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Driven Liouville von Neumann Equation in Lindblad Form

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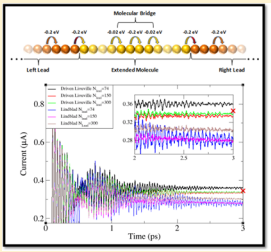
ABSTRACT: The Driven Liouville von Neumann approach [*J. Chem. Theory Comput.* **2014**, *10*, 2927−2941] is a computationally efficient simulation method for modeling electron dynamics in molecular electronics junctions. Previous numerical simulations have shown that the method can reproduce the exact single-particle dynamics while avoiding density matrix positivity violation found in previous implementations. In this study we prove that in the limit of infinite lead models the underlying equation of motion can be cast in Lindblad form. This provides a formal justification for the numerically observed density matrix positivity conservation.



$$\dot{\rho}(t) = -\frac{i}{\hbar}[H,\rho] + \mathcal{L}\{\rho\}$$

$$\mathcal{L}\{\rho\} = -\Gamma \begin{pmatrix} (\rho_L - \rho_L^0) & \frac{1}{2}\rho_{L,EM} & \rho_{L,R} \\ \frac{1}{2}\rho_{EM,L} & 0_{EM} & \frac{1}{2}\rho_{EM,R} \\ \rho_{R,L} & \frac{1}{2}\rho_{R,EM} & (\rho_R - \rho_R^0) \end{pmatrix}$$

INTRODUCTION

Since its inception over 40 years ago[1] the field of molecular electronics has held the promise to use individual molecular entities and their assemblies as active components in electronic devices.[2−4] Molecules are often characterized by their miniature size, quantum-mechanical nature, well-defined chemical composition, highly efficient and accurate synthesis procedures, as well as self-assembly capabilities. These properties open the door for the design of novel molecular-scale electronic components that may present unique functionality with high sensitivity toward external perturbations and fast response time. Furthermore, such systems are expected to be energetically efficient and to allow for cost-effective reproducible device fabrication.

Steady-state transport properties of molecular junctions remain the main focus of both experimental and theoretical efforts in this field. Nevertheless, the study of dynamical transport phenomena in nanoscale junctions has recently gained increasing attention from the scientific community.[5−32] Research in this direction explores the effects of time-dependent perturbations such as alternating currents, bias pulses, and external electromagnetic fields on the transient response of the system. This involves complex physical processes that can be harnessed for the design of miniaturized electronic devices such as optoelectronic ultrafast molecular switches and nanoscale rectifiers.[7,8,14,22,24−27,29,31]

Considering the temporal degree of freedom poses new challenges on the experimental efforts that theory and simulation may help resolve via the prediction of optimal junction configurations and operation conditions and the interpretation of experimental findings. To this end, various methods aiming to simulate electron dynamics in molecular junctions have been developed.[31−90] These approaches either consider the detailed atomistic structure of the junction or introduce model Hamiltonians to study specific transport phenomena. Furthermore, they vary in the level of treatment of electron−electron interactions and effects of bath memory.

Recently, we proposed the Driven Liouville von Neumann approach that imposes dynamic nonequilibrium boundary conditions on finite atomistic models of realistic molecular junctions.[91,92] This method was shown to provide a decent compromise between computational efficiency and physical accuracy when modeling single-electron dynamics in molecular junctions subjected to time-dependent external perturbations.[93] Notably, the underlying equation of motion was numerically shown to solve the density matrix positivity conservation violation found in previous related implementations.[80] This gained further formal support when the equation was explicitly derived as an approximate form of nonequilibrium Green's function formalism.[93] Nevertheless, no direct rigorous proof was offered to support the general validity of the positivity condition for this method. In the present study, we show that in the limit of infinite lead models the Driven Liouville von Neumann equation can be written in Lindblad form. The latter guarantees preservation of density matrix positivity[94−96] as well as *N*-representability of the *N*-electron density matrix and, under certain conditions, also of the one-electron reduced density matrix[97] throughout the dynamics thus justifying the numerical findings.

DERIVATION

Consider the system depicted in Figure 1. Here a molecule bridges the gap between two leads that are connected to two external baths. We formally divide the system into five sections including the left and right semi-infinite reservoirs, the left and

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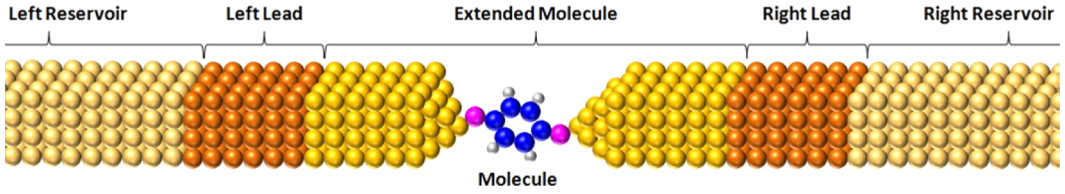

Figure 1. Real-space representation of a typical molecular junction model divided into the extended molecule, left and right leads, and external reservoirs.

right leads, and the extended molecule region, which is the molecule itself augmented by its adjacent lead sections. The size of these lead sections is chosen such that the electronic properties of the full extended molecule converge to within a desired accuracy. In the present derivation we do not treat the reservoirs explicitly and instead we take them into account implicitly by considering their effect on their adjacent lead sections. So, in practice, we consider a system constructed from the finite left and right lead models connected by the extended molecule. The corresponding sets of orthonormal eigenstates of each individual section are marked as $\{|l\rangle\}$, $\{|r\rangle\}$, and $\{|m\rangle\}$, respectively.

We aim at showing that the driven Liouville von Neumann equation that was previously derived both heuristically[91] and explicitly[93] can be written in Lindblad form, thus proving that the corresponding nonunitary evolution of the density matrix is indeed completely positive. To this end, we start from the Lindblad super operator that has the following general form

$$\mathcal{L}\{\hat{\rho}\} = \sum_{\alpha}\left[\hat{L}_{\alpha}\hat{\rho}\hat{L}_{\alpha}^{\dagger} - \frac{1}{2}\hat{L}_{\alpha}^{\dagger}\hat{L}_{\alpha}\hat{\rho} - \frac{1}{2}\hat{\rho}\hat{L}_{\alpha}^{\dagger}\hat{L}_{\alpha}\right] \tag{1}$$

where $\hat{\rho}$ is the density operator and $\hat{L}_{\alpha}$ are Lindblad operators that we choose in the form previously suggested by Dubi and Di Ventra[98]

$$\hat{L}_{k,k'} = \sqrt{\gamma_{k,k} f_K(E_k, \mu_K)}\,|k\rangle\langle k'| \tag{2}$$

Here $|k\rangle \in \{|l\rangle\}$ or $\{|r\rangle\}$ are single-particle states in the left (K = L) or right (K = R) noninteracting lead sections, respectively. The action of these operators is to exchange charge between each finite lead model levels with (real) transition rates $\{\gamma_{k,k'}\}$ so as to maintain, as close as possible, their Fermi–Dirac equilibrium distribution $f_K(E, \mu_K) = [1 + e^{(E-\mu_K)/(k_B T_K)}]^{-1}$ induced by their implicit coupling to the corresponding reservoirs. Here, T_K and μ_K are the electronic temperature and chemical potential of reservoir K and k_B is Boltzmann's constant. With this choice the Lindblad superoperator can be split into the individual contributions of the left and right leads $\mathcal{L}\{\hat{\rho}\} = \mathcal{L}_L\{\hat{\rho}\} + \mathcal{L}_R\{\hat{\rho}\}$ with

$$\mathcal{L}_K\{\hat{\rho}\} = \sum_{k=1}^{N_K}\sum_{k'=1,k'\neq k}^{N_K}\left[\hat{L}_{k,k'}\hat{\rho}\hat{L}_{k,k'}^{\dagger} - \frac{1}{2}\hat{L}_{k,k'}^{\dagger}\hat{L}_{k,k'}\hat{\rho} - \frac{1}{2}\hat{\rho}\hat{L}_{k,k'}^{\dagger}\hat{L}_{k,k'}\right] \tag{3}$$

where the sums run over all N_K levels of lead K with $k' \neq k$. To obtain the driven Liouville von Neumann equation we write this superoperator in matrix form. Using eq 2, the first term in the double sum can be written as

$$\begin{aligned}\hat{L}_{k,k'}\hat{\rho}\hat{L}_{k,k'}^{\dagger} &= \left[\sqrt{\gamma_{k,k} f_K(E_k, \mu_K)}\,|k\rangle\langle k'|\right]\hat{\rho}\left[|k'\rangle\right.\\ &\quad\left.\langle k|\sqrt{\gamma_{k,k} f_K(E_k, \mu_K)}\right]\\ &= \gamma_{k,k} f_K(E_k, \mu_K)\rho_{k',k'}|k\rangle\langle k|\end{aligned} \tag{4}$$

where we have denoted the matrix element $\rho_{k',k'} \equiv \langle k'|\hat{\rho}|k'\rangle$. The second term is given by

$$\begin{aligned}-\frac{1}{2}\hat{L}_{k,k}^{\dagger}\hat{L}_{k,k}\hat{\rho} &= -\frac{1}{2}\left[\sqrt{\gamma_{k,k} f_K(E_k, \mu_K)}\,|k'\rangle\langle k|\right]\left[|k\rangle\langle k'|\right.\\ &\quad\left.\sqrt{\gamma_{k,k} f_K(E_k, \mu_K)}\right]\hat{\rho}\\ &= -\frac{1}{2}\gamma_{k,k} f_K(E_k, \mu_K)|k'\rangle\langle k'|\hat{\rho}\hat{I}\\ &= -\frac{1}{2}\gamma_{k,k} f_K(E_k, \mu_K)\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}\rho_{k',n}|k'\rangle\langle n|\end{aligned} \tag{5}$$

where we introduced the identity operator within the subspace of system states: $\hat{I} = \sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}|n\rangle\langle n|$. Accordingly, the third term can be written as

$$-\frac{1}{2}\hat{\rho}\hat{L}_{k,k}^{\dagger}\hat{L}_{k,k'} = -\frac{1}{2}\gamma_{k,k} f_K(E_k, \mu_K)\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}\rho_{n,k'}|n\rangle\langle k'| \tag{6}$$

Substituting eqs 4–6 in eq 3 we obtain an expression for the Lindblad superoperator of lead K

$$\begin{aligned}\mathcal{L}_K\{\boldsymbol{\rho}\} &= \sum_{k=1}^{N_K}\sum_{k'=1}^{N_K}\gamma_{k,k'} f_K(E_k, \mu_K)\left[\rho_{k',k'}|k\rangle\langle k|\right.\\ &\quad\left. - \frac{1}{2}\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}\left(\rho_{k',n}|k'\rangle\langle n| + \rho_{n,k'}|n\rangle\langle k'|\right)\right]\\ &\quad - \sum_{k=1}^{N_K}\gamma_{k,k} f_K(E_k, \mu_K)\left[\rho_{k,k}|k\rangle\langle k|\right.\\ &\quad\left. - \frac{1}{2}\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}\left(\rho_{k,n}|k\rangle\langle n| + \rho_{n,k}|n\rangle\langle k|\right)\right]\end{aligned} \tag{7}$$

where we have added and subtracted the terms with $k' = k$. The eigenstates of each section ($\{|l\rangle\}$, $\{|m\rangle\}$, $\{|r\rangle\}$) form an orthogonal set within themselves by construction. Furthermore, assuming a tight-binding approximation, the overlap between states of different sections is neglected, thus making them mutually orthogonal. Therefore, the diagonal elements of the matrix representation of $\mathcal{L}_K\{\hat{\rho}\}$ are given by

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$$\langle i|\mathcal{L}_K|i\rangle = \sum_{k=1}^{N_K}\sum_{k'=1}^{N_K}\gamma_{k,k'}f_K(E_k,\mu_K)\Bigg[\rho_{k',k'}\delta_{ik}\delta_{ki} - \frac{1}{2}\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}(\rho_{k',n}\delta_{ik}\delta_{ni} + \rho_{n,k'}\delta_{in}\delta_{k'i})\Bigg] - \sum_{k=1}^{N_K}\gamma_{k,k}f_K(E_k,\mu_K)\Bigg[\rho_{k,k}\delta_{ik}\delta_{ki} - \frac{1}{2}\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}(\rho_{k,n}\delta_{ik}\delta_{ni} + \rho_{n,k}\delta_{in}\delta_{ki})\Bigg] \tag{8}$$

Clearly, if $|i\rangle$ does not belong to the set of eigenstates $\{|k\rangle\}$ of lead K this term completely vanishes, whereas when $|i\rangle \in \{|k\rangle\}$ the second sum vanishes and the only terms that survive are

$$\langle i|\mathcal{L}_K|i\rangle = \sum_{k=1}^{N_K}\gamma_{i,k}f_K(E_i,\mu_K)\rho_{k,k} - \sum_{k=1}^{N_K}\gamma_{k,i}f_K(E_k,\mu_K)\rho_{i,i} \tag{9}$$

where, for brevity, we have replaced the summation index k' by k in the first sum.

For the off-diagonal matrix elements of $\mathcal{L}_K\{\hat{\rho}\}$ we obtain

$$\langle i|\mathcal{L}_K|j\neq i\rangle = -\frac{1}{2}\sum_{k=1}^{N_K}\sum_{k'=1}^{N_K}\gamma_{k,k'}f_K(E_k,\mu_K)\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}(\rho_{k',n}\delta_{ik}\delta_{nj} + \rho_{n,k'}\delta_{in}\delta_{k'j}) + \frac{1}{2}\sum_{k=1}^{N_K}\gamma_{k,k}f_K(E_k,\mu_K)\sum_{n\in\{|l\rangle\},\{|m\rangle\},\{|r\rangle\}}(\rho_{k,n}\delta_{ik}\delta_{nj} + \rho_{n,k}\delta_{in}\delta_{kj}) \tag{10}$$

where terms involving $\delta_{ik}\delta_{kj}$ have been omitted. When $|i\rangle$, $|j\rangle \in \{|k\rangle\}$ this expression yields

$$\langle i|\mathcal{L}_K|j\rangle = \frac{1}{2}[\gamma_{i,i}f_K(E_i,\mu_K) + \gamma_{j,j}f_K(E_j,\mu_K) - \sum_{k=1}^{N_K}(\gamma_{k,i}+\gamma_{k,j})f_K(E_k,\mu_K)]\rho_{i,j} \tag{11}$$

For $|i\rangle \in \{|k\rangle\}$ and $|j\rangle \notin \{|k\rangle\}$ this term gives

$$\langle i|\mathcal{L}_K|j\rangle = -\frac{1}{2}[\sum_{k\neq i}^{N_K}\gamma_{k,i}f_K(E_k,\mu_K)]\rho_{i,j} \tag{12}$$

Similarly, for $|i\rangle \notin \{|k\rangle\}$ and $|j\rangle \in \{|k\rangle\}$ we obtain

$$\langle i|\mathcal{L}_K|j\rangle = -\frac{1}{2}[\sum_{k\neq j}^{N_K}\gamma_{k,j}f_K(E_k,\mu_K)]\rho_{i,j} \tag{13}$$

and when $|i\rangle$, $|j\rangle \notin \{|k\rangle\}$

$$\langle i|\mathcal{L}_K|j\rangle = 0 \tag{14}$$

Collecting all of the terms appearing in eqs 9 and 11−14 we obtain the following expression for the matrix elements of the Lindblad super operator defined by eqs 2 and 3 on the basis of single-particle states of the separate system sections (left and right leads and the extended molecule)

$$\langle i|\mathcal{L}_K|j\rangle = \begin{cases} \sum_{k=1}^{N_K}\gamma_{i,k}f_K(E_i,\mu_K)\rho_{k,k} - \sum_{k=1}^{N_K}\gamma_{k,i}f_K(E_k,\mu_K)\rho_{i,i} & i=j;\ |i\rangle,|j\rangle\in\{|k\rangle\} \\ 0 & i=j;\ |i\rangle,|j\rangle\notin\{|k\rangle\} \\ \frac{1}{2}\Big[\gamma_{i,i}f_K(E_i,\mu_K) + \gamma_{j,j}f_K(E_j,\mu_K) - \sum_{k=1}^{N_K}(\gamma_{k,i}+\gamma_{k,j})f_K(E_k,\mu_K)\Big]\rho_{i,j} & i\neq j;\ |i\rangle,|j\rangle\in\{|k\rangle\} \\ -\frac{1}{2}\Big[\sum_{k\neq i}^{N_K}\gamma_{k,i}f_K(E_k,\mu_K)\Big]\rho_{i,j} & i\neq j;\ |i\rangle\in\{|k\rangle\},\ |j\rangle\notin\{|k\rangle\} \\ -\frac{1}{2}\Big[\sum_{k\neq j}^{N_K}\gamma_{k,j}f_K(E_k,\mu_K)\Big]\rho_{i,j} & i\neq j;\ |i\rangle\notin\{|k\rangle\},\ |j\rangle\in\{|k\rangle\} \\ 0 & i\neq j;\ |i\rangle,|j\rangle\notin\{|k\rangle\} \end{cases} \tag{15}$$

At this point we assume that all interstate transition rates are equal and constant such that $\gamma_{k,k'} = \gamma_K = \text{Const}$ giving

$$\langle i|\mathcal{L}_K|j\rangle = \gamma_K\begin{cases} f_K(E_i,\mu_K)\sum_{k=1}^{N_K}\rho_{k,k} - \Big[\sum_{k=1}^{N_K}f_K(E_k,\mu_K)\Big]\rho_{i,i} & i=j;\ |i\rangle,|j\rangle\in\{|k\rangle\} \\ 0 & i=j;\ |i\rangle,|j\rangle\notin\{|k\rangle\} \\ \frac{1}{2}\Big[f_K(E_i,\mu_K)+f_K(E_j,\mu_K) - 2\sum_{k=1}^{N_K}f_K(E_k,\mu_K)\Big]\rho_{i,j} & i\neq j;\ |i\rangle,|j\rangle\in\{|k\rangle\} \\ -\frac{1}{2}\Big[\sum_{k\neq i}^{N_K}f_K(E_k,\mu_K)\Big]\rho_{i,j} & i\neq j;\ |i\rangle\in\{|k\rangle\},\ |j\rangle\notin\{|k\rangle\} \\ -\frac{1}{2}\Big[\sum_{k\neq j}^{N_K}f_K(E_k,\mu_K)\Big]\rho_{i,j} & i\neq j;\ |i\rangle\notin\{|k\rangle\},\ |j\rangle\in\{|k\rangle\} \\ 0 & i\neq j;\ |i\rangle,|j\rangle\notin\{|k\rangle\} \end{cases} \tag{16}$$

The partial trace of the density matrix over the states of lead K appearing in the expression for the nonzero diagonal terms in eq 16 provides the instantaneous number of electrons in the finite lead model $\sum_{k=1}^{N_K}\rho_{k,k} = N_K$. Similarly, the sum over Fermi−Dirac weights results in the corresponding equilibrium number of electrons $\sum_{k=1}^{N_K}f_K(E_k,\mu_K) = N_K^{\text{Eq}}$. Hence, for $i \in \{|k\rangle\}$ we obtain

$$\langle i|\mathcal{L}_L|i\rangle = \gamma_K[f_K(E_i,\mu_K)N_K - N_K^{\text{Eq}}\rho_{i,i}] = \gamma_K N_K^{\text{Eq}}\left[f_K(E_i,\mu_K)\frac{N_K}{N_K^{\text{Eq}}} - \rho_{i,i}\right] \tag{17}$$

In the limit of infinite lead models the effect of the extended molecule on the leads becomes negligible and the Lindblad

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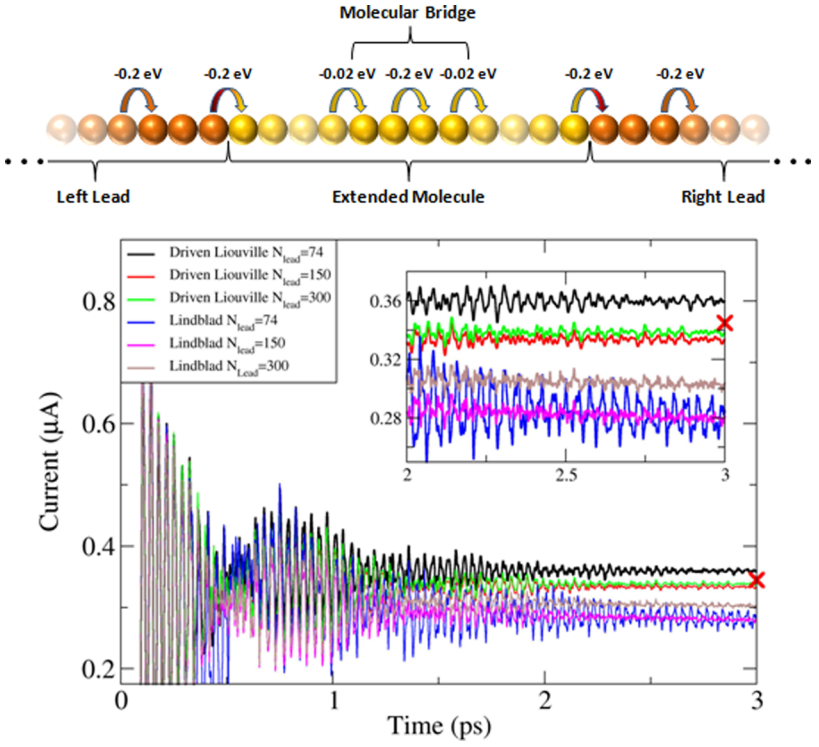

Figure 2. Current versus time of a tight-binding atomic chain calculated using the driven Liouville von Neumann equation (black, red, and green) and the Lindblad equation (blue, violet, and brown). Three different lead model sizes with increasing length of 74 (black and blue), 150 (red and violet), and 300 (green and brown) sites are considered. The Landauer stead-state value is presented for reference as the red ×. The extended molecule length is 110 sites with 10 sites representing the molecular bridge and 50 sites on each of the bridge sides to represent the lead sections within the extended molecule region. All onsite energies are set to zero, the hopping integrals within the left, right, and extended molecule sections are taken to be −0.2 eV, and the hopping integral between the two edge sites of the molecular bridge and the corresponding edge sites of the lead sections in the extended molecule is taken as −0.02 eV (see illustration above the diagram). The bias voltage considered is 0.2 V and the lead electronic temperatures are set to 0 K. The inset provides a zoom-in on the steady-state transport region.

operators of eq 2 drive the lead occupations toward their equilibrium state such that $\frac{N_K}{N_K^{Eq}} \to 1$, and thus we obtain

$$\langle i|\mathcal{L}_L|i\rangle \xrightarrow[N_K\to\infty]{} \gamma_K N_K^{Eq}[f_K(E_i,\mu_K) - \rho_{i,i}] \tag{18}$$

Accordingly, for the off-diagonal terms with $|i\rangle, |j\rangle \in \{|k\rangle\}$ we have

$$\langle i|\mathcal{L}_K|j\rangle = \frac{\gamma_K N_K^{Eq}}{2}\left[\frac{f_K(E_i,\mu_K) + f_K(E_j,\mu_K)}{N_K^{Eq}} - 2\right]\rho_{i,j} \tag{19}$$

Because $f_K(E_i,\mu_K)$ and $f_K(E_j,\mu_K)$ are both positive fractions, in the limit of infinite lead models the first term in the square brackets in eq 19 vanishes, leaving

$$\langle i|\mathcal{L}_K|j\rangle \xrightarrow[N_K^{Eq}\to\infty]{} -\gamma_K N_K^{Eq}\rho_{i,j} \tag{20}$$

The remaining nonzero off-diagonal terms of $\mathcal{L}_K$ have either the form

$$\begin{aligned}\langle i|\mathcal{L}_K|j\rangle &= -\frac{\gamma_K}{2}[\sum_{k\neq i}^{N_K} f_K(E_k,\mu_K)]\rho_{i,j}\\ &= -\frac{\gamma_K}{2}[\sum_{k=1}^{N_K} f_K(E_k,\mu_K) - f_K(E_i,\mu_K)]\rho_{i,j}\\ &= -\frac{\gamma_K}{2}[N_K^{Eq} - f_K(E_i,\mu_K)]\rho_{i,j}\\ &= -\frac{\gamma_K N_K^{Eq}}{2}\left[1 - \frac{f_K(E_i,\mu_K)}{N_K^{Eq}}\right]\rho_{i,j} \xrightarrow[N_K^{Eq}\to\infty]{} -\frac{\gamma_K N_K^{Eq}}{2}\rho_{i,j}\end{aligned} \tag{21}$$

when $i \in \{|k\rangle\}$, $j \notin \{|k\rangle\}$ or

$$\langle i|\mathcal{L}_K|j\rangle = -\frac{\gamma_K N_K^{Eq}}{2}\left[1 - \frac{f_K(E_j,\mu_K)}{N_K^{Eq}}\right]\rho_{i,j} \xrightarrow[N_K^{Eq}\to\infty]{} -\frac{\gamma_K N_K^{Eq}}{2}\rho_{i,j} \tag{22}$$

when $i \notin \{|k\rangle\}$, $j \in \{|k\rangle\}$, thus yielding the same expression.

Collecting all terms appearing in eqs 18 and 20−22 and substituting in eq 16, we finally obtain

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$$\langle i|\mathcal{L}_K|j\rangle = -\gamma_K N_K^{\mathrm{Eq}} \begin{cases} [\rho_{i,i} - f_K(E_i, \mu_K)] & i = j;\ |i\rangle, |j\rangle \in \{|k\rangle\} \\ \rho_{i,j} & i \neq j;\ |i\rangle, |j\rangle \in \{|k\rangle\} \\ \frac{1}{2}\rho_{i,j} & i \neq j;\ |i\rangle \in \{|k\rangle\},\ |j\rangle \notin \{|k\rangle\} \\ \frac{1}{2}\rho_{i,j} & i \neq j;\ |i\rangle \notin \{|k\rangle\},\ |j\rangle \in \{|k\rangle\} \\ 0 & \text{otherwise} \end{cases} \tag{23}$$

In matrix form the Lindblad superoperator is thus given by

$$\mathcal{L}\{\rho\} = \mathcal{L}_L\{\rho\} + \mathcal{L}_R\{\rho\} = \begin{pmatrix} -\Gamma_L(\rho_L - \rho_L^0) & -\frac{\Gamma_L}{2}\rho_{L,EM} & -\left(\frac{\Gamma_L}{2} + \frac{\Gamma_R}{2}\right)\rho_{L,R} \\ -\frac{\Gamma_L}{2}\rho_{EM,L} & \mathbf{0}_M & -\frac{\Gamma_R}{2}\rho_{EM,R} \\ -\left(\frac{\Gamma_L}{2} + \frac{\Gamma_R}{2}\right)\rho_{R,L} & -\frac{\Gamma_R}{2}\rho_{R,EM} & -\Gamma_R(\rho_R - \rho_R^0) \end{pmatrix} \tag{24}$$

where we have defined $\rho_K^0 \equiv \mathrm{diag}\{f_K(E_k, \mu_K)\}$ as a diagonal matrix of dimensions $K \times K$, whose kth diagonal element is given by $f_K(E_k, \mu_K)$ and $\Gamma_K \equiv \gamma_K N_K^{\mathrm{eq}}$. If we further assume that $\Gamma_L = \Gamma_R \equiv \Gamma$, eq 24 reduces to

$$\mathcal{L}\{\rho\} = -\Gamma \begin{pmatrix} (\rho_L - \rho_L^0) & \frac{1}{2}\rho_{L,EM} & \rho_{L,R} \\ \frac{1}{2}\rho_{EM,L} & \mathbf{0}_M & \frac{1}{2}\rho_{EM,R} \\ \rho_{R,L} & \frac{1}{2}\rho_{R,EM} & (\rho_R - \rho_R^0) \end{pmatrix} \tag{25}$$

which has the exact same structure as the driving term of the driven Liouville von Neumann equation,[91−93] thus completing the derivation.

NUMERICAL DEMONSTRATION

To demonstrate the correspondence between the Lindblad superoperator defined by eqs 1 and 2 and the driving term appearing in eq 25, we used both to perform comparative numerical simulations of the electronic transport through a tight-binding atomic chain with increasing lead models size. To this end, we propagate the quantum master equation

$$\dot{\rho}(t) = -\frac{i}{\hbar}[\boldsymbol{H}, \boldsymbol{\rho}] + \mathcal{L}\{\boldsymbol{\rho}\} \tag{26}$$

where the matrix elements of the superoperator $\mathcal{L}$ are given by either eq 16 or eq 25. Figure 2 compares the time-dependent current obtained by the two methods for increasing lead model systems.[99] The model parameters are detailed in the Figure caption. Constant driving rates of $\gamma_L = \gamma_R = \gamma = 1 \times 10^{-4}$ fs^{-1} are used in all Lindblad equation calculations, and the corresponding driving rate used for the driven Liouville von Neumann equation calculations is $\Gamma = 0.015$ fs^{-1}. The two values are related via $\Gamma \equiv \gamma N^{\mathrm{eq}}$ for the 150 sites lead model system where the average lead equilibrium occupation is $N^{\mathrm{eq}} = 150$. As can be seen, the results of the driven Liouville von Neumann calculations quickly converge with lead size such that already for a lead of 150 sites good agreement is obtained with the Landauer steady-state current value. The Lindblad currents, which are consistently smaller than the Driven Liouville von Neumann results, gradually approach the correct steady-state value and the Driven Liouville von Neumann current traces with increasing lead size. This indicates that indeed at sufficiently large lead models the methods become equivalent. Nevertheless, even at a lead size of 300 sites the Lindblad results are not fully converged and deviate from the Landauer value.

To better understand this behavior we analyze the steady-state populations as obtained by the two methods with increasing lead size. In Figure 3a we present the lead and extended molecule-state occupations obtained at steady-state using the Driven Liouville von Neumann equation of motion for the three tight-binding chain lead sizes. Notably, all populations are between 0 and 1, indicating that N representability is conserved. Furthermore, the molecular occupations are converged already for the shortest lead model considered of 74 sites, while the lead occupation deviations from the target equilibrium distribution reduce with increasing lead size.

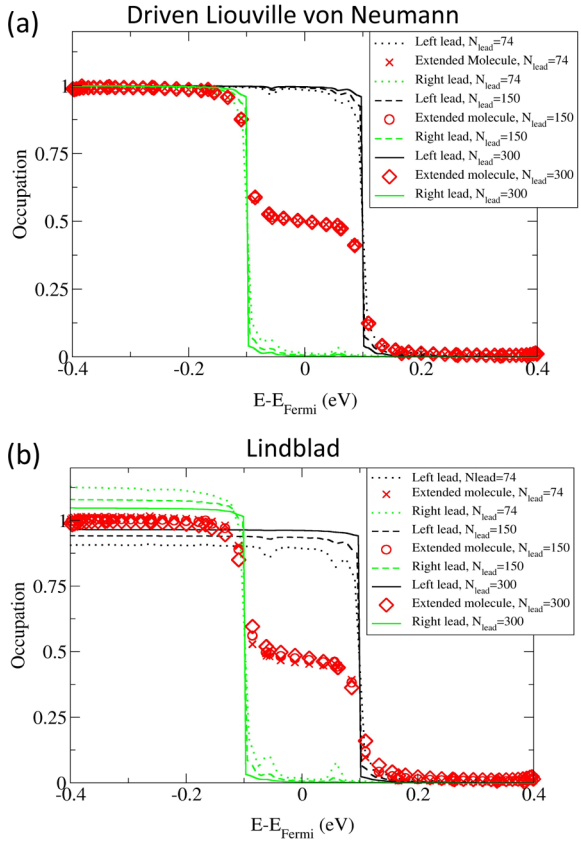

Figure 3. Steady-state occupations of the left lead (black), extended molecule (red), and right lead (green) single-particle states as obtained using the driven Liouville von Neumann (a) and the Lindblad (b) master equations for increasing lead sizes of 74 (dotted lines), 150 (dashed lines), and 300 (full lines) sites. The model parameters are detailed in the caption of Figure 2.

The corresponding results for the Lindblad equation are presented in Figure 3b. As may be expected, all state occupations are positive. Nevertheless, large deviations of the lead steady-state occupations from the target Fermi−Dirac distributions appear. These are characterized by clear violations

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J. Phys. Chem. A 2016, 120, 3278−3285

of the *N*-representability condition leading to occupations that exceed one particle per state in disagreement with Pauli's exclusion principle.[97] The deviations reduce with increasing lead size but are still quite significant, even at a lead model size of 300 sites. Accordingly, the extended molecule steady-state occupations, that resemble those obtained by the driven Liouville von Neumann approach, are not fully converged at this lead size. These results further indicate the robustness of the driven Liouville von Neumann equation for describing time-dependent transport in molecular junctions.

It is important to note that in order to provide an appropriate comparison between the driven Liouville von Neumann and the Lindblad equations we restrict the calculation to a single driving rate applied uniformly to all lead model eigenstates. Reference 98 provides a scheme to calculate state-dependent transition rates within the Lindblad formalism. These may reduce deviations from *N*-representability conservation and improve convergence of the Lindblad calculation. In fact, the reason that a single driving rate description works well for the driven Liouville von Neumann approach within the tight-binding Hamiltonian is the uniform density of states of the finite lead models. From an energy perspective, the driving parameter serves to broaden the lead eigenstates so as to obtain a continuous spectrum as required from any descent lead model. When the lead density of states is uniform, a single broadening factor is sufficient to achieve this goal. For more advanced Hamiltonian models, such as those obtained within nonorthogonal basis set representations, that produce a nonuniform density of states, the single driving rate description is insufficient and more advanced schemes to calculate state-dependent broadening factors are required. This, indeed, is a subject of current research.

SUMMARY AND CONCLUSIONS

We have shown that in the limit of infinite lead model size the driven Liouville von Neumann equation of motion can be written in Lindblad form. This rationalizes the numerical observation of density matrix positivity conservation exhibited by this equation. Furthermore, it establishes a link between the exact equation of motion, to which the driven Liouville von Neumann equation was shown to be an approximation,[93] and the Lindblad operators adopted herein.

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Notes

The authors declare no competing financial interest.

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J. Phys. Chem. A 2016, 120, 3278−3285