Probing electronic excitations in molecular conduction

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We identify experimental signatures in the current-voltage (I-V) characteristics of weakly contacted molecules directly arising from excitations in their many electron spectrum. The current is calculated using a multielectron master equation in the Fock space of an exact diagonalized model many-body Hamiltonian for a prototypical molecule. Using this approach, we explain several nontrivial features in frequently observed I-Vs in terms of a rich spectrum of excitations that may be hard to describe adequately with standard one-electron self-consistent field (SCF) theories.

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Theoretical efforts to model molecular conduction have largely been based on SCF models for electron-electron interactions. While they have been fairly successful in describing both shapes and magnitudes of various I-V characteristics, notable exceptions include low-temperature measurements on unconjugated and weakly coupled molecules, as well as short conjugated molecules where there are clear disagreements between theory and experiment. Some disagreements could be attributed to uncertainties in geometry or parasitic resistances; nevertheless the applicability of SCF approaches need to be scrutinized, especially in the weak coupling regime. Charging energies of short molecules (~3 eV for benzene) are often larger than their contact induced broadenings (~0.2 eV for benzene dithiol on gold), while couplings between various molecular units (~2 eV for conjugated molecules, much less for non-conjugated species) can be tuned widely using synthetic chemistry. It is thus debatable whether a molecule acts as a quantum wire in the SCF regime, or as a quantum dot in the Coulomb Blockade (CB) regime.

In this paper, we employ a multielectron master equation in the Fock space of a prototypical molecular Hamiltonian to describe conduction through molecules with weak contact couplings or poor conjugation. A full many-body treatment of transport even with a small molecule, modeled simply as an array of quantum dots, yields many features with compelling similarities (Fig. 1a) to relevant experiments [1,2]. These features, however, are quite difficult to obtain using a traditional non-equilibrium Green’s function (NEGF) treatment of transport, being only perturbative in the interaction parameter [11]. A spin restricted (RSCF) calculation (inset in Fig. 1c) typically creates slow current onsets spread over several volts by Coulomb costs for adiabatic charging. The high zero-bias conductances, in clear variance with experiments, could be removed by incorporating self-interaction correction for integer charge addition in the CB regime. However, crucial to experiments in this regime is the fact that the molecule can also execute transitions between various excited states of the neutral and singly charged species at no additional Coulomb cost, making it possible to directly probe a rich spectrum of such transition levels within a small bias window.

FIG. 1: (color online) (a, b) Experimental and (c, d) theoretical I-Vs for a molecular ring weakly coupled with a backbone or with conducting electrodes. Many nontrivial, features such as low zero-bias conductance, sharp current onset, and a subsequent quasilinear region spanning several volts with multiple closely spaced features (a-d) arise in our treatment of CB from excitations, but not even qualitatively in a spin restricted SCF (RSCF) treatment for the same parameter set (inset in c). For asymmetric contacts, there are additional features (b, d) including current step heights (as opposed to widths) that are asymmetric in bias, are modulated with a gate voltage [4], and reverse polarity for gate voltages on either side of the charge degeneracy point [12].

It seems difficult to capture this rich spectrum adequately within any SCF theory even with self interaction correction or effective one electron potentials, especially under non-equilibrium conditions. A single spin-degenerate level (Fig. 2) illustrates the problem. While the deficiencies of SCF (e.g. adiabatically smeared steps) are rectified with self-interaction correc-
tive justice to chemistry would possibly require looking that captures the conjugation chemistry and electrostatics and yet allows exact diagonalization within a multiorbital description. Our aim is to solve the transport problem exactly for a simple system, rather than do an approximate SCF calculation of a more elaborate quantum chemical system.

**Approach.** We start with a tight-binding model for benzene (one orbital per atom), with onsite, hopping, and Hubbard parameters that can be benchmarked with separate LDA calculations. In contrast with single dot studies, long-ranged Coulomb terms (modeled with the Mataga-Nishimoto approximation and hopping are responsible for off-diagonal correlations in the charging term of the molecular eigenspace. Exact diagonalizing this Hamiltonian yields a large spectrum of closely spaced excitations in every charged configuration of the molecule. Using the equation of motion of the density matrix of the composite molecule and leads and assuming no molecule-lead correlations, one can derive a simple master equation in terms of the occupation probabilities of each N electron many-body state $|N,i\rangle$ with total energy $E_i^N$. The master equation then involves transition rates $R_{|N,i\rangle\rightarrow|N\pm 1,j\rangle}$ between states differing by a single electron, leading to a set of independent equations defined by the size of the Fock space.

$$\frac{dP_i^N}{dt} = -\sum_j \left[ R_{|N,i\rangle\rightarrow|N\pm 1,j\rangle} P_i^N - R_{|N\pm 1,j\rangle\rightarrow|N,i\rangle} P_j^{N\pm 1} \right]$$

along with the normalization equation $\sum_i P_i^N = 1$. For weakly coupled dispersionless contacts, parameterized using bare-electron tunneling rates $\gamma_{\alpha}$, ($\alpha$: left/right contact), we define rate constants

$$\Gamma_{ij\alpha}^{\text{NR}} = \gamma_{\alpha}|\langle N,i|c_{\alpha}^\dagger|N-1,j\rangle|^2$$

$$\Gamma_{ij\alpha}^{\text{NS}} = \gamma_{\alpha}|\langle N,i|c_{\alpha}|N+1,j\rangle|^2,$$

where $c_{\alpha}^\dagger$, $c_{\alpha}$ are the creation/annihilation operators for an electron on the molecular end atom coupled with the corresponding electrode. The transition rates are given by

$$R_{|N,i\rangle\rightarrow|N-1,j\rangle} = \sum_{\alpha=L,R} \Gamma_{ij\alpha}^{\text{NS}} \left[ 1 - f(\epsilon_{ij}^{\text{NR}}) - \mu_{\alpha} \right]$$

$$R_{|N-1,j\rangle\rightarrow|N,i\rangle} = \sum_{\alpha=L,R} \Gamma_{ij\alpha}^{\text{NR}} f(\epsilon_{ij}^{\text{NR}} - \mu_{\alpha}).$$

for the removal levels ($N,i \rightarrow N-1,j$), and replacing ($r \rightarrow a, f \rightarrow 1 - f$) for the addition levels ($N,i \rightarrow N+1,j$). $\mu_{\alpha}$ are the contact electrochemical potentials, $f$ is the corresponding Fermi function, with single particle removal and addition transport channels $\epsilon_{ij}^{\text{NR}} = E_i^N - E_j^{N-1}$, and $\epsilon_{ij}^{\text{NS}} = E_j^{N+1} - E_i^N$. Finally, the steady-state solution to Eq. (1) is used to get the left terminal current

$$I = \frac{\pm e}{h} \sum_{ij} \left[ R_{|N,i\rangle\rightarrow|N\pm 1,j\rangle}^L P_i^N - R_{|N\pm 1,j\rangle\rightarrow|N,i\rangle}^L P_j^{N\pm 1} \right]$$

FIG. 2: (color online) (a) Fock space, (b) equilibrium occupancy $N - \mu$ and (c) nonequilibrium I-V of a spin degenerate level $\epsilon = 1\text{eV}$ with a single electron charging energy $U = 1\text{eV}$. A restricted SCF (RSCF) (pink) calculation shows fractional charge occupation and is inappropriate in the weak coupling limit. A Spin Unrestricted SCF (blue) describes integer charge transfer and matches the many-body $N - \mu$ (black) plot; however, it yields equal current steps corresponding to sequential removal of two electrons, as opposed to a many-body calculation (shown in black) in which step heights are in the ratio of 2:1. Including correlations in SCF alters the current onsets and the plateau widths, but misses the essential point that consecutive removal of spins need not carry equal current.
where states corresponding to a removal of electrons by the left electrode involve a negative sign.

**Results.** We calculate currents in a break-junction configuration with equal electrostatic coupling with the leads, setting $\mu_{L,R} = E_F + eV_d/2$, and equal resistive couplings set by the ratio $\gamma = \gamma_L/\gamma_R = 1$. $\gamma_L = 0.6$ meV. Coulomb Blockade with integer charge transfer manifests itself as a vanishing pre-threshold current followed by a step-wise increase in current for positive drain bias for the source to access the transport channel marked $e_{00}^{Nr}$ (shown in the state transition diagram). The onset of conduction is established by the offset between the equilibrium Fermi energy $E_F$ and the first accessible transition energy (focussing on removal levels for concreteness, this corresponds to the transport channel marked $e_{00}^{Nr}$ in Figs. 3a and 3c). The onset can be varied by varying the gate voltage, thereby accounting for the variation in conductance gap with gate bias.

The simplest impact of Coulomb Blockade on the I-Vs of short molecular wires is a clear suppression of zero-bias conductance, often seen experimentally. Indeed, a spin unrestricted SCF with self-interaction corrections can yield a Coulomb staircase with intervening plateaus through the Coulomb cost of adding or removing an electron to the molecular ground state.

However, integer charge transfer can also occur between various electronic excitations of the neutral and singly charged species at marginal correlation costs. Specifically, a quasilinear regime resulting from very closely spaced transport channels ($\epsilon_{10}^{N0}$) via excitations. The crucial step is the access of the first excited state via channel $e_{00}^{Nr}$, following which transport channels involving higher excitations are accessible in a very small bias window. The sequence of access of transport channels upon bias, enumerated in the state transition diagrams shown in Figs. 3a and 3b, determines the shape of the I-V. When the Fermi energy $E_F$ lies closer to the threshold transport channel $e_{00}^{Nr}$ (Fig. 3a), it takes an additional positive drain bias for the source to access the first excited state of the neutral system via the transition $e_{10}^{Nr}$, as shown in the state transition diagram in Fig. 3a. The I-V shows a sharp rise followed by a plateau (Fig. 3c), as seen in various experiments. However, when transport channels that involve low lying excitations such as $\epsilon_{10}^{N0}$ are closer to the Fermi energy $E_F$ than $e_{00}^{Nr}$ (Fig. 3b), the excitations get populated by the left contact immediately when the right contact intersects the threshold channel $e_{00}^{Nr}$, allowing for a simultaneous population of both the ground and first excited states via $\epsilon_{10}^{N0}$ and $\epsilon_{10}^{Nr}$ at threshold. Under these conditions the I-V shows a sharp onset followed immediately by a quasilinear regime (Fig. 3c) with no intervening plateaus, as observed frequently in I-Vs of molecules weakly coupled with a backbone.

The direct role of excitations in conduction becomes particularly striking under asymmetric coupling ($\gamma = \gamma_L \gg \gamma_R$), including the possibility of populating higher excitations (b), say, via transport channel $e_{10}^{Nr}$ at threshold. For positive bias charge removal is the rate limiting process, while for negative bias addition dominates, accounting thus for the corresponding I-V asymmetry in (c). Progressive access of higher excitations also accounts for the observed gate modulation of the current steps, as shown in (d).
This predicts a peak current \( \sim \) larger than experiments [8], indicating that one needs fur-
rnering as in chemisorbed benzene dithiol [20], still much
peak currents through a level since those depend only
For instance, correlation alone cannot explain ultralow
[6]) can vary and will be discussed in detail elsewhere [22].
larization asymmetries [5] and temperature dependences
details specific to experiments (e.g. onset voltages, po-
tally [12]. While the qualitative features of our I-Vs are
charge degeneracy point, as is also observed experimen-
4d). Furthermore, it is easy to show that the asymme-
try will flip on gate voltages between either sides of the
charge degeneracy point, as is also observed experimen-
tally [12]. While the qualitative features of our I-Vs are
robust with respect to variation of our model parameters,
details specific to experiments (e.g. onset voltages, po-
larization asymmetries [3] and temperature dependences
) can vary and will be discussed in detail elsewhere [22].
For instance, correlation alone cannot explain ultralow
peak currents through a level since those depend only
on contact couplings through the ratio \( \gamma_L \gamma_R/\gamma_L + \gamma_R \). This predicts a peak current \( \sim 3 \mu A \) for a 0.1eV broad-
easing as in chemisorbed benzene dithiol [21], still much
larger than experiments [6], indicating that one needs fur-
ther to postulate weak couplings due to non-ideal contact
couplings or perhaps parasitic resistances from multiple
molecules [22]. Further complications could arise from
strong electron-phonon interactions [4] that smoothen
out the first few conduction plateaus (Fig. 1d) due to
low lying excitations over phonon energies significantly
smaller than their Coulomb counterparts at tens of meV.

In summary, we have used a rate equation in the Fock
space of a molecular Hamiltonian to address significant
experimental features like suppressed zero-bias conduc-
tances, sharp steps that are often asymmetric, gate mod-
ulated and interchangeable, and followed occasionally by
extended quasiohmic regimes. While our method is par-
icularly suited to systems with large charging and small
coupling, the opposite regime is usually handled pertur-
batively by SCF-NEGF. Developing the transport formal-
ism for the intermediate coupling regime could be
nontrivial [31], involving novel physics due to the inter-
play between charging (localization) and hybridization
(delocalization), and may be crucial to understanding a
variety of other molecular switching and sensing-based
phenomena already being explored experimentally.

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oration \( \Delta e = 0.9eV \), while for calculations on porphyrin
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