Nonadiabatic corrections to electric current in molecular junction due to nuclear motion at the molecule-electrode interfaces

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We present quantum electron transport theory that incorporates dynamical effects of motion of atoms on electrode-molecule interfaces in the calculations of the electric current. The theory is based on nonequilibrium Green’s functions. We separate time scales in the Green’s functions on fast relative time and slow central time. The derivative with respect to the central time serves as a small parameter in the theory. We solve the real-time Dyson equations for molecular Green’s functions using Wigner representation and keep terms up to the second order with respect to the central time derivatives. Molecular Green’s functions and consequently the electric current are expressed as functions of molecular junction coordinates as well as velocities and accelerations of molecule-electrode interface nuclei. We apply the theory to model a molecular system and show that the nonadiabatic effects of nuclear motion of interfacial atoms generally reduce electrical conductivity in the resonance transport regime.
I. INTRODUCTION

Quantum transport of electrons through nanoscale molecular systems is an active field of research, which has made remarkable fundamental advances in recent years. This includes not only developing, after a decade of struggle, robust and reproducible experimental measurements but also obtaining the fundamental theoretical understanding of microscopic mechanisms of molecular quantum transport.\textsuperscript{1,2}

Unfortunately, this scientific progress has not been transplanted in electronic devices for real world applications. Molecular electronics has for decades been touted as something to replace semiconductor electronics, but one major difficulty has dampened hopes. Single-molecular junctions are sensitive to every microscopic static and dynamical detail of the electrode-molecule interface with the details not being possible to control that are not possible to control. The thorough scientific understanding of molecular contacts is still required before the commercial potential of single-molecular technologies can be realised in electronics.

Not only is the interface geometry largely not known in a molecular junction but nuclear dynamics for the interfacial atoms play a critical role (owing to the gold-electron plasticity, significant voltage drop on molecule-metal interface creating a strong electric field, and comparative weakness of the molecule-metal bonds).\textsuperscript{3,4} The nuclear motion of molecule-electrode interfacial atoms can be considered as vibrational motion and standard theoretical techniques, such as nonequilibrium Green’s functions,\textsuperscript{5–13} master equations,\textsuperscript{14–23} or scattering theory,\textsuperscript{24–27} can, in principle, be applied to treat it (although the problem is technically harder for the theoretical treatment, since the vibrations are not localized in the central region).\textsuperscript{26,28} With only a few recent exceptions,\textsuperscript{29–34} all these standard theoretical approaches have to assume that the amplitudes of nuclear motions are small, in addition, they require that either electron-vibration coupling or interaction between the molecule and electrodes should be small in comparison with other energy scales in the system.

In this paper, we continue our development of a non-equilibrium Green’s function based transport theory, which takes into consideration nonadiabatic effects of nuclear motion.\textsuperscript{34} In our previous paper\textsuperscript{34} we computed the nonadiabatic correction to the electric current from nonadiabatic effects associated with nuclear motion in the central region. Here we extend the theory to include the interfacial nuclear dynamics from nonrigid molecule-electrode bonding.
Our approach is not based on the typical assumption that the amplitude of nuclear motion is either small or harmonic; nor is it required that the electron-nuclear coupling is small. The theory uses the velocity of nuclear motion as a small parameter and, consequently, there are no restrictions on the scale of possible molecular conformational changes or strength of electron-vibrational interaction in our approach.

The outline of the paper is as follows. Section II contains the theory: separable approximation for electrode self-energies, solution of real-time Dyson’s equation for molecular Green’s functions using Wigner representation, and the derivation of nonadiabatic formulae for electric current. In section III, we illustrate the proposed theory by the application to electron transport through a single resonant-level molecular junction with non-rigid molecule-electrode linkage. Section IV gives conclusions and a summary of the main results. We use atomic units in the derivations throughout the paper ($\hbar = |e| = m_e = 1$).

II. THEORY

A. Model Hamiltonian

We consider a molecular junction: a single molecule connected to two macroscopic leads. It is described by the following Hamiltonian

$$H = H_M + H_L + H_R + H_{LM} + H_{RM}, \quad (1)$$

where $H_M$ is the Hamiltonian for the molecule, $H_L$ is the Hamiltonian for the left lead, $H_R$ is the Hamiltonian for the right lead, $H_{LM}$ and $H_{RM}$ are interactions between the molecule and left and right leads, respectively. The molecule is modelled by a single molecular orbital with energy $\epsilon$

$$H_M = \epsilon d^\dagger d + V_N(q_L, q_R). \quad (2)$$

Here $d^\dagger$ and $d$ are fermionic creation and annihilation operators for a molecular electron. Classical variables $q_L$ and $q_R$ describe dynamical changes in the bond lengths between the molecule and left and right leads, respectively, and $V_N$ is the potential energy surface for these two variables.

The left and right leads of the molecular junction are modelled as macroscopic reservoirs.
of noninteracting electrons

\[ H_L + H_R = \sum_{k\alpha} \epsilon_{k\alpha} a_{k\alpha}^\dagger a_{k\alpha}, \quad (3) \]

where \( a_{k\alpha}^\dagger \) creates an electron in the single-particle state \( k \) with energy \( \epsilon_{k\alpha} \) of \( \alpha = L/R \) left/right leads and \( a_{k\alpha} \) is the corresponding electron annihilation operator. The lead-molecule couplings are described by the tunneling interaction

\[ H_{LM}(t) + H_{RM}(t) = \sum_{k\alpha} (v_{\alpha}(q_{\alpha}) a_{k\alpha}^\dagger d + v_{\alpha}^*(q_{\alpha}) d^\dagger a_{k\alpha}), \quad (4) \]

where \( v_{\alpha}(q_{\alpha}) \) are the tunnelling amplitudes between leads single-particle states and molecular orbital. The molecule-lead interaction is explicitly time-dependent due to the changes of the corresponding bond lengths from the equilibrium values \( q_{\alpha} = x_{\alpha} - x_{0\alpha} \), where \( x_{0\alpha} \) is the equilibrium bond length and we assume that

\[ v_{\alpha}(q_{\alpha}) = v_{\alpha}(1 + \lambda_{\alpha} q_{\alpha}). \quad (5) \]

Here \( \lambda_{\alpha} \) is the real parameter which describes the modulation of tunnelling amplitude due to the changes of the molecule-lead geometry. The assumption of the linear dependence of the tunneling amplitude on the nuclear coordinates is not critical for the derivation of the main equations, we can also carry out the similar derivations for completely arbitrary dependence of \( v_{\alpha} \) on \( q_{\alpha} \).

B. Green’s functions and self-energies

1. Green’s functions

We define exact (nonadiabatic, computed with full time-dependent Hamiltonian along given trajectory \( q(t) = (q_L(t), q_R(t)) \)) retarded, advanced, and lesser Green’s functions in a standard way as \(^{35}\)

\[ \mathcal{G}^R(t, t') = -i\theta(t - t') \langle \{ d(t), d^\dagger(t') \} \rangle, \quad (6) \]

\[ \mathcal{G}^A(t, t') = \left( \mathcal{G}^R(t', t) \right)^* \quad (7) \]

\[ \mathcal{G}^<(t, t') = i \langle d^\dagger(t') d(t) \rangle. \quad (8) \]
2. **Self-energies in time domain**

The influence of the electrodes on the molecular Green’s function is taken into account via electrodes self-energies. Left and right retarded self-energies are

\[
\Sigma^R_{\alpha}(t, t') = -i\theta(t - t')v^\ast_{\alpha}(t)v_{\alpha}(t') \sum_k e^{-i\epsilon_k(t-t')}.
\] (9)

Here \(v_{k\alpha}(t)\) means \(v_{k\alpha}(q_{\alpha}(t))\). The advanced and retarded self-energies are related to each other via Hermitian conjugation:

\[
\Sigma^A_{\alpha}(t, t') = (\Sigma^R_{\alpha}(t', t))^*.
\] (10)

The lesser self-energy is defined as

\[
\Sigma^<_{\alpha}(t, t') = iv^\ast_{\alpha}(t)v_{\alpha}(t') \sum_k f_{\alpha}(\epsilon_k)e^{-i\epsilon_k(t-t')}.
\] (11)

where \(f_{\alpha}\) is Fermi-Dirac occupation number for \(\alpha = L, R\) electrodes. The total self-energies are the sum of contributions from the left and right electrodes

\[
\Sigma^{R,A,\alpha}(t, t') = \Sigma^{L,A,\alpha}(t, t') + \Sigma^{R,A,\alpha}(t, t').
\] (12)

3. **Self-energies in Wigner representation and separable approximation**

We will solve the real-time Dyson equations using Wigner representation and to be able to do so, first, we need to convert electrode self-energies to the Wigner representation. Let us introduce central and relative times

\[
T = \frac{1}{2}(t + t'), \quad \tau = t - t'
\] (13)

for Green’s functions \(\mathcal{G}(t, t')\) and self-energies \(\Sigma(t, t')\). Wigner transformation is defined as the Fourier transformation with respect to relative time:

\[
\tilde{\Sigma}(T, \omega) = \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau}\Sigma(T, \tau).
\] (14)

For the calculation of the Wigner transformed self-energies we propose separable approximation (separable functional form with respect to central \(T\) and relative \(\tau\) times):

\[
\Sigma^R_{\alpha}(T, \tau) = -i\theta(\tau)v^\ast_{\alpha}(T + \tau/2)v_{\alpha}(T - \tau/2) \sum_k e^{-i\epsilon_k\tau} \simeq -i\theta(\tau)|v_{\alpha}(T)|^2 \sum_k e^{-i\epsilon_k\tau},
\] (15)
\[ \Sigma^<_\alpha(T, \tau) = iv^*_\alpha(T + \tau/2)v_\alpha(T - \tau/2) \sum_k f_\alpha(\epsilon_k)e^{-i\epsilon_k\tau} \approx i|v_\alpha(T)|^2 \sum_k f_\alpha(\epsilon_k)e^{-i\epsilon_k\tau}. \] 

(16)

The separable approximation does not violate the standard relations between self-energies, for example \( \Sigma^A_\alpha(T, \tau) = (\Sigma^R_\alpha(T, -\tau))^\dagger \). We justify the use of separable approximation based on the following considerations. For the smooth lead’s density of state both sums \( \sum_k e^{-i\epsilon_k\tau} \) and \( \sum_k f(\epsilon_k)e^{-i\epsilon_k\tau} \) are peaked around \( \tau = 0 \), thereby removing \( \pm \tau/2 \) time shifts from the tunnelling coupling amplitudes \( v_\alpha \).

The use of the separable approximation yields the following self-energies in Wigner space;

\[ \tilde{\Sigma}^A_\alpha(T, \omega) = \Lambda_\alpha(T, \omega) + \frac{i}{2}\Gamma_\alpha(T, \omega), \] 

(17)

\[ \tilde{\Sigma}^R_\alpha(T, \omega) = \Lambda_\alpha(T, \omega) - \frac{i}{2}\Gamma_\alpha(T, \omega), \] 

(18)

\[ \tilde{\Sigma}^<_\alpha(T, \omega) = f_\alpha(\omega) (\Sigma^A(T, \omega) - \Sigma^R(T\omega)) = if_\alpha(\omega)\Gamma_\alpha(T, \omega). \] 

(19)

Here

\[ \Gamma_\alpha(T, \omega) = 2\pi|v_\alpha(T)|^2\rho_\alpha(\omega) = (1 + \lambda_\alpha q_\alpha(T^2)\Gamma_\alpha(\omega), \] 

(20)

where

\[ \Gamma_\alpha(\omega) = 2\pi|v_\alpha|^2\rho_\alpha(\omega). \] 

(21)

is the standard level-broadening functions for static molecular junction.

We will use the wide-band limit (that means we assume that \( \rho_\alpha(\omega) = \text{constant} \)) for the self-energies in the derivations and calculation in the paper:

\[ \tilde{\Sigma}^A_\alpha(T) = \frac{i}{2}\Gamma_\alpha(1 + \lambda_\alpha q_\alpha(T))^2, \] 

(22)

\[ \tilde{\Sigma}^R_\alpha(T) = -\frac{i}{2}\Gamma_\alpha(1 + \lambda_\alpha q_\alpha(T))^2, \] 

(23)

\[ \tilde{\Sigma}^<_\alpha(T, \omega) = if_\alpha(\omega)\Gamma_\alpha(1 + \lambda_\alpha q_\alpha(T))^2. \] 

(24)

Notice, that the retarded and advanced self-energies do not depend on \( \omega \) in the wide-band limit, they depend only on central time \( T \).

C. Solution of real time Dyson equation via separation of time-scales

We begin with the equation of motion for the nonadiabatic retarded Green’s function (only this type of Green’s functions will be later required for the electric current calculations)

\[ (i\partial_t - \epsilon)G^R(t, t') = \delta(t - t') + \int^{+\infty}_{-\infty} dt_1 \Sigma^R(t, t_1)G^R(t_1, t'). \] 

(25)
The equation of motion in the Wigner representation becomes

\[
\left( \omega + \frac{i}{2} \partial_T - \epsilon \right) \tilde{G}_R(T, \omega) = I + e^{\frac{1}{2i} \left( \partial_T^2 \partial_\omega^2 - \partial_T^2 \partial_\omega^2 \right)} \tilde{\Sigma}^R(T, \omega) \tilde{G}_R(T, \omega).
\]  

(26)

Here \( \partial^R \) means the derivative acting on the self-energy only and \( \partial^G \) denotes the derivative acting on the Green’s function. In the wide-band approximation \( \tilde{\Sigma}^R \) depends on the central time \( T \) only, therefore, the exponential operator acting on the retarded self-energy is simplified and we get

\[
\left( \omega + \frac{i}{2} \partial_T - \epsilon \right) \tilde{G}_R(T, \omega) = I + e^{\frac{1}{2i} \partial_T^2 \partial_\omega^2} \tilde{\Sigma}^R(T) \tilde{G}_R(T, \omega).
\]  

(27)

We solve this Dyson’s equation using the time derivative with respect to the central time as a small parameter. It means we assume that the changes of the self-energies and the Green’s functions are slow with respect to the central time and fast with respect to the relative time. The central time dependence is associated with slow nuclear dynamics (through the dependence of the self energy on classical variable \( q(t) \)) and relative time oscillations are related to electronic time-scale (in our case the characteristic tunneling time for the electron to transport across the molecule). The solution described below follows the general ideas discussed in our previous paper.\textsuperscript{34} Expanding the exponential operator up to the second order in the time derivatives, we get a truncated equation of motion for the retarded Green’s function

\[
\left( \omega + \frac{i}{2} \partial_T - \epsilon \right) \tilde{G}_R(T, \omega) = I + e^{\frac{1}{2i} \partial_T^2 \partial_\omega^2} \tilde{\Sigma}^R(T) \tilde{G}_R(T, \omega) + \frac{1}{8} \partial_T^2 \tilde{\Sigma}^R(T) \tilde{G}_R(T, \omega) \tilde{G}_R(T, \omega).
\]  

(28)

Here we omit \( T \) and \( \omega \) variables from Green’s functions and self energies for brevity. Looking for the solution that contains the time derivatives up to the second order, we use the following ansatz for the retarded Green’s function

\[
\tilde{G}_R = \tilde{G}^{R(0)} + \tilde{G}^{R(1)} + \tilde{G}^{R(2)},
\]  

(29)

where the term \( \tilde{G}^{R(0)} \) depends on nuclear geometry only, \( \tilde{G}^{R(1)} \) depends on nuclear geometry and is linearly proportional to the nuclear velocities, and \( \tilde{G}^{R(2)} \) depends on the geometry, and either depends quadratically on nuclear velocities or linearly on nuclear accelerations.

Substituting (29) into (28) we obtain a system of three equations based on order of the derivatives with respect to the central time

\[
\left( \omega - \epsilon \right) \tilde{G}^{R(0)} = 1 + \tilde{\Sigma}^R \tilde{G}^{R(0)},
\]  

(30)
\[\frac{i}{2} \partial_T \tilde{G}^R_{(0)} + (\omega - \epsilon) \tilde{G}^R_{(1)} = \tilde{\Sigma}^R \tilde{G}^R_{(1)} + \frac{1}{2i} \partial_T \tilde{\Sigma}^R \partial_\omega \tilde{G}^R_{(0)} \]  

(31)

and

\[\frac{i}{2} \partial_T \tilde{G}^R_{(1)} + (\omega - \epsilon) \tilde{G}^R_{(2)} = \tilde{\Sigma}^R \tilde{G}^R_{(2)} + \frac{1}{2i} \partial_T \tilde{\Sigma}^R \partial_\omega \tilde{G}^R_{(1)} - \frac{1}{8} \partial_T^2 \tilde{\Sigma}^R \partial_\omega^2 \tilde{G}^R_{(0)} \]  

(32)

The equation for the zeroth order Green’s function is easily solved and gives

\[\tilde{G}^R_{(0)} = \left(\omega - \epsilon - \tilde{\Sigma}^R\right)^{-1} = G^R,\]  

(33)

which is the standard adiabatic retarded Green’s function \(G^R\). To solve for the first order correction we rearrange the respective equation in terms of \(\tilde{G}^R_{(1)}\) to get

\[\tilde{G}^R_{(1)} = -\frac{i}{2} G^R \partial_T G^R + \frac{1}{2i} G^R \partial_T \tilde{\Sigma}^R \partial_\omega G^R.\]  

(34)

We note that

\[\partial_\omega G^R = -\left(\partial_\omega G^R\right)^2\]  

(35)

and

\[\partial_T G^R = \partial_T \tilde{\Sigma}^R \left(\partial_\omega G^R\right)^2.\]  

(36)

Substituting these derivatives we find that

\[\tilde{G}^R_{(1)} = 0.\]  

(37)

Therefore, the first order nonadiabatic correction to the retarded Green’s function vanishes. Now considering the second order correction, we rearrange for \(\tilde{G}^R_{(2)}\) and make a substitution for \(\tilde{G}^R_{(1)}\) to get

\[\tilde{G}^R_{(2)} = -\frac{1}{8} G^R \partial_T^2 \tilde{\Sigma}^R \partial_\omega^2 G^R,\]  

(38)

which, after computing the double derivative of the adiabatic retarded Green’s function, can be easily shown to produce

\[\tilde{G}^R_{(2)} = -\frac{1}{4} \left(\partial_\omega G^R\right)^4 \partial_T^2 \tilde{\Sigma}^R,\]  

(39)

where \(\partial_T^2 \tilde{\Sigma}^R\) is given by

\[\partial_T^2 \tilde{\Sigma}^R = -i q^2 \Gamma_\alpha \lambda_\alpha^2 - i q^2 \Gamma_\alpha \lambda_\alpha (1 + \lambda_\alpha q_\alpha).\]  

(40)
D. Formula for electric current

We begin with the general expression for the electric current at time \( t \) flowing from \( \alpha = L, R \) electrode to the molecule

\[
J_\alpha(t) = C_\alpha(t, t),
\]  

(41)

where

\[
C_\alpha(t, t') = 2 \int_{-\infty}^{+\infty} dt_1 \text{Re} \left\{ G^<(t, t_1) \Sigma^A_\alpha(t_1, t') + G^R(t, t_1) \Sigma^<_\alpha(t_1, t') \right\},
\]  

(42)

In Wigner representation the expression for the current becomes

\[
J_\alpha(T) = \int_{-\infty}^{+\infty} d\omega \tilde{C}_\alpha(T, \omega),
\]  

(43)

where \( \tilde{C}_\alpha(T, \omega) \) is the Wigner transformation of the two-time function \( C_\alpha(t, t') \):

\[
\tilde{C}_\alpha(T, \omega) = 2 \text{Re} \left\{ e^{\frac{i}{\hbar} (\partial_T^2 - \partial_\omega^2)} \left( \tilde{G}^< \tilde{\Sigma}^A_\alpha + \tilde{G}^R \tilde{\Sigma}^<_\alpha \right) \right\}.
\]  

(44)

Taking a second order gradient expansion for the exponential derivatives as well as expanding the Green’s function up to the second order (note that we use the expansion for the lesser Green’s function \( G^< = G^<_{(0)} + \tilde{G}^<_{(1)} + \tilde{G}^<_{(2)} \) similar to (29) but the particular form of the terms in this expansion is not required for our final expression), we now break this equation for the current based on order to get

\[
J^{(0)}_\alpha(q) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re} \left\{ G^< \tilde{\Sigma}^A_\alpha + G^R \tilde{\Sigma}^<_\alpha \right\},
\]  

(45)

\[
J^{(1)}_\alpha(q, \dot{q}) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re} \left\{ \tilde{G}^< \tilde{\Sigma}^A_\alpha + \tilde{G}^R \tilde{\Sigma}^<_\alpha + \frac{1}{2i} \left( \partial_T G^R \right) \left( \partial_\omega \tilde{\Sigma}^<_\alpha \right) - \frac{1}{2i} \left( \partial_\omega G^< \right) \left( \partial_T \tilde{\Sigma}^A_\alpha \right) \right\}
\]  

(46)

and

\[
J^{(2)}_\alpha(q, \dot{q}, \ddot{q}) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re} \left\{ \tilde{G}^< \tilde{\Sigma}^A_\alpha + \tilde{G}^R \tilde{\Sigma}^<_\alpha + \frac{1}{2i} \left( \partial_T \tilde{G}^R_{(1)} \right) \left( \partial_\omega \tilde{\Sigma}^<_\alpha \right) \right. \\
- \frac{1}{2i} \left( \partial_\omega \tilde{G}^<_{(1)} \right) \left( \partial_T \tilde{\Sigma}^A_\alpha \right) - \frac{1}{2i} \left( \partial_\omega \tilde{G}^R_{(1)} \right) \left( \partial_T \tilde{\Sigma}^<_\alpha \right) - \frac{1}{8} \left( \partial^2 G^R \right) \left( \partial_\omega^2 \tilde{\Sigma}^<_\alpha \right) \\
+ \frac{1}{4} \left( \partial_T \partial_\omega G^R \right) \left( \partial_{\omega T} \tilde{\Sigma}^<_\alpha \right) - \frac{1}{8} \left( \partial^2 G^< \right) \left( \partial_\omega^2 \tilde{\Sigma}^A_\alpha \right) - \frac{1}{8} \left( \partial^2 G^R \right) \left( \partial_\omega^2 \tilde{\Sigma}^<_\alpha \right) \right\}.
\]  

(47)
By considering the identities with $\tilde{A}$ as a combination of molecular Green's functions in the Wigner representation (owing to the fact that the Green's functions vanish as $|t-t'| \rightarrow \pm \infty$)

$$\int_{-\infty}^{\infty} d\omega \tilde{A}(\partial_\omega \tilde{\Sigma}) = - \int_{-\infty}^{\infty} d\omega (\partial_\omega \tilde{A}) \tilde{\Sigma}$$  \hspace{1cm} (48)$$

and

$$\int_{-\infty}^{\infty} d\omega \tilde{A}(\partial^2_\omega \tilde{\Sigma}) = \int_{-\infty}^{\infty} d\omega (\partial^2_\omega \tilde{A}) \tilde{\Sigma},$$  \hspace{1cm} (49)

we simplify the equations to

$$J^{(0)}_{\alpha}(q) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re}\left\{ G^< \tilde{\Sigma}^A_{\alpha} + G^R \tilde{\Sigma}^<_{\alpha} \right\},$$  \hspace{1cm} (50)$$

$$J^{(1)}_{\alpha}(q, \dot{q}) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re}\left\{ \tilde{G}^< (1) \tilde{\Sigma}^A_{\alpha} + \tilde{G}^R (2) \tilde{\Sigma}^<_{\alpha} -\frac{1}{2t} \left( \tilde{G}^R + \tilde{G}^R \right) \tilde{\Sigma}^<_{\alpha} - \frac{1}{2t} \left( \partial_\omega G^R \right) \left( \partial_\tau \tilde{\Sigma}^<_{\alpha} \right) \right\},$$  \hspace{1cm} (51)$$

and

$$J^{(2)}_{\alpha}(q, q', \dot{q}) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re}\left\{ \tilde{G}^< (2) \tilde{\Sigma}^A_{\alpha} + \tilde{G}^R (2) \tilde{\Sigma}^<_{\alpha} \right\}$$

$$+ \frac{1}{4} \left( \partial_\tau \partial^2_\omega G^R \right) \left( \partial_\tau \tilde{\Sigma}^<_{\alpha} \right) - \frac{1}{8} \left( \partial^2_\omega G^R \right) \left( \partial^2_\tau \tilde{\Sigma}^<_{\alpha} \right).$$  \hspace{1cm} (52)

Consider the net second order nonadiabatic current as

$$J^{(2)}(q, q', \dot{q}) = y(q) J^{(2)}_{L}(q, \dot{q}, \ddot{q}) - (1 - y(q)) J^{(2)}_{R}(q, \dot{q}, \ddot{q}),$$  \hspace{1cm} (53)$$

where $y(q)$ is arbitrary function of $q$. Function $y(q)$ can be chosen such that the final expression for the current has a particularly simple form. Substituting in explicit expressions for $J^{(2)}_{L}(q, \dot{q}, \ddot{q})$ and $J^{(2)}_{R}(q, \dot{q}, \ddot{q})$ we find that $J^{(2)}(q, \dot{q}, \ddot{q})$ becomes

$$J^{(2)}(q, q', \dot{q}) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \text{Re}\left\{ \tilde{G}^< (2) \left( y \Sigma^A_L - (1 - y) \Sigma^A_R \right) + \left[ \tilde{G}^R (2) - \frac{1}{8} \partial^2_\tau \partial^2_\omega G^R \right] \right\}$$

$$\left( y \Sigma^< L - (1 - y) \Sigma^< R \right) + \frac{1}{4} \partial_\tau \partial^2_\omega G^R \left( y \partial_\tau \Sigma^< L - (1 - y) \partial_\tau \Sigma^< R \right) - \frac{1}{8} \partial^2_\omega G^R \left( y \partial^2_\tau \Sigma^< L - (1 - y) \partial^2_\tau \Sigma^< R \right).$$  \hspace{1cm} (54)$$

We now choose $y$ such that the lesser Green’s function term disappears. This is done by solving for $y$ given

$$y \Sigma^A_L - (1 - y) \Sigma^A_R = 0.$$  \hspace{1cm} (55)$$
This can be easily solved to give
\[ y = \frac{\overline{\Sigma}_R^A}{\overline{\Sigma}_L^A + \overline{\Sigma}_R^A} = \frac{\Gamma_R(1 + \lambda_R q_R)^2}{\Gamma_L(1 + \lambda_L q_L)^2 + \Gamma_R(1 + \lambda_R q_R)^2}. \] (56)

By making substitutions for \( y(q) \), we find that (54) becomes
\[
J^{(2)}(q, \dot{q}^2, \ddot{q}) = \frac{1}{\pi} \int d\omega \text{Re}\left\{ \left[ \frac{\tilde{G}_R^{(2)}}{8 \partial^2 T \omega} \right] \frac{\Gamma_R(q_R) \tilde{\Sigma}_L^<(q_L) - \Gamma_L(q_L) \tilde{\Sigma}_R^<(q_R)}{\Gamma_L(q_L) + \Gamma_R(q_R)} \right. \\
+ \frac{1}{4} \partial_T \partial^2 G^R \left[ \frac{\Gamma_R(q_R) \partial_T \tilde{\Sigma}_L^<(q_L) - \Gamma_L(q_L) \partial_T \tilde{\Sigma}_R^<(q_R)}{\Gamma_L(q_L) + \Gamma_R(q_R)} \right. \\
- \frac{1}{8} \partial^2 G^R \left[ \frac{\Gamma_R(q_R) \partial_T^2 \tilde{\Sigma}_L^<(q_L) - \Gamma_L(q_L) \partial_T^2 \tilde{\Sigma}_R^<(q_R)}{\Gamma_L(q_L) + \Gamma_R(q_R)} \right. \\
\left. \left. \left. \right. \right. \right\}. \] (57)

We now make substitutions for the self-energy terms where we use the form
\[ \Sigma^A = \frac{i}{2} \Gamma_\alpha(q_\alpha) \] (58)

and
\[ \Sigma^<_L/R = i \Gamma_\alpha(q_\alpha) f_\alpha, \] (59)

where \( \Gamma_\alpha(q_\alpha) = \Gamma_\alpha(1 + \lambda_\alpha q_\alpha)^2 \) and the associated derivatives in this form are obvious. We find that
\[
J^{(2)}(q, \dot{q}^2, \ddot{q}) = \frac{1}{\pi \Gamma(q)} \int d\omega \text{Re}\left\{ \frac{i}{2} \Gamma_L(q) \Gamma_R(q_R) \left[ \tilde{G}_R^{(2)} - \frac{1}{8} \partial^2 T \omega \right] \right. \\
+ \frac{i}{4} \partial_T \partial^2 G^R \left( \Gamma_L(q) \Gamma_R(q_R) f_L - \Gamma_L(q) \Gamma_R(q_R) f_R \right) \\
- \frac{i}{8} \partial_T^2 G^R \left( \Gamma_L(q) \Gamma_R(q_R) f_L - \Gamma_L(q) \Gamma_R(q_R) f_R \right) \right\}. \] (60)

In the equation above we have used the quantity
\[ \Gamma(q) = \Gamma_L(q_L) + \Gamma_R(q_R). \] (61)

We now take a detour and search for explicit forms for all \( \Gamma(q) \) terms and their associated derivatives. Consider first
\[ \Gamma_\alpha(q_\alpha) = \Gamma_\alpha(1 + \lambda_\alpha q_\alpha)^2, \] (62)

where its central time derivatives are given by
\[ \dot{\Gamma}_\alpha(q_\alpha) = 2 \Gamma_\alpha \lambda_\alpha \dot{q}_\alpha (1 + \lambda_\alpha q_\alpha), \] (63)
and
\[ \tilde{\Gamma}_\alpha(q) = 2\Gamma_\alpha \lambda_\alpha^2 \dot{q}_\alpha^2 + 2\Gamma_\alpha \lambda_\alpha \dot{q}_\alpha (1 + \lambda_\alpha q_\alpha). \] (64)

Making substitutions (neglecting acceleration terms since they will disappear once averaged over time), we find that
\[
J^{(2)}(q, q') = \frac{\Gamma_L \Gamma_R}{2\pi \Gamma(q)} \int d\omega \text{Re} \left\{ i(1 + \lambda_L q_L)^2 (1 + \lambda_R q_R)^2 \left[ \tilde{G}^{R(2)}(q) - \frac{1}{8} \partial^2 \omega G^R \right] (f_L - f_R) \right. \\
+ i(1 + \lambda_L q_L)(1 + \lambda_R q_R) \partial_\omega \partial^2 \omega G^R \left( \dot{q}_L \lambda_L (1 + \lambda_R q_R) f_L - \dot{q}_R \lambda_R (1 + \lambda_L q_L) f_R \right) \\
- \frac{i}{2} \partial^2 \omega G^R \left( \dot{q}_L^2 \lambda_L^2 f_L - \dot{q}_R^2 \lambda_R^2 f_R \right) \left. \right\}. \tag{65}
\]

In order to simplify the presentation of the expressions we introduce the quantity
\[ \Lambda_\alpha = 1 + \lambda_\alpha q_\alpha. \tag{66} \]

We now substitute in the explicit forms of \( \tilde{G}^{R(2)} \) and all Green’s function derivatives to find
\[
J^{(2)}(q, q') = \frac{\Gamma_L \Gamma_R}{2\pi \Gamma(q)} \int d\omega \text{Re} \left\{ -i\Lambda_L^2 \Lambda_R^2 \left[ (G^R)^4 \partial_\omega^2 \Sigma^R + 3(G^R)^5 \partial_\omega \Sigma^R \right] (f_L - f_R) \right. \\
+ 6i\Lambda_L \Lambda_R (G^R)^4 \partial_\omega \Sigma^R \left( \dot{q}_L \lambda_L \Lambda_R f_L - \dot{q}_R \lambda_R \Lambda_L f_R \right) \\
- i(G^R)^3 \left( \dot{q}_L^2 \lambda_L^2 f_L - \dot{q}_R^2 \lambda_R^2 f_R \right) \left. \right\}. \tag{67}
\]

Making a substitution for the self energy components yields
\[
J^{(2)}(q, q') = \frac{\Gamma_L \Gamma_R}{2\pi \Gamma(q)} \int d\omega \text{Re} \left\{ -\Lambda_L^2 \Lambda_R^2 \left[ (G^R)^4 \left( \dot{q}_L^2 \lambda_L^2 \Gamma_L + \dot{q}_R^2 \lambda_R^2 \Gamma_R \right) \right. \\
+ 3(G^R)^5 \left( \dot{q}_L \lambda_L \Gamma_L \Lambda_R + \dot{q}_R \lambda_R \Gamma_R \Lambda_L \right) \left( f_L - f_R \right) \\
+ 6\Lambda_L \Lambda_R (G^R)^4 \left( \dot{q}_L \lambda_L \Gamma_L \Lambda_R + \dot{q}_R \lambda_R \Gamma_R \Lambda_L \right) \left( \dot{q}_L \lambda_L \Lambda_R f_L - \dot{q}_R \lambda_R \Lambda_L f_R \right) \\
- i(G^R)^3 \left( \dot{q}_L^2 \lambda_L^2 \Lambda_R f_L - \dot{q}_R^2 \lambda_R^2 \Lambda_L f_R \right) \left. \right\}. \tag{68}
\]

We now average over nuclear velocities and remove terms which do not preserve the continuity equation, to find
\[
J^{(2)}(q, q') = -\frac{\Gamma_L \Gamma_R \Lambda_L^2 \Lambda_R^2}{\pi \Gamma(q)} \int d\omega \text{Re} \left\{ \left( G^R \right)^4 \left( \dot{q}_L^2 \lambda_L^2 \Gamma_L + \dot{q}_R^2 \lambda_R^2 \Gamma_R \right) \right\} (f_L - f_R). \tag{69}
\]

Combining all non-vanishing terms together we obtain the following expression for the total current
\[
J(q, q') = J(q) + J^{(2)}(q, q') = \int_{-\infty}^{+\infty} d\omega \mathcal{T}(\omega) (f_L - f_R), \tag{70}
\]
\[ 12 \]
where
\[
T(\omega) = -\frac{1}{\pi} \frac{\Gamma_L(q_L) \Gamma_R(q_R)}{\Gamma_L(q_L) + \Gamma_R(q_R)} \left( \text{Im}\{G^R(\omega)\} + \left( \frac{\lambda_L^2 \Gamma_L + \lambda_R^2 \Gamma_R}{\Gamma_L + \Gamma_R} \right) \text{Re}\{[G^R(\omega)]^4\} \right)
\]  
(71)
with \(\Gamma_\alpha(q_\alpha) = \Gamma_\alpha(1 + \lambda_\alpha q_\alpha)^2\).

Equations (70,71) are the main results of the paper. Notice that despite its similar appearance to the Landauer formula, \(T(\omega)\) given by (71) should not be viewed as the transmission probability for electron with energy \(\omega\). The inelastic effects are present in our model (interaction between electronic and nuclear degrees of freedom) and, therefore, generally there is no connection between \(T(\omega)\) (71) and the probability for an electron with energy \(\omega\) to be transferred across the molecular bridge.

III. RESULTS

The proposed theory is illustrated in the single molecular orbital and single nuclear degree of freedom case. As such we choose parameters \(q = q_L = -q_R\) – it means if the left bond stretches than the right bond contracts, and vice versa and \(\lambda = \lambda_L = \lambda_R\). In this limit we compute the following expression for \(T(\omega)\) using (71)
\[
T(\omega) = -\frac{1}{\pi} \frac{\Gamma_L(q) \Gamma_R(-q)}{\Gamma_L(q) + \Gamma_R(-q)} \left( \text{Im}\{G^R(\omega)\} + \frac{\lambda^2 (\Gamma_L + \Gamma_R)}{\Gamma_L + \Gamma_R} \text{Re}\{[G^R(\omega)]^4\} \right).
\]  
(72)
The first term represents the elastic transmission coefficient for electron transport in a frozen molecular junction geometry and the second term gives nonadiabatic corrections that arise from dynamical variations in molecule-electrode interfacial atomic configuration. Computing this case exactly at resonance \(\omega = \epsilon\), and where the geometry is taken at the equilibrium configuration \(q = 0\), we find that this further reduces to
\[
T(\omega) = \frac{1}{\pi} \frac{\Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)^2} \left( 1 - \frac{16 \bar{q}^2 \lambda^2}{(\Gamma_L + \Gamma_R)^2} \right).
\]  
(73)
Equation (73) demonstrates that the nonadiabatic contribution to the quantity \(T(\omega)\) always plays the destructive role at the resonance regime suppressing the “transparency” of the molecular junction for tunneling electrons.

Through the use of (72), we evaluate the quantity \(T(\omega)\) to investigate the adiabatic and nonadiabatic contributions. We choose level broadening \(\Gamma_L = \Gamma_R = 0.5\) and average classical kinetic energy \(\bar{q}^2 = 0.1\) with these quantities being chosen to reflect possible experimental
FIG. 1. Function $T(\omega)$ computed for electron-nuclei coupling strength $\lambda$. Parameters used in calculations: $\Gamma_L = \Gamma_R = 1$, $\bar{q}_L = \bar{q}_R = 0.1$, $\epsilon = 0$.

values. Calculations are conducted for a range of values of $\lambda$, namely we consider $\lambda = 0$, which corresponds to fully adiabatic transport, and $\lambda = 1, 2$ as seen in Fig. 1.

Let us now consider the case of electron transport where the molecular junction interface is no longer confined to its equilibrium geometry. We do this by averaging the system over nuclear position and velocity according to the Boltzmann factor for a quadratic potential $V(q) = \frac{1}{2}kq^2$, where the spring constant $k$ describes the rigidity of the molecule-electrode linkage bonds. In Fig. 2, we plot the transmission coefficient for three values of the spring constant $k = 0.2, 2, 20$. We see in Fig. 2 that the adiabatic and nonadiabatic effects take on larger values for molecular junctions of increasing rigidity of molecule-electrode interfaces. The dip in the transmission coefficient at the resonance is not affected by the flexibility of molecule-electrode linkages, but on overall a molecular junction with soft bonds on the
FIG. 2. Function $T(\omega)$ computed for different values of the electrode-molecule bond spring constant $k$. Parameters used in calculations: $\Gamma_L = \Gamma_R = 0.5$, $\bar{q}_L^2 = \bar{q}_R^2 = 0.1$, $\epsilon = 0$, $\lambda = 1$.

molecule-electrode interfaces is less conductive.

IV. CONCLUSION

This paper has detailed a quantum transport theory that computes the electronic current while taking into account the nonadiabatic dynamical effects of motion of atoms on the molecule-electrode interfaces. Our approach makes use of the Keldysh nonequilibrium Green’s functions technique where the equations of motion are mapped into the Wigner space such that fast and slow time scales are easily identifiable. The equations of motion are then solved in the limit that interfacial nuclear dynamics are slow, where, as a result, a systematic perturbative expansion is developed about the small parameter to compute the adiabatic
molecular Green’s functions with first and second order nonadiabatic corrections. These components are used to compute the electric current as a function of molecular geometry, velocities and accelerations of nuclei contained in the molecule-lead interface. Our equations allow for the calculations of electronic transport characteristics of molecular junctions where we do not need to assume that the molecular deformation about the equilibrium geometry is small or harmonic, neither do we need to assume that coupling between the nuclear and electronic degrees of freedom is small.

The proposed theory is applied to a simple transport model with a single molecular and a single classical degree of freedom. We find that the motion of nuclei in the molecule-lead interface leads to a destructive contribution in molecular conductivity which mathematically arose from the presence of the second order nonadiabatic corrections in the retarded molecular Green’s functions. Furthermore, we find that more flexible molecule-electrode linkage bonds result in less transparent for electron tunneling molecular junctions.

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