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Current-constrained one-electron reduced density-matrix theory for non-equilibrium steady-state molecular conductivity

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In the effort to create ever smaller electronic devices, the idea of single molecule circuit elements has sparked the imagination of scientists for nearly fifty years. While traditional theories for non-equilibrium steady-state molecular conductivity like the non-equilibrium Green's function density functional theory determine the current from an applied voltage, the recently proposed current-constrained density-matrix theory computes the voltage from a current constraint on the molecule. In the present paper we extend the current-constrained density-matrix theory from its two-electron reduced density-matrix (2-RDM) formulation to a one-electron reduced density matrix (1-RDM) formulation that is applicable to Hartree-Fock, density functional, and tight-binding theories. We demonstrate the current-constrained 1-RDM method through the computation of the theoretical, intrinsic resistance of acenes and phenacenes.

I. INTRODUCTION

When Aviram and Ratner suggested the possibility of a single molecule diode in 1974 [1], the concept of molecular-scale electronics was entirely theoretical. The development of single molecule measurement techniques[2, 3] made the testing of such components an experimental reality [4, 5]. Since then, a number of molecules have been found to function as molecular wires [6], switches [7, 8], and diodes [9, 10]. Current theoretical studies generally use density functional theory (DFT) [11–18] or reduced density matrix (RDM) theory [19, 20] to approximate the non-equilibrium Green's functions. Just as in experiment, these methods calculate the current flow through a system which results from setting a particular bias voltage.

Recent work proposed a different paradigm to study single molecule conductance, the current-constrained reduced-density-matrix theory. This method imposes a current on the molecule and measures the bias voltage required to generate the current-constrained non-equilibrium steady state. In the previous work, the current constraint is added to a variational minimization of the 2-electron reduced-density-matrix or 2-RDM [21]. Here, we extend the theory to a one-electron reduced density matrix (1-RDM) form. The 1-RDM,

$$^{1}D(1:\bar{1}) = \int {}^{N}D(1,...N;\bar{1},...N)d2..dN, \tag{1}$$

which is obtained by integrating the N-particle density matrix over all particles save one, contains all the information needed to study one-electron properties. By analogy with the 2-RDM stationary-state [22–39] and steady-state work [21], we perform a variational minimization of the energy of the molecule as a functional of the 1-RDM which is subject to the N-representability conditions [34, 40–42], ensuring that the 1-RDM represents at least one N-electron density matrix, but also a current constraint that sets the average current fluxing through the molecule. The 1-RDM current-constrained theory is compatible with any one-electron electronic structure theory including Hartree-Fock, density functional [43, 44], and tight-binding [45, 46] methods. While the 1-RDM method does not include an explicit description of electron correlation, it provides a qualitatively correct description of single molecule conductivity at low computational cost.

After deriving the current-constrained 1-RDM method in section II, we apply it in section III to compute the steady-state, intrinsic resistance of the acenes and phenacenes in the Hartree-Fock approximation as a function of their length. The intrinsic resistance of a molecule is its resistance to the flow of electrons along a chosen direction where the current is added to the isolated molecule as a constraint. Both acenes and phenacenes exhibit trends in their intrinsic resistance that reflect trends in available experimental data [47].

II. THEORY

To define a 1-RDM theory of molecular conductivity, we begin with variational principle in the absence of electron transport. The energy of the system, given by

$$E = \mathrm{Tr}(^{1}K\,^{1}D). \tag{2}$$

where ^{1}K is a one-electron reduced Hamiltonian matrix such as the Fock or Kohn-Sham matrix. The energy is minimized subject to N-representability conditions known as the 1-positivity constraints, which ensure that the 1-RDM generated in the minimization arises from the integration of at least one N-electron density

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matrix [40, 41, 48–50]. These conditions have the form,

$$^{1}D^{i}_{j} \succeq 0 \tag{3}$$

$$^{1}Q^{i}_{j} \succeq 0 \tag{4}$$

where ^{1}D and ^{1}Q are the one-particle and one-hole reduced density matrices and the symbol $\succeq$ indicates that they must remain positive semidefinite, that is, they must have nonnegative eigenvalues. These conditions can be expressed as a single semidefinite constraint

$$M \succeq 0 \tag{5}$$

in which M is a block-diagonal matrix

$$M = \begin{pmatrix} ^{1}D & 0 \\ 0 & ^{1}Q \end{pmatrix} \tag{6}$$

with ^{1}D and ^{1}Q matrices on the diagonal.

To set the current for the system, we define the one-electron current matrix as the matrix representation of the one-electron gradient in a specified direction $\hat{\kappa}$, given by

$$^{1}J^{p}_{q} = \frac{1}{L}\int_{dr} \phi_{p}(r)(\nabla \cdot \hat{\kappa})\phi_{q}(r)dr, \tag{7}$$

where L is the length of the molecule, r represents the electronic coordinates, $\hat{\kappa}$ is the vector direction of the current, and ϕ_p are the molecular orbitals [21]. We add this to the energy minimization by requiring that

$$\mathrm{Tr}(^{1}J\ \mathrm{Im}(^{1}\mathrm{D})) = \mathrm{I}, \tag{8}$$

where ^{1}J is given above. This method of energy minimization is a special type of convex optimization known as semidefinite programming (SDP) [26, 27, 32, 34]. The current constraint generates a complex-valued SDP that can be mapped to a real-valued SDP by representing the complex matrix M by a larger real-valued matrix S,

$$S = \begin{pmatrix} \mathrm{Re(M)} & \mathrm{Im(M)} \\ -\mathrm{Im(M)} & \mathrm{Re(M)}. \end{pmatrix} \tag{9}$$

The S matrix is positive semidefinite if and only if the M matrix is positive semidefinite.

Solving this semidefinite program generates the reorganization energy due to the current constraint. Since charge polarization is the microscopic starting point for conductivity, we follow Ref. [21] in assuming that the energetic response ΔE_{curr} of a molecule to a current constraint is comparable to its energetic response $\Delta E_{\mathrm{field}}$ to an electric field ϵ applied in the same direction,

$$\Delta E_{\mathrm{curr}} \approx \Delta E_{\mathrm{field}} = \alpha\epsilon^{2} = \alpha\frac{V^{2}}{L^{2}}, \tag{10}$$

where L is the length of the molecule and α is its electric field polarizability. Solving for the voltage V, we obtain the following formula [21] for V in terms of ΔE_{curr}, L, and α

$$V \approx L\left(\frac{\Delta E_{\mathrm{curr}}}{\alpha}\right)^{1/2}. \tag{11}$$

Thus, the voltage required to generate a current-constrained steady state in an isolated molecule may be estimated from the reorganization energy due to the current constraint and the electric field polarizability.

To determine the length dependence of conductance in the acene chains, we calculate the current through the atomic orbitals of the atoms of the edge rings of each acene

$$\tilde{I} = \mathrm{Tr}(^{1}\tilde{J}\mathrm{Im}(^{1}D)), \tag{12}$$

where

$$\tilde{J} = C^{AO}_{MO}PJ \tag{13}$$

in which P is the projector onto selected orbitals at the edge of each acene. The estimated voltage in Eq. (11) and this edge current can then be used to compute the conductance (or resistance) of the system.

III. APPLICATIONS

Graphene [51], and its acene precursors [52] are of particular interest in the field of molecular electronics. Recently, linear acenes have been used to create stable and highly conductive molecular junctions at room temperature, without the need for thiol linkers between the molecule and the metal leads [53]. In this work, we calculate the response energy and voltage of linear acene and phenacene chains, shown in Fig. 1, of three to seven phenyl rings in length over a current range of 0 to 20 μA. Geometries of the linear acenes and phenacenes were obtained by optimization at the B3LYP/cc-pVDZ level of theory. All molecules are centered at the origin and the vector direction of the current ($\hat{\kappa}$) is set as the y-axis.We generate the Hamiltonian from the Fock matrix from a minimization of the Hartree-Fock energy of each molecule at the 6-31G level of theory. Since we are interested in a qualitative description of the conductivity which arises only from the molecule itself, we compute the intrinsic conductance of the molecule, omitting the thiol linkers and metal leads.

The voltage required to support a particular edge current increases exponentially with the number rings in both the acenes and the phenacenes. For a given number of phenyl rings, acenes require a lower voltage than phenacenes to support a given current, indicating that as a whole acenes have higher conductivity than the corresponding phenacenes, as shown by the current-voltage plots for the acenes and phenacenes in Fig. 2. While phenacenes have a lower reorganization energy at a particular current, their lower electric field polarizability results in a higher voltage requirement. For both the acenes

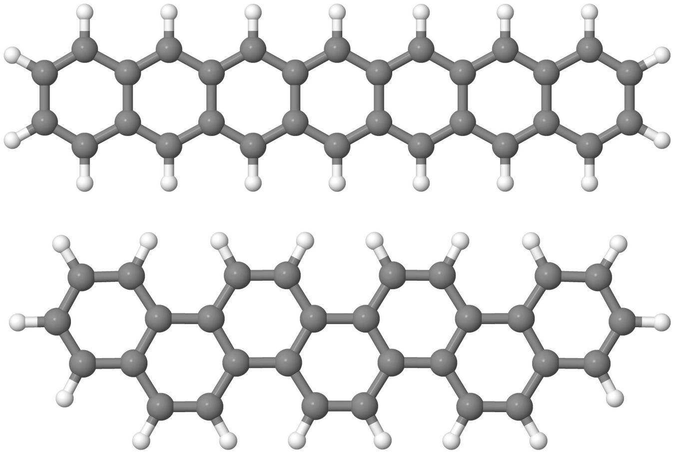

FIG. 1. Ball and stick representations of 7-acene (top) and 7-phenacene (bottom)

and the phenacenes the voltage necessary to achieve a particular current is directly proportional to chain length, as has been shown in experiment for the acenes [47].

In single molecule junctions, a variety of conductance mechanisms have been observed, but in general, the conductance is dominated by non-resonant tunneling. This results in an exponential decay in conductance with increasing molecular length (L) across a series such as the acenes or oligothiophenes as given by

$$G \propto e^{-\beta L} \tag{14}$$

where β is the decay constant [54]. As shown in Fig. 3, we recover the expected exponential decay from conductances calculated using the edge current, indicating that the edge behavior of single molecules is retained without including explicit leads in the calculation.

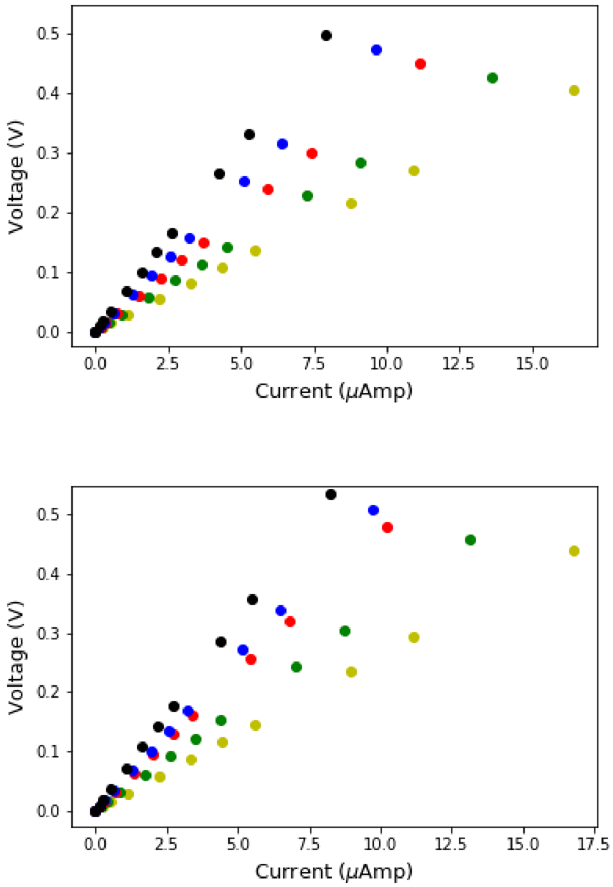

FIG. 2. Edge current plotted as a function of voltage for the N-acenes (top) and N-phenacenes (bottom), where N is 3 (yellow), 4 (green), 5 (red), 6 (blue), and 7 (black). The edge is taken to be the outermost phenyl ring on each side of the molecule.

IV. DISCUSSION AND CONCLUSIONS

In this work we extend the current-constrained reduced-density-matrix theory for non-equilibrium, steady-state molecular conductivity from its original 2-RDM formulation to a 1-RDM formulation. We show that, like the 2-RDM version, this formulation gives ohmic current-voltage relationships in the low bias region and captures the tunneling effect in the edge conductance of the linear acenes. This method achieves a qualitatively correct description of the length dependence of conductivity in the linear acenes. The data presented here cannot be directly compared to data obtained from the 2-RDM formulation, as the 2-RDM method uses an active set of orbitals while the present 1-RDM method uses all of the orbitals. We also find that linear aromatic chains of phenyl rings are more effective conductors than alternating aromatic chains.

Traditional theories of molecular conductivity add a voltage to the molecule to compute the current. In the current-constrained RDM theories the current is added as a constraint to compute the reorganization energy and the voltage. This change in paradigm allows us to compute an intrinsic resistance (or conductance) for each molecule that depends only upon a molecule's energetic response to the imposed current constraint as well as its intrinsic properties such as length and polarization. Importantly, as shown in the results, the intrinsic resistance reflects key qualitative features of molecular conductivity, features that are determined mainly by the electronic properties of the molecule. Even the exponential decay in the edge current, observed experimentally in acene chains, is qualitatively captured by the current-constrained computation of each chain's intrinsic resistance. The computation of intrinsic resistance provides a useful metric by which to compare the intrinsic capacity of molecules and materials for efficient electron transport.

While in this work, we use Hartree-Fock theory to generate the Hamiltonian, the theory can be interfaced with other one-electron-based electronic structure methods,

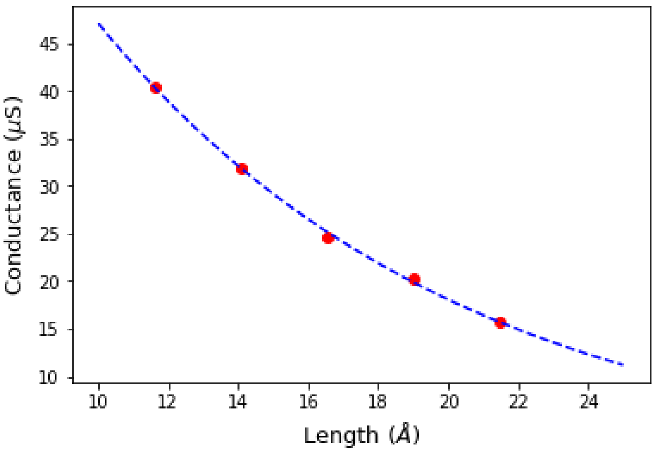

FIG. 3. Molecular conductance plotted as a function of length for 3-acene through 7-acene (red). In all cases, the current is set to 0.662 μA and the atomic orbitals selected are those of the 12 carbons and 8 hydrogens in the outermost phenyl ring on each end of the molecule. A least-squares exponential fit with a β value of 0.009568 1/Å is shown in blue.

including DFT and semi-empirical tight binding methods. The current-constrained 1-RDM theory provides a qualitatively correct description of single molecule conductivity at low computational cost.

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