Nonequilibrium diagrammatic technique for Hubbard Green functions

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Abstract

We introduce diagrammatic technique for Hubbard nonequilibrium Green functions (NEGF). Within the technique intra-system interactions are taken into account exactly, while molecular coupling to contacts is used as a small parameter in perturbative expansion. We demonstrate the viability of the approach with numerical simulations for a generic junction model of quantum dot coupled to two electron reservoirs.

Introduction

The nonequilibrium Green function (NEGF) technique is the usual choice in *ab-initio* simulations in the field of molecular electronics. But in many cases of practical importance, especially in treating strong intra-molecular interactions, a nonequilibrium theory based on the many-body states of the isolated molecule is preferable.

The Hubbard NEGF utilizes Hubbard operators $\hat{X}_{S_1S_2} \equiv |S_1\rangle\langle S_2|$, where $|S_{1,2}\rangle$ are many-body states of the system. The Hubbard Green function is defined as

$$G_{(S_1S_2),(S_3S_4)}(\tau,\tau') \equiv -i\left\langle T_c\, \hat{X}_{S_1S_2}(\tau)\, \hat{X}^{\dagger}_{S_3S_4}(\tau')\right\rangle \tag{1}$$

Since for quasiparticle excitation, $\hat{c}_i = \sum_{S_1,S_2}\langle S_1|\hat{c}_i|S_2\rangle \hat{X}_{S_1S_2}$, Hubbard NEGF yields spectral decomposition of the excitations into underlying transitions between many-body states, and knowing it one always can reconstruct the NEGF

$$G_{ij}(\tau,\tau') = -i\left\langle T_c\, \hat{c}_i(\tau)\, \hat{c}^{\dagger}_j(\tau')\right\rangle \tag{2}$$

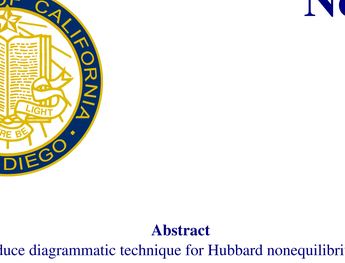

Figure 1: NEGF uses quasiparticle states while Hubbard Green functions utilize many-body states

We present first nonequilibrium diagrammatic technique applicable to multi-time correlation functions of Hubbard operators. The formulation is an extension of equilibrium considerations for strongly correlated lattice models. Contrary to standard diagrammatic techniques it utilizes system-bath coupling as a small parameter of expansion with intra-system interactions taken into account exactly.

Diagrammatic technique for NEGF is based on Wick's theorem which relies on commutation relations $[\hat{c}_i;\hat{c}_j^{\dagger}]_{\pm} = \delta_{ij}$. The corresponding commutators for Hubbard operators are

$$[\hat{X}_{S_1S_2};\hat{X}_{S_3S_4}]_{\pm} = \delta_{S_2,S_4}\hat{X}_{S_1S_3} \pm \delta_{S_1,S_3}\hat{X}_{S_4S_2} \tag{3}$$

The commutator is an operator (not a number), which makes standard Wick's theorem inapplicable. Nevertheless, a variant of Wick's theorem for equilibrium systems was developed [2, 4]. Here, we generalize the consideration to non-equilibrium systems.

Diagrammatic Technique for Hubbard NEGF

We consider generic model of a molecular junction consisting of a molecule M coupled to two contacts L and R:

$$\begin{aligned}\hat{H} &= \hat{H}_M + \sum_{K=L,R}\hat{H}_K + \hat{V}, \qquad \hat{H}_M = \sum_S E_S \hat{X}_{SS}\\ \hat{H}_K &= \sum_{k\in K}\epsilon_k \hat{c}^{\dagger}_k\hat{c}_k, \qquad \hat{V} = \sum_{K=L,R}\sum_{k\in K}\sum_{m\in M}\left(V_{km}\,\hat{c}^{\dagger}_k\hat{X}_m + H.c.\right)\end{aligned} \tag{4}$$

Here m are single electron transitions between many-body states of the molecule.

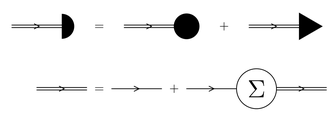

Figure 2: Graphical representation of the modified Dyson equation, Eqs. 6

Perturbative expansion of the Hubbard Green function (1) in system-bath interaction $\hat{V}$ is

$$\begin{aligned}G_{(S_1S_2),(S_3S_4)}(\tau,\tau') = \sum_{n=0}^{\infty}\frac{(-i)^{n+1}}{n!}\int_c d\tau_1 ... \int_c d\tau_n\\ \left\langle T_c\, \hat{X}_{S_1S_2}(\tau)\hat{X}^{\dagger}_{S_3S_4}(\tau')\,\hat{V}(\tau_1)...\hat{V}(\tau_n)\right\rangle_0\end{aligned} \tag{5}$$

Decoupling molecular and contacts degrees of freedom and following a set of contraction rules formulated in Ref. [1] leads to a modified Dyson equation for the Hubbard Green function (see Fig. 2)

$$\begin{aligned}G_{mm'}(\tau,\tau') &= \sum_{m_1}\int_c d\tau_1 g_{mm_1}(\tau,\tau_1)P_{m_1m'}(\tau_1,\tau')\\ g_{mm'}(\tau,\tau') &= g^{(0)}_{mm'}(\tau,\tau') + \sum_{m_1,m_2}\int_c d\tau_1\int_c d\tau_2\\ &\quad g^{(0)}_{mm'}(\tau,\tau_1)\Sigma_{m_1,m_2}(\tau_1,\tau_2)g_{m_2,m'}(\tau_2,\tau')\end{aligned} \tag{6}$$

In the resulting diagrams one can distinguish three types of contributions: self-energy $\Sigma(\tau,\tau')$, spectral weight $F(\tau)$ (circle in Fig. 2) and vertex $\Delta(\tau,\tau')$ (triangle in Fig. 2). Self-energies due to coupling to the contacts

$$\sigma^K_{mm'}(\tau,\tau') = \sum_{k\in K} V_{mk}\, g_k(\tau,\tau')\, V_{km'} \tag{7}$$

play a role of time-nonlocal interaction in the expansion.

Quantum Dot Model

Molecular (quantum dot) subspace is spanned by four many-body states: $|0\rangle \equiv |0,0\rangle, |a\rangle \equiv 1,0,|b\rangle \equiv |0,1\rangle, |2\rangle \equiv |1,1\rangle$. Their energies are: $E_0 = 0$, $E_a = \varepsilon_a$, $E_b = \varepsilon_b$, and $E_2 = \varepsilon_a + \varepsilon_b + U$. Correspondingly, there are four single-electron transitions: $|0\rangle\langle a|, |b\rangle\langle 2|, |0\rangle\langle b|, |a\rangle\langle 2|$

Performing expansion up to second order in molecular coupling to contacts for the Hubbard Green function $G_{mm'}$ leads to the set of diagrams shown in Fig. 5

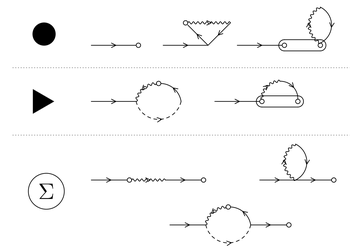

Figure 3: Non-dressed diagrams up to second order in molecule-contacts coupling for Fermi-type Hubbard Green function $G_{mm'}$. Parts are spectral weight F (circle, top panel), vertex Δ (triangle, middle panel), and self-energy Σ (bottom panel). Solid line represents Fermi type Green function $g^{(0)}_m$, wavy line is the interaction (7), dashed line represents Bose type Green function for two-particle scattering $d^{(0)}_{02}$, and oval stands for the correlation function $C^{(0)}$.

Numerical Results

We start from a non-interacting case, $U = 0$, where exact solution is known from the usual NEGF.

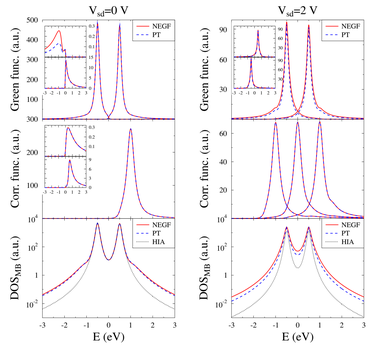

Figure 4: Non-degenerate two-level system. $T = 300K, \epsilon_a = -0.5eV, \epsilon_b = 0.5eV, U = 0, \Gamma^K_{aa} = \Gamma^K_{bb} = 0.1eV$ and $\Gamma^K_{ab} = \Gamma^K_{ba} = 0$. Top graphs show Green function $\mathrm{Im}(G^<_{11}(E)$, $-\mathrm{Im}(G^>_{44}(E)$ (main panel), $\mathrm{Im}(G^<_{33}(E)$ (top inset), and $-\mathrm{Im}G^>_{11}(E)$ (bottom inset). Middle graphs show correlation function $C^>_{31,13}(E)$ (rightmost peak in the main panel), $C^>_{12,21}(E)$ (top inset or leftmost peak in the main panel), and $C^>_{33,33}(E)$ (bottom inset or central peak in the main panel). Bottom graph show many-body spectral function, $i\sum_m(G^>_{mm}(E) - G^<_{mm}(E))$;

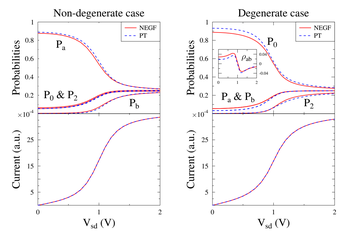

Figure 5: Non-interacting junction. Exact NEGF results (solid line, red) are compared with diagrammatic perturbation theory (PT) (dashed line, blue). Shown are state probabilities (top panels) and current (bottom panels) vs. applied bias V_{sd} for non-degenerate (left) and degenerate (right) cases. Inset in the top right panel shows coherence vs. applied bias.

We now consider regime of pair electron tunneling in junctions (negative U model).

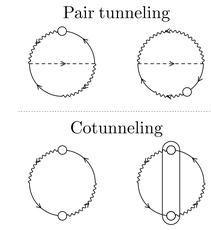

Figure 6: Diagrams responsible for pair and cotunneling transport in the negative-U model

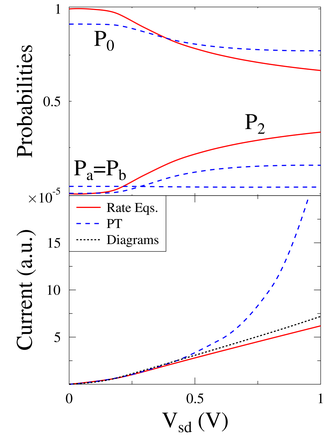

Figure 7: Pair electron tunneling in junction. Diagrammatic perturbation theory (PT) simulations are compared with the rate equation results [3]. Parameters are $\epsilon_a = \epsilon_b = 2eV$ and $U = -3.8eV$

Conclusions

We present a nonequilibrium flavor of diagrammatic technique for Hubbard Green functions, and illustrate the viability of such approach with several numerical examples of transport in molecular junctions. This technique is suitable for description of nonequilibrium steady-states in junctions and is applicable to multi-time correlation functions

References

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