

Simulations of Correlated Electronic Transport Across Molecular Junctions

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INTRODUCTION

Measurement and theoretical prediction of current-voltage (IV) characteristics for molecular-scale electronic devices remains a challenge. A physical scheme for transport at the many-body level and its implementation leading to calculation of IV curves for molecular scale systems is presented. Open boundary conditions are applied to a many-body wavefunction calculated by the configuration interaction (CI) technique. Our aim is to remove as many approximations from the calculation of the current carrying many-body wavefunction as possible, and to allow for a systematic treatment of electron correlation.

METHOD

A constraint *Ansatz* is made to incorporate open-system boundary conditions for the calculation of the subsystem reduced density matrix that describes the device region (typically the molecule plus part of the electrodes) at each value of applied voltage. The N -body reduced density matrix operator for the device region is written $\hat{\gamma}_N = |\Psi\rangle\langle\Psi|$, where $|\Psi\rangle$ is the best approximation to an N -body wavefunction of the subsystem with constraints.

However, application of scattering boundary conditions is not conceptually tractable. For example, what is meant by incoming electrons on the left (or right)? All electrons are indistinguishable, and there is no localization of a single electron beyond the one-body density $\rho(\mathbf{r})$ yielding the probability of finding *any* electron at position \mathbf{r} . To this end, our approach relies on the use of the first order Wigner function $f(\mathbf{q}, \mathbf{p})$, which is the Wigner-Weyl transform of $\rho(\mathbf{r})$, in order to fix the incoming electron momentum distributions.

Finally, $|\Psi\rangle$ is represented by a CI expansion written as a sum of spin-projected Slater determinants. This enables us to adjust the electronic correlations between the HF exact-exchange level and improve to approach the in principle exact treatment of full CI limit.

DISCUSSION

We review the method and discuss our most recent results for correlated electron transport in nanoscale systems (see Fig. 1 and 2). Application of our many-body formalism to the study of transport across single aromatic molecules like benzene dithiol(Fig. 3), short oligomer chains of alkanes and point contacts all lead to results that compare well to the best experimental data available. In particular, we discuss the influence of electron-electron interactions on tunneling through molecular junctions and determine the validity of independent particle models for tunneling quantifying respective deviations of tunneling currents magnitudes. To this end, we thoroughly examine the properties of the one-particle reduced density matrix and its corresponding eigenvalues and eigenvectors.

ACKNOWLEDGMENT

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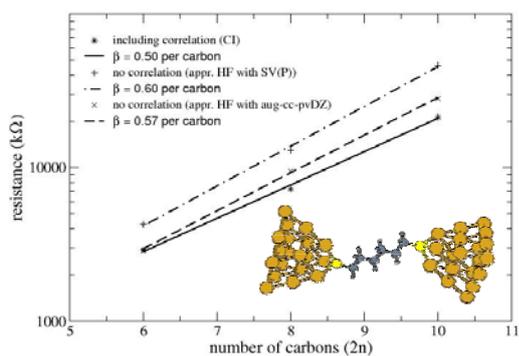


Fig. 1. Resistance-increase exponential law at different levels of theory. Inset: Typical geometry of the studied $\text{Au}_{\text{tip}}\text{-S-(C}_2\text{H}_4)_n\text{-S-Au}_{\text{tip}}$ molecular junctions ($n = 3$).

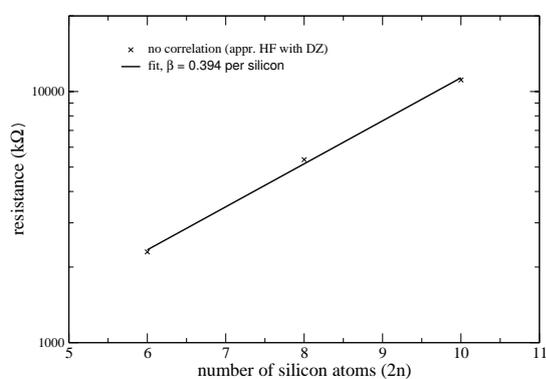


Fig. 2. Resistance-increase exponential law for silicon hydrate molecular junctions ($\text{Au}_{\text{tip}}\text{-S-(Si}_2\text{H}_4)_n\text{-S-Au}_{\text{tip}}$). Note that $\beta(\text{\AA}^{-1}) \approx 0.2$ much smaller than that of alkanes $\beta(\text{\AA}^{-1}) \approx 0.45$.

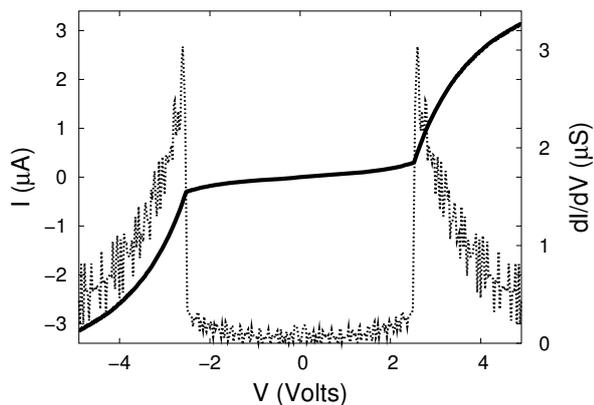


Fig. 3. Predicted current voltage characteristics of benzene dithiol attached to Au electrodes.