Describing non-Hermitian dynamics using a Generalized Three-Time NEGF for a Partition-free Molecular Junction with Electron-Phonon Coupling

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In this paper we develop the Non-Equilibrium Green’s Function (NEGF) formalism for a dissipative molecular junction that consists of a central molecular system with one-dimensional electronic transport coupled to a phonon environment and attached to multiple electronic leads. Our approach is partitionless – initial preparation of the system places the whole system in the correct canonical equilibrium state – and is valid for an external bias with arbitrary time dependence. Using path integrals as an intermediary tool, we apply a two-time Hubbard-Stratonovich transformation to the phonon influence functional with mixed real and imaginary times to obtain an exact expression for the electronic density matrix at the expense of introducing coloured Gaussian noises whose properties are rigorously derived from the environment action. This results in a unique stochastic Hamiltonian on each branch of the Konstantinov-Perel’ contour (upper, lower, vertical) such that the time evolution operators in the Liouville equation no longer form a Hermitian conjugate pair, thus corresponding to non-Hermitian dynamics. To account for this we develop a generalized three-time NEGF which is sensitive to all branches of the contour, and relate it to the standard NEGF in the absence of phonons via a perturbative expansion of the noises. This approach is exact and fully general, describing the non-equilibrium driven dynamics from an initial thermal state while subject to inelastic scattering, and can be applied to non-Hermitian dynamics in general.
I. INTRODUCTION

In the age of nanofabrication and molecular devices, the electronic transport properties of molecular structures and one-dimensional materials has become an appealing theoretical question, rooted in its applications to electronic engineering\(^1\). Of particular interest are conducting structures where the strong confinement of electrons across two dimensions is of the order of atomic diameters, rendering current flow to be effectively one-dimensional; henceforth, such structures shall be referred to as **molecular junctions**. The conductance of various current-carrying molecular junctions has been measured using scanning probe spectroscopy or nanolithography, with measurements including: scanning probe spectroscopy for single molecules, molecular junctions, and simultaneous measurement of charge and heat transport through single molecules\(^{10–14}\). Determining the current in such molecular junctions is not a purely electronic problem: the electrons interact inelastically with vibrations of the atomic lattice so that the properties of the junction must be understood in the context of open quantum systems, where dissipative effects play an important role in the system’s properties, for example, in scanning tunneling microscopy where an atomic chain forms at the contact between the tip and sample with vibrations\(^{25}\).

The advancement of theoretical approaches for actually calculating these electronic transport properties was kick-started by the development of phenomenological models for elastic transport in static junctions due to Landauer and Buttiker (LB) in the LB formalism\(^{30–37}\) which relates the scattering properties of a conductor to its conductance. More generally, considering elastic transport with rigid atoms has led to an ontology of scattering approaches\(^{30–37}\), predominantly for one dimensional transport, but which are elastic in the sense that they consider electron-electron interactions in the absence of any dissipation/inelastic processes, with some notable exceptions\(^{38–43}\). In fact, formally inelastic effects can be included to all orders in electron-phonon coupling within the multichannel scattering method\(^{43–45}\). Other elastic methods include quantum master equations\(^{46,47}\) and the Non-Equilibrium Green’s Function (NEGF) formalism\(^{48–57}\), where the latter represents a powerful generalization of the scattering matrix method\(^{37–59}\). Crucially, first principles approaches based on NEGFs such as DFT have been very successful at describing the electronic properties for a wide range of systems\(^{60–62}\), and are easily combined with elastic scattering. Of course, the reality is that atomic lattice vibrations (phonons) and inelastic electron-phonon interactions are fundamental to any description of a molecular junction\(^{43,64}\) at finite temperature since the coupling between electrons and phonons is strongly enhanced for one-dimensional and molecular scale systems. The NEGF formalism has proven a fruitful method for the inclusion of interactions within the junction\(^{39,64–71}\), in particular for inelastic effects. In fact, the latter effects are naturally treated within the NEGF using diagrammatic methods\(^{45,72}\).

Using the Feynman-Vernon influence functional formalism\(^{73}\), the effect of the phonon environment on the electronic open system can be calculated exactly using path integrals. Specifically, the quantum-mechanical propagators are expressed as phase-weighted sums over trajectories, where the phase associated with each trajectory is proportional to the action of that trajectory in the classical system\(^{74}\). This approach has since been greatly expanded upon\(^{75–78}\) and applied to many open quantum systems in first quantization, focusing on the rigorous derivation of quantum Langevin equations for the reduced density matrix\(^{79–83}\) or stochastic Liouville von-Neumann equations\(^{84–86}\) via the application of a Hubbard-Stratonovich (HS) transformation\(^{87,88}\). The obtained equations of motion for the density matrix or wavefunction\(^{86,89–95}\) are stochastic in the sense that they contain coloured Gaussian noises, but whose properties are analytically derived from the propagator path integral rather than being introduced artificially. These schemes all exhibit non-Hermitian dynamics associated with a Liouville equation where the time evolution operators do not form a Hermitian conjugate pair, a feature which manifests in dynamics which does not preserve the trace and can lead to numerical instability\(^{86,89}\). Extending this procedure to an electronic open system interacting with the nuclear lattice and heat bath\(^{86}\) has only recently been done for molecular junctions and applied to thermal and electronic transport\(^{69,97}\). The initial condition in this approach has the potential to be generalised so that the electronic and phonon sub-spaces are not partitioned but are jointly thermalized\(^{75,76,98,99}\), though the issue of non-Hermiticity remains a serious point.

In this work, we integrate out the phonon environment directly and generalise the NEGF to account for the resulting non-Hermiticity; even with the tools of the NEGF formalism, the inclusion of phonons leading to non-Hermitian dynamics is formidable. Therefore, our approach is to marry together the advantages of the path integral and NEGF representations of the system, using path integrals to integrate out the atomic vibrations exactly, while the NEGF allows us to construct a consistent and elegant framework for the electronic dynamics in the presence of phonons. The result is the reduction of the system to an electron-only problem in which phonons have been replaced with Gaussian noises in the Hamiltonian, achieved via the application of a generalized HS transformation with respect to two times rather than one\(^{86,90,99,100}\); one real time associated with the open system dynamics, and one imaginary time associated with thermal preparation. This provides an exact procedure for the joint thermal preparation of the electronic and phonon subsystems together in the correct canonical equilibrium state, ensuring that quantum coherence is retained with no adiabatic separation between electronic states and phonons, even at the initial time. The appearance of the Gaussian noises and non-Hermiticity of the Hamiltonian requires a generalisation of the NEGF and the Kadanoff-Baym equations of motion, resulting in a stochastically unravelled\(^{86,101–103}\) three-time Green’s function in which time reversibility with respect to real times is broken\(^{69,100,104,105}\). We emphasise that this three-time NEGF is a rather different kind of NEGF and that its calculation requires the introduction of...
new self-energies, auxiliary functions, and use of the generalized Langreth rules. The purpose of this paper is to present a generalization of the NEGF formalism capable of handling non-Hermitian dynamics, such as in a molecular junction in the presence of electron-phonon coupling within the framework of stochastic unravelling. The paper is organized as follows. We begin in Section II with a description of the model for a current junction that includes a phonon environment in the central region which is coupled to electrons. The result of applying the stochastic unravelling procedure to this model, transforming phonons into coloured Gaussian noises, is presented in Section III, with a detailed derivation in Appendix A. We then develop the three-time NEGF which accounts for the additional branch dependence introduced by stochasticity/non-Hermiticity in Sec IV A, followed by a series expansion appropriate for numerical simulation for the three-time NEGF in terms of the noises and phonon-free NEGF in Section IV B with a summary of the Generalized Langreth Rules in Appendix B. An expression for the non-linear current response to an external bias on the leads in the presence of inelastic scattering is derived in Section IV C, with a subtlety of the derivation explained in Appendix C, and expressions for the components of the self energies given in terms of energy integrals in Appendix D. Finally, in Sections V and VI, we present a discussion of the overall procedure and our conclusions, respectively. At the time of publication, no implementation of this method is available so calculations will not be presented here; this is left for future work.

II. MODEL

We consider a molecular junction comprised of an interacting central region \( C \) connected to any number of non-interacting leads \( \{ L \} \), where each lead is under the influence of an external time-dependent spatially homogeneous bias potential \( V_L(t) \). This set-up is depicted schematically in Figure 1. The system Hamiltonian in the absence of phonons (denoted by the superscript 0) is given by

\[
\hat{H}_0(t) = \sum_{L,i \in L} \left[ \epsilon_i + V_L(t) \right] \hat{c}_i^\dagger \hat{c}_i + \sum_{mn \in C} T_{mn} \hat{d}_m^\dagger \hat{d}_n + \sum_{L,i \in L; n \in C} \left( T_{ni} \hat{d}_n^\dagger \hat{c}_i + T_{in} \hat{c}_i^\dagger \hat{d}_n \right)
\]

where \( \hat{H}_L(t) \) is the Hamiltonian of the \( L^{th} \) lead which includes the bias \( V_L(t) \), \( \hat{H}_0^C \) is the Hamiltonian of the central region which refers to hopping events between eigenstates \( n \) and \( m \), and \( \hat{H}_{LC} \) contains the coupling of the \( L^{th} \) lead to the central region. Here, \( \hat{c}_i^\dagger (\hat{c}_i) \) creates (annihilates) a non-interacting electron with energy eigenvalue \( \epsilon_i \) for any \( i \in L \) in the \( L^{th} \) lead, while an interacting electron in the central region \( C \) of the electronic level \( n \) is created (annihilated) by the operators \( \hat{d}_n^\dagger (\hat{d}_n) \). For the sake of clarity, electronic state indices will be restricted to specific subsystems within the molecular junction, so that \( i, j, k \in L \), while \( n, m \in C \), and \( p, q \in C \cap \{ L \} \).

Figure 1: (Colour online) Schematic of the molecular junction with an atomic chain (grey circles) as the central region connected to an arbitrary number of semi-infinite leads (orange blocks, only two are shown); the \( L^{th} \) lead has chemical potential \( \mu_L \) and external bias \( V_L \) which is switched on at \( t_0 \). Phonons (blue rings) in the central region couple to electronic states in the central region via the electronic coupling operator \( \hat{\sigma} \).

In first quantization, atomic vibrations can be introduced to the Hamiltonian Eq. (1) via each atom \( A \) (of mass \( m_A \)) displacement coordinate \( u_{A\alpha} \) defined relative to the equilibrium position within the lattice \( \alpha \), and the conjugated momentum

\[
\hat{H}_0(t) = \sum_{L,i \in L} \left[ \epsilon_i + V_L(t) \right] \hat{c}_i^\dagger \hat{c}_i + \sum_{mn \in C} T_{mn} \hat{d}_m^\dagger \hat{d}_n + \sum_{L,i \in L; n \in C} \left( T_{ni} \hat{d}_n^\dagger \hat{c}_i + T_{in} \hat{c}_i^\dagger \hat{d}_n \right)
\]
where the third term describes harmonic phonons in the central region, and the third term \( \hat{H}_{el-ph} \) describes the electron-phonon interaction,

\[
\hat{H}_{el-ph} = -\sum_{A} \sum_{nm} \gamma_{nm} \hat{\delta}_{m} \hat{d}_{n} u_{A} = -\sum_{A} \hat{\sigma}_{A} u_{A},
\]

where \( \gamma_{nm} = \langle \phi_{n} | \gamma_{A} | \phi_{m} \rangle \) are the matrix elements of the coupling potential \( \gamma_{A} \) on the orbitals \( \{ \phi_{n}(r) \} \) in the central region, and \( \hat{\sigma}_{A} = \sum_{nm} \gamma_{nm} \hat{\delta}_{m} \) is the electronic coupling operator to the \( A \) displacement.

At thermal equilibrium, the total density matrix of the electronic and phonon subsystems together is given by

\[
\rho_{tot}(t_{0}) = \frac{1}{Z_{tot,0}} e^{-\beta \hat{H}_{0}},
\]

where \( \hat{H}_{0} = \hat{H}^{0}(t_{0}) - \mu \hat{N} \) is the Hamiltonian of the Grand Canonical Ensemble at \( t_{0} \), characterised by the chemical potential \( \mu \) and the number operator \( \hat{N} \), and \( Z_{tot,0} = \text{Tr} \left[ e^{-\beta \hat{H}_{0}} \right] \) is the partition function of the total system.

Note that this is a phenomenological description of phonons in a coupled electron-phonon system since the force-constant matrix is already defined in our Hamiltonian (and thus so are the harmonic frequencies); the full characterisation of lattice vibrations which are caused by ion-electron interactions\(^{63,106,107}\) goes well beyond the scope of this paper. Instead we have assumed that when the lattice is properly dressed with electrons, lattice vibrations which are harmonic emerge and couple with the electrons linearly with respect to their displacements but arbitrarily with respect to the electrons, i.e. there are no limitations applied to the coupling strength.

It is also assumed that up until \( t_{0} \) the total system was in thermodynamic equilibrium characterized by the chemical potential \( \mu_{L} = \mu \) (the same for all leads) and inverse temperature \( \beta \), and not in a partitioned state, before each lead \( L \) was subjected to the potential \( V_{L}(t) \) with subsequently arbitrary time dependence. The physical reality\(^{108}\) of switching on the bias at \( t_{0} \) means that the energy levels in the \( L^{th} \) lead are shifted by \( V_{L}(t_{0}) \), causing a rearrangement of electrons in the junction and the leads, with electronic screening ensuring that the internal electric field well inside any leads will be zero. Consequently, any potential difference introduced as a result of the bias will be confined to the central region. This is avoided by choosing a sufficiently large central region so that the boundary layer of each lead which is most affected by the charge redistribution is incorporated directly into the central region and any modulation of the bias by the charge redistribution can be neglected, with \( V_{L}(t) \) once again being uniform within the \( L \)-th lead.

### III. Unravelling the Phonon Influence Functional

The central region Hamiltonian including phonons Eq. (3) corresponds to harmonic bath degrees of freedom \( \{ A_{\omega} \} \) coupled to electronic states \( \{ nm \} \) in the central region, where the coupling strength is arbitrary in the central region’s coordinates but linear in the bath displacement. Although Eq. (3) is presented in second quantization, there is of course a corresponding Hamiltonian in first quantization which consists of an electronic sub-system made up of one-particle bra-ket states coupled to a classical harmonic bath. As a result, the first quantization version of Eq. (3) is a more general form of the Caldeira-Leggitt Hamiltonian\(^{79}\) for which the process of stochastic unravelling is well known\(^{73,75,83}\). Applied to Eq. (3), stochastic unravelling replaces the sum over phonon degrees of freedom in the electron-phonon interaction of Eq. (4) with a stochastic Hamiltonian that couples the central region electron states to a set of stochastic potential fields in the form of coloured noises, with the physical properties of the system being recovered exactly by averaging over all possible manifestations of these noises.

To do this (see Appendix A), we derive an exact expression for the reduced density matrix by taking the partial trace over the atomic vibrations by means of the path integral method, expressing the influence functional in the quadratic (bi-linear) form needed to apply the HS transformation to introduce the noises. This reduced density matrix is therefore reduced with respect to the atomic displacements, so can be thought of as the electron-only density matrix. By then returning to the operator language from the path integrals representation, two stochastic propagators can be introduced, \( \hat{U}^{\pm} \), which enable one to write an exact expression for the time evolution of the reduced (electronic) density matrix from its initial value, \( \rho_{0} \).
at time $t_0$ (as a formal solution of a stochastic Liouville equation) as
\[ \tilde{\rho}(T) = \hat{U}^+(t, t_0^+) \tilde{\rho}_0 \hat{U}^-(t_0^-, T), \] (6)
where the tilde has been introduced to denote the fact that this is not the physical density matrix but a stochastic one corresponding to a single realization of the noises. Physical quantities are only recovered after averaging over the noises and appropriate normalization (see below) Eq. (6) corresponds to stochastic dynamics along the horizontal branches of the Konstantinov-Perel’ contour $\kappa$ depicted in Figure 2, first evolving chronologically along $\kappa^+$ by $\hat{U}^+$ up to the observation time $\bar{T}$, introduced here as the right-most real time on the contour, before evolving anti-chronologically along $\kappa^-$ by $\hat{U}^-$. These propagators take the form
\[ \hat{U}^\pm(t, t') = \hat{T}_\pm \exp \left\{ \pm \frac{i}{\hbar} \int_{t'}^{t} dt_1 \hat{H}^\pm(t_1) \right\}, \] (7)
where the Hamiltonian $\hat{H}^\pm$ is now branch dependent,
\[ \hat{H}^\pm(t) = \hat{H}_0 + \hat{H}_{cl-ph}^\pm(t) \] (8)
\[ \hat{H}_{cl-ph}^\pm = - \sum_{\alpha} \left[ \eta_{\alpha}(t) \pm \frac{\hbar}{2} \nu_{\alpha}(t) \right] \hat{\sigma}_{\alpha}. \] (9)
This corresponds to removing the harmonic phonon part from Eq. (3) and replacing the original electron-phonon interaction Hamiltonian with an unravelled coupling term $\hat{H}_{cl-ph}^\pm$ that contains the sets of noises $\{\eta_{\alpha}(t)\}$ and $\{\nu_{\alpha}(t)\}$, so that Eq. (8) is for electrons only. Crucially, the stochastic propagators on either side of $\tilde{\rho}_0$ in Eq. (6) are not each other’s Hermitian conjugate, that is, $\hat{U}^+$ is not the Hermitian conjugate of $\hat{U}^-$. As such, the dynamics described in Eq. (6) is not Hermitian, with Hermicity only being recovered after taking the stochastic average $\langle ... \rangle_{\xi_\xi}$. This represents a significant deviation from standard NEGF theories, and is the main feature of this approach which requires a generalization of the NEGF.

Similarly, the equilibrium density matrix $\tilde{\rho}_0$ at $t_0$ is obtained by a stochastic evolution in imaginary time,
\[ \rho(\tau) = \tilde{U}(\tau, 0), \] (10)
with $\rho(\beta\hbar) = \tilde{\rho}_0$, where the over-bar denotes imaginary time stochasticity, and
\[ \tilde{U}(\tau, \tau') = \hat{T}_M \exp \left\{ - \frac{1}{\hbar} \int_{\tau'}^{\tau} d\tau_1 \hat{H}(\tau_1) \right\}. \] (11)
is a stochastic propagator in imaginary time from \( \tau' \) and \( \tau \) along the vertical branch of the contour \( \kappa^M = \{ \tau \in [0, \beta \hbar] \} \) (see Figure 2) serving to thermalize the total system into the correct initial canonical equilibrium state corresponding to a particular realization of the imaginary time noises, \( \{ \overline{\mu}_{\text{AA}}(\tau) \} \). The Hamiltonian on the vertical branch inherits this set of imaginary time noises, which replace the corresponding displacement operators in the electron-phonon coupling term:

\[
\hat{H}(\tau) = \hat{H}^0 + \overline{H}_{\text{el-ph}}(\tau),
\]

\[
\overline{H}_{\text{el-ph}}(\tau) = - \sum_{A\alpha} \overline{\mu}_{\text{AA}}(\tau) \hat{\sigma}_{\alpha A},
\]

so that there are three sets of noises \( \{ \eta_{\text{AA}}(t) \}, \{ \nu_{\text{AA}}(t) \} \) and \( \{ \overline{\mu}_{\text{AA}}(\tau) \} \), with three noises \( \eta_{\text{AA}}, \nu_{\text{AA}}, \overline{\mu}_{\text{AA}} \) per atomic displacement \( u_{\alpha A} \).

Collectively, Eqs. (6)-(13) correspond to evolution via a complex time propagator \( \hat{U}(z, z') \), where \( z, z' \) can take any position on the contour, with contour ordering operator \( \hat{T}_R \) which considers ascending times to run from \( t^*_0 \) to \( \tilde{t} \), then \( \tilde{t} \) to \( t^*_0 \), then \( t^*_0 \) to \( t^*_0 - i\beta \hbar \), so satisfies \( \hat{T}_R \) and \( \hat{T}_M \) on the horizontal and vertical branches, respectively. It will be useful to introduce the general creation(annihilation) operators \( \hat{a}^\dagger_p (\hat{a}_p) \in \{ c_{\eta}(\hat{c}_i), \hat{d}_n^\dagger (\hat{d}_n) \} \) where the states \( p, p' \) can be in any region (lead or central) of the total system. In doing so, the stochastic Hamiltonian can be more compactly expressed,

\[
\hat{H}^\kappa(z) = \sum_{pp'} h_{pp'}(z) \hat{a}^\dagger_p \hat{a}_{p'}
\]

\[
= \begin{cases} 
\hat{H}^\pm(t) = \hat{H}^0(t) + \hat{H}_{\text{el-ph}}(t), & \text{on } \kappa^\pm \\
\hat{H}(\tau) = \hat{H}^0 + \overline{H}_{\text{el-ph}}(\tau), & \text{on } \kappa^M.
\end{cases}
\]

Writing the Hamiltonian in this way makes it possible to construct blocks of the matrix \( h_{pp'}(t) \) projected onto the lead and central region subspaces for any combination of times on the contour,

\[
\{ h_{pp'}(z) \} = \begin{cases} 
\{ h_{LL}(t) = \{ c_{ij}(t) \} = \{ \delta_{ij} [ \epsilon_i + V_L(t) ] \} \}, & \text{where } i, j \in L \text{ and } t \in \kappa^\pm \\
\{ h_{LM}(\tau) = \{ h_{\text{el}}(\tau) \} = \{ \delta_{ij} \epsilon^M \} \}, & \text{where } i, j \in L, \tau \in \kappa^M \\
\{ h_{LC} = \{ \epsilon_{in} \} = \{ T_{in} \} \}, & \text{where } i \in L, n \in C \text{ and } z \in \kappa = \kappa^\pm \cup \kappa^M \\
\{ h_{CC}(t) = \{ h_{nm}(t) \} = \{ T_{nm} + w_{nm}(t) \} \}, & \text{where } n, m \in C \text{ and } t \in \kappa^\pm \\
\{ \overline{H}_{CC}(\tau) = \{ \overline{h}_{nm}(\tau) \} = \{ T_{nm} + \overline{w}_{nm}(\tau) \} \}, & \text{where } n, m \in C, \tau \in \kappa^M.
\end{cases}
\]

Above, \( \epsilon^M_i = \epsilon_i - \mu_L \) and the stochastic part of \( h_{CC}(z) \) is contained within the unravelling matrix \( w_{CC}(z) \) which is given by:

\[
w_{CC}^\pm(t) = - \sum_{A\alpha} \left[ \eta_{\text{AA}}(t) \pm \frac{\hbar}{2} \nu_{\text{AA}}(t) \right] \psi_{CC}^{A\alpha}(t) \quad \text{on } \kappa^\pm
\]

\[
\overline{w}_{CC}(\tau) = - \sum_{A\alpha} \overline{\mu}_{\text{AA}}(\tau) \psi_{CC}^{A\alpha}(\tau) \quad \text{on } \kappa^M.
\]

We take a moment to emphasise this notation. The labels \( \pm \) indicate the presence of stochasticity on the upper and lower horizontal branches, while the over-bar indicates stochasticity on the vertical branch. This is distinct from the label \( M \) for the regular Matsubara branch which does not have any stochasticity associated with it.

The physical density matrix is then recovered by the stochastic average,

\[
\hat{\rho}(t) = \mathbb{N} \langle \hat{\rho}(t) \rangle_{\xi, \bar{\xi}},
\]

where \( \xi \) and \( \bar{\xi} \) represent the noises in real and imaginary time, respectively (Eq. (A32) in Appendix A) and

\[
\mathbb{N} = \langle \rho(\beta \hbar) \rangle_{\xi, \bar{\xi}}^{-1} = \langle \hat{U}(\beta \hbar, 0) \rangle_{\xi, \bar{\xi}}^{-1}
\]

is a normalisation factor which ensures that \( \text{Tr} [ \hat{\rho}] = 1 \), and is needed because of the non-Hermicity of the stochastic dynamics. The noises themselves have non-trivial correlation functions (Eqs. (A33)-(A36) in Appendix A), and are in no way arbitrary or introduced ad hoc. Rather, they are related to the actual phonon dynamics and require knowledge of the phonon eigenstates. Note that this is the only place where actual information of the phonons appears.
IV. THE THREE-TIME GREEN'S FUNCTION

A. Additional Branch Dependence

To justify an introduction of the three-time Green’s function, let us calculate the electronic population matrix at time \( \bar{t} \),

\[
P_{pp'}(\bar{t}) = \text{Tr} \left[ \hat{\rho}(\bar{t}) \hat{a}_p^\dagger \hat{a}_{p'} \right].
\]

Using the stochastic unravelling procedure laid out in Section III, the population matrix is unravelled as

\[
P_{pp'}(\bar{t}) = \mathbb{H} \left\langle \text{Tr} \left[ \hat{U}(\beta h, 0) \hat{U}^-(t_0^-, \bar{t}) \hat{a}_p \hat{a}_{p'} \hat{U}^+(\bar{t}, t_0^+) \right] \right \rangle_{\tilde{\mathcal{G}}}
\]

\[
= \langle \tilde{P}_{pp'}(\bar{t}) \rangle_{\tilde{\mathcal{G}}},
\]

where the tilde on \( \tilde{P} \) again indicates that it is a stochastic quantity; it corresponds to the population calculated for the Hamiltonian (16) in which the atomic displacements in the electron-phonon coupling were replaced with the noises and hence corresponds to a particular stochastic realisation.

In order to calculate the populations \( \tilde{P}_{pp'}(\bar{t}) \) appearing in Eq. (22), we define the three-time NEGF,

\[
G_{pp'}(z, z' | \bar{t}) = -\frac{i}{\hbar} \frac{1}{\Pi(\bar{t})} \left\{ \text{Tr} \left[ \hat{U}(t_0^-, i\beta h, z) \hat{a}_p \hat{U}(z, z') \hat{a}_{p'} \hat{U}(z', t_0^+) \right] \right\}, \quad \text{for } z > z' \text{ w.r.t } \bar{T}_\kappa
\]

\[
-\text{Tr} \left[ \hat{U}(t_0^-, i\beta h, z') \hat{a}_{p'} \hat{U}(z', z) \hat{a}_p \hat{U}(z, t_0^+) \right], \quad \text{for } z < z' \text{ w.r.t } \bar{T}_\kappa,
\]

where the function \( \Pi(\bar{t}) \) (given below in Eq. (34)) is introduced to ensure that the Green’s function still satisfies the regular equations of motion,

\[
i\hbar \partial_z G_{pp'}(z, z' | \bar{t}) = \delta(z - z') \delta_{pq} + \sum_q h_{pq}(z) G_{qp'}(z, z' | \bar{t})
\]

\[
-ih \partial_z G_{pp'}(z, z' | \bar{t}) = \delta(z - z') \delta_{pq} + \sum_q G_{pq}(z, z' | \bar{t}) h_{qp'}(z),
\]

and the \( h_{pq}(z) \) are from Eq. (14). Here, the third time \( \bar{t} \) has been introduced, and is referred to as the observation time (see Figure 2), and the full time evolution operator across the contour \( \kappa \) is required, defined by the equations of motion \( (z \in \kappa) \),

\[
i\hbar \partial_t \hat{U}(t, z) = \hat{H}^z(t) \hat{U}(t, z)
\]

\[
i\hbar \partial_t \hat{U}(z, t) = -\hat{U}(z, t) \hat{H}^t(t)
\]

\[
-i\hbar \partial_t \hat{U}(t_0^- - i\tau, z) = \hat{H}(\tau) \hat{U}(t_0^- - i\tau, z)
\]

\[
-i\hbar \partial_z \hat{U}(z, t_0^- - i\tau) = - \hat{U}(z, t_0^- - i\tau) \hat{H}(\tau),
\]

which have the solution,

\[
\hat{U}(z, z') = \tilde{T}_\kappa \exp \left\{ -\frac{i}{\hbar} \int_{z_0}^z dz_1 \hat{H}(z_1) \right\}.
\]

For instance, when both times are on the horizontal branches \( \kappa^\pm \), we arrive at \( \hat{U}^{\pm}(t, t') \), where \( \tilde{T}_\kappa \to \tilde{T}^{\pm} \) and \( \hat{H}^{\kappa} \to \hat{H}^{\pm}(t) \), while when both time arguments are on the vertical track \( \kappa^M \), we have \( \hat{U}(\tau, \tau') \), in which \( \tilde{T}_\kappa \to \tilde{T}^M \) and \( \hat{H}^{\kappa} \to \hat{H}(\tau) \). When both times \( z \) and \( z' \) belong to different tracks on the contour \( \kappa \), an integration over the appropriate part of the contour from \( z' \) to \( z \) is implied, with appropriate Hamiltonian on each part of the relevant tracks.

The dependence on the observation time \( \bar{t} \) which appears as the third time is a subtle point that must be emphasized. Since the Hamiltonians on the upper and lower branches are now unique, there is no cancellation for regions of the contour which would normally be shared between them, for example the deterministic dynamics of the regular Green’s function from \( t' \) to \( t \) on \( \kappa^+ \) would annul the dynamics from \( \bar{t} \) to \( t' \) on \( \kappa^- \). Instead, the full dynamics of the three-time Green’s function on \( \kappa^+ \) and \( \kappa^- \) must be considered independently, with \( \bar{t} \) parameterizing the dynamics up to some upper time limit \( t_{max} \). This means that the Heisenberg representation cannot be used in the normal way, since \( \hat{H}^{\kappa} \neq \hat{H}^{\bar{t}} \) and \( \hat{U}^+ \) and \( \hat{U}^- \) no longer form a Hermitian conjugate pair; hence the need for the introduction of this new kind of three-time NEGF.
The stochastic population matrix is then obtained via relation to a particular component of this NEGF,

\[
\tilde{P}(\bar{t}) = -i\hbar \Pi(\bar{t}) G^< (\bar{t}, \bar{t}) = -i\hbar \Pi(\bar{t}) G^{+ -} (\bar{t}, \bar{t}),
\]

(32)

where \( \bar{t}^- \) and \( \bar{t}^+ \) are the observation times taken on the lower and upper horizontal branches, respectively, with \( \bar{t}^+ \) being just before and \( \bar{t}^- \) just after the actual observation time \( \bar{t} \) on the contour. The calculation requires the specific lesser Green’s function \( G^{+ -} \) (see\(^{105}\)) with the first argument on the upper and the second on the lower horizontal branches, but when both tend to the observation time. Hence, the task becomes calculating the desired blocks of this lesser component of the Green’s function Eq. (24) such as \( G_{LL}, G_{CC}, \) etc. when all three times are equal to the observation time.

At the same time, one needs to calculate the prefactor \( \Pi(\bar{t}) \). In the rest of this section we shall consider how to calculate this prefactor, while the method of calculating the three-time Green’s function will be considered in the next section.

The function \( \Pi(\bar{t}) \) takes the form

\[
\Pi(\bar{t}) = \text{Tr} \left[ \hat{U}(t_0^- - i\beta\hbar, t_0^+) \right]
\]

(33)

\[
= \text{Tr} \left[ \hat{U}(t_0^- - i\beta\hbar, t_0^-) \hat{U}(t_0^+, \bar{t}) \hat{U}(\bar{t}, t_0^+) \right]
\]

(34)

where the \( \bar{t} \) dependence has been made explicit by showing the shared time in the propagators. Hence, the trace in Eq. (34) is calculated over the complete propagation along the contour, from the initial time \( t_0^- \) to the final \( t_0^- - i\beta\hbar \) passing through the observation time \( \bar{t} \) on the way. Differentiating \( \Pi(\bar{t}) \) with respect to \( \bar{t} \) yields

\[
i\hbar \partial_{\bar{t}} \Pi(\bar{t}) = h \left[ i\hbar \Pi(\bar{t}) \right] \sum_{A\alpha} \nu_{A\alpha}(\bar{t}) \text{tr} \left[ V^{A\alpha} G^{+\alpha}_{CC}(\bar{t}, \bar{t}|\bar{t}) \right],
\]

(35)

which has the formal solution:

\[
\Pi(\bar{t}) = \Pi_0 \exp \left\{ h \int_{t_0}^{\bar{t}} dt \sum_{A\alpha} \nu_{A\alpha}(t) \text{tr} \left[ V^{A\alpha} G^{+\alpha}_{CC}(t, t|t) \right] \right\},
\]

(36)

where we distinguish between the trace of a matrix and the quantum-mechanical trace by writing the former using small letters. Since the electron-phonon coupling matrix \( V \) is only non-zero for electronic states in the central region, only the central region Green’s function appears in the trace.

Here, \( \Pi_0 = \Pi(t_0^-) \) is the initial value of \( \Pi \) when \( \bar{t} = t_0^- = t_0^+ \), that is, when there are no horizontal branches and only the Matsubara branch remains. To calculate \( \Pi_0 \), it is convenient to introduce yet another three-time Green’s function which exists only on the vertical branch which we shall refer to as the thermal Green’s function:

\[
\tilde{G}_{pp'}(\tau, \tau'|\tau) = -\frac{1}{\hbar} \frac{1}{\Pi(\tau)} \left\{ \text{Tr} \left[ \hat{U}(t_0^-, \tau) \hat{a}_p \hat{U}(\tau, \tau') \hat{a}_{p'} \hat{U}(\tau', t_0^- - i\tau) \right] \right. \quad \text{for } \tau > \tau', \tau, \tau' \in (0, \beta\hbar)
\]

\[
- \left. \text{Tr} \left[ \hat{U}(t_0^-, \tau') \hat{a}_{p'} \hat{U}(\tau', \tau) \hat{a}_p \hat{U}(\tau, t_0^- - i\tau) \right] \right\} \quad \text{for } \tau < \tau', \tau, \tau' \in (0, \beta\hbar)
\]

(37)

which involves the imaginary time propagator Eq. (11) defined on the vertical track only, \( \hat{U}(\tau, \tau') \). Note that this \( \tilde{G} \) is not the same as the normal Matsubara component of the regular Green’s function whose arguments \( \tau, \tau' \) are defined on the entire vertical branch \( \kappa^M \), \( \tau, \tau' \in (0, \beta\hbar) \). Instead, the thermal three-time Green’s function contains \( 0 \leq \tau \leq \beta\hbar \) as the third imaginary time, and hence is defined on the subbranch within \( \kappa^M \) from \( 0 \) to \( \tau \) only. Since \( \tau \) is responsible for extending the subbranch up to \( \kappa^M \), it is responsible for the thermalization of the total system including phonons into the canonical equilibrium state, and shall be referred to as the preparation time.

With these definitions, \( \Pi_0 \) is related to the imaginary time propagator for \( \bar{\tau} = \beta\hbar \),

\[
\Pi_0 = \text{Tr} \left[ \hat{U}(t_0^- - i\beta\hbar, t_0^-) \hat{U}(t_0^+, 0) \right]
\]

(38)

\[
= \text{Tr} \left[ \hat{U}(\beta\hbar, 0) \right],
\]

(39)

since \( \hat{U}(t_0^-, t_0^+) = 1 \). This leads to the definition of a similar function to Eq. (34), only this time on the vertical branch,

\[
\tilde{\Pi}(\tau) = \text{Tr} \left[ \hat{U}(\tau, 0) \right],
\]

(40)
so that
\[ \Pi_0 = \Pi(\beta \hbar). \]  

The auxiliary function \( \Pi(\tau) \) has the equation of motion,
\[ -\hbar \partial_\tau \Pi(\tau) = \hbar \Pi(\tau) \text{tr} \left[ \bar{\mathcal{G}}(\tau) \mathcal{G}^< (0, 0^+|\tau) \right], \]  
in which the lesser component of the three-time thermal Green’s function appears. Note that since \( \mathcal{G}^< \) is defined only on the vertical branch, both its arguments belong to the same branch making it clearly determined. Integrating Eq. (42) yields
\[ \Pi(\tau) = \Pi_0 \exp \left\{ - \int_0^\tau d\tau' \text{tr} \left[ \bar{\mathcal{G}}(\tau') \mathcal{G}^< (0, 0^+|\tau') \right] \right\}, \]
where \( \Pi_0 = \Pi(0) = \text{Tr} [\mathcal{U}(0, 0)] = 1. \)

Crucially, \( \Pi(\tau) \) depends on the entire three-time thermal Green’s function across all regions of the junction. Expanding the trace using block notation for the matrices of each region of the junction, each block of \( \mathcal{G} \) can be expressed in terms of the central region \( G_{CC} \) by first introducing the three-time isolated lead Green’s function \( \mathcal{G}_{LL}^0(\tau, \tau'|\tau) \), defined on the subbranch of \( \kappa^M \) between 0 and \( \tau \). Its equation of motion (in obvious symbolic notation) is
\[ -(\hbar \partial + \hbar^M_{LL} \mathcal{G})_{LL}^0 = \delta, \]  
which has the solution
\[ \mathcal{G}_{ij}(\tau, \tau'|\tau) = -\frac{1}{\hbar} \delta_{ij} e^{-\epsilon^M_{ij}(\tau' - \tau)/\hbar} \left[ \Theta(\tau - \tau') \left[ 1 - \bar{\mathcal{G}}_{LL}^0(\tau) \right] - \Theta(\tau' - \tau) \bar{\mathcal{G}}_{LL}^0(\tau) \right], \]
where \( \bar{\mathcal{G}}(\epsilon|\tau) \) is just the ordinary Fermi function but with \( \beta \hbar \) replaced by \( \tau \). Note that \( \mathcal{G}_{LL}^0 \) is not a stochastic Green’s function; the \( \tau \) dependence comes solely from these modified Fermi functions.

The equation of motion for \( \mathcal{G}_{LC} \) is
\[ -(\hbar \partial + \hbar^M_{LL} \mathcal{G})_{LC} = \hbar_{LC} \mathcal{G}_{CC}, \]
which by inverting Eq. (44) becomes
\[ \mathcal{G}_{LC} = \mathcal{G}_{LL}^0 \hbar_{LC} \mathcal{G}_{CC}, \]
and similarly for \( \mathcal{G}_{CL} \),
\[ \mathcal{G}_{CL} = \mathcal{G}_{CC}^0 \hbar_{CL} \mathcal{G}_{LL}^0. \]
Then finally for \( \mathcal{G}_{LL} \),
\[ -(\hbar \partial + \hbar^M_{LL} \mathcal{G})_{LL} = \delta_L + \hbar_{LC} \mathcal{G}_{CL}, \]
applying Eqs. (44) and (48) gives
\[ \mathcal{G}_{LL} = \mathcal{G}_{LL}^0 + \mathcal{G}_{LL}^0 \hbar_{LC} \mathcal{G}_{CC}^0 \hbar_{CL} \mathcal{G}_{LL}^0. \]

Substituting these into Eq. (43) and using cyclic permutations of the trace and the fact that different leads do not interact, \( \hbar_{LL'} = 0 \) for \( L \neq L' \), we obtain
\[ \Pi(\tau) = \exp \left\{ - \int_0^\tau d\tau' \left[ \text{tr} \left[ \bar{\mathcal{G}}_{CC}(\tau) \mathcal{G}_{CC}^< (0, 0^+|\tau) \right] + \sum_L \text{tr} \left[ \hbar^M_{LL} \mathcal{G}_{LL}^0 < (0, 0^+|\tau) \right] \right] + \int_0^\tau d\tau_1 \left[ \text{tr} \left[ \mathcal{G}_{CC}^< (0, \tau_1|\tau) \mathcal{G}_{CC}^> (\tau_1, 0^+|\tau) + \mathcal{G}_{CC}^> (0, \tau_1|\tau) \mathcal{G}_{CC}^< (\tau_1, 0^+|\tau) \right] \right] + \int_0^\tau d\tau_1 \int_0^\tau d\tau_2 \left[ \text{tr} \left[ \mathcal{G}_{CC}^< (\tau_2, \tau_1|\tau) \mathcal{G}_{CC}^> (\tau_1, \tau_2|\tau) \right] \right] \right\}, \]
where $\bar{\eta}_{CC}(\tau)$ contains the noises $\{\eta_{A}(\tau)\}$ and two new imaginary time self-energies $\Sigma_{CC}$ and $\Lambda_{CC}$ have been defined:

$$\Sigma_{CC}(\tau,\tau'|\bar{\tau}) = \sum_{L} \Sigma_{CLC}(\tau,\tau'|\bar{\tau}) = \sum_{L} h_{CLL} g_{LL}(\tau,\tau'|\bar{\tau}) h_{LC}$$

and

$$\Lambda_{CC}(\tau,\tau'|\bar{\tau}) = \sum_{L} \Lambda_{CLC}(\tau,\tau'|\bar{\tau}) = \sum_{L} h_{CLL} g_{LL}(\tau,\tau'|\bar{\tau}) h_{LC}.$$  (52)

Returning to Eq. (51), the presence of the term containing $\sum_{L} \text{tr} \left[ h_{LL} g_{LL}(0, 0^+|\tau) \right]$ is concerning at first glance as the semi-infinite nature of the leads means it will in general be infinity. Since it does not depend on the noises, it can be taken outside of any stochastic averages as a noise-independent pre-factor,

$$Y(\tau) = \exp \left\{ -\int_{0}^{\tau} d\tau \sum_{L} \text{tr} \left[ h_{LL} g_{LL}(0, 0^+|\tau) \right] \right\},$$

so that $\Pi(\tau) = Y(\tau)\Pi_{1}(\tau)$, where $\Pi_{1}$ is the remaining noise-dependent part. When calculating the population matrix (see Eqs. (32), (36) and (41)), this infinite prefactor appears in two places. First, it appears in the normalisation constant $\mathcal{N}$ in Eq. (32), defined in Eq. (20), which takes the value

$$\mathcal{N} = \langle \Pi(\beta h) \rangle^{-1} = Y(\beta h)^{-1}\langle \Pi_{1}(\beta h) \rangle^{-1},$$

since $\mathcal{P}(\tau) = \bar{U}(\tau, 0)$. And second, it appears in the factor $\Pi_{0} = \bar{\Pi}(\beta h)$ within the definition of $\Pi(\bar{t})$. Hence, substituting these results into Eq. (32), the physical population matrix after stochastic averaging becomes

$$P_{pp'}(\bar{t}) = -ih \frac{\langle \Pi_{1}(\beta h)G^{+}(\bar{t},\bar{t}')\Pi(\beta h) \rangle_{\xi}}{\langle \Pi_{1}(\beta h) \rangle_{\xi}},$$

where $\Pi_{1}(\bar{t})$ is simply $\Pi(\bar{t})$ but with the factor of $Y(\beta h)$ removed from $\Pi_{0}$. The factors of $Y(\beta h)$ thus appear in both the numerator and denominator and cancel out, so it is convenient to redefine $\Pi(\tau)$ to only include the stochastic part $\Pi_{1}(\tau)$, as well as redefining $\Pi(\bar{t})$ to only include $\Pi_{1}(\beta h)$ in $\Pi_{0}$. For completeness, the final form of $\Pi(\tau)$ is

$$\Pi(\tau) = \exp \left\{ -\int_{0}^{\tau} d\tau \left( \text{tr} \left[ \bar{\eta}_{CC}(\tau)\Sigma_{CC}(0, 0^+|\tau) \right] \right) \right.$$  
$$+ \int_{0}^{\tau} d\tau_{1} \text{tr} \left[ \Sigma_{CC}(0, \tau_{1}|\tau)\Sigma_{CC}(\tau_{1}, 0^+|\tau) + \Sigma_{CC}(0, \tau_{1}|\tau)\Sigma_{CC}(\tau_{1}, 0^+|\tau) \right] \right.$$  
$$+ \int_{0}^{\tau} d\tau_{1} \int_{0}^{\tau} d\tau_{2} \text{tr} \left[ \Lambda_{CC}(\tau_{2}, \tau_{1}|\tau)\Sigma_{CC}(\tau_{1}, \tau_{2}|\tau) \right] \right\},$$  (56)

which can be calculated as long as the three-time thermal Green’s function in the central region $\bar{G}_{CC}$ is known.

B. Series Expansion in $W$

The equations of motion for blocks of the three-time NEGF in different regions of the junction (in obvious symbolic notation) are:

$$(ih\partial - h_{CC})G_{CC} = \delta_{C} + \sum_{L} h_{CL} G_{LC}$$

$$(ih\partial - h_{CC})G_{CL} = h_{LL} G_{LL}$$

$$(ih\partial - h_{CC})G_{LC} = h_{LC} G_{CC}$$

$$(ih\partial - h_{LL})G_{LL} = \delta_{L} + h_{LC} G_{CL}.$$  (57)

Here, $h_{CC}(z)$ can be split into the phonon-free part $h^{0}_{CC} = \{T_{nm}\}$ and the unravelled part from Eqs. (17) and (18) which contain the noises. Substituting Eq. (59) into Eq. (57) yields

$$(ih\partial - h^{0}_{CC})G_{CC} = \delta_{C} + W_{CC} G_{CC} + \Sigma_{CC} G_{CC},$$

(61)
where the general two-time unravelling matrix \( W_{CC}(z, z') \) has been introduced,

\[
W_{CC}(z, z') = \begin{cases} 
\delta(t-t')w_{CC}^\pm(t) & z, z' = t, t' \in \kappa^\pm \\
\delta(\tau-\tau')\Pi_{CC}(\tau) & z, z' = \tau, \tau' \in \kappa^M \\
0 & \text{otherwise},
\end{cases}
\]

in place of Eqs. (17) and (18) for ease of notation when appearing in contour integrals, and

\[
\Sigma_{CC}(z, z') = \sum_L h_{CL}g_{LL}^0(z, z')h_{LC},
\]

is the regular embedding self-energy containing the Green's function of the isolated leads \( g_{LL}^0 \) under the bias. Similarly, the equation of motion for the phonon-free Green's function in which phonons are not accounted for (with the same bias) is

\[
(i\hbar\partial - h_{CC}^0)G_{CC}^0 = \delta C + \Sigma_{CC}G_{CC}^0.
\]

Comparing this with Eq. (61) one obtains a self-consistent Dyson-like formal equation for \( G_{CC} \),

\[
G_{CC} = G_{CC}^0 + G_{CC}^0W_{CC}G_{CC},
\]

which can be used to generate a Born-like series expansion of the full three-time NEGF in terms of the noises and the phonon-free Green's function, which in the symbolic form reads:

\[
G_{CC} = G_{CC}^0 + G_{CC}^0W_{CC}G_{CC}^0 + G_{CC}^0W_{CC}G_{CC}^0W_{CC}G_{CC}^0 + \ldots.
\]

Writing the times in Eq. (65) explicitly,

\[
G_{CC}(z, z'|\bar{T}) = G_{CC}^0(z, z') + \int_\kappa dz_1dz_2G_{CC}^0(z, z_1)W_{CC}(z_1, z_2)G_{CC}(z_2, z'|\bar{T}),
\]

the integrals over \( \kappa \) must be taken with respect to the generalized Langreth rules\(^{105} \) for the specific component of \( G_{CC} \) of interest. As an example, an expansion for the lesser component \( G^{-+}(z, z'|\bar{T}) \) is presented in Appendix B.

Eq. (67) generates a perturbative expansion with respect to the unravelling matrix \( W_{CC} \). The expansion for the purposes of the calculation must be truncated at certain order with respect to the unravelling matrix \( W_{CC} \) that is linear with respect to the noises. Note that this also requires knowledge of the components of the phonon-free Green’s function \( G_{CC}^0 \) for a variable bias; these expressions are readily available, e.g., in the wide band approximation\(^{106} \). Hence, the three-time Green’s function can be written explicitly in a Born-like series with respect to the electrons-only Green’s function of the junction (which is assumed known) and the noises, so that \( G_{CC} \) is expressed as a power series with respect to the noises.

In addition to the three-time Green’s function \( G_{CC} \), we also need a working expression for the thermal three-time Green’s function; this can also be expanded in a similar fashion,

\[
\bar{G}_{CC}(\tau, \tau'|\bar{T}) = G_{CC}^{0M}(\tau, \tau') + \int_0^\tau d\tau_1 G_{CC}^{0M}(\tau, \tau_1)\Pi_{CC}(\tau_1)\bar{G}_{CC}(\tau_1, \tau'|\bar{T}),
\]

where this time generalised Langreth rules are not required as the integration is performed over the subbranch of \( \kappa^M \) from 0 up to the preparation time \( \bar{T} \).

### C. The Current

Now that the central region three-time Green’s function can be calculated, any block of the Green’s function can be found. For example, the Green’s function for the \( L^{th} \) lead,

\[
G_{LL} = g_{LL}^0 + g_{LL}^0h_{LC}G_{CC}h_{CL}g_{LL}^0.
\]

appears in the unravelled number operator which is just the trace of the population matrix Eq. (32) of the lead,

\[
\bar{N}_{L}(\bar{T}) = -i\hbar\Pi(\bar{T}) \text{ tr } \left[ G_{LL}^{-+}(\bar{T}, \bar{T}|\bar{T}) \right]
\]
\[= -i\hbar n\Pi(\mathcal{T}) \left( \text{tr} \left[ g_{LL}^{0L}(\mathcal{T}, \mathcal{T}) \right] + \int_{\mathcal{K}} d\tau_1 d\tau_2 \text{tr} \left[ g_{LL}^{0L}(\mathcal{T}^+, \mathcal{T}_1) h_{LL} G_{CC}(\mathcal{T}_1, \mathcal{T}_2) h_{LL} g_{LL}^{0L}(\mathcal{T}_2, \mathcal{T}^-) \right] \right) \] (71)

where the double contour integral is again taken with respect to the generalized Langreth rules, and the expression in the square brackets is understood as the +− projection; this is stated explicitly by the time arguments of the \(g_{LL}^{0L}\), the first one containing \(\mathcal{T}^+\) and the second \(\mathcal{T}^-\). Now, using cyclic invariance of the trace, we can rearrange:

\[\bar{N}_L(\mathcal{T}) = -i\hbar n\Pi(\mathcal{T}) \left( \text{tr} \left[ g_{LL}^{0L}(\mathcal{T}, \mathcal{T}) \right] + \int_{\mathcal{K}} d\tau_1 d\tau_2 \text{tr} \left[ \Upsilon_{CLC}(\mathcal{T}_2, \mathcal{T}_1) G_{CC}(\mathcal{T}_1, \mathcal{T}_2) \right] \right) \] (72)

having introduced a new self-energy with components

\[\Upsilon_{CLC}^{\gamma\gamma'}(\mathcal{T}_2, \mathcal{T}_1) = h_{CL} g_{LL}^{0\gamma}(\mathcal{T}_2, \mathcal{T}_1) g_{LL}^{0\gamma'}(\mathcal{T}_1^+, \mathcal{T}_2^-) h_{LL},\] (73)

where the superscripts \(\gamma, \gamma'\) specify the projections of the isolated lead Green’s functions onto the different branches of the contour, as well as their ordering with respect to \(\mathcal{T}_c\). Note that this self-energy depends on only two times on the contour \(z\) and \(z'\), rather than all four of the arguments which appear on the right hand side as the inner two times are explicitly set to the observation time \(\mathcal{T}_c^\pm\) of the indicated branch (upper and lower).

The first term in Eq. (72) involving the isolated lead \(g_{LL}^{0L}\) will be infinite due to the trace over the orbitals in a semi-infinite lead, where for equal arguments, \(g_{LL}^{0L}\) is time-independent and is just the Fermi function (Eq. (D7)). However, it can be shown that this term, after stochastic averaging, represents the total number of electrons in the isolated lead which is a time-independent quantity (see Appendix C). Hence, only the second term in Eq. (72) is time-dependent and responsible for the current.

Hence, differentiating the second term in the number operator of the lead and multiplying by the electron charge, \(-e\), we obtain the current (note that the derivative is a linear operator which commutes with the stochastic average):

\[\mathcal{J}_L(\mathcal{T}) = \frac{ie\hbar}{\langle \Pi(\beta) \rangle_{\xi_2}} \left( \text{tr} \left[ \Pi(\mathcal{T}) \int_{\mathcal{K}} d\tau_1 d\tau_2 \text{tr} \left[ \Upsilon_{CLC}(\mathcal{T}_2, \mathcal{T}_1) G_{CC}(\mathcal{T}_1, \mathcal{T}_2) \right] \right] \right).\] (74)

Note that the double contour integral over both the inner and outer times of \(\Upsilon_{CLC}(\mathcal{T}_2, \mathcal{T}_1) G_{CC}(\mathcal{T}_1, \mathcal{T}_2)\) cannot be written by applying the generalized Langreth rules alone. Instead, all possible combinations of times on the contour with all possible time orderings must be separately considered, introducing the need for the \(\gamma, \gamma'\) indices in Eq. (73). An explicit expression for the trace in the integrand via various components of the Green’s function is given in Appendix B, while the derivation of the components \(\Upsilon_{CLC}^{\gamma\gamma'}\) are presented in Appendix D.

V. DISCUSSION

Having derived the three-time NEGF and it’s associated functions, we should review how it is different from previous approaches. We began by including a phonon bath in the central region Hamiltonian using phonon displacements from equilibrium where the coupling between the bath and central region electrons is linear with respect to these displacements but arbitrary with respect to electrons. Using path integrals to integrate out the effect of the phonons on the electronic system, we were able to apply a HS transformation to the influence functional which exactly removed the phonon degrees of freedom all together, replacing them with three sets of coloured Gaussian noises \(\{\eta_{\alpha}(t)\}, \{\nu_{\alpha}(t)\} \text{ and } \{\pi_{\alpha}(\tau)\}\). There are two key points here.

The first and less important point is that this transformation included the path integral representation of the equilibrium partition function, resulting in the introduction of the set of imaginary time noises. The dynamics associated with these noises is responsible for the joint preparation of the total system (electrons and phonons), initialised in the correct equilibrium state which includes quantum correlations between the electronic and phonon sub-spaces rather than the two sub-spaces being thermalized separately in the so-called partitioned approach. This formulation of the equilibrium density matrix was first derived in the 1990s and then again later in the 2000s, and used by Tanimura to develop hierarchical equations of motion for fermionic systems with an Ohmic spectral density for the environment, and by Lane et al. to quantify deviations from expected asymptotic results which occur as a result of system memory of the nonphysical partitioned state. As a result of this formulation, the contact between electrons and phonons in the molecular junction is neither partitioned nor approximate, removing any spurious transient dynamics associated with the initial mixing of artificially separated sub-spaces which would always otherwise be present. In fact, in the approach we have developed, memory of the initial preparation appears explicitly in the form of the cross-time correlation function between the set of real time noises \(\{\eta_{\alpha}(t)\}\) and imaginary time
noises \( \{ \mathcal{P}_{AA}(\tau) \} \), which is equivalent to the initial entanglement between electrons and phonons having a direct impact on the subsequent system dynamics.

The second and more important point is that the introduction of these noises causes the system dynamics to be non-Hermitian, a property which manifests in three main features: the Hamiltonian is different on the upper and lower horizontal branches of the contour; the forward and backward propagators of the electronic density matrix in the Liouville equation are no longer Hermitian conjugates of each other; and the trace of the electronic density matrix is not preserved over the dynamics. Dealing with this non-Hermiticity issues requires the generalization of the NEGF formalism to include the stochastic branch dependent time evolution operators that we have presented here.

The first of these three features, that the Hamiltonian is now sensitive to the upper and lower branches, supersedes the other two as it is in some sense responsible for them. Since the dynamics over shared periods of time on the branches no longer annul each other, we introduced a third time argument into the NEGF, the observation time \( \bar{t} \), which is the right most time on the contour, as this controls the extent of the full dynamics on the horizontal branches of the contour. The definition of this three-time Green’s function \( G(z, z' | \bar{t}) \) in Eq. (24) requires the introduction of a multiplicative prefactor which is a function of the observation time alone, \( \Pi(\bar{t}) \), which would otherwise appear in its equation of motion. Though an expression for \( \Pi(\bar{t}) \) was found, Eq. (36), its initial value when \( \bar{t} = t_0 \) was not immediately obvious, and required the definition of a similar function \( \Pi(\tau) \), this time a function of the preparation time \( \tau \) which defines a subbranch within the vertical branch, \( \tau \in (0, \tau) \). This provided the initial value, \( \Pi(t_0) = \Pi(\beta \hbar) \), but the expression for \( \Pi(\tau) \) Eq. (56) introduced new imaginary time self-energies \( \Sigma_{CC}(\tau, \tau' | \tau) \) and \( \Lambda_{CC}(\tau, \tau' | \tau) \) and, more importantly, a second three-time thermal NEGF \( \mathcal{G}(\tau, \tau' | \bar{t}) \), defined exclusively on the subbranch parameterized by the preparation time.

Using the Kadanoff-Baym equations of motion for these three-time Green’s functions, we obtained a perturbative expansion Eq. (67) in terms of the unravelling matrix which contains the noises and the phonon-free Green’s function for the molecular junction in the absence of phonons. With a procedure to compute the three-time NEGFs in place, we derived an expression for the non-equilibrium current response to an external bias on the leads in Eq. (74) which involves the three-time Green’s functions leading to an approximate solution, the inelastic dynamics of an electronic open system coupled to a phonon environment. Of course, in practice one would need to use a finite number of terms in the Born-like expansion of the Green’s functions leading to an approximate solution, and this finite expansion would need to converge.

For clarity, we present here a condensed form of the procedure to calculate the non-equilibrium current response to an external bias through the leads using this method:

1. Compute quantities which are independent of the noises: components of the phonon-free NEGF \( G_{CC}^0(z, z') \) from Eq. (D22) and \( \Sigma_{CC}(0, \tau | \tau) \) Eq. (D23), \( \Lambda_{CC}(\tau, \tau' | \tau) \) Eq. (D24) and various components of \( \Upsilon_{CLC}(z, z') \) (Appendix D).

2. Generate realizations of \( \eta_{AA}, \nu_{AA} \) and \( \mathcal{P}_{AA} \). For each realization:
   
   I For \( \tau \in (0, \beta \hbar) \):
   
   i. Use Born-like expansion Eq. (67) on the subbranch of \( k^M \) up to \( \tau \) to calculate the three-time thermal NEGF \( \mathcal{G}_{CC}(\tau, \tau' | \tau) \).
   
   ii. Calculate \( \Pi(\tau) \) Eq. (56).

   II Initialize \( \Pi(t_0) = \Pi(\beta \hbar) \).

   III For \( t \in (t_0, t_{\text{max}}) \):
   
   i. Use Born-like expansion Eq. (67) on the entire contour \( k \) to calculate the three-time NEGF \( G_{CC}(z, z' | \bar{t}) \).
   
   ii. Calculate \( \Pi(\bar{t}) \) Eq. (36).
   
   iii. Evaluate \( \int_k d\zeta_1 d\zeta_2 \Upsilon_{CLC}(z_2, z_1) G_{CC}(z_1, z_2 | \bar{t}) \).

3. Evaluate stochastic averages \( \langle \Pi(\beta \hbar) \rangle_{\xi^2} \) and \( \langle \Pi(\bar{t}) \rangle \int_k d\zeta_1 d\zeta_2 \Upsilon_{CLC}(z_2, z_1) G_{CC}(z_1, z_2 | \bar{t}) \xi_\zeta \).

4. Differentiate the latter with respect to \( \bar{t} \).

5. Evaluate the current Eq. (74).

The feasibility of a numerical scheme involving the three-time NEGF depends on the size of the phonon environment, since there are three noises per phonon, and the computational cost scales with the total number of noises that must be generated, as well as the number of noises involved in a single realization of the system dynamics. Generating the noises themselves should not be a problem, as optimized schemes for generating noises of this kind already exist, and should be
easily extendable to the NEGF framework. It will also require evaluation of the integrals in Appendix D for the self energies, which may in some cases involve the use of Matsubara sums, the Padé approximation, or an extension of the wide band approximation (WBA); this is left for future work. Therefore, the first application of the three-time NEGF is likely to be for a small molecular junction whose central region is on the order of single atoms, with a minimal number of phonon modes.

We are currently working on a numerical implementation of this method for a simple junction, as well as on its further development in which the noises are integrated out analytically.

VI. CONCLUSION

Using the influence functional formalism, the electronic density matrix was obtained by reducing the total density matrix with respect to phonons for a molecular junction with electrons coupled to a phonon environment in the central region, attached to an arbitrary number of leads. Phonon degrees of freedom were fully removed and replaced by complex coloured Gaussian noises via application of a two-time HS transformation, leading to a stochastic Liouville equation for the dynamics of the electronic density matrix. This prompted the definition of a three-time stochastic NEGF $G(z, z'|\tilde{t})$ to account for the non-Hermicity of the dynamics, encapsulated by the dependence on the third time $\tilde{t}$ which is the rightmost time on the Konstantinov-Perel’ contour, or the *observation time*. Initialization of this three-time NEGF involved the definition of a second three-time *thermal* NEGF $\overline{G}(\tau, \tau'|\tau)$, defined only on a subbranch of the Matsubara branch up to the third time $\tau$, the *preparation time*. A perturbative expansion for these new NEGFs in terms of the noises and the regular phonon-free Green’s function was derived, as well as an expression for the non-linear current response to an arbitrary external bias applied to the leads. Physical quantities are recovered by integrating over the functional distribution of the noises. This represents an extension of the NEGF formalism to include stochastic dynamics, or more generally any non-Hermitian dynamics that is sensitive to the upper and lower horizontal branches.

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APPENDICES

Appendix A: Hubbard-Stratonovich and the Influence Functional

By transforming into the normal mode coordinates of the bath $q_\lambda$, the central region Hamiltonian becomes diagonal with respect to the phonons (indicated by $\lambda$),

$$H_C = H_C^0 + \frac{1}{2} \sum \lambda \left[ p_{q_\lambda}^2 + \omega_{q_\lambda}^2 q_{q_\lambda}^2 \right] - \sum \lambda \hat{\sigma}_\lambda q_{q_\lambda},$$  \hspace{1cm} (A1)

$$q_{q_\lambda} = \sum_{A\alpha} \sqrt{m_{A\alpha}} c_{\lambda,A\alpha} u_{A\alpha},$$  \hspace{1cm} (A2)

where $\epsilon_\lambda = \{ e_{\lambda,A\alpha} \}$ are the eigenvectors of the bath’s dynamical matrix $D_{A\alpha}^{A\alpha'} = \lambda_{A\alpha}^{A\alpha'} / \sqrt{m_{A\alpha} m_{A\alpha'}}$ with associated eigenvalues $\omega_{q_\lambda}^2$.

The density matrix of the entire system, being a solution of the Liouville equation, evolves in time via (in this Appendix, we use $\bar{t}$ instead of the observation time $t$ to avoid cumbersome notations)

$$\rho_{tot}(\bar{t}) = \hat{U}(t, \bar{t}) \rho_{tot}(t) \hat{U}(t, \bar{t})$$  \hspace{1cm} (A3)

and therefore, can be thought of as a forward propagation along the real time from $t_0$ to $\bar{t}$ by the regular time evolution operator $\hat{U}(t, \bar{t})$ which is not stochastic (this corresponds to the upper branch $\kappa^+$) followed by the backward propagation from $\bar{t}$ to $t_0$ via $\hat{U}(t_0, \bar{t}) = U^\dagger(t, t_0)$ (this corresponds to the lower branch $\kappa^-$). In the coordinate representation the density matrix depends on the initial and final coordinates of both the electrons and phonons, with all electronic variables $x$ and phonon variables $q$ carrying a superscript $\pm$ which corresponds to the upper and lower horizontal branches, respectively.

The forward propagator of the total system from some initial time $t_1$ up to a later time $t_2$ along the upper branch $\kappa^+$, written in the coordinate representation with respect to electronic coordinates $x$ and phonon coordinates $q$, can be expressed as a path integral over electronic trajectories $x^+(s)$ and phonon trajectories $q^+(s)$,

$$\langle x_2, q_2 | \hat{U}(t_2, t_1) | x_1, q_1 \rangle = \int_{x^+(t_1)=x_1}^{x^+(t_2)=x_2} D\left[x^+(s)\right] \int_{q^+(t_1)=q_1}^{q^+(t_2)=q_2} D\left[q^+(s)\right] e^{\frac{i}{\hbar} S_{tot}[x^+(s), q^+(s)]},$$  \hspace{1cm} (A4)

where $S_{tot}[x^+(s), q^+(s)]$ is the action of the total system of electrons and phonons,

$$S_{tot}[x(s), q(s)] = S^0_{el}[x(s)] + S_{ph}[x(s), q(s)].$$  \hspace{1cm} (A5)

Here, $S^0_{el}[x(s)]$ is the classical action associated with the isolated electronic subsystem of Eq. (1), and the action $S_{ph}[x(s), q(s)]$ contains all terms which depend on the phonons from Eq. (A2). Note that, since phonons and electrons are coupled together, $S_{ph}$ must also depend on the electronic trajectories.

Similarly, the backwards propagator of the total system is

$$\langle x_1, q_1 | \hat{U}(t_1, t_2) | x_2, q_2 \rangle = \int_{x^-(t_2)=x_2}^{x^-(t_1)=x_1} D\left[x^-(s)\right] \int_{q^-(t_1)=q_1}^{q^-(t_2)=q_2} D\left[q^-(s)\right] e^{-\frac{i}{\hbar} S_{tot}[x^-(s), q^-(s)]},$$  \hspace{1cm} (A6)

where the use of the $\pm$ superscripts clearly indicates which branch $\kappa^\pm$ the evolution is on, and with respect to which time ordering. For the backwards propagator, the limits of integration are reversed to reflect the anti-chronological time ordering, with the minus sign in the exponent coming from the time integral in the action going from $t_2$ to $t_1$ with $t_1 < t_2$.

The path integrals are performed with respect to both the open system electronic trajectories and the phonon trajectories. However, the integration over the environment (phonons) can be performed exactly as the part of the Hamiltonian which involves phonons in Eq. (A2) is that of a set of independent displaced harmonic oscillators. Consequently the path integral is Gaussian and its result is well known$^{73-75}$, so that the propagators becomes path integrals over the open system electronic trajectories only. For example, the forward propagator is now given by,

$$\langle x_2, q_2 | \hat{U}(t_2, t_1) | x_1, q_1 \rangle = A^+ \int_{x^+(t_1)=x_1}^{x^+(t_2)=x_2} D\left[x^+(s)\right] e^{\frac{i}{\hbar}\left(S^0_{el}[x^+(s)] + S_{ph}[q_2^+, q_2^-, x^+(s)]\right)},$$  \hspace{1cm} (A7)

where and $q_1^+$ and $q_2^+$ are initial and final phonon normal mode coordinates associated with the initial and final time argu-
ments in the time evolution operator, and

$$A^+ = \prod_\lambda A^+_{\lambda} = \prod_\lambda \frac{1 + i}{2\sqrt{\pi\hbar}} \sqrt{\frac{\omega_\lambda}{\sin(\omega_\lambda(t_2 - t_1))}}$$  \hspace{1cm} (A8)$$

is an oscillating amplitude which arises from a closed loop path integral for each mode. The phonon part of the action, $S_{\text{ph}}[q^0_2, q^0_1, x^+(s)]$, depends only on the initial and final values of the phonon variables, but is still a functional of the electronic coordinates $x^+[s]$ along the trajectory.

The corresponding backwards propagator takes the same form, with the replacement $+ \rightarrow -$, a minus sign in the exponent, and the limits of integration reversed as before.

The electronic only density matrix is obtained by taking the diagonal element of the total density matrix with respect to the phonon coordinates at the final time $\tau$ and integrating over them

$$\rho(x_t, t; x_0, t_0) = \int dq_1 dq_{1t} \rho_{\text{tot}}(t) |x_0,q_1\rangle \langle x_0,q_1|$$

$$= \int dq_1 dq_1 dq_2 dq_2 dq_2 \langle x_1, q_1 | \hat{U}(t,t_0) | x_2, q_2 \rangle \langle x_2, q_2 | \rho_{\text{tot}}(t_0) | x_1, q_1 \rangle \langle x_1, q_1 | \hat{U}(t_0,t) | x_0, q_0 \rangle ,$$ \hspace{1cm} (A10)$$

that is, Eq. (A10) is the reduced density matrix with respect to the phonons.

Assuming that the total system was initially in thermal equilibrium,

$$\rho_{\text{tot}}(t_0) = \frac{1}{Z_{\text{tot},0}} e^{-\beta H_0},$$ \hspace{1cm} (A11)$$

the part associated with the equilibrium density matrix at time $t_0$, after integration over phonons, can also be expressed as an electronic path integral, this time with a dummy imaginary time variable $\tau$,

$$\langle x_2, q^M_{\beta \hbar} | \rho_{\text{tot}}(t_0) | x_1, q^0_0 \rangle = \frac{A^M}{Z_{\text{tot},0}} \int_{x^M(0) = x_1}^{x^M(\beta \hbar) = x_2} D[x^M(\tau)] e^{-\frac{\beta}{\hbar} \left( S^E[x^M(\tau)] + S^M_{\text{ph}}[q^M_0, q^M_\beta, x^M(\tau)] \right)},$$ \hspace{1cm} (A12)$$

where $S^E[x^M(\tau)]$ is the Euclidean action where the electronic Hamiltonian Eq. (1) is used in place of the Lagrangian in an integral over $\tau$ from 0 to $\beta \hbar$, and $S^M_{\text{ph}}[q^M_0, q^M_\beta, x^M(\tau)]$ is the same but for the part of Eq. (A2) that involves phonons and depends on the initial and final values of the phonon coordinates at to $\tau = 0$ and $\tau = \beta \hbar$, respectively. Here, the label $M$ serves the same role as the $\pm$ labels used previously, indicating that this imaginary time evolution can be thought of as evolution along the vertical branch $\kappa^{M}$, and

$$A^M = \prod_{\lambda} A^+_{\lambda} = \prod_\lambda \frac{1}{\sqrt{\sinh(\beta \hbar \omega_\lambda)}}.$$ \hspace{1cm} (A13)$$

Eq. (A10) now becomes

$$\rho(x_t, t; x_0, t_0) = \frac{1}{Z_0} \int dx_1 dx_2 \int_{x^+(t_0) = x_2}^{x^+(t) = x_1} D[x^+(s)] \int_{x^M(0) = x_1}^{x^M(\beta \hbar) = x_2} D[x^M(\tau)] \int_{x^-(t) = x_1}^{x^-(t_0) = x_2} D[x^-(s')] \exp \left\{ \frac{i}{\hbar} \left( S^0_{\text{el}}[x^+(s)] - S^0_{\text{el}}[x^-(s')] + i S^E_{\text{el}}[x^M(\tau)] \right) \right\} \mathcal{F}[x^+(s), x^-(s'), x^M(\tau)]$$ \hspace{1cm} (A14)$$

where

$$\mathcal{F}[x^+(s), x^-(s'), x^M(\tau)] = \frac{A^+ A^M A^-}{Z_{\text{ph}}} \prod_{\lambda} \int dq_{\lambda} dq^+ dq^- dq_{\lambda} F^+_\lambda[q, q^+(s)] F^-_{\lambda}[q, q, x^M(\tau)] F^-_{\lambda}[q, q, x^-(s')]$$ \hspace{1cm} (A15)$$

is the influence functional which contains all the information about the effect of the electron-phonon coupling on the electronic junction, having already performed the path integration over the phonon trajectories. Here, the total partition function $Z_{\text{tot},0}$ has been split into the partition function for the isolated phonon subsystem $Z_{\text{ph}}$,

$$Z_{\text{ph}} = \frac{1}{2} \prod_{\lambda} \cosh \left( \frac{1}{2} \beta \hbar \omega_\lambda \right),$$ \hspace{1cm} (A16)$$
and the partition function for the remaining part $Z_0$, so that $Z_{tot,0} = Z_0 Z_{ph}$. The three functions $F^\pm, M$ come from the path integrals on the three branches of the contour and are exponential functions whose exponents are quadratic in the integration variables. Integration is performed for each phonon mode $\lambda$ separately, and the quadratic structure of the exponent makes the integrals Gaussian and therefore directly integrable, resulting in a single exponential of a sum over modes,

$$F[x^+(s), x^-(s'), x^M(\tau)] = \frac{A^+ A^M A^-}{Z_{ph}} \exp \left\{ -\frac{1}{\hbar} \sum_\lambda \Phi_\lambda [x^+(s), x^-(s'), x^M(\tau)] \right\}, \tag{A17}$$

where $\Phi = \sum_\lambda \Phi_\lambda$ is the influence phase and the prefactor $A^+ A^M A^- / Z_{ph} = 1$, as can be shown by a simple algebra, so that $F[x^+(s), x^-(s'), x^M(\tau)] = \exp (-\Phi/\hbar)$.

This influence phase will depend on the coupling between the electronic subsystem and the phonons. Recalling the electronic coupling operator to the $A\alpha$ phonon $\hat{\sigma}_{A\alpha}$ from Eq. (4), the operators associated with electronic states have been replaced by classical trajectories in the path integrals, leading to the definition of the branch dependent coupling functions $\sigma_\lambda^\pm (s) = \sigma_\lambda^\pm [x^\pm (s)]$ and $\sigma_\lambda^M (\tau) = \sigma_\lambda^M [x^M (\tau)]$ which couple each phonon mode $\lambda$ to the electronic trajectory on one of the three branches $x^\pm (s)$ or $x^M (\tau)$. After much algebra, each mode of the influence phase becomes

$$\Phi_\lambda = \frac{1}{2} \int_{t_0}^t dt_1 dt_2 K_\lambda^{Re} (t_1 - t_2) v_\lambda (t_1) v_\lambda (t_2) + 2i \int_{t_0}^t dt_1 dt_2 \Theta (t_1 - t_2) K_\lambda^{Im} (t_1 - t_2) v_\lambda (t_1) w_\lambda (t_2)$$

$$- i \int_{0}^{\beta \hbar} d\tau_1 \int_{t_0}^{\tau_1} dt_1 K_\lambda (t_1 - i \tau_1) \sigma_\lambda^M (\tau_1) v_\lambda (t_1)$$

$$- \frac{1}{2} \int_{0}^{\beta \hbar} d\tau_1 d\tau_2 [K_\lambda^\ast (\tau_1 - \tau_2) - K_\lambda^\ast (\tau_1 - \tau_2)] \sigma_\lambda^M (\tau_1) \sigma_\lambda^M (\tau_2), \tag{A18}$$

where

$$v_\lambda (t) = \sigma_\lambda^+ (t) - \sigma_\lambda^- (t) \quad \text{and} \quad w_\lambda (t) = \frac{1}{2} [\sigma_\lambda^+ (t) + \sigma_\lambda^- (t)] \tag{A19}$$

$$K_\lambda^{Re} (t) = \frac{1}{2 \omega_\lambda} \cos (\omega_\lambda t) \coth \left( \frac{1}{2} \omega_\lambda \beta \hbar \right) \tag{A20}$$

$$K_\lambda^{Im} (t) = - \frac{1}{2 \omega_\lambda} \sin (\omega_\lambda t) \tag{A21}$$

$$K_\lambda (z) = \frac{1}{2 \omega_\lambda} \cosh \left( \frac{\omega_\lambda}{2 \beta \hbar} (z - i) \right) \tag{A22}$$

$$K_\lambda^\ast (\tau) = \frac{1}{2 \omega_\lambda} \coth \left( \frac{1}{2} \omega_\lambda \beta \hbar \right) \cosh (\omega_\lambda \tau) \tag{A23}$$

$$K_\lambda^a (\tau) = \frac{1}{2 \omega_\lambda} \sinh (\omega_\lambda \tau). \tag{A24}$$

Notably, these kernels satisfy the following relationships: that $K_\lambda (t) = K_\lambda^{Re} (t) + i K_\lambda^{Im} (t)$, and $K_\lambda (i \tau) = K_\lambda^\ast (\tau) + K_\lambda^a (\tau)$, with $K_\lambda^\ast$ and $K_\lambda^a$ being even and odd functions, respectively. The first two terms in Eq. (A18) are the regular integrals which appear in the Feynman-Vernon influence functional, while the remaining terms arise from considering the total system to be in thermal equilibrium at $t_0$ rather than artificially partitioned.

Returning to the site representation for the phonons with the joint index $a = (A \alpha)$, the total influence phase in Eq. (A17) is now

$$-\frac{1}{\hbar} \Phi = -\frac{1}{\hbar} \sum_{aa'} \Phi_{aa'} = -\frac{1}{2} \left[ \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 v_\alpha^T (t_1) C_{aa'} (t_1 - t_2) v_{a'} (t_2) + \int_{0}^{\beta \hbar} d\tau_1 \int_{t_0}^{\tau_1} dt_1 v_\alpha^T (t_1) C_{aa'} (t_1, \tau_1) v_{a'} (t_1) \right. \tag{A25}$$

$$+ 2 \int_{0}^{\beta \hbar} d\tau_1 \int_{t_0}^t dt_1 v_\alpha^T (t_1) C_{aa'} (t_1, \tau_1) v_{a'} (t_1) + \int_{0}^{\beta \hbar} d\tau_1 \int_{0}^{\beta \hbar} d\tau_2 v_\alpha (t_1) \overline{C}_{aa'} (t_1, \tau_1 - \tau_2) v_{a'} (\tau_2) \right]$$
where

\[ \mathbf{v}_a(t) = \begin{pmatrix} v_a(t)/\hbar \\ 0 \\ w_a(t) \end{pmatrix} \quad \text{and} \quad \mathbf{v}_a(\tau) = \begin{pmatrix} i\sigma_a^M(\tau)/\hbar \end{pmatrix} \]  

(A26)

\[ \mathbf{C}_{aa'}(t) = \begin{pmatrix} \hbar K_{aa'}^{Re}(t) & 0 & 2i\Theta(t)K_{aa'}^{Im}(t) \\ 0 & 0 & 0 \\ 2i\Theta(-t)K_{aa'}^{Im}(-t) & 0 & 0 \end{pmatrix} \]  

(A27)

\[ \mathbf{C}_{aa'}^{\times}(t, \tau) = \begin{pmatrix} -\hbar K_{aa'}(t-i\tau) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]  

(A28)

\[ \mathbf{C}(\tau) = \begin{pmatrix} \hbar [K_{aa'}(\tau) - K_{aa'}(|\tau|)] & 0 \\ 0 & 0 \end{pmatrix} \]  

(A29)

so that the total influence phase is now \( \Phi = \sum_{aa'} \Phi_{aa'} \), having used transformations of the form

\[ K_{aa'} = \frac{1}{\sqrt{m_a m_{a'}}} \sum_{\lambda} \epsilon_{\lambda a} \epsilon_{\lambda a'} K_{\lambda}. \]  

(A30)

As before, the \( \epsilon_{\lambda a} \) are the elements of the eigenvectors of the bath’s dynamical matrix.

The equations above have been written specifically in the form most suitable for the Hubbard-Stratonovich transformation\(^{88,90}\) with complex multivariate Gaussian noises\(^94\) that is applied with respect to the real and imaginary times\(^99\). This transformation maps the bi-linear exponent in Eq. (A25) (the total phase in Eq. (A17)) onto a stochastic exponent which is linear in the noises, at the expense of then averaging over all realizations of those noises,

\[ \exp \left\{ -\frac{1}{\beta} \sum_{aa'} \Phi_{aa'} \right\} = \langle \exp \left\{ \sum_a \int_0^{t_1} dt_1 \mathcal{E}^T a(t_1) \mathbf{v}_a(t_1) + \int_0^{\beta \hbar} d\tau_1 \bar{\xi}_a^T(\tau_1) \mathbf{v}_a(\tau_1) \right\} \rangle_{\xi \bar{\xi}}, \]  

(A31)

where

\[ \xi_a(t) = \begin{pmatrix} \eta_a(t) \\ \eta_a^*(t) \\ \nu_a(t) \\ \nu_a^*(t) \end{pmatrix} \quad \text{and} \quad \bar{\xi}_a(\tau) = \begin{pmatrix} \bar{\eta}_a(\tau) \\ \bar{\eta}_a^*(\tau) \\ \bar{\nu}_a(\tau) \\ \bar{\nu}_a^*(\tau) \end{pmatrix} \]  

(A32)

are vectors of the noises and their complex conjugates, and \( \langle \ldots \rangle_{\xi \bar{\xi}} \) indicates the average over \( \xi \) and \( \bar{\xi} \). It is worth emphasizing the structure of the noise vectors \( \xi_a \) and \( \bar{\xi}_a \): they contain complex conjugate pairs of the noises. This gives meaning to the matrices in Eqs. (A27)-(A29), which up until now have simply been algebraic, when in fact they are the precision matrices of the distribution functional of the noises. For example, for \( C_{aa'}^{\times} \), the 11 component is the correlation function of \( \eta_a \) and \( \eta_{a'} \); the 12 component is the correlation function of \( \eta_a \) and \( \nu_{a'} \); the 13 component is the correlation function of \( \eta_a \) and \( \nu_{a'} \), and so on.

The noises therefore have the following correlation functions,

\[ \langle \eta_a(t) \eta_{a'}(t') \rangle_{\xi \bar{\xi}} = \hbar K_{aa'}^{Re}(t-t') \]  

(A33)

\[ \langle \eta_a(t) \nu_{a'}(t') \rangle_{\xi \bar{\xi}} = 2i\Theta(t-t') K_{aa'}^{Im}(t-t') \]  

(A34)

\[ \langle \eta_a(t) \bar{\eta}_{a'}(\tau) \rangle_{\xi \bar{\xi}} = -\hbar K_{aa'}(t-i\tau) \]  

(A35)

\[ \langle \bar{\nu}_a(\tau) \bar{\nu}_{a'}(\tau') \rangle_{\xi \bar{\xi}} = \hbar [K_{aa'}(\tau_1-\tau_2) - K_{aa'}(|\tau_1-\tau_2|) ] \]  

(A36)

with all other correlations not shown being zero. The matrix elements \( C_{aa'}, C_{aa'}^{\times} \) and \( C_{aa'}^{\times T} \) of Eqs. (A27)-(A29) are therefore identified as the correlations between the \( a \) and \( a' \) noises, which appear as elements of a \( 2 \times 2 \) block in the partitioned covariance matrix between the noises,

\[ \Sigma_{aa'} = \begin{pmatrix} C_{aa'} & C_{aa'}^{\times T} \\ C_{aa'}^{T} & C_{aa'}^{\times} \end{pmatrix}, \]  

(A37)
having been partitioned with respect to the real-time vector noises \( \xi_a(t) \) and the imaginary time vector noises \( \tilde{\xi}_a(\tau) \). The full covariance matrix for all the \( a \) and \( a' \) is thus \( \Sigma = (\Sigma_{aa'}) \).

It is worth emphasising the equality between Eq. (A31) and Eq. (A25): this is not an approximation. Rather, the noises have been introduced in a mathematically exact way and their properties rigorously derived from the theory, with the average of Eq. (A31) over the Gaussian distribution functional of the noises being formally equivalent to Eq. (A25). Reincorporating the influence functional back into the path integrals by inserting Eqs. (A31) and (A17) into Eq. (A14), we obtain

\[
\tilde{\rho}(x_t, t; x_0, t_0) = \frac{1}{Z_0} \int dx_1 dx_2 \int_{x_{x_0=\tau}}^{x_{x_t=x}} \mathcal{D} [x^+ (s)] \mathcal{D} [x^M(\beta \hbar)] \mathcal{D} [x^M(0) = x_1] \mathcal{D} [x^M(\tau)] \mathcal{D} [x^- (s')] \exp \left\{ \frac{i}{\hbar} \left( S^+ [x^+ (s)] - S^- [x^- (s')] + i \mathcal{S} [x^M(\tau)] \right) \right\}
\]

for the electronic density matrix, where the three actions \( S^\pm \) and \( \mathcal{S} \) are now stochastic - hence the tilde over the \( \rho \) to indicate that it is a non-physical stochastic quantity - and correspond to stochastic potentials in the Lagrangians,

\[
S^\pm [x^\pm (s)] = \int_{t_0}^t ds \left( L_{el}^0 [x^\pm (s)] + \sum_{Aa} \left[ \eta_{Aa}(s) \pm \frac{\hbar}{2} \gamma_{Aa}(s) \right] \sigma^\pm_{Aa}(s) \right)
\]

(A39)

\[
\mathcal{S}[x^M(\tau)] = \int_0^{\beta \hbar} d\tau \left( L_{el}^0 [x^M(\tau)] + \sum_{Aa} \mathcal{P}_{Aa}(\tau) \sigma^M_{Aa}(\tau) \right)
\]

(A40)

where \( L_{el}^0 \) is the purely electronic (phonon-free) Lagrangian associated with the Hamiltonian in Eq. (1). The new stochastic Lagrangians which are the full integrands of Eqs. (A39) and (A40) have the corresponding stochastic Hamiltonians that are precisely those of Eq. (15).

Returning to the propagators associated with each of the path integrals, and using the same coordinates as in Eq. (A10), we obtain

\[
\langle x_1 | \hat{U}^+(t, t_0) | x_2 \rangle = \int x_{x_{t_0}=x_2}^{x_{x_t=\tau}} D [x^+(s)] e^{i \tilde{S}^+[x^+(s)]}
\]

(A41)

\[
\langle x_2 | \tilde{\rho}_0 | x_1 \rangle = \int x_{x_{x_0=\tau}}^{x_{x_0=x_1}} D [x^M(\tau)] e^{-i \mathcal{S} [x^M(\tau)]}
\]

(A42)

\[
\langle x_1 | \tilde{U}^- (t_0, t) | x_0 \rangle = \int x_{x_{x_0=\tau}}^{x_{x_0=x_1}} D [x^- (s)] e^{-i \mathcal{S} [x^- (s)]}
\]

(A43)

where \( \hat{U}^\pm \) and \( \mathcal{P}(\beta \hbar, 0) = \tilde{\rho}_0 \) are the stochastic time evolution operators on the upper and lower horizontal branches and the vertical branch, respectively, which use these new stochastic Hamiltonians. This brings us to the Liouville equation of Eq. (6) and completes the transformation.

**Appendix B: Contour Integrals**

The regular Langreth rules cannot be applied when expanding the contour integrals in Eqs. (67) and (74) since the unravelled Hamiltonian of Eqs. (14)-(15) is sensitive to all three of the branches \( \kappa^\pm \) and \( \kappa^M \). Instead, the generalized Langreth rules\(^\text{105}\) must be applied to consider all possible combinations of complex times where real times on the upper and lower branches are treated separately due to the different values of the unraveling matrix \( W_{CC} \), and always ordered with respect to the contour time ordering \( \tilde{T}_\kappa \).

Adopting the following convention for the integration of three-time quantities such as with the unravelling matrix \( W_{CC}(z_1, z_2) \) in the expansion for \( G_{CC} \) (Eq. (67)),

\[
\int_{\kappa} dz_1 dz_2 A(z, z_1|\tilde{T}) W(z_1, z_2) B(z_2, z'|\tilde{T}) = \begin{cases} 
(A \bullet w \bullet B) (z, z', \tilde{T}) & t \in \kappa^+ \\
(A \circ w \circ B) (z, z', \tilde{T}) & t \in \kappa^- \\
(A \bullet w \star B) (z, z', \tilde{T}) & \tau \in \kappa^M,
\end{cases}
\]

(B1)
with

\[ (A \bullet w \bullet B) (z, z', \bar{t}) \equiv \int_{t_0}^{\bar{t}} dt A (z, t | \bar{t}) w(t) B (t, z' | \bar{t}), \quad t \in \kappa^+ \]  

(B2)

\[ (A \circ w \circ B) (z, z', \bar{t}) \equiv - \int_{t_0}^{\bar{t}} dt A (z, t | \bar{t}) w(t) B (t, z' | \bar{t}), \quad t \in \kappa^- \]  

(B3)

\[ (A \star w \star B) (z, z', \bar{t}) \equiv -i \int_0^{\beta h} d\tau A (z, \tau | \bar{t}) \bar{w} (\tau) B (\tau, z' | \bar{t}), \quad \tau \in \kappa^M, \]  

(B4)

where we have exploited the \( \delta \)-functions in the definition of \( W_{CC} \) in Eq. (62), we can write down integrals of the product of functions defined on the contour explicitly. Using the fact that only the unravelling matrix depends on the particular horizontal branch, with the phonon-free Green’s function \( G^0_0 \) being the same on both branches, the perturbative expansion for the \( + - \) component of the three-time NEGF in the central region is readily expanded out, e.g., to first order, as

\[
G_{CC}^{+-}(t, t' | \bar{t}) = G_{CC}^{00}(t, t') + \big[(G_{CC}^{0r} + G_{CC}^{0<}) \bullet w_{CC} \bullet G_{CC}^{0<} + G_{CC}^{0<} \circ w_{CC} \circ (G_{CC}^{0r} - G_{CC}^{0<}) \big]
+ G_{CC}^{0r} \star w_{CC} \star G_{CC}^{0r} \big)(t, t') + \ldots ,
\]

(B5)

where the dependence on the observation time \( \bar{t} \) on the right hand side is hidden in the definitions for \( \bullet \) and \( \circ \). The expressions for the components of the phonon-free NEGF (e.g., in the wide band approximation) they are given in Ref. then be used to compute the three-time Green’s function as required. Higher order terms can be written similarly by a repetitive application of the generalised Langreth rules.

The contour integral which appears in the current Eq. (74) is less straightforward since it involves integrating over both the inner and outer times of \( \Upsilon_{CLC} (z_2, z_1) G_{CC} (z_2, z_1) \bar{t} \). This calculation is easier to perform by representing each \( z \) integral as a sum over either of the three branches, leading to 9 terms. Since one of the times in each of the two isolated lead Green’s function \( g_{LL} \) in the definition of \( \Upsilon_{CLC} (z_2, z_1) \) is fixed just before or after the observation time, Eq. (73), it is possible to indicate explicitly as superscripts in the self-energy the particular components of the isolated leads Green’s function,

\[
\Upsilon_{CLC}^{\gamma \gamma'} (z_2, z_1) = h_{CL} g_{LL}^{0\gamma} (z_2, \bar{t}) g_{LL}^{0\gamma'} (\bar{t}', z_1) h_{LC} ,
\]

(B6)

where \( \gamma, \gamma' = <, >, \downarrow, \uparrow \). Then, by considering each possible combination of the branches, one obtains

\[
\int_{\kappa} d\xi_1 d\xi_2 \text{tr} \left[ \Upsilon_{CLC} (z_2, z_1) G_{CC} (z_2, z_1) \bar{t} \right] = \int_{t_0}^{\bar{t}} dt_1 dt_2 \text{tr} \left[ \Upsilon_{CLC}^{<\gamma} (t_2, t_1) G_{CC}^{+-} (t_1, t_2 \bar{t}) - \Upsilon_{CLC}^{\gamma<} (t_2, t_1) G_{CC}^{-+} (t_1, t_2 \bar{t}) \right]
- \Upsilon_{CLC}^{>\gamma} (t_2, t_1) G_{CC}^{--} (t_1, t_2 \bar{t}) + \Upsilon_{CLC}^{\gamma>} (t_2, t_1) G_{CC}^{++} (t_1, t_2 \bar{t})
- i \int_{t_0}^{\beta h} d\tau \text{tr} \left[ \Upsilon_{CLC}^{<\gamma} (t, \tau) G_{CC}^{M+} (t, \tau \bar{t}) - \Upsilon_{CLC}^{\gamma<} (t, \tau) G_{CC}^{M-} (t, \tau \bar{t}) \right]
+ \Upsilon_{CLC}^{>\gamma} (t, \tau) G_{CC}^{MM} (t, \tau \bar{t}) - \Upsilon_{CLC}^{\gamma>} (t, \tau) G_{CC}^{MM} (t, \tau \bar{t})
- \int_{0}^{\beta h} d\tau_1 d\tau_2 \text{tr} \left[ \Upsilon_{CLC}^{M+} (t_2, \tau_1) G_{CC}^{M+} (t_1, \tau_2 \bar{t}) \right].
\]

(B7)

The components of \( \Upsilon_{CLC} \) are given in Appendix D. This expression shows that alongside the component \( G_{CC}^{-+} \) of the central region Green’s function obtained in Eq. (B5), one also needs similar expressions for other components, such as \( G_{CC}^{+<} \), \( G_{CC}^{<+} \), \( G_{CC}^{++} \) and \( G_{CC}^{MM} \). These can be obtained using rules presented in in a straightforward manner.

**Appendix C: Girsanov Transformation of the Noise Measure**

Taking the average of \( \Pi (\bar{t}) \) in Eq. (72), the average can be treated as either a statistical average over realizations of the noises, or as the functional integral over their distribution \( M \),

\[
\langle \Pi (\bar{t}) \rangle_{\bar{\xi}} = \int_{\bar{\xi}} \mathcal{D}[\xi (\bar{t})] \mathcal{D}[\bar{\xi} (\bar{t})] M [\xi (\bar{t}), \bar{\xi} (\bar{t})] \Pi (\bar{t}),
\]

(C1)
where $\xi_a$ and $\tilde{\xi}_a$ are the vector noises of the $a = (A\alpha)$ displacement from Eq. (A32), and $\xi = \{\xi_a\}$ and $\tilde{\xi} = \{\tilde{\xi}_a\}$ are the sets of noises over all the displacements. The noise measure takes the form

\[
\mathcal{M}[\xi(t), \tilde{\xi}(\tau)] = \mathcal{M} \exp \left\{ -\frac{1}{2} \sum_{aa'} \left[ \frac{1}{2} \left( \sum_{\alpha} \xi_a(t) A_{aa'}^T B_{aa'} \right) \right] \right\}
\]

and

\[
\mathcal{M} \exp \left\{ -\frac{1}{2} \sum_{aa'} \left[ \int_{t_0}^{T} dt_1 \int_{t_0}^{T} \int_{t_0}^{T} dt_2 \xi_a(t_1) A_{aa'}(t_1 - t_2) \xi_a(t_2) + \int_{t_0}^{T} dt_1 \int_{t_0}^{T} \int_{t_0}^{T} dt_2 \xi_a(t_1) B_{aa'}(t_1, \tau) \tilde{\xi}_a'(\tau) \right] \right\},
\]

where $\mathcal{M}$ is the Gaussian normalization factor, and the matrix

\[
P_{aa'}(z, z') = \begin{pmatrix} A_{aa'}(t, t') & B_{aa'}(t, \tau) \\ B_{aa'}^T(\tau, t) & D_{aa'}(\tau, \tau') \end{pmatrix}
\]

is the precision matrix of the distribution; specifically, it is the particular component of the full precision matrix $P = (P_{aa'})$, between the $a$ and $a'$ noises. This matrix shares the same structure as the covariance matrix $\Sigma_{aa'}$ (Eq. (A37)), in which the blocks are matrices themselves which correspond to the different pairs of times $(t, \tau), (t, \tau')$ and $(\tau, \tau')$. The precision matrix $P$ therefore has components for both the sets of noises and pairs of times. For example, $(P_{11})_{aa'} = P_{1a,1a'}$ is the precision matrix between noises $\xi_a(t)$ and $\xi_a'(t')$ for both times being real (which is still a $4 \times 4$ matrix with respect to the components of the noises), $(P_{12})_{aa'} = P_{1a,2a'}$ is the rectangular $4 \times 2$ matrix block for the noises $\xi_a(t)$ and $\tilde{\xi}_a'(\tau)$ corresponding to one time real and one imaginary, and, finally, $(P_{22})_{aa'} = P_{2a,2a'}$ is the $2 \times 2$ block corresponding to the noises $\tilde{\xi}_a(\tau)$ and $\tilde{\xi}_a'(\tau')$ for both imaginary times. The full matrix $P$ is directly related to the covariance matrix $\Sigma$ of Eq. (A37) by its inverse, $P_{aa'} = (\Sigma^{-1})_{aa'}$. Thus the block matrices $C_{aa'}, C_{aa'}^\perp$ and $\overline{C}_{aa'}$ which contain the correlation functions between the noises are related to the precision matrix by $C_{aa'} = (P^{-1})_{1a,1a'}$, $C_{aa'}^\perp = (P^{-1})_{1a,2a'}$ and $\overline{C}_{aa'} = (P^{-1})_{2a,2a'}$.

To simplify the notation, we shall henceforth ignore the complex conjugate components since all correlation functions which involve complex conjugate noises are equal to zero. The vector $\xi_a(t)$ then has only two components $\eta_a$ and $\nu_a$, and $\tilde{\xi}_a(\tau)$ has only one component $\pi_a$. Next, we shall discretise both real and imaginary times and introduce three blocks for the noises: $\eta = (\eta_a(t))$, $\nu = (\nu_a(t))$, and $\pi = (\pi_a(\tau))$, with the full noise vector $\chi = (\eta \; \nu \; \pi)^T$. The noise measure can then be compactly written as

\[
\mathcal{M}[\xi(t), \tilde{\xi}(\tau)] = \mathcal{M} \exp \left\{ -\frac{1}{2} \chi^T P \chi \right\}.
\]

Given that $\Pi(\tilde{t})$ of Eq. (36) is an exponential which is linear in the $\nu_a(t)$ noises (which are the second component of $\chi$), it can be written as

\[
\Pi(\tilde{t}) = \Pi_0 \exp \left( \chi^T L \right),
\]

where we have introduced a 3-component vector $L = (0 \; \gamma \; 0)^T$, with

\[
\gamma = (\gamma_a(t)) = (\hbar \; \text{tr} \; [\nu_{aC}^\perp \overline{G}_{aCC}^\perp(t, t)])
\]

The Girsanov transformation\textsuperscript{86,113} can then be applied such that the average taken over the transformed measure $\mathcal{M}'$ with respect to the transformed noises $\xi', \tilde{\xi}'$ is analytically equivalent to the original average in Eq. (C1) taken over the original measure $\mathcal{M}$ with respect to the un-transformed noises $\xi, \tilde{\xi}$:

\[
\mathcal{M}[\xi(\tilde{t}), \tilde{\xi}(\tau)] \Pi[\xi(\tilde{t})] = \Pi_0 \mathcal{M}'[\xi'(\tilde{t}), \tilde{\xi}'(\tau)].
\]

This transformation is achieved by completing the square in the total exponent of the right hand side of Eq. (C8) to introduce a new vector of noises,

\[
\chi' = \chi - P^{-1} L = \chi - \Sigma L,
\]

where $\Sigma$ is the precision matrix.
which transforms the quadratic form in the exponential $-\frac{1}{2} \chi^T P \chi + \chi^T L$ into $\phi = -\frac{1}{2} (\chi')^T P \chi'$, where the free (noise independent) term,

$$\phi = \frac{1}{2} L^T P^{-1} L = \frac{1}{2} L^T \Sigma L$$

$$= \frac{1}{2} \begin{pmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & \mathcal{C} \end{pmatrix} \begin{pmatrix} C_{\eta \eta} & C_{\eta \nu} & C_{\times} \\ C_{\nu \eta} & 0 & 0 \\ C_{\times T} & 0 & \mathcal{C} \end{pmatrix} \begin{pmatrix} 0 \\ \gamma \\ 0 \end{pmatrix} = 0,$$

is equal to zero since the correlation functions between the $\nu$ noises, $C_{\nu \nu}'(t_1, t_2) = \langle \nu_{\alpha}(t_1) \nu_{\alpha'}(t_2) \rangle$, is itself equal to zero.

This is a very important point that the free term $\phi = 0$; without it, the application of the Girsanov transformation would introduce an additional time dependence to Eq. (71) when differentiating to obtain the current.

It is clear from Eq. (C9) that only the $\eta$ noises are affected by the transformation:

$$\begin{pmatrix} \eta' \\ \nu' \end{pmatrix} = \begin{pmatrix} \eta \\ \nu \end{pmatrix} - \begin{pmatrix} C_{\eta \eta} & C_{\eta \nu} & C_{\times} \\ C_{\nu \eta} & 0 & 0 \\ C_{\times T} & 0 & \mathcal{C} \end{pmatrix} \begin{pmatrix} 0 \\ \gamma \\ 0 \end{pmatrix},$$

$$= \begin{pmatrix} \eta_{a}(t) - \sum_{a'} \int_{0}^{t} dt' \gamma_{a'}(t') \eta_{a'}(t') \\ \nu_{a}(t) - \sum_{a'} \int_{0}^{t} dt' \gamma_{a'}(t') \nu_{a'}(t) \\ \bar{\nu}_{a}(t) - \sum_{a'} \int_{0}^{t} dt' \gamma_{a'}(t') \bar{\nu}_{a'}(t) \end{pmatrix},$$

where $C_{\eta \eta}' = 2i \Theta K_{\eta \eta}'$ is the $\eta - \nu_{\alpha'}$ correlation function of Eq. (A34). Hence, when written explicitly, the new $\eta_{a}$ noises are

$$\eta'_{a}(t) = \eta_{a}(t) - 2ih \int_{t_{0}}^{t} dt_{1} \Theta(t-t_{1}) \sum_{a'} K_{\eta \eta}'(t-t_{1}) \text{tr} \left[ \gamma'_{a'} G_{CC}(t_{1}, t_{1}|t_{1}) \right],$$

and all the other noises are left unchanged $\nu'_{a} = \nu_{a}, \bar{\nu}'_{a} = \bar{\nu}_{a}$.

For the integral over $\mathcal{M}'$ with respect to the primed noises to be analytically equivalent to the integral over $\mathcal{M}$ with respect to the original noises, the Jacobian of the transformation $J$ must be equal to unity. It is convenient to split the Jacobian matrix into block matrices which correspond to derivatives of the different noises within the primed and original sets. Using obvious notation, this is

$$J = \begin{bmatrix} J_{\eta \eta} & J_{\eta \nu} & J_{\eta \pi} \\ J_{\nu \eta} & J_{\nu \nu} & J_{\nu \pi} \\ J_{\pi \eta} & J_{\pi \nu} & J_{\pi \pi} \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

where the second equality is obtained since the $\eta$ noises are the only set of noises altered by the transformation; so, $J_{\nu \nu}$ and $J_{\pi \pi}$ are the identity matrices, while the other blocks in the second and third rows must be zero. By considering the elements of the $\eta' \eta$ block matrix, $J_{\eta \eta}' = [\delta \eta'_{a}/\delta \eta_{b}(t')]$, using Eq. (C14), and discretising times,

$$\frac{\delta \eta'_{a}(t)}{\delta \eta_{b}(t')} = \delta_{ab} \delta_{t' t} - 2ih \int_{t_{0}}^{t} dt_{1} \Theta(t-t_{1}) \sum_{a'} K_{\eta \eta}'(t-t_{1}) \text{tr} \left[ \gamma'_{a'} \frac{\delta G_{CC}(t_{1}, t_{1}|t_{1})}{\delta \eta_{b}(t')} \right],$$

it is clear that the Heaviside function bounds the integral from from above so that $t_{1} < t$, while the kernel $K_{\eta \eta}'$ is a known correlation function which is independent of any individual realization of any specific noise in the set, so the derivative is applied to the three-time NEGF instead. The NEGF must satisfy causality: it can only depend on noises from the past, which bounds the integral from below, $t_{1} > t'$, meaning that the integral corresponds to an upper-triangular matrix with zeros on the diagonal, so that its contribution to the determinant is zero. Therefore the second term does not contribute to the Jacobian, leaving $J_{\eta \eta}' = \delta_{ab} \delta_{t' t}$ which means that $J_{\eta \eta}'$ is the identity matrix. The other two blocks, $J_{\nu \nu}$ and $J_{\pi \pi}$, are irrelevant since the total Jacobian matrix Eq. (C15) is an upper triangular matrix with identities along the diagonal and hence has determinant equal to one. Finally, the simple change of variables $\eta_{a} \rightarrow \eta'_{a}$ completes the transformation with the consequence that the regular stochastic average over realizations of the noises with the transformed $\{\eta'_{a}\}$ must be equivalent to the stochastic average over realizations of the original noises, in the limit of sampling over all possible
realizations. Therefore Eq. (C1) becomes
\[
\langle \Pi(t) \rangle_{\xi\bar{\xi}} = \langle \Pi_0 \rangle_{\xi\bar{\xi}} = n^{-1},
\]  
(C17)
and so the product of \( n \) and \( \langle \Pi_0 \rangle_{\xi\bar{\xi}} \) in the first term in Eq. (72) is equal to one, and the infinite term in the population in Eq. (72) becomes
\[
-i\hbar n \Pi(t) \text{tr} \left[ g_{LL}^{0\infty}(\bar{\tau}, \tau) \right] = -i\hbar \text{tr} \left[ g_{LL}^{0\infty}(\bar{\tau}, \tau) \right],
\]  
(C18)
which is the total number of electrons in the \( L \)-th lead. Since \( g_{LL}^{0\infty}(\bar{\tau}, \tau) \) does not depend on time \( \tau \), this term is constant and does not contribute to the current. Concluding, the infinite term in the number operator Eq. (72) vanishes in the current through the \( L \)th lead after performing the average. This gives the final form Eq. (74).

Appendix D: Self-Energies in the WBA

As well as the regular embedding self-energy, three additional self energies have been introduced: \( \Sigma_{CC} \) and \( \overline{\Sigma}_{CC} \) in Eq. (56) for \( \Pi(\tau) \), and \( \Upsilon_{CLC} \) in the expression for the current, Eq. (74). Note that the regular embedding self-energy is still required to calculate the components of the phonon-free NEGF, see, e.g., Ref. 109. The self-energies are reproduced here for convenience (we here set \( \hbar = 1 \)):

\[
\Sigma_{CC}(z_1, z_2) = \sum_L h_{CL} g_{LL}^0(z_1, z_2) h_{LC}
\]  
(D1)
\[
\overline{\Sigma}_{CC}(\tau_1, \tau_2 | \tau) = \sum_L h_{CL} \overline{g}_{LL}^0(\tau_1, \tau_2 | \tau) h_{LC}
\]  
(D2)
\[
\overline{\Upsilon}_{CC}(\tau_1, \tau_2 | \tau) = \sum_L h_{CL} \overline{g}_{LL}^0(\tau_1, 0 | \tau) h_{LL}^0 \overline{g}_{LL}^0(0, \tau_2 | \tau) h_{LC}
\]  
(D3)
\[
\Upsilon_{CLC}(z_1, z_2) = h_{CL} \overline{g}_{LL}^0(z_1, \bar{\tau} | \tau) \overline{g}_{LL}^0(\bar{\tau}, z_2) h_{LC}.
\]  
(D4)

Using the equation of motion for the isolated lead Green’s function (the index \( L \) of the lead is omitted),
\[
(i\hbar \partial - h_{LL}) g_{LL}^0 = \delta,
\]  
(D5)
its different components are:
\[
g_{ij}^L(t_1, t_2) = \frac{i}{\hbar} \delta_{ij} e^{-i\phi_i(t_1, t_2)} \left[ 1 - f(\epsilon_i^M) \right]
\]  
(D6)
\[
g_{ij}^C(t_1, t_2) = \frac{i}{\hbar} \delta_{ij} e^{-i\phi_i(t_1, t_2)} f(\epsilon_i^M)
\]  
(D7)
\[
g_{ij}^{L\tau}(t_1, t_2) = -\frac{i}{\hbar} \delta_{ij} \Theta(t_1 - t_2) e^{-i\phi_i(t_1, t_2)}
\]  
(D8)
\[
g_{ij}^{L\tau}(t_1, t_2) = \delta_{ij} \Theta(t_2 - t_1) e^{-i\phi_i(t_1, t_2)}
\]  
(D9)
\[
g_{ij}^{\tau M}(t, \tau) = -\frac{i}{\hbar} \delta_{ij} e^{-\epsilon_i^M \tau} e^{i\phi_i(t, t_0)} \left[ 1 - f(\epsilon_i^M) \right]
\]  
(D10)
\[
g_{ij}^{\tau M}(t, \tau) = \frac{i}{\hbar} \delta_{ij} e^{\epsilon_i^M \tau} e^{-i\phi_i(t, t_0)} f(\epsilon_i^M)
\]  
(D11)
\[
g_{ij}^{\tau M}(\tau_1, \tau_2) = -\frac{1}{\hbar} \delta_{ij} e^{-\epsilon_i^M (\tau_1 - \tau_2)} \left\{ \Theta(\tau_1 - \tau_2) \left[ 1 - f(\epsilon_i^M) \right] - \Theta(\tau_2 - \tau_2) f(\epsilon_i^M) \right\}.
\]  
(D12)

Here,
\[
\phi_i(t, t') = \int_{t'}^t dt_1 [\epsilon_i + V_L(t_1)] = \epsilon_i(t - t') + \psi_L(t, t')
\]  
(D13)
for \( i \in L, f(\omega) = (1 + e^{\beta \omega})^{-1} \) is the Fermi function, and \( \epsilon_i^M = \epsilon_i - \mu \) as before, and we also note the useful relationship \( \left[ 1 - f(\omega) \right] = e^{\beta \omega} f(\omega) \). There is also the isolated Green’s function on the vertical subbranch up to the preparation time,
defined in Eq. (45),
\[
\mathcal{g}_{ij}(\tau_1, \tau_2|\tau) = -\frac{1}{\hbar} \delta_{ij} e^{-\epsilon_i^M(\tau_1-\tau_2)} \left\{ \Theta(\tau_1 - \tau_2) \left[ 1 - \bar{f}(\epsilon_i^M|\tau) \right] - \Theta(\tau_2 - \tau_1) \bar{f}(\epsilon_i^M|\tau) \right\}. \tag{D14}
\]

All the necessary components of the self-energies can now be obtained. For the retarded and advanced components which involve the Heaviside function, the part that depends exclusively on a time difference must be Fourier transformed to properly account for the Heaviside function. This gives for the two components:
\[
\Sigma^r_{nm}(t_1, t_2) = \sum_L e^{-i\psi_L(t_1, t_2)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_1-t_2)} \left[ \Phi_{nm}(\omega) - \frac{i}{2} \Gamma_{nm}(\omega) \right],
\]
\[
\Sigma^a_{nm}(t_1, t_2) = \sum_L e^{-i\psi_L(t_1, t_2)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_1-t_2)} \left[ \Phi_{nm}(\omega) + \frac{i}{2} \Gamma_{nm}(\omega) \right],
\]
where we introduced the level width matrix in terms of the elements \( T_{ni} \) of the transmission matrix of the lead and central regions:
\[
\Gamma_{nm}(\omega) = \sum_L \Gamma^L_{nm}(\omega) = 2 \pi \sum_{L,i \in L} T_{ni} T_{im} \delta(\epsilon_i - \omega), \tag{D15}
\]
and
\[
\Phi_{nm}(\omega) = \int \frac{d\omega'}{2\pi} \frac{\Gamma_{nm}(\omega')}{\omega - \omega'}
\]
is basically the Gilbert transform of the level width matrix.

Other components of the self energy are obtained directly by introducing integration over the energies \( \omega \) by means of the delta function \( \delta(\omega - \epsilon_i) \). This enables one to essentially replace the sum over the lead’s states \( i \) with the \( \omega \) integration of the level width matrix:
\[
\Sigma^r_{CC}(t_1, t_2) = -ie^{-i\mu(t_1-t_2)} \sum_L e^{-i\psi_L(t_1, t_2)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_1-t_2)} \Gamma^L_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right] \tag{D16}
\]
\[
\Sigma^a_{CC}(t_1, t_2) = ie^{-i\mu(t_1-t_2)} \sum_L e^{i\psi_L(t_1, t_2)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_1-t_2)} \Gamma^L_{CC}(\omega + \mu) f(\omega) \tag{D17}
\]
\[
\Sigma_{CC}^\Gamma(t,t) = -ie^{i\mu(t-t_1)} \sum_L e^{i\psi_L(t,t_1)} \int \frac{d\omega}{2\pi} e^{i\omega(t-t_1)} e^{-\omega\tau} \Gamma^L_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right] \tag{D18}
\]
\[
\Sigma_{CC}^\Gamma(t,t) = ie^{-i\mu(t-t_1)} \sum_L e^{-i\psi_L(t,t_1)} \int \frac{d\omega}{2\pi} e^{-i\omega(t-t_1)} e^{\omega\tau} \Gamma^L_{CC}(\omega + \mu) f(\omega) \tag{D19}
\]
\[
\Sigma^M_{CC}>(\tau_1, \tau_2) = -i \int \frac{d\omega}{2\pi} e^{-\omega(\tau_1-\tau_2)} \Gamma_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right] \tag{D20}
\]
\[
\Sigma^M_{CC}<_{CC}(\tau_1, \tau_2) = i \int \frac{d\omega}{2\pi} e^{-\omega(\tau_1-\tau_2)} \Gamma_{CC}(\omega + \mu) f(\omega). \tag{D21}
\]

The same is done for the necessary components of the thermal self-energies on the subbranch up to the preparation time, \( \Sigma_{CC} \) and \( \bar{\Sigma}_{CC} \), by using \( g_{LLL} \) rather than \( g_{LLM} \),
\[
\Sigma^r_{CC}(\tau_1, 0^+|\tau) = - \int \frac{d\omega}{2\pi} e^{-\omega\tau_1} \Gamma_{CC}(\omega + \mu) \left[ 1 - \bar{f}(\omega|\tau) \right] \tag{D22}
\]
\[
\Sigma^\Lambda_{CC}(0, \tau_1|\tau) = \int \frac{d\omega}{2\pi} e^{\omega\tau_1} \Gamma_{CC}(\omega + \mu) \bar{f}(\omega|\tau) \tag{D23}
\]
\[
\bar{\Sigma}_{CC}(\tau_1, \tau_2|\tau) = - \int \frac{d\omega}{2\pi} e^{\omega(\tau_1-\tau_2)} \Gamma_{CC}(\omega + \mu) \bar{f}(\omega|\tau) \left[ 1 - \bar{f}(\omega|\tau) \right]. \tag{D24}
\]

Substituting in the \( <, >, \Gamma \) and \( \bar{\tau} \) projections of the isolated lead Green’s functions (Eqs. (D6), (D7), (D10), and (D11),...
respectively) into \( \Upsilon^{\gamma'}_{CLC}(z_2, z_1) \), where \( \gamma \) and \( \gamma' \) represent these projections, and then introducing the \( \omega \) integration by means of \( \delta(\omega - \epsilon_i) \) as above, the components which appear in Eq. (B7) are obtained:

\[
\begin{align*}
\Upsilon^{< >}_{CLC}(t_2, t_1) &= e^{-i\mu(t_2-t_1)}e^{-i\psi_L(t_2,t_1)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_2-t_1)} \Gamma^L_{CC}(\omega + \mu) f(\omega) \left[ 1 - f(\omega) \right] \\
&= \Upsilon^{< >}_{CLC}(t_2, t_1) \\
\Upsilon^{< <}_{CLC}(t_2, t_1) &= e^{-i\mu(t_2-t_1)}e^{-i\psi_L(t_2,t_1)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_2-t_1)} \Gamma^L_{CC}(\omega + \mu) f(\omega)^2 \\
\Upsilon^{> >}_{CLC}(t_2, t_1) &= e^{-i\mu(t_2-t_1)}e^{-i\psi_L(t_2,t_1)} \int \frac{d\omega}{2\pi} e^{-i\omega(t_2-t_1)} \Gamma^L_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right]^2 \\
\Upsilon^{< >}_{CLC}(t, \tau) &= e^{-i\mu(t-t_0)}e^{-i\psi_L(t,t_0)} \int \frac{d\omega}{2\pi} e^{-i\omega(t-t_0)} e^{i\omega t} \Gamma^L_{CC}(\omega + \mu) f(\omega) \left[ 1 - f(\omega) \right] \\
\Upsilon^{> >}_{CLC}(t, \tau) &= e^{-i\mu(t-t_0)}e^{-i\psi_L(t,t_0)} \int \frac{d\omega}{2\pi} e^{-i\omega(t-t_0)} e^{i\omega t} \Gamma^L_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right]^2 \\
\Upsilon^{< >}_{CLC}(\tau, t) &= e^{i\mu(t-t_0)}e^{i\psi_L(t,t_0)} \int \frac{d\omega}{2\pi} e^{i\omega(t-t_0)} e^{-i\omega t} \Gamma^L_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right] \\
\Upsilon^{> >}_{CLC}(\tau, t) &= e^{i\mu(t-t_0)}e^{i\psi_L(t,t_0)} \int \frac{d\omega}{2\pi} e^{i\omega(t-t_0)} e^{-i\omega t} \Gamma^L_{CC}(\omega + \mu) \left[ 1 - f(\omega) \right]^2 \\
\Upsilon^{< >}_{CLC}(\tau_2, \tau_1) &= \int \frac{d\omega}{2\pi} e^{-i\omega(\tau_2-\tau_1)} e^{i\omega t} \Gamma^L_{CC}(\omega + \mu) f(\omega) \left[ 1 - f(\omega) \right].
\end{align*}
\]
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