\tilde{Q}\tilde{\rho}\tilde{P}+\gamma\tilde{Q}\tilde{\rho}^F\tilde{Q}, \tag{20}$$

where we define

$$\tilde{\rho}=X\rho U^{-1},\quad \tilde{\rho}^F=X\rho^F U^{-1}, \tag{21}$$

$$\tilde{P}=XPU^{-1},\quad \tilde{Q}=XQU^{-1}. \tag{22}$$

Solving Eqs. (19) and (20) iteratively and self-consistently is very quick since Λ and Ω are diagonal operators.

B. Numerical results

In our theoretical development of equilibrium, detailed above in the SS-RDM equation, one must choose both (i) a discrete number of states to describe the bath or continuum reservoir (N_{bath}), and (ii) a value for the damping parameter γ. We must now show that these numbers can be chosen so that our model has physical meaning.

We first consider the density of states used to model the bath. In Fig. 1, we show that the population on the system is affected only marginally by increasing the number of bath states in Eq. (9). We compare our SS-RDM results with the result obtained by direct diagonalization of the Hamiltonian H in Eq. (1) for a finite system (without any broadening or complex energies). It should be noted that allowing an increase in the density of bath states (η) must be done while also keeping $\Gamma=2\pi\eta V^2$ a constant in accordance with the Golden rule. From the data in Fig. 1, we may conclude that, above a certain threshold number of states, we are modeling a picture of a continuous bath.

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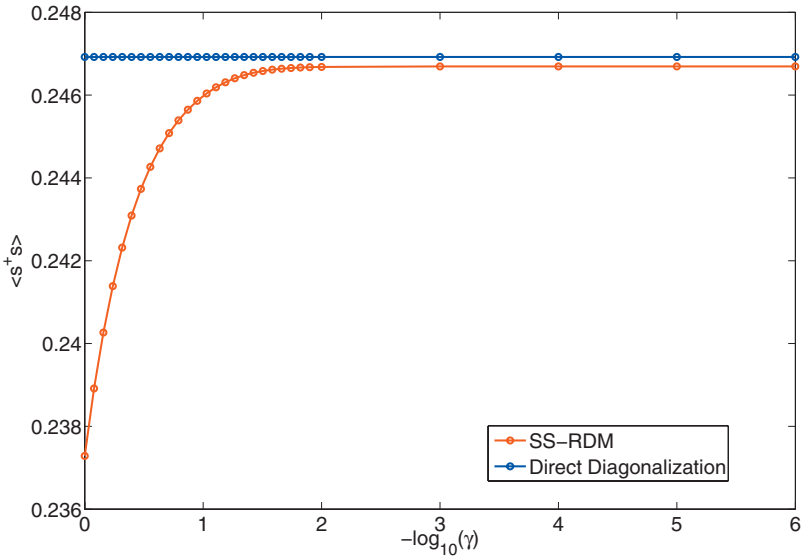


FIG. 2. (Color) Population of the system $\langle s^{\dagger}s\rangle$ plotted as a function of γ. Here we choose the system energy $\epsilon_s=1$, the Fermi energy of the bath to be $\mu_F=0.5$, and the temperature to be $T=0.1$. The number of states is $N_{\text{bath}}=200$, and all states are spaced evenly between the band edges of the continuum (chosen as $[-10,10]$). The coupling of the system to the bath is fixed by $\Gamma=2\pi\eta V^2=1$. The direct diagonalization curve assumes the entire system is finite and points on this curve are obtained by diagonalizing the real, symmetric Hamiltonian in Eq. (1), filling up all eigenstates of H according to a Fermi distribution with a given Fermi level, and transforming all population information back to the original basis of separate, orthogonal, bath and systems states.

Next, we turn to γ. The exact answer to the problem of one state coupled to a discrete set of bath states requires $\gamma=0$, so that $[\rho,H]=0$. In general, we should expect that, in order to capture the correct physical description of a finite system interacting with a continuum, a good choice of γ should depend on the energy spacing between states in the bath: $\Delta\epsilon_k=(\text{bandwidth}/N_{\text{bath}})$. According to standard methodologies for discretizing a metal into a finite number of states, introducing an imaginary energy [i.e., self-energy $\Sigma(E)=E_0+iE_1$] in the Hamiltonian reflects a broadening of energy levels, and a metal should be correctly described when $E_1\approx\Delta\epsilon_k$.[3] Although, as written in Eq. (9), the parameter γ is not a self-energy, we will interpret γ as broadening of bath states. The interesting result in Fig. 2 is that the system population $\langle s^{\dagger}s\rangle$ is very insensitive to γ over a wide range of γ values, provided that $\Gamma\geq\gamma$, $\Delta\epsilon_k$. This can be explained in two ways.

First, from a physical perspective, provided $\Gamma\geq\gamma$, we know that the rate at which an electron moves to and from the system is faster than the rate at which the bath (as a whole) relaxes toward a Fermi distribution with a fixed Fermi level. Suppose that at time $t=-\infty$, there is no system-bath coupling, the system is unoccupied, and the bath is equilibrated. Now, we switch on the system-bath coupling at $t=0$. For the case of equilibrium, if an electron moves from the bath to the system at time $t=\hbar/\Gamma$, it will return to the bath at time $t=2\hbar/\Gamma$, well before any appreciable bath relaxation. Because the population of the system is determined from this electron transfer back and forth, we conclude that the result must be determined almost entirely by the Fermi level of the bath and depend only minimally on bath relaxation. Second, from a computational perspective, if we consider propagating the density matrix ρ forward in time with $\gamma=0$, we will never reach steady state, but rather we will find Poincaré recurrences with period $\Delta\epsilon_k^{-1}$ on top of the relaxation rate Γ.[3] By introducing a small $\gamma>0$, we can eliminate these recurrences and drive the system to the correct steady state. The result for system population will be nearly independent of γ.

Note that the limit $\gamma\to\infty$, $\gamma\gg\Gamma$ is an incorrect choice for γ. In such a case, the SS-RDM equation does not allow for bath relaxation, but rather enforces equilibrium conditions on the bath [Eq. (8)], and, as shown in the Appendix, this restriction does not describe the broadening of the system state.

For nonequilibrium problems, there are more than two competing rates, for example, charge injection from one bath versus charge ejection into another bath versus energetic relaxation of the bath, and this can lead to nonzero current density. For nonequilibrium problems, we expect (and find) that not all dynamical observables will be independent of γ as $\gamma\to 0$. Nevertheless, the insensitivity of the population $\langle s^{\dagger}s\rangle$ to γ for equilibrium problems (in Fig. 2) strongly suggests that Eq. (9) is correctly capturing the physical picture of a molecule interacting with a continuous bath.

III. NONEQUILIBRIUM: A SINGLE STATE COUPLED TO TWO RESERVOIRS

A. Theory

At first glance, Eq. (9) would appear a very inefficient approach toward solving many-body problems, especially problems where finite systems interact with a continuous bath. After all, Eq. (9) treats bath degrees of freedom explicitly, and thus, one is forced to manipulate and diagonalize large operators with both bath and system degrees of freedom. For the equilibrium problem, standard Green's functions techniques avoid treating bath degrees of freedom almost entirely by defining self-energies. Moreover, the most elementary approach—constructing and diagonalizing the Hamiltonian to find the population of the system—is faster than solving Eq. (9). Solving Eq. (9) appears to be the most tedious and least efficient approach.

That being said, however, the strength of Eq. (9) is that it is easily generalized to nonequilibrium steady state problems. As an example, we now solve the problem of a single level coupled to two reservoirs (left and right), which can be out of equilibrium: $\mu_F^L\neq\mu_F^R$. The Hamiltonian we consider is

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$$H = H_0 + H_1,$$

$$H_0 = \epsilon_s s^\dagger s + \sum_{k\in L} \epsilon_k b_k^\dagger b_k + \sum_{k\in R} \epsilon_k c_k^\dagger c_k, \tag{23}$$

$$H_1 = \sum_{k\in L} V_k (s^\dagger b_k + b_k^\dagger s) + \sum_{k\in R} W_k (s^\dagger c_k + c_k^\dagger s).$$

We use b_k to represent the bath on the left, and c_k the bath on the right. This Hamiltonian ignores both spin degeneracy and coupling to vibronic motion, even though both are crucial components of molecular conduction experiments. Nuclear motion is especially important near resonance. For simplicity and pedagogical purposes, however, we study the Hamiltonian in Eq. (23), and we will compare the SS-RDM result for current through the system to the exact (Landauer) result.

For this model problem of two baths not at equilibrium, we first define two equilibrium distribution functions for the baths, one for the left and one for the right:

$$\rho_{kk'}^{F,L} \equiv \delta_{kk'} \frac{1}{1 + e^{\beta(\epsilon_k - \mu_F^L)}} \equiv f_L(\epsilon_k), \tag{24}$$

$$\rho_{kk'}^{F,R} \equiv \delta_{kk'} \frac{1}{1 + e^{\beta(\epsilon_k - \mu_F^R)}} \equiv f_R(\epsilon_k). \tag{25}$$

Then, in analogy to Eq. (9), the steady state density matrix is the solution to

$$i\left\{\begin{pmatrix} H_{ss} & H_{sb} & H_{sc} \\ H_{bs} & H_{bb} & 0 \\ H_{cs} & 0 & H_{cc} \end{pmatrix}\begin{pmatrix} \rho_{ss} & \rho_{sb} & \rho_{sc} \\ \rho_{bs} & \rho_{bb} & \rho_{bc} \\ \rho_{cs} & \rho_{cb} & \rho_{cc} \end{pmatrix} - \begin{pmatrix} \rho_{ss} & \rho_{sb} & \rho_{sc} \\ \rho_{bs} & \rho_{bb} & \rho_{bc} \\ \rho_{cs} & \rho_{cb} & \rho_{cc} \end{pmatrix}\begin{pmatrix} H_{ss} & H_{sb} & H_{sc} \\ H_{bs} & H_{bb} & 0 \\ H_{cs} & 0 & H_{cc} \end{pmatrix}\right\} - \gamma\left\{\begin{pmatrix} 0 & 0 & 0 \\ 0 & \rho_{bb} & \rho_{bc} \\ 0 & \rho_{cb} & \rho_{cc} \end{pmatrix} - \begin{pmatrix} 0 & 0 & 0 \\ 0 & \rho_{bb}^F & 0 \\ 0 & 0 & \rho_{cc}^F \end{pmatrix}\right\} = 0. \tag{26}$$

Like Eq. (9), Eq. (26) will also be referred to as an SS-RDM equation. An element of the density matrix (e.g., $\rho_{ss} = \langle s^\dagger s \rangle$) is an average over nonequilibrium steady state ensembles. The strength of Eq. (26) is that, by setting the entire expression on the left to zero, the equation describes steady state nonequilibrium phenomena without explicitly doing time dynamics.

Now, for the nonequilibrium case where $\mu_F^L \neq \mu_F^R$, we have $\rho_{bb}^F \neq \rho_{cc}^F$ in Eq. (26), and there will be a nonzero current. The steady state current can be calculated as

$$I_L = -e\frac{d}{dt}\left(\sum_{k\in L} \langle b_k^+ b_k \rangle\right) \tag{27}$$

$$= \frac{ei}{\hbar} \sum_{k\in L} V_k (\langle b_k^+ s \rangle - \langle s^+ b_k \rangle) \tag{28}$$

$$= -\frac{2e}{\hbar} \sum_{k\in L} V_k \, \mathrm{Im}(\langle b_k^+ s \rangle). \tag{29}$$

B. Numerical results

Just as before, in order to justify the validity of Eq. (26), we must investigate the dependence of the solution on the parameter γ. As discussed above in the equilibrium case and in the Appendix, in order to describe broadening correctly, we should never choose $\gamma \gg \Gamma$. This choice applies both to equilibrium and nonequilibrium boundary conditions. In the opposite limit (i.e., $\gamma \to 0$), whereas all physical properties at equilibrium are not sensitive to the choice of γ, some physical properties for nonequilibrium conditions are extremely sensitive to γ. In particular, while the nonequilibrium steady state population of the system is rather insensitive to the size of γ, the current [Eq. (29)] is incredibly sensitive to γ, and for $\gamma \ll \Delta\epsilon_k$, we find $I_L \propto \gamma$.

The behavior of the current for $\gamma \to 0$ can be explained in two ways. Empirically, when we investigate the solution to Eq. (26), we find that unless $\gamma \geq \Delta\epsilon_k$, we cannot enforce nonequilibrium conditions. Instead, we find, for $\gamma \ll \Delta\epsilon_k$, assuming that both baths are equally coupled to the system ($V = W$) and have the same density of states, the solution to Eq. (26) (which we denote ρ_{sol}) empirically has the incorrect trace over the bath states

$$\sum_{k\in L} \langle b_k^\dagger b_k \rangle \approx \sum_{k\in R} \langle c_k^\dagger c_k \rangle \approx N_{\mathrm{bath}} \sum_{k\in L} \theta(\mu_F^{\mathrm{av}} - \epsilon_k)(\text{wrong!}), \tag{30}$$

$$\mu_F^{\mathrm{av}} = \frac{\mu_F^L + \mu_F^R}{2}. \tag{31}$$

Here, θ is the Heavyside function. For γ close to zero, ρ_{sol} bares some resemblance to the equilibrium problem where the two baths have one averaged Fermi energy (μ_F^{av}), whereas we seek the solution to the nonequilibrium problem where there are two different Fermi energies.

Physically, the need to choose $\gamma > \epsilon_k$ can be argued as follows: We interpret γ as a rate for bath relaxation and Γ as the rate of movement to and from the system. Because system relaxation involves $\Gamma/\Delta\epsilon_k$ bath states, the rate at which population changes in a single bath level is $\Gamma/(\Gamma/\Delta\epsilon_k) = \Delta\epsilon_k$. Thus, choosing $\gamma > \Delta\epsilon_k$ allows us to maintain local equilibrium in each bath. Conversely, if we choose $\gamma \ll \Delta\epsilon_k$, then the bath does not relax fast enough to maintain local equilibrium and the current will distort the population levels in each bath. As a result, the baths will be equilibrated together and the solution ρ_{sol} will have the wrong behavior in each bath, namely, the behavior found empirically in Eq. (30). This explains why the current $I_L \to 0$ as $\gamma \to 0$.

We now show numerically that when we choose γ over a limited range such that $\Gamma > \gamma \geq \Delta\epsilon_k$, all physical properties are mostly independent of γ. As a side note, this justifies our use of a single damping parameter to damp all bath reservoirs. Although, in principle, we could use different damping parameters for the left bath (γ_{LL}), the right bath (γ_{RR}), and

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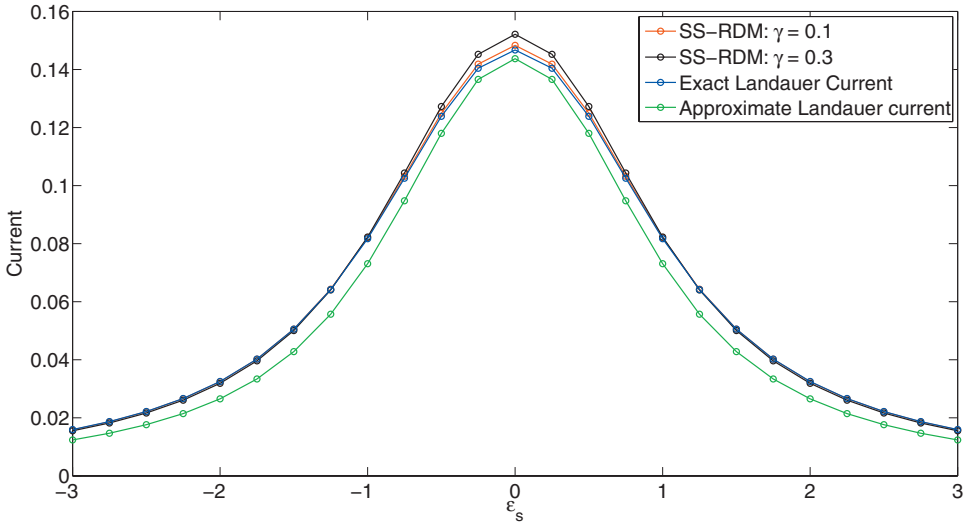


FIG. 3. (Color) The current [Eq. (29)] as a function of the energy of the level system s. Here we choose the Fermi energies of the baths to be $\mu_F^L=0.5$, $\mu_F^R=-0.5$ and the coupling of the system to the bath is fixed by $\Gamma^L=\Gamma^R=2\pi\eta V^2=1$ (and $V=W$). The number of states is $N_{\text{bath}}=100$ and all states are evenly spaced between the band edges of the continuum (chosen as $[-5,5]$). The temperature is $T=0.1$.

the left-right mixed bath density matrix (γ_{LR}), we may safely ignore this degree of freedom so long as all results are roughly independent of the choice of γ.

We begin with the coherent (Landauer) current flowing between the left and right bath reservoirs. The exact expression for the current (as calculated by steady state quantum mechanics[3] or nonequilibrium Green's functions[5,22] (NEGFs) is

$$I_{\text{exact}} = e\int \frac{d\epsilon}{2\pi\hbar}\frac{\Gamma^L(\epsilon)\Gamma^R(\epsilon)}{(\epsilon-\epsilon_s-\Lambda^{\text{tot}}(\epsilon))^2+(\Gamma^{\text{tot}}(\epsilon)/2)^2} \times(f_L(\epsilon)-f_R(\epsilon)), \tag{32}$$

where we define

$$\sum_{k\in L}\frac{V_k^2}{\epsilon-\epsilon_k+i\gamma_0}=\Sigma^L(\epsilon)=\Lambda^L(\epsilon)-\frac{i}{2}\Gamma^L(\epsilon), \tag{33}$$

$$\sum_{k\in R}\frac{W_k^2}{\epsilon-\epsilon_k+i\gamma_0}=\Sigma^R(\epsilon)=\Lambda^R(\epsilon)-\frac{i}{2}\Gamma^R(\epsilon), \tag{34}$$

$$\Lambda^{\text{tot}}(\epsilon)=\Lambda^L(\epsilon)+\Lambda^R(\epsilon), \tag{35}$$

$$\Gamma^{\text{tot}}(\epsilon)=\Gamma^L(\epsilon)+\Gamma^R(\epsilon). \tag{36}$$

A simple approximation for the current replaces $\Lambda(\epsilon)$ by $\Lambda(\epsilon_s)$ and $\Gamma(\epsilon)$ by $\Gamma(\epsilon_s)$ in the equation above:

$$I_{\text{approx}} = e\int \frac{d\epsilon}{2\pi\hbar}\frac{\Gamma^L(\epsilon_s)\Gamma^R(\epsilon_s)}{(\epsilon-\epsilon_s-\Lambda^{\text{tot}}(\epsilon_s))^2+(\Gamma^{\text{Tot}}(\epsilon_s)/2)^2} \times(f_L(\epsilon)-f_R(\epsilon)). \tag{37}$$

The expressions for the exact and approximate currents in Eqs. (32) and (37), and the corresponding self-energies in Eqs. (33) and (34), can be evaluated by discretization on an energetic grid. For added accuracy, we have chosen this discretization grid to be three times denser than our grid for the bath states. The value of γ_0 in Eqs. (33) and (34) is fixed as 0.1, our common choice of γ in Eq. (26).

In Fig. 3, we plot the current [Eq. (29)] coming from the model Hamiltonian [Eq. (23)] as a function of ϵ_s, which effectively is a gate voltage, as well as the exact and approximate currents [Eqs. (32) and (37)]. We calculate the current for two different values of γ (0.1 and 0.3) in the range Γ^L, $\Gamma^R \geq \gamma \geq \Delta\epsilon_k$, demonstrating that the results are nearly independent of γ. Moreover, one sees that the current from Eq. (29) is very close to the exact result, closer even than the approximate solution [Eq. (37)]. This should convince the reader that, by introducing imaginary terms to the Liouville equation, we are sampling a continuum of states rather than a discrete number.

In Fig. 4, we plot the current as a function of source–drain voltage: $V_{sd}=\mu_F^L-\mu_F^R$. Again, one sees agreement between the SS-RDM result and the exact result.

While many standard physical approaches can solve for the current between baths in the Landauer regime, one strength of Eq. (26) is that one may calculate both nonequilibrium currents and populations simultaneously for the Hamiltonian in Eq. (23). Standard steady state quantum mechanical[3] approaches can calculate current in terms of transmission but cannot capture steady state population. Admittedly, for molecular conduction experiments, the Hamiltonian in Eq. (23) may be too simple because the energy of the system (ϵ_s) can depend implicitly on the Fermi levels in the baths. Nevertheless, our intuition is that any computational approach which aims to eventually tackle the problem of electron-electron correlation in molecular conduction must be able to solve for steady state populations in addition to the bulk current. This necessity mirrors the conclusion in quantum chemistry that, in order to obtain an accurate post Hartree–Fock correction to account for electron-electron correlation, one requires first a mean-field method with a decent energy *and* wave function (the latter being more difficult to obtain).

In Fig. 5, we show that, when Eq. (26) is solved numerically, the resulting nonequilibrium population of the system site $\langle s^\dagger s\rangle$ is nearly independent of γ. Furthermore, when we compare our numerical results to the exact result as calculated by NEGF,

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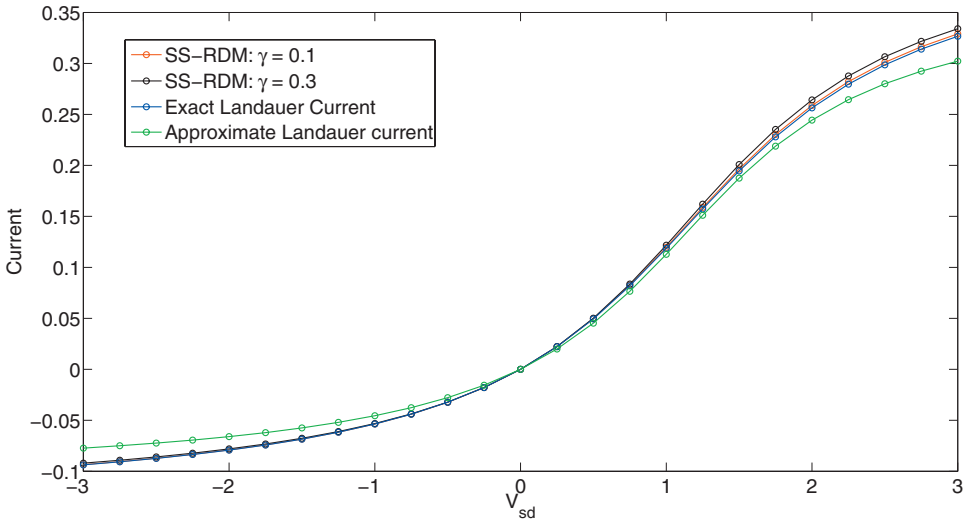


FIG. 4. (Color) The current [Eq. (29)] as a function of source–drain voltage. Here we fix the energy of the level system $\epsilon_s=1$ and the Fermi energy of the right-hand bath $\mu_F^R=0$, while varying the Fermi energy of the left-hand bath μ_F^L. The number of states is $N_{\text{bath}}=100$ and all states are evenly spaced between the band edges of the continuum (chosen as $[-5,5]$). The coupling of the system to the bath is fixed by $\Gamma^L=\Gamma^R=2\pi\eta V^2=1$ and the temperature is $T=0.1$.

$$\langle s^\dagger s\rangle_{\text{NEGF}}=\int \frac{d\epsilon}{2\pi}\frac{f_L(\epsilon)\Gamma^L(\epsilon)+f_R(\epsilon)\Gamma^R(\epsilon)}{(\epsilon-\epsilon_s-\Lambda^{\text{tot}}(\epsilon))^2+(\Gamma^{\text{tot}}(\epsilon)/2)^2}, \tag{38}$$

we find that the SS-RDM solution approximates the NEGF answer very accurately.

IV. DISCUSSION

Even though we cannot solve Eqs. (9) and (26) completely analytically, we believe the SS-RDM equations themselves capture the essential physics for understanding steady state nonequilibrium current flow, provided that we ignore electron-electron correlation. Moreover, because the equations themselves do not distinguish between fermions and bosons, they should be applicable toward understanding heat flow between two baths of bosons which are at different temperatures and thus out of equilibrium. We will now characterize the solution (ρ_{sol}) of the SS-RDM equations in greater detail.

A. Energy conservation

Using the system-system component of the SS-RDM equations

$$0=\frac{d}{dt}\langle s^\dagger s\rangle=\sum_{k\in L}V_k\,\text{Im}\langle b_k^\dagger s\rangle+\sum_{k\in R}W_k\,\text{Im}\langle c_k^\dagger s\rangle \tag{39}$$

and Eq. (29) as an expression for current, it is easy to show that charge is conserved during steady state by the SS-RDM equation: $I_L+I_R=0$.

Similarly, we can also show that energy is conserved. To do so, we repeat the analysis leading to Eq. (29) for charge current, only now we differentiate the energy stored in the left-hand reservoir (rather than the number of particles):

$$J_L^E=-\frac{d}{dt}\left(\sum_{k\in L}\epsilon_k\langle b_k^+b_k\rangle\right) \tag{40}$$

$$=-2\sum_{k\in L}V_k\epsilon_k\,\text{Im}(\langle b_k^+s\rangle). \tag{41}$$

There is an analogous expression for the flux of energy into the right-hand bath:

$$J_R^E=-2\sum_{k\in R}W_k\epsilon_k\,\text{Im}(\langle c_k^+s\rangle). \tag{42}$$

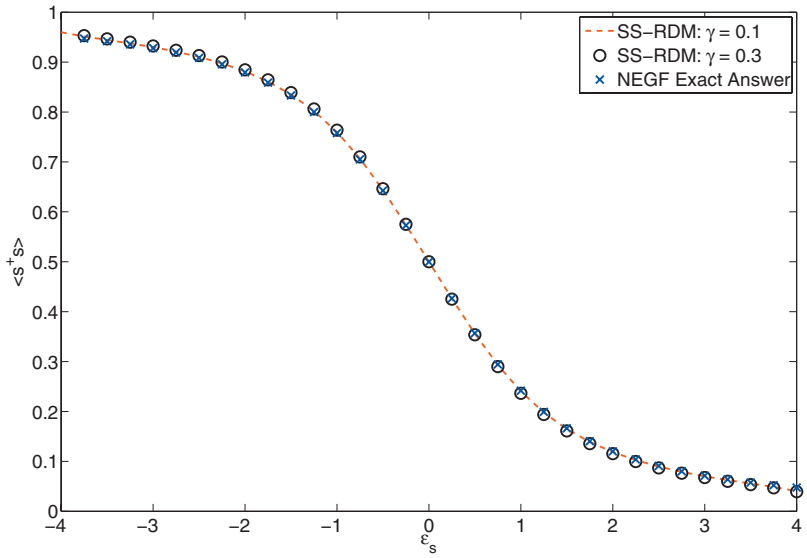


FIG. 5. (Color) The population of the system site $\langle s^\dagger s\rangle$ plotted as a function of the energy of the level system s (i.e., gate voltage). Here we choose the Fermi energies of the baths to be $\mu_F^L=0.5$, $\mu_F^R=-0.5$, the coupling of the system to the bath is fixed by $\Gamma^L=\Gamma^R=2\pi\eta V^2=1$, and the temperature is $T=0.1$. The number of states is $N_{\text{bath}}=100$ and all states are evenly spaced between the band edges of the continuum (chosen as $[-5, 5]$). The exact NEGF answer for the population is given in Eq. (38).

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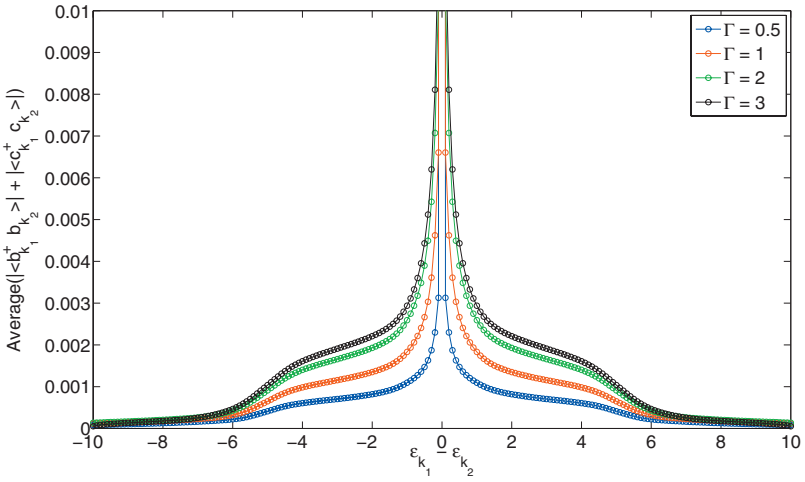


FIG. 6. (Color) Analysis of the bath relaxation according to the SS-RDM equation. Here, we plot the average value of the bath-bath correlations in the same bath as a function of the energy difference for different Γ values. See Eq. (48). We choose the system energy to be $\epsilon_s=1$ and the Fermi energies of the baths to be $\mu_F^L=0.5$, $\mu_F^R=-0.5$. The number of states is $N_{\text{bath}}=100$ and all states are evenly spaced between the band edges of the continuum (chosen as $[-5,5]$). The temperature is $T=0.1$ and $\gamma=0.1$. Note that the intermediate decay of the bath-bath correlations depends strongly on Γ.

To show that $J_L^E+J_R^E=0$, consider the system-bath component in Eq. (26) written out explicitly for the right-hand bath as

$$0=\frac{d}{dt}\langle c_r^\dagger s\rangle=\langle c_r^\dagger s\rangle(\epsilon_r-\epsilon_s)+W_r\langle s^\dagger s\rangle - \sum_{k\in R} W_k\langle c_r^\dagger c_k\rangle-\sum_{k\in L} V_k\langle c_r^\dagger b_k\rangle. \tag{43}$$

If we multiply both sides by W_r and sum over r, we find

$$0=\sum_{r\in R} W_r\langle \dot{c}_r^\dagger s\rangle(\epsilon_r-\epsilon_s)+\sum_{r\in R} W_r^2\langle s^\dagger s\rangle - \sum_{k,r\in R} W_kW_r\langle c_r^\dagger c_k\rangle-\sum_{k\in L,r\in R} V_kW_r\langle c_r^\dagger b_k\rangle. \tag{44}$$

Taking the imaginary part of Eq. (44), we see that the second and third terms vanish (because they are strictly real), leaving us with

$$J_R^E=-2\ \mathrm{Im}\left(\epsilon_s\sum_{r\in R} W_r\langle c_r^\dagger s\rangle+\sum_{k\in L,r\in R} V_kW_r\langle c_r^\dagger b_k\rangle\right) \tag{45}$$

$$=I_R\epsilon_s-2\ \mathrm{Im}\left(\sum_{k\in L,r\in R} V_kW_r\langle c_r^\dagger b_k\rangle\right). \tag{46}$$

Similarly, the expression for J_L^E is

$$J_L^E=I_L\epsilon_s-2\ \mathrm{Im}\left(\sum_{k\in L,r\in R} V_kW_r\langle b_k^\dagger c_r\rangle\right). \tag{47}$$

Because $I_L+I_R=0$ and $\langle c_r^\dagger b_k+b_k^\dagger c_r\rangle$ is real, it follows that $J_L^E+J_R^E=0$.

B. Bath relaxation

In standard treatments of steady state charge transport, the baths or reservoirs are assumed to be infinite and always in equilibrium. According to the SS-RDM equations, however, we choose a finite, discrete basis for our baths and then we force these baths to relax. In so doing, the one-electron density matrix for the bath-bath correlations is not the Fermi distribution, e.g., $\langle b_k^\dagger b_{k'}\rangle\neq\rho_{kk'}^{F,L}\equiv\delta_{kk'}(1/1+e^{\beta(\epsilon_k-\mu_F^L)})$ and $\langle b_k^\dagger c_{k'}\rangle\neq 0$. This has immediate physical implications, as shown for energy transfer in Eqs. (46) and (47) and for charge transfer in the Appendix. Bath relaxation is the crucial ingredient that allows the SS-RDM equation to correctly describe broadening of the system state.

In Figs. 6–9, we analyze the bath-bath correlations that arise according to the SS-RDM equation. For different values of Γ and γ, we calculate the average magnitude of the correlations that arise between different states in the same bath:

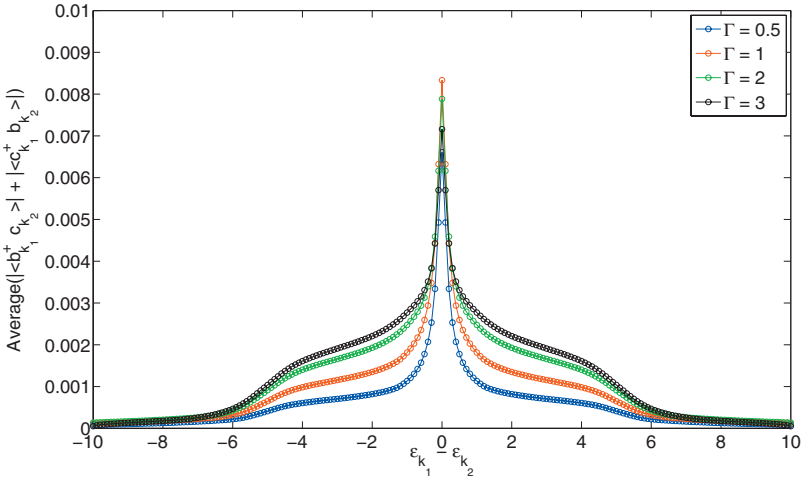


FIG. 7. (Color) Analysis of the bath relaxation according to the SS-RDM equation. Here, we plot the average value of the bath-bath correlations in opposite baths as a function of the energy difference for different Γ values. See Eq. (49). All parameters are the same as for Fig. 6.

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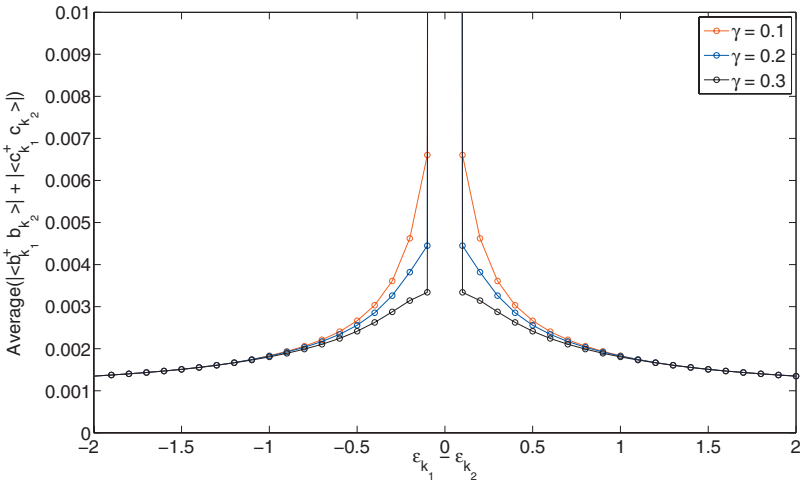


FIG. 8. (Color) Analysis of the bath relaxation according to the SS-RDM equation. Here, we plot the average value of the bath-bath correlations in the same bath as a function of the energy difference for different γ values. See Eq. (48). We choose the system energy to be $\epsilon_s=1$ and the Fermi energies of the baths to be $\mu_F^L=0.5$, $\mu_F^R=-0.5$. The number of states is $N_{\text{bath}}=100$ and all states are evenly spaced between the band edges of the continuum (chosen as $[-5, 5]$). The temperature is $T=0.1$ and $\Gamma=1$. Note that the decay of the bath-bath correlations (e.g., $\langle b_{k_1}^\dagger b_{k_2}\rangle$) depends strongly on γ for ϵ_{k_1} very close to ϵ_{k_2}.

$$A_{\text{same}}(\Delta\epsilon)=\frac{\sum_{\substack{k_1,k_2\in L\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}|\langle b_{k_1}^\dagger b_{k_2}\rangle|+\sum_{\substack{k_1,k_2\in R\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}|\langle c_{k_1}^\dagger c_{k_2}\rangle|}{\sum_{\substack{k_1,k_2\in L\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}1+\sum_{\substack{k_1,k_2\in R\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}1} \tag{48}$$

and for different states in different baths:

$$A_{\text{opp}}(\Delta\epsilon)=\frac{\sum_{\substack{k_1\in L,k_2\in R\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}|\langle b_{k_1}^\dagger c_{k_2}\rangle|+\sum_{\substack{k_1\in R,k_2\in L\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}|\langle c_{k_1}^\dagger b_{k_2}\rangle|}{\sum_{\substack{k_1\in L,k_2\in R\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}1+\sum_{\substack{k_1\in R,k_2\in L\\ \epsilon_{k_1}-\epsilon_{k_2}=\Delta\epsilon}}1}. \tag{49}$$

We plot the function $A_{\text{same}}(\Delta\epsilon)$ in Figs. 6 and 8 and $A_{\text{opp}}(\Delta\epsilon)$ in Figs. 7 and 9.

From Figs. 6–9, the clear conclusion is that, in the SS-RDM analysis, the bath-bath correlation functions (e.g., $\langle b_k^\dagger b_{k'}\rangle$) decay first according to the size of γ and next according to the size of Γ. There are two time scales of interest here. One important conclusion of our research, however, is that, provided $\Gamma>\gamma>\Delta\epsilon_k$, the current does not depend strongly on γ, even if the bath-bath off-diagonal correlations (for states very close in energy) do depend strongly on γ.

Regarding the decay of the bath-bath correlations for states far apart in energy, there are very strong implications caused by the observation that

$$\langle b_{k_1}^\dagger b_{k_2}\rangle\approx 0, \quad \text{when } |\epsilon_{k_1}-\epsilon_{k_2}|\gg\Gamma. \tag{50}$$

Because of this decay, one need not include all $\langle b_{k_1}^\dagger b_{k_2}\rangle$ (and similar) terms as variables in the SS-RDM equations. Thus, Eq. (50) should allow for large computational savings, either for large band calculations (with many states) or for calculations that include electron-electron correlation, as discussed below. Equation (50) is a statement of locality in energy space, asserting that bath states of very different energies are correlated together very weakly. Thus, Eq. (50) appears to be the steady state equivalent of local correlation theory from quantum chemistry,[23–25] where one asserts that localized orbitals that are far away from each other in real space are uncorrelated. Local correlation theory has transformed the exponentially scaling problem of electron correlation into a linear-scaling problem,[24,26,27] and we are hopeful that Eq. (50) will have similarly significant implications for the steady state problem.

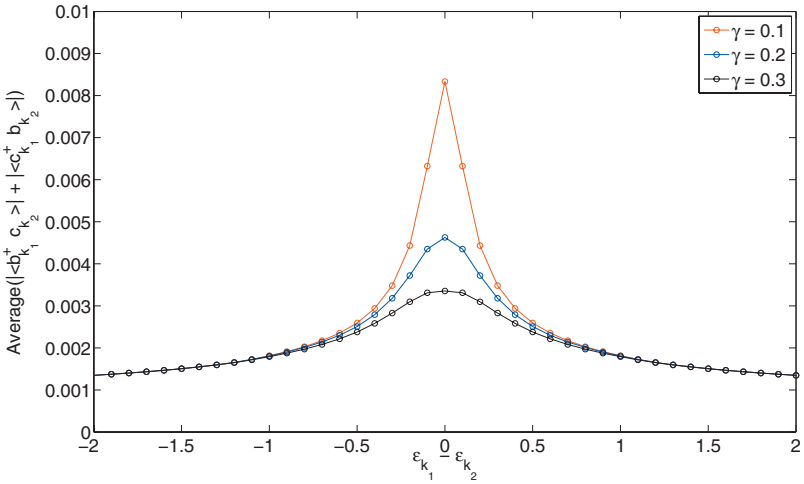


FIG. 9. (Color) Analysis of the bath relaxation according to the SS-RDM equation. Here, we plot the average value of the bath-bath correlations in opposite baths as a function of the energy difference for different γ values. See Eq. (49). All parameters are the same as for Fig. 8.

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V. FUTURE DIRECTIONS: ELECTRON-ELECTRON CORRELATION AND THE ANTI-HERMITIAN CONTRACTED SCHRODINGER EQUATION

We now briefly discuss how we might construct SS-RDM equations when there is a two-electron potential energy term in the Hamiltonian (e.g., a Coulomb operator).

Future work on steady state dynamics through the SS-RDM equation will no doubt seek to incorporate the effects of electron-electron correlation, which has been a difficult problem to solve thus far.[28–39] To do so, we are now investigating whether or not we can refashion Eqs. (9) and (26) so that we use the two-particle reduced density matrix (D) instead of the one-particle reduced density matrix (ρ):

$$\rho_{uv} = \langle a_u^\dagger a_v \rangle, \tag{51}$$

$$D_{pqrs} = \langle a_p^\dagger a_q^\dagger a_s a_r \rangle. \tag{52}$$

In such an application, we will no longer damp the bath-bath piece of the one-particle density matrix, as in Eq. (9):

$$Q_{rs} = \begin{cases} \delta_{rs}, & \text{if } r,s \in \text{bath}, \\ 0, & \text{otherwise}, \end{cases}$$

$$\dot{\rho}_{uv} = i(H\rho - \rho H)_{uv} - \gamma \sum_{r,s} Q_{ur} Q_{vs} (\rho_{rs} - \rho_{rs}^F) = 0. \tag{53}$$

Instead, we will damp the bath-bath-bath-bath piece of the two-particle density matrix D:

$$\dot{D}_{pqrs} = i\langle [H, a_p^\dagger a_q^\dagger a_s a_r] \rangle - \gamma \sum_{e,f,g,h} Q_{pe} Q_{qf} Q_{rg} Q_{sh} \times (D_{efgh} - \rho_{eg}^F \rho_{fh}^F + \rho_{eh}^F \rho_{fg}^F) = 0. \tag{54}$$

Here, we use Wick's theorem to simplify the bath-bath-bath-bath piece of the 2-RDM for a Fermi metal.

From the perspective of quantum chemistry, Eq. (54) is the ACSE equation, $[H,D]=0$, plus damping terms that enforce open boundary conditions appropriate for molecular conduction and nonequilibrium transport. Because we will focus on nonequilibrium problems, we will call this equation a SS-RDM equation [like Eqs. (9) and (26)].

Although Eq. (54) scales formally as the number of bath states to the sixth power, we hope to employ local correlation theory as detailed in Sec. IV B to solve the SS-RDM equation in a faster amount of time. The biggest difficulty, however, in solving Eq. (54) is that the 3-RDM appears in $[H,D]$, and in order to close Eq. (54), the 3-RDM must be reconstructed in terms of the 2-RDM and 1-RDM, as discussed in Refs. 20, 40, and 41. Luckily, such reconstruction of the 3-RDM has already been explored for the ACSE. For the case of an isolated molecule, D denotes the electronic 2-RDM and solutions to the ACSE represent stationary states of the electronic Hamiltonian. Recent work has solved the ACSE for the electronic ground-states of a variety of isolated molecules with very good accuracy.[8–15] Although Rosina's theorem[40] guarantees the uniqueness of the exact 3-RDM reconstruction only for the ground state of an isolated molecule, our hope is that an approximate reconstruction will work for the conduction problem, thus allowing for a meaningful solution of Eq. (54). Because of the large damping terms in Eq. (54), we may need to modify the Mazziotti algorithm for solving the ACSE (where these terms are absent).

Finally, it is interesting to speculate that, in the limit $\gamma \to 0$, Eq. (54) describes a closed system and becomes exactly the ASCE with infinitesimal constraints. Although solutions to the ACSE do not require these constraints, these constraints might help to find excited state solutions. Usually, the ACSE is applied to electronic ground state problems.[42]

VI. CONCLUSIONS

This paper has presented a very elementary theory of how one may describe out-of-equilibrium current flow in terms of the one-particle reduced density matrix. Solving Eq. (26) recovers the correct population on the system site as well as the correct Landauer current for a one-state model system. Moreover, the SS-RDM formalism presented here can be extended to a system with arbitrarily many states interacting via a mean-field potential. Ongoing research will explore whether analogous equations [e.g., Eq. (54)] can correctly account for electron-electron correlation in molecular conduction within a reasonable amount of computational time.

ACKNOWLEDGMENTS

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APPENDIX: APPROXIMATE ANALYTICAL SOLUTION OF THE SS-RDM EQUATION IGNORING BATH RELAXATION

In order to gain intuition for the approach outlined above, we will solve Eq. (26) approximately using the Hamiltonian in Eq. (23). In so doing, we will show that one can derive very approximate (and very incorrect) expressions for the current and steady state population on the system when one makes the assumption that bath states are uncorrelated with each other. In other words, the conclusion of our analytical treatment is that, if we solve the SS-RDM equations for finite baths, the bath-bath correlations are crucial in order to recover the correct current and steady state population. This emphasizes the importance of Figs. 6 and 7, where we plot the decay of bath-bath correlations as a function of the difference in energy between bath states.

We will write b and c to denote a singe-particle bath state on the left and right, respectively. Using the Hamiltonian in Eq. (23) and our notation from above, we can also write $H_{sb}=V_b$, $H_{sc}=W_c$, $H_{ss}=\epsilon_s$, $H_{bb'}=\delta_{bb'}\epsilon_b$, etc. Consider the equations associated with $\dot{\rho}_{ss}=0$, $\dot{\rho}_{sb}=0$, and $\dot{\rho}_{sc}=0$.

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$$\dot{\rho}_{ss}=0\Rightarrow\sum_b\left(H_{sb}\rho_{bs}-\rho_{sb}H_{bs}\right)+\sum_c\left(H_{sc}\rho_{cs}-\rho_{sc}H_{cs}\right)=0, \tag{A1}$$

$$\dot{\rho}_{sb}=0\Rightarrow\left(H_{ss}-H_{bb}\right)\rho_{sb}-H_{sb}\left(\rho_{ss}-\rho_{bb}\right)+\sum_c H_{sc}\rho_{cb}+\sum_{b'\neq b}H_{sb'}\rho_{b'b}=0, \tag{A2}$$

$$\dot{\rho}_{sc}=0\Rightarrow\left(H_{ss}-H_{cc}\right)\rho_{sc}-H_{sc}\left(\rho_{ss}-\rho_{cc}\right)+\sum_b H_{sb}\rho_{bc}+\sum_{c'\neq c}H_{sc'}\rho_{c'c}=0. \tag{A3}$$

We now assume that, to a first approximation, the two baths dephase very quickly relative to any time scale of the system. Thus, in Eqs. (A2) and (A3), we set

$$\rho_{bc}=\rho_{cb}=\rho_{b'b}=\rho_{c'c}=0 \tag{A4}$$

for $b'\neq b$, and $c'\neq c$. Effectively, Eq. (A4) implies we are ignoring bath relaxation. We can then solve for ρ_{sb} and ρ_{sc}:

$$\rho_{sb}=\frac{V_b\left(\rho_{ss}-\rho_{bb}\right)}{\epsilon_s-\epsilon_b+i\delta}, \tag{A5}$$

$$\rho_{sc}=\frac{V_c\left(\rho_{ss}-\rho_{cc}\right)}{\epsilon_s-\epsilon_c+i\delta}, \tag{A6}$$

where we have added a complex infinitesimal δ in the denominator to avoid the pole when ϵ_b or ϵ_c is equal to ϵ_s.

Plugging Eqs. (A5) and (A6) into Eq. (A1) written in the form

$$\mathrm{Im}\left(\sum_b H_{bs}\rho_{sb}\right)+\mathrm{Im}\left(\sum_c H_{cs}\rho_{sc}\right)=0, \tag{A7}$$

we find:

$$\mathrm{Im}\left(\sum_b\frac{|V_b|^2\left(\rho_{ss}-\rho_{bb}\right)}{\epsilon_s-\epsilon_b+i\delta}\right)+\mathrm{Im}\left(\sum_c\frac{|W_c|^2\left(\rho_{ss}-\rho_{cc}\right)}{\epsilon_s-\epsilon_c+i\delta}\right)=0. \tag{A8}$$

We now apply Eqs. (33) and (34), assuming that ρ_{bb}, ρ_{cc} are slowly varying functions of ϵ_b, ϵ_c respectively, so that

$$\sum_b\frac{|V_b|^2\rho_{bb}}{\epsilon_s-\epsilon_b+i\delta}=\left(\Lambda^L(\epsilon_s)-\frac{i}{2}\Gamma^L(\epsilon_s)\right)\rho_{bb}(\epsilon_s), \tag{A9}$$

$$\sum_c\frac{|W_c|^2\rho_{cc}}{\epsilon_s-\epsilon_c+i\delta}=\left(\Lambda^R(\epsilon_s)-\frac{i}{2}\Gamma^R(\epsilon_s)\right)\rho_{cc}(\epsilon_s). \tag{A10}$$

Then, if we denote $\rho_{bb}(\epsilon_s)\equiv\rho_s^L$, $\rho_{cc}(\epsilon_s)\equiv\rho_s^R$, $\Gamma_s^L\equiv\Gamma^L(\epsilon_s)$, and $\Gamma_s^R\equiv\Gamma^R(\epsilon_s)$, Eq. (A8) becomes

$$\Gamma_s^L\left(\rho_{ss}-\rho_s^L\right)+\Gamma_s^R\left(\rho_{ss}-\rho_s^R\right)=0, \tag{A11}$$

$$\rho_{ss}=\frac{\Gamma_s^L\rho_s^L+\Gamma_s^R\rho_s^R}{\Gamma_s^L+\Gamma_s^R}. \tag{A12}$$

Plugging back into Eq. (A5), we find

$$\rho_{sb}=V_b\frac{\left(\frac{\Gamma_s^L\rho_s^L+\Gamma_s^R\rho_s^R}{\Gamma_s^L+\Gamma_s^R}-\rho_{bb}\right)}{\epsilon_s-\epsilon_b+i\delta}. \tag{A13}$$

According to Eq. (29) and the approximations in Eqs. (A9) and (A10), we can express the bulk current as

$$I_L=\frac{2e}{\hbar}\sum_b\mathrm{Im}\;V_b\rho_{sb} \tag{A14}$$

$$=\frac{e}{\hbar}\frac{\Gamma_s^L\Gamma_s^R}{\Gamma_s^L+\Gamma_s^R}\left(\rho_s^L-\rho_s^R\right) \tag{A15}$$

Finally, if we assume that $\rho_s^{L,R}=f_{L,R}(\epsilon_s)$ and we use the Lorentzian identity:

$$\frac{1}{y}=\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{d\epsilon}{(\epsilon-x)^2+y^2}, \tag{A16}$$

we find [setting $y=(\Gamma_s^L+\Gamma_s^R)/2$]

$$I_L=\frac{e}{2\pi\hbar}\int_{-\infty}^{+\infty}d\epsilon\frac{\Gamma_s^L\Gamma_s^R}{(\epsilon-\epsilon_s)^2+\left(\frac{\Gamma_s^L+\Gamma_s^R}{2}\right)^2}\times\left(f_L(\epsilon_s)-f_R(\epsilon_s)\right). \tag{A17}$$

Equations (A12) and (A17) are inaccurate expressions for they do not account for the broadening of the system state when coupled to the bath. In particular, Eq. (A17) is a poor approximation to the Landauer current [either Eq. (32) and (37)]. As we have shown numerically above, one can arrive at the exact steady-state population and Landauer current if one does not assume that the baths dephase instantaneously [Eq. (A4)], but rather relax toward equilibrium with a rate determined by the γ parameter, $\gamma\geq\Delta\epsilon_k$. This emphasizes the importance of bath relaxation and the bath-bath correlation functions plotted in Figs. 6 and 7 in the discussion section. Unfortunately, we do not know how to solve the SS-RDM equations exactly without invoking the dephasing approximations in Eq. (A4).

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[42] Work is currently in progress by Gidofalvi and Mazziotti for the excited state problem using the ACSE without any damping terms.

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