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:

\[ G_{\mu}(\tau_1, \tau_2) = \langle \hat{\psi}_{\mu}^{+}(\tau_1) \hat{\psi}_{\mu}(\tau_2) \rangle \]

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

\[ \hat{c}_{\mu} = \sum_{m_{\mu}} c_{m_{\mu}} \hat{c}_{m_{\mu}} \]

The pseudoparticle Green's function satisfies the usual Dyson equation:

\[ G_{\mu}(\omega) = G_{\mu}(\omega) G_{\mu}(\omega) \]

Inelastic Electron Transport
Coupling of conducting electrons to molecular vibrations (vibrons) is the cause 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.

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 plasmonic systems far from equilibrium, and demonstrate the sensitivity of the junction optical properties to electron transport through the molecule.

Conclusion
We have applied a state based approach to calculating junction properties for systems in which a traditional NEGF method is inconvenient. This formulation 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
We gratefully acknowledge support from the Department of Energy (Early Career Award, DE-SC0006422), the National Science Foundation (grant No. CHE-1007030), U.S.-Israel Binational Science Foundation (grant No. 2008282), and the Hellmann Family Foundation.