

## CHAPTER 14

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# *Superoperator many-body theory of molecular currents: non-equilibrium Green functions in real time*

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## Abstract

The electric conductance of a molecular junction is calculated by recasting the Keldysh formalism in Liouville space. Dyson equations for non-equilibrium many-body Green functions (NEGF) are derived directly in real (physical) time. The various NEGFs appear naturally in the theory as time-ordered products of superoperators, while the Keldysh forward/backward time loop is avoided.

## 14.1 INTRODUCTION

Recent advances in the fabrication and measurements of nanoscale devices have led to a considerable interest in non-equilibrium current carrying states of single molecules. The tunneling of electrons between two metals separated by a thin oxide layer was first observed experimentally by Giaever [1] and later by others [2]. Vibrational resonances can be observed for molecules absorbed at the metal–oxide interface by analyzing the tunneling current as a function of the applied bias [3,4]. More recent development of scanning tunneling microscopy (STM) led to a direct, real space determination of surface structures. A metal tip is brought near the surface so that tunneling resistance is measurable. A contour map of the surface is obtained by recording the tunneling resistance as the tip scans the surface. The tunneling electrons interact and may exchange energy with the nuclear degrees of freedom of the absorbed molecule. This opens up inelastic channels for electron transmission from the tip to the surface, leading to inelastic electron tunneling (IET). IET may play an important role in manipulating molecules with STM [5,6]. Recently, IET was combined with STM for the chemical analysis of a single absorbed molecule with atomic spatial resolution [7,8]. The atomic scale images of STM

46 have been useful in analyzing different binding configurations of the molecule  
47 chemisorbed on a semiconductor surface [9,10]. Recent advances in the theory of  
48 STM are reviewed in Ref. [11].

49 Electron tunneling was first analyzed by Bardeen [12] and Cohen et al. [13] using the  
50 perturbative transfer Hamiltonian (TH) approach and more recently by many other  
51 authors [14–16]. Although the TH gives, in most cases, a good description of the  
52 observed effects, it lacks a firm first principles theoretical basis and does not account  
53 properly for many-body effects [17]. An improved form of TH [18] that involved energy  
54 dependent transfer matrix elements was used to incorporate many-body effects. However,  
55 this model does not describe the electron–phonon interaction properly [19].

56 A many-body non-equilibrium Green functions (NEGF) formulation of electron  
57 tunneling was proposed by Caroli et al. [20]. The NEGF theory was originated by  
58 Schwinger [21] and Kadanoff and Baym [22], and developed further by Keldysh [23] and  
59 Craig [24]. This formalism involves the calculation of four basic Green functions, time  
60 ordered ( $G^T$ ), anti-time ordered ( $G^{\bar{T}}$ ), lesser ( $G^<$ ) and greater ( $G^>$ ). Additional retarded  
61 ( $G^r$ ) and advanced ( $G^a$ ) Green functions are defined as specific combinations of these  
62 **Q1** basic functions. At equilibrium suffice it to know only the retarded or advanced Green  
63 functions; all other Green functions simply follow from the fluctuation–dissipation  
64 theorem that connects the ‘lesser’ and ‘greater’ with the retarded Green function through  
65 the equilibrium Fermi distribution function ( $f_0(E)$ ) [25]. However, for non-equilibrium  
66 measurements, where the distribution function is not known *a priori*, one needs to solve  
67 for the various NEGFs self-consistently.

68 Electronic transport in molecular wires and STM currents of single molecules have  
69 received considerable attention [26–31]. Electron transport through a single molecule  
70 [32–34] or a chain of several atoms [35] was studied. From a theoretical point of view,  
71 this is very similar to the electron tunneling in semiconductor junctions and various  
72 theories developed for STM [36,37] can directly be applied to molecular wires. The  
73 NEGF technique developed for tunneling currents has been used to analyze the electron  
74 conduction through a single molecule attached to electrodes [26,36,38–42]. The method  
75 has also been combined with density functional theory for the modeling of transport in  
76 molecular devices [43,44].

77 In this chapter, we develop a non-equilibrium superoperator Green function theory  
78 [23,25,45] (NESGF) of molecular currents [46]. A notable advantage of working with  
79 superoperators in the higher dimensional Liouville space [44,47] is that we need to  
80 consider only time-ordered quantities in real (physical) time; all NEGFs show up  
81 naturally without introducing artificial time variables. Observables can be expressed in  
82 terms of various *Liouville space pathways* (LSP) [46]. The ordinary (causal) response  
83 function which represents the density response to an external field is one particular  
84 combination of these LSPs. Other combinations represent the spontaneous density  
85 fluctuations and the response of these fluctuations to the external field [47,48]. A simple  
86 time ordering operation of superoperators in real time is all it takes to derive the non-  
87 equilibrium theory, avoiding the Keldysh loop or Matsubara imaginary time. The NESGF  
88 theory provides new physical insights into the mechanism of the current. It can also be  
89 more naturally used to interpret time domain experiments involving external pulses.  
90

In Section 14.2, we give a brief introduction to the superoperator formalism and recast the NEGF theory in terms of the superoperator Green functions. Starting from the microscopic definitions for various NESGF, we construct dynamical equations of motion and obtain the Dyson matrix equation of Keldysh which couples the various NESGFs. In Section 14.3, we apply the NESGF theory to the conduction through a molecular junction. In Section 14.4 we end with a discussion.

## 14.2 DYSON EQUATIONS FOR SUPEROPERATOR GREEN FUNCTIONS

We consider a system of externally driven electrons and phonons described by the Hamiltonian [16,23,26,38],

$$H = H_0 + H_{\text{ep}} + H_{\text{ex}} \quad (1)$$

where  $H_0$  represents the non-interacting electrons and phonons,

$$H_0 = \int d\mathbf{r} \psi^\dagger(\mathbf{r}) h_0(\mathbf{r}) \psi(\mathbf{r}) + \int d\mathbf{r} \phi^\dagger(\mathbf{r}) \Omega_0(\mathbf{r}) \phi(\mathbf{r}) \quad (2)$$

$h_0(\mathbf{r}) = (-\hbar^2/2m)\nabla^2$  is the kinetic energy and  $m$  is the electron mass.  $\psi(\psi^\dagger)$  represent the annihilation (creation) operators which satisfy the Fermi anticommutation relations,

$$\begin{aligned} \psi(\mathbf{r})\psi^\dagger(\mathbf{r}') + \psi^\dagger(\mathbf{r}')\psi(\mathbf{r}) &= \delta(\mathbf{r} - \mathbf{r}') \\ \psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}') + \psi^\dagger(\mathbf{r}')\psi^\dagger(\mathbf{r}) &= 0 \\ \psi(\mathbf{r})\psi(\mathbf{r}') + \psi(\mathbf{r}')\psi(\mathbf{r}) &= 0 \end{aligned} \quad (3)$$

and  $\phi(\phi^\dagger)$  are boson operators with the commutation relations,

$$\begin{aligned} \phi(\mathbf{r})\phi^\dagger(\mathbf{r}') - \phi^\dagger(\mathbf{r}')\phi(\mathbf{r}) &= \delta(\mathbf{r} - \mathbf{r}') \\ \phi^\dagger(\mathbf{r})\phi^\dagger(\mathbf{r}') - \phi^\dagger(\mathbf{r}')\phi^\dagger(\mathbf{r}) &= 0 \\ \phi(\mathbf{r})\phi(\mathbf{r}') - \phi(\mathbf{r}')\phi(\mathbf{r}) &= 0 \end{aligned} \quad (4)$$

The second term in Eq. (1) denotes the electron–phonon interaction,

$$H_{\text{ep}} = \int d\mathbf{r} \lambda(\mathbf{r}) [\phi^\dagger(\mathbf{r}) + \phi(\mathbf{r})] \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) \quad (5)$$

where  $\lambda(\mathbf{r})$  is the coupling strength. Finally,  $H_{\text{ex}}$  represents the coupling to a time-dependent external potential  $\xi(\mathbf{r}, t)$ ,

$$H_{\text{ex}} = \int d\mathbf{r} \xi(\mathbf{r}, t) \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) \quad (6)$$

We next briefly survey some properties of Liouville space superoperators that will be useful in the following derivations [49]. The elements of the Hilbert space  $N \times N$  density matrix,  $\rho(t)$ , are arranged as a Liouville space vector (bra or ket) of length  $N^2$ . Operators of  $N^2 \times N^2$  dimension in this space are denoted as superoperators. With any Hilbert space operator  $A$ , we associate two superoperators  $A_L$  (left) and  $A_R$  (right) defined through their

action on another operator  $X$  as

$$A_L X \equiv AX \quad \text{and} \quad A_R X \equiv XA \quad (7)$$

We further define symmetric and antisymmetric combinations of these superoperators

$$A_+ = \frac{1}{2}(A_L + A_R) \quad \text{and} \quad A_- = (A_L - A_R) \quad (8)$$

The commutator and anticommutator operations in Hilbert space can thus be implemented with a single multiplication by a ‘-’ and ‘+’ superoperator, respectively. We further introduce the Liouville space–time ordering operator  $\mathcal{T}$ . This is a key ingredient for extending NEGF to superoperators: when applied to a product of superoperators it reorders them so that time increases from right to left. We define  $\langle A(t) \rangle \equiv \text{Tr}\{A(t)\rho_{\text{eq}}\}$  where  $\rho_{\text{eq}} = \rho(t=0)$  represents the equilibrium density matrix of the interacting system. It is straightforward to see that for any two operators  $A$  and  $B$  we have

$$\langle \mathcal{T} A_+(t) B_-(t') \rangle = 0, \quad t' > t \quad (9)$$

$\langle \mathcal{T} A_+(t) B_-(t') \rangle$  is thus always a retarded function. This follows from the definitions (8). Since a ‘-’ superoperator corresponds to a commutator in Hilbert space, this implies that for  $t < t'$ ,  $\langle A_+(t) B_-(t') \rangle$  becomes a trace of a commutator and must vanish, i.e.

$$\begin{aligned} \langle \mathcal{T} A_+(t) B_-(t') \rangle &= \text{Tr}\{B_-(t') A_+(t) \rho_{\text{eq}}\} \quad t < t' \\ &= \frac{1}{2} \text{Tr}\{[B(t'), A(t) \rho_{\text{eq}} + \rho_{\text{eq}} A(t)]\} = 0 \end{aligned}$$

Similarly, it follows that the trace of two ‘minus’ operators always vanishes

$$\langle \mathcal{T} A_-(t) B_-(t') \rangle = 0 \quad \text{for all } t \text{ and } t' \quad (10)$$

We shall make use of Eqs. (9) and (10) for discussing the retarded and advanced Green functions in Appendix 14D. Superoperator algebra was surveyed in Ref. [49].

In Liouville space the density matrix,  $\rho(t)$  is a vector whose time dependence is given by

$$\rho(t) = \mathcal{G}(t, t_0) \rho(t_0) \quad (11)$$

with the Green function,

$$\mathcal{G}(t, t_0) = \mathcal{T} \exp\left\{-\frac{i}{\hbar} \int_{t_0}^t \mathcal{H}_-(\tau) d\tau\right\} \quad (12)$$

and  $\mathcal{H}_-$  is the superoperator corresponding to the Hamiltonian (Eq. (1)). Note that unlike Hilbert space, where time dependence of the ket and the bra is governed by forward and backward time-evolution operators, respectively, in Liouville space one keeps track of both bra and ket simultaneously and the density matrix needs only to be propagated forward in time (Eq. (11)).

To introduce the interaction picture in Liouville space we partition  $\mathcal{H}_- = \mathcal{H}_{0-} + \mathcal{H}'_-$  corresponding to the non-interacting and interaction Hamiltonians.

181 With this partitioning, Eq. (12) can be written as

$$182 \quad \mathcal{G}(t, t_0) = \mathcal{G}_0(t, t_0)\mathcal{G}_1(t, t_0) \quad (13)$$

183 where  $\mathcal{G}_0$  represents the time evolution with respect to  $H_0$ ,

$$184 \quad \mathcal{G}_0(t, t_0) = \theta(t - t_0) \exp\left\{-\frac{i}{\hbar} \mathcal{H}_{0-}(t - t_0)\right\} \quad (14)$$

185  $\mathcal{G}_1(t, t_0)$  is the time evolution operator in the interaction picture,

$$186 \quad \mathcal{G}_1(t, t_0) = \mathcal{T} \exp\left\{-\frac{i}{\hbar} \int_{t_0}^t \tilde{\mathcal{H}}'_-(\tau) d\tau\right\} \quad (15)$$

187 and  $\tilde{\mathcal{H}}'_-$  is the interaction picture representation of  $\mathcal{H}'_-$ . We shall denote superoperators  
188 in the interaction picture by a  $(\tilde{\phantom{x}})$ ,

$$189 \quad \tilde{A}_\alpha(t) \equiv \mathcal{G}_0^\dagger(t, t_0) A_\alpha(t_0) \mathcal{G}_0(t, t_0) \quad (16)$$

190 where  $\alpha = +, -$  or L, R. Superoperators in the Heisenberg picture will be represented  
191 by a caret

$$192 \quad \hat{A}_\alpha(t) \equiv \mathcal{G}^\dagger(t, t_0) A_\alpha(t_0) \mathcal{G}(t, t_0) \quad (17)$$

193 By adiabatic switching of the interaction  $\mathcal{H}'_-$  starting at  $t_0 = -\infty$  we have

$$194 \quad \rho(t) = \rho_0 - \frac{i}{\hbar} \int_{-\infty}^t d\tau \mathcal{G}_0(t, \tau) \mathcal{H}'_-(\tau) \rho(\tau) \quad (18)$$

195 where  $\rho_0 = \rho(-\infty)$  is the equilibrium density matrix of the non-interacting system

$$196 \quad \rho_0 = \frac{\exp(-\beta H_0)}{\text{Tr}\{\exp(-\beta H_0)\}} \quad (19)$$

197 An iterative solution of Eq. (18) yields

$$198 \quad \rho(t) = \mathcal{G}_1(t, -\infty)\rho_0 \quad (20)$$

199 which can also be obtained by applying the time evolution operator (15) to  $\rho(t_0)$  and  
200 setting  $t_0 = -\infty$ . Using Eq. (20), the equilibrium density matrix of the interacting system  
201 can be generated from the non-interacting one by switching on the interactions  
202 adiabatically, starting at  $t = -\infty$ . The external potential is constant in time for  $t < 0$  and  
203 is assumed to be time dependent only for  $t > 0$ . We then get

$$204 \quad \rho_{\text{eq}} = \mathcal{G}_1(0, -\infty)\rho_0 \quad (21)$$

205 This *adiabatic connection formula* has been shown [49] to be very useful for calculating  
206 expectation values using the interaction picture. In the corresponding Gellman-law  
207 expression in Hilbert space [50] there is an extra denominator that takes care of the phase

of the wavefunction. This is not necessary in Liouville space since the density matrix does not acquire such a phase.

In the Heisenberg picture, the expectation value of an operator  $\hat{A}_\alpha(t)$  is given by

$$\langle \hat{A}_\alpha(t) \rangle \equiv \text{Tr}\{\hat{A}_\alpha(t)\rho_{\text{eq}}\} \quad (22)$$

where  $\rho_{\text{eq}} = \rho(t = 0)$ . Using Eqs. (16), (17) and (20), this can be recast in the interaction picture as

$$\langle \hat{A}_\alpha(t) \rangle = \text{Tr}\{\tilde{A}_\alpha(t)\mathcal{G}_1(t, -\infty)\rho_0\} \equiv \langle \tilde{A}_\alpha(t)\mathcal{G}_1(t, -\infty) \rangle_0 \quad (23)$$

Eq. (23) is a good starting point for developing a perturbation theory around the non-interacting system. Through Eqs. (22) and (23) we also define the expectation values  $\langle \dots \rangle$  and  $\langle \dots \rangle_0$ . While the former represents the trace with respect to the interacting density matrix, the latter is defined with respect to the non-interacting density matrix. This will be used in the following.

Corresponding to the Hilbert space electron and phonon operators,  $\hat{\psi}$ ,  $\hat{\psi}^\dagger$ ,  $\hat{\phi}$  and  $\hat{\phi}^\dagger$  we define ‘left’ ( $\alpha = \text{L}$ ) and ‘right’ ( $\alpha = \text{R}$ ) superoperators,  $\hat{\psi}_\alpha$ ,  $\hat{\psi}_\alpha^\dagger$ ,  $\hat{\phi}_\alpha$  and  $\hat{\phi}_\alpha^\dagger$ . The dynamics of a superoperator,  $\hat{\psi}_\alpha$ , is described by the generalized Liouville equation,

$$-i\hbar \frac{\partial \hat{\psi}_\alpha(t)}{\partial t} = [\mathcal{H}_-(t), \hat{\psi}_\alpha(t)] = \mathcal{H}_-(t)\hat{\psi}_\alpha(t) - \hat{\psi}_\alpha(t)\mathcal{H}_-(t) \quad (24)$$

where  $\mathcal{H}_-$  is the superoperator corresponding to the Hamiltonian given in Eq. (1). A similar equation can be written down for the phonon superoperators. In order to evaluate the commutator appearing in the RHS of Eq. (1), we need the commutation relations of superoperators [51]. The ‘left’ and the ‘right’ operators always commute. Thus, for  $\alpha \neq \beta$  we have

$$\begin{aligned} [\psi_\alpha(\mathbf{r}), \psi_\beta(\mathbf{r}')] &= [\psi_\alpha^\dagger(\mathbf{r}), \psi_\beta^\dagger(\mathbf{r}')] = [\psi_\alpha^\dagger(\mathbf{r}), \psi_\beta(\mathbf{r}')] = 0 \\ [\phi_\alpha(\mathbf{r}), \phi_\beta(\mathbf{r}')] &= [\phi_\alpha^\dagger(\mathbf{r}), \phi_\beta^\dagger(\mathbf{r}')] = [\phi_\alpha^\dagger(\mathbf{r}), \phi_\beta(\mathbf{r}')] = 0 \end{aligned} \quad (25)$$

For Fermi superoperators we have

$$\begin{aligned} \psi_\alpha(\mathbf{r})\psi_\alpha(\mathbf{r}') + \psi_\alpha(\mathbf{r}')\psi_\alpha(\mathbf{r}) &= 0 \\ \psi_\alpha^\dagger(\mathbf{r})\psi_\alpha^\dagger(\mathbf{r}') + \psi_\alpha^\dagger(\mathbf{r}')\psi_\alpha^\dagger(\mathbf{r}) &= 0 \\ \psi_\alpha(\mathbf{r})\psi_\alpha^\dagger(\mathbf{r}') + \psi_\alpha(\mathbf{r}')\psi_\alpha^\dagger(\mathbf{r}) &= \delta(\mathbf{r} - \mathbf{r}') \end{aligned} \quad (26)$$

Similarly for the boson operators

$$\begin{aligned} \phi_\alpha^\dagger(\mathbf{r})\phi_\alpha^\dagger(\mathbf{r}') - \phi_\alpha^\dagger(\mathbf{r}')\phi_\alpha^\dagger(\mathbf{r}) &= 0 \\ \phi_\alpha(\mathbf{r})\phi_\alpha(\mathbf{r}') - \phi_\alpha(\mathbf{r}')\phi_\alpha(\mathbf{r}) &= 0 \\ \phi_\alpha(\mathbf{r})\phi_\alpha^\dagger(\mathbf{r}') - \phi_\alpha^\dagger(\mathbf{r}')\phi_\alpha(\mathbf{r}) &= \kappa_\alpha\delta(\mathbf{r} - \mathbf{r}') \end{aligned} \quad (27)$$

Here  $\kappa_\alpha = -1$  for  $\alpha = \text{R}$  and unity for  $\alpha = \text{L}$ .

Using the commutation relations (25) and (26) and the identity

$$(XY\dots Z)_\alpha = X_\alpha Y_\alpha \dots Z_\alpha, \quad \alpha = L, R \quad (28)$$

we can recast  $\mathcal{H}_-$  in terms of the elementary field superoperators,

$$\mathcal{H}_- = \mathcal{H}_{0-} + \mathcal{H}_-^{\text{ep}} + \mathcal{H}_-^{\text{ex}} \quad (29)$$

with

$$\begin{aligned} \mathcal{H}_{0-} &= \sum_{\alpha=L,R} \kappa_\alpha \int d\mathbf{r} (\psi_\alpha^\dagger(\mathbf{r}) h_0(\mathbf{r}) \psi_\alpha(\mathbf{r}) + \phi_\alpha^\dagger(\mathbf{r}) \Omega_0(\mathbf{r}) \phi_\alpha(\mathbf{r})) \\ \mathcal{H}_-^{e-p} &= \sum_{\alpha=L,R} \kappa_\alpha \int d\mathbf{r} \lambda(\mathbf{r}) \hat{\Phi}_\alpha(\mathbf{r}) \psi_\alpha^\dagger(\mathbf{r}) \psi_\alpha(\mathbf{r}) \\ \mathcal{H}_-^{\text{ex}} &= \sum_{\alpha=L,R} \kappa_\alpha \int d\mathbf{r} \psi_\alpha^\dagger(\mathbf{r}) \xi(\mathbf{r}, t) \psi_\alpha(\mathbf{r}) \end{aligned} \quad (30)$$

where  $\hat{\Phi}_\alpha = \phi_\alpha + \phi_\alpha^\dagger$ .

We next define electron and phonon superoperator Green functions

$$\begin{aligned} G_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= -\frac{i}{\hbar} \langle \mathcal{T} \hat{\psi}_\alpha(\mathbf{r}, t) \hat{\psi}_\beta^\dagger(\mathbf{r}', t') \rangle \\ D_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= -\frac{i}{\hbar} \langle \mathcal{T} \hat{\Phi}_\alpha(\mathbf{r}, t) \hat{\Phi}_\beta^\dagger(\mathbf{r}', t') \rangle \end{aligned} \quad (31)$$

As shown in Ref. [44] (see Appendix 14A),  $G_{LL}$ ,  $G_{RR}$ ,  $G_{LR}$  and  $G_{RL}$ , respectively, coincide with the standard Hilbert space–time ordered  $G^T$ , antitime ordered  $G^{\tilde{T}}$ , lesser  $G^<$  and greater  $G^>$  Green functions defined on a closed time loop.

Using the commutation relations (3), the Heisenberg equations of motion for superoperator  $\hat{\psi}_\alpha(t)$  reads

$$i\hbar \kappa_\alpha \frac{\partial \hat{\psi}_\alpha(\mathbf{r}, t)}{\partial t} = h(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) + \lambda(\mathbf{r}) \hat{\Phi}_\alpha(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) \quad (32)$$

where  $h(\mathbf{r}, t) = h_0(\mathbf{r}) + \xi(\mathbf{r}, t)$ . By taking the time derivative of the electron Green function in Eq. (31) and using Eq. (32), we obtain the equation of motion for  $G_{\alpha\beta}$ ,

$$\begin{aligned} \left( i\hbar \frac{\partial}{\partial t} - \kappa_\alpha h(\mathbf{r}, t) \right) G_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= \delta_{\alpha\beta} \delta(\mathbf{x} - \mathbf{x}') - \frac{i}{\hbar} \kappa_\alpha \lambda(\mathbf{r}) \\ &\times \langle \mathcal{T} \hat{\Phi}_\alpha(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) \hat{\psi}_\beta^\dagger(\mathbf{r}', t') \rangle \end{aligned} \quad (33)$$

In order to derive the equation of motion for the phonon Green function  $D_\alpha$ , we add the following coupling term

$$\int d\mathbf{r} J(\mathbf{r}, t) \Phi(\mathbf{r}) \quad (34)$$

to the Hamiltonian. Here  $J(\mathbf{r}, t)$  is some artificial field that will be set to zero at the end of calculations. This new term does not effect the electron Green function since  $\Phi$  and  $\psi$

commute. Thus, superoperator  $\mathcal{H}_-^{\text{ex}}$  in Eq. (30) takes the form

$$\mathcal{H}_-^{\text{ex}} = \sum_{\alpha=L,R} \kappa_\alpha \int d\mathbf{r} [\psi_\alpha^\dagger(\mathbf{r}) \xi(\mathbf{r}, t) \psi_\alpha(\mathbf{r}) + J_\alpha(\mathbf{r}, t) \Phi_\alpha(\mathbf{r})] \quad (35)$$

where fields  $J_L$  and  $J_R$  couple to the ‘left’ and ‘right’ boson operators, respectively. Using the boson commutation (Eq. (26)), the Heisenberg equation for superoperator  $\phi_\alpha$  is obtained as

$$-i\hbar\kappa_\alpha \frac{\partial \hat{\phi}_\alpha(\mathbf{r}, t)}{\partial t} = \Omega_0(\mathbf{r}) \hat{\phi}_\alpha(\mathbf{r}, t) + \lambda(\mathbf{r}) \hat{\psi}_\alpha^\dagger(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) + J_\alpha(\mathbf{r}, t) \quad (36)$$

Using Eq. (36) we next obtain the equation of motion for operator  $\hat{\Phi}_\alpha$

$$-\frac{\hbar^2 \kappa_\alpha}{\Omega_0(\mathbf{r})} \frac{\partial^2 \hat{\Phi}_\alpha(\mathbf{r}, t)}{\partial t^2} = \Omega_0(\mathbf{r}) \hat{\Phi}_\alpha(\mathbf{r}, t) + 2\lambda(\mathbf{r}) \hat{\psi}_\alpha^\dagger(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) + 2J_\alpha(\mathbf{r}, t) \quad (37)$$

Taking trace with respect to the density matrix  $\rho(t=0)$  we obtain

$$-\frac{1}{2} \left( \frac{\hbar^2 \kappa_\alpha}{\Omega_0(\mathbf{r})} \frac{\partial^2}{\partial t^2} + \Omega_0(\mathbf{r}) \right) \langle \hat{\Phi}_\alpha(\mathbf{r}, t) \rangle = \lambda(\mathbf{r}) \langle \hat{\psi}_\alpha^\dagger(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) \rangle + J_\alpha(\mathbf{r}, t) \quad (38)$$

Using the interaction picture representation (Eq. (23)) with  $\mathcal{H}_-^{\text{ex}}$  given by Eq. (35) we can write

$$\langle \hat{\Phi}_\alpha(\mathbf{r}, t) \rangle = \langle \tilde{\Phi}(\mathbf{r}, t) \mathcal{G}_I(t, -\infty) \rangle_0 \quad (39)$$

By taking the functional derivative with respect to  $J_\beta$ , and setting  $J_L = J_R = 0$ , we obtain

$$\begin{aligned} \left. \frac{\delta}{\delta J_\beta(\mathbf{r}', t')} \langle \hat{\Phi}_\alpha(\mathbf{r}, t) \rangle \right|_{J_L=J_R=0} &= -\frac{i}{\hbar} \epsilon_\beta \langle \mathcal{T} \tilde{\Phi}_\alpha(\mathbf{r}, t) \tilde{\Phi}_\beta^\dagger(\mathbf{r}', t') \mathcal{G}_I(t, -\infty) \rangle_0 \\ &= \kappa_\beta D_{\alpha\beta}(\mathbf{r}\mathbf{t}, \mathbf{r}'\mathbf{t}') \end{aligned} \quad (40)$$

Using Eqs. (38)–(40), the equation of motion for the phonon Green function is obtained as

$$\begin{aligned} -\frac{1}{2} \left( \frac{\hbar^2 \kappa_\beta}{\Omega_0(\mathbf{r})} \frac{\partial^2}{\partial t^2} + \Omega_0(\mathbf{r}) \right) D_{\alpha\beta}(\mathbf{r}\mathbf{t}, \mathbf{r}'\mathbf{t}') &= \delta_{\alpha\beta} \delta(\mathbf{x} - \mathbf{x}') + \frac{i}{\hbar} \lambda(\mathbf{r}) \kappa_\alpha \\ &\quad \times \langle \mathcal{T} \hat{\psi}_\alpha^\dagger(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) \hat{\Phi}_\beta^\dagger(\mathbf{r}', t') \rangle \end{aligned} \quad (41)$$

We shall denote the space and time coordinates collectively by  $\mathbf{x} = \mathbf{r}, t$ ; thus in Eqs. (33) and (41)  $\delta(\mathbf{x} - \mathbf{x}') \equiv \delta(\mathbf{r} - \mathbf{r}') \delta(t - t')$ .

Following Keldysh, we shall rearrange the superoperator Green functions in a  $2 \times 2$  matrix  $\bar{G}$ ,

$$\bar{G}(\mathbf{x}, \mathbf{x}') = \begin{pmatrix} G_{LL}(\mathbf{x}, \mathbf{x}') & G_{LR}(\mathbf{x}, \mathbf{x}') \\ G_{RL}(\mathbf{x}, \mathbf{x}') & G_{RR}(\mathbf{x}, \mathbf{x}') \end{pmatrix} \quad (42)$$



and similarly the phonon Green function matrix  $\bar{D}$  with elements  $D_{\alpha\beta}$ . The corresponding Green functions of the non-interacting system described by the Hamiltonian (2) are denoted by  $\bar{G}^0$  and  $\bar{D}^0$ , respectively. These are given by

$$\begin{aligned} G_{\alpha\beta}^0(\mathbf{r}t, \mathbf{r}'t') &= \left( i\hbar \frac{\partial}{\partial t} - \kappa_\alpha h(\mathbf{r}, t) \right)^{-1} \delta_{\alpha\beta} \delta(\mathbf{x} - \mathbf{x}') \\ D_{\alpha\beta}^0(\mathbf{r}t, \mathbf{r}'t') &= -\frac{1}{2} \left( \frac{\hbar^2 \kappa_\beta}{\Omega_0(\mathbf{r})} \frac{\partial^2}{\partial t^2} + \Omega_0(\mathbf{r}) \right)^{-1} \delta_{\alpha\beta} \delta(\mathbf{x} - \mathbf{x}') \end{aligned} \quad (43)$$

Using our matrix notation, we can recast Eqs. (33) and (41) in the form of Dyson equations

$$\begin{aligned} \bar{G} &= \bar{G}^0 + \bar{G}^0 \bar{\Sigma} \bar{G}, \\ \bar{D} &= \bar{D}^0 + \bar{D}^0 \bar{\Pi} \bar{D} \end{aligned} \quad (44)$$

The effect of all interactions is now included in the electron ( $\bar{\Sigma}$ ) and phonon ( $\bar{\Pi}$ ) self-energies. Exact expressions for the self-energies are obtained by comparing Eqs. (33) and (41) with Eq. (44)

$$\begin{aligned} \Sigma_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= -\frac{i}{\hbar} \kappa_\alpha \lambda(\mathbf{r}) \sum_{\beta'} \int d\tau \int d\mathbf{r}_1 \langle \mathcal{T} \hat{\Phi}_\alpha^\dagger(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) \hat{\psi}_{\beta'}^\dagger(\mathbf{r}_1, \tau) G_{\beta'\beta}^{-1}(\mathbf{r}_1 \tau, \mathbf{r}'t') \rangle \\ \Pi_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= \frac{i}{\hbar} \kappa_\alpha \lambda(\mathbf{r}) \sum_{\beta'} \int d\tau \int d\mathbf{r}_1 \langle \mathcal{T} \hat{\psi}_\alpha^\dagger(\mathbf{r}, t) \hat{\psi}_\alpha(\mathbf{r}, t) \hat{\Phi}_{\beta'}^\dagger(\mathbf{r}_1, \tau) D_{\beta'\beta}^{-1}(\mathbf{r}_1 \tau, \mathbf{r}'t') \rangle \end{aligned} \quad (45)$$

Eqs. (43)–(45) are exact and constitute the NESGF formalism.

In order to evaluate the self-energies perturbatively, we rewrite the Green functions, Eq. (31), in the interaction picture

$$\begin{aligned} G_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= -\frac{i}{\hbar} \langle \mathcal{T} \tilde{\psi}_\alpha(\mathbf{r}, t) \tilde{\psi}_\beta^\dagger(\mathbf{r}', t') \mathcal{G}_1(t, -\infty) \rangle_0 \\ D_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= -\frac{i}{\hbar} \langle \mathcal{T} \tilde{\Phi}(\mathbf{r}, t) \tilde{\Phi}_\beta^\dagger(\mathbf{r}', t') \mathcal{G}_1(t, -\infty) \rangle_0 \end{aligned} \quad (46)$$

where  $\mathcal{G}_1(t, -\infty)$  is given by Eq. (15) with  $t_0 = -\infty$ . Using Eqs. (13), (16) and (20), the self-energies (45) can also be expressed in the interaction picture as

$$\begin{aligned} \Sigma_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= -\frac{i}{\hbar} \kappa_\alpha \lambda(\mathbf{r}) \sum_{\beta'} \iint d\tau d\mathbf{r}_1 \langle \mathcal{T} \tilde{\Phi}_\alpha^\dagger(\mathbf{r}, t) \tilde{\psi}_\alpha(\mathbf{r}, t) \tilde{\psi}_{\beta'}^\dagger(\mathbf{r}_1, \tau) \mathcal{G}_1(t, -\infty) \rangle_0 G_{\beta'\beta}^{-1}(\mathbf{r}_1 \tau, \mathbf{r}'t') \\ \Pi_{\alpha\beta}(\mathbf{r}t, \mathbf{r}'t') &= \frac{i}{\hbar} \kappa_\alpha \lambda(\mathbf{r}) \sum_{\beta'} \iint d\tau d\mathbf{r}_1 \langle \mathcal{T} \tilde{\psi}_\alpha^\dagger(\mathbf{r}, t) \tilde{\psi}_\alpha(\mathbf{r}, t) \tilde{\Phi}_{\beta'}^\dagger(\mathbf{r}_1, \tau) \mathcal{G}_1(t, -\infty) \rangle_0 D_{\beta'\beta}^{-1}(\mathbf{r}_1 \tau, \mathbf{r}'t') \end{aligned} \quad (47)$$

Eq. (47) together with Eq. (46) constitutes closed form equations for the self-energies where all the averages are given in the interaction picture,  $\langle \dots \rangle_0$ , with respect to

the non-interacting density matrix. By expanding  $\mathcal{G}_I$  (Eq. (15)) perturbatively in  $\tilde{\mathcal{H}}'_-$  we can obtain perturbative expansion for the self-energies. Each term in the expansion can be calculated using Wick's theorem for superoperators [49] which is given in Appendix 14E. This results in a perturbative series in terms of the zeroth order Green functions.

### 14.3 THE CALCULATION OF MOLECULAR CURRENTS

We have applied the NESGF to study the charge conductivity of a molecular wire attached to two perfectly conducting leads. In the simplest approach the leads 'a' and 'b' are treated as two free electron reservoirs. Nuclear motions in the molecular region are described as harmonic phonons which interact with the surrounding electronic structure and the environment (secondary phonons) [26]. We first recast the general Hamiltonian, Eq. (1), in a single electron local basis and partition it as

$$H = H_f + H_{\text{int}} \quad (48)$$

where  $H_f$  represents the free, non-interacting electrons and phonons and with no coupling between molecule and leads

$$H_f = \sum_{i,j} E_{i,j} \psi_i^\dagger \psi_j + \sum_{k \in \text{a,b}} \epsilon_k \psi_k^\dagger \psi_k + \sum_l \Omega_l \phi_l^\dagger \phi_l + \sum_m \omega_m \phi_m^\dagger \phi_m \quad (49)$$

The indices  $(i,j)$  represent the electronic basis states corresponding to the molecule,  $k$  labels the electronic states in the leads (a and b),  $l$  denotes primary phonons which interact with the electrons and  $m$  denotes the secondary phonons which are coupled to the primary phonons and constitute a thermal bath. The applied external voltage  $V$  maintains a chemical potential difference,  $\mu_a - \mu_b = eV$ , between the two leads and also modifies the single electron energies. In addition it provides an extra term  $\sum_i V_i \psi_i^\dagger \psi_i$  which is included in the zeroth order Hamiltonian,  $H_f$ , by modifying the single electron energies. The interaction Hamiltonian is given by

$$H_{\text{int}} = \sum_{k \in \text{a,b}; i} (V_{ki} \psi_k^\dagger \psi_i + h.c.) + \sum_{l,i} \lambda_{li} \Phi_l \psi_i^\dagger \psi_i + \sum_{l,m} U_{lm} \Phi_l \Phi_m \quad (50)$$

The three terms represent the molecule/lead interaction, coupling of primary phonons with the molecule and the interaction of primary and secondary phonons, respectively.

The total current passing through the junction can be expressed in terms of the electron Green functions and the corresponding self-energies. At steady state it is given by (see Appendix 14B, Eq. (B22))

$$I_T = \frac{2e}{\hbar} \sum_{ij} \int \frac{d\omega}{2\pi} \left[ \Sigma_{\text{LR}}^{ij'}(\omega) G_{\text{RL}}^{j'i}(\omega) - \Sigma_{\text{RL}}^{ij'}(\omega) G_{\text{LR}}^{j'i}(\omega) \right] \quad (51)$$

The electron Green functions  $G_{\text{LR}}^0$  and  $G_{\text{RL}}^0$  correspond to the free Hamiltonian,  $H_f$ , and the self-energies  $\Sigma_{\text{LR}}$  and  $\Sigma_{\text{RL}}$  represent the effects of all interactions (Eq. (50)).

$\Sigma_{\alpha\beta}^{ij}$  has contributions from the electron-lead ( $\sigma$ ) and electron-phonon ( $\Xi$ ) interactions

$$\Sigma_{\alpha\beta}^{ij}(\omega) = \sigma_{\alpha\beta}^{ij}(\omega) + \Xi_{\alpha\beta}^{ij}(\omega) \quad (52)$$

These are given in Eqs. (C29) and (C38). The self-energy expressions (C38) and (C40) are calculated perturbatively to second order in the electron–phonon coupling in terms of the zeroth order Green functions (Eq. (55)). The simplest expression for current is obtained by substituting Eqs. (55), (C29) and (C38) in Eq. (51). This zeroth order result can be improved by using the renormalized Green functions obtained from the self-consistent solution of the Dyson equation (44).

In order to solve self-consistently for the electron Green functions that appear in the current formula, Eq. (51), the self-energy is calculated under the Born approximation by replacing the zeroth order Green functions,  $G_{\alpha\beta}^0$  and  $D_{\alpha\beta}^0$  with the corresponding renormalized Green functions,  $G_{\alpha\beta}$  and  $D_{\alpha\beta}$ , as is commonly done in mode-coupling theories [52,53]. This approximation sums an infinite set of non-crossing diagrams [54,55] that appear in the perturbation expansion of the many-body Green function,  $G_{\alpha\beta}$ .

Since the electron self-energy (Eq. (C38)) also depends on the phonon Green function, the phonon self-energy,  $\Pi_{\alpha\beta}^{ll'}$ , is also required for a self-consistent solution of the electron Green functions. The phonon self-energy calculated in Appendix 14C is given by

$$\Pi_{\alpha\beta}^{ij}(\omega) = \gamma_{\alpha\beta}^{ij}(\omega) + \Lambda_{\alpha\beta}^{ij}(\omega) \quad (53)$$

where  $\gamma_{\alpha\beta}^{ij}(\omega)$  (Eq. (C30)) and  $\Lambda_{\alpha\beta}^{ij}(\omega)$  (Eq. (C40)) represent the contributions from the phonon–phonon and the electron–phonon interactions, respectively.

Computing the renormalized electron and phonon Green functions and the corresponding self-energies involves the self-consistent solution of the following coupled equations for the Green functions:

$$\begin{aligned} G_{LR}(\omega) &= G_{LL}^0(\omega)\Sigma_{LL}(\omega)G_{LR}(\omega) + G_{LL}^0(\omega)\Sigma_{LR}(\omega)G_{RR}(\omega) \\ G_{RL}(\omega) &= G_{RR}^0(\omega)\Sigma_{RL}(\omega)G_{LL}(\omega) + G_{RR}^0(\omega)\Sigma_{RR}(\omega)G_{RL}(\omega) \\ G_{LL}(\omega) &= G_{LL}^0(\omega) + G_{LL}^0(\omega)\Sigma_{LL}(\omega)G_{LL}(\omega) + G_{LL}^0(\omega)\Sigma_{LR}(\omega)G_{RL}(\omega) \\ G_{RR}(\omega) &= G_{RR}^0(\omega) + G_{RR}^0(\omega)\Sigma_{RL}(\omega)G_{LR}(\omega) + G_{RR}^0(\omega)\Sigma_{RR}(\omega)G_{RR}(\omega) \end{aligned} \quad (54)$$

Similarly the equations for the phonon Green functions are obtained by replacing  $G_{\alpha\beta}$  with  $D_{\alpha\beta}$  and  $\Sigma_{\alpha\beta}$  with  $\Pi_{\alpha\beta}$ . Here Green functions corresponding to the free Hamiltonian  $G_{\alpha\beta}^{0ij}$  and  $D_{\alpha\beta}^{0ll'}$  are given by

$$G_{\alpha\beta}^{0ij}(\omega) = \frac{\delta_{\alpha\beta}}{\omega\delta_{ij} - \kappa_{\alpha}E_{ij} + i\eta}, \quad D_{\alpha\beta}^{0ll'}(\omega) = \frac{2\Omega_l\delta_{\alpha\beta}\delta_{ll'}}{\kappa_{\alpha}\hbar^2\omega^2 - \Omega_l^2 + i\eta} \quad (55)$$

where we set  $\hbar = 1$  and  $\eta \rightarrow 0$ .  $E_{ij} = E_i - E_j$  is the energy difference between single electron  $i^{\text{th}}$  and  $j^{\text{th}}$  states.  $\Omega_i$  denotes the molecular phonon eigenstates.

Once the Green functions,  $G_{LR}$ ,  $G_{RL}$  and the corresponding self-energies  $\Sigma_{LR}$ ,  $\Sigma_{RL}$ , are obtained from the self-consistent solution of Eq. (54) together with Eq. (52), formula (51) can be used to calculate the total current through the molecular junction.

## 14.4 DISCUSSION

In this chapter, we have developed the NESGF formalism and applied it to the computation of molecular current. The Liouville space–time ordering operator provides an elegant way for performing calculations in real time, thus avoiding the artificial backward and forward time evolution required in Hilbert space (Keldysh loop). Wick’s theorem for superoperators is used to compute the self-energies perturbatively to the second order in phonon–electron coupling. Eq. (54) have been derived earlier by many authors [19,43,55]. Recently, Galperin et al. [26] have used a fully self-consistent solution to study the influence of different interactions on molecular conductivity for a strong electron–phonon coupling. The main aim of the present work is to demonstrate that by doing calculations in Liouville space one can avoid the backward/forward time evolution (Keldysh loop) required in Hilbert space. This originates from the fact that in Liouville space both ket and bra evolve forward in time. Thus, one can couple the system with two independent fields, ‘left’ and ‘right’. This property of Liouville space can be used to construct real (physical) time generating functionals for the non-perturbative calculation of the self-energies.

The present model [37–39] ignores electron–electron interactions. These may be treated using the GW technique [56–58] formulated in terms of the superoperators and extended to non-equilibrium situations. All non-equilibrium observables can be obtained from a single generating functional in terms of ‘left’ and ‘right’ operators. The retarded (advance) Green function that describes the forward (backward) motion of the system particle can also be calculated in terms of the basic Green functions,  $G_{\alpha\beta}$  (see Appendix 14D).

The NESGF formulation can also be recast in terms of the + and – (rather than L/R) superoperators which are more directly related to observables. This is done in Appendix 14D. We focused on the primary quantities that are represented in terms of the ‘left’ and ‘right’ superoperators and all other quantities are obtained as the linear combination of these basic operators.

## 14.5 ACKNOWLEDGEMENTS

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**APPENDIX 14A: SUPEROPERATOR EXPRESSIONS FOR THE KELDYSH GREEN FUNCTIONS**

The standard NEGF theory formulated in terms of the four Hilbert space Green functions: time ordered ( $G^T$ ), anti-time ordered ( $G^{\tilde{T}}$ ), greater ( $G^{>}$ ) and lesser ( $G^{<}$ ) [23,25]. These are defined in the Heisenberg picture as

$$\begin{aligned}
 G^T(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \langle T \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle \\
 &= -\frac{i}{\hbar} \theta(t - t') \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle + \theta(t' - t) \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle \\
 G^{\tilde{T}}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \langle \tilde{T} \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle \\
 &= -\frac{i}{\hbar} \theta(t' - t) \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle + \theta(t - t') \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle \\
 G^{>}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle \\
 G^{<}(\mathbf{x}, \mathbf{x}') &\equiv \frac{i}{\hbar} \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle
 \end{aligned}
 \tag{A1}$$

These are known as  $T$  ( $\tilde{T}$ ) is the Hilbert space–time (anti-time) ordering operator: when applied to a product of operators, it reorders them in ascending (descending) times from right to left.

The four Green functions that show up naturally in Liouville space are defined as

$$\begin{aligned}
 G_{LL}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle \mathcal{T} \hat{\psi}_L(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rangle \\
 G_{RR}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle \mathcal{T} \hat{\psi}_R(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rangle \\
 G_{LR}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle \mathcal{T} \hat{\psi}_L(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rangle \\
 G_{RL}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle \mathcal{T} \hat{\psi}_R(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rangle
 \end{aligned}
 \tag{A2}$$

$\mathcal{T}$  is the Liouville space–time ordering operator, which rearranges all superoperators in increasing order of time from right to left.

To establish connection between Liouville space and Hilbert space Green functions we shall convert superoperators back to ordinary operators [44]. For  $G_{LR}$ , and  $G_{RL}$ , we obtain

$$\begin{aligned}
 G_{LR}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr}\{ \mathcal{T} \hat{\psi}_L(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} \text{Tr}\{ \hat{\psi}(\mathbf{x}) \rho_{\text{eq}} \hat{\psi}^\dagger(\mathbf{x}') \} \\
 &= -\frac{i}{\hbar} \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle = G^<(\mathbf{x}, \mathbf{x}') \\
 G_{RL}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr}\{ \mathcal{T} \hat{\psi}_R(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} \text{Tr}\{ \hat{\psi}^\dagger(\mathbf{x}') \rho_{\text{eq}} \hat{\psi}(\mathbf{x}) \} \\
 &= -\frac{i}{\hbar} \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle = G^>(\mathbf{x}, \mathbf{x}')
 \end{aligned}
 \tag{A3}$$

where  $\rho_{\text{eq}}$  is the fully interacting many body equilibrium density matrix.

For  $G_{LL}$  and  $G_{RR}$  we have two cases

(i) For  $t > t'$ , we get

$$\begin{aligned}
 G_{LL}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr}\{ \mathcal{T} \hat{\psi}_L(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} \text{Tr}\{ \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rho_{\text{eq}} \} = -\frac{i}{\hbar} \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle \\
 G_{RR}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr}\{ \mathcal{T} \hat{\psi}_R(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} \text{Tr}\{ \rho_{\text{eq}} \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \} = -\frac{i}{\hbar} \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle
 \end{aligned}
 \tag{A4}$$

(ii) For the reverse case,  $t < t'$ , we get

$$\begin{aligned}
 G_{LL}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr}\{ \mathcal{T} \hat{\psi}_L(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} \text{Tr}\{ \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rho_{\text{eq}} \} = -\frac{i}{\hbar} \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle \\
 G_{RR}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr}\{ \mathcal{T} \hat{\psi}_R(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} \text{Tr}\{ \rho_{\text{eq}} \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \} = -\frac{i}{\hbar} \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle
 \end{aligned}
 \tag{A5}$$

Combining Eqs. (A4) and (A5) we can write

$$\begin{aligned}
 G_{LL}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr} \{ \mathcal{T} \hat{\psi}_L(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} [\theta(t-t') \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle - \theta(t'-t) \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle] \\
 &= G^T(\mathbf{x}, \mathbf{x}') \\
 G_{RR}(\mathbf{x}, \mathbf{x}') &\equiv -\frac{i}{\hbar} \text{Tr} \{ \mathcal{T} \hat{\psi}_R(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rho_{\text{eq}} \} \\
 &= -\frac{i}{\hbar} [\theta(t-t') \langle \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \rangle - \theta(t'-t) \langle \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \rangle] \\
 &= G^{\bar{T}}(\mathbf{x}, \mathbf{x}')
 \end{aligned}
 \tag{A6}$$

Eqs. (A3) and (A6) establish the equivalence of Hilbert and Liouville space Green functions and they can be summarized as

$$\begin{aligned}
 G_{LL}(\mathbf{x}, \mathbf{x}') &= G^T(\mathbf{x}, \mathbf{x}'), & G_{RR}(\mathbf{x}, \mathbf{x}') &= G^{\bar{T}}(\mathbf{x}, \mathbf{x}') \\
 G_{LR}(\mathbf{x}, \mathbf{x}') &= G^<(\mathbf{x}, \mathbf{x}'), & G_{RL}(\mathbf{x}, \mathbf{x}') &= G^>(\mathbf{x}, \mathbf{x}')
 \end{aligned}
 \tag{A7}$$

## APPENDIX 14 B: SUPEROPERATOR GREEN FUNCTION EXPRESSION FOR THE CURRENT

In this appendix, we present a formal microscopic derivation for the current flowing through a conductor. The conductor could be a molecule or a metal or any conducting material attached to two electrodes held at two different potentials.

In Hilbert space the charge current-density is given by

$$\mathbf{j}(\mathbf{r}, t) = -\frac{ie\hbar}{2m} \langle [\hat{\psi}^\dagger(\mathbf{r}, t) \nabla \hat{\psi}(\mathbf{r}, t) - (\nabla \hat{\psi}^\dagger(\mathbf{r}, t)) \hat{\psi}(\mathbf{r}, t)] \rangle
 \tag{B8}$$

where  $e$  and  $m$  are the electron charge and mass, respectively. Eq. (B8) can also be expressed in a slightly modified form as

$$\mathbf{j}(\mathbf{r}, t) = \frac{ie\hbar}{2m} [ \langle (\nabla - \nabla') \hat{\psi}^\dagger(\mathbf{r}, t) \hat{\psi}(\mathbf{r}', t') \rangle ]_{\mathbf{x}'=\mathbf{x}}
 \tag{B9}$$

where  $\nabla'$  represents the derivative with respect to  $\mathbf{r}'$ .

Using relation (A7) the current density can be expressed in terms of the superoperator Green function as

$$\mathbf{j}(\mathbf{r}, t) = -\frac{e\hbar^2}{2m} [ \langle (\nabla - \nabla') G_{LR}(\mathbf{r}t, \mathbf{r}'t') \rangle ]_{\mathbf{x}'=\mathbf{x}}
 \tag{B10}$$

At steady state, the Green functions only depend on the time difference ( $t - t'$ ) and the total current density ( $\mathbf{J}_T$ ) becomes time independent. Transforming to the frequency (energy) domain, the current density per unit energy is

$$\mathbf{j}(\mathbf{r}, E) = -\frac{e\hbar}{2m} [(\nabla - \nabla')G_{LR}(\mathbf{r}\mathbf{r}', E)]_{\mathbf{r}'=\mathbf{r}} \quad (\text{B11})$$

and the total current density

$$\mathbf{J}_T(\mathbf{r}) = \int \frac{dE}{2\pi} \mathbf{j}(\mathbf{r}, E) \quad (\text{B12})$$

Eq. (B12) provides a recipe for calculating the current profile across the conductor once the Green function  $G_{LR}$  is known from the self-consistent solution of the Dyson equation. For computing the total current passing through the conductor, Eq. (B11) can be expressed in the form of Eq. (51). In order to get the total current per unit energy ( $I_T(E)$ ) passing between electrode and conductor we need to integrate the current density over the surface area of the conductor–electrode contact

$$I_T(E) = \int_S \mathbf{j}(\mathbf{r}, E) \cdot \hat{\mathbf{n}} dS = \int \nabla \cdot \mathbf{j}(\mathbf{r}, E) d\mathbf{r} \quad (\text{B13})$$

where  $\hat{\mathbf{n}}$  is the unit vector normal to surface  $S$ . Substituting into Eq. (B13) from Eq. (B11), we get

$$I_T(E) = -\frac{e\hbar}{2m} \text{Tr}[(\nabla^2 - \nabla'^2)G_{LR}(\mathbf{r}\mathbf{r}', E)] \quad (\text{B14})$$

In general, a conductor–electrode system can be described by the Hamiltonian

$$H = H_0 + H_{\text{int}} \quad (\text{B15})$$

where  $H_0$  represents the non-interacting part

$$H_0 = \int d\mathbf{r} \psi^\dagger(\mathbf{r}) h_0(\mathbf{r}) \psi(\mathbf{r}) \quad (\text{B16})$$

where  $h_0(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2$  and all the interaction terms (conductor–electrode, electron–phonon) are included in  $H_{\text{int}}$ . The total current per unit energy, Eq. (B14), is

$$I_T(E) = -\frac{e}{\hbar} \text{Tr}[(h_0(\mathbf{r}) - h_0^*(\mathbf{r}'))G_{LR}(\mathbf{r}\mathbf{r}', E)] \quad (\text{B17})$$

The Dyson equations for the retarded Green function (see Appendix 14D, Eq. (D48)) in frequency (energy) can be expressed in the matrix form as

$$h_0 G_r = E G_r - \mathbf{I} - \sigma_r G_r \quad (\text{B18})$$

where  $\mathbf{I}$  is the identity matrix and  $\Sigma_r$  is the retarded self-energy, Eq. (D50).  $E = \hbar\omega$  is a number. Henceforth, we write all the expressions in the matrix notation. Taking



721 the complex conjugate of Eq. (B18), we obtain the Dyson equation for the advanced  
722 Green function,

$$723 \quad G_a h_0 = E G_a - \mathbf{I} - G_a \sigma_a \quad (B19)$$

726 with the corresponding advanced self-energy,  $\Sigma_a$ . From the matrix Dyson equation  
727 (D48), we also have the relation

$$728 \quad G_{LR} = G_r \Sigma_{LR} G_a \quad (B20)$$

731 Using the relations (B18)–(B20), it is easy to see that

$$732 \quad h_0 G_{LR} - G_{LR} h_0 = G_{LR} \Sigma_a + G_r \Sigma_{LR} - \Sigma_r G_{LR} - \Sigma_{LR} G_a \quad (B21)$$

735 Substituting this in Eq. (B17), the total current per unit energy becomes

$$736 \quad I_T(E) = \frac{2e}{\hbar} \text{Tr}[\Sigma_{LR}(E)G_{RL}(E) - \Sigma_{RL}(E)G_{LR}(E)] \quad (B22)$$

740 where a factor of 2 is introduced to account for the spin degeneracy.

741 We have calculated the total current in real space. In practice, the Green functions and  
742 the self-energy matrices are calculated in an electronic basis ( $i, j$ ). The total current  
743 through the conductor is obtained by integrating Eq. (B22) over energy resulting in  
744 Eq. (51).

## 747 APPENDIX 14C: SELF-ENERGIES FOR SUPEROPERATOR GREEN 748 FUNCTIONS

750 The basic quantities required for describing the coupled molecule–lead system are the  
751 one particle electron and the phonon Green functions. Following the steps outlined in  
752 Section 14.2, the time development for various superoperators (Heisenberg equations) is  
753 (all primed indices should be summed over)

$$754 \quad \begin{aligned} 755 \quad i\hbar\kappa_\alpha \frac{\partial}{\partial t} \hat{\psi}_{i\alpha}(t) &= E_{ij} \hat{\psi}_{j\alpha}(t) + V_{k'i} \hat{\psi}_{k'\alpha}(t) + \lambda_{l'i} \hat{\phi}_{l'\alpha}(t) \hat{\psi}_{i\alpha}(t) \\ 757 \quad -i\hbar\kappa_\alpha \frac{\partial}{\partial t} \hat{\phi}_{l\alpha}(t) &= \lambda_{l'i} \hat{\psi}_{i\alpha}^\dagger(t) \hat{\psi}_{l'\alpha}(t) + \Omega_l \hat{\phi}_{l\alpha}(t) + U_{lm'} \hat{\phi}_{m'\alpha}(t) \\ 759 \quad i\hbar\kappa_\alpha \frac{\partial}{\partial t} \hat{\psi}_{k\alpha}(t) &= \epsilon_k \hat{\psi}_{k\alpha}(t) + V_{k'i} \hat{\psi}_{i\alpha}(t) \\ 761 \quad -i\hbar\kappa_\alpha \frac{\partial}{\partial t} \hat{\phi}_{m\alpha}(t) &= \omega_m \hat{\phi}_{m\alpha}(t) + U_{l'm} \hat{\phi}_{l'\alpha}(t) \end{aligned} \quad (C23)$$

764 Using Eq. (C23) and following the procedure described in Section 14.2, it is  
765 straightforward to write the matrix Dyson equation (44) for the electron and phonon

Green functions defined as

$$\begin{aligned}
 G_{\alpha\beta}^{ij}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle \mathcal{T} \psi_{i\alpha}(\mathbf{r}, t) \psi_{j\beta}^\dagger(\mathbf{r}', t') \rangle \\
 D_{\alpha\beta}^{ll'}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle \mathcal{T} \Phi_{l\alpha}(\mathbf{r}, t) \Phi_{l'\beta}^\dagger(\mathbf{r}', t') \rangle
 \end{aligned}
 \tag{C24}$$

with the corresponding self-energy matrix elements

$$\begin{aligned}
 \Sigma_{\alpha\beta}^{ij}(t, t') &= -\frac{i}{\hbar} \kappa_\alpha \sum_{\beta', j'} \int d\tau \left[ \sum_{l'} \lambda_{l'i} \langle \mathcal{T} \hat{\Phi}_{l'\alpha}(t) \hat{\psi}_{i\alpha}(t) \hat{\psi}_{j'\beta'}^\dagger(\tau) \rangle + \sum_{k'} V_{k'i} \langle \mathcal{T} \hat{\psi}_{k'\alpha}(t) \hat{\psi}_{j'\beta'}^\dagger(\tau) \rangle \right] \\
 &\quad \times G_{\beta'\beta}^{j'j-1}(\tau, t') \equiv \Xi_{\alpha\beta}^{ij}(t, t') + \sigma_{\alpha\beta}^{ij}(t, t') \\
 \Pi_{\alpha\beta}^{ll'}(t, t') &= \frac{i}{\hbar} \int d\tau \sum_{\beta', j''} \left[ \sum_{m'} U_{lm'} \langle \mathcal{T} \hat{\Phi}_{m'\alpha}(t) \hat{\Phi}_{\beta''j''}^\dagger(\tau) \rangle + \sum_{i'} \lambda_{i'l} \langle \mathcal{T} \hat{\psi}_{i'\alpha}(t) \hat{\psi}_{i'\alpha}(t) \hat{\Phi}_{\beta''j''}^\dagger(\tau) \rangle \right] \\
 &\quad \times D_{\beta'\beta}^{j''j-1}(\tau, t') \equiv \gamma_{\alpha\beta}^{ll'}(t, t') + \Lambda_{\alpha\beta}^{ll'}(t, t')
 \end{aligned}
 \tag{C25}$$

The two terms in the electron self-energy represent the contributions from the phonon–electron ( $\Xi$ ) and molecule–lead ( $\sigma$ ) interactions. Similarly, the phonon self-energy has contributions from the electron–phonon ( $\Lambda$ ) and the primary–secondary phonon ( $\gamma$ ) couplings. The self-energy due to the molecule–lead coupling can be calculated exactly. To this end we need to obtain the quantity  $\langle \mathcal{T} \hat{\psi}_{k'\alpha}(t) \hat{\psi}_{j'\beta'}^\dagger(\tau) \rangle$ . By multiplying the third equation in Eq. (C23) by  $\hat{\psi}_{j'\beta'}^\dagger(\tau)$  from the left and from the right, taking trace and subtracting, we get (here primed indices are not summed over)

$$\begin{aligned}
 \left( i\hbar \kappa_\alpha \frac{\partial}{\partial t} - \epsilon_{k'} \right) \langle \mathcal{T} \hat{\psi}_{k'\alpha}(t) \hat{\psi}_{j'\beta'}^\dagger(\tau) \rangle &= \sum_{i'} V_{k'i} \langle \mathcal{T} \hat{\psi}_{i'\alpha}(t) \hat{\psi}_{j'\beta'}^\dagger(\tau) \rangle \\
 \Rightarrow \langle \mathcal{T} \hat{\psi}_{k'\alpha}(t) \hat{\psi}_{j'\beta'}^\dagger(\tau) \rangle &= i\hbar \sum_{i'} V_{k'i} g_{k'}(t) G_{\alpha\beta}^{i'j'}(t, \tau)
 \end{aligned}
 \tag{C26}$$

where  $g_k(t) = (i\hbar \kappa_\alpha \frac{\partial}{\partial t} - \epsilon_{k'})^{-1}$ . Substituting expression (C26) in Eq. (C25) gives for the molecule–lead self-energy

$$\sigma_{\alpha\beta}^{ij}(t, t') = \kappa_\alpha \delta_{\alpha\beta} \sum_{k' \in \text{a,b}} V_{k'i} V_{k'j} g_{k'}(t) \delta(t - t')
 \tag{C27}$$

Similarly, the contribution to the phonon self-energy from the interaction with secondary phonons can be calculated exactly

$$\gamma_{\alpha\beta}^{ll'} = -\kappa_\alpha \delta_{\alpha\beta} \sum_{m'} U_{lm'} U_{l'm'} g_{m'}(t) \delta(t - t')
 \tag{C28}$$

where  $g_{m'}(t) = (i\hbar \kappa_\alpha \frac{\partial}{\partial t} + \omega_{m'})^{-1}$ . At steady state all Green functions and self-energies depend only on the time difference ( $t_1 - t_2$ ) and it is very convenient to express them in the frequency space. The self-energy contributions due to molecule–lead ( $\sigma_{\alpha\beta}^{ij}$ ) and phonon–phonon ( $\gamma_{\alpha\beta}^{ll'}$ ) interactions, Eqs. (C27) and (C28), can be represented in

811 frequency space as

$$812 \sigma_{\alpha\beta}^{ij}(\omega) = \kappa_{\alpha} \delta_{\alpha\beta} \sum_{k'} \frac{V_{k'i} V_{k'j}}{\kappa_{\alpha} \omega - \epsilon_{k'} + i\eta} \quad (C29)$$

$$814 \gamma_{\alpha\beta}^{ll'}(\omega) = -\kappa_{\alpha} \delta_{\alpha\beta} \sum_{m'} \frac{U_{lm'} U_{l'm'}}{\kappa_{\alpha} \omega + \omega_{m'} + i\eta} \quad (C30)$$

815  
816 where  $\eta \rightarrow 0$ . However, in real calculations it is a common practice to calculate self-energies  $\sigma_{\alpha\beta}$  and  $\gamma_{\alpha\beta}$  in the wide band approximation, implying that the real parts of the self-energies can be ignored and the imaginary parts are considered as frequency independent. Eqs. (C29) and (C30) then reduce to simpler forms

$$822 \sigma_{\alpha\beta}^{ij} = \kappa_{\alpha} \delta_{\alpha\beta} \frac{i}{2} \Gamma^{ij}, \quad \gamma_{\alpha\beta}^{ll'} = -\kappa_{\alpha} \delta_{\alpha\beta} \frac{i}{2} \tilde{\Gamma}^{ll'} \quad (C31)$$

823  
824 where  $\Gamma^{ij} (2\pi \sum_{k'} V_{k'i} V_{k'j})$  and  $\tilde{\Gamma}^{ll'} = 2\pi \sum_{m'} U_{m'l} V_{m'l'}$ .

825 The phonon contribution to the electronic self-energy is obtained perturbatively in the phonon–electron coupling. We recast the phonon contribution (first term on the RHS of Eq. (C25) for  $\Sigma_{\alpha\beta}^{ij}$ ) in the interaction picture by writing

$$827 \langle \mathcal{T} \hat{\Phi}_{l\alpha}(t) \hat{\psi}_{l\alpha}(t) \hat{\psi}_{j\beta}^{\dagger}(t') \rangle = \langle \mathcal{T} \tilde{\Phi}_{l\alpha}(t) \tilde{\psi}_{l\alpha}(t) \tilde{\psi}_{j\beta}^{\dagger}(t') \mathcal{G}_I(t, -\infty) \rangle_0 \quad (C32)$$

828  
829 where

$$830 \mathcal{G}_I(t, -\infty) = \exp \left\{ -\frac{i}{\hbar} \int d\tau \sum_{i'\alpha'} \kappa_{\alpha'} \left[ \sum_{l'} \lambda_{l'i'} \tilde{\Phi}_{l'\alpha'}(\tau) \tilde{\psi}_{i'\alpha'}^{\dagger}(\tau) \tilde{\psi}_{l'\alpha'}(\tau) \right. \right. \\ \left. \left. + \sum_{k'} V_{k'i'} (\tilde{\psi}_{k'\alpha'}^{\dagger}(\tau) \tilde{\psi}_{i'\alpha'}(\tau) + \tilde{\psi}_{i'\alpha'}^{\dagger}(\tau) \tilde{\psi}_{k'\alpha'}(\tau)) \right] \right\} \quad (C33)$$

831  
832 Substituting Eq. (C33) in Eq. (C32), expanding the exponential to first order in  $\lambda_{li}$  and using Wick's theorem for superoperators [49] we obtain

$$833 \langle \mathcal{T} \hat{\Phi}_{l\alpha}(t) \hat{\psi}_{l\alpha}(t) \hat{\psi}_{j\beta}^{\dagger}(t') \rangle = -\hbar^2 \sum_{i'\alpha'} \kappa_{\alpha'} \lambda_{i'l'} \int d\tau \mathcal{D}_{\alpha\alpha'}^{0ll'}(t, \tau) \left[ G_{\alpha\beta}^{0ij}(t, t') G_{\alpha'\alpha'}^{0i'l'}(\tau, \tau^+) \right. \\ \left. + G_{\alpha\alpha'}^{0ii'}(t, \tau) G_{\alpha'\beta}^{0i'j}(\tau, t') \right] \quad (C34)$$

834 Here the superscript '0' represents the trace with respect to the non-interacting density matrix. The zeroth order Green functions are given in Eq. (55). The terms coming from the lead-molecule coupling ( $V_{ki}$ ) vanish because they are odd in creation and annihilation operators. Substituting Eq. (C34) in Eq. (C25) gives for the phonon contribution

to the self-energy

$$\begin{aligned} \Xi_{\alpha\beta}^{ij}(t, t') = & i\hbar \sum_{l_1 l_2} \kappa_\alpha \lambda_{l_1 i} \left[ \kappa_\beta \lambda_{l_2 j} D_{\alpha\beta}^{0l_1 l_2}(t, t') G_{\alpha\beta}^{0ij}(t, t') \right. \\ & \left. + \delta_{ij} \delta_{\alpha\beta} \delta(t - t') \sum_{i_1 \alpha'} \lambda_{l_2 i_1} \kappa_{\alpha'} \int d\tau D_{\alpha\alpha'}^{0l_1 l_2}(t, \tau) G_{\alpha'\alpha'}^{0i_1 i_1}(\tau, \tau^+) \right] \end{aligned} \quad (C35)$$

In the derivation of Eq. (C35), we have used the identity

$$\int d\tau \sum_{\alpha' j'} G_{\alpha\beta'}^{0ij'}(t, \tau) G_{\beta'\beta}^{-1 0j'j}(\tau, t') = \delta_{\alpha\beta} \delta_{ij} \delta(t - t') \quad (C36)$$

Similarly the contribution of the electron–phonon interaction to the phonon self-energy (second term in Eq. (C25) for  $\Pi_{\alpha\beta}^{ij}$ ) can be obtained perturbatively. To the second order in phonon–electron coupling, we obtain

$$\Lambda_{\alpha\beta}^{ll'}(t, t') = -i\hbar \sum_{ij} \kappa_\alpha \kappa_\beta \lambda_{li} \lambda_{l'j} [G_{\beta\alpha}^{0ji}(t', t) G_{\alpha\beta}^{0ij}(t, t') + G_{\alpha\alpha}^{0ii}(t, t^+) G_{\beta\beta}^{0jj}(t', t'^+)] \quad (C37)$$

To second order in electron–phonon coupling, the electronic self-energy depends on both the electron and phonon green functions while the phonon self-energy contains only the electron Green functions.

At steady state we shift to the frequency domain and obtain

$$\begin{aligned} \Xi_{\alpha\beta}^{ij}(\omega) = & i\hbar \sum_{l_1 l_2} \kappa_\alpha \kappa_\beta \lambda_{l_1 i} \lambda_{l_2 j} \int \frac{d\omega'}{2\pi} D_{\alpha\beta}^{0l_1 l_2}(\omega') G_{\alpha\beta}^{0ij}(\omega - \omega') \\ & + \delta_{ij} \delta_{\alpha\beta} \sum_{l_1, l_2, i_1, \alpha'} \kappa_{\alpha'} \lambda_{l_1 i} \lambda_{l_2 i_1} \rho_{i_1 i_1}^0 D_{\alpha\alpha'}^{0l_1 l_2}(\omega = 0) \end{aligned} \quad (C38)$$

where

$$\rho_{ii}^0 \equiv i\hbar G_{\alpha\alpha}^{ii}(t = 0) = i \int \frac{dE}{2\pi} G_{\alpha\alpha}^{ii}(E) \quad (C39)$$

The phonon self-energy becomes

$$\begin{aligned} \Lambda_{\alpha\beta}^{ll'}(\omega) = & -i\hbar \sum_{ij} \kappa_\alpha \kappa_\beta \lambda_{li} \lambda_{l'j} \int \frac{d\omega'}{2\pi} G_{\alpha\beta}^{0ij}(\omega') G_{\beta\alpha}^{0ji}(\omega' - \omega) \\ & + \frac{i}{\hbar} \sum_{ij} \kappa_\alpha \epsilon_\beta \lambda_{li} \lambda_{l'j} \rho_{ii}^0 \rho_{jj}^0 \delta(\omega = 0) \end{aligned} \quad (C40)$$

## APPENDIX 14D: DYSON EQUATIONS IN THE +/- REPRESENTATION

In this appendix, we define the retarded and advance Green's functions and the corresponding self-energies and relate them to the basic Green functions and self-energies obtained in Appendix 14C. From definition (9), the Liouville space retarded ( $G_r$ ) and advance ( $G_a$ ) Green functions are defined as

$$G_r^{ij}(t, t') \equiv -\frac{i}{\hbar} \langle \mathcal{T} \psi_{i+}(t) \psi_{j-}^\dagger(t') \rangle \quad (D41)$$

$$G_a^{ij}(t, t') \equiv -\frac{i}{\hbar} \langle \mathcal{T} \psi_{i-}(t') \psi_{j+}^\dagger(t) \rangle \quad (D42)$$

We further introduce the correlation function

$$G_c^{ij}(t, t') \equiv -\frac{2i}{\hbar} \langle \mathcal{T} \psi_{i+}(t') \psi_{j+}^\dagger(t) \rangle \quad (D43)$$

It follows from Eq. (10) that there are only three Green functions in the +/- representation. These are given by Eqs. (D41)–(D43). Using Eq. (8) these can be represented in terms of the basic Green functions (31) as

$$\begin{aligned} G_r^{ij}(t, t') &= \frac{1}{2} [G_{LL}^{ij}(t, t') - G_{LR}^{ij}(t, t') + G_{RL}^{ij}(t, t') - G_{RR}^{ij}(t, t')] \\ &= G_{LL}^{ij}(t, t') - G_{LR}^{ij}(t, t') \\ G_a^{ij}(t, t') &= \frac{1}{2} [G_{LL}^{ij}(t, t') - G_{RR}^{ij}(t, t') - G_{RL}^{ij}(t, t') + G_{LR}^{ij}(t, t')] \\ &= -G_{RR}^{ij}(t, t') + G_{LR}^{ij}(t, t') = G_{LL}^{ij}(t, t') - G_{RL}^{ij}(t, t') \\ G_c^{ij}(t, t') &= \frac{1}{2} [G_{LL}^{ij}(t, t') + G_{RR}^{ij}(t, t') + G_{LR}^{ij}(t, t') + G_{RL}^{ij}(t, t')] \\ &= G_{LL}^{ij}(t, t') + G_{RR}^{ij}(t, t') \end{aligned} \quad (D44)$$

where we have used the identity  $G_{LL} + G_{RR} = G_{LR} + G_{RL}$  which can be verified using Eq. (10). A Dyson equation corresponding to  $G_r$ ,  $G_a$  and  $G_c$  can be obtained from Eq. (44) using unitary transformation

$$G = S \bar{G} S^{-1} \quad (D45)$$

where  $G$  represents the matrix

$$G = \begin{pmatrix} 0 & G_a \\ G_r & G_c \end{pmatrix} \quad (D46)$$

and

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \quad (D47)$$

The transformed Dyson equation (44) reads

$$G = G^0 + G^0 \tilde{\Sigma} G \quad (\text{D48})$$

and the corresponding self-energy matrix reduces to

$$\tilde{\Sigma} = \begin{pmatrix} \Sigma_c & \Sigma_r \\ \Sigma_a & 0 \end{pmatrix} \quad (\text{D49})$$

with the matrix elements given by

$$\begin{aligned} \Sigma_r^{ij}(t, t') &= \Sigma_{LL}^{ij}(t, t') + \Sigma_{LR}^{ij}(t, t') \\ \Sigma_a^{ij}(t, t') &= \Sigma_{RR}^{ij}(t, t') + \Sigma_{LR}^{ij}(t, t') \\ \Sigma_c^{ij}(t, t') &= \Sigma_{RR}^{ij}(t, t') + \Sigma_{LL}^{ij}(t, t') \end{aligned} \quad (\text{D50})$$

Similar relations also hold for the phonon Green functions and self-energies.

Using Eqs. (D44) and (D50), the retarded self-energies for electron and phonon Green functions (retarded) coming from the electron–phonon coupling are obtained as

$$\begin{aligned} \tilde{\Xi}_r^{ij}(\omega) &= i\hbar \sum_{l'} \lambda_{l'i} \lambda_{lj} \int \frac{d\omega'}{2\pi} [D_r^{0l'}(\omega') G_r^{0ij}(\omega - \omega') + D_r^{0l'}(\omega') G_{LR}^{0ij}(\omega - \omega') \\ &\quad + D_{LR}^{0l'}(\omega') G_r^{0ij}(\omega - \omega')] \end{aligned} \quad (\text{D51})$$

$$\begin{aligned} \Lambda_r^{ll'}(\omega) &= -i\hbar \sum_{ij} \lambda_{ij} \lambda_{li} \lambda_{lj} \int \frac{d\omega'}{2\pi} [G_{LR}^{0ij}(\omega') G_a^{0ij}(\omega - \omega') \\ &\quad + G_r^{0ij}(\omega') (G_{RL}^{0ij}(\omega - \omega') + G_a(\omega - \omega'))] \end{aligned}$$

Similarly the retarded self-energies due to the lead and secondary phonons can be written in the wide band limit as

$$\sigma_r^{ij} = \frac{i}{2} \Gamma^{ij} \quad \text{and} \quad \gamma_r^{ll'} = -\frac{i}{2} \tilde{\Gamma}^{ll'} \quad (\text{D52})$$

where  $\Gamma^{ij}$  includes contributions from both the leads a and b, i.e.  $\Gamma^{ij} = \Gamma_a^{ij} + \Gamma_b^{ij}$ .

## APPENDIX 14E: WICK'S THEOREM FOR SUPEROPERATORS

Wick's theorem for superoperators was formulated in Ref. [49]. Using Eqs. (8) and (27), it can be shown that similar to the L and R superoperators, the commutator of '+' and '-' boson superoperators are also numbers. Thus, boson superoperators follow Gaussian statistics and Wick's theorem holds for both the L, R and '+', '-' representations. However, for Fermi superoperators life is more complicated. The anticommutator corresponding to only the 'left' or the 'right' Fermi superoperators are numbers but that for the 'left' and 'right' superoperators, in general, is not a number. Thus, the Fermi superoperators are not Gaussian. However, since the left and right superoperators always commute, the following Wick's theorem [49] can be applied to the time-ordered product

of any number of ‘left’ and ‘right’ superoperators, e.g.

$$\langle \mathcal{T} A_{i_1 \nu_1}(t_1) A_{i_2 \nu_2}(t_2) \cdots A_{i_n \nu_n}(t_n) \rangle_0 = \sum_p \langle \mathcal{T} A_{i_a \nu_a}(t_a) A_{i_b \nu_b}(t_b) \rangle_0 \cdots \langle \mathcal{T} A_{i_p \nu_p}(t_p) A_{i_q \nu_q}(t_q) \rangle_0 \quad (\text{E53})$$

Here  $A_{i_n \nu_n}$ ,  $\nu_n = \text{L, R}$ , represents either a boson or a fermion superoperator.  $i_a \nu_a \dots i_q \nu_q$  is a permutation of  $i_1 \nu_1 \dots i_n \nu_n$  and sum on  $p$  runs over all possible permutations, keeping the time ordering. In case of fermions, each term should be multiplied by  $(-1)^P$ , where  $P$  is the number of permutations of superoperators required to put them into a particular order. Only permutations among either ‘left’ or among ‘right’ superoperators count in  $P$ . The permutations among ‘L’ and ‘R’ operators leave the product unchanged.

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1081 **Author Queries**

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1083 *JOB NUMBER:* 9585

1084 *JOURNAL:* Superoperator many-body theory of molecular currents: non-equilibrium  
1085 Green functions in real time

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1087 **Q1** Please check sense of the sentence ‘At equilibrium suffice it to know only the...’

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