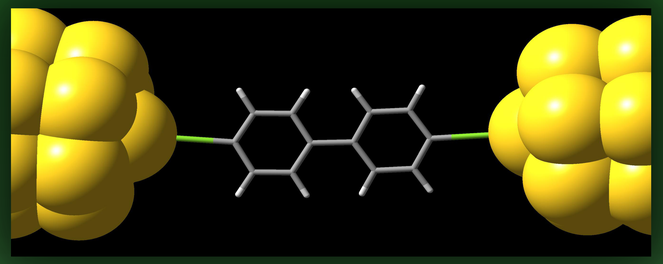
Electron and Energy Transfer in Molecular Junctions

Alexander J. White and Michael Galperin

Department of Chemistry and Biochemistry,
University of California San Diego, La Jolla, CA



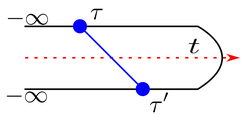
Abstract

Study of the properties of single-molecule transport junctions (SMJ) is important to the understanding of the quantum nature of nanoscale devices and to the fundamental processes of charge and energy transfer. We seek methods to calculate the properties of the molecular junction in terms of the molecular many-body states. These methods are exact in their description of the on-the-molecule correlations but are perturbative in the molecule-bath coupling. Due to the molecular sensitivity to oxidation/reduction and/or excitation, such methods are especially convenient for description of SMJ's operation at resonance. We apply one such approach, the pseudoparticle nonequilibrium Green's functions, to inelastic electron transfer and hybrid plasmon-exciton systems (energy transfer).

Theory

The single molecule junction is composed of two, or more, leads connected by a molecule. Theoretical treatment of the SMJ is based on the approximate separation of the whole junction into the interacting system (the molecule) and idealized baths (the leads). Usual non-equilibrium Green's function is a quantum field theory method utilizing the language of quasiparticles (elementary excitations). The single particle GF is a two time correlation function of excitation operators defined on the Keldysh contour.

$$G_{\nu,\nu'}(\tau,\tau') = -i\langle T_c\, \hat{c}_\nu(\tau)\hat{c}^\dagger_{\nu'}(\tau')\rangle$$



Every creation or annihilation operator in the system can be expressed in terms of pseudoparticle operators via spectral decomposition.

$$\hat{c}^\dagger_\nu \equiv \sum_{m_1,m_2} \xi^\nu_{m_1m_2}\hat{d}^\dagger_{m_1}\hat{d}_{m_2}$$

$$\xi^\nu_{m_1m_2} \equiv \langle m_1|\hat{c}^\dagger_\nu|m_2\rangle$$

The pseudoparticle operator, $\hat{d}^\dagger_m$, creates the many-body system state m, $\hat{d}^\dagger_m|0\rangle \equiv |m\rangle$. The pseudoparticle Green's function

$$G_{m_1m_2}(\tau_1,\tau_2) = -i\langle T_c \hat{d}_{m_1}(\tau_1)\hat{d}^\dagger_{m_2}(\tau_2)\rangle$$

satisfies the usual Dyson equation $\mathbf{G} = \mathbf{g} + \mathbf{g}\boldsymbol{\Sigma}\mathbf{G}$ within an extended Hilbert space. Here, $\Sigma_{m_1m_2}$ is the pseudoparticle self-energy. As with the standard NEGF approach, the pseudoparticle NEGF must be projected from the Kelysh contour onto the real time axis. For the steady state consideration, the projections are calculated using the Fourier transform of the Dyson and Keldysh equations:

$$\mathbf{G}^r(E) = [E\mathbf{I} - \mathbf{H}_M - \boldsymbol{\Sigma}^r(E)]^{-1}$$
$$\mathbf{G}^<(E) = \mathbf{G}^r(E)\boldsymbol{\Sigma}^<(E)\mathbf{G}^a(E)$$

The imaginary parts of the retarded, $\mathbf{G}^r$ and lesser, $\mathbf{G}^<$, pseudoparticle NEGFs tell about the state density and population respectively. Within the non-crossing approximation (dressed second-order perturbation in the coupling to the bath) the connection between the usual NEGF (for the excitation operators) and the pseudoparticle NEGF is (ζ_m is +1 (-1) if m is a bosonic (fermionic) state)

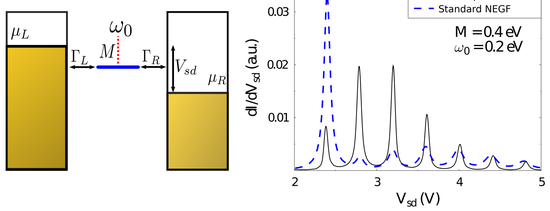
$$G^{</>}_{\nu,\nu'}(E) = i\sum_{\substack{m_1,m_1'\\ m_2,m_2'}} \zeta_{m_2}\overset{*}{\xi}{}^\nu_{m_1m_2}\xi^{\nu'}_{m_1'm_2'} \times \int_{-\infty}^{\infty}\frac{dE'}{2\pi}G^{>/<}_{m_1m_1'}(E'+E)G^{</>}_{m_2'm_2}(E')$$

Inelastic Electron Transport

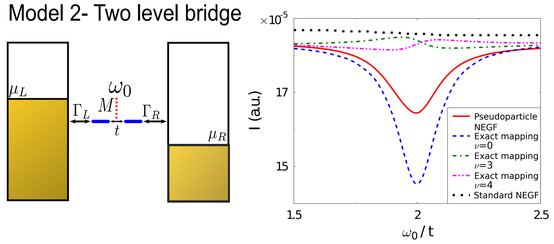
Coupling of conducting electrons to molecular vibrations (vibrons) is the cuase of inelastic transport features in molecular devices. Utilizing the pseudoparticle NEGF technique, the electron-vibron interaction is described nonperturbatively. Contrary to the usual treatments, the pseudoparticle NEGF allows us to account for strong electron-vibron coupling of arbitrary form. The method goes beyond the usual Born-Oppenheimer approximation.We calculate the steady state current for several models of molecular devices.

$$I_K = \sum_{\nu_1,\nu_2}\int_{-\infty}^{\infty}\frac{dE}{2\pi}\,[\Sigma^{K<}_{\nu_1,\nu_2}(E)G^{>}_{\nu_2,\nu_1}(E) - G^{<}_{\nu_1,\nu_2}(E)\Sigma^{K>}_{\nu_2,\nu_1}(E)]$$

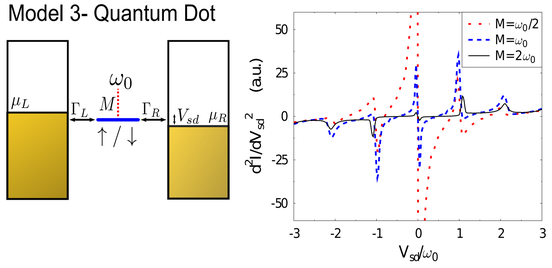
Model 1- Single level



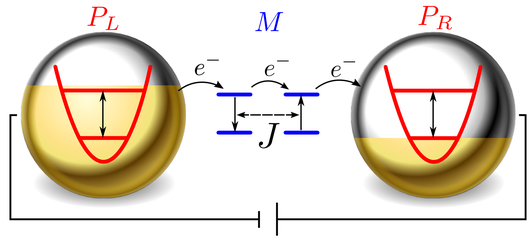
Model 2- Two level bridge



Model 3- Quantum Dot



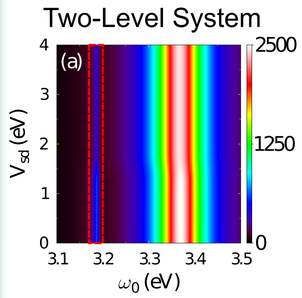
Plasmon-Exciton Interaction



Description of plasmon-molecule interaction on a fully quantum mechanical level is important for the study of surface enhanced and single molecule spectroscopy. This interaction also allows for coherent control of molecular systems. We consider open plexcitonic systems far from equilibrium, and demonstrate the sensitivity of the junction optical properties to electron transport through the molecule.

$$P^>(\omega) = \sum_{\substack{K,K'\in[L,R]\\ m_1,m_1',m_2,m_2'\in M}} \overset{*}{\beta}{}^K_{m_1m_2}\beta^{K'}_{m_1'm_2'}\zeta_{m_2} \times \int_{-\infty}^{\infty} dE\frac{-1}{\pi}\mathrm{Im}[G^r_{m_1m_1'}(E+\omega)]G^<_{m_2'm_2}(E)$$

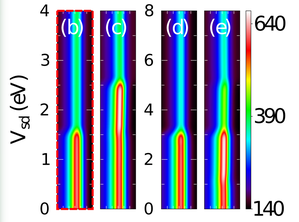
Two-Level System



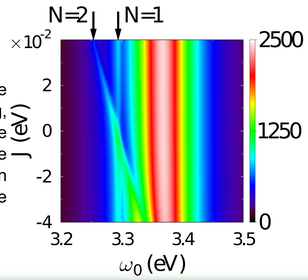
$$I_{abs}(\omega_0) = -\int_0^\infty \frac{d\omega}{2\pi}\gamma(\omega)N_{\omega_0}(\omega)\mathrm{Im}P^>(\omega)$$

$$N_{\omega_0}(\omega) \equiv N_0\frac{1}{\pi}\frac{\delta^2}{(\omega-\omega_0)^2+\delta^2}$$

Plasmon absorption spectrum $I_{abs}(\omega_0)/\gamma N_0\delta$ as a function of bias (a) and close up of the Fano resonance (b)-(e). Calculations with an asymmetrically applied bias are preformed without, (b), and with electron-electron repulsion, U=1 eV (c). (d) and (e) show the results of calculations with a symmetrically applied bias with U=0 eV and with U=1 eV respectively.



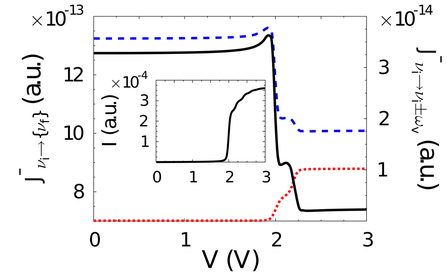
TLS Dimer



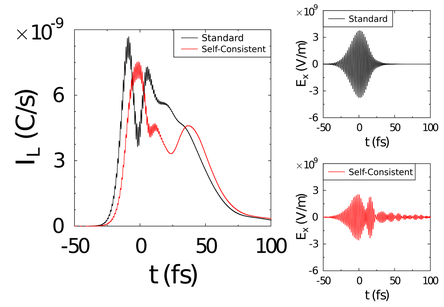
Plasmon absorption spectrum as a function of the intramolecular exciton coupling, J. The system is under large symmetric bias, and with a large on-site electron-electron repulsion. N is the total charge on the dimer.

Additional Research Areas

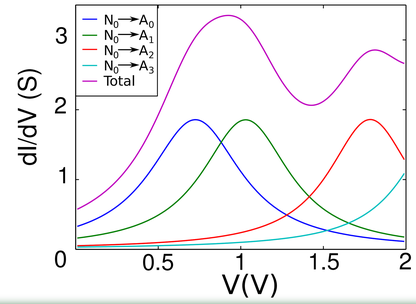
Raman Spectroscopy in molecular junctions



Time-Dependent Transport and Interaction with External Fields (Molecular Nanoplasmonics)



Ab Initio Simulations in Realistic Molecular Junctions



Conclusion

We have applied a state based approach to calculating junction properties for systems in which a traditional NEGF method is inconvenient. This formalism is exact in its description of all in-the-system interactions. We demonstrate our ability to operate beyond the Born-Oppenheimer approximation and in the strong electron-vibration coupling regime. We also apply this method to investigate hybrid plasmon-exciton systems under non-equilibrium transport conditions. The optical properties of the system under bias may reveal additional information on intra-molecular interactions. The application of the pseudoparticle NEGF to the study of transient behavior in molecular junctions is an ongoing project.

Acknowledgments

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