LOCAL FLUXES AND NOISE SPECTROSCOPY IN MOLECULAR JUNCTIONS

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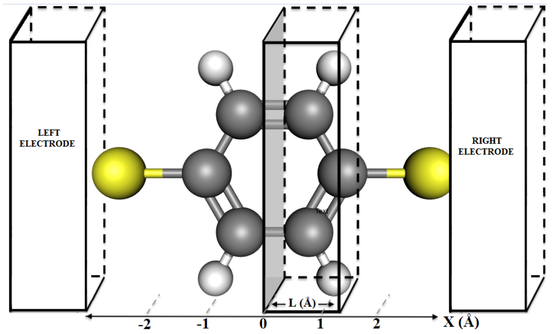
INTRODUCTION

Theoretical characterization of local junction properties is instrumental in understanding the overall junction response. Significant number of studies utilize bond currents to understand effects of quantum coherence on transport in junctions. However, the concept has two significant shortcomings: (a) bond currents can be formulated only in non-interacting systems and (b) they are useful only when electron flow is dominated by through-bond contributions. Here we present a more general current density analysis for elastic and inelastic flow and introduce, for the first time, concept of local noise spectroscopy.

MODEL and METHOD

We consider a junction consisting of a molecule M attached to two contacts L and R. Electron repulsion and interaction of electrons with vibrational degrees of freedom are assumed to be confined to the molecular part. Contacts are reservoirs of free electrons each at its own thermodynamic equilibrium. A difference in chemical potentials induces electron flux through the junction. The full Hamiltonian operator of the junction is

$$\hat{H} = \hat{H}_M + \hat{H}_L + \hat{H}_R + \hat{V}_{LM} + \hat{V}_{MR}$$



Coupling to the contacts and electron-vibration interaction enter reduced description of molecular electron degrees of freedom via electron self-energy

$$\Sigma = \Sigma^{e-e} + \Sigma^{e-vib} + \Sigma^{L} + \Sigma^{R}$$

We treat electron-electron interactions at the Hartree-Fock level of theory (the self-energy was calculated as the difference between the Fock matrix and part of the Hamiltonian representing electronic kinetic energy plus its potential in nuclear frame), electron coupling to molecular vibrations is accounted for within the self-consistent Born approximation (SCBA)

$$\Sigma^{e-vib}_{nm} = i\sum_{\alpha}[\sum_{u,v} D_{\alpha}(\tau_1,\tau_2) M^{\alpha}_{nu} G_{uv}(\tau_1,\tau_2) M^{\alpha}_{vm} + i\delta(\tau_1,\tau_2)\sum_{s,t} M^{\alpha}_{nm} M^{\alpha}_{ts} \int_{\tau_3} d\tau_3 D^{\alpha}(\tau_1,\tau_3) G_{st}(\tau_3,\tau_3)]$$

Here M^{α}_{ij} are electron coupling constants associated with normal mode α,

$$G_{ij}(\tau_1,\tau_2) = -i < \hat{T}_c \hat{c}_i(\tau_1)\hat{c}^{\dagger}_j(\tau_2) >$$

$$D_{\alpha}(\tau_1,\tau_2) = -i < T_c a_{\alpha}(\tau_1) a^{\dagger}_{\alpha}(\tau_2) >$$

are is the single-particle electron and phonon Green function, respectively. $\hat{T}_c$ is the contour ordering operator, $\tau_{1,2}$ are the contour variables, and $\hat{c}^{\dagger}_i$ ($\hat{c}_i$) creates (annihilates) electron in orbital i, $\hat{a}^{\dagger}_{\alpha}$ ($\hat{a}_{\alpha}$) creates (annihilates) quantum of molecular vibration in the normal mode α. The electron Green function satisfies the Dyson equation

$$G_{i,j}(\tau_1,\tau_2) = G^0_{i,j}(\tau_1,\tau_2) + \sum_{n,m\in M}\int_{\vec{\tau}} d\tau_3 d\tau_4 G^0_{i,j}(\tau_1,\tau_3)\Sigma_{n,m}(\tau_3,\tau_4) G_{i,j}(\tau_4,\tau_2)$$

Vibrational degrees of freedom are modeled as set of normal modes at thermal equilibrium.

REFERENCES

1. G. Cabra, A. Jensen, and M. Galperin, *On simulation of local fluxes in molecular junctions* J. Chem. Phys. **148**, 204103 (2018)

2. G. Cabra, M. Di Ventra, and M. Galperin, *Local-noise spectroscopy for nonequilibrium systems* submitted (2018)

CONTINUITY EQUATION

In molecular junctions, the presence of contacts and intra-molecular interactions leads to necessity to account for the source term P

$$\frac{\partial \rho(\vec{r},t)}{\partial t} + \vec{\nabla} \bullet \vec{J}(\vec{r},t) = P(\vec{r},t)$$

Here ρ is electron density and $\vec{J}$ is current density.
At steady state

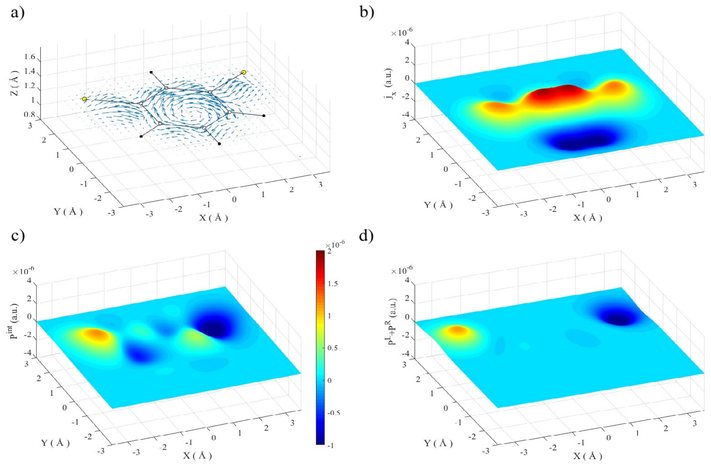
$$\rho(\vec{r}) = -i\sum_{n,m\in M}\int \frac{dE}{2\pi}\chi_n(\vec{r}) G^{<}_{n,m}(E)\chi^{*}_m(\vec{r})$$

$$\vec{J}(\vec{r}) = -\frac{1}{2}\sum_{n,m\in M}\int \frac{dE}{2\pi} G^{<}_{n,m}(E)[(\vec{\nabla}\chi^{*}_m(\vec{r}))\chi_n(\vec{r}) - \chi^{*}_m(\vec{r})(\vec{\nabla}\chi_n(\vec{r}))]$$

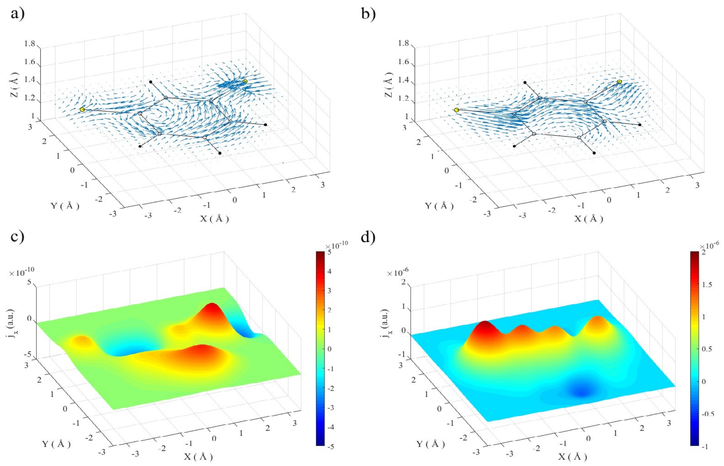
$$P(\vec{r}) = \sum_{n,m,k\in M}\chi_n(\vec{r})\chi^{*}_m(\vec{r})\int\frac{dE}{2\pi}[\Sigma^{<}_{n,k}(E)G^{a}_{k,m}(E) + \Sigma^{r}_{n,k}(E)G^{<}_{k,m}(E) - G^{r}_{n,k}(E)\Sigma^{<}_{k,m}(E) + G^{<}_{n,k}(E)\Sigma^{a}_{k,m}(E)]$$

LOCAL FLUX

Elastic Transport in a MBDT junction



Inelastic Transport in a MBDT junction



LOCAL NOISE SPECTROSOCPY

Local noise is defined as

$$S^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2;t_1,t_2) = \frac{1}{4}[C^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2,t_1,t_2) + C^{J}_{i_2 i_1}(\vec{r}_2,\vec{r}_1;t_1,t_2) + C^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2;t_2,t_1) + C^{J}_{i_2 i_1}(\vec{r}_2,\vec{r}_1,t_2,t_1)]$$

where

$$C^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2;t_1,t_2) = \langle \delta\hat{j}_{i_1}(\vec{r}_1,t_1)\,\delta\hat{j}_{i_2}(\vec{r}_2,t_2)\rangle$$

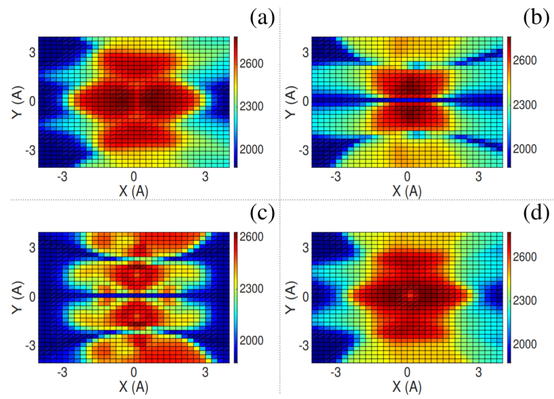
Here $i_1, i_2 \in x,y,z$ and $\delta\hat{j}_i(\vec{r},t)$ is the operator of projection i of the local flux fluctuation, $\delta\hat{j}_i = \hat{j}_i - \langle\hat{j}_i\rangle$, in the Heisenberg picture.
At steady-state,

$$S^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2;\omega) = 2\int_{-\infty}^{\infty} dt e^{i\omega t} S^{J}_{i_1,i_2}(\vec{r}_1,\vec{r}_2;t) = \frac{1}{8}\sum_{n,m,u,v\in M}[(\vec{\nabla}\chi^{*}_m)\chi_n - \chi^{*}_m(\vec{\nabla}\chi_n)]_{i_1}[(\vec{\nabla}\chi^{*}_v)\chi_u - \chi^{*}_v(\vec{\nabla}\chi_u)]_{i_2} \times \int_{-\infty}^{+\infty}\frac{dE}{2\pi}[G^{>}_{n,v}(E+\omega)G^{<}_{u,m}(E) + G^{>}_{u,m}(E+\omega)G^{<}_{n,v}(E) + G^{>}_{n,v}(E-\omega)G^{<}_{u,m}(E) + G^{>}_{u,m}(E-\omega)G^{<}_{n,v}(E)]$$

LOCAL NOISE THERMOMETRY

Effective local temperature

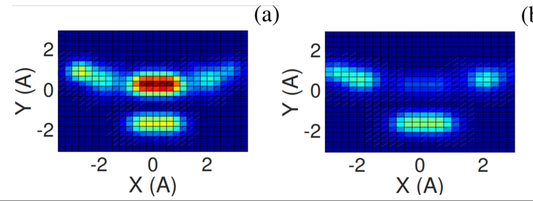
$$T_M = T_{EQ}\frac{\int_A d\vec{s}_1\int_A d\vec{s}_2\, S^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2;\omega=0)|_{V_{sd}}}{\int_A d\vec{s}_1\int_A d\vec{s}_2\, S^{J}_{i_1 i_2}(\vec{r}_1,\vec{r}_2;\omega=0)|_{V_{sd}=0}}$$



Bias-Induced Heating The above figure demonstrates the bias-induced heating of PBDT junction for different orientations of a non-invasive probe: (a) perpendicular to tunneling direction, (b) parallel to junction tunneling direction and perpendicular to molecular plane, (c) parallel to molecular plane, (d) perpendicular to local current.

LOCAL ELECTROLUMINESCENCE

Electroluminescence is associated with the positive frequency part of the current noise. Local noise spectroscopy yields information on local emission patern in the junction.



ACKNOWLEDGEMENTS

The M.G. group research is supported by the National Science Foundation (Grant No. CHE-1565939) and U.S. Department of Energy (Grant No. DE-SC0018201).