Nonequilibrium superoperator Green's function approach to inelastic resonances in STM currents

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(Received 29 May 2005; revised manuscript received 11 January 2006; published 5 May 2006)

Closed expressions for tunneling currents in molecular junctions are derived to the fourth-order in electron-phonon coupling. The Keldysh-Schwinger formalism is recast in terms of density matrices in Liouville space, and the calculation only involves forward propagation in real time and is represented by the double sided Feynman diagrams commonly used for computing optical response functions. The current is related to the decay of coherences in Fock space between many-body molecular states with N and $N \pm 1$ electrons. Application is made to the fundamental and overtone vibrational resonances of methane.

I. INTRODUCTION

Scanning tunneling microscopy (STM) is a sensitive tool for characterizing the electronic structure of surfaces and adsorbates. The remarkable precision with which single atoms and molecules can be imaged[1–4] and manipulated[5–7] has been clearly demonstrated time and again. There has been much interest in the simulation of electronic transport in STM junctions[8–10] and molecular wires.[11] Tersoff and Hamann (TH) (Ref. 12) adopted the electron tunneling formulation of Bardeen and Cohen *et al.*[13,14] to compute the STM images of molecules on surfaces. The STM tip was approximated by a spherical potential well and the conductance was assumed to be proportional to the density of states (DOS) of the surface at the tip position. Owing to its simple structure, the TH approach, which neglects many-body interactions in the tunneling region, has been widely used. An alternative single-body approach to elastic STM currents[15–18] describes the tunneling as scattering of electrons by the defect (vacuum gap) in the periodic structure of the surface and the tip. The transmission probability for electrons to scatter between a tip and a surface channel with the same energy depends on the corresponding scattering matrix element, and the current is calculated via the Landauer-Buttiker (LB) formula.[19,20] Inelastic scattering has been included phenomenologically by introducing an imaginary self-energy in the elastic transmission probability.[18]

Vibrational spectroscopy of molecules absorbed on metal surfaces reveals their bonding environment through inelastic electron tunneling (IET) resonances in STM currents.[3,4,21,22] The tunneling electrons exchange energy with the phonons, opening up inelastic channels for electron transmission from the tip to the surface. Predicting IET resonances in molecular wires and STM junctions[20] has received considerable theoretical attention.[10,23–26] Nonequilibrium Green's function theory (NEGFT) (Refs. 27–29) provides a formally exact framework for computing elastic and inelastic currents.[20] It involves the self-consistent computation of various nonequilibrium Green's functions whose self-energies account for all interactions. Caroli *et al.*[30] were the first to use that approach to compute the current in a one-dimensional metal-insulator-metal junction. Many applications have subsequently been made to molecular or atomic wire configurations.[25,31–33] Recently, Lorente and Persson[34] have extended the TH approach by including the phonon corrections to the total conductance perturbatively to second order in the electron-phonon coupling using the NEGF formulation. This calculation predicts the discontinuities in the conductance as the voltage, eV, is scanned across a phonon energy, $\hbar\Omega$.

The standard NEGFT is based on the Schwinger-Keldysh time loop[29] which includes both forward and backward time propagations. In this paper we develop a nonequilibrium superoperator Green's function theory (NESGFT) (Refs. 35–37) in real time. The present formalism, which is based on the density matrix and its evolution in Liouville space, lends itself more easily to physical intuition and establishes a formal connection between the calculation of molecular currents and nonlinear optical spectroscopy.[38] The inelastic contribution to the tunneling current due to the molecular vibrations is computed as a function of the applied bias and shows both the fundamental and overtone vibronic peaks.

All observables of a system whose coupling to a classical external field E is given by $E(t) \cdot A$, where A is an operator, can be expressed in terms of ordinary (linear or nonlinear) response functions. Dynamical properties of two systems interacting via a direct-product coupling of the form $\lambda A \cdot B$ can be calculated by adiabatically switching their interaction, starting with the noninteracting system at $t \to -\infty$. In that case the ordinary response functions of the two systems do not carry all the necessary information and all observables can be expressed in terms of *generalized response functions* (GRF) of both systems.[39,40] This may be most clearly seen by formulating the problem in Liouville space: An ordinary response function is a specific combination of more elementary quantities, known as *Liouville space pathways* (LSP). The GRF are various combinations of the LSP. Intermolecular forces have been expressed using GRF,[41,42] generalizing the McLachlan's[43] expressions for van der Waals forces to all orders. We extend the same approach to open systems where we allow for charge transfer between the two subsystems, resulting in molecular currents. The four Hilbert space Green's functions (retarded, advanced, lesser, and greater), commonly used in standard NEGFT,[28] appear naturally in Liouville space as a consequence of the time ordered inter-

actions of field operators with the ket and bra of the density matrix, responsible for its forward evolution in real (physical) time. Each time-ordered evolution sequence of the system constitutes a distinct LSP. Keldysh Green's functions are obtained directly in real time as combinations of different LSPs. We provide physical interpretation for the various contributions to the second derivative of the tunneling current with respect to the applied bias and generalize the expressions of Lorente and Persson[34] to fourth order in electron-phonon coupling, to reveal vibrational overtones in the IET spectrum.

The paper is organized as follows: In the next section we present the model Hamiltonian for the tunneling process and introduce the Liouville space superoperators. In Sec. III, the tunneling current is expressed in terms of Liouville space Green's functions. The IET spectrum is computed perturbatively to fourth order in electron-phonon coupling in Sec. IV. Applications to methane are discussed in Sec. V. We conclude in Sec. VI with a discussion.

II. LIOUVILLE SPACE CALCULATION OF MOLECULAR CURRENTS

The STM setup consisting of a metal tip and a substrate (a molecule adsorbed on a metal surface) can be described by the total Hamiltonian,[30,31,44,45]

$$H_T = H_t + H_s + H_{ts}. \tag{1}$$

where the three terms represent the tip, the substrate, and their coupling. The isolated tip Hamiltonian is

$$H_t = \sum_\mu \epsilon_\mu \psi^\dagger{}_\mu \psi_\mu, \tag{2}$$

where ϵ_μ are the orbital energies. We use Latin (i,j,k,l) and Greek (μ,ν,η,κ) indices to represent the substrate and the tip orbitals, respectively. $\psi_\mu(\psi_i)$ are the Fermi annihilation operators which satisfy the anticommutation relations,

$$\{\psi^\dagger_p, \psi_q\} = \delta_{pq}, \quad \{\psi^\dagger_p, \psi^\dagger_q\} = \{\psi_p, \psi_q\} = 0, \quad p,q = i,j,\mu,\eta. \tag{3}$$

The substrate Hamiltonian is

$$H_s = \sum_i \epsilon_i \psi^\dagger_i \psi_i + \sum_m \hbar \, \Omega_m \phi^\dagger_m \phi_m + \sum_{ijm} \lambda^m_{ij} \psi^\dagger_i \psi_j (\phi_m + \phi^\dagger_m), \tag{4}$$

where Ω_m is the frequency of mth phonon mode. $\phi_m(\phi^\dagger_m)$, the annihilation (creation) operators for the mth phonon mode, satisfy the boson commutation relations

$$[\phi_m, \phi^\dagger_n] = \delta_{mn}, \quad [\phi_m, \phi_n] = [\phi^\dagger_m, \phi^\dagger_n] = 0, \tag{5}$$

and λ^m_{ij} is the electron-phonon coupling.

$$H_{ts} = \sum_{i\mu} (V_{i\mu} \psi^\dagger{}_i \psi_\mu + V_{\mu i} \psi^\dagger{}_\mu \psi_i) \tag{6}$$

is the tip-substrate coupling where $V_{\mu i}$ are the tunneling matrix elements. The current across the STM junction through the ith substrate orbital is described by the operator,

$$J_i = \frac{ie}{\hbar} \sum_\mu [V_{i\mu} \psi^\dagger{}_i \psi_\mu - V_{\mu i} \psi^\dagger{}_\mu \psi_i]. \tag{7}$$

The current passing through the ith substrate orbital at time t, $I_i(t)$ is obtained by taking the trace of J_i with respect to the density matrix $[\rho(t)]$ of the coupled system and the total current is given by summing over all substrate states,

$$I(t) = \sum_i \text{Tr}\{J_i \rho(t)\} = \sum_i I_i(t). \tag{8}$$

The current will be calculated using time-ordered superoperator Green's functions in Liouville space.[35,36,38] We briefly review the properties of superoperators. With each Hilbert space Fermi operator, $\psi(\psi^\dagger)$, we associate two Liouville space superoperators, "left" $(\psi_L(\psi^\dagger_L))$ and "right" $(\psi_R(\psi^\dagger_R))$, defined through their action on some Hilbert space operator $|m\rangle\langle n|$,[46]

$$\psi_L|m\rangle\langle n| \equiv \psi|m\rangle\langle n|, \quad \psi^\dagger_L|m\rangle\langle n| \equiv \psi^\dagger|m\rangle\langle n|,$$

$$\psi_R|m\rangle\langle n| \equiv (-1)^{m+n}|m\rangle\langle n|\psi, \tag{9}$$

$$\psi^\dagger_R|m\rangle\langle n| \equiv (-1)^{(m+n+1)}|m\rangle\langle n|\psi^\dagger,$$

where $|m\rangle$ is an eigenstate of the number operator with m electrons with the sign convention in Eq. (9). ψ_L and ψ_R satisfy the same anticommutation rules as their Hilbert space counterparts,

$$\{\psi_{p\alpha}, \psi^\dagger_{q\beta}\} = \delta_{\alpha\beta}\delta_{pq}, \quad \{\psi^\dagger_{p\alpha}, \psi^\dagger_{q\beta}\} = \{\psi_{p\alpha}, \psi_{q\beta}\} = 0. \tag{10}$$

We further define the linear combinations of "left" and "right" superoperators corresponding to any function A of Fermi operators,

$$A^+ = \frac{1}{2}(A_L + A_R),$$

$$A^- = A_L - A_R. \tag{11}$$

One notable advantage of the $+/-$, compared to the L/R representation, is the more natural bookkeeping of causal and noncausal functions.[47] An important tool used in the following manipulations is the time-ordering operator in Liouville space, $\mathcal{T}$; when acting on a product of superoperators, it reorders them so that time increases from right to left.[46]

Since the trace of a product of operators is invariant to a cyclic permutation, we can recast the expectation value of J_i, Eq. (7), using the $+$ operator

$$I_i(t) = \text{Tr}\{J^+_i \rho(t)\}. \tag{12}$$

We shall evaluate Eq. (12) following the procedure of Caroli et al.[30] whereby the junction is biased at $t \to -\infty$, and the tip-substrate coupling is adiabatically switched on. Using the interaction picture representation in Liouville space,[35,41] $\rho(t)$ can be obtained from $\rho(t_0)$ using the adiabatic connection formula,[35]

$$\rho(t) = \mathcal{G}_0(t,t_0)\mathcal{G}_I(t,t_0)\rho(t_0), \tag{13}$$

with

$$\mathcal{G}_0(t,t_0) = \mathcal{T}\exp\left\{-\frac{i}{\hbar}\int_{t_0}^t \tilde{H}^-(\tau)\right\},$$

$$\mathcal{G}_I(t,t_0) = \mathcal{T}\exp\left\{-\frac{i}{\hbar}\int_{t_0}^t d\tau \tilde{H}_{ts}^-(\tau)\right\}, \quad (14)$$

where $H = H_t + H_s$ represent the noninteracting tip and the substrate, and H^- and H_{ts}^- are the superoperators corresponding to H and H_{ts}, respectively. $\tilde{A}_{i\alpha}(t)$ denotes the superoperator $A_{i\alpha}$ in the interaction picture,

$$\tilde{A}_{i\alpha}(t) = \mathcal{G}_0^\dagger(t,t_0)A_{i\alpha}(t_0)\mathcal{G}_0(t,t_0). \quad (15)$$

Equation (15) also holds for $+/-$ superoperators. Using Eqs. (12), (13), and (15), and setting $t_0 \to -\infty$, we obtain

$$I_i(t) = \left\langle \mathcal{T}\tilde{J}_i^+(t)\exp\left[-\frac{i}{\hbar}\int_{-\infty}^t d\tau \tilde{H}_{ts}^-(\tau)\right]\right\rangle_0, \quad (16)$$

where $\langle A_{i\alpha}(t)\rangle_0 = \text{Tr}\{A_{i\alpha}(t)\rho(t\to-\infty)\}$ denotes an expectation value with respect to the noninteracting substrate/tip density matrix with $\alpha = (L,R)$ or $(+,-)$. Equation (16) will be used in the calculation of the current.

III. GREEN'S FUNCTION EXPRESSION FOR THE TUNNELING CURRENT

The tip and the substrate are initially decoupled and the density matrix $\rho(t\to-\infty)$ is given by the direct product of density matrices for the free tip and the free substrate. We shall first expand the exponential in Eq. (16) perturbatively in $\tilde{H}_{ts}^-$ (adiabatic switching). At steady state, the current is independent on time. In each order we can factorize the product of operators into tip and substrate Green's functions. To second order in V, the current through the ith state of the substrate is given by

$$I_i \equiv \langle J_i^+\rangle = e\int dt \sum_{j\mu\eta} V_{i\mu}V_{j\eta}[G_{LL}^{0ij}(t)G_{LL}^{0\mu\eta}(-t) - G_{LL}^{0\eta\mu}(t)$$
$$\times G_{LL}^{0ji}(-t) - G_{LR}^{0ij}(t)G_{RL}^{0\mu\eta}(-t) + G_{LR}^{0\eta\mu}(t)G_{RL}^{0ji}(-t)], \quad (17)$$

where the Green's function, $G_{\alpha\beta}^{0mn}(t,t')$, is defined as

$$G_{\alpha\beta}^{0mn}(t,t') \equiv -\frac{i}{\hbar}\langle\mathcal{T}\tilde{\psi}_{m\alpha}(t)\tilde{\psi}_{n\beta}^\dagger(t')\rangle_0. \quad (18)$$

When the total current is calculated by summing Eq. (17) over i we find (see Appendix A) that the G_{LL} contributions vanish. We transform to the frequency domain

$$G_{\alpha\beta}(E) = \int dt G_{\alpha\beta}(t)\exp\left\{\frac{i}{\hbar}Et\right\}, \quad \alpha,\beta = L,R. \quad (19)$$

To derive an approximate nonperturbative expression for the current we replace all zero-order Green's functions G^0 by the actual Green's functions G which include tip-substrate and electron-phonon self-energies. Equation (17) then gives

$$I = \frac{e}{2\pi\hbar}\int dE\sum_{ij\mu\eta} V_{i\mu}V_{j\eta}[G_{LR}^{\eta\mu}(E)G_{RL}^{ji}(E) - G_{LR}^{ij}(E)G_{RL}^{\mu\eta}(E)], \quad (20)$$

where $G_{\alpha\beta}^{ij}$ and $G_{\alpha\beta}^{\mu\eta}$ are the substrate and tip Green's functions, respectively.

We next use the fluctuation-dissipation relation (Appendix B) to express the tip Green's functions in terms of its density of states (DOS), $\rho_{\mu\eta}$ [Eq. (B10)]. We further assume that $\rho_{\mu\eta}$ is independent of energy to obtain

$$I = \frac{ie}{\hbar}\sum_{ij\mu\eta}\rho_{\mu\eta}V_{\eta i}V_{\mu j}\int dE[f(E+eV)G_{RL}^{ji}(E)$$
$$- (1 - f(E+eV))G_{LR}^{ij}(E)], \quad (21)$$

where $f(E)$ is the Fermi distribution function

$$f(E) = \frac{1}{1 + \exp[\beta(E-E_F)]} \quad (22)$$

and E_F is the tip Fermi energy. An alternative derivation of Eq. (21), based on an equation of motion technique, is given in Appendix C.

Equation (21) can be understood using the double-sided Feynman diagrams shown in Fig. 1. G_{LR} and G_{RL} correspond to processes that change the number of electrons in the molecule. The first term inside the brackets in Eq. (21) represents electron transfer from an occupied state of the tip at energy $E+eV$ to the substrate, hence the Fermi function $f(E+eV)$. The second term represents the reverse process which must involve an unoccupied tip state, ensured by the multiplicative factor $[1-f(E+eV)]$. This interpretation comes naturally in the real-time Liouville space picture but is harder to see in the Hilbert space Keldysh loop which involves a backward propagation. It is also clear from the diagrams why G_{LL} and G_{RR} do not contribute to the total current. These Green's functions represent a virtual charge transfer process where a coherence is created in Fock space and is then destroyed; the number of electrons in the substrate does not change.

At zero temperature, Eqs. (21) and (22) give for the derivative of the total current with respect to the applied bias

$$\frac{dI}{dV} = \frac{e^2}{2\hbar}\sum_{ij\mu\eta}\rho_{\mu\eta}V_{\eta i}V_{\mu j}[A_{ij}(E_F-eV) + A_{ji}(E_F-eV)], \quad (23)$$

where

$$A_{ij}(E) \equiv -i[G_{RL}^{ij}(E) + G_{LR}^{ij}(E)]. \quad (24)$$

The Green's functions $G_{\alpha\beta}, (\alpha,\beta=L,R)$ satisfy a 2×2 matrix Dyson equation given in Appendix D. By transforming to the $+/-$ representation, we find that the conductance, Eq. (23), can be calculated in terms of G^- and G^+ alone (see Appendix E)
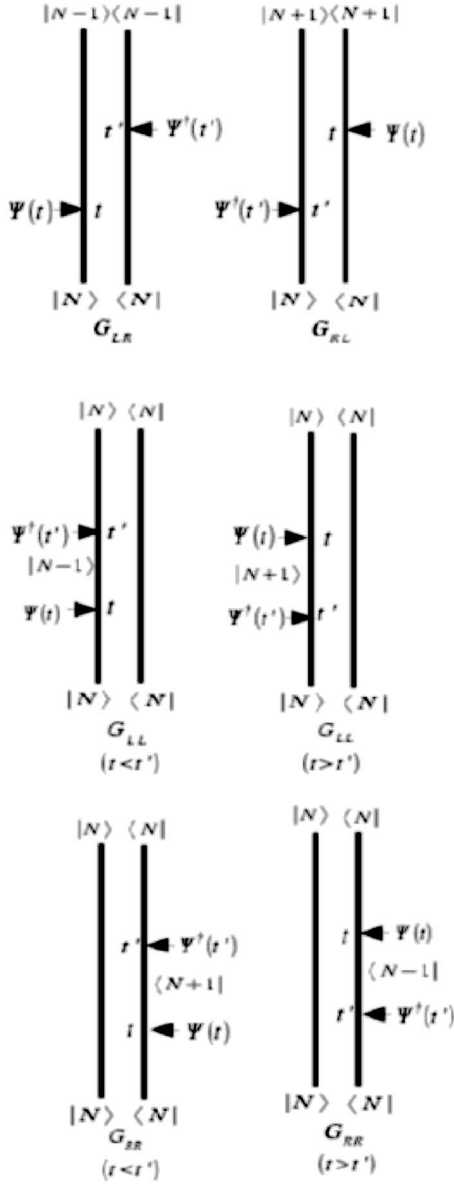
FIG. 1. Double-sided Feynman diagrams for the four Liouville space substrate Green's functions. Time moves from bottom to top. $|N\rangle\langle N|$ denotes a many electron density matrix of the substrate with N electrons. G_{LR} and G_{RL} represent processes where the final states are negatively and positively charged, reflecting the transfer of an electron and a hole from the tip to the substrate, respectively. G_{LL} and G_{RR} represent virtual processes where no real electron transition takes place and the number of elctrons in the substrate remains the same.

$$A(E) = 2\pi\left[\rho_0 + 2\rho_0\,\mathrm{Re}\{\Sigma^{--}G^{--}\} + G^{--}\Sigma^{--}\rho_0\Sigma^{++}G^{++}\right.$$

$$\left. - \frac{1}{\pi}G^{--}\,\mathrm{Im}\{\Sigma^{--}\}G^{++}\right], \tag{25}$$

where $\rho_0 = (G^0_{LR}+G^0_{RL})/2i\pi$ represents the electronic DOS of the free substrate. The DOS can be expressed in terms of the Kohn-Sham orbitals and energies as

$$\rho_0(\mathbf{r},\mathbf{r}',E) = \frac{1}{\pi}\sum_i \langle\mathbf{r}|i\rangle\langle i|\mathbf{r}'\rangle \frac{\sigma_{ii}}{(E-\epsilon_i)^2 + \sigma_{ii}^2}. \tag{26}$$

$\langle\mathbf{r}|i\rangle$ is the substrate orbital in the coordinate representation and $\sigma_{ii} = 2\pi\Sigma_\mu|V_{\mu i}|^2$ is the imaginary part of the retarded self-energy (wide band approximation) due to electrode-molecule coupling.

The Dyson equations for the retarded G^{--} and the advanced G^{++} Green's functions are decoupled,

$$G^{--} = G^{--}_0 + G^{--}_0\Sigma^{--}G^{--}, \tag{27}$$

$$G^{++} = G^{++}_0 + G^{++}_0\Sigma^{++}G^{++}, \tag{28}$$

and the advanced and retarded functions are related by, $G^{++} = [G^{--}]^\dagger$ and $\Sigma^{++} = [\Sigma^{--}]^\dagger$. The reference Green's function G^{--}_0 includes the tip-substrate coupling and can be expressed in terms of Kohn-Sham substrate energies and orbitals (Appendix E)

$$G^{--}_0(\mathbf{r},\mathbf{r}',E) = \sum_i \frac{\langle\mathbf{r}|i\rangle\langle i|\mathbf{r}'\rangle}{E - \epsilon_i + i\sigma_{ii}}. \tag{29}$$

The retarded self-energy Σ^{--} is expressed in terms of the electron and phonon Green's functions (Appendix F)

$$\Sigma^{--}_{ij}(E) = i\int\frac{dE'}{2\pi}\sum_{mni'j'}\lambda^m_{ii'}\lambda^n_{jj'}[D^{mn}_{LR}(E-E')G^{--}_{i'j'}(E')$$

$$- D^{--}_{mn}(E-E')G^{i'j'}_{RL}(E')], \tag{30}$$

with $\Phi_{m\alpha} = \phi_{m\alpha} + \phi^\dagger_{n\alpha}$, and $D^{--}_{mn} = D^{mn}_{LL} - D^{mn}_{LR}$ is the retarded phonon Green's function, where

$$D^{mn}_{\alpha\beta}(t,t') = -\frac{i}{\hbar}\langle\mathcal{T}\Phi_{m\alpha}(t)\Phi^\dagger_{n\beta}(t')\rangle. \tag{31}$$

These will be calculated in the next section.

IV. THE INELASTIC RESONANCES

When the electron-phonon interaction is switched off ($\Sigma=0$), $A(E)=2\pi\rho_0(E)$, and Eq. (23) reduces to the Tersoff-Hamann[12] expression. By expanding the self-energies, Σ^{--} and Σ^{++}, and the corresponding Green's functions perturbatively in electron-phonon coupling, we can study its effect on the tunneling current.

We shall compute the retarded self-energy due to phonons Σ^{--}, Eq. (30), and electron Green's functions to fourth order in electron-phonon coupling. We ignore the effect of electron-phonon interaction in the phonon Green's functions and use the zeroth-order result[31]

$$D^{--}_{0mn}(E) = \delta_{mn}\left[\frac{1}{E-\hbar\Omega_m+i\eta} - \frac{1}{E+\hbar\Omega_m+i\eta}\right], \tag{32}$$

$$D^{mn}_{0LR}(E) = -2\pi i\delta_{mn}\{N(\Omega_m)\delta(E-\hbar\Omega_m) + [1+N(\Omega_m)]$$

$$\times\delta(E+\hbar\Omega)\}, \tag{33}$$

where $N(\Omega_m) = [\exp(\hbar\Omega_m/k_BT)-1]^{-1}$ is the boson distribu-

tion function and η is a positive infinitesimal real number. Using the fluctuation-dissipation relation, Eq. (B11), at zero temperature, the imaginary part of the self-energy is obtained as $\Sigma''_{ij} = W^{(2)}_{ij} + W^{(4)}_{ij}$, where $W^{(n)}$ represents the self-energy to nth order in electron-phonon coupling λ^m_{ij}, with

$$W^{(2)}_{ij}(E) = -\pi \sum_{i'j'm} \lambda^m_{ii'} \lambda^m_{jj'} [\rho^{i'j'}_0 (E + \hbar\Omega_m)\theta(E + \hbar\Omega_m - E_F)$$

$$+ \rho^{i'j'}_0 (E - \hbar\Omega_m)\theta(E - \hbar\Omega_m - E_F)], \qquad (34)$$

$$W^{(4)}_{ij}(E) = -\pi \,\mathrm{Re} \sum_{mn} \sum_{i'j'k'l'} \lambda^m_{ii'} \lambda^m_{i'j} \lambda^n_{j'l'} \lambda^n_{k'l'} [\theta(E - \hbar\Omega_m - E_F)$$

$$\times \theta(E - \hbar\Omega_{mn} - E_F) G^{--}_{0i'j'}(E - \hbar\Omega_m)$$

$$\times \rho_{0l'l'}(E - \hbar\Omega_{mn}) G^{--}_{0k'i'}(E - \hbar\Omega_m)$$

$$+ \theta(E_F - \hbar\Omega_m - E)$$

$$\times \theta(E_F - \hbar\Omega_{mn} - E) G^{--}_{0i'j'}(E + \hbar\Omega_m)$$

$$\times \rho_{0l'l'}(E + \hbar\Omega_{mn}) G^{--}_{0k'i'}(E + \hbar\Omega_m)], \qquad (35)$$

where $\Omega_{mn} = \Omega_m + \Omega_n$.

$W^{(2)}$ contains discontinuities at $E = E_F \pm \hbar\Omega_m$ while $W^{(4)}$ has additional singularities at $E = E_F \pm \hbar\Omega_{mn}$, which give vibrational overtones in the IET spectrum. The real part of Σ^{--} is a continuous function of the bias and will be neglected.

Substituting Eqs. (34), (35), and (25) in Eq. (23), we obtain

$$\frac{dI}{dV} = \frac{2\pi e^2}{\hbar} \,\mathrm{Re} \sum_{ij\mu\eta} \rho_{\mu\eta} V_{\mu i} V_{\eta j} \left[\frac{1}{\pi} \delta_{ij} |\langle i|j\rangle| \mathcal{D}_i(E_F - eV) + \sum_m \{Q^m_{ij+}(E_F - eV)\theta(eV - \hbar\Omega_m) + Q^m_{ij-}(E_F - eV)\theta(-eV - \hbar\Omega_m)\} \right.$$

$$+ \sum_{m,n} \{P^{mn}_{ij+}(E_F - eV)\theta(eV - \hbar\Omega_m)\theta(eV - \hbar\Omega_n) + P^{mn}_{ij-}(E_F - eV)\theta(-eV - \hbar\Omega_m)\theta(-eV - \hbar\Omega_n)$$

$$\left. + R^{mn}_{ij+}(E_F - eV)\theta(eV - \hbar\Omega_m)\theta(eV - \hbar\Omega_{mn}) + R^{mn}_{ij-}(E_F - eV)\theta(-eV - \hbar\Omega_m)\theta(-eV - \hbar\Omega_{mn})\} \right], \qquad (36)$$

where the auxiliary functions $Q^m_{ij\pm}$, $P^{mn}_{ij\pm}$, and $R^{mn}_{ij\pm}$ are given by

$$Q^m_{ij\pm}(E) = -\frac{2}{\pi} \sum_k \lambda^m_{ik} \lambda^m_{kj} \mathcal{D}_i(E) \mathcal{D}_j(E) \mathcal{D}_k(E \pm \hbar\Omega_m) + \frac{1}{\pi} \sum_k \frac{\lambda^m_{ik} \lambda^m_{jk}}{(E - \epsilon_i + i\sigma_{ii})(E - \epsilon_j - i\sigma^*_{jj})} \mathcal{D}_k(E \pm \hbar\Omega_m), \qquad (37)$$

$$P^{mn}_{ij\pm}(E) = \frac{2}{\pi} \sum_{i'j'k'} \left[\frac{1}{2} \frac{\lambda^m_{ij'} \lambda^m_{j'i'} \lambda^n_{i'k'} \lambda^n_{k'j} \mathcal{D}_{i'}(E)}{(E - \epsilon_i + i\sigma_{ii})(E - \epsilon_j - i\sigma^*_{jj})} - \mathrm{Re} \left\{ \frac{\lambda^m_{ij'} \lambda^m_{j'i'} \lambda^n_{i'k'} \lambda^n_{k'j} \mathcal{D}_i(E)}{(E - \epsilon_{i'} + i\sigma_{i'i'})(E - \epsilon_j + i\sigma_{jj})} \right\} \right.$$

$$\left. - \mathrm{Im} \left\{ \frac{\lambda^m_{ij'} \lambda^m_{j'i'} \lambda^n_{i'k'} \lambda^n_{k'j}}{(E - \epsilon_i + i\sigma_{ii})(E - \epsilon_{i'} - i\sigma^*_{i'i'})(E - \epsilon_j - i\sigma^*_{jj})} \right\} \mathcal{D}_{j'}(E \pm \hbar\Omega_m) \mathcal{D}_{k'}(E \pm \hbar\Omega_n) \right], \qquad (38)$$

$$R^{mn}_{ij\pm}(E) = \frac{1}{\pi} \sum_{i'j'k'} \lambda^m_{ij'} \lambda^n_{j'i} \lambda^n_{i'k'} \lambda^m_{k'j} \mathcal{D}_{i'}(E \pm \hbar\Omega_{mn}) \mathrm{Re} \left\{ \frac{1}{E - \epsilon_{j'} \pm \hbar\Omega_m + i\sigma_{j'j'}} \frac{1}{E - \epsilon_{k'} \pm \hbar\Omega_m + i\sigma_{k'k'}} \right.$$

$$\left. \times \left(\frac{1}{(E - \epsilon_i + i\sigma_{ii})(E - \epsilon_j - i\sigma^*_{jj})} - 2\mathcal{D}_i(E)\mathcal{D}_j(E) \right) \right\}, \qquad (39)$$

with $\mathcal{D}_i(E) = \sigma_{ii}/[(E - \epsilon_i)^2 + \sigma^2_{ii}]$.

The second derivative of the current with respect to the applied bias is obtained from Eq. (36) by ignoring the voltage dependence of Q^m_{ij}, P^{mn}_{ij}, and R^{mn}_{ij}, since these are smooth functions of V compared to the step functions. We obtain

$$\frac{d^2I}{dV^2} = \frac{2\pi e^3}{\hbar} \,\mathrm{Re} \sum_{ij\mu\eta m} \rho_{\mu\eta} V_{\mu i} V_{\eta j} \left\{ Q^m_{ij+}(E_F - eV)\delta(eV - \hbar\Omega_m) - Q^m_{ij-}(E_F - eV)\delta(eV + \hbar\Omega_m) \right.$$

$$+ \sum_n (P^{mn}_{ij+}(E_F - eV)[\delta(eV - \hbar\Omega_m)\theta(eV - \hbar\Omega_n) + (m \leftrightarrow n)] - P^{mn}_{ij-}(E_F - eV)[\delta(\hbar\Omega_m + eV)\theta(-eV - \hbar\Omega_n) + (m \leftrightarrow n)]$$

$$+ R^{mn}_{ij+}(E_F - eV)[\delta(eV - \hbar\Omega_m)\theta(eV - \hbar\Omega_{mn}) + \delta(eV - \hbar\Omega_{mn})\theta(eV - \hbar\Omega_m)]$$

$$\left. - R^{mn}_{ij-}(E_F - eV)[\delta(eV + \hbar\Omega_m)\theta(-eV - \hbar\Omega_{mn}) + \delta(eV + \hbar\Omega_{mn})\theta(-eV - \hbar\Omega_m)]) \right\}. \qquad (40)$$

Equations (36) and (40) are our final expressions for the current derivatives. Equation (40) contains peaks at $eV = \hbar\Omega_m$ and $eV = \hbar\Omega_{mn}$ whose amplitudes are determined by Q_{ij}^m, P_{ij}^{mn}, and R_{ij}^{mn}, respectively. Similar peaks but with negative amplitude are observed at $eV = -\hbar\Omega_m$. Q_{ij}^m represents single phonon processes, while P_{ij}^{mn} and R_{ij}^{mn} involve two phonon processes. In P_{ij}^{mn}, an electronic transition is accompanied by the absorption (or creation) of a phonon with energy $\hbar\Omega_m$ and the creation (or absorption) of another phonon with energy $\hbar\Omega_n$. In R_{ij}^{mn} both the phonons are either emitted or absorbed during an electronic transition. Note that peaks in IET spectrum corresponding to fundamental molecular vibrations have contributions from the second (Q_{ij}^m) as well as the fourth order terms (P_{ij}^{mn} and R_{ij}^{mn}) while overtone peaks only involve the function R_{ij}^{mn}. Vibrational overtones in the IET spectrum have been observed recently.[48] In the next section we present a numerical simulation of the IET spectrum of methane based on Eqs. (36) and (40).

V. COMPUTATIONAL RESULTS

In this section we examine the inelastic contributions to the electron tunneling current through a single methane molecule and describe the steps leading up to the evaluation of the inelastic conductance Eq. (36) and the IET spectrum Eq. (40). We neglect the details of the STM tip's electronic structure and the contact geometry and focus instead on the inelastic contributions to the current arising from the internal vibrations of an isolated methane molecule. Thus, bouncing and rotational modes which involve the motion of the molecule relative to the surface are not included.

First, the GAUSSIAN 03 package[49] was used to minimize the ground state energy at the Hartree-Fock (HF) level with a 3-21G basis set and obtain the molecular geometry, normal mode frequencies, and atomic displacements. We take the Fermi energy E_F of the system to be at the midpoint between the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals and we set the linewidths $\sigma_{ii} = 0.2$ eV for all orbital energies. An additional Lorentzian line shape with a width of 0.005 eV for all vibrational transition energies is used in place of the delta functions in Eq. (40). The electronic coupling to the STM tip $V_{\eta i}$ and the tip's density of states $\rho_{\mu\eta}$ must also be calculated. The simplest approach follows from the Tersoff-Hamann (TH) theory.[12] The electronic structure of the tip is reduced to a single s-type orbital $|\mathbf{r}_0\rangle$ at the Fermi energy E_F and the electronic coupling elements are proportional to the overlap of $|\mathbf{r}_0\rangle$ with the molecular orbitals of the substrate

$$V_{i\mu} \approx \delta_{\mu\mathbf{r}_0} V_{\mathbf{r}_0} \propto \langle \mathbf{r}_0 | i \rangle = \sum_\alpha c_{i\alpha} \langle \mathbf{r}_0 | \alpha \rangle, \qquad (41)$$

where $c_{i\alpha}$ are the molecular orbital coefficients and $\langle \mathbf{r}_0 | \alpha \rangle$ are the overlap integrals between the tip orbital and the atomic basis functions. In our calculations, we assume that the tip's density of states is constant over the range of applied bias energies. The tip is represented by a ghost atom centered at $\mathbf{r}_0$ bearing a single $1s$ orbital; the overlap with

atomic basis functions for the molecule are then computed and stored. The Q_{ij}^m, P_{ij}^{mn}, and R_{ij}^{mn} factors in Eqs. (36) and (40) depend on the electron-phonon coupling matrices λ^m. In the atomic orbital basis representation the electron-phonon coupling matrix elements are given by[50]

$$\lambda_{\alpha\beta}^m = \sum_n \sqrt{\frac{\hbar}{2M_n\Omega_m}} \Delta_{nm} \cdot \langle \alpha | \nabla_{X_n} H | \beta \rangle, \qquad (42)$$

where the sum runs over all atoms, M_n is the atomic weight of the nth atom, Δ_{nm} is the dimensionless displacement vector of the nth atom for the mth normal mode, and $\nabla_{X_n} H$ is the gradient of the electronic Hamiltonian with respect to the Cartesian coordinates of the nth atom at the equilibrium nuclear configuration. Using the output of our HF calculations, the electron-phonon matrices are calculated according to Eq. (42) and then transformed to the molecular orbital representation.

Using these parameters, the inelastic conductance Eq. (36) and the IETS intensity Eq. (40) were calculated as a function of applied bias for a given tip position. In Fig. 2 we show the inelastic conductance and IETS spectrum. The tip orbital is positioned such that it bisects one of the H-C-H angles at a distance of 2 Å from the carbon atom. Panels (a) and (b) show only the second order contribution to the inelastic conductance and IETS spectrum, respectively. Steps (peak) are found in the conductance (IETS spectrum) when the applied bias energy is resonant with a vibrational transition energy. In contrast, to IR and Raman spectroscopies all nine vibrational modes of methane show some activity in the calculated inelastic tunneling signals. The four peaks seen in the second order IETS arise from single quantum vibrational transitions: the peak at 208 mV is due to the triply degenerate asymmetric C-H bending modes, the peak at 236 mV involves the doubly degenerate C-H scissoring and twisting, the peak at 437 mV comes from the symmetric C-H stretch, and finally the peak at 469 mV is due to the set of triply degenerate asymmetric C-H stretching vibrations. Panels (c) and (d) show the fourth order contribution to the inelastic conductance and IETS spectrum, respectively. The fourth order contribution to the IETS is negligible for the fundamental transitions but exhibits a fairly large intensity when the applied bias energy is resonant with transitions that involve two quanta of vibrational energy: the bending overtones and bending/bending combinations at 416, 444, and 472 mV, the combination of bending and C-H stretching modes with peaks at 645, 673, 677, and 705 mV, and the overtones/combinations of the C-H stretching modes at 874, 906, and 938 mV. Panels (e) and (f) include terms up to fourth order in the electron-phonon coupling.

VI. DISCUSSION

We have employed the Liouville space formulation of nonequilibrium Green's function theory to calculate tunneling currents. NESGFT provides physical insights into the tunneling process in terms of Liouville space pathways. Each
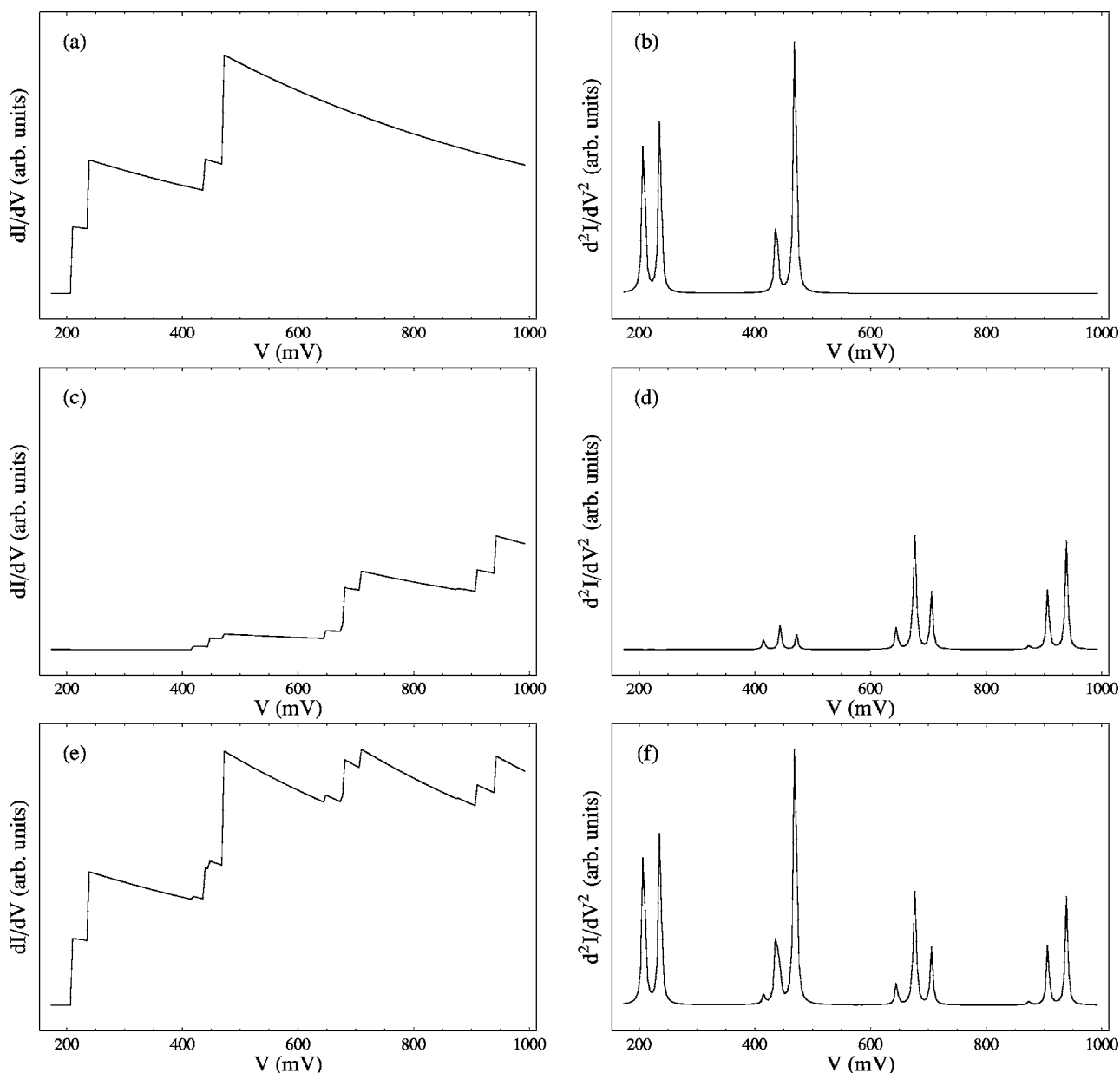
FIG. 2. Calculated conductance Eq. (36) and IETS spectrum Eq. (40) for an isolated molecule of methane. Panels (a) and (b) show only the second order terms in conductance and IETS spectra, respectively, which give rise to steps/peaks at the fundamental vibrational transition energies. Panels (c) and (d) show only the fourth order component which exhibit moderate intensity for several of the combination and overtone transition energies. Panels (e) and (f) show the conductance and IETS spectrum, respectively, which include both the second and fourth terms in the electron-phonon coupling.

pathway represents a physical, real-time sequence of interactions involving either the ket or the bra of the density matrix. The four Hilbert space Green's functions of standard NEGFT appear naturally in NESGFT using a single time-ordering operation without resorting to any artificial time variables, as required in the Hilbert space formulation.

Equation (36) is a generalization of Lorente and Persson's[34] result for the differential conductance. To recover their result, we first ignore the self-energy η_i so that $\mathcal{D}_i(E) \rightarrow \pi \delta(E - \epsilon_i)$, and neglect the fourth order terms in λ_{ij}^m, $P_{ij}^{mn} = 0$ in Eq. (36). This gives

$$
\begin{aligned}
\frac{dI}{dV} = \frac{2\pi e^2}{\hbar} \sum_{ij\mu\eta} \rho_{\mu\eta} V_{\mu i} V_{\eta j} \Bigg[& \delta_{ij} |\langle i|j\rangle| \delta(E_F + eV - \epsilon_i) \\
& + \sum_m \mathrm{Re}\{Q_{ij+}^m(E_F - eV)\,\theta(eV - \hbar\Omega_m) + Q_{ij-}^m(E_F - eV) \\
& \times \theta(-eV - \hbar\Omega_m)\} \Bigg].
\end{aligned}
\tag{43}
$$

We further assume a single phonon mode with frequency Ω and a single tip orbital (s-wave) coupled to one isoenergetic

substrate orbital, so that $\rho_{\mu\eta} = \delta_{\mu\eta}$ and $V_{i\mu} \sim \langle i|\mu\rangle\delta(\epsilon_i - \epsilon_\mu)$. Equation (43) then takes the form,

$$\frac{dI}{dV} \sim \sum_i |\langle\mu|i\rangle|^2\delta(E_F - eV - \epsilon_i) + Q_+(E_F - eV)\theta(eV - \hbar\Omega)$$
$$+ Q_-(E_F - eV)\theta(-eV - \hbar\Omega). \tag{44}$$

The first term on the RHS is simply the projected density of state $[\rho_{i\mu}(E_F - eV)]$ of the substrate on the tip orbital (μ) and is independent on the phonons. The other two terms depend on electron-phonon interaction. Ignoring the phonon contributions, we recover the Tersoff-Hamann[12] result for the derivative of current, $dI/dV \sim \rho_{ik}(E_F - eV)$. Under these approximations, the functions $Q_\pm$ are obtained from $Q_{ij\pm}^m$ as

$$Q_\pm(E) = -2\pi^2\sum_j \left|\sum_i \lambda_{ij}\langle i|\mu\rangle\delta(\epsilon_i - \epsilon_j \pm \hbar\Omega)\right|^2\delta(\epsilon_\mu - \epsilon_i)$$
$$+ \sum_j \left|\sum_i \frac{\lambda_{ij}\langle i|\mu\rangle}{E - \epsilon_i - i\eta}\right|^2\delta(E \pm \hbar\Omega - \epsilon_j). \tag{45}$$

Equations (44) and (45) were obtained by Lorente $et\ al.$[34]

In Eq. (32) we have ignored the self-energy in the phonon Green's functions, implying that the tunneling electrons interact with the equilibrium phonon distribution throughout the process. This is justified provided the electron residence time in the tunneling region is short compared to the phonon response time, and the tunneling rate is small compared to the decay rate of the excited phonon states so that incoming electrons feel the same equilibrium phonon bath. The treatment of nonequilibrium phonon bath requires a full self-consistent calculation in both electron and phonon Green's functions which is relevant to the "molecular wire" configuration where the molecule is more strongly coupled to two leads and the tunneling rate of electrons can be comparable to the phonon relaxation time scale. This simplification leads to the dependence of the electronic DOS in Eq. (34) on Ω_m (frequency of mth phonon mode). Using the complete Green's functions [Eq. (30)] the electronic DOS depends on all phonon modes in a more complex way.

Neglecting the self-energy in the phonon Green's functions greatly simplifies the calculation. One can then easily estimate the effect of broadening in the electronic system due to the coupling with equilibrium phonon bath and its consequences on the tunneling current. This can be achieved via a self-consistent calculation[26] for the retarded electronic Green's function, Eq. (29), together with the self-energy given in Eq. (34) after replacing ρ_0 with full density of states (ρ). Using the retarded Green's function and self-energy, one can directly compute A_{ij} in Eq. (25), and hence the differential conductance from Eq. (23).

In the present work, as in the TH approximation, we have ignored the bias dependence of electronic orbitals and energies. Its only effect is to shift the relative chemical potentials of the tip and the substrate. However the large local electric field in the point contact regime, where the tip is close to the substrate (4–5 Å),[24] can perturb the local electronic structure. The effect of bias on the molecular orbitals and energies can be incorporated in a self-consistent $ab\ initio$ electronic structure calculation. Performing a self-consistent calculation for each applied bias is computationally expensive. Yang[51] has recently proposed a practical scheme that includes the effect of external bias into the self-energy of the two leads, and a self-consistent calculation is done for the electron Green's function and the charge density outside the $ab\ initio$ calculation. A self-consistent solution of the electron and phonon Green's functions can lead to many interesting phenomena such as, negative resistance in the IET spectrum.[31]

APPENDIX A: DERIVATION OF EQ. (20)

In order to show that the first two terms inside the bracket in Eq. (17) do not contribute to the total current, Eq. (20), we first sum these terms over i (which is needed to compute the total current) to get

$$I^{(1)} = -\frac{e}{\hbar}\int dt\sum_{ij\mu\eta} V_{i\mu}V_{\eta j}[G_{LL}^{ij}(t)G_{LL}^{\mu\eta}(-t) - G_{LL}^{\eta\mu}(t)G_{LL}^{ji}(-t)]. \tag{A1}$$

Upon interchanging the dummy indices $i \leftrightarrow j$, $\mu \leftrightarrow \eta$ and substituting $t = -t'$, we find

$$I^{(1)} = -\frac{e}{\hbar}\int dt'\sum_{ij\mu\eta} V_{i\mu}V_{\eta j}[G_{LL}^{ji}(-t')G_{LL}^{\eta\mu}(t')$$
$$- G_{LL}^{\mu\eta}(-t')G_{LL}^{ij}(t')]. \tag{A2}$$

Comparing Eqs. (A2) and (A1), we obtain $I^{(1)} = -I^{(1)}$, so that $I^{(1)}$ must vanish identically.

APPENDIX B: THE FLUCTUATION-DISSIPATION RELATION FOR THE GRAND CANONICAL GREEN'S FUNCTIONS

From the definition of Green's functions [Eq. (18)] we have

$$G_{LR}(\mathbf{r}t, \mathbf{r}'t') = -\frac{i}{\hbar}\langle\mathcal{T}\hat{\psi}_L(\mathbf{r}, t)\hat{\psi}_R^\dagger(\mathbf{r}', t')\rangle,$$

$$G_{RL}(\mathbf{r}t, \mathbf{r}'t') = -\frac{i}{\hbar}\langle\mathcal{T}\hat{\psi}_R(\mathbf{r}, t)\hat{\psi}_L^\dagger(\mathbf{r}', t')\rangle. \tag{B1}$$

In terms of ordinary operators in Hilbert space, we have

$$G_{LR}(\mathbf{r}t, \mathbf{r}'t') \equiv \frac{i}{\hbar}\langle T\hat{\psi}^\dagger(\mathbf{r}', t')\hat{\psi}(\mathbf{r}, t)\rangle,$$

$$G_{RL}(\mathbf{r}t, \mathbf{r}'t') \equiv \frac{i}{\hbar}\langle T\hat{\psi}(\mathbf{r}, t)\hat{\psi}^\dagger(\mathbf{r}', t')\rangle, \tag{B2}$$

where T is the Hilbert space time-ordering operator; when acting on a product of operators it rearranges them in in-

creasing order of time from right to left. We further define the field operators in the Heisenberg picture

$$\hat{\psi}(\mathbf{r},t) = e^{iHt}\psi(\mathbf{r})e^{-iHt},\tag{B3}$$

where $\psi(\mathbf{r}) = \psi(\mathbf{r},t=0)$.

We shall use the grand canonical density matrix

$$\hat{\rho} = \frac{1}{Z}e^{-\beta(H-\mu N)},\tag{B4}$$

where H, N, and μ are the Hamiltonian, the number operator, and the chemical potential, respectively. $Z=\mathrm{Tr}\{e^{-\beta(H-\mu N)}\}$ is the partition function. $|i\rangle$ represents the eigenstate of both H and N with eigenvalues ϵ_i and N_i, respectively.

At steady state we can transform the Green's functions to energy space, Eq. (19). Using Eq. (B4) in Eq. (19) and making use of Eq. (B3), we get

$$G_{LR}(\mathbf{r},\mathbf{r}',E) = \frac{i}{Z\hbar}\sum_{i,j}\delta(E+\epsilon_i-\epsilon_j)e^{-\beta(\epsilon_j-\mu N_j)}$$
$$\times\langle j|\psi^\dagger(\mathbf{r}')|i\rangle\langle i|\psi(\mathbf{r})|j\rangle.\tag{B5}$$

Note that only states with $N_j-N_i=1$ contribute to Eq. (B5). Similarly, we find for G_{RL},

$$G_{RL}(E) = -\frac{i}{Z\hbar}\sum_{i,j}\delta(E+\epsilon_j-\epsilon_i)e^{-\beta(\epsilon_j-\mu N_i)}$$
$$\times\langle i|\psi^\dagger(\mathbf{r}')|j\rangle\langle j|\psi(\mathbf{r})|i\rangle,\tag{B6}$$

where only states with $N_i-N_j=1$ contribute. Interchanging $i\leftrightarrow j$ in Eq. (B6) and making use of the fact that $N_j-N_i=1$, $\epsilon_i-\epsilon_j=E$, we get,

$$G_{RL}(E) = -\frac{i}{Z\hbar}e^{\beta(E-\mu)}\sum_{i,j}\delta(E+\epsilon_i-\epsilon_j)e^{-\beta(\epsilon_j-\mu N_j)}$$
$$\times\langle j|\psi^\dagger(\mathbf{r}')|i\rangle\langle i|\psi(\mathbf{r})|j\rangle.\tag{B7}$$

Comparing Eqs. (B7) and (B5), we obtain

$$G_{RL}(E) = -e^{\beta(E-\mu)}G_{LR}(\mathbf{r},\mathbf{r}',E).\tag{B8}$$

We also have the relation[39]

$$G_{RL}(\mathbf{r},\mathbf{r}',E) + G_{LR}(\mathbf{r},\mathbf{r}',E) = 2\pi i\rho(\mathbf{r},\mathbf{r}',E),\tag{B9}$$

where

$$\rho(\mathbf{r},\mathbf{r}',E) \equiv -\frac{1}{\pi}\mathrm{Im}\{G^{--}(\mathbf{r},\mathbf{r}',E)\}\tag{B10}$$

is the density of states.

Solving Eqs. (B8) and (B9) for G_{LR} and G_{RL}, we obtain[29,30]

$$G_{LR}(\mathbf{r},\mathbf{r}',E) = 2\pi i f(E)\rho(\mathbf{r},\mathbf{r}',E),$$

$$G_{RL}(\mathbf{r},\mathbf{r}',E) = 2\pi i[1-f(E)]\rho(\mathbf{r},\mathbf{r}',E),\tag{B11}$$

where $f(E)$ is the Fermi distribution function [Eq. (22)]. The fluctuation-dissipation relations, Eq. (B11), connects the correlations of the number fluctuations (G_{LR} and G_{RL}) to the dissipation ($\rho\sim\mathrm{Im}\{G^{--}\}$) in the system.

APPENDIX C: EQUATION OF MOTION DERIVATION OF EQ. (21)

We start with the total Hamiltonian,

$$H_T = \sum_i \epsilon_i\psi_i^\dagger\psi_i + \sum_\mu \epsilon_i\psi_\mu^\dagger\psi_\mu + \sum_{ijn}\lambda_{ij}^n\psi_i^\dagger\psi_j\Phi_n$$
$$+ \sum_{i\mu}(V_{i\mu}\psi_i^\dagger\psi_\mu + \mathrm{h.c.}).\tag{C1}$$

The current is defined as the rate of change of the charge through the molecular junction,

$$I = e\sum_i \frac{d}{dt}\langle\psi_i^\dagger\psi_i\rangle = -\frac{ie}{\hbar}\sum_{i\mu}V_{i\mu}[\langle\psi_\mu^\dagger\psi_i\rangle - \langle\psi_i^\dagger\psi_\mu\rangle]$$
$$= -\frac{2e}{\hbar}\mathrm{Im}\left\{\sum_{i\mu}V_{i\mu}\langle\psi_i^\dagger\psi_\mu\rangle\right\}.\tag{C2}$$

We define Liouville space Green's functions,

$$G_{\alpha\beta}^{mn}(t,t') = -\frac{i}{\hbar}\langle\mathcal{T}\psi_{m\alpha}(t)\psi_{n\beta}^\dagger(t')\rangle,$$

$$m,n = (i,j,\mu)\text{ and }\alpha,\beta = L,R,\tag{C3}$$

where $\psi_\alpha, \alpha=L,R$ are superoperators corresponding to the Hilbert space Fermi operator ψ. They satisfy anticommutation relations [Eq. (10), Refs. 46 and 47]. The current, Eq. (C2), can then be expressed as

$$I = \frac{2e}{\hbar}\mathrm{Re}\left\{\sum_{i\mu}V_{i\mu}\int dE\,G_{LR}^{\mu i}(E)\right\}.\tag{C4}$$

The Green's function $G_{LR}^{\mu i}$, defined in the space of substrate +tip, can be expressed in terms of the Green's functions defined in substrate and tip subspaces.

The superoperator $\psi_{\mu\alpha}$ satisfies the equation of motion,

$$-i\hbar\frac{\partial}{\partial t}\psi_{\mu\alpha}(t) = [H_T^-,\psi_{\mu\alpha}],\tag{C5}$$

where $H_T^- = H_t^- + H_s^- + H_{\mathrm{int}}^-$ is the superoperator corresponding to the total Hamiltonian, Eq. (C1), where[47]

$$H_t^- = \sum_\mu \epsilon_\mu(\psi_{\mu L}^\dagger\psi_{\mu L} - \psi_{\mu R}\psi_{\mu R}^\dagger),$$

$$H_s^- = \sum_i \epsilon_i(\psi_{iL}^\dagger\psi_{iL} - \psi_{iR}\psi_{iR}^\dagger) + \sum_m \hbar\,\Omega_m(\phi_{mL}^\dagger\phi_{mL} - \phi_{mR}\phi_{mR}^\dagger),$$

$$H_{\mathrm{int}}^- = \sum_{ijm}\lambda_{ij}^m(\psi_{iL}^\dagger\psi_{jL}\Phi_{mL} - \psi_{jR}\psi_{iR}^\dagger\Phi_{mR})$$
$$+ \sum_{i\mu}V_{i\mu}(\psi_{iL}^\dagger\psi_{\mu L} - \psi_{\mu R}\psi_{iR}^\dagger) + \mathrm{h.c.}\tag{C6}$$

We start with the tip variable, $\psi_{\mu\alpha}$. Substituting Eqs. (C6) in (C5) and using commutation relations for superoperators, Eq. (10), we get

$$-i\hbar\frac{\partial}{\partial t}\psi_{\mu\alpha}(t)=\epsilon_{\mu}\psi_{\mu\alpha}(t)+\sum_{i}V_{i\mu}\psi_{i\alpha}(t). \qquad \text{(C7)}$$

Multiplying Eq. (C7) by $\psi_{i\beta}^{\dagger}(t')$ from the right, taking a trace and using Eq. (C3), we get

$$\left(i\hbar\frac{\partial}{\partial t}+\epsilon_{\mu}\right)G_{\alpha\beta}^{\mu i}(t,t')=-\sum_{j}V_{\mu j}G_{\alpha\beta}^{ji}(t,t'). \qquad \text{(C8)}$$

We can write Eq. (C8) in the matrix form

$$G_{\alpha\beta}^{\mu i}(E)=-\sum_{j\mu'\beta}g_{\alpha\beta'}^{\mu\mu'}(E)V_{\mu'j}G_{\beta'\beta}^{ji}(E), \qquad \text{(C9)}$$

where $g_{\alpha\beta}^{\mu\mu'}$ is the Green's function for the free electrode defined as

$$\left(i\hbar\frac{\partial}{\partial t}+\epsilon_{\mu}\right)g_{\alpha\beta}^{\mu\mu'}(t,t')=\delta_{\alpha\beta}\delta_{\mu mu'}\delta(t-t'). \qquad \text{(C10)}$$

The current, Eq. (C4) is then expressed as

$$I=-\frac{2e}{\hbar}\text{Re}\left\{\sum_{ij\mu\mu'}V_{i\mu}\int\frac{dE}{2\pi}\sum_{\beta}g_{L\beta}^{\mu\mu'}(E)V_{\mu'j}G_{\beta R}^{ji}(E)\right\}. \qquad \text{(C11)}$$

It can also be written as

$$I=-\frac{2e}{\hbar}\text{Re}\left\{\sum_{ij\mu\mu'}V_{i\mu}V_{\mu'j}\int\frac{dE}{2\pi}[g_{LL}^{\mu\mu'}(E)G_{LR}^{ji}(E)\right.$$
$$\left.+g_{LR}^{\mu\mu'}(E)G_{RR}^{ji}(E)]\right\}. \qquad \text{(C12)}$$

The Liouville space Green's functions are connected by the relation[47]

$$G_{LL}+G_{RL}=G_{RR}+G_{LR}. \qquad \text{(C13)}$$

We further define the retarded and advanced Green's functions (Appendix E),[47]

$$G^{--}=G_{LL}-G_{LR}, \quad G^{++}=G_{LL}+G_{RL}. \qquad \text{(C14)}$$

Making use of these relations we can recast Eq. (C12) as

$$I=\frac{2e}{\hbar}\text{Re}\sum_{ij\mu\mu'}V_{i\mu}V_{j\mu'}\int\frac{dE}{2\pi}(g_{\mu\mu'}^{--}(E)G_{LR}^{ij}(E)$$
$$+g_{LR}^{\mu\mu'}(E)G_{ij}^{-+}(E)). \qquad \text{(C15)}$$

Using the fluctuation-dissipation relation $g_{LR}^{\mu\mu'}(E)=2\pi if(E)\rho_{\mu\mu'}(E)$, where f and ρ are Fermi distribution function and density of states [Eq. (B1)], respectively, we get Eq. (21).

APPENDIX D: THE DYSON MATRIX EQUATION

In this appendix functions without subscripts or superscripts (i,j) are to be understood as functions of space points $(\mathbf{r},\mathbf{r}')$, e.g., $G_{\alpha\beta}=G_{\alpha\beta}(\mathbf{r},\mathbf{r}',E)$, etc. The current in Eq. (20)

is completely specified by the Green's functions G_{LR} and G_{RL}. These satisfy a matrix Dyson equation [Eq. (F6)] for the four Green's functions G_{LR}, G_{RL}, G_{LL}, and G_{RR}. This can be written explicitly as

$$\begin{pmatrix}G_{LL} & G_{LR}\\ G_{RL} & G_{RR}\end{pmatrix}=\begin{pmatrix}G_{LL}^0 & G_{LR}^0\\ G_{RL}^0 & G_{RR}^0\end{pmatrix}+\begin{pmatrix}G_{LL}^0 & G_{LR}^0\\ G_{RL}^0 & G_{RR}^0\end{pmatrix}\begin{pmatrix}\Sigma_{LL} & \Sigma_{LR}\\ \Sigma_{RL} & \Sigma_{RR}\end{pmatrix}$$
$$\times\begin{pmatrix}G_{LL} & G_{LR}\\ G_{RL} & G_{RR}\end{pmatrix}, \qquad \text{(D1)}$$

where the zero-order Green's function $G_{\alpha\beta}^0$ are defined for interacting tip-substrate system. Thus $G_{\alpha\beta}^0$ include the tip self-energy, σ, and can be expressed in terms of substrate Kohn-Sham orbitals and energies,

$$G_{LL}^0(\mathbf{r},\mathbf{r}',E)=\sum_i\langle\mathbf{r}|i\rangle\langle i|\mathbf{r}'\rangle\left[\frac{1-f(E)}{E-\epsilon_i+i\sigma_{ii}}+\frac{f(E)}{E-\epsilon_i-i\sigma_{ii}}\right], \qquad \text{(D2)}$$

$$G_{RR}^0(\mathbf{r},\mathbf{r}',E)=\sum_i\langle\mathbf{r}|i\rangle\langle i|\mathbf{r}'\rangle\left[\frac{1-f(E)}{E-\epsilon_i-i\sigma_{ii}}+\frac{f(E)}{E-\epsilon_i+i\sigma_{ii}}\right], \qquad \text{(D3)}$$

$$G_{LR}^0(\mathbf{r},\mathbf{r}',E)=-2i\sum_i\langle\mathbf{r}|i\rangle\langle i|\mathbf{r}'\rangle f(E)\mathcal{D}_i(E), \qquad \text{(D4)}$$

$$G_{RL}^0(\mathbf{r},\mathbf{r}',E)=-2i\sum_i\langle\mathbf{r}|i\rangle\langle i|\mathbf{r}'\rangle[1-f(E)]\mathcal{D}_i(E). \qquad \text{(D5)}$$

In Eq. (D2) we have ignored the real part of the tip self-energy (wide-band approximation[31]). More generally, to compute $G_{\alpha\beta}^0$, one must solve the Dyson matrix equation with tip self-energy given in Appendix C, Eq. (F13), and the zeroth-order Green's function defined for a noninteracting molecular system. However, assuming that tip self-energy matrix is diagonal (contains only one atom which couples to one molecular orbital at a time), we obtain Eq. (D2). The electron-phonon interaction is incorporated through self-energies $\Sigma_{\alpha\beta}$ which are expressed in terms of the Green's functions [Eq. (F11)]. Thus one can compute G_{RL} and G_{LR}, and hence the current, by solving Eq. (D1) self-consistently for all Green's functions and the corresponding self-energies. This calculation is greatly simplified by switching to the +/− representation as shown in Appendix E.

APPENDIX E: TRANSFORMATION FROM L/R TO THE +/− REPRESENTATION

The Dyson equation (D1) can be transformed to +/− representation by a unitary transformation $\bar{G}=SGS^{-1}$, where G is the Green's function matrix in L/R, Eq. (D1), and[47]

$$S=\frac{1}{\sqrt{2}}\begin{pmatrix}-1 & -1\\ 1 & -1\end{pmatrix} \qquad \text{(E1)}$$

is the transformation matrix. In this representation we only have three (rather than four) Green's functions[47]

$$G^{--} = G_{LL} - G_{LR}, \tag{E2}$$

$$G^{++} = G_{LL} + G_{RL}, \tag{E3}$$

$$G^{-+} = G_{LR} - G_{RL}. \tag{E4}$$

$G^{--}(G^{++})$ is a retarded (advanced) function while G^{-+} is symmetric in time, and G^{+-} vanishes identically.[47] Substituting for G^0_{LL} and G^0_{LR} from Eqs. (D2) into Eq. (E2), we obtain Eq. (29). Applying the transformation to Eq. (D1), we find that self-energy matrix also has only three elements corresponding to the three Green's functions defined above, Eqs. (E2)–(E4). This results in decoupled equations for G^{--} and G^{++},

$$G^{--} = G^{--}_0 + G^{--}_0 \Sigma^{--} G^{--}, \tag{E5}$$

$$\Sigma^{--} = \Sigma_{LL} - \Sigma_{LR} \tag{E6}$$

and

$$G^{++} = G^{++}_0 + G^{++}_0 \Sigma^{++} G^{++}, \tag{E7}$$

$$\Sigma^{++} = \Sigma_{LL} + \Sigma_{RL} \tag{E8}$$

with $G^{++} = [G^{--}]^\dagger$ and $\Sigma^{++} = [\Sigma^{--}]^\dagger$. We further have

$$G^{++} = G^{++}_0 + G^{+-}_0 [\Sigma^{++} G^{-+} + \Sigma^{+-} G^{++}] + G^{++}_0 \Sigma^{-+} G^{-+}, \tag{E9}$$

$$\Sigma^{++} = \Sigma_{LL} + \Sigma_{RR}. \tag{E10}$$

Using the matrix Dyson equation, Eq. (D1), and Eqs. (E2)–(E5), G_{LR} can be expressed as

$$G_{LR} = (1 + G^{--}\Sigma^{--})G^0_{LR}(1 + \Sigma^{++}G^{++}) + G^{--}\Sigma_{LR}G^{++}. \tag{E11}$$

G_{RL} is similarly obtained by interchanging $R \leftrightarrow L$ in Eq. (E11). Since $G^{--} = [G^{++}]^*$, Eq. (E11) expresses G_{LR} in terms of G^{--} alone which, in turn, can be obtained by solving the Dyson equation (E5). This is much simpler than the direct solution of Eq. (D1), which requires the self-consistent computation of four Green's functions and four self-energies.

Using Eq. (E11), and the identities $G_{LR} + G_{RL} \equiv -2i \, \text{Im}\{G^{--}\}$ and $\Sigma_{LR} + \Sigma_{RL} \equiv -2i \, \text{Im}\{\Sigma^{--}\}$,[39] $A(E)$ [Eq. (24)] can be expressed in terms of retarded and advanced functions, resulting in Eq. (25).

APPENDIX F: CALCULATION FOR SELF-ENERGY Σ AND σ

We compute the self-energy for the electron Green's function due to electron-phonon (Σ) and tip-substrate (σ) interactions. To that end, we start with the equation of motion for $G_{\alpha\beta}$ derived from the equation of motion for $\psi_{i\alpha}$. Replacing $\psi_{\mu\alpha}$ by $\psi_{i\alpha}$ in Eq. (C5) we obtain,

$$-i\hbar \frac{\partial}{\partial t}\psi_{i\alpha}(t) = \epsilon_i \psi_{i\alpha}(t) + \sum_k V_{ki}\psi_{k\alpha}(t) + \sum_{mj}\lambda^m_{ij}\Phi_{m\alpha}(t)\psi_{j\alpha}(t). \tag{F1}$$

Taking the time derivative of the Green's function, Eq. (C3), and using Eq. (F1), the equation of motion for $G_{\alpha\beta}$ is obtained as[47]

$$\left(i\hbar\frac{\partial}{\partial t} + \epsilon_i\right)G^{ij}_{\alpha\beta}(t,t') = \delta_{\alpha\beta}\delta_{ij}\delta(t-t') + \Sigma^{ij'}_{\alpha\beta'}(t,t_1)G^{j'j}_{\beta'\beta}(t_1,t')$$
$$- \sum_\mu V_{i\mu}G^{\mu j}_{\alpha\beta}(t,t'), \tag{F2}$$

where Σ is the self-energy due to electron-phonon interaction defined by the ansatz

$$\Sigma^{ij'}_{\alpha\beta'}(t,t'_1)G^{j'j}_{\beta'\beta}(t'_1,t') \equiv -i\sum_{mk}\lambda^m_{ik}\langle \mathcal{T}\Phi_{m\alpha}(t)\psi_{k\alpha}(t)\psi^\dagger_{j\beta}(t')\rangle. \tag{F3}$$

By substituting Eq. (C9), the last term in Eq. (F2) can be written in terms of the electrode and molecule Green's functions, and we get,

$$\left(i\hbar\frac{\partial}{\partial t} + \epsilon_i\right)G^{ij}_{\alpha\beta}(t,t') = \delta_{\alpha\beta}\delta_{ij}\delta(t-t') + \Sigma^{ij'}_{\alpha\beta'}(t,t_1)G^{j'j}_{\beta'\beta}(t_1,t')$$
$$+ \sigma^{ii'}_{\alpha\beta'}(t,t_1)G^{i'j}_{\beta'\beta}(t_1,t'), \tag{F4}$$

where $\sigma_{\alpha\beta}$ is the self-energy due to the tip interaction

$$\sigma^{ij}_{\alpha\beta}(t,t') = \sum_{\mu\mu'}V_{i\mu}V_{j\mu'}g^{\mu\mu'}_{\alpha\beta}(t,t_1). \tag{F5}$$

Note that the self-energy $\sigma_{\alpha\beta}$ is exact. The reason that σ can be obtained exactly is that the tip-substrate interaction is quadratic in ψ's, the same as the Green's function itself. Equation (F4) can be put into the form of the Dyson equation,

$$G^{ij}_{\alpha\beta}(t,t') = G^{0ij}_{\alpha\beta}(t,t') + G^{0ij'}_{\alpha\beta'}(t,t_1)\Xi^{j'i'}_{\beta'\alpha'}(t_1,t_2)G^{i'j}_{\alpha'\beta}(t_2,t'), \tag{F6}$$

where $\Xi = \Sigma + \sigma$ and the zero-order Green's functions G^0 corresponds to noninteracting electrons defined as[28,47]

$$\left(i\hbar\frac{\partial}{\partial t} + \epsilon_i\right)G^{0ij}_{\alpha\beta}(t,t') = \delta_{\alpha\beta}\delta_{ij}\delta(t-t'). \tag{F7}$$

To compute the phonon self-energy, we express the right-hand-side of Eq. (F3) in the interaction picture as,

$$\Sigma^{ij'}_{\alpha\beta'}(t,t'_1)G^{j'j}_{\beta'\beta}(t'_1,t')$$
$$= -\frac{i}{\hbar}\sum_{mk}\lambda^m_{ik}\langle \mathcal{T}\tilde{\Phi}_{m\alpha}(t)\tilde{\psi}_{k\alpha}(t)\tilde{\psi}^\dagger_{j\beta}(t')\mathcal{G}_I(t,-\infty)\rangle_0, \tag{F8}$$

where $\mathcal{G}_I(t,-\infty)$ is the Liouville space-time evolution operator in the interaction picture and can be obtained from Eq. (14) by replacing $\tilde{H}^-_{ts}$ with $\tilde{H}^-_{\text{int}}$. By expanding $\mathcal{G}_I$, the r.h.s. in Eq. (F8) can be expressed perturbatively in electron-phonon

coupling. This perturbation series involves averages of the higher order (three and more) products of phonon and electron operators, which can be factorized into the averages of products of two operators using the Wick's theorem for superoperators.[46] This allows us to compute the self-energy, Σ, to the desired order in λ_{ij}^m in terms of the zeroth-order Green's functions. Let $M^{(p)}$ represent the pth order term in λ_{ij}^m on the r.h.s. in Eq. (F8), and $\Sigma^{(p)}$ be the corresponding term in the self-energy expansion, Eq. (F8) can then be rewritten as (we do not write indices i, j, α, β explicitly)

$$(\Sigma^{(1)} + \Sigma^{(2)} + \cdots)(G^0 + G^0\Sigma^{(1)}G^0 + \cdots) = M^{(1)} + M^{(2)} + \cdots.$$

(F9)

Since $\langle \Phi(t) \rangle_0 = 0$, the odd terms $M^{(2n+1)}$ vanish. Equating the two sides of Eq. (F9) we obtain

$$\Sigma^{(1)}G^0 = 0, \quad \Sigma^{(2)}G^0 = M^{(2)},$$

$$\Sigma^{(2)}G^0\Sigma^{(2)}G^0 + \Sigma^{(4)}G^0 = M^{(4)}, \quad \text{etc.} \quad (F10)$$

Once $M^{(2p)}$ are computed, Eqs. (F10) can be used to obtain $\Sigma^{(2n)}$. We compute the self-energy within the self-consistent Born-approximation.[31] By replacing zero-order Green's functions in $\Sigma^{(2)}$ with the full Green's functions, we obtain

$$\Sigma_{\alpha\beta}^{ij}(t,t') = i \sum_{mnkl} \lambda_{ik}^m \lambda_{lj}^n (\delta_{L\beta} D_{\alpha L}^{mn}(t,t') G_{\alpha L}^{kl}(t,t')$$

$$+ \delta_{R\beta} D_{\alpha R}^{mn}(t,t') G_{\alpha R}^{kl}(t,t')) - i\delta_{\alpha\beta}\delta(t-t')$$

$$\times \sum_{mnkl} \lambda_{ij}^m \lambda_{kl}^n \int d\tau (D_{\alpha L}^{mn}(t,\tau) G_{LL}^{kl}(\tau,\tau^+)$$

$$+ D_{\alpha R}^{mn}(t,\tau) G_{RR}^{kl}(\tau,\tau^+)). \quad (F11)$$

We next derive an equation of motion for the retarded Green's function. Since $G^{--} = G_{LL} - G_{LR}$, we get from Eq. (F4)

$$\left(i\hbar \frac{\partial}{\partial t} + \epsilon_i \right) G_{ij}^{--}(t,t') = \delta_{ij}\delta(t-t') + \Sigma_{ij'}^{--}(t,t_1) G_{j'j}^{--}(t_1,t')$$

$$+ \sigma_{ij'}^{--}(t,t_1) G_{j'j}^{--}(t_1,t'), \quad (F12)$$

where we have used $\Sigma^{--} = \Sigma_{LL} - \Sigma_{LR}$ (Ref. 47) and similar relations hold for σ. The retarded self-energy due to coupling with the electrode is

$$\sigma_{ik}^{--}(t,t') = \sigma_{LL}^{ik}(t,t') - \sigma_{LR}^{ik}(t,t') = \sum_{\mu\mu'} V_{i\mu} V_{k\mu'} g_{\mu\mu'}^{--}(t,t'),$$

(F13)

where $g_{\mu\mu'}^{--}(t,t')$ is the retarded Green's function for the free electrode

$$g_{\mu\mu'}^{--}(t,t') = -i\theta(t-t')\delta_{\mu\mu'} \exp\{-i\epsilon_\mu(t-t')\}. \quad (F14)$$

In frequency space, Eq. (19), we get

$$g_{\mu\mu'}^{--}(E) = \frac{\delta_{\mu\mu'}}{\omega - \epsilon_\mu + i\eta} \quad (F15)$$

and the imaginary part of the tip self-energy which defines the broadening in the electronic states is then

$$\sigma_{ij}(E) = -2 \, \text{Im} \, \sigma_{ij}^{--}(E) = 2\pi \sum_\mu V_{i\mu} V_{\mu j} \delta(E - \epsilon_\mu).$$

(F16)

In the wide-band approximation, the energy dependence of σ_{ij} is ignored. Equation (F16) is used to write the electron DOS [Eq. (26)] and the Green's function [Eq. (29)].

The retarded phonon self-energy, $\Sigma^{--} = \Sigma_{LL} - \Sigma_{LR}$ is obtained from Eq. (F11) as

$$\Sigma_{ij}^{--}(t,t') = i \sum_{mnkl} \lambda_{ik}^m \lambda_{lj}^n (D_{LR}^{mn}(t,t') G_{kl}^{--}(t,t')$$

$$- D_{mn}^{--}(t,t') G_{RL}^{kl}(t,t')) + \delta(t-t')$$

$$\times \sum_{mnkl} \lambda_{ij}^m \lambda_{kl}^n \rho_{kl} \int d\tau D_{mn}^r(\tau), \quad (F17)$$

where ρ_{kl} is the charge density matrix. Transforming to frequency space and neglecting the second term, which is frequency independent and does not involve discontinuities, we obtain Eq. (30).

APPENDIX G: MAPPING BETWEEN THE LIOUVILLE SPACE AND HILBERT SPACE GREEN'S FUNCTIONS

The standard NEGF theory is formulated in terms of four Hilbert space Green's functions: time ordered (G^T), antitime ordered ($G^{\tilde{T}}$), greater ($G^>$), and lesser ($G^<$).[28,29] These are defined in the Heisenberg picture as

$$G^T(\mathbf{x},\mathbf{x}') \equiv -\frac{i}{\hbar} \langle T\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}') \rangle$$

$$= -\frac{i}{\hbar} \theta(t-t') \langle \hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}') \rangle$$

$$+ \frac{i}{\hbar} \theta(t'-t) \langle \hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}) \rangle,$$

$$G^{\tilde{T}}(\mathbf{x},\mathbf{x}') \equiv -\frac{i}{\hbar} \langle \tilde{T}\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}') \rangle$$

$$= -\frac{i}{\hbar} \theta(t'-t) \langle \psi(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}') \rangle$$

$$+ \frac{i}{\hbar} \theta(t-t') \langle \hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}) \rangle,$$

$$G^>(\mathbf{x},\mathbf{x}') \equiv -\frac{i}{\hbar} \langle \hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}') \rangle,$$

$$G^<(\mathbf{x},\mathbf{x}') \equiv \frac{i}{\hbar} \langle \hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}) \rangle. \quad (G1)$$

Here T ($\tilde{T}$) 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 Green's functions that show up naturally in Liouville space are defined using a positive time ordering operator $\mathcal{T}$ as,

$$G_{\alpha\beta}(\mathbf{x},\mathbf{x}') = -\frac{i}{\hbar}\langle \mathcal{T}\hat{\psi}_\alpha(\mathbf{x})\hat{\psi}_\beta^\dagger(\mathbf{x}')\rangle; \quad \alpha,\beta = L,R. \quad (G2)$$

The equivalence of the Hilbert space and the Liouville space Green's functions i has been shown in Refs. 37 and 47,

$$G_{LL}(\mathbf{x},\mathbf{x}') = G^T(\mathbf{x},\mathbf{x}'), \quad G_{RR}(\mathbf{x},\mathbf{x}') = -G^{\tilde{T}}(\mathbf{x},\mathbf{x}')$$

$$G_{LR}(\mathbf{x},\mathbf{x}') = G^<(\mathbf{x},\mathbf{x}'), \quad G_{RL}(\mathbf{x},\mathbf{x}') = -G^>(\mathbf{x},\mathbf{x}').$$
$$(G3)$$

We next turn to the $+/-$ representation where we have only three Liouville space Green's functions,

$$G^{--}(\mathbf{x},\mathbf{x}') = -\frac{i}{\hbar}\langle \mathcal{T}\hat{\psi}^-(\mathbf{x})\hat{\psi}^{-\dagger}(\mathbf{x}')\rangle,$$

$$G^{++}(\mathbf{x},\mathbf{x}') = -\frac{i}{\hbar}\langle \mathcal{T}\hat{\psi}^+(\mathbf{x})\hat{\psi}^{+\dagger}(\mathbf{x}')\rangle,$$

$$G^{-+}(\mathbf{x},\mathbf{x}') = -\frac{2i}{\hbar}\langle \mathcal{T}\hat{\psi}^-(\mathbf{x})\hat{\psi}^{+\dagger}(\mathbf{x}')\rangle, \quad (G4)$$

since G^{+-} vanishes identically.[49] The operators $\psi^\pm$ were defined in Eq. (11).

We next show the equivalence of G^{--}, G^{++}, and G^{-+} with the Hilbert space retarded (G^r), advanced (G^a), and correlation functions (G^c), defined as

$$G^r(\mathbf{x},\mathbf{x}') = -\frac{i}{\hbar}\theta(t-t')\langle\{\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{x}')\}\rangle,$$

$$G^a(\mathbf{x},\mathbf{x}') = \frac{i}{\hbar}\theta(t'-t)\langle\{\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{x}')\}\rangle,$$

$$G^c(\mathbf{x},\mathbf{x}') = -\frac{i}{\hbar}\langle[\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{x}')]\rangle. \quad (G5)$$

Using the definition of $+/-$ operators, Eq. (11), and Eq. (G2), we obtain

$$G^{+-}(\mathbf{x},\mathbf{x}') \equiv -\frac{i}{\hbar}\langle \mathcal{T}\hat{\psi}^+(\mathbf{x})\hat{\psi}^{-\dagger}(\mathbf{x}')\rangle$$

$$\equiv G_{LL}(\mathbf{x},\mathbf{x}') - G_{RR}(\mathbf{x},\mathbf{x}')$$

$$- G_{LR}(\mathbf{x},\mathbf{x}') + G_{RL}(\mathbf{x},\mathbf{x}'). \quad (G6)$$

Since $G^{+-}=0$, Eq. (G6) gives

$$G_{LL}(\mathbf{x},\mathbf{x}') + G_{RL}(\mathbf{x},\mathbf{x}') = G_{LR}(\mathbf{x},\mathbf{x}') + G_{RR}(\mathbf{x},\mathbf{x}'). \quad (G7)$$

Similarly, using Eq. (G6), we obtain linear relations between $+/-$ and L/R Green's functions, $G_{\alpha\beta},\alpha,\beta=L,R$ as given in Eq. (E2).

Substituting Eqs. (G8) and (G3) in Eq. (E2), we get

$$G^{--} = G_{LL} - G_{LR}$$

$$\equiv -\frac{i}{\hbar}\theta(t-t')\langle\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\rangle - \frac{i}{\hbar}\theta(t-t')\langle\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\rangle$$

$$= -\frac{i}{\hbar}\theta(t-t')\langle\{\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{x}')\}\rangle = G^r(\mathbf{x},\mathbf{x}'),$$

$$G^{++} \equiv G_{LL} + G_{RL}$$

$$= \frac{i}{\hbar}\theta(t'-t)\langle\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\rangle + \frac{i}{\hbar}\theta(t'-t)\langle\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\rangle$$

$$= \frac{i}{\hbar}\theta(t'-t)\langle\{\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{x}')\}\rangle = G^a(\mathbf{x},\mathbf{x}'),$$

$$G^{-+} \equiv G_{LL} - G_{RR}$$

$$= -\frac{i}{\hbar}\theta(t-t')(\langle\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\rangle - \langle\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\rangle)$$

$$- \frac{i}{\hbar}\theta(t'-t)(\langle\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\rangle - \langle\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\rangle)$$

$$= -\frac{i}{\hbar}\langle[\hat{\psi}(\mathbf{x}),\hat{\psi}^\dagger(\mathbf{x}')]\rangle = G^c(\mathbf{x},\mathbf{x}'). \quad (G8)$$

We can summarize these relations as

$$G^{--}(\mathbf{x},\mathbf{x}') \equiv G^r(\mathbf{x},\mathbf{x}'), \quad G^{++}(\mathbf{x},\mathbf{x}') \equiv G^a(\mathbf{x},\mathbf{x}'),$$

$$G^{-+}(\mathbf{x},\mathbf{x}') \equiv G^c(\mathbf{x},\mathbf{x}'), \quad G^{+-}(\mathbf{x},\mathbf{x}') = 0. \quad (G9)$$

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