Nonequilibrium atomic limit
Projection operators NEGF-EOM approach to quantum transport

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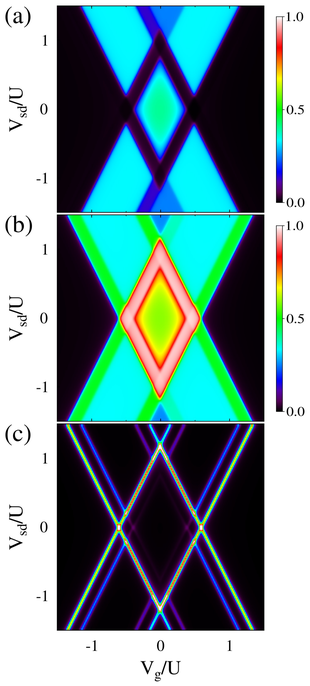
Development of theoretical methods capable of describing transport in molecular junctions in the language of many-body states of an isolated molecule is necessary for an adequate description of RIETS with strong electron-vibration coupling and/or anharmonic effects, of situations when the BO approximation breaks down, of energy transport in junctions with strong covalent bonding between the molecule and the contacts, and for the description of single-molecule magnet devices.

Within the projection operators approach we derive a canonical form of NEGF-EOMs, thus explicitly demonstrating proper formulation of the nonequilibrium atomic limit in junction problems.

QUANTUM DOT: COULOMB BLOCKADE REGIME.

As our first example, we investigate a single quantum dot (QD) with a strong Coulomb interaction parameter U and weak coupling to the contacts Γ.



Under these conditions the QD is close to the nonequilibrium atomic limit and the state-resolved system excitations are the right choice for our initial vector of operators.

$$\hat{A}_1 = \left((1-\hat{n}_\downarrow)\hat{d}_\uparrow,\ (1-\hat{n}_\uparrow)\hat{d}_\downarrow,\ \hat{n}_\downarrow\hat{d}_\uparrow,\ \hat{n}_\uparrow\hat{d}_\downarrow\right)^T$$

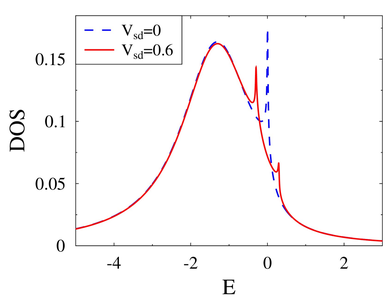
Shown are the maps for the
(a) probability of state “spin up”
(b) probability of state “spin down”
(c) conductance, dI/dV$_{sd}$.

Parameters are (in units of U): T=0.001, E_{up} =-0.4 E_{down} =-0.6, Γ_K =0.01. E_F=0. Bias is applied symmetrically with splitting factor ½. Energy grid spanning region from -3 to 3.

QUANTUM DOT: KONDO REGIME.

Next, we investigate a single quantum dot (QD) with an *infinitely* strong Coulomb interaction and weak coupling to the contacts. Then double occupancy is forbidden and the Kondo effect is the result of bath-induced correlations in the system. Assumptions for this model lead us to choose

$$\hat{A}_1 = \left((1-\hat{n}_{\bar{\sigma}})\hat{d}_\sigma,\ (1-\hat{n}_{\bar{\sigma}})\hat{c}_{k\sigma},\ \hat{d}^\dagger_{\bar{\sigma}}\hat{c}_{k\bar{\sigma}}\hat{d}_\sigma\right)^T$$



This Figure shows the density of states, in equilibrium (blue) and under symmetrically-applied bias (red).

Parameters for this calculation are (in units of Γ): T=0.005, E_{up}=E_{down}=-2, $\Gamma_{R,L}$=0.5 E_F=0, splitting factor equal to ½ and an enegy grid spanning form -5 to 3.

THEORY AND METHODOLOGY

The EOM technique provides a way to study correlation functions of any set of operators

$$\mathbf{G}_{a,b}(\tau,\tau') = -i\left\langle T_c\, \hat{a}(\tau)\,\hat{b}^\dagger(\tau')\right\rangle$$

yielding (in general) an infinite chain of equations of motion. The main drawback of the method is the necessity to make *uncontrolled approximations* in order to truncate the chain of equations.

Uncontrolled decoupling of correlation functions may result in complications related to loss of proper commutation relations between the decoupled operators. Here we present a methodology that solves these problems.

Heisenberg EOMs introduce an infinite sequence of operators $\hat{a}_n(\tau)$

$$i\frac{\partial}{\partial\tau}\hat{a}_n(\tau) = \varepsilon_n(\tau)\hat{a}_n(\tau) + \nu_{n,n+1}(\tau)\hat{a}_{n+1}(\tau)$$
$$-i\frac{\partial}{\partial\tau'}\hat{a}^\dagger_n(\tau') = \hat{a}^\dagger_n(\tau')\bar{\varepsilon}_n(\tau') + \hat{a}^\dagger_{n+1}(\tau')\nu_{n+1,n}(\tau')$$

Utilizing the scalar product

$$\mathbf{P}_{a,b} = \left\langle\left[\hat{a};\hat{b}^\dagger\right]_\pm\right\rangle$$

we orthogonalize vectors in generation *n* relative to all previous generations

$$\hat{A}_n \equiv \hat{a}_n - \sum_{i=1}^{n-1}\mathbf{P}_{a_n,A_i}\,\mathbf{P}^{-1}_{A_i,A_i}\,\hat{A}_i$$

Introducing irreducible Green functions

$$\mathbf{G}^{(n)}_{\mathbf{a},\mathbf{b}}(\tau,\tau') = \mathbf{G}^{(n-1)}_{\mathbf{a},\mathbf{b}}(\tau,\tau') - \int_c \mathbf{d}\tau_1\int_c \mathbf{d}\tau_2\ \mathbf{G}^{(n-1)}_{a,A_n}(\tau,\tau_1)\hat{\mathbf{G}}^{-1\,(n-1)}_{A_n,A_n}(\tau_1,\tau_2)\mathbf{G}^{(n-1)}_{A_n,b}(\tau_2,\tau')$$

and performing a local gauge transformation.

$$\mathcal{G}^{(n-1)}_{A_n,A_n}(\tau,\tau') = \mathbf{P}^{-1/2}_{A_n,A_n}(\tau)\,\mathbf{G}^{(n-1)}_{A_n,A_n}(\tau,\tau')\,\mathbf{P}^{-1/2}_{A_n,A_n}(\tau')$$

We arrive at a set of EOMs of the canonical (Dyson) type for arbitrary operators describing the system

$$\left(i\frac{\vec{\partial}}{\partial\tau} - \mathcal{W}_n(\tau)\right)\mathcal{G}^{(n-1)}_{A_n,A_n}(\tau,\tau') = \delta(\tau,\tau')\,\mathbf{I}_n + \int_c d\tau_1\,\mathcal{S}^{(n-1)}_{A_n,A_n}(\tau,\tau_1)\,\mathcal{G}^{(n-1)}_{A_n,A_n}(\tau_1,\tau')$$

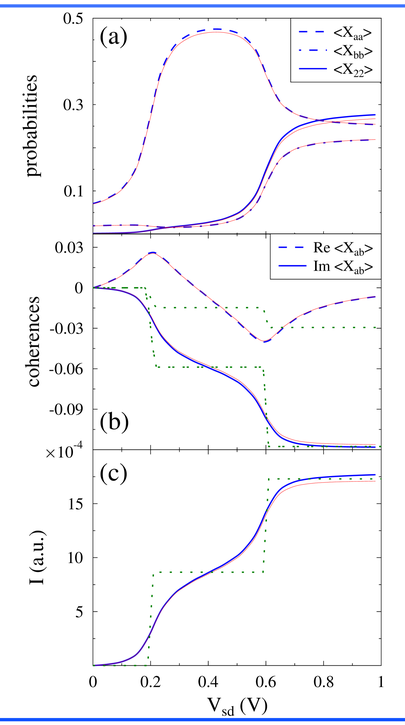
This set of equations allows for a controlled decoupling of the EOM chain and resolves symmetry violations present in the standard NEGF-EOM approaches.

TWO-LEVEL SYSTEM

We study a model for a junction with only two levels within this methodology. In this case, we describe the system in terms of Hubbard operators

$$\hat{A}_1 = \left(\hat{X}_{0a},\hat{X}_{0b},\hat{X}_{b2},\hat{X}_{a2}\right)^T$$

The Figure presents simulations within the standard NEGF (red) and the projection operator scheme (blue). Shown are (a) the probabilities and (b) the coherences of the many-body eigenstates of the TLS, and (c) current vs. applied bias V$_{sd}$.
Panels (b) and (c) show also results of the Redfield QME simulation (dotted and double-dotted lines, green)

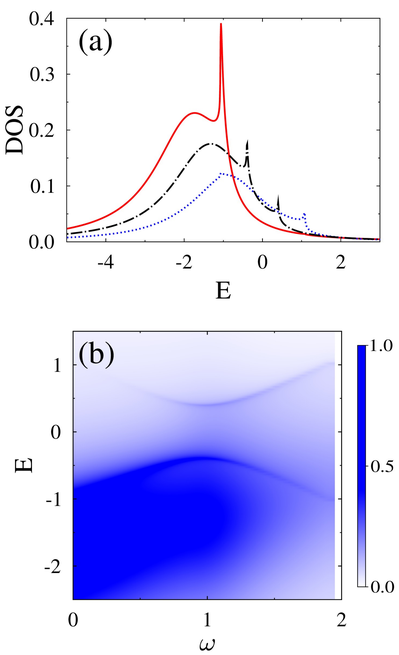


QD UNDER AN *ac* MAGNETIC FIELD IN KONDO REGIME

The presence of an *ac* magnetic field with frequency ω brings additional time-dependent dynamics. In this case, treatment within the projection operator NEGF EOM method is possible with the following choice

$$\hat{A}_1 = \Big((1-\hat{n}^c_{\bar{\sigma}})\hat{c}_\sigma,\ (1-\hat{n}^c_{\bar{\sigma}})\hat{c}_{k\sigma},\ \hat{c}^\dagger_{\bar{\sigma}}\hat{c}_{k\bar{\sigma}}\hat{c}_\sigma,\ (1-\hat{n}^c_\sigma)\hat{c}_{k\sigma},\ \hat{c}^\dagger_{\bar{\sigma}}\hat{c}_{k\sigma}\hat{c}_\sigma\Big)^T$$

Here we illustrate (a) The density of states for ω=0 spin up (red), ω=0 spin down (blue) and for both with ω=1 (black). (b) DOS for the spin up as a function of ω and Energy E.



Parameters for this calculation are (in units of Γ): E_{up}=-2.5, E_{down}= -1.5, g μ_B B_{ac}=0.2 and V_{sd}=0. This figure illustrates avoided crossing demonstrated by the Kondo peaks of the two densities when the frequency of the *ac* magnetic field approached the molecular resonance.