

# Nonequilibrium superoperator GW equations

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Hedin's equations [Phys. Rev. **139**, 796 (1965)] for the one-particle equilibrium Green's function of a many-electron system are generalized to nonequilibrium open systems using two fields that separately control the evolution of the bra and the ket of the density matrix. A closed hierarchy is derived for the Green's function, the self-energy, the screened potential, the polarization, and the vertex function, all expressed as Keldysh matrices in Liouville space. © 2006 American Institute of Physics. [DOI: 10.1063/1.2161177]

## I. INTRODUCTION

Equilibrium, zero and finite temperature Green function techniques are widely used in electronic-structure calculations.<sup>1-4</sup> Hedin's GW formulation<sup>5</sup> closes the many-body hierarchy by expanding the self-energy of the one-particle Green function in terms of the screened Coulomb interaction. This provides a convenient starting point for many useful approximations and applications<sup>6</sup> to photoemission spectroscopy and optical absorption in metals,<sup>7-10</sup> semiconductors,<sup>11-16</sup> and molecules.<sup>17,18</sup>

Treating externally driven open systems, such as current-carrying states of molecular wires coupled to electrodes<sup>19-23</sup> requires an extension of the GW approach to nonequilibrium conditions. Nonequilibrium Green function theory (NEGFT) is widely used for computing molecular currents,<sup>20,23-29</sup> plasmas, quantum transport in semiconductors,<sup>30</sup> and high-energy processes in nuclear physics.<sup>31</sup> Most molecular current simulations assume noninteracting electrons but include electron-phonon interactions. Few studies<sup>30,32</sup> have incorporated electron-electron interactions using Anderson's slave boson model. The NEGFT calculation of molecular currents is based on the Keldysh's Green function technique, also known as the closed time-path formalism,<sup>33</sup> which depends on an artificial time parameter ( $\tau$ ) that runs on an imaginary contour (Keldysh loop).<sup>30,34</sup>  $\tau$  is a formal device that has no direct physical meaning, but was introduced in order to obtain a self-consistent Dyson-type equations for the Keldysh Green function using Schwinger's functional derivative technique.<sup>35</sup> Transforming the Dyson equations to real time by varying  $\tau$  over the Keldysh loop results in a self-consistent matrix equation for nonequilibrium Green functions.<sup>36</sup> It was shown by Schmutz<sup>37</sup> that the Keldysh artificial-time formulation of NEGFT can be avoided by reformulating quantum statistical mechanics in terms of superoperators acting in Liouville space.<sup>38</sup> One can then work directly in physical time and no analytical continuation from artificial (real or imaginary) time is required. A perturbative scheme based on Wick's theorem was suggested for computing the superoperator Greens functions.<sup>37</sup> This expansion in

Liouville space is analogous to the standard expansion of the equilibrium zero temperature Green function.

In this paper we extend Hedin's approach to superoperators in Liouville space and combine it with NEGFT to derive a closed hierarchy which incorporates electron-electron interactions in nonequilibrium Green's functions.<sup>35</sup> This is accomplished by introducing two external potentials, the "left" ( $\phi_L$ ) and the "right" ( $\phi_R$ ), that control the evolution of the bra and the ket of the density matrix, respectively. In the next section, we summarize the Liouville space superoperator algebra. In Sec. III, we use Schwinger's functional derivative technique to close the Liouville space hierarchy. We conclude with a discussion in Sec. IV.

## II. THE INTERACTION PICTURE FOR FERMION SUPEROPERATORS IN LIOUVILLE SPACE

We consider a many-electron system subjected to an external potential  $\phi(t)$  and described by the Hamiltonian

$$H = H_0 + H' + H'' \quad (1)$$

The reference ( $H_0$ ) and interaction ( $H' + H''$ ) parts are given by

$$H_0 = \int d\mathbf{r}_1 h_0(\mathbf{r}_1) \psi^\dagger(\mathbf{r}_1) \psi(\mathbf{r}_1),$$

$$H' = \int \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) \psi^\dagger(\mathbf{r}_1) \psi^\dagger(\mathbf{r}_2) \psi(\mathbf{r}_2) \psi(\mathbf{r}_1), \quad (2)$$

$$H'' = \int d\mathbf{r}_1 \phi(\mathbf{x}_1) \psi^\dagger(\mathbf{r}_1) \psi(\mathbf{r}_1),$$

where  $h_0(\mathbf{r}) = -\hbar^2 \nabla^2 / (2M) + U(\mathbf{r})$  with electron mass  $M$ , and  $v(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$  is the bare Coulomb potential.  $U$  is an external time-independent potential. We further use abbreviated notation for space-time coordinates,  $\mathbf{x}_n = (\mathbf{r}_n, t_n)$ .  $\phi(\mathbf{x}_1) = 0$  for  $t_1 < 0$ .

In Liouville space, the elements of the  $N \times N$  density matrix,  $\rho(t)$ , or any Hilbert space operator, are arranged as a vector (bra or ket) of length  $N^2$ . Operators of  $N^2 \times N^2$  dimension in this higher-dimensional space are denoted superoperators. We define a Liouville space vector  $|A\rangle = |m, n\rangle$

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which corresponds to the Hilbert space operator  $A=|m\rangle\langle n|$ , where  $|n\rangle$  is the particle number eigenstate,  $\psi_i^\dagger\psi_i|n\rangle=n_i|n\rangle$ . With any Hilbert space Fermi operator  $\psi$ , we associate two superoperators, the left ( $\psi_L$ ) and the right ( $\psi_R$ ), defined through their action on the state vector  $|A\rangle\rangle$  as<sup>37</sup>

$$\psi_{iL}|m,n\rangle\equiv\psi_i|m\rangle\langle n|, \quad \psi_{iL}^\dagger|m,n\rangle\equiv\psi_i^\dagger|m\rangle\langle n|, \quad (3)$$

$$\psi_{iR}|m,n\rangle\equiv(-1)^\mu|m\rangle\langle n|\psi_i, \quad (4)$$

$$\psi_{iR}^\dagger|m,n\rangle\equiv(-1)^{\mu+1}|m\rangle\langle n|\psi_i^\dagger,$$

where  $\mu=m-n$ . The  $n$ -electron state  $|n\rangle$  is constructed by applying  $n$  creation operators,  $\psi_i^\dagger$ , to the vacuum state,  $|n\rangle=\psi_{i_1}^\dagger\cdots\psi_{i_n}^\dagger|0\rangle$ . Thus  $m+n$  permutations of Fermi operators are required to bring the  $\psi_R$  to rightmost in Eq. (4). Each permutation gives a negative sign, which is taken care by the factor  $(-1)^\mu$  in Eq. (4). Using Eqs. (3) and (4), it can be seen that Fermi superoperators,  $\psi_\alpha$ ,  $\alpha=L, R$ , satisfy the same anticommutation relations as their Hilbert space counterparts,

$$\{\psi_{i\alpha},\psi_{j\beta}^\dagger\}=\delta_{\alpha\beta}\delta_{ij}, \quad (5)$$

$$\{\psi_{i\alpha},\psi_{j\beta}\}=\{\psi_{i\alpha}^\dagger,\psi_{j\beta}^\dagger\}=0.$$

These simple anticommutation relations, which are identical for those of ordinary Fermi operators, are the consequence of the  $(-1)^\mu$  factors in Eq. (4). For a product of operators, we have the identity,

$$(\psi_i\cdots\psi_j)_L=\psi_{iL}\cdots\psi_{jL}, \quad (\psi_i\cdots\psi_j)_R=\psi_{jR}\cdots\psi_{iR}. \quad (6)$$

The same relations hold if we change any of the  $\psi_i$  to  $\psi_i^\dagger$ . We next define ‘‘plus’’ and ‘‘minus’’ linear combinations of left and right superoperators

$$A_-=A_L-A_R, \quad A_+=\frac{1}{2}(A_L+A_R), \quad (7)$$

where  $A$  is any function of Fermi operators. The plus and minus operators obey same anticommutation relations as operators  $L$  and  $R$ , Eq. (5). This is very convenient because Eq. (5) holds when the indices  $\alpha, \beta$  are either  $+, -$  or  $L, R$ . In other words, this is simply a basis set transformation of superoperators. The formulation in terms of  $+$  and  $-$  operators is particularly useful if one wants to work directly with the observables (response and correlation functions) (see Appendix B).

In previous studies<sup>39,40</sup> we used an alternative definition for the right operators, which does not include the  $(-1)^\mu$  factors in Eq. (4). All  $L$  superoperators then commute with  $R$  superoperators while two ‘‘L’’ or two ‘‘R’’ superoperators ( $\alpha=\beta$ ) follow the same anticommutation relations as in Eq. (5). Since no simple commutation (or anticommutation) relation can be defined for  $+$  and  $-$  operators, in that case it becomes difficult to work with them. With the current definitions, Eqs. (3) and (4), both  $L, R$  and  $+, -$  operators satisfy the same anticommutation relations and one can work with either representations.

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

$$\frac{d\rho}{dt}=-\frac{i}{\hbar}\mathcal{H}_-\rho, \quad (8)$$

whose solution is

$$\rho(t_1)=S(t_1,t_0)\rho(t_0), \quad (9)$$

with the propagator

$$S(t_1,t_0)=\mathcal{T}\exp\left\{-\frac{i}{\hbar}\int_{t_0}^{t_1}\mathcal{H}_-(\tau)d\tau\right\}, \quad (10)$$

and  $\mathcal{H}_-$  is the superoperator corresponding to the Hamiltonian [Eq. (2)].  $\mathcal{T}$  is the Liouville space time-ordering operator; when acting on a product of superoperators, it rearranges them in increasing order of time from right to left. Unlike Hilbert space, where the time dependence of the ket and the bra is governed by forward and backward time-evolution operators, respectively, in Liouville space one keeps track simultaneously of both bra and ket, and all observables can be calculated by propagating the density matrix forward in time. Note that, since the Hamiltonian, Eq. (2), contains products of equal number of  $\psi$  and  $\psi^\dagger$  operators (electrons are conserved), the  $(-1)^\mu$  factor in Eq. (4) does not affect  $\mathcal{H}_-$  and Eq. (8).

To introduce the interaction picture in Liouville space, we extend the partitioning, Eq. (1), to superoperators,

$$\mathcal{H}_-=\mathcal{H}_{0-}+\mathcal{H}'_-+\mathcal{H}''_-. \quad (11)$$

Substituting Eqs. (6) and (7) in Eq. (2), the superoperator  $\mathcal{H}_-$  can be expressed in terms of  $\psi_\alpha$  ( $\alpha=L, R$ ) as

$$\begin{aligned} \mathcal{H}_{0-} &= \int d\mathbf{r}_1 h_0(\mathbf{r}_1) [\psi_L^\dagger(\mathbf{r}_1)\psi_L(\mathbf{r}_1) - \psi_R(\mathbf{r}_1)\psi_R^\dagger(\mathbf{r}_1)], \\ \mathcal{H}'_- &= \int \int d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1, \mathbf{r}_2) [\psi_L^\dagger(\mathbf{r}_1)\psi_L^\dagger(\mathbf{r}_2)\psi_L(\mathbf{r}_2)\psi_L(\mathbf{r}_1) \\ &\quad - \psi_R(\mathbf{r}_1)\psi_R(\mathbf{r}_2)\psi_R^\dagger(\mathbf{r}_2)\psi_R^\dagger(\mathbf{r}_1)], \\ \mathcal{H}''_- &= \int d\mathbf{r}_1 [\phi_L(\mathbf{x}_1)\psi_L^\dagger(\mathbf{r}_1)\psi_L(\mathbf{r}_1) \\ &\quad - \phi_R(\mathbf{x}_1)\psi_R(\mathbf{r}_1)\psi_R^\dagger(\mathbf{r}_1)]. \end{aligned} \quad (12)$$

In Eq. (12) we allow the potentials acting from the left ( $\phi_L$ ) and from the right ( $\phi_R$ ) to be different. This gives a formal flexibility in the following manipulations by allowing to independently control the ket and the bra.

Using the partitioning (11), Eq. (10) can be written in the interaction picture,

$$S(t_1,t_0)=\mathcal{S}_0(t_1,t_0)\mathcal{S}_I(t_1,t_0), \quad (13)$$

where  $\mathcal{S}$  is the generalization of Eq. (10) to allow for two different external fields.  $\mathcal{S}_0$  is the time evolution with respect to  $H_0$ ,

$$\mathcal{S}_0(t_1,t_0)=\theta(t_1-t_0)\exp\left\{-\frac{i}{\hbar}\mathcal{H}_{0-}(t_1-t_0)\right\}. \quad (14)$$

The interaction picture propagator can be factorized as

$$S_I(t_1, t_0) = \mathcal{T}S'_I(t_1, t_0)S''_I(t_1, t_0), \quad (15)$$

where

$$S'_I(t_1, t_0) = \exp\left\{-\frac{i}{\hbar} \int_{t_0}^{t_1} d\tau \tilde{\mathcal{H}}'_-(\tau)\right\},$$

$$S''_I(t_1, t_0) = \exp\left\{-\frac{i}{\hbar} \int_{t_0}^{t_1} d\tau \tilde{\mathcal{H}}''_-(\tau)\right\}. \quad (16)$$

We shall label superoperators in the interaction picture by a  $(\sim)$ ,

$$\tilde{A}_\alpha(t_1) \equiv S_0^\dagger(t_1, t_0)A_\alpha(t_0)S_0(t_1, t_0), \quad (17)$$

where  $\alpha = +, -$  or  $L, R$ .  $\tilde{\mathcal{H}}'_-(\tilde{\mathcal{H}}''_-)$  is the interaction picture representation of  $\mathcal{H}'_-(\mathcal{H}''_-)$ . Superoperators in the Heigenberg picture will be similarly represented by a caret,

$$\hat{A}_\alpha(t_1) \equiv S^\dagger(t_1, t_0)A_\alpha(t_0)S(t_1, t_0). \quad (18)$$

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

$$\rho(t_1) = \rho_0 - \frac{i}{\hbar} \int_{-\infty}^t d\tau S_0(t_1, \tau) \mathcal{H}'_-(\tau) \rho(\tau), \quad (19)$$

where  $\rho_0 = \rho(-\infty)$  is the equilibrium density matrix of our reference system,

$$\rho_0 = \frac{\exp(-\beta H_0)}{\text{Tr}[\exp(-\beta H_0)]}. \quad (20)$$

The formal solution of Eq. (19) yields,

$$\rho(t_1) = S_0(t_1, -\infty)S_I(t_1, -\infty)\rho_0. \quad (21)$$

The adiabatic connection formula, Eq. (21),<sup>39</sup> is very useful for calculating interaction picture expectation values. The equilibrium density matrix of the interacting system can

be generated at  $t=0$  from the noninteracting one, by starting at  $t=-\infty$ , switching on the electron-electron interactions ( $\mathcal{H}'$ ) adiabatically, and taking the limit  $\phi_L = \phi_R = \phi$ . The external potential  $\phi(t)$  is applied starting at  $t=0$ , i.e.,  $\mathcal{H}''_- = 0$  for  $t < 0$ .

### III. THE NONEQUILIBRIUM GW EQUATIONS

We shall define the “expectation value” of an operator  $\hat{A}_\alpha(t)$  in the interaction picture by combining Eqs. (17), (18), and (21),

$$\langle \hat{A}_\alpha(t_1) \rangle \equiv \frac{\text{Tr}[\tilde{A}_\alpha(t_1)S_I(t_1, -\infty)\rho_0]}{\text{Tr}\{S_I(t_1, -\infty)\rho_0\}} = \frac{\langle \tilde{A}_\alpha(t_1)S_I(t_1, -\infty) \rangle_0}{\langle S_I(t_1, -\infty) \rangle_0}. \quad (22)$$

$\langle \hat{A}_\alpha(t_1) \rangle$  is a functional of  $\phi_L$  and  $\phi_R$  that serves as a generating functional for various observables as will be shown in the following.  $\langle \cdots \rangle_0$  represents the trace over  $\rho_0$  [Eq. (20)]. For  $\phi_L = \phi_R$ , the denominator in Eq. (22) is unity and  $\langle \hat{A}_\alpha(t_1) \rangle$  reduces to the usual definition for the trace of an operator in Liouville space.<sup>38</sup>

Equation (22) is a convenient starting point for developing a perturbation theory. To that end we define a generalized Liouville space nonequilibrium Green function,

$$\mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = \frac{-i}{\hbar} \langle \mathcal{T} \hat{\psi}_\alpha(\mathbf{x}_1) \hat{\psi}_\beta^\dagger(\mathbf{x}_2) \rangle. \quad (23)$$

Using Eqs. (21)–(23) gives

$$\mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = \frac{-i}{\hbar I[\phi_L, \phi_R]} \langle \mathcal{T} \tilde{\psi}_\alpha(\mathbf{x}_1) \tilde{\psi}_\beta^\dagger(\mathbf{x}_2) \times S'_I(t_1, -\infty) \mathcal{Z}[\phi_L, \phi_R] \rangle_0, \quad (24)$$

with

$$\mathcal{Z}[\phi_L, \phi_R] = \mathcal{T} \exp\left\{-\frac{i}{\hbar} \int dx'_1 [\phi_L(\mathbf{x}'_1) \tilde{\psi}_L^\dagger(\mathbf{x}'_1) \tilde{\psi}_L(\mathbf{x}'_1) - \phi_R(\mathbf{x}'_1) \tilde{\psi}_R(\mathbf{x}'_1) \tilde{\psi}_R^\dagger(\mathbf{x}'_1)]\right\} \quad (25)$$

and

$$I[\phi_L, \phi_R] = \langle \mathcal{T} S'_I(\infty, -\infty) \mathcal{Z}[\phi_L, \phi_R] \rangle_0. \quad (26)$$

The deviation of the normalization factor  $I[\phi_L, \phi_R]$  from unity arises from the different phase accumulated by the ket and the bra and allows us to independently control their time evolution.

In Appendix B, we use Eq. (24) to derive a closed hierarchy of equations for the generalized Green functions,  $\mathcal{G}$  [Eq. (B14)], the self-energy,  $\Xi$  [Eq. (B19)], the screened potential,  $\mathcal{W}$  [Eq. (B23)], the polarization potential,  $\tilde{P}$  [Eq. (B25)], and the vertex function,  $\mathcal{L}$  [Eq. (27)]. Using different potentials ( $\phi_L$  and  $\phi_R$ ) is crucial for this derivation. How-

ever, at the end, we can compute observables by setting the two fields equal  $\phi_L = \phi_R = \phi$ ,  $I[\phi_L, \phi_R] = 1$ . The Liouville space nonequilibrium Green's function  $\mathcal{G}_{\alpha\beta}$  will then be denoted  $G_{\alpha\beta}$  and the equations of Appendix B then assume the form

$$G = G^0 + G^0 \Sigma G, \quad (27)$$

$$\Sigma = G \Lambda W, \quad (28)$$

$$W = vI + vPW, \quad (29)$$

$$P = GG\Lambda, \quad (30)$$

$$\Lambda = I + \frac{\delta\Sigma}{\delta G}GG\Lambda, \quad (31)$$

where  $G$ ,  $G^0$ ,  $\Sigma$ ,  $W$ ,  $P$ , and  $\Lambda$  represent matrices in  $\alpha, \beta = L, R$ .  $\Sigma$  is the self-energy of the single-particle nonequilibrium Green function,  $G$ , and accounts for the many-body interactions.  $W$ ,  $P$ , and  $\Lambda$  are the screened Coulomb potential, the polarization, and the vertex functions, respectively, defined through the functional derivatives (Appendix B),

$$\Sigma = v \frac{\delta G}{\delta \phi} G^{-1}, \quad W = v \frac{\delta V^T}{\delta \phi}, \quad (32)$$

$$P = \frac{\delta \rho}{\delta V^T}, \quad \Lambda = \frac{\delta G^{-1}}{\delta V^T}$$

where  $V^T$  and  $\rho$  are the total effective potential (sum of the external potential and the induced potential) and the charge density, respectively.

Writing Eqs. (27)–(31) explicitly gives (primed indices are summed over)

$$G_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = G_{\alpha\beta}^0 + \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 G_{\alpha\alpha'}^0(\mathbf{x}_1, \mathbf{x}'_1) \Sigma_{\alpha'\beta'}(\mathbf{x}'_1, \mathbf{x}'_2) G_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2), \quad (33)$$

$$\Sigma_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = i\hbar \int \int d\mathbf{x}'_2 d\mathbf{x}'_3 G_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \Lambda_{\beta'\gamma'}(\mathbf{x}'_2, \mathbf{x}_2, \mathbf{x}'_3) W_{\gamma'\alpha}(\mathbf{x}'_3, \mathbf{x}_1), \quad (34)$$

$$W_{\alpha\beta}(\mathbf{x}_2, \mathbf{x}_1) = \delta_{\alpha\beta} \delta(t_1 - t_2) v(\mathbf{r}_1, \mathbf{r}_2) + \int \int d\mathbf{x}'_1 d\mathbf{r}'_2 v(\mathbf{r}_2, \mathbf{r}'_2) P_{\alpha\beta'}(\mathbf{r}'_2, t_2, \mathbf{x}'_1) W_{\beta'\beta}(\mathbf{x}'_1, \mathbf{x}_1), \quad (35)$$

$$P_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = -i\hbar \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 G_{\alpha\alpha'}(\mathbf{x}_1, \mathbf{x}'_1) G_{\beta'\alpha}(\mathbf{x}'_2, \mathbf{x}_1) \Lambda_{\alpha'\beta'}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_2), \quad (36)$$

$$\Lambda_{\alpha\beta\gamma}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \epsilon_\alpha \delta_{\alpha\beta} \delta_{\alpha\gamma} \delta(\mathbf{x}_1, \mathbf{x}_2) \delta(\mathbf{x}_1, \mathbf{x}_3) + \int \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 d\mathbf{x}'_3 d\mathbf{x}'_4 \frac{\delta \Sigma_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2)}{\delta G_{\alpha'\delta'}(\mathbf{x}'_1, \mathbf{x}'_2)} \times G_{\alpha'\gamma'}(\mathbf{x}'_1, \mathbf{x}'_3) G_{\delta'\beta'}(\mathbf{x}'_2, \mathbf{x}'_4) \Lambda_{\gamma'\beta'}(\mathbf{x}'_3, \mathbf{x}'_4, \mathbf{x}_3). \quad (37)$$

These equations extend Hedin's Hilbert space equations<sup>5</sup> to include the superoperator indices  $\alpha$ ,  $\beta$ ,  $\gamma$ . They have one-to-one correspondence with the Hilbert space Keldysh nonequilibrium Green's functions as shown in Appendix C.

Equations (27)–(31) form an exact closed hierarchy and can be solved iteratively for  $G_{\alpha\beta}$ . We start with the Green functions,  $G^0$ , for a reference system whose properties are known. Since  $G^0$  corresponds to a system of noninteracting electrons, it can be easily expressed in terms of the orbitals ( $\phi_i$ ) and energies ( $\epsilon_i$ ) obtained from a density-functional theory calculation. In the Kohn-Sham molecular-orbital basis set,<sup>41</sup> denoted by Latin indices  $i$ ,  $j$ ,  $k$ , all the zeroth-order Green functions are diagonal:

$$G_{LR}^0(i, j, E) = 2\pi i \delta_{ij} f_i \delta(E - \epsilon_i), \quad (38)$$

$$G_{RL}^0(i, j, E) = 2\pi i \delta_{ij} (1 - f_i) \delta(E - \epsilon_i), \quad (39)$$

$$G_{LL}^0(i, j, E) = \delta_{ij} \left[ \frac{f_i}{E - \epsilon_i - i\eta} + \frac{1 - f_i}{E - \epsilon_i + i\eta} \right], \quad (40)$$

$$G_{RR}^0(i, j, E) = \delta_{ij} \left[ \frac{1 - f_i}{E - \epsilon_i - i\eta} + \frac{f_i}{E - \epsilon_i + i\eta} \right], \quad (41)$$

where  $\eta$  is an infinitesimal, positive, real number and  $f_i$  is the Fermi distribution function

$$f_i = \frac{1}{1 + \exp\{\beta(\epsilon_i - E_F)\}}, \quad (42)$$

with  $\beta = 1/k_B T$  and  $E_F$  the Fermi energy. In the  $+$ ,  $-$  representation we only have three Green's functions since  $G_{+-} = 0$  (Appendix A). To zero order they are given by

$$G_{--}^0(i, j, E) = \frac{\delta_{ij}}{E - \epsilon_i + i\eta}, \quad (43)$$

$$G_{++}^0(i, j, E) = \frac{\delta_{ij}}{E - \epsilon_i - i\eta}, \quad (44)$$

$$G_{-+}^0(i, j, E) = 2\pi i \delta_{ij} [2f_i - 1] \delta(E - \epsilon_i). \quad (45)$$

In zero order,  $G_{\alpha\beta} = G_{\alpha\beta}^0$ ,  $\Sigma^0 = W^0 = 0$ ,  $\Lambda^0$  is the unit matrix [first term in the right-hand side of Eq. (31)], and  $P^0$  is simply the product of two zeroth-order Green functions. We substitute  $P^0$  and  $\Lambda^0$  in Eqs. (28) and (29) to obtain updated

self-energy  $\Sigma^{(1)}$  and screened potential  $W^{(1)}$ , respectively. Using  $\Sigma^{(1)}$  in Eq. (27) gives the updated Green's function  $G_{\alpha\beta}^{(1)}$ . We next compute the derivative,  $\delta\Sigma/\delta G$ , numerically, where  $\delta G = G^{(1)} - G_0$  and  $\delta\Sigma = \Sigma^{(1)} - \Sigma^{(0)}$ , which is used to update  $\Lambda$  from Eq. (31). The updated vertex function  $\Lambda^{(1)}$  when substituted in Eq. (30) gives  $P^{(1)}$ . These updated functions  $P^{(1)}$  and  $\Lambda^{(1)}$  are substituted in Eqs. (27) and (28) to obtain new  $W^{(2)}$  and  $\Sigma^{(2)}$ , respectively. These give updated Greens functions  $G^{(2)}$  from Eq. (27). These steps are repeated until a desired convergence is reached between the input and the output Green's functions.

## IV. DISCUSSION

By working in Liouville space we derived closed Dyson equations for the nonequilibrium Green functions in real time. This formulation does not involve artificial time variables, thus avoiding the Keldysh loop. Note that in Liouville space both fields  $\phi_L$  and  $\phi_R$  have a physical meaning; they control the time evolution of the bra and the ket of the density matrix, respectively. The independent control of the bra and the ket allows to construct a real time generating functional<sup>37,39</sup> for different *Liouville space pathways* (LSPs).<sup>38</sup> The superoperator Green's functions are given by linear combinations of these LSPs. We emphasize that using a single external potential ( $\phi_L = \phi_R = \phi$ ), as done in time-dependent density-functional theory (TDDFT),<sup>42</sup> one only obtains the ordinary response functions which are specific combinations of the individual LSPs. These are not sufficient to derive a closed Dyson-type equation for NESGF.

All experimental observables can be expressed in terms of LSP.<sup>43,44</sup> Response and correlation functions are intimately connected. In linear order, they are related through the fluctuation-dissipation theorem.<sup>45,46</sup> This is, however, no longer the case for nonlinear fluctuations and responses which do not have a unique simple relation.<sup>47</sup> In Liouville space both response and the correlations are naturally treated on the same footing<sup>48,49</sup> through the LSP. This property of Liouville space turned out to be very useful for many physical observables, e.g., resolving the causality paradox of TDDFT (Ref. 48) and calculating intermolecular interactions,<sup>43,49</sup> which require both the correlations of spontaneous fluctuations of the charge density and their responses to an external field.

The equilibrium Green functions can be generated from the nonequilibrium Green functions ( $\phi_\alpha \neq 0$ ) by simply setting  $\phi_L = \phi_R = 0$ . Equations (33)–(37) constitute closed matrix equations that can be transformed using the matrix  $Q$  [Eq. (A5)] to obtain the celebrated Hedin's equations<sup>5</sup> for the ordinary (causal) equilibrium Green's function. At equilibrium, unlike Hilbert space, we still have a matrix Dyson equation in Liouville space. However, the fluctuation-dissipation relation,<sup>30</sup>

$$G^<(\mathbf{r}, \omega) = -f_{\text{eq}}(\omega)[G_r(\mathbf{r}, \omega) - G_a(\mathbf{r}, \omega)], \quad (46)$$

$$G^<(\mathbf{r}, \omega) = (1 - f_{\text{eq}}(\omega))[G_r(\mathbf{r}, \omega) - G_a(\mathbf{r}, \omega)],$$

connects “lesser” ( $G_{LR}$ ) and “greater” ( $G_{RL}$ ) functions with the retarded and advanced Green functions through the Fermi equilibrium distribution function,<sup>30</sup>

$$f_{\text{eq}}(\omega) = \frac{1}{1 + e^{\beta(\omega - E_F)}}, \quad (47)$$

where  $\beta$  is the inverse temperature. This is why at equilibrium, the Dyson equation can be recast solely for the retarded (or advanced) Green's functions.

This formulation can be used to compute the effect of electron-electron interactions on molecular currents and fluorescence induced by currents.<sup>50</sup> We briefly outline the possible application of the present formalism to currents in molecular junctions (scanning tunneling microscopy and molecular wires), electronic tunneling through single molecules,<sup>51</sup> chains of atoms,<sup>52</sup> and self-assembled monolayers of molecules<sup>53</sup> under an externally applied bias. A molecule attached to two metal electrodes is described by the Hamiltonian,  $H_T = H_m + H_t + H_{ts}$ , with molecular Hamiltonian ( $H_m$ ), electrode Hamiltonian ( $H_t$ ), and their coupling<sup>24,30</sup>

$$H_{ts} = \sum_{i\mu} J_{i\mu} \psi_i^\dagger \psi_\mu + \text{H.c.}, \quad (48)$$

where we use Greek ( $\mu, \nu, \kappa$ ) and Latin ( $i, j, k$ ) indices to denote electrode and molecule orbitals, respectively.  $J_{i\mu}$  are the tunneling matrix elements.  $\psi_i^\dagger$  ( $\psi_i$ ) are the Fermi creation (annihilation) operators and satisfy usual anticommutation relations.

An external bias ( $V$ ) maintains a chemical potential difference of eV, creating a nonequilibrium steady state where the electrons flow from a higher to a lower chemical potential through the molecule. The total current  $I$  is given by the rate of change of occupation number operator of electrons in the molecule,

$$I = \frac{dN}{dt} = \frac{ie}{\hbar} \sum_{i\mu} (J_{\mu i} \langle \psi_i^\dagger \psi_\mu \rangle_T - \text{H.c.}), \quad (49)$$

where  $N = \sum_i \psi_i^\dagger \psi_i$  is the number operator and  $\langle \cdots \rangle_T$  is the trace with respect to the density matrix of the interacting electrodes+molecule system. In Eq. (49), the current  $I$  represents the rate of flow of electrons from the left electrode to the molecule. The sum  $\mu$  runs over only one of the electrodes. At steady state, current through the other electrode is the same but negative.

Using the Liouville space interaction picture,<sup>24,37,38</sup> we can compute the average in Eq. (49) perturbatively in the electrode-molecule coupling. By switching the coupling adiabatically starting at  $t \rightarrow -\infty$ , each term in the perturbation series can be expressed in terms of products of Green's functions of the electrode and the molecule. To lowest (second) order in electrode-molecule coupling, the current depends on the one-body NESGFs for the electrode and the molecule [see Eq. (52)] which includes all many-body interactions.

Using the definitions, Eqs. (3) and (4), the current, Eq. (49), can be expressed in terms of the superoperators,

$$I = \frac{ie}{\hbar} \sum_{i\mu} (J_{i\mu} \langle \psi_{iL}^\dagger \psi_{\mu L} \rangle_T - \text{H.c.}), \quad (50)$$

where  $\langle \cdots \rangle_T$  is trace over the density matrix of the entire electrode+molecule system. Current can be computed perturbatively in electrode-molecule coupling ( $J_{i\mu}$ ) by expressing Eq. (50) in the interaction picture,

$$I = \frac{ie}{\hbar} \sum_{i\mu} J_{i\mu} \left\langle \mathcal{T} \psi_{iL}^\dagger(t) \psi_{\mu L}(t) \exp \left\{ \frac{-i}{\hbar} \int_{-\infty}^t d\tau H_-^{ts}(\tau) \right\} \right\rangle + \text{c.c.}, \quad (51)$$

where  $H_-^{ts}$  is the superoperator corresponding to  $H_{ts}$ , Eq. (48), and the trace in Eq. (51) is with respect to the initial ( $t \rightarrow -\infty$ ) density matrix of the electrode+molecule system.

By expanding the exponential, we can express the current as a power series in coupling element  $J_{i\mu}$ . Since the initial density matrix is a direct product of the density matrices of the electrode and the molecule, each term of the series can be expressed as a product of averages for the electrode and the molecule separately. To lowest (second) order, the contribution from the term containing the Green functions  $G_{LL}$  and  $G_{RR}$  vanishes<sup>54</sup> and we obtain

$$I = e \sum_{ii'\mu\mu'} J_{i\mu} J_{i'\mu'} \int d\tau [G_{LR}^{ii'}(t\tau) G_{RL}^{\mu'\mu}(\tau, t) - G_{RL}^{i'i}(\tau, t) G_{LR}^{\mu\mu'}(t, \tau)], \quad (52)$$

where  $G^{ii'}$  and  $G^{\mu\mu'}$  are the NESGFs for the molecule and the electrode, respectively. The next (fourth-order) contribution involves higher-order Green's functions of the molecule and the electrode.

Most theoretical studies of molecular wires include electron-phonon but neglect electron-electron interactions within the molecule. The electrodes are modeled as a free-electron gas. The average in Eq. (49) can then be factorized into a product of Green functions of the noninteracting electrode and the molecule.<sup>20,30</sup> Once many-body interactions in the electrodes and the molecule are included, such factorization is no longer possible and the present hierarchy of Green's functions needs to be solved.

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## APPENDIX A: THE RETARDED AND THE ADVANCED GREEN FUNCTIONS

The retarded and the advanced Green functions represent the forward and the backward propagation of a quasiparticle (i.e., a dynamically screened particle) in a many-body system, respectively. In this section we obtain these functions in

Liouville space. The Liouville space retarded ( $G_r$ ) and advanced ( $G_a$ ) Green functions are defined in terms of the “+” and “-” superoperators,

$$G_r(t_1, t_2) = G^-(t_1, t_2) \equiv -\frac{i}{2\hbar} \langle \mathcal{T} \psi_-(t_1) \psi_-^\dagger(t_2) \rangle, \quad (A1)$$

$$G_a(t_1, t_2) = G^{++}(t_1, t_2) \equiv -\frac{2i}{\hbar} \langle \mathcal{T} \psi_+(t_1) \psi_+^\dagger(t_2) \rangle.$$

Similarly, the correlation function (noncausal),  $G_c$ , can be defined as

$$G_c(t_1, t_2) = G^{-+}(t_1, t_2) \equiv -\frac{i}{\hbar} \langle \mathcal{T} \psi_-(t_1) \psi_+^\dagger(t_2) \rangle, \quad (A2)$$

and the Green function,  $G^{+-}=0$ . Using Eqs. (7), the retarded and advanced Green functions can be expressed in terms of the Green functions,  $G_{\alpha\beta}$ ,  $\alpha, \beta=L, R$ ,

$$G_r(t_1, t_2) = G_{LL}(t_1, t_2) - G_{LR}(t_1, t_2),$$

$$G_a(t_1, t_2) = G_{LL}(t_1, t_2) + G_{RL}(t_1, t_2), \quad (A3)$$

$$G_c(t_1, t_2) = G_{LR}(t_1, t_2) - G_{RL}(t_1, t_2),$$

where we have used the identity,  $G_{LL}+G_{RL}=G_{RR}+G_{LR}$  (which reflects the fact that  $G^{+-}=0$ ). Thus a Dyson equation for the retarded and advanced Green functions can be obtained using the transformation,

$$G = Q \bar{G} Q^{-1} \quad (A4)$$

where

$$\bar{G} = \begin{pmatrix} G_{LL} & G_{LR} \\ G_{RL} & G_{RR} \end{pmatrix}, \quad G = \begin{pmatrix} G_a & 0 \\ -G_c & G_r \end{pmatrix}, \quad (A5)$$

$$Q = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix}.$$

Applying this transformation to Eq. (33), we obtain the Dyson equations for retarded and advanced Green functions which can be expressed in the matrix form as

$$G = G^0 + G^0 \Sigma G, \quad (A6)$$

with

$$\Sigma = \begin{pmatrix} \Sigma_a & 0 \\ -\Sigma_c & \Sigma_r \end{pmatrix}. \quad (A7)$$

The elements of the self-energy matrix are given by

$$\begin{aligned}\Sigma_r(t_1, t_2) &= \Sigma_{LL}(t_1, t_2) - \Sigma_{LR}(t_1, t_2), \\ \Sigma_a(t_1, t_2) &= \Sigma_{LL}(t_1, t_2) + \Sigma_{RL}(t_1, t_2),\end{aligned}\quad (\text{A8})$$

$$\Sigma_c(t_1, t_2) = \Sigma_{LR}(t_1, t_2) - \Sigma_{RL}(t_1, t_2).$$

The closed set, Eqs. (33)–(37) together with Eqs. (A6) and (A8), may be solved to yield the retarded (advanced) Green functions. Using these transformations to Eq. (33) and setting the external field to zero ( $\phi=0$ ), we obtain set of equations for the equilibrium retarded Green's function,

$$G_r(\mathbf{x}_1, \mathbf{x}_2) = G_r^0 + \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 G_r^0(\mathbf{x}_1, \mathbf{x}'_1) \Sigma_r(\mathbf{x}'_1, \mathbf{x}'_2) G_r(\mathbf{x}'_2, \mathbf{x}_2). \quad (\text{A9})$$

An equation corresponding to the advanced Green functions can be obtained from Eq. (A9) by replacing all retarded functions with advanced functions.

## APPENDIX B: CLOSED MATRIX EQUATIONS FOR $\mathcal{G}_{\alpha\beta}$

Closed matrix-Dyson equation for generalized Green's functions, Eq. (23), will be derived using the Schwinger's functional derivative technique. We start with the time derivative of Eq. (23), we get

$$i\hbar \frac{\partial}{\partial t_1} \mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = \delta_{\alpha\beta} \delta(\mathbf{x}_1 - \mathbf{x}_2) + \left\langle \mathcal{T} \frac{\partial \hat{\psi}_\alpha(\mathbf{x}_1)}{\partial t_1} \hat{\psi}_\beta^\dagger(\mathbf{x}_2) \right\rangle. \quad (\text{B1})$$

We next consider the Heisenberg equation of motion for superoperator  $\tilde{\psi}_\alpha$  (Refs. 37 and 38)

$$\frac{\partial \hat{\psi}_\alpha(\mathbf{x}_1)}{\partial t_1} = \frac{i}{\hbar} [\mathcal{H}_-, \hat{\psi}_\alpha(\mathbf{x}_1)]. \quad (\text{B2})$$

Using the (anti)commutation relations (5), this gives

$$\begin{aligned}i\hbar \frac{\partial \hat{\psi}_L(\mathbf{x}_1)}{\partial t_1} &= h_L(\mathbf{x}_1) \hat{\psi}_L(\mathbf{x}_1) \\ &+ \int d\mathbf{x}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \hat{\psi}'_L(\mathbf{x}'_1) \hat{\psi}_L(\mathbf{x}'_1) \hat{\psi}_L(\mathbf{x}_1),\end{aligned}\quad (\text{B3})$$

$$\begin{aligned}-i\hbar \frac{\partial \hat{\psi}_R(\mathbf{x}_1)}{\partial t_1} &= h_R(\mathbf{x}_1) \hat{\psi}_R(\mathbf{x}_1) \\ &+ \int d\mathbf{x}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \hat{\psi}_R(\mathbf{x}_1) \hat{\psi}_R(\mathbf{x}'_1) \hat{\psi}'_R(\mathbf{x}'_1),\end{aligned}\quad (\text{B4})$$

where  $h_\alpha(\mathbf{x}_1) = -\nabla_1^2/(2m) + U(\mathbf{r}_1) + \phi_\alpha(\mathbf{x}_1)$ . Substituting Eqs. (B3) and (B4) in (B1) and using Eq. (24) we obtain the Dyson equation for  $\mathcal{G}_{\alpha\beta}$ ,

$$\begin{aligned}\left( i\hbar \frac{\partial}{\partial t_1} + \epsilon_\alpha h_\alpha(\mathbf{x}_1) \right) \mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) \\ = \delta_{\alpha\beta} \delta(\mathbf{x}_1 - \mathbf{x}_2) + \int d\mathbf{x}'_2 M_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2),\end{aligned}\quad (\text{B5})$$

where  $\epsilon_L=1$  and  $\epsilon_R=-1$ . The elements  $M_{\alpha\beta}$  of the self-energy are defined by

$$\begin{aligned}\int d\mathbf{x}'_2 M_{L\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2) \\ \equiv \frac{i}{\hbar} \int d\mathbf{x}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \langle \mathcal{T} \hat{\psi}'_L(\mathbf{x}'_1) \hat{\psi}_L(\mathbf{x}'_1) \hat{\psi}_L(\mathbf{x}_1) \hat{\psi}'_\beta(\mathbf{x}_2) \rangle,\end{aligned}\quad (\text{B6})$$

$$\begin{aligned}\int d\mathbf{x}'_2 M_{R\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2) \\ \equiv \frac{-i}{\hbar} \int d\mathbf{x}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \langle \mathcal{T} \hat{\psi}_R(\mathbf{x}_1) \hat{\psi}_R(\mathbf{x}'_1) \hat{\psi}'_R(\mathbf{x}'_1) \hat{\psi}'_\beta(\mathbf{x}_2) \rangle.\end{aligned}$$

Using Eq. (22), Eqs. (B6) assume the form

$$\begin{aligned}\int d\mathbf{x}'_2 M_{L\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2) \\ = \frac{i}{\hbar I[\phi_L, \phi_R]} \int d\mathbf{x}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \\ \times \langle \mathcal{T} \tilde{\psi}'_L(\mathbf{x}'_1) \tilde{\psi}_L(\mathbf{x}'_1) \tilde{\psi}_L(\mathbf{x}_1) \tilde{\psi}'_\beta(\mathbf{x}_2) \mathcal{S}'_I(t_1, -\infty) \\ \times \mathcal{Z}[\phi_L, \phi_R] \rangle_0,\end{aligned}\quad (\text{B7})$$

$$\begin{aligned}\int d\mathbf{x}'_2 M_{R\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2) \\ = \frac{-i}{\hbar I[\phi_L, \phi_R]} \int d\mathbf{x}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \\ \times \langle \mathcal{T} \tilde{\psi}_R(\mathbf{x}_1) \tilde{\psi}_R(\mathbf{x}'_1) \tilde{\psi}'_R(\mathbf{x}'_1) \tilde{\psi}'_\beta(\mathbf{x}_2) \mathcal{S}'_I(t_1, -\infty) \\ \times \mathcal{Z}[\phi_L, \phi_R] \rangle_0.\end{aligned}$$

Taking the functional derivative of  $\mathcal{G}_{\alpha\beta}$  [Eq. (24)] with respect to  $\phi_L$  and  $\phi_R$  gives

$$\begin{aligned} \frac{\delta}{\delta\phi_L(\mathbf{x}_3)}\mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= -\mathcal{G}_{LL}(\mathbf{x}_3, \mathbf{x}_3^\dagger)\mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) \\ &+ \left(\frac{i}{\hbar}\right)^2 \frac{1}{I[\phi_L, \phi_R]} \\ &\times \langle T\tilde{\psi}_L^\dagger(\mathbf{x}_3)\tilde{\psi}_L(\mathbf{x}_3)\tilde{\psi}_\alpha(\mathbf{x}_1)\tilde{\psi}_\beta^\dagger(\mathbf{x}_2) \\ &\times S'_I(t_1, -\infty)\mathcal{Z}[\phi_L, \phi_R]\rangle_0, \end{aligned} \quad (\text{B8})$$

$$\begin{aligned} \frac{\delta}{\delta\phi_R(\mathbf{x}_3)}\mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= -\mathcal{G}_{RR}(\mathbf{x}_3, \mathbf{x}_3^\dagger)\mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) \\ &+ \left(\frac{i}{\hbar}\right)^2 \frac{1}{I[\phi_L, \phi_R]} \\ &\times \langle T\tilde{\psi}_\alpha(\mathbf{x}_1)\tilde{\psi}_R(\mathbf{x}_3)\tilde{\psi}_R^\dagger(\mathbf{x}_3)\tilde{\psi}_\beta^\dagger(\mathbf{x}_2) \\ &\times S'_I(t_1, -\infty)\mathcal{Z}[\phi_L, \phi_R]\rangle_0. \end{aligned}$$

Using Eqs. (B7) and (B8), the Dyson equation (B5) can be recast as

$$\begin{aligned} \left(i\hbar\frac{\partial}{\partial t_1} + \epsilon_\alpha h_\alpha(\mathbf{x}_1) + V_\alpha^H(\mathbf{x}_1)\right)\mathcal{G}_{\alpha\beta} \\ = \delta_{\alpha\beta}\delta(\mathbf{x}_1 - \mathbf{x}_2) + \int d\mathbf{x}'_2 \Xi_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2)\mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2), \end{aligned} \quad (\text{B9})$$

where

$$V_\alpha^H(\mathbf{x}_1) = -i\hbar \int d\mathbf{r}'_1 v(\mathbf{r}'_1, \mathbf{r}_1)\mathcal{G}_{\alpha\alpha}(\mathbf{r}'_1 t_1, \mathbf{r}'_1 t_1^\dagger). \quad (\text{B10})$$

Note that when  $\phi_L = \phi_R$ ,  $V_\alpha^H$  reduces to Hartree (time-dependent) potential.<sup>55</sup> The self-energy  $\Xi_{\alpha\beta}$  is given by

$$\begin{aligned} \Xi_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= -i\hbar \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 v(\mathbf{r}_1, \mathbf{r}'_1) \\ &\times \sum_{\beta'} \frac{\delta\mathcal{G}_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2)}{\delta\phi_\alpha(\mathbf{x}'_1)}\mathcal{G}_{\beta'\beta}^{-1}(\mathbf{x}'_2, \mathbf{x}_2). \end{aligned} \quad (\text{B11})$$

We next define the zeroth-order Green function,  $\mathcal{G}_{0\alpha\beta}$ ,

$$\left(i\hbar\frac{\partial}{\partial t_1} + \epsilon_\alpha h_\alpha(\mathbf{x}_1) + V_\alpha^H(\mathbf{r}_1)\right)\mathcal{G}_{0\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = \delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (\text{B12})$$

corresponding to the reference system of noninteracting particles subjected to the (total) potential

$$V_\alpha^T(\mathbf{x}_1) = U(\mathbf{r}_1) + \phi_\alpha(\mathbf{x}_1) + V_\alpha^H(\mathbf{x}_1). \quad (\text{B13})$$

Multiplying Eq. (B9) from the right by  $\mathcal{G}_{\alpha\beta}^{-1}$  gives

$$\mathcal{G}_{\alpha\beta}^{-1}(\mathbf{x}_1, \mathbf{x}_2) = \mathcal{G}_{0\alpha\beta}^{-1}(\mathbf{x}_1, \mathbf{x}_2) - \Xi_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) \quad (\text{B14})$$

or equivalently,

$$\begin{aligned} \mathcal{G}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= \mathcal{G}_{0\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) \\ &+ \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 \sum_{\alpha'\beta'} \mathcal{G}_{0\alpha\alpha'}(\mathbf{x}_1, \mathbf{x}'_1)\Xi_{\alpha'\beta'}(\mathbf{x}'_1, \mathbf{x}'_2) \\ &\times \mathcal{G}_{\beta'\beta}(\mathbf{x}'_2, \mathbf{x}_2). \end{aligned} \quad (\text{B15})$$

Taking the functional derivative of the identity,

$$\sum_{\beta'} \int d\mathbf{x}'_2 \mathcal{G}_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2)\mathcal{G}_{\beta'\beta}^{-1}(\mathbf{x}'_2, \mathbf{x}_2) = \delta_{\alpha\beta}\delta(\mathbf{x}_1 - \mathbf{x}_2) \quad (\text{B16})$$

with respect to  $V_\alpha^T$ , we obtain

$$\begin{aligned} \sum_{\beta'} \int d\mathbf{x}'_2 \left[ \mathcal{G}_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \frac{\delta\mathcal{G}_{\beta'\alpha}^{-1}(\mathbf{x}'_2, \mathbf{x}_2)}{\delta V_\alpha^T(\mathbf{x}'_1)} \right. \\ \left. + \frac{\delta\mathcal{G}_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2)}{\delta V_\alpha^T(\mathbf{x}'_1)} \mathcal{G}_{\beta'\beta}^{-1}(\mathbf{x}'_2, \mathbf{x}_2) \right] = 0. \end{aligned} \quad (\text{B17})$$

Changing variables from  $\phi_\alpha$  to  $V_\alpha^T$  using the chain rule,

$$\frac{\delta}{\delta\phi_\alpha(\mathbf{x}_1)} = \int d\mathbf{x}_2 \sum_\beta \frac{\delta V_\beta^T(\mathbf{x}_2)}{\delta\phi_\alpha(\mathbf{x}_1)} \frac{\delta}{\delta V_\beta^T(\mathbf{x}_2)} \quad (\text{B18})$$

and using Eq. (B17), the self-energy [Eq. (B11)] assumes the form

$$\begin{aligned} \Xi_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= i\hbar \sum_{\beta'\gamma'} \int \int d\mathbf{x}'_2 d\mathbf{x}'_3 \mathcal{G}_{\alpha\beta'}(\mathbf{x}_1, \mathbf{x}'_2) \\ &\times \mathcal{L}_{\beta'\beta\gamma'}(\mathbf{x}'_2, \mathbf{x}_2, \mathbf{x}'_3)\mathcal{W}_{\gamma'\alpha}(\mathbf{x}'_3, \mathbf{x}_1), \end{aligned} \quad (\text{B19})$$

where  $\mathcal{W}_{\alpha\beta}$  is the screened Coulomb potential

$$\mathcal{W}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = \int d\mathbf{r}'_1 v(\mathbf{r}_1, \mathbf{r}'_1) \frac{\delta V_\alpha^T(\mathbf{x}_1)}{\delta\phi_\beta(\mathbf{r}'_1, t_2)} \quad (\text{B20})$$

and  $\mathcal{L}_{\alpha\beta\gamma}$  is the vertex function,

$$\mathcal{L}_{\alpha\beta\gamma}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \frac{\delta\mathcal{G}_{\alpha\beta}^{-1}(\mathbf{x}_1, \mathbf{x}_2)}{\delta V_\gamma^T(\mathbf{x}_3)}. \quad (\text{B21})$$

To derive a closed equation for the Green functions, we need to express  $\mathcal{W}_{\alpha\beta}$  and  $\mathcal{L}_{\alpha\beta\gamma}$  in terms of  $\mathcal{G}_{\alpha\beta}$ . To that end we take the functional derivative of Eq. (B13) with respect to the external potential ( $\phi_\alpha$ ), and make use of Eq. (B10) to obtain

$$\begin{aligned} \frac{\delta V_\alpha^T(\mathbf{x}_1)}{\delta\phi_\beta(\mathbf{r}'_1, t_2)} &= \delta_{\alpha\beta}\delta(t_2 - t_1)\delta(\mathbf{r}_1 - \mathbf{r}'_1) \\ &- i\hbar \int d\mathbf{r}'_2 v(\mathbf{r}'_2, \mathbf{r}_1) \frac{\delta\mathcal{G}_{\alpha\alpha}(\mathbf{r}'_2 t_1, \mathbf{r}'_2 t_1^\dagger)}{\delta\phi_\alpha(\mathbf{r}'_1, t_2)}. \end{aligned} \quad (\text{B22})$$

Substituting Eq. (B22) in (B20) and changing variables from  $\phi_\alpha$  to  $V_\alpha^T$ , the screened Coulomb potential,  $\mathcal{W}_{\alpha\beta}$  satisfies the self-consistent equation

$$\begin{aligned} \mathcal{W}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= \delta_{\alpha\beta} \delta(t_1 - t_2) v(\mathbf{r}_1, \mathbf{r}_2) \\ &+ \int \int d\mathbf{x}'_1 d\mathbf{r}'_2 \sum_{\beta'} v(\mathbf{r}_2, \mathbf{r}'_2) \tilde{P}_{\alpha\beta'}(\mathbf{r}'_2 t_2, \mathbf{x}'_1) \\ &\times \mathcal{W}_{\beta'\beta}(\mathbf{x}'_1, \mathbf{x}_1), \end{aligned} \quad (\text{B23})$$

where

$$\tilde{P}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) = -i\hbar \frac{\delta \mathcal{G}_{\alpha\alpha}(\mathbf{x}_1, \mathbf{x}_1^\dagger)}{\delta V_{\beta}^T(\mathbf{x}_2)}. \quad (\text{B24})$$

$\tilde{P}_{\alpha\beta}$  reduces to the polarizability in the limit  $\phi_L = \phi_R$ . To express  $\tilde{P}_{\alpha\beta}$  in terms of Green function,  $\mathcal{G}_{\alpha\beta}$ , we again make use of Eqs. (B17) and (B21). Equation (B24) then gives

$$\begin{aligned} \tilde{P}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) &= i\hbar \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 \mathcal{G}_{\alpha\alpha'}(\mathbf{x}_1, \mathbf{x}'_1) \mathcal{G}_{\beta'\alpha}(\mathbf{x}'_2, \mathbf{x}_1) \\ &\times \mathcal{L}_{\alpha'\beta'\beta}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_2). \end{aligned} \quad (\text{B25})$$

Finally, the vertex function  $\mathcal{L}_{\alpha\beta\gamma}$  defined in Eq. (B21) can be expressed in terms of the Green functions and the self-energy in a closed form. For this purpose, we start with the Dyson equation (B14). Differentiating with respect to  $V_{\gamma}^T(\mathbf{x}_3)$  gives

$$\frac{\delta \mathcal{G}_{\alpha\beta}^{-1}(\mathbf{x}_1, \mathbf{x}_2)}{\delta V_{\gamma}^T(\mathbf{x}_3)} = \epsilon_{\alpha} \delta_{\alpha\beta} \delta_{\alpha\gamma} \delta(\mathbf{x}_1, \mathbf{x}_2) \delta(\mathbf{x}_1, \mathbf{x}_2) - \frac{\delta \Xi_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2)}{\delta V_{\gamma}^T(\mathbf{x}_3)}. \quad (\text{B26})$$

Substituting Eq. (B26) in (B21), the vertex function can be expressed in a closed form as

$$\begin{aligned} \mathcal{L}_{\alpha\beta\gamma}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) &= \epsilon_{\alpha} \delta_{\alpha\beta} \delta_{\alpha\delta} \delta(\mathbf{x}_1, \mathbf{x}_2) \delta(\mathbf{x}_1, \mathbf{x}_3) \\ &+ \int \int \int \int d\mathbf{x}'_1 d\mathbf{x}'_2 d\mathbf{x}'_3 d\mathbf{x}'_4 \\ &\times \frac{\delta \Xi_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2)}{\delta \mathcal{G}_{\alpha'\delta'}(\mathbf{x}'_1, \mathbf{x}'_2)} \\ &\times \mathcal{G}_{\alpha'\gamma'}(\mathbf{x}'_1, \mathbf{x}'_3) \mathcal{G}_{\delta'\beta'}(\mathbf{x}'_4, \mathbf{x}'_2) \\ &\times \mathcal{L}_{\gamma'\delta'\gamma}(\mathbf{x}'_3, \mathbf{x}'_4, \mathbf{x}_3). \end{aligned} \quad (\text{B27})$$

The Dyson equation (B14) together with Eqs. (B19), (B23), (B25), and (B27) provide a closed, self-consistent prescription for calculating the Liouville space generalized Green functions,  $\mathcal{G}_{\alpha\beta}$ .

### APPENDIX C: CONNECTION WITH HILBERT SPACE GREEN FUNCTIONS

We demonstrate the equivalence of the Liouville space and the Hilbert space Green functions.  $G_{\alpha\beta}$  are identical to the Hilbert space Keldysh Green functions.<sup>40</sup> Standard

NEGF theory is formulated in terms of four Hilbert space Green functions: time ordered ( $G^T$ ), antitime ordered ( $G^{\bar{T}}$ ), greater ( $G^>$ ), and lesser ( $G^<$ ).<sup>30,36</sup> These are defined in the Heisenberg picture as

$$\begin{aligned} G^T(t_1, t_2) &\equiv -\frac{i}{\hbar} \langle T \hat{\psi}(t_1) \hat{\psi}^\dagger(t_2) \rangle \\ &= -\frac{i}{\hbar} \theta(t_1 - t_2) \langle \hat{\psi}(t_1) \hat{\psi}^\dagger(t_2) \rangle + \theta(t_2 - t_1) \\ &\quad \times \langle \hat{\psi}^\dagger(t_2) \hat{\psi}(t_1) \rangle, \\ G^{\bar{T}}(t_1, t_2) &\equiv -\frac{i}{\hbar} \langle \bar{T} \hat{\psi}(t_1) \hat{\psi}^\dagger(t_2) \rangle \\ &= -\frac{i}{\hbar} \theta(t_2 - t_1) \langle \hat{\psi}(t_1) \hat{\psi}^\dagger(t_2) \rangle + \theta(t_1 - t_2) \\ &\quad \times \langle \hat{\psi}^\dagger(t_2) \hat{\psi}(t_1) \rangle, \\ G^>(t_1, t_2) &\equiv -\frac{i}{\hbar} \langle \hat{\psi}(t_1) \hat{\psi}^\dagger(t_2) \rangle, \end{aligned} \quad (\text{C1})$$

$$G^<(t_1, t_2) \equiv \frac{i}{\hbar} \langle \hat{\psi}^\dagger(t_2) \hat{\psi}(t_1) \rangle.$$

$T(\bar{T})$  is the Hilbert space time (antitime) ordering operator: When applied to a product of operators, it reorders them in ascending (descending) times from right to left.

The four Liouville space Green functions are

$$\begin{aligned} G_{LL}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle T \hat{\psi}_L(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rangle, \\ G_{RR}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle T \hat{\psi}_R(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rangle, \\ G_{LR}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle T \hat{\psi}_L(\mathbf{x}) \hat{\psi}_R^\dagger(\mathbf{x}') \rangle, \\ G_{RL}(\mathbf{x}, \mathbf{x}') &= -\frac{i}{\hbar} \langle T \hat{\psi}_R(\mathbf{x}) \hat{\psi}_L^\dagger(\mathbf{x}') \rangle. \end{aligned} \quad (\text{C2})$$

To establish the connection between the Liouville space and Hilbert space Green functions we shall convert the superoperators back to ordinary operators by using definitions for the superoperators and their anticommutation relations. For  $G_{LR}$  and  $G_{RL}$ , we obtain

$$\begin{aligned}
G_{LR}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_L(t_1)\hat{\psi}_R^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \left[ \theta(t_1 - t_2) \text{Tr}\{\hat{\psi}_L(t_1)\hat{\psi}_R^\dagger(t_2)\rho\} \right. \\
&\quad \left. - \theta(t_2 - t_1) \text{Tr}\{\hat{\psi}_R^\dagger(t_2)\hat{\psi}_L(t_1)\rho\} \right] \\
&= \frac{i}{\hbar} \text{Tr}\{\hat{\psi}(t_1)\rho\hat{\psi}^\dagger(t_2)\} \\
&= \frac{i}{\hbar} \langle \hat{\psi}^\dagger(t_2)\hat{\psi}(t_1) \rangle \\
&= G^<(\mathbf{x}, \mathbf{x}'),
\end{aligned}
\tag{C3}$$

$$\begin{aligned}
G_{RL}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_R(t_1)\hat{\psi}_L^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \left[ \theta(t_1 - t_2) \text{Tr}\{\hat{\psi}_R(t_1)\hat{\psi}_L^\dagger(t_2)\rho\} \right. \\
&\quad \left. - \theta(t_2 - t_1) \text{Tr}\{\hat{\psi}_L^\dagger(t_2)\hat{\psi}_R(t_1)\rho\} \right] \\
&= \frac{i}{\hbar} \text{Tr}\{\hat{\psi}^\dagger(t_2)\rho\hat{\psi}(t_1)\} \\
&= \frac{i}{\hbar} \langle \hat{\psi}(t_1)\hat{\psi}^\dagger(t_2) \rangle \\
&= -G^>(t_1, t_2),
\end{aligned}$$

where  $\rho = |n\rangle\langle n|$  is the fully interacting density matrix in terms of the many-body states  $|n\rangle$ .

For  $G_{LL}$  and  $G_{RR}$  we need to distinguish between the following two cases:

(i) For  $t_1 > t_2$ , we get

$$\begin{aligned}
G_{LL}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_L(t_1)\hat{\psi}_L^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \text{Tr}\{\hat{\psi}(t_1)\hat{\psi}^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \langle \hat{\psi}(t_1)\hat{\psi}^\dagger(t_2) \rangle, \\
G_{RR}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_R(t_1)\hat{\psi}_R^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \text{Tr}\{\rho\hat{\psi}^\dagger(t_2)\hat{\psi}(t_1)\} \\
&= -\frac{i}{\hbar} \langle \hat{\psi}^\dagger(t_2)\hat{\psi}(t_1) \rangle.
\end{aligned}
\tag{C4}$$

(ii) For the reverse case,  $t_1 < t_2$ , we get

$$\begin{aligned}
G_{LL}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_L(t_1)\hat{\psi}_L^\dagger(t_2)\rho\} \\
&= \frac{i}{\hbar} \text{Tr}\{\hat{\psi}^\dagger(t_2)\hat{\psi}(t_1)\rho\} = \frac{i}{\hbar} \langle \hat{\psi}^\dagger(t_2)\hat{\psi}(t_1) \rangle, \\
G_{RR}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_R(t_1)\hat{\psi}_R^\dagger(t_2)\rho\} \\
&= \frac{i}{\hbar} \text{Tr}\{\rho\hat{\psi}(t_1)\hat{\psi}^\dagger(t_2)\} = \frac{i}{\hbar} \langle \hat{\psi}(t_1)\hat{\psi}^\dagger(t_2) \rangle.
\end{aligned}
\tag{C5}$$

Combining Eqs. (C4) and (C5) we can write

$$\begin{aligned}
G_{LL}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_L(t_1)\hat{\psi}_L^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \left[ \theta(t_1 - t_2) \langle \hat{\psi}(t_1)\hat{\psi}^\dagger(t_2) \rangle - \theta(t_2 - t_1) \right. \\
&\quad \left. \times \langle \hat{\psi}^\dagger(t_2)\hat{\psi}(t_1) \rangle \right] \\
&= G^T(t_1, t_2), \\
G_{RR}(t_1, t_2) &\equiv -\frac{i}{\hbar} \text{Tr}\{\mathcal{T}\hat{\psi}_R(t_1)\hat{\psi}_R^\dagger(t_2)\rho\} \\
&= -\frac{i}{\hbar} \left[ \theta(t_1 - t_2) \langle \hat{\psi}^\dagger(t_2)\hat{\psi}(t_1) \rangle - \theta(t_2 - t_1) \right. \\
&\quad \left. \times \langle \hat{\psi}(t_1)\hat{\psi}^\dagger(t_2) \rangle \right] \\
&= -G^{\bar{T}}(t_1, t_2).
\end{aligned}
\tag{C6}$$

Equations (C3) and (C6) establish the equivalence of the Hilbert and Liouville space Green functions.

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