

# Current profiles of molecular nanowires: Density-functional theory Green's function representation

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(Received 20 August 2003; published 30 April 2004)

The Liouville-space Green function formalism is used to compute the current-density profile across a single molecule attached to electrodes. Time ordering is maintained in real, physical, time, avoiding the use of artificial time loops and backward propagations. Closed expressions for molecular currents, which only require density-functional theory calculations for the isolated molecule, are derived to fourth order in the molecule/electrode coupling.

DOI: 10.1103/PhysRevB.69.155430

PACS number(s): 85.65.+h, 73.63.Nm, 71.10.-w, 73.40.Cg

## I. INTRODUCTION

There is a considerable interest in measuring<sup>1-14</sup> and computing<sup>15-22</sup> currents in single molecules attached to electrodes. The current-voltage ( $I$ - $V$ ) characteristics of such devices are strongly nonlinear, and should be recast in terms of high-order conductivities.<sup>12-14</sup> Controlling molecular currents has important applications to nanodevices such as molecular wires and rectifiers.<sup>12-14</sup>

The first-principles computation of molecular currents poses a serious challenge that was addressed by many approaches.<sup>17,18</sup> Standard quantum chemistry packages are not designed to compute current-carrying states. Nonequilibrium Green function techniques widely used for computing currents in macroscopic systems, e.g., semiconductors,<sup>23,24</sup> were adopted for single-molecular currents.<sup>15-17</sup> The underlying diagrammatic perturbative expansion requires the computation of extra information in the intermediate steps, which is not needed for computing the current. This includes the dependence of the Green function on two times, involving coherence between states with a different number of electrons.<sup>17</sup> In a different approach the time-dependent charge distribution in a donor-acceptor junction was studied by calculating the tunneling currents at the Hartree-Fock level in terms of the donor and acceptor states.<sup>25</sup>

An *ab initio* algorithm for calculating molecular currents developed by Lang<sup>21,22</sup> is based on the self-consistent solution of a system of four equations: (1) The Kohn-Sham integral equation for the wave function of the molecule + electrodes [Eq. (3.1) in Ref. 21], (2) Equation for the potential difference between the complete (molecule + electrodes) system and the bare electrodes [Eq. (3.2) in Ref. 21], (3) Equation for the Green function of the molecule in an effective potential given by the sum of the exchange correlation and the electrostatic potential [Eq. (3.13) in Ref. 21]. The latter is determined by (4) the Poisson equation with boundary conditions setting the potential to be equal to the chemical potentials difference of the electrodes [Eq. (6) in this paper]. These equations, together with the boundary conditions, yield the wave function of the entire (molecule + electrodes) system which can be used to compute the finite current. This algorithm was applied for calculating the current in a chain of three Al atoms with the substitution of one atom

by sulfur, and for a chain of ten carbon atoms. The electrodes were modeled as a semi-infinite ideal metal (homogeneous electron gas or Jellium model). The same approach was subsequently applied to calculate the current in a benzene-1,4-dithiol molecule connected to ideal metal electrodes, and the effect of inserting a single gold atom between the molecule and a metallic surface was investigated.<sup>4</sup>

Mujica, Kemp, Roitberg, and Ratner<sup>20</sup> proposed to solve self-consistently the Hartree-Fock equation for the Green function of the complete (molecule + electrodes) system and the Poisson equation for the electrostatic potential, with the same boundary conditions of Lang.<sup>21,22</sup> The molecule was described by the Hubbard Hamiltonian, the electrodes were taken to be an ideal metal, and the current is computed from the Green function. This approach is easier to implement compared to density-functional theory (DFT),<sup>21,22</sup> since it only requires the solution of two rather than four self-consistent equations. However, DFT<sup>21,22</sup> takes into account exchange-correlation effects more rigorously.

Kosov applied a variational Kohn-Sham density-functional (DFT) equation for electrons in molecular wires (benzene-1,4-dithiolate molecule covalently bonded to two gold electrodes).<sup>18</sup> By variational minimization of the total energy, where an arbitrary given current is imposed as a constraint,<sup>18</sup> a ten atom gold cluster participates in the bonding with a molecule. The device contains 32 atoms. This results in a system of two self-consistent equations, similar to the Hartree-Fock approach,<sup>20</sup> which is simpler than the equations of Refs. 21, 22, yet treats exchange-correlation effects as rigorously as DFT.<sup>21,22</sup>

All these approaches, which employ DFT for the molecule + electrodes, require the solution of a system of self-consistent equations, but do not give closed expressions for the current.

In this paper we compute the current profile in a molecule perturbatively in the ratio of the coupling of the molecular electrons with the electrodes and the separation between Kohn-Sham orbital energies. Our approach yields a closed expression for the current density  $\langle \hat{J}(\mathbf{r}) \rangle$  in terms of Kohn-Sham orbitals of the molecule alone, which enter various Green functions in the frequency domain. The molecule/electrodes coupling potential of Lang's approach<sup>21</sup> is treated to the lowest order required to yield a finite current. We use

a Liouville-space (superoperator) many-body Green function technique, which provides a convenient description of non-equilibrium effects.<sup>26,27</sup> The Liouville-space TDDFT (time-dependent density-functional theory) formulation of nonlinear response based on the single electron density matrix was developed in Refs. 28, 29, and subsequently extended to superconductors.<sup>30</sup> One advantage of working in the higher-dimensional Liouville space is that we need only consider time-ordered quantities in real (physical) time and Wick's theorem therefore assumes a particularly compact form,<sup>27</sup> in contrast to Hilbert-space Green function perturbation theory<sup>24,31,32</sup> no special contours or analytic continuations are necessary.

## II. THE MODEL HAMILTONIAN

We shall partition the electronic Hamiltonian of a molecule with  $N$  electrons connected to two electrodes  $A$  and  $B$ , in the form

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (1)$$

where  $\hat{H}_0$  represents the noninteracting molecule and electrodes and  $\hat{V}$  is the molecule/electrodes coupling,

$$\hat{V} = \int dx \int dx' U(x, x') [\psi^\dagger(x) [\psi^A(x') + \psi^B(x')] + [\psi^{A\dagger}(x') + \psi^{B\dagger}(x')] \psi(x)]. \quad (2)$$

The spatial coordinates  $x$  and  $x'$  run over the molecule and the electrode regions, respectively [ $x \equiv (\mathbf{r}, t)$  is a coordinate of electrons within the molecule and  $x' \equiv (\mathbf{r}', t)$  is a coordinate of electrons in the electrodes region].  $U(x, x')$  is the coupling potential between the molecule and electrodes,  $\psi(x)$  is the field operator of electrons in the molecule, whereas  $\psi^A(x')$  and  $\psi^B(x')$  are the field operators of electrons in the two electrodes. These operators satisfy Fermi anticommutation relations,<sup>33,34</sup>

$$\begin{aligned} \psi(\mathbf{r}_1) \psi^\dagger(\mathbf{r}_2) + \psi^\dagger(\mathbf{r}_2) \psi(\mathbf{r}_1) &= \delta(\mathbf{r}_1 - \mathbf{r}_2), \\ \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) + \psi(\mathbf{r}_2) \psi(\mathbf{r}_1) &= 0, \\ \psi^\dagger(\mathbf{r}_1) \psi^\dagger(\mathbf{r}_2) + \psi^\dagger(\mathbf{r}_2) \psi^\dagger(\mathbf{r}_1) &= 0. \end{aligned} \quad (3)$$

We assume that the electrodes interact with the molecule only at two points of contact ( $\mathbf{r}_0^A$  and  $\mathbf{r}_0^B$ ). Kosov considered the coupling between the molecule and the electrodes represented by 10 gold atoms;<sup>18</sup> participation of only a restricted domain of the electrodes in the molecule/electrode coupling was also assumed in the "extended molecule" model.<sup>17</sup> We then have

$$U(\mathbf{r}, \mathbf{r}') = \phi(\mathbf{r}) [\delta(\mathbf{r}' - \mathbf{r}_0^A) + \delta(\mathbf{r}' - \mathbf{r}_0^B)], \quad (4)$$

where  $\phi(\mathbf{r})$  is defined as the potential, induced by the difference between the charge density of the isolated molecule  $\varrho_0(\mathbf{r})$  and of the molecule coupled to the electrodes  $\varrho(\mathbf{r})$ .<sup>17</sup>  $\phi(\mathbf{r})$  is obtained by solving the Poisson equation in the molecule ( $r_0^A < r < r_0^B$ ) [Eq. (5.3) in Ref. 17],

$$\nabla^2 \phi(\mathbf{r}) = -e(\varrho(\mathbf{r}) - \varrho_0(\mathbf{r})), \quad (5)$$

with the boundary conditions  $\phi(\mathbf{r}_0^A) = \mu_A$  and  $\phi(\mathbf{r}_0^B) = \mu_B$ . Here  $\mu_A$  and  $\mu_B$  are the chemical potentials of electrodes  $A$  and  $B$ , respectively,  $W = \mu_A - \mu_B$  is the external voltage, and  $e$  is electron charge.

The Poisson equation for the total electrostatic potential in the molecule coupled to the electrodes  $U_{el}(\mathbf{r})$  is<sup>17,19</sup>

$$\nabla^2 U_{el}(\mathbf{r}) = -e\varrho(\mathbf{r}), \quad (6)$$

with the boundary conditions  $U_{el}(\mathbf{r}_0^A) = \mu_A$  and  $U_{el}(\mathbf{r}_0^B) = \mu_B$ . The boundary conditions should reflect the change of the electrostatic potential in the interior of the left (right) electrodes when current is flowing, which is smaller than the chemical potential difference of electrodes [Eq. (5.4) in Ref. 17].<sup>35</sup> This difference should be negligible for large electrode spacings, for which the current is small, but should be notable for small spacings. Our boundary conditions thus hold in the small current limit (large electrode spacings).

To lowest order in the molecule/electrodes coupling we use the unperturbed charge density of the isolated molecule in the right-hand-side (rhs) of the Poisson equation  $\varrho(\mathbf{r}) = \varrho_0(\mathbf{r})$ , and Eq. (6) gives

$$\nabla^2 U_{el}(\mathbf{r}) = -e \sum_{\alpha} \varphi_{\alpha}(\mathbf{r}) \varphi_{\alpha}^*(\mathbf{r}), \quad (7)$$

where the sum runs over all occupied molecular Kohn-Sham orbitals  $\varphi_{\alpha}(\mathbf{r})$ . Using  $\varrho(\mathbf{r}) = \varrho_0(\mathbf{r})$ , we obtain from Eq. (5) [Eq. (5.6) in Ref. 17]  $\nabla^2 \phi(\mathbf{r}) = 0$ ,  $\phi(\mathbf{r}_0^A) = \mu_A$ ,  $\phi(\mathbf{r}_0^B) = \mu_B$ . By solving this equation, we obtain that the coupling potential is linear in  $\mathbf{r}$ ,

$$\phi(\mathbf{r}) = (\mathbf{r}_0^A - \mathbf{r}_0^B)^{-1} [\mu_B \mathbf{r}_0^A - \mu_A \mathbf{r}_0^B + (\mu_A - \mu_B) \mathbf{r}]. \quad (8)$$

There are two contributions to the charge density in the Poisson equation [Eq. (6)]: The charge density of the isolated molecule and the variation of the charge density due to the coupling with the electrodes induced by the external voltage.<sup>17,21</sup> To lowest order in the coupling potential we neglect the latter, and the electrostatic potential in the molecule is calculated using the unperturbed charge density [Eq. (7)]. We thus neglect all screening effects and the potential profile across the junction is assumed to be linear [Eq. (8)]. This holds for low voltages. The electronic structure of the molecule enters in  $\hat{H}_0$ . The external voltage, which is the difference between the chemical potentials of the electrodes ( $W \equiv \mu_A - \mu_B$ ), enters in the Hamiltonian of the molecule/electrodes coupling  $\hat{V}$  in Eq. (1) through the coupling potential  $U$  [Eqs. (4) and (8)]. Our perturbative approach holds provided the coupling potential of the molecular electrons with the electrodes (the external voltage [Eq. (8)]) is smaller than the difference between Kohn-Sham orbital energies. It corresponds to lowest-order expansion in the molecule/electrodes coupling potential of Lang's approach.<sup>21</sup>

### III. PERTURBATIVE CALCULATION OF THE CURRENT

Our goal is to compute the expectation value of the current operator

$$\hat{J}(x) = -\frac{ie\hbar}{2m}(\nabla_{\mathbf{r}} - \nabla_{\mathbf{r}'})\psi(x)\psi^\dagger(\bar{x})|_{x=\bar{x}}, \quad (9)$$

where  $e$  and  $m$  are the electron charge and mass, respectively.

We start with the interaction picture expression for the expectation value of  $\hat{J}(x)$ , using the partitioning [Eq. (1)] of the Hamiltonian.<sup>27</sup> We define the Liouville operators  $L = L_0 + V_-$  corresponding to Eq. (1) where  $L_0 \equiv (H_0)_-$  i.e.,  $L_0 X \equiv H_0 X - X H_0$ . The zero-order time evolution operator is defined as

$$\mathcal{G}_0(\tau_2, \tau_1) \equiv \theta(\tau_2 - \tau_1) \exp\left[-\frac{i}{\hbar}L_0(\tau_2 - \tau_1)\right], \quad (10)$$

where  $\theta(t)$  is the Heaviside step function. Throughout this paper we denote operators in the interaction picture by a tilde ( $\tilde{\phantom{x}}$ ), i.e.,

$$\tilde{A}_\nu(\tau) \equiv \mathcal{G}_0^\dagger(\tau, 0) A_\nu \mathcal{G}_0(\tau, 0) \quad \nu = +, - \text{ or } \nu = L, R. \quad (11)$$

The current is given by

$$\langle \hat{J}(x) \rangle = -\left\langle \hat{T} \tilde{J}_+(x) \exp\left[-\frac{i}{\hbar} \int_{-\infty}^t d\tau \tilde{V}_-(\tau)\right] \right\rangle, \quad (12)$$

where the Liouville-space superoperators with indices  $+$  and  $-$  are defined in Appendix A,<sup>27</sup> and the time-ordering operator in Liouville-space  $\hat{T}$  is defined in Eq. (B11).<sup>27</sup> This natural time ordering follows chronologically the various interactions with the electrodes. The precise order in which superoperators appear next to a  $\hat{T}$  operator is immaterial since at the end the order will be fixed by  $\hat{T}$ .  $\hat{T}$  before an exponent means that each term in the Taylor expansion of this exponent should be time ordered.

The current can be also expressed in terms of the molecular electron density matrix  $\tilde{\rho}(\mathbf{r}, \mathbf{r}', t)$  in the interaction picture

$$\tilde{\rho}(\mathbf{r}, \bar{\mathbf{r}}, t) \equiv \text{Tr}[\tilde{\psi}(\mathbf{r}, t)\tilde{\psi}^\dagger(\bar{\mathbf{r}}, t)\rho_0], \quad (13)$$

where  $\rho_0$  is unperturbed many-electron density matrix of the isolated molecule uncoupled to the electrodes, and the current is

$$\langle \hat{J}(x) \rangle = -\frac{ie\hbar}{2m}(\nabla_{\mathbf{r}} - \nabla_{\mathbf{r}'})\tilde{\rho}(\mathbf{r}, \bar{\mathbf{r}}, t)|_{x=\bar{x}}. \quad (14)$$

A finite current requires at least two interactions with each electrode. We, therefore, computed the current to fourth order in  $\tilde{V}$ ,

$$\langle \hat{J}(x) \rangle = -\frac{ie\hbar}{2m}(\nabla_{\mathbf{r}} - \nabla_{\mathbf{r}'}S(x, \bar{x})|_{x=\bar{x}}, \quad (15)$$

where

$$\begin{aligned} S(x, \bar{x}) = & -\frac{1}{4!} \left(\frac{i}{\hbar}\right)^4 \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 \int_{-\infty}^{\tau_3} d\tau_4 \int d\mathbf{r}_1 \\ & \times \int d\mathbf{r}'_1 \int d\mathbf{r}_2 \int d\mathbf{r}'_2 \int d\mathbf{r}_3 \int d\mathbf{r}'_3 \int d\mathbf{r}_4 \int d\mathbf{r}'_4 \\ & \times \langle \hat{T} \tilde{\rho}(x, \bar{x}, t) \tilde{V}_-(\mathbf{r}_4, \tau_4) \tilde{V}_-(\mathbf{r}_3, \tau_3) \tilde{V}_-(\mathbf{r}_2, \tau_2) \\ & \times \tilde{V}_-(\mathbf{r}_1, \tau_1) \rangle_0, \end{aligned} \quad (16)$$

where  $\tilde{\rho}(x, \bar{x}, t) = \tilde{\psi}(x)\tilde{\psi}^\dagger(\bar{x})$ .

We next expand  $S(x, \bar{x})$  in Eq. (16) in ‘‘left’’ and ‘‘right’’ operators in Liouville space.<sup>27</sup> To that end we introduce the field operator corresponding to both electrodes

$$\psi^M(x') \equiv \psi^A(x') + \psi^B(x'). \quad (17)$$

Substituting Eq. (2) into Eq. (17) we get

$$\begin{aligned} S(x, \bar{x}) = & \frac{1}{4!} \left(\frac{i}{\hbar}\right)^4 \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 \int_{-\infty}^{\tau_3} d\tau_4 \int d\mathbf{r}_1 \\ & \times \int d\mathbf{r}'_1 \int d\mathbf{r}_2 \int d\mathbf{r}'_2 \int d\mathbf{r}_3 \int d\mathbf{r}'_3 \int d\mathbf{r}_4 \int d\mathbf{r}'_4 \\ & \times U(x_4, x'_4) U(x_3, x'_3) U(x_2, x'_2) U(x_1, x'_1) \\ & \times I(x_1, x'_1, x_2, x'_2, x_3, x'_3, x_4, x'_4, x, \bar{x}), \end{aligned} \quad (18)$$

where  $I$  is given by Eq. (A4). In Appendix A we use superoperator algebra to bring it to the form of Eq. (A8). Factorizing that equation, using Wick’s theorem for fermion superoperators [Eq. (74) in Ref. 27], we obtain

$$\begin{aligned} I = & \frac{1}{4!} \sum_{\nu_\eta, \nu_\kappa=0,1; i,j=0,1} (-1)^P \\ & \times \left[ \prod_{\eta, \kappa=0, \dots, 4; k, l=0,1} \langle \hat{T}(\psi_{\nu_\eta}^{M_k \alpha_i}(x^k) \psi_{\nu_\kappa}^{M_l \alpha_j}(x^l)) \rangle \right] \\ & \times (1 - \delta_{\eta,0} \delta_{\nu_\kappa,1} \delta_{k,1}) (1 - \delta_{\kappa,0} \delta_{\nu_\eta,1} \delta_{l,1}), \end{aligned} \quad (19)$$

where  $\delta$  is the Kronecker symbol: for  $\nu_\eta=0$   $\psi_{\nu_\eta} = \psi_L$  and for  $\nu_\eta=1$   $\psi_{\nu_\eta} = \psi_R$ , for  $k=1$   $\psi^{M_k}(x^k) = \psi^M(x')$  and for  $k=0$   $\psi^{M_k}(x^k) = \psi(x)$ , for  $i=0$   $\psi^{\alpha_i} = \psi$  and for  $i=1$   $\psi^{\alpha_i} = \psi^\dagger$ .  $P = 1/2(n_L^{dif} + n_R^{dif})$  is a number of sum of permutations of  $\psi_L$  and  $\psi_R$ , where  $n_L^{dif}$  is a number of contractions in the rhs of Eq. (19)  $\langle \hat{T}(\psi_L(x_n) \psi_L(x_m)) \rangle$ , when  $n \neq m$ , and  $n_R^{dif}$  is a number of contractions in the rhs of Eq. (19)  $\langle \hat{T}(\psi_R(x_n) \psi_R(x_m)) \rangle$ , when  $n \neq m$ .

We assume that the molecule contacts each electrode at a single point ( $\mathbf{r}_0^A$  and  $\mathbf{r}_0^B$ ) with the coupling potential

$$U(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} U_{\alpha\beta} \varphi_\alpha^*(\mathbf{r}) \varphi_\beta(\mathbf{r}'), \quad (20)$$

where  $U(\mathbf{r}, \mathbf{r}')$  is determined by Eq. (4),  $\varphi_\alpha(\mathbf{r})$  is the  $\alpha$ th Kohn-Sham orbital of the molecule, and

$$\begin{aligned}
U_{\alpha\beta} &= \int d\mathbf{r}' \int d\mathbf{r} U(\mathbf{r}, \mathbf{r}') \varphi_\alpha(\mathbf{r}) \varphi_\beta^*(\mathbf{r}') \\
&= (\varphi_\beta^*(\mathbf{r}_0^A) + \varphi_\beta^*(\mathbf{r}_0^B)) \int d\mathbf{r} \phi(\mathbf{r}) \varphi_\alpha(\mathbf{r}), \quad (21)
\end{aligned}$$

where  $\phi(\mathbf{r})$  is determined by Eq. (8). Below we denote  $U_\alpha \equiv U_{\alpha\alpha}$ .

Substituting the expansion of the frequency domain Green functions and coupling potential in Kohn-Sham orbitals [Eqs. (C4) and (20)] in the expressions for  $I$  (Appendixes B and C), and substituting  $I$  in Eq. (18) and  $S$  in Eq. (15), we obtain

$$\begin{aligned}
\langle \hat{J}(x) \rangle &= -\frac{e}{m\hbar^3} (\nabla_{\bar{\mathbf{r}}} - \nabla_{\mathbf{r}}) \Big|_{\mathbf{r}=\bar{\mathbf{r}}} \int \frac{d\omega}{2\pi} \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} \\
&\times \delta(\omega - \omega_1 - \omega_2) \left[ \sum_{\beta=1}^N \sum_{i=1}^{21} I_i \varphi_\beta(\mathbf{r}) \varphi_\beta^*(\bar{\mathbf{r}}) \right]. \quad (22)
\end{aligned}$$

Equation (22) is our final expression for the current. The twenty one terms  $I_i$  contributing to the current are given in Appendix D.

If the external voltage is zero,  $\mu_A = \mu_B = \mu_0$ . Setting  $\mu_0 = 0$ , Eq. (8) gives  $\phi(\mathbf{r}) = 0$  and  $U(\mathbf{r}, \mathbf{r}') = 0$  everywhere in the molecule. All twenty one terms  $I_i$  contributing to the current Eqs. (D2)–(D22) then vanish.

#### IV. DISCUSSION

In this paper we have derived a closed expression [Eq. (22)] for the current profile within a molecule attached to electrodes, in terms of Green functions of the isolated molecule. The external voltage  $W \equiv \mu_A - \mu_B$  is equal to the difference between the chemical potentials of electrodes  $A$  and  $B$ . Only one characteristic of the electrodes, the Fermi energy levels  $\mu_A$  and  $\mu_B$ , enters these Green functions, the molecule/electrodes coupling potential and the final expression for the molecular current [Eqs. (C15)–(C19)]. This expression only requires DFT calculations for the molecule alone (which enters in the Green functions of the molecule in the expression for the current) rather than the molecule and electrodes as used in Refs. 17, 18, 20–22. The derivation employs the Liouville-space Green function technique,<sup>27</sup> and the current is expanded to fourth order in the molecule/electrodes coupling our formula for the current [Eq. (22)] should agree with Lang's approach<sup>21</sup> to lowest order in the molecule/electrodes coupling potential.

We have established a one-to-one correspondence between Liouville-space and Hilbert-space Green functions for fermions (Appendixes B and C). For completeness, similar relations for boson Green functions are given in Appendix E. The only difference is the definition of the time ordering in Liouville space [Eq. (B11) for fermions vs Eq. (E1) for bosons].

Liouville space provides a fully time-ordered description of the current since we only need to propagate the density matrix forward in time. In contrast, the wave function in

Hilbert space involves both forward and backward propagations. The choice is between following the ket only, moving forward and backward or following the joint dynamics of the ket and the bra and moving only forward.<sup>27</sup> Artificial time variables (Keldysh loops) commonly used in many-body theory,<sup>24,31,32</sup> which are necessary for the wave function picture, are avoided by the density matrix in Liouville space which uses the real laboratory time scale throughout the calculation.

#### ACKNOWLEDGMENTS

The support of the National Science Foundation NIRT Grant No. EEC 0303389 is gratefully acknowledged.

#### APPENDIX A: SUPEROPERATOR ALGEBRA FOR THE CURRENT

A Liouville-space operator  $A_\alpha$  is labeled by a Greek subscript where  $\alpha = L, R, +, -$ . It is defined by its action on an ordinary (Hilbert-space) operator  $X$ ,<sup>27</sup>

$$(A_\alpha X)_{ij} \equiv \sum_{\kappa\ell} (A_\alpha)_{ij,\kappa\ell} X_{\kappa\ell}. \quad (A1)$$

$A_\alpha$  is thus a *tetradic* operator with four indices.  $A_L X \equiv A X$  denotes action from the left and  $A_R X \equiv X A$  denotes action from the right. We then obtain using Eq. (A1),

$$(A_L)_{ij,\kappa\ell} = A_{i\kappa} \delta_{j\ell}, \quad (A2)$$

$$(A_R)_{ij,\kappa\ell} = A_{\ell j} \delta_{i\kappa}. \quad (A3)$$

Note that the order of the  $j\ell$  indices in Eq. (A3) has been reversed.

We further define the symmetric and the antisymmetric combinations  $A_+ \equiv \frac{1}{2}(A_L + A_R)$  and  $A_- \equiv A_L - A_R$ . We then have the tetradic matrix elements  $(A_-)_{ij,\kappa\ell} = A_{i\kappa} \delta_{j\ell} - A_{\ell j} \delta_{i\kappa}$ ,  $(A_+)_{ij,\kappa\ell} = \frac{1}{2}[A_{i\kappa} \delta_{j\ell} + A_{\ell j} \delta_{i\kappa}]$ . Note that  $[A_L, A_R] = 0$ . This commutativity of left and right operators is made possible by the larger dimensionality of Liouville space, simplifies algebraic manipulations and results in many useful relations.<sup>27</sup>

Using the above definitions of the Liouville-space algebra, we can represent  $I$  in Eq. (18) in the form

$$\begin{aligned}
I &= \frac{1}{4!} \sum_{\alpha \neq \beta = 0,1} \langle \hat{T} \psi(x) \psi^\dagger(\bar{x}) (\psi^\alpha(x_1) \psi^{M\beta}(x'_1))_- \\
&\times (\psi^\alpha(x_2) \psi^{M\beta}(x'_2))_- (\psi^\alpha(x_3) \psi^{M\beta}(x'_3))_- \\
&\times (\psi^\alpha(x_4) \psi^{M\beta}(x'_4))_- \rangle. \quad (A4)
\end{aligned}$$

Here, for  $\alpha = 1$   $\psi^\alpha(x_1) = \psi^\dagger(x_1)$ , and, for  $\alpha = 0$   $\psi^\alpha(x_1) = \psi(x_1)$ . In the rhs of Eq. (A4) there are sixteen terms.

We can now expand Eq. (A4) in “left” and “right” Liouville-space operators.<sup>27</sup> We note that the superoperator corresponding to any function  $f$  of an operator  $Q_j$  can be expressed in terms of  $Q_{j+}$  and  $Q_{j-}$ , i.e.,<sup>27</sup>

$$[f(Q_j)]_- \equiv f(Q_{jL}) - f(Q_{jR}) = f(Q_{j+} + \frac{1}{2}Q_{j-}) - f(Q_{j+} - \frac{1}{2}Q_{j-}), \quad (\text{A5})$$

and

$$2[f(Q_j)]_+ \equiv f(Q_{jL}) + f(Q_{jR}) = f(Q_{j+} + \frac{1}{2}Q_{j-}) + f(Q_{j+} - \frac{1}{2}Q_{j-}). \quad (\text{A6})$$

Using these relations, we have

$$\begin{aligned} (\psi^\alpha(x_1)\psi^{M\beta}(x'_1))_- &= (\psi^\alpha(x_1)\psi^{M\beta}(x'_1))_L - (\psi^\alpha(x_1)\psi^{M\beta}(x'_1))_R \\ &= \psi_L^\alpha(x_1)\psi_L^{M\beta}(x'_1) - \psi_R^{M\beta}(x'_1)\psi_R^\alpha(x_1), \end{aligned} \quad (\text{A7})$$

substituting Eq. (A7) in Eq. (A4), we obtain

$$\begin{aligned} I &= \frac{1}{4!} \sum_{\eta,\kappa,\lambda,\nu=L,R} \sum_{\alpha \neq \beta=0,1} \langle \hat{T}(\psi_L(x)\psi_L^\dagger(\bar{x})\psi_\eta^\alpha(x_1) \\ &\quad \times \psi_\eta^{M\beta}(x'_1)\psi_\kappa^\alpha(x_2)\psi_\kappa^{M\beta}(x'_2)\psi_\lambda^\alpha(x_3) \\ &\quad \psi_\lambda^{M\beta}(x'_3)\psi_\nu^\alpha(x_4)\psi_\nu^{M\beta}(x'_4)) \rangle. \end{aligned} \quad (\text{A8})$$

Equation (A8) which has 196 terms is used to derive Eq. (19).

## APPENDIX B: RELATIONS BETWEEN LIOUVILLE- AND HILBERT-SPACE GREEN FUNCTIONS

In this appendix we establish a one-to-one correspondence between Liouville- and Hilbert-space Green functions.

Standard field theory is formulated in terms of four types of Hilbert-space Green functions.<sup>24,31,32</sup> Using the notation of Ref. 24, they are

$$\begin{aligned} G^c(x,\bar{x}) &\equiv -i\langle T\psi(x)\psi^\dagger(\bar{x}) \rangle \\ &= -i\theta(t-\bar{t})\langle \psi(x)\psi^\dagger(\bar{x}) \rangle + i\theta(\bar{t}-t)\langle \psi^\dagger(\bar{x})\psi(x) \rangle, \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} G^{\tilde{c}}(x,\bar{x}) &\equiv -i\langle \tilde{T}\psi(x)\psi^\dagger(\bar{x}) \rangle \\ &= -i\theta(\bar{t}-t)\langle \psi(x)\psi^\dagger(\bar{x}) \rangle + i\theta(t-\bar{t})\langle \psi^\dagger(\bar{x})\psi(x) \rangle, \end{aligned} \quad (\text{B2})$$

$$G^>(x,\bar{x}) \equiv -i\langle \psi(x)\psi^\dagger(\bar{x}) \rangle, \quad (\text{B3})$$

$$G^<(x,\bar{x}) \equiv i\langle \psi^\dagger(\bar{x})\psi(x) \rangle, \quad (\text{B4})$$

$G^c$ ,  $G^{\tilde{c}}$ ,  $G^>$  and  $G^<$  are known as the time-ordered, antitime-ordered, “greater” and “lesser” Keldysh Green functions, respectively.  $T$  is a time-ordering operator in Hil-

bert space, which takes any product of Fermi field operators  $\zeta$  and  $\chi$  and reorders them in ascending times from right to left, i.e.,

$$T\zeta(\tau_1)\chi(\tau_2) \equiv \begin{cases} \zeta(\tau_1)\chi(\tau_2) & \tau_2 < \tau_1 \\ -\chi(\tau_2)\zeta(\tau_1) & \tau_1 < \tau_2 \\ \frac{1}{2}[\zeta(\tau_1)\chi(\tau_1) - \chi(\tau_1)\zeta(\tau_1)] & \tau_2 = \tau_1. \end{cases} \quad (\text{B5})$$

$\tilde{T}$  is an antitime-ordering operator in Hilbert space, which reorders any product of Fermi field operators in descending times from right to left, i.e.,

$$\tilde{T}\zeta(\tau_1)\chi(\tau_2) \equiv \begin{cases} -\chi(\tau_2)\zeta(\tau_1) & \tau_2 < \tau_1 \\ \zeta(\tau_1)\chi(\tau_2) & \tau_1 < \tau_2 \\ \frac{1}{2}[\zeta(\tau_1)\chi(\tau_1) - \chi(\tau_1)\zeta(\tau_1)] & \tau_2 = \tau_1. \end{cases} \quad (\text{B6})$$

Four types of the Green functions naturally appear in Liouville space,

$$G_{LL}(x,\bar{x}) = -i\langle \hat{T}(\psi_L(x)\psi_L^\dagger(\bar{x})) \rangle, \quad (\text{B7})$$

$$G_{RR}(x,\bar{x}) = -i\langle \hat{T}(\psi_R(x)\psi_R^\dagger(\bar{x})) \rangle, \quad (\text{B8})$$

$$G_{LR}(x,\bar{x}) = -i\langle \hat{T}(\psi_L(x)\psi_R^\dagger(\bar{x})) \rangle, \quad (\text{B9})$$

$$G_{RL}(x,\bar{x}) = -i\langle \hat{T}(\psi_R(x)\psi_L^\dagger(\bar{x})) \rangle, \quad (\text{B10})$$

where  $\hat{T}$  is a time-ordering operator in Liouville space, which rearranges all superoperators so that time decreases from left to right, i.e.,<sup>27</sup>

$$\begin{aligned} \hat{T}\zeta_\nu(\tau_1)\chi_\mu(\tau_2) &= \begin{cases} \zeta_\nu(\tau_1)\chi_\mu(\tau_2) & \tau_2 < \tau_1 \\ -\chi_\mu(\tau_2)\zeta_\nu(\tau_1) & \tau_1 < \tau_2 \\ \frac{1}{2}[\zeta_\nu(\tau_1)\chi_\mu(\tau_1) - \chi_\mu(\tau_1)\zeta_\nu(\tau_1)] & \tau_2 = \tau_1, \end{cases} \end{aligned} \quad (\text{B11})$$

where  $\zeta_\nu(\tau)$  is a Liouville-space Fermi superoperator, and  $\nu$  and  $\mu$  can be either +, -, or  $L$  or  $R$ .

We next establish the connection between the Hilbert-space [Eqs. (B1)–(B4)] and Liouville-space [Eqs. (B7)–(B10)] Green functions. For  $G_{RL}$  and  $G_{LR}$  we have

$$\begin{aligned} G_{RL}(x,\bar{x}) &= -iTr[\hat{T}\psi_R(x)\psi_L^\dagger(\bar{x})\rho_0] = -iTr[\psi^\dagger(\bar{x})\rho_0\psi(x)] \\ &= -iTr[\psi(x)\psi^\dagger(\bar{x})\rho_0] = G^>(x,\bar{x}), \end{aligned} \quad (\text{B12})$$

$$\begin{aligned} G_{LR}(x,\bar{x}) &= -iTr[\hat{T}\psi_L(x)\psi_R^\dagger(\bar{x})\rho_0] = -iTr[\psi(x)\rho_0\psi^\dagger(\bar{x})] \\ &= -iTr[\psi^\dagger(\bar{x})\psi(x)\rho_0] = G^<(x,\bar{x}), \end{aligned} \quad (\text{B13})$$

where  $\rho_0$  is unperturbed many-electron density matrix of the isolated molecule uncoupled to the electrodes.

We next turn to  $G_{RR}$  and  $G_{LL}$ . For  $x > \bar{x}$ , we have

$$\begin{aligned} G_{RR}(x, \bar{x}) &= -iTr[\hat{T}\psi_R(x)\psi_R^\dagger(\bar{x})\rho_0] = -iTr[\rho_0\psi^\dagger(\bar{x})\psi(x)] \\ &= -iTr[\psi^\dagger(\bar{x})\psi(x)\rho_0], \end{aligned} \quad (\text{B14})$$

$$G_{LL}(x, \bar{x}) = -iTr[\hat{T}\psi_L(x)\psi_L^\dagger(\bar{x})\rho_0] = -iTr[\psi(x)\psi^\dagger(\bar{x})\rho_0]. \quad (\text{B15})$$

For  $x < \bar{x}$  we analogously obtain

$$G_{RR}(x, \bar{x}) = -iTr[\psi(x)\psi^\dagger(\bar{x})\rho_0], \quad (\text{B16})$$

$$G_{LL}(x, \bar{x}) = -iTr[\psi^\dagger(\bar{x})\psi(x)\rho_0]. \quad (\text{B17})$$

Comparing Eqs. (B14), (B16) with Eq. (B2), we see that  $G_{RR}(x, \bar{x}) = G^c(x, \bar{x})$ . Combining Eqs. (B15), (B17) with Eq. (B1), we get  $G_{LL}(x, \bar{x}) = G^c(x, \bar{x})$ . Equations (B12) and (B13) provide the other relation  $G_{RL}(x, \bar{x}) = G^>(x, \bar{x})$  and  $G_{LR}(x, \bar{x}) = G^<(x, \bar{x})$ .

### APPENDIX C: DFT KELDYSH GREEN FUNCTIONS IN HILBERT SPACE

The four Hilbert-space Green functions [Eqs. (B1)–(B4)] are not independent. To obtain the relations between them we introduce the retarded  $G^r$  and the advanced  $G^a$  Green functions<sup>24</sup>

$$G^r(x, \bar{x}) \equiv \theta(t - \bar{t})[G^>(x, \bar{x}) - G^<(x, \bar{x})], \quad (\text{C1})$$

$$G^a(x, \bar{x}) \equiv \theta(\bar{t} - t)[G^<(x, \bar{x}) - G^>(x, \bar{x})]. \quad (\text{C2})$$

The retarded DFT Green function in real space is given by Eq. (3.2) of Ref. 17 (see Refs. 24,33,34,36)

$$G^r(x, \bar{x}) = \int \frac{d\omega}{2\pi} e^{i\omega(\bar{t}-t)} \sum_{\alpha} \frac{\varphi_{\alpha}(\mathbf{r})\varphi_{\alpha}^*(\bar{\mathbf{r}})}{\omega - (\omega_{\alpha} - \omega_F) + i\delta}, \quad (\text{C3})$$

where  $\delta \rightarrow 0$ ,  $\omega_{\alpha}$  is the energy of  $\alpha$  Kohn-Sham orbital molecular orbital, and  $\omega_F$  is the Fermi energy of the molecule.

We define retarded DFT Green function  $G_{\alpha}^r(\omega)$  of the Kohn-Sham orbital  $\alpha$  in the frequency domain

$$G^r(x, \bar{x}) = \int \frac{d\omega}{2\pi} e^{-i\omega(t-\bar{t})} \sum_{\alpha} \varphi_{\alpha}(\mathbf{r})\varphi_{\alpha}^*(\bar{\mathbf{r}})G_{\alpha}^r(\omega), \quad (\text{C4})$$

where

$$G_{\alpha}^r(\omega) = (\omega - \omega_{\alpha} + \omega_F + i\delta)^{-1}. \quad (\text{C5})$$

To connect  $G^r$ ,  $G^a$ ,  $G^>$ ,  $G^<$ ,  $G^c$ , and  $G^{\tilde{c}}$  (Refs. 24,32) we use Eqs. (C1) and (C2) together with

$$G^c(x, \bar{x}) = -G^{\tilde{c}}(\bar{x}, x), \quad (\text{C6})$$

$$G^a(x, \bar{x}) = G^{r*}(\bar{x}, x), \quad (\text{C7})$$

$$G^c(x, \bar{x}) + G^{\tilde{c}}(x, \bar{x}) = G^<(x, \bar{x}) + G^>(x, \bar{x}). \quad (\text{C8})$$

Since  $G^r(x, \bar{x})$  is given by Eq. (C3), we can use the system of five equations (C1), (C2), (C6)–(C8) to obtain all Keldysh DFT Green functions for the molecule alone  $G^a$ ,  $G^>$ ,  $G^<$ ,  $G^c$ , and  $G^{\tilde{c}}$ . Solving these equations, and switching to the Kohn-Sham orbital representation in the frequency domain [see Eqs. (C3)–(C5)] we obtain all Keldysh DFT Green functions for the molecule,

$$\begin{aligned} G_{\alpha}^c(\omega) &= (\omega + \omega_F - \omega_{\alpha} + i\delta)^{-1}\theta(\omega_F - \omega_{\alpha}) \\ &\quad + (\omega + \omega_F - \omega_{\alpha} - i\delta)^{-1}\theta(\omega_{\alpha} - \omega_F), \end{aligned} \quad (\text{C9})$$

$$\begin{aligned} G_{\alpha}^{\tilde{c}}(\omega) &= -(\omega + \omega_F - \omega_{\alpha} - i\delta)^{-1}\theta(\omega_F - \omega_{\alpha}) \\ &\quad - (\omega + \omega_F - \omega_{\alpha} + i\delta)^{-1}\theta(\omega_{\alpha} - \omega_F), \end{aligned} \quad (\text{C10})$$

$$G_{\alpha}^a(\omega) = (\omega - \omega_{\alpha} + \omega_F - i\delta)^{-1}, \quad (\text{C11})$$

$$G_{\alpha}^>(\omega) = -2\pi i(1 - \theta(\omega_{\alpha} - \omega_F))\delta(\omega - \omega_{\alpha} + \omega_F), \quad (\text{C12})$$

and

$$G_{\alpha}^<(\omega) = 2\pi i\theta(\omega_{\alpha} - \omega_F)\delta(\omega - \omega_{\alpha} + \omega_F). \quad (\text{C13})$$

The Keldysh Green functions for the electrode  $A$  can be obtained analogously by replacing  $G^r(x, \bar{x})$  with  $D_A^r(x, \bar{x})$ . The retarded Green function of an electron  $D_A^r(\omega)$  in a metal electrode in frequency domain is

$$D_A^r(\omega) \simeq (\omega - \mu_A + i\delta)^{-1}, \quad (\text{C14})$$

where  $\mu_A$  is the Fermi energy level of electrons in electrode  $A$  ( $B$ ). The difference between the chemical potentials of the electrodes  $A$  and  $B$  is given by the external voltage  $U = \mu_A - \mu_B$ . In Eq. (C14) we assumed that the electrons in the metal are at the Fermi level,

$$\begin{aligned} D_A^c(\omega) &= (\omega - \mu_A + i\delta)^{-1}\theta(\omega - \mu_A) + (\omega - \mu_A - i\delta)^{-1} \\ &\quad \times \theta(\mu_A - \omega), \end{aligned} \quad (\text{C15})$$

$$\begin{aligned} D_A^{\tilde{c}}(\omega) &= -(\omega - \mu_A - i\delta)^{-1}\theta(\omega - \mu_A) \\ &\quad - (\omega - \mu_A + i\delta)^{-1}\theta(\mu_A - \omega), \end{aligned} \quad (\text{C16})$$

$$D_A^a(\omega) = (\omega - \mu_A - i\delta)^{-1}, \quad (\text{C17})$$

$$D_A^>(\omega) = -2\pi i(1 - \delta(\omega - \mu_A)), \quad (\text{C18})$$

$$D_A^<(\omega) = 2\pi i\delta(\omega - \mu_A). \quad (\text{C19})$$

Similar expressions apply to electrode  $B$ . The final expression for the molecular current only depends on the sum of the Green functions of electrodes  $A$  and  $B$  ( $D^c = D_A^c + D_B^c$ ,  $D^{\tilde{c}} = D_A^{\tilde{c}} + D_B^{\tilde{c}}$ ,  $D^> = D_A^> + D_B^>$ , and  $D^< = D_A^< + D_B^<$ ).

#### APPENDIX D: THE VARIOUS CONTRIBUTIONS TO THE MOLECULAR CURRENT

Only terms which contain the contractions  $\langle \hat{T}(\psi_L(x_n)\psi_L^\dagger(x_m)) \rangle$ ,  $\langle \hat{T}(\psi_R(x_n)\psi_R^\dagger(x_m)) \rangle$ ,  $\langle \hat{T}(\psi_R(x_n)\psi_L^\dagger(x_m)) \rangle$ , and  $\langle \hat{T}(\psi_L(x_n)\psi_R^\dagger(x_m)) \rangle$  (and similar contractions for the electrodes) can contribute to  $I$  in Eq. (19), because all other contractions vanish. Therefore, only twenty one terms survive in the rhs of Eq. (19). These terms contain the four types of Liouville-space Green functions of the molecule  $G_{LL}$ ,  $G_{RR}$ ,  $G_{LR}$ , and  $G_{RL}$  introduced in Appendix B and of the electrodes  $D_{LL}=D_{LL(A)}+D_{LL(B)}$ ,  $D_{RR}=D_{RR(A)}+D_{RR(B)}$ ,  $D_{LR}=D_{LR(A)}+D_{LR(B)}$ , and  $D_{RL}=D_{RL(A)}+D_{RL(B)}$ .

As an illustration we write the expression for one of the terms contributing to  $S$ ,

$$I_{15} = -iU(x_1, x'_1)U(x_2, x'_2)U(x_3, x'_3)U(x_4, x'_4)G_{RL}(x_1, x_2) \\ \times G_{LR}(x_3, x_4)G_{LL}(x, \bar{x})D_{LR}(x'_2, x'_1)D_{RL}(x'_4, x'_3). \quad (D1)$$

Using the relations of Appendix B, we can recast this in the form of Eq. (D16).

Below we present all twenty one terms which contribute to the current [Eq. (22)], using the Kohn-Sham orbitals representation in the frequency domain. The Greek indices run over the occupied Kohn-Sham orbitals  $\alpha, \beta, \gamma = 1, \dots, N$ ,

$$I_1 = -i \sum_{\alpha} U_{\beta} U_{\alpha}^3 G_{\beta}^{>}(\omega) G_{\alpha}^c(\omega_1) G_{\alpha}^{\sim}(\omega_2) \\ \times D^{\sim*}(-\omega_2) D^{<}(-\omega_1), \quad (D2)$$

$$I_2 = -i \sum_{\alpha} U_{\beta} U_{\alpha}^3 G_{\beta}^{>}(\omega) G_{\alpha}^c(\omega_1) G_{\alpha}^c(\omega_2) \\ \times D^{<}(-\omega_2) D^{c*}(-\omega_1), \quad (D3)$$

$$I_3 = -i \sum_{\alpha} U_{\beta}^3 U_{\alpha} G_{\beta}^{>}(\omega) G_{\alpha}^{<}(\omega_1) G_{\beta}^{>}(\omega_2) \\ \times D^{\sim*}(-\omega_2) D^{<}(-\omega_1), \quad (D4)$$

$$I_4 = i \sum_{\alpha} U_{\beta}^2 U_{\alpha}^2 G_{\beta}^c(\omega_2) G_{\alpha}^c(\omega) G_{\alpha}^{>}(\omega_1) \\ \times D^{c*}(-\omega_2) D^{<}(-\omega_1), \quad (D5)$$

$$I_5 = -i \sum_{\alpha} U_{\beta} U_{\alpha}^3 G_{\beta}^c(\omega_1) G_{\alpha}^{>}(\omega) G_{\alpha}^c(\omega_2) \\ \times D^{<}(-\omega_2) D^{c*}(-\omega_1), \quad (D6)$$

$$I_6 = -i \sum_{\alpha} U_{\beta}^2 U_{\alpha}^2 G_{\beta}^c(\omega_1) G_{\alpha}^{>}(\omega) G_{\alpha}^{\sim}(\omega_2) \\ \times D^{<}(-\omega_2) D^{\sim*}(-\omega_1), \quad (D7)$$

$$I_7 = -i \sum_{\alpha} U_{\beta} U_{\alpha}^3 G_{\beta}^{<}(\omega) G_{\alpha}^c(\omega_1) G_{\alpha}^{\sim}(\omega_2) \\ \times D^{\sim*}(-\omega_2) D^{>}(-\omega_1), \quad (D8)$$

$$I_8 = -i \sum_{\alpha} U_{\beta}^3 U_{\alpha} G_{\beta}^{<}(\omega) G_{\alpha}^c(\omega_1) G_{\beta}^c(\omega_2) \\ \times D^{>}(-\omega_2) D^{*}(-\omega_1), \quad (D9)$$

$$I_9 = -i \sum_{\alpha} U_{\beta} U_{\alpha}^3 G_{\beta}^{<}(\omega) G_{\alpha}^{>}(\omega_1) G_{\alpha}^{<}(\omega_2) \\ \times D^{*}(-\omega_2) D^{>}(-\omega_1), \quad (D10)$$

$$I_{10} = i \sum_{\alpha} U_{\beta}^2 U_{\alpha}^2 G_{\beta}^c(\omega_2) G_{\alpha}^c(\omega) G_{\alpha}^{<}(\omega_1) \\ \times D^{c*}(-\omega_2) D^{>}(-\omega_1), \quad (D11)$$

$$I_{11} = -i \sum_{\alpha} U_{\beta} U_{\alpha}^3 G_{\beta}^c(\omega_1) G_{\alpha}^{<}(\omega) G_{\alpha}^c(\omega_2) \\ \times D^{>}(-\omega_2) D^{c*}(-\omega_1), \quad (D12)$$

$$I_{12} = -i \sum_{\alpha} U_{\beta}^2 U_{\alpha}^2 G_{\beta}^c(\omega_1) G_{\alpha}^{<}(\omega) G_{\alpha}^{\sim}(\omega_2) \\ \times D^{>}(-\omega_2) D^{\sim*}(-\omega_1), \quad (D13)$$

$$I_{13} = -i \sum_{\alpha\gamma} U_{\beta} U_{\gamma} U_{\alpha}^2 G_{\beta}^c(\omega) G_{\alpha}^c(\omega_1) G_{\gamma}^c(\omega_2) \\ \times D^{c*}(-\omega_2) D^{c*}(-\omega_1), \quad (D14)$$

$$I_{14} = -i \sum_{\alpha\gamma} U_{\beta} U_{\gamma} U_{\alpha}^2 G_{\beta}^c(\omega) G_{\alpha}^c(\omega_1) G_{\gamma}^{\sim}(\omega_2) \\ \times D^{c*}(-\omega_1) D^{\sim*}(-\omega_2), \quad (D15)$$

$$I_{15} = -i \sum_{\alpha\gamma} U_{\beta} U_{\gamma} U_{\alpha}^2 G_{\beta}^c(\omega) G_{\alpha}^{<}(\omega_1) G_{\gamma}^{>}(\omega_2) \\ \times D^{<}(-\omega_2) D^{>}(-\omega_1), \quad (D16)$$

$$I_{16} = -i \sum_{\alpha\gamma} U_{\beta} U_{\gamma} U_{\alpha}^2 G_{\beta}^{\sim}(\omega_2) G_{\alpha}^{<}(\omega_1) G_{\gamma}^{>}(\omega) \\ \times D^{\sim*}(-\omega_2) D^{>}(-\omega_1), \quad (D17)$$

$$I_{17} = i \sum_{\alpha\gamma} U_{\beta} U_{\gamma} U_{\alpha}^2 G_{\beta}^{<}(\omega_1) G_{\alpha}^{\sim}(\omega) G_{\gamma}^{>}(\omega_2) \\ \times D^{<}(-\omega_2) D^{>}(-\omega_1), \quad (D18)$$

$$I_{18} = i \sum_{\alpha\gamma} U_{\beta} U_{\gamma} U_{\alpha}^2 G_{\beta}^{\sim}(\omega_1) G_{\alpha}^{\sim}(\omega_2) G_{\gamma}^c(\omega) \\ \times D^{\sim*}(-\omega_2) D^{\sim*}(-\omega_1), \quad (D19)$$

$$I_{19} = -i \sum_{\alpha\gamma} U_\beta U_\gamma U_\alpha^2 G_\beta^<(\omega) G_\alpha^>(\omega_2) G_\gamma^c(\omega_1) \times D^<(-\omega_2) D^{c*}(-\omega_1), \quad (\text{D20})$$

$$I_{20} = -i \sum_{\alpha\gamma} U_\beta U_\gamma U_\alpha^2 G_\beta^>(\omega_1) G_\alpha^>(\omega_2) G_\gamma^<(\omega) \times D^<(-\omega_2) D^{c*}(-\omega_1), \quad (\text{D21})$$

$$I_{21} = -i \sum_{\alpha\gamma} U_\beta U_\gamma U_\alpha^2 G_\beta^<(\omega) G_\alpha^c(\omega_2) G_\gamma^>(\omega_1) \times D^{c*}(-\omega_2) D^<(-\omega_1). \quad (\text{D22})$$

### APPENDIX E: RELATION BETWEEN BOSON GREEN FUNCTIONS IN LIOUVILLE AND HILBERT SPACE

The relations between Liouville-space Green functions and Keldysh Hilbert-space Green functions for fermions also apply to boson fields. We consider a system of identical atoms in an external potential.<sup>37</sup> The definitions for the Liouville space Green functions  $G_{LL}$ ,  $G_{LR}$ ,  $G_{RL}$ , and  $G_{RR}$  [Eqs. (B7)–(B10)] are the same for bosons as for fermions with the only difference that a time-ordering operator in Liouville-space  $\hat{T}_B$  is defined as<sup>27</sup>

$$\hat{T}_B \zeta_\nu(\tau_1) \chi_\mu(\tau_2) \equiv \begin{cases} \zeta_\nu(\tau_1) \chi_\mu(\tau_2) & \tau_2 < \tau_1 \\ \chi_\mu(\tau_2) \zeta_\nu(\tau_1) & \tau_1 < \tau_2 \\ \frac{1}{2} [\zeta_\nu(\tau_1) \chi_\mu(\tau_1) + \chi_\mu(\tau_1) \zeta_\nu(\tau_1)] & \tau_2 = \tau_1, \end{cases} \quad (\text{E1})$$

where  $\zeta_\nu(\tau)$  is a Liouville-space Bose superoperator, and  $\nu$  and  $\mu$  can be either +, -, or L or R.

The four types of Hilbert-space Green functions for bosons are defined as<sup>32</sup>

$$G^c(x_1, x_2) \equiv -i \langle T_B \psi(x_1) \psi^\dagger(x_2) \rangle = -i \theta(t_1 - t_2) \times \langle \psi(x_1) \psi^\dagger(\bar{x}) \rangle - i \theta(t_2 - t_1) \langle \psi^\dagger(x_2) \psi(x_1) \rangle, \quad (\text{E2})$$

$$G^{\tilde{c}}(x, \bar{x}) \equiv -i \langle \tilde{T}_B \psi(x) \psi^\dagger(\bar{x}) \rangle = -i \theta(t_6 - t_5) \langle \psi(x) \psi^\dagger(\bar{x}) \rangle - i \theta(t_5 - t_6) \langle \psi^\dagger(\bar{x}) \psi(x) \rangle, \quad (\text{E3})$$

$$G^>(x_1, x_2) \equiv -i \langle \psi(x_1) \psi^\dagger(x_2) \rangle, \quad (\text{E4})$$

$$G^<(x_1, x_2) \equiv -i \langle \psi^\dagger(x_2) \psi(x_1) \rangle. \quad (\text{E5})$$

In Eq. (E2)  $T_B$  is a time-ordering operator in Hilbert space for bosons, which takes any product of Bose field operators  $\zeta$ ,  $\chi$  and reorders them in ascending times from right to left, i.e.,

$$T_B \zeta(\tau_1) \chi(\tau_2) \equiv \begin{cases} \zeta(\tau_1) \chi(\tau_2) & \tau_2 < \tau_1 \\ \chi(\tau_2) \zeta(\tau_1) & \tau_1 < \tau_2 \\ \frac{1}{2} [\zeta(\tau_1) \chi(\tau_1) + \chi(\tau_1) \zeta(\tau_1)] & \tau_2 = \tau_1. \end{cases} \quad (\text{E6})$$

$\tilde{T}_B$  is an antitime-ordering operator in Hilbert space for bosons, which reorders any product of Bose field operators in descending times from right to left, i.e.,

$$\tilde{T}_B \zeta(\tau_1) \chi(\tau_2) \equiv \begin{cases} \chi(\tau_2) \zeta(\tau_1) & \tau_2 < \tau_1 \\ \zeta(\tau_1) \chi(\tau_2) & \tau_1 < \tau_2 \\ \frac{1}{2} [\zeta(\tau_1) \chi(\tau_1) + \chi(\tau_1) \zeta(\tau_1)] & \tau_2 = \tau_1. \end{cases} \quad (\text{E7})$$

In analogy with Appendix B, we can show that for bosons  $G_{LL}(x_1, x_2) = G^c(x_1, x_2)$ ,  $G_{RR}(x_1, x_2) = G^{\tilde{c}}(x_1, x_2)$ ,  $G_{RL}(x_1, x_2) = G^>(x_1, x_2)$ ,  $G_{LR}(x_1, x_2) = G^<(x_1, x_2)$ .

The retarded boson Green function in real space is given by<sup>32</sup>

$$G^r(x_1, x_2) = \int \frac{d\omega}{2\pi} e^{i\omega(t_2 - t_1)} \sum_\alpha \frac{\varphi_\alpha(\mathbf{r}_1) \varphi_\alpha^*(\mathbf{r}_2)}{\omega - (\omega_\alpha - \mu) + i\delta}, \quad (\text{E8})$$

where  $\delta \rightarrow 0$ ,  $\omega_\alpha$  is the energy of  $\alpha$  eigenvalue,  $\mu$  is the chemical potential,  $\varphi_\alpha(\mathbf{r}_1)$  is the wave function corresponding to  $\alpha$  eigenvalue of the external potential.

We define retarded boson Green function  $G_\alpha^r(\omega)$  in the frequency domain,

$$G^r(x_1, x_2) = \int \frac{d\omega}{2\pi} e^{-i\omega(t_1 - t_2)} \sum_\alpha \varphi_\alpha(\mathbf{r}_1) \varphi_\alpha^*(\mathbf{r}_2) G_\alpha^r(\omega), \quad (\text{E9})$$

where

$$G_\alpha^r(\omega) = (\omega - \omega_\alpha + \mu + i\delta)^{-1}. \quad (\text{E10})$$

The Keldysh Green functions for bosons are<sup>32</sup>

$$G_\alpha^c(\omega) = (\omega + \mu - \omega_\alpha + i\delta)^{-1} - 2\pi i n_\alpha \delta(\omega - \omega_\alpha + \mu), \quad (\text{E11})$$

$$G_\alpha^{\tilde{c}}(\omega) = -(\omega + \mu - \omega_\alpha - i\delta)^{-1} - 2\pi i n_\alpha \delta(\omega - \omega_\alpha + \mu), \quad (\text{E12})$$

$$G_\alpha^a(\omega) = (\omega - \omega_\alpha + \mu - i\delta)^{-1}, \quad (\text{E13})$$

$$G_\alpha^>(\omega) = -2\pi i (1 + n_\alpha) \delta(\omega - \omega_\alpha + \mu), \quad (\text{E14})$$

$$G_\alpha^<(\omega) = -2\pi i n_\alpha \delta(\omega - \omega_\alpha + \mu), \quad (\text{E15})$$

where  $n_\alpha = (\exp[(\omega_\alpha - \mu)/(k_B T)] - 1)^{-1}$  is the occupation number of the  $\alpha$  harmonic oscillator ( $T$  is temperature and  $k_B$  is Boltzmann constant).



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