Microscopic study of electrical transport through individual molecules with metallic contacts. 
I. Band lineup, voltage drop, and high-field transport

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We present the first in a series of microscopic studies of electrical transport through individual molecules with metallic contacts. We view the molecules as “heterostructures” composed of chemically well-defined atomic groups, and analyze the device characteristics in terms of the charge and potential response of these atomic groups to the perturbation induced by the metal-molecule coupling and the applied bias voltage, which are modeled using a first-principles based self-consistent matrix Green’s function (SCMGF) method. As the first example, we examine the devices formed by attaching two benzene-based molecular radicals—phenyl dithiol (PDT) and biphenyl dithiol (BPD)—symmetrically onto two semi-infinite gold electrodes through the end sulfur atoms. We find that both molecules acquire a fractional number of electrons with similar magnitude and spatial distribution upon contact with the electrodes. The charge transfer creates a potential barrier at the metal-molecule interface that modifies significantly the frontier molecular states depending on the corresponding electron density distribution. For both molecules, the metal Fermi level is found to lie closer to the highest-occupied-molecular-orbital (HOMO) than to the lowest-unoccupied-molecular-orbital (LUMO). Transmission in the HOMO-LUMO gap for both molecules is due to the metal-induced gap states arising from the hybridization of the metal surface states with the occupied molecular states. Applying a finite bias voltage leads to only minor net charge injection due to the symmetric device structure assumed in this work. But as current flows, the electrons within the molecular junction redistribute substantially, with resistivity dipoles developing in the vicinity of potential barriers. Only the delocalized $\pi$ electrons in the benzene ring can effectively screen the applied electric field. For the PDT molecule, the majority of the bias voltage drops at the metal-molecule interface. But for the BPD molecule, a significant amount of the voltage also drops in the molecule core. The field-induced modification of the molecular states (the static Stark effect) becomes significant as the bias voltage increases beyond the linear-transport region. A bias-induced reduction of the HOMO-LUMO gap is observed for both molecules at large bias. The Stark effect is found to be stronger for the BPD molecule than the PDT molecule despite the longer length of the former. For both molecules, the peaks in the conductance are observed for both molecules at large bias. The Stark effect is found to be stronger for the BPD molecule than the PDT molecule despite the longer length of the former. For both molecules, the peaks in the conductance are due to electron transmission through the occupied rather than the unoccupied molecular states. The calculation is done at room temperature, and we find that the thermionic-emission contribution to the current-voltage characteristics of both molecules is negligible.

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I. INTRODUCTION

Exploring the use of individual molecules as active components in electronic devices has been at the forefront of nanoelectronics research in recent years due to the potential advantage of ultrahigh density/speed and low-cost device fabrication through self-assembly/self-organization processes that such molecular-scale devices may bring. Numerous useful device characteristics including molecular rectifying diodes, negative differential resistance and field-effect transistors have been demonstrated using molecular-scale structures including small conjugated molecules, single- and multiple-wall carbon nanotubes and macromolecules such as DNA. A quantitative understanding of the physical mechanisms underlying the operation of such diverse molecular-scale devices has been and remains a major challenge in nanoelectronics research.

The electrical characteristics of molecular devices are usually measured by sandwiching the molecules between two metallic electrodes. The measured transport characteristics reflect both the nature of the metal-molecule interface and the properties of the molecular layer. There are basically three electronic processes of interest in such metal-molecule-metal junctions: charge transfer between the metals and the molecules, the change of the electrostatic potential, and the modification of the molecular geometry and electronic states. The nature of these processes under both zero and nonzero bias determines the electrical characteristics of the molecular junction. Here it is natural to separate the problem into device at equilibrium and device out of equilibrium since (1) the linear dc-transport property of the molecular device probes the equilibrium charge distribution of the molecular junction established by adsorption onto the electrodes and (2) the nonlinear transport probes the charge response of the molecular junction to the applied electrical field established through a finite bias voltage. A microscopic theory of molecular electronics will therefore need to (1) determine the appropriate geometry of the molecular junction, (2) determine the self-consistent charge transfer and the resulting lineup of the molecular levels relative to the metal Fermi level and the modification of the molecular states upon formation of the metal-molecule-metal junction, and (3) determine the molecular screening of the applied electric field, the field-induced modification of molecular states.
Stark effect), and the nonequilibrium electron distribution when current is flowing, and (4) determine the current/conductance-voltage characteristics and their correlation with the molecular and device structures. None of these issues has been satisfactorily solved such that theory can be used in conjunction with experiment for an unambiguous identification of the device operation mechanism. The purpose of our work is to elucidate the above device electronic processes and their dependence on the given molecular and device structures under both equilibrium and nonequilibrium conditions within a well-defined theoretical model. Specifically, we will investigate the different aspects of molecular transport due to the interplay between the electronic processes at the metal-molecule interface, the electronic processes in the molecule core and the molecular response to the applied electrical field when current is flowing. Correspondingly, we focus our attention on the electron dynamics and calculate the device characteristics within the coherent transport regime. Our emphasis is on the conceptual understanding and the chemical trends obtained from detailed microscopic calculation of simple but representative molecular and device structures. Our work can therefore be considered as a "minimal" microscopic model of single-molecule electronics.

The ionic dynamics of the metal-molecule-metal junction can also be affected by the above electronic processes both at equilibrium and out of equilibrium, i.e., the adsorption and bias/current-induced conformation change. Neither aspect will be treated here. By confining ourselves to the coherent transport regime, we also neglect the effect of electron-vibrational coupling on transport. Solving the adsorption-induced conformation change requires an accurate knowledge of the surface lattice structure at the atomic scale for devices under applied voltage. This is almost never known in typical molecular transport measurement. Since one goal of such a calculation is to provide the input nuclear configuration for transport calculation, our purpose can be served equally well by examining the effect that different adsorption and molecular geometries may have on the device characteristics, which will be treated in subsequent papers of the series. A rigorous solution of the bias/current-induced conformational change and the general solution of inelastic contribution to nonlinear current due to electron-vibrational coupling is a challenging topic which requires solving the nonequilibrium dynamics of the coupled electron-nuclei systems since the molecular potential energy surface is affected by the nonequilibrium electron dynamics and electron energy is dissipated in moving the atoms. By focusing on the electron dynamics in the molecular junction with fixed geometry, the present work will provide a reference for evaluating the importance of such additional complications and provide the necessary input for further investigation in situations where they are indeed critical.

In typical molecular junction measurement, conjugated molecules are attached to the metallic electrodes through appropriate end groups. In this paper we will consider current transport through two benzene-based molecular radicals—phenylene dithiol (PDT) and biphenylene dithiol (BPD)—adsorbed symmetrically onto two semi-infinite gold (111) electrodes through the end sulfur atoms. These structures chosen are among the simplest possible but are still representative of current experimental works. For the device at equilibrium, we obtain the self-consistent charge transfer, the adsorption-induced change in the electrostatic potential, the lineup of the molecular level relative to the metal Fermi level, and the modification of the individual molecular states due to the metal-molecule coupling. For the device out of equilibrium, we obtain the charge injection/redistribution within the metal-molecule-metal junction, the molecular screening of the applied field and the resulting voltage drop, the modification of the molecular states by the applied field, the nonequilibrium occupation of molecular orbitals, and the current/conductance-voltage characteristics for the given contact geometry.

The calculation we present is performed using a recently developed self-consistent matrix Green’s function (SCMGF) method, which is based on the nonequilibrium generalization of the quasiparticle Green’s function theory (NEGF) and uses a finite local-orbital basis set. By replacing the quasiparticle exchange-correlation self-energy with the exchange-correlation potential within the density functional theory, the well-established technique of self-consistent field theory of molecular electronic structure can then be utilized for transport calculations. The real-space formulation of our approach allows us to provide an intuitive and coherent physical picture of the molecular transport by analyzing the device electronic processes both at the atomic scale and on the basis of individual molecular orbitals. We view the molecules as comprised of chemically well-defined atomic groups and interpret their electrical characteristics in terms of the response of these atomic groups to the perturbation induced by the metal-molecule coupling and the applied bias voltage. We emphasize the insight obtained with such atomic-scale analysis and show the important effect of atomic-scale charge and potential inhomogeneity on device characteristics at the molecular scale, which may otherwise be obscured by the molecular-level analysis treating the molecules as a whole. In particular, two important conclusions come out of this work: (1) the adsorption-induced modification of molecular states is larger than the field-induced effect unless we go to large bias, so accurate modeling of the electronic processes at equilibrium is critical for determining the low-bias transport characteristics and (2) the effect of both the metal-molecule coupling and the applied electric field in turning the individual molecular orbitals into effective conduction channels depends on the detailed charge and potential distribution across the metal-molecule-metal junction and may be different for different molecular orbitals. “Engineering” the charge and potential inhomogeneity as commonly done in quantum semiconductor heterostructures will be equally important at the molecular scale. Both aspects have been largely neglected in the past. We therefore hope the results obtained here will provide an useful guide regarding the nature of electron transport at the ultimate limit of device scaling and the prospect of device engineering through molecular design.
II. THEORETICAL MODEL

A. The self-consistent matrix Green’s function theory

The details of the self-consistent matrix Green’s function theory have been described elsewhere,18,19 so we only give a brief summary here to clarify the assumptions and approximations and to show how the physical observables are computed. Similar but different methods based on the NEGF approach have been developed independently by other research groups.20,23,24 We feel that this approach provides a natural link between quantum transport, first-principles electronic structure theory, and qualitative molecular orbital theory.25,26 A comparison between the present approach and other related experimental and theoretical works will be given at the end of the paper.

Due to metallic screening in the electrodes, the charge and potential perturbations induced by molecular adsorption extend only over a finite region into the metal surface.43,44 We define an “extended molecule” which includes both the molecule and the surface atoms perturbed by molecular adsorption.25,26 The surface atoms also form an adiabatic reflectionless contact with the rest of the electrodes, which can then be modeled as infinite electron reservoirs commonly assumed for mesoscopic transport problems.19,47 The size of the “extended molecule” is chosen such that charge neutrality is maintained approximately under both zero and finite biases. The central quantities in the NEGF theory are the retarded and correlation Green’s function $G^r$ and $G^c$.37,36 We expand both the wave functions $\psi_{\mu}$ and the Green’s functions using a finite set of local orbital functions $\phi_i$,

$$G^r(\vec{r},\vec{r}';E) \equiv \sum_{ij} G^r_{ij}(E) \phi_i(\vec{r}) \phi_j^*(\vec{r}') , \quad (1)$$

$$G^c(\vec{r},\vec{r}';E) \equiv \sum_{ij} G^c_{ij}(E) \phi_i(\vec{r}) \phi_j^*(\vec{r}') , \quad (2)$$

where $\sigma$ is the spin index. We obtain the retarded and correlation matrix Green’s function by solving the Keldysh-Kadanoff-Baym (KKB) equation in the matrix form19

$$G^r_{MM} = \{E^+ S_{MM} - H^\sigma_{MM} - V^\text{ext,}\sigma - \Sigma_L^\sigma(E) - \Sigma_R^\sigma(E)\}^{-1} , \quad (3)$$

$$G^c_{MM} = -i[\Sigma_L^\sigma(E) - \Sigma_R^\sigma(E)] f(E - \mu_L) + i[\Sigma_L^\sigma(E) - \Sigma_R^\sigma(E)] f(E - \mu_R) , \quad (4)$$

where the effect of the contact is incorporated as the self-energy operators $\Sigma_{L(R)}^\sigma$,

$$\Sigma_L^\sigma(E) = (E^+ S_{ML} - H^\sigma_{ML}) G^r_{LL} (E^+ S_{LM} - H^\sigma_{LM}) ,$$

$$\Sigma_R^\sigma(E) = (E^+ S_{MR} - H^\sigma_{MR}) G^r_{RR} (E^+ S_{RM} - H^\sigma_{RM}) ,$$

$$\Gamma^\sigma_{L(R)} = i(\Sigma_L^\sigma - \Sigma_R^\sigma)_{L(R)} . \quad (5)$$

Here $G^r_{LL(RR)} = (E^+ S_{LL(RR)} - H^\sigma_{LL(RR)})^{-1}$ are the surface Green’s functions of the left (L) and right (R) contacts (the electrodes with the perturbed surface atoms removed) which can be obtained from that of the semi-infinite surface. The self-energy operators $\Sigma^\sigma_{L(R)}$ characterizes the interaction between the molecule and the left (right) contacts, the real part of which leads to an effective shift of the molecular level while the imaginary part $\Gamma^\sigma_{L(R)}$ describes an effective energy level broadening due to the finite probability of electrons escaping into the respective contact (for details see Ref. 19). $H^\sigma_{MM}$ represents the part of the Fock matrix contributed by the charge distributions (both nuclei and electron) in the “extended molecule” only, while $V^\text{ext,}\sigma(\vec{r})$ represents the long-range coulomb potential due to the equilibrium charge (ionic and electronic) distribution in the contact region, which includes the linear voltage drop due to the applied bias. The $S$ are overlap matrices. The applied potential $V^\text{ext,}\sigma$ changes the charge and potential in the “extended molecule,” requiring a self-consistent solution.

Given the electron density or the density matrix in the “extended molecule,” the calculation of the Fock matrix $H^\sigma_{MM}$ is the same as that of standard molecular electronic structure calculation, which greatly facilitates the implementation of our procedure using standard molecular electronic structure codes.19 The self-consistent calculation proceeds by computing the input density matrix to the next iteration from the correlation matrix Green’s function computed in the current iteration

$$\rho_{ij}^\sigma = \int \frac{dE}{2\pi} G^c_{ij}(E) . \quad (6)$$

The density matrix is simply the energy integration of the matrix correlation function. The integration over energy can be performed conveniently in the complex energy plane.19,48 Once the self-consistent calculation converges, we can calculate all the physical observables from the matrix retarded Green’s function and the density matrix.

B. Analyzing molecular transport

We calculate the charge density using

$$\rho(\vec{r}) = \sum_{ij,\sigma} \rho_{ij}^\sigma \phi_i(\vec{r}) \phi_j^*(\vec{r}) , \quad (7)$$

from which we can obtain the electrostatic potential in the molecular junction from the Poisson equation. We can also calculate charges associated with each atom using Becke’s atomic-partition scheme49

$$N = \int d\vec{r} \rho(\vec{r}) = \sum_i \int d\vec{r} W_i(\vec{r}) \rho(\vec{r}) = \sum_i N_i . \quad (8)$$

Here the atomic weight function $W_i(\vec{r})$, which satisfies $\Sigma_i W_i(\vec{r}) = 1$ everywhere in space, is determined such that it is centered on the atom $i$ and is non-negligible only in a region close to its atomic center.49

The local density of states (LDOS) gives the energy-resolved charge density distribution.
nonorthogonal basis functions. To identify the contribution of the individual molecular orbitals to the total density of states, we project it onto the basis of molecular orbitals. This is done by transforming $G'$ into the basis of the molecular orbitals obtained by diagonalizing the (self-consistent) Fock matrix corresponding to the molecule. The imaginary part of the diagonal element of the transformed $G'$ gives the projected density of states (PDOS) of the corresponding molecular orbitals. The peak position of the PDOS characterizes the perturbed molecular energy level, while the broadness reflects the coupling strength of the molecular orbitals with the metallic surface states.

A critical question in molecular transport is how the electron occupation of the molecular orbitals changes as the molecule is driven out of equilibrium by a finite bias voltages. This information is contained in the nonequilibrium density matrix $\rho'_{ij}$ [Eq. (6)]. Transforming to the basis of molecular orbitals, the diagonal elements of the density matrix give the nonequilibrium electron occupation of the corresponding molecular levels.

A general formula for the current through a mesoscopic system with arbitrary interaction in contact with two noninteracting electrodes is

$$ I = \frac{e}{\hbar} \int dE \sum_{\sigma} \text{Tr} \left[ \left( \Gamma_L^{\sigma} - \Gamma_R^{\sigma} \right)(E,V) i G^{<:\sigma}(E,V) \right] $$

\[ + \left[ f(E - \mu_L) \Gamma_L^{\sigma}(E,V) - f(E - \mu_R) \Gamma_R^{\sigma}(E,V) \right] \]

\[ \times A^{\sigma}(E,V) \}, \quad (11) \]

where $A^{\sigma} = i (G^{\sigma\sigma} - G^{\sigma\sigma})$ is the spectral function. Since the only scattering mechanism in the coherent transport regime is that by the contacts (introducing additional scattering mechanisms within the molecule will lead to additional terms in self-energy and current), we arrive at the familiar Landauer-type current formula

$$ I = \frac{e}{\hbar} \int dE \sum_{\sigma} T^{\sigma}(E,V) \left[ f(E - \mu_L) - f(E - \mu_R) \right], \quad (12) $$

where the transmission probability $T^{\sigma}$ through the molecule is obtained from

$$ T^{\sigma}(E,V) = \text{Tr} \left[ \hat{T}^{\sigma}(E,V) \right] = \text{Tr} \left[ (i\tau^{\sigma})^T \tau^{\sigma} \right] $$

\[ = \text{Tr} \left[ \Gamma_L^{\sigma}(E,V) G^{\sigma\sigma}(E,V) \Gamma_R^{\sigma}(E,V) [G^{\sigma\sigma} \Gamma_L^{\sigma}(E,V)] (E,V) \right]. \quad (13) \]

Note that equations (12), (13) hold for both orthogonal and nonorthogonal basis functions. To identify the contribution of individual molecular orbitals to the transmission, we transform the transmission matrix $\hat{T}^{\sigma}(E,V)$ into the basis of the molecular orbitals whose diagonal elements give the transmission probability through the corresponding molecular orbitals.

Combined with the spatially resolved LDOS and charge density, the total DOS, the transmission coefficient and their projection onto individual molecular orbitals provide a set of useful qualitative analysis tools to establish the connection between the molecular electronic structure and the transport characteristics of the metal-molecule-metal junction, similar to the use of qualitative molecular orbital theory in quantum chemistry. A caveat of projecting the physical observable onto the individual molecular orbitals is that phase interference information is lost. Only the summation over all molecular orbitals (conserved by the matrix transformation), not the individual components, corresponds to the quantum mechanical physical observable. The situation is similar to what we met when we try to decompose the electron density of the molecule into the contribution of individual atoms through a Mulliken-type population analysis or other charge partition schemes as we used here. Only the total density but not the atom-partitioned density corresponds to a physical observable.

Within the coherent transport model, the only temperature effect is from the two electrode Fermi-Dirac distributions associated with the electronic temperature in the electrodes. We can separate the current into two components, the “tunneling” component $I_{\text{tun}}$ and the “thermionic emission” component $I_{\text{th}}$ as follows:

$$ I = I_{\text{tun}} + I_{\text{th}} = \frac{e}{R} \int \left[ \mu_L + \mu_R \right] \left[ \mu_L + \mu_R \right] \int dE \left[ f(E - \mu_L) - f(E - \mu_R) \right] \times \left( [f(E - \mu_L) - f(E - \mu_R)] \right). \quad (14) $$

C. Device model

A convenient way of characterizing the “band” lineup problem at any interface is to find a reference level to put all materials forming the interface on a common absolute energy scale. For the metal-molecule-metal junction considered here, the occupation of the electron states is determined by the electrochemical potential of the two metallic electrodes, which are treated as large electron reservoirs. So it is natural to choose the reference level being determined by the property of (empty) bimetallic junction alone, which is not affected by the choice of the molecules or the nature of metal-molecule interaction. Therefore we choose the electrostatic potential energy in the middle of the (empty) bimetallic junction as the energy reference, then the equilibrium Fermi level $E_f$ is fixed at the negative of the metal work function $-5.31$ eV for single-crystal gold (111) electrodes. The electrochemical potential of the two electrodes is fixed by the applied bias voltage $V$ at $\mu_L = E_f - eV/2$ and $\mu_R = E_f + eV/2$. Here the bias polarity is chosen such that for positive bias the electron is injected from the right electrode. Note the Fermi-level positions are fixed by the bimetallic junction alone without the molecular insertion. The symmetrization shift of the electrochemical potential of the two electrodes
from the equilibrium Fermi level $E_f$ is independent of the property of the molecule as well as its interaction with the electrodes, and has nothing to do with the common assumption of symmetric shift of molecular levels with respect to the metal Fermi levels at nonzero bias which is an approximation that is not correct in general. Instead, the symmetric shift of the electrochemical potential of the two electrodes determines the electrostatic boundary condition from which the self-consistent electrochemical potential of the two electrodes Fermi distribution. Both aspects are affected by the bias voltage and the thermal broadening through the metal-molecule-metal junction, as will be detailed in this series of work.

In this work, the electronic structure of the “extended molecule” is described using the Becke-Perdew-Wang (BPW91) (Refs. 53,54) parameterization of the spin-polarized density-functional theory (SDFT) (Refs. 39,55) within the generalized-gradient approximation (GGA).54 We also replace the atomic core by an appropriate pseudopotential56 with the corresponding optimized Gaussian basis sets.57,58 The geometry of the adsorbed molecule is taken to be the same as the singlet geometry of the free molecule optimized at the BPW91/6–31G* level (we assume the bare molecule to be the molecular biradical with the end H atoms removed). The adsorption geometry is chosen such that the end atoms sit in front of the center of the triangular pad of the three gold atoms on the Au(111) surface (the end sulfur-surface distance is 1.9 Å). Six nearest-neighbor gold atoms on each metal surface are included into the “extended molecule.” Within the range of second-nearest-neighbor coupling, there are 12 metal atoms in the first surface layer and 14 metal atoms on the second surface layers on each side coupled to the “extended molecule.” Only the blocks of the surface Green’s function corresponding to these atoms are needed, which in turn can be calculated from the surface Green’s function of the semi-infinite metal using tight-binding method parametrized by fitting accurate bulk band structure calculations.18,19,59 The results and conclusions given in the following are not affected significantly by small changes in the molecular and adsorption geometry. The structures of the molecule junction are shown in Figs. 1 and 2. The calculation is performed using a modified version of GAUSSIAN98.18,19,60

III. DEVICE AT EQUILIBRIUM

The problem for device at equilibrium is a generalization of the familiar chemisorption problem in surface science since two metallic surfaces are involved. For a molecular orbital to be turned into an effective conduction channel of the metal-molecule-metal junction (within the coherent transport regime), it needs to couple to both electrode states and its energy must lie within the energy window determined by the bias voltage and the thermal broadening through the electrodes Fermi distribution. Both aspects are affected by the molecular adsorption, which may well be more significant than the subsequent application of the bias voltage, as detailed in subsequent sections.

FIG. 1. (Color online) Atomic geometry of the gold-PDT-gold junction. Six gold atoms closest to the end sulfur atoms on each electrode are included into the “extended molecule.”

FIG. 2. (Color online) Atomic geometry of the gold-BPD-gold junction. Six gold atoms closest to the end sulfur atoms on each electrode are included into the “extended molecule.”
molecules can be viewed as “heterostructures” composed of the end sulfur atoms and the benzene rings. Due to the non-coplanar geometry of the two benzenes in BPD molecule (the torsion angle is 37°), the orbital overlap between the corresponding π electrons is weak. Our analysis of the electrical transport through the two molecules will be based on the electrical response of these chemical units.

B. Charge transfer and electrostatic potential change in the molecular junction

The adsorption-induced charge transfer across the metal-molecule interface is the central quantity for the device at equilibrium since the linear-response transport probes the equilibrium charge distribution of the molecular junction. The perturbation introduced by the metal-molecule coupling is largely a localized interaction. The corresponding charge-transfer process is determined by the interfacial chemistry and can be understood qualitatively from the local bonding analysis across the metal-molecule interface as in the chemisorption problem.18,41

Due to the identical end group/bonding configuration across the metal-molecule interface and similar charge distribution of the frontier molecular states, both the magnitude and the spatial distribution of the transferred charge for the two molecules are quite similar. This is illustrated in Figs. 5, 6, where we plotted the difference between the self-consistent charge distribution in the gold-molecule-gold junction and the charge distribution in the isolated molecule plus the charge distribution of the isolated bimetallic junction. For clarity and to aid visualization, we have plotted both the regions where charge accumulation and depletion occur and the spatial distribution of the transferred charge as a function of position in the xy plane after integrating over the z axis.

This is clearly seen for the BPD molecule where the charge perturbation induced by the two metal-molecule contacts decays into the interior of the molecule without effectively interfering with each other (Fig. 6). Note this is not necessarily due to the noncoplanar geometry. The decay of charge perturbation is already obvious for the PDT while for BPD it becomes negligible before reaching the interbenzene bonding region. The number of electrons increases in the sulfur-gold bonding region due to the rehybridization of the sulfur \( P_z \) orbital in forming gold-sulfur bond and the transfer of charge from gold atom to sulfur atom due to electronegativity difference. Electron density also increases in the neighbor

![Image](54x534 to 294x733)

![Image](54x86 to 294x284)

![Image](318x537 to 558x733)

FIG. 3. (Color online) Orbital shape of the HOMO-1, HOMO, LUMO, and LUMO+1 states of PDT.

FIG. 4. Orbital shape of the HOMO-1, HOMO, LUMO, and LUMO+1 states of BPD.

![Image](115406-6)
carbon $P_z$ orbital since the HOMO level has large weights on both the sulfur and carbon $P_z$ orbitals. The electron density decreases in the sulfur-carbon $\sigma$-bonding region, the sulfur $P_x$ orbitals and also the gold $s$ orbitals. This is because the formation of surface gold-sulfur bond involves charges originally residing in the sulfur $P_x$ and gold $s$ orbitals thus weakening the bonding between sulfur and carbon. The direction of charge transfer is from the gold electrodes to the molecules.

Accompanying the charge transfer across the gold-molecule interface, the electrostatic potential also changes. The difference of the electrostatic potential in the junction and the electrostatic potential in the isolated molecule plus that in the isolated bimetallic junction gives the potential perturbation due to the formation of the contact. A cross-sectional view of the change in the electrostatic potential in the $xy$ plane as defined by the benzene ring (the left benzene ring for the BPD molecule) is plotted in Figs. 7 and 8. The net transfer of electrons into the molecule increases the electrostatic potential inside the molecule creating a potential barrier between the metal surface and the end sulfur atom. There is also a potential well between the sulfur atom and the benzene ring because of the decrease of electron density in the sulfur-carbon bonding region. Although the pattern of charge transfer at the metal-molecule interface is similar for the two molecules, the long-range electrostatic potential perturbation is quite different. For the BPD molecule, the electrostatic potential profile inside the two benzene rings becomes quite complicated which creates additional barrier for the electron motion within the molecule core. Due to the noncoplanar geometry, the barrier for injection from the right metal into the right half of the molecule is larger than that from the left metal to the left half (the right benzene ring gives a slightly smaller orbital overlap with the right electrode). Since the probability of electron tunneling through a potential barrier is sensitive to its shape, the charge-transfer induced potential change will have a profound influence on the electron transmission through the metal-molecule-metal junction. The presence of the potential barrier at the interface (and also in the molecule core for BPD) will affect the charge redistribution within the molecule when an additional field is applied, since it impedes the flow of electrons across the metal-molecule-metal junction. This will be discussed in the next section.
C. Contact-induced modification of molecular states, band lineup, and conductance of the metal-molecule-metal junction

The coupling between the gold electrodes and the molecule (reflected in the self-energy operator of the electrodes) and the induced potential change in the molecule (reflected in the self-consistent molecular Fock matrix) modify both the charge distribution and the energy of the molecular states relative to the metal Fermi level. They also broaden the discrete molecular electronic spectrum into a quasicontinuous one. These effects can be analyzed through the local density of states, the transmission coefficient and their projection onto the individual molecular orbitals.

The transmission versus energy ($T$-$E$) and the projected DOS (PDOS) corresponding to the five frontier molecular states of the two molecules (LUMO+1, LUMO, HOMO, HOMO-1, and HOMO-2) closest to the Fermi-level for spin-up electrons are shown in Figs. 9 and 10. The molecules studied here contain an even number of electrons and the spin-up and spin-down channels show identical characteristics. For other molecules in contact with ferromagnetic electrodes, the spin-resolved analysis is essential for understanding the transport characteristics.

From both the transmission versus energy curve and the projected DOS curve, we find the Fermi level lies closer to the HOMO state than to the LUMO state for both molecules. Comparing the peak position in the PDOS plot with the energy levels of the isolated molecule, we find that the contact with the metallic electrodes significantly shifts the energy levels of the frontier molecular states. The change is found to be larger for the occupied states than for the unoccupied states since the unoccupied states are benzene based (which also leads to sharper peaks in the PDOS plot).

The contact with the electrodes also modifies the charge distribution of the molecular states. This is illustrated by examining the LDOS at energies corresponding to the peak positions of the PDOS of the HOMO and LUMO for both molecules in Figs. 11 and 12, where we show both the shape and the spatial distribution of the surface-perturbed molecular states. The spatial distribution is obtained by integrating the three-dimensional (3D) LDOS with respect to the $z$ axis and plotted as a function of position in the $xy$ plane. The perturbation of the molecular states due to the coupling to the electrodes is different for the two molecules. In general, the surface-induced change in the charge distribution associated with the molecular states correlates closely with the change in the electrostatic potential. For the PDT molecule, the large increase of the electrostatic potential in the middle of the benzene rings pushes the electrons located on the carbon atoms to the peripheral hydrogen atoms for both the HOMO and the LUMO states (Fig. 11). The LUMO level remains highly localized giving rise to sharp peak in both PDOS and $T$-$E$ plots. For the BPD molecule, electrons also move from the right benzene to the left benzene for both the HOMO and LUMO states due to the difference in potential.
arising from the difference in local geometries. Similar analysis applies to other molecular states.

The peak positions in the PDOS plots of the HOMO and LUMO states align closely with the two peak positions in the $T-E$ plot around the Fermi level, corresponding to the onset of resonant transmission. By projecting the total transmission coefficient onto the individual molecular orbitals, we find the first transmission peak above $E_F$ at $E = 2.45 \text{ eV}$ arises mainly from the nearly degenerate LUMO and LUMO1 states. The first transmission peak below $E_F$ at $E = 6.5 \text{ eV}$ instead arises mainly from the HOMO state. In addition to the transmission peak at the HOMO and LUMO states, there is also a transmission peak in the HOMO-LUMO gap of the PDT molecule at energy $E = 3.6 \text{ eV}$ (Fig. 9). This peak corresponds to transmission through metal-induced gap states (MIGS) (Refs. 61–64) due to the hybridization of metal surface states with the occupied molecular states, which is significant for such a short molecule as PDT. The projected transmission analysis shows contribution coming mainly from the HOMO and also other occupied molecular states. The nature of the MIGS state is most clearly seen in the corresponding LDOS plot (Fig. 13), which shows similar charge distribution to the HOMO state. This is the case for both the LDOS and the transmission coefficient throughout the HOMO-LUMO gap region including that at the Fermi level. For such a short molecule as PDT, the transmission through the metal-induced gap states in the HOMO-LUMO gap is significant. A similar situation occurs also for the BPD molecule except that the transmission through the HOMO-LUMO gap of the BPD molecule is much reduced (Fig. 10). The molecule is longer and the orbital overlap with the right electrode states is weaker, so the transmission probability in the gap is much smaller.

The magnitude of the transmission coefficient at the Fermi level determines the zero-bias conductance at low temperature. We find a conductance of 4.8 and 1.4 $\mu \text{S}$ for the PDT and BPD molecules. Since the length of the molecules are 6.4 and 10.7 Å, respectively, the resistance is not proportional to the conjugation length, as expected for tunneling transport.

IV. DEVICE OUT OF EQUILIBRIUM

A. Current-voltage and conductance-voltage characteristics

The current-voltage ($I-V$) and differential conductance-voltage ($dI/dV-V$ or $G-V$) characteristics are calculated for the two molecules using the method described in Sec. II in the bias range from $-4$ to 4 $\text{V}$ and plotted in Figs. 14 and 15. Due to the symmetric device structure, the current-voltage and conductance-voltage characteristics for both molecules are nearly symmetric with respect to bias polarity. In the low bias regime, current changes approximately linearly with the bias voltage for both molecules, corresponding to tunneling transport in the HOMO-LUMO gap. Both tun-
neling and thermionic emission contribution to the total current are shown. As expected, for tunneling transport through a large and thin barrier, the thermionic emission contribution to the current is negligible even at low bias shown in the insets. Since the variation of the thermionic emission contribution with bias voltage is small in the coherent transport regime, this further reduces its contribution at high bias. Since this is the only temperature dependence in the coherent transport model, we expect the temperature dependence of the coherent current transport through the two molecules to be weak ignoring any disorder effects. Within the coherent transport model, the thermionic emission and, correspondingly, the temperature dependence of the current transport can be important only if the barrier for electron transmission is small and/or thick.

FIG. 14. $I$-$V$ (upper figure) and $G$-$V$ (lower figure) characteristics of the gold-PDT-gold device. The inset in the $I$-$V$ plot gives the magnified view at low bias. The dotted line in the $G$-$V$ plot is obtained assuming the transmission-energy relation to be bias independent.

For comparison, we have also plotted the conductance-voltage characteristics obtained using the equilibrium transmission coefficient, i.e., replacing $T(E,V)$ in Eq. (12) with $T(E,V=0)$. Since the gold surface density of states are approximately symmetric with respect to the Fermi level (the gold surface band around the Fermi level is due primarily to the $sp$ electrons), the difference between the $G$-$V$ characteristics thus obtained and the self-consistent $G$-$V$ characteristics reflects the effect of the bias-induced modification of molecular states.

For both molecules, only the low-bias conductance-voltage characteristics (before reaching the first conductance peak) can be reasonably well reproduced by the equilibrium transmission characteristics. The deviation in both the magnitude and the peak position of the conductance becomes significant at large bias, there are also more conductance peaks than would be obtained from the equilibrium transmission characteristics. So any attempt to predicting the nonlinear transport characteristics from the equilibrium transmission characteristics combined with an assumption about the voltage drop will lead to significant error. The effect of the bias-induced modification of molecular states is also obvious from looking at the shift of the frontier molecular levels by the applied voltage, as shown in Fig. 16. The molecular levels plotted are obtained by diagonalizing the molecular part of the self-consistent Fock matrices at each bias voltage, i.e., the submatrix of $H_{MM}$ containing only the molecule itself [since the molecular levels thus obtained do not include the effect of self-energy induced shift, their values don’t match the peaks in the PDOS or $T(E,V)$ plot shown later]. The molecular levels are nearly constant at low voltages, but begin to shift before reaching the first conductance peak. The voltage at which the shift occurs corresponds to the voltage where major deviation in the $G$-$V$ characteristics occurs.

FIG. 15. $I$-$V$ (upper figure) and $G$-$V$ (lower figure) characteristics of the gold-BPD-gold device as in Fig. 14.

FIG. 16. Bias-induced modification of molecular levels at gold-PDT-gold junction (left figure) and gold-BPD-gold junction (right figure). We have also shown the position of the equilibrium Fermi level $E_F$ and the electrochemical potential of the two electrode $\mu_{L,R}$ in the plot.
An important question in current transport through molecules is which molecular states are responsible for the observed conductance peak. From the position of the plotted molecular levels [and also from the $T(E,V)$ plots shown later], we expect that for both molecules, the peaks in the conductance are due to the occupied molecular levels, in disagreement with previous calculation where a jellium model of the electrode is used.$^{21,22}$ We believe this is because the jellium model underestimates the metal work function which effectively pushes the HOMO level down relative to the metal Fermi level.$^{18}$ The shifts in the individual molecular levels are not identical in either direction or magnitude, so a rigid shift in energy levels as occurring in a planar metal-semiconductor contact does not apply here. Instead the shift of the individual molecular states will depend on the detailed charge and potential distributions. For the two molecules considered here, there is an effective reduction in the HOMO-LUMO gap as bias increases (Fig. 16).

### B. Charge response and voltage drop

The charge response of the molecule to the applied electrical field is reflected in both the net charge injection into the molecule and the charge redistribution inside the molecule. For PDT molecule, we find there is only slight additional charge injection into the molecule as we apply the bias voltage. For BPD molecules, the net charge injection becomes important only when we go to high bias ($>2.5$ eV). The charge injection under nonzero bias voltage is determined by the balance of charge injection and extraction at the source-molecule and drain-molecule contacts. Since for the PDT molecule the contact geometries are identical and the gold surface density of states are approximately symmetric with respect to the Fermi levels, little net charge accumulation will be induced by the applied bias voltages. For the BPD molecule, the two rings are noncoplanar, but due to the largely localized nature of the charge injection process, the difference in the two contact becomes non-negligible only at high bias voltages. In addition to the total net charge in the molecule, we can also calculate the nonequilibrium occupation of the individual orbitals from the nonequilibrium density matrix [Eq. (6)] as a function of the bias voltage (Fig. 17). We find the change in the electron occupation is fractional and small, with the maximum being $\leq 0.2$. The electron occupation of the molecular orbital is fractional due to the broadening of the molecular level by the coupling to the contact. The difference in the voltage dependence of the occupation of the four molecular states is due to the difference in the voltage dependence of their energies and their different broadening. Note the change in the electron occupation of the molecular states is rather gradual, far less than the unit change implied by electron oxidization or reduction.

Although the net charge injection due to applied voltage is negligible, there can be significant charge redistribution within the molecule. This calls for closer investigation into the spatial distribution of the charge and potential distribution within the molecule as a function of applied voltage.$^{65}$ Samples of the spatial distributions of the transferred charge and the electrostatic potential drop for both molecules at bias voltage of $3.0$ V are shown in Fig. 18. Similar charge and potential distributions are obtained for all bias voltages. The spatial distribution of charge transfer is obtained by integrating the difference in electron density at finite and zero biases along the $z$ axis and plotted as a function of position in the $xy$ plane (defined by the left benzene ring). The potential drop is obtained by evaluating the difference between the electrostatic potential at finite and zero biases, which obeys the boundary condition of approaching $+V/2$ ($-V/2$) at the left (right) electrode. The molecules exhibit different conductance at different voltages, but the calculated charge and potential distributions show similar patterns and do not depend on whether the molecules are in low or high conductance state. The reason is as follows: The charge and potential

FIG. 17. Nonequilibrium occupation of molecular orbitals as a function of voltage for the PDT (left figure) and BPD (right figure) molecules in the molecular junction. Here we show the electron occupation of the HOMO-1, HOMO, LUMO, and LUMO+1 states.

FIG. 18. (Color online) Spatial distribution of charge transfer and potential drop at the gold-PDT-gold and gold-BPD-gold contacts for bias voltage of $3.0$ V.
response of the molecular junction is determined by the total electron population. But to be in high conductance state, one molecular orbital needs to align with one of the metal Fermi levels. As it moves away from alignment, the change in the electron population is gradual (Fig. 17), in contrast with the change in conductance. Given the net charge injected into the molecule, the determination of the electrostatic charge and potential response of the molecule in contact with the two electrodes will be equivalent to that of an isolated charged molecule under the same boundary conditions of charge and potential.

The nature of the charge redistribution can be understood readily by partitioning the molecules into the atomic groups, i.e., the benzene rings and the end sulfur atoms. As bias voltage increases, electrons move from the source-side carbon and sulfur to the drain-side carbon and sulfur. This is due to the fact that the \( \pi \) electrons in the carbon \( P_x \) orbitals can move freely under the applied electric field. This flow of \( \pi \) electrons is impeded at the molecule-drain contact because the presence of potential barrier there, which inhibits the charge flow into the drain electrode. Similar considerations apply to the molecule-source contact. This leads to the creation of two resistivity dipoles at the metal-molecule interface, i.e., the accumulation of electrons on the injecting side and the depletion of electrons on the extracting side of the potential barrier. For the BPD molecule, where the two benzene rings are noncoplanar, the charge response of the two benzene rings show identical behavior and are similar to the benzene ring in the PDT molecule. The weak orbital overlap between the two benzene rings disrupts the flow of \( \pi \) electrons across the interbenzene bonding region, which creates another potential barrier with corresponding resistivity dipole and partially insulates the two benzene rings from each other.

The spatial variation of the current-induced electron redistribution could also have a significant effect on the structural stability of the molecule under high bias. As shown in Fig. 18, applying bias voltage increases the electron density in the sulfur-carbon bond at the source-molecule contact but decreases the electron density in the sulfur-carbon bond at the drain-molecule contact. According to Hellman-Feynman theorem,\(^{66}\) this would lead to stronger attractive forces and consequently shorter sulfur-carbon bond at the source-molecule contact but weaker forces and longer sulfur-carbon bond at the drain-molecule contact. For the BPD molecule, there is also a shift of electron density in the carbon-carbon bond connecting the two benzene rings which may affect the inter-ring spacing. Since the magnitude of the electron redistribution increases with the bias voltage, we expect this bias-induced modification of structural change will have stronger effect at high bias. The problem of current-induced conformational change is the molecular analog of the more familiar electromigration problem in metallic systems.\(^{67}\) Although this problem has been treated recently by several groups,\(^{115406-12,22,68}\) we feel that much needs to be done before a satisfactory theory emerges.

The resistivity dipole is a well known concept in mesoscopic electron transport\(^{47}\) and is common in inhomogeneous transport media where their presence in the vicinity of local scattering center helps to overcome the barrier for transport and ensure current continuity. This can lead to a nonlinear transport effect due to the strong spatial variations in local carrier density and transport field. Such nonlinear transport characteristics induced by the device charge and potential inhomogeneity are a hallmark of band “engineering” through mesoscopic semiconductor heterostructures.\(^{69}\) Molecular junctions are an analog of the mesoscopic “heterostructures,” since the choice of the component functional and structural groups allows the possibility of “engineering” charge and potential inhomogeneity within a single molecule, suggesting the possibility of device “engineering” through molecular design and permitting the extension of device concepts to the molecular scale. This effect can be further elucidated by examining the potential response of the two molecules.

The mobile \( \pi \) electrons of the benzene ring effectively screen the applied field, leading to rather flat electrostatic potential drop across the benzene rings. The electrostatic potential drops rapidly in the molecule-electrode contact region, and becomes flat again as it approaches the boundary of the electrode where strong screening of the applied electric field occurs. For the PDT molecule, the majority of the voltage therefore drops across the molecule-electrode contact region.\(^{20,65}\) Since the unoccupied molecular states of the PDT molecule are located mainly on the benzene ring where the screened electric field is small, their energy levels do not change much as bias voltage increases. The HOMO-1 state shows stronger voltage dependence than the HOMO state because it is end-sulfur based where the potential variation is the strongest. For the BPD molecule, although the \( \pi \) electrons of each benzene ring can screen the applied field effectively, the potential barrier between the two benzene rings prevents the electron from flowing freely across, leading to significant voltage drop across the molecule core. As a result, there exists strong spatial variation of the electrostatic potential across the molecule core in addition to the metal-molecule contact. Since the four frontier molecular states of the BPD molecule are either sulfur based or have charge distributed across the entire molecule core, they all show clear voltage dependence. An empirical model of rigid shift of the molecular level relative to the Fermi levels of the two electrodes has often been assumed,\(^{6}\) with the proportion of the voltage drop being associated with the contact geometry. It is clear that this model can only be utilized as a crude check of the device characteristics, since it neglects the possible voltage drop across the molecules and the different effects this may have on different molecular states.

C. Bias-induced modification of molecular states and transmission characteristics

The molecular charge and potential response to the applied electrical field will affect the transport characteristics in two ways: (1) it shifts the molecular levels relative to the Fermi levels of the two electrodes and, (2) it modifies the charge distribution of the molecular states and therefore their capability for carrying current. The bias-induced modification of molecular states can be analyzed by examining the
local density of states and its projection onto the individual molecular orbitals at finite bias voltages.

A snapshot of the bias dependence of the transmission characteristics and the projected DOS corresponding to the five frontier molecular orbitals is shown for the PDT molecule at bias voltages of 1.6, 3.0, and 4.0 V (Fig. 19) and for the BPD molecule at bias voltages of 1.4, 3.0, and 4.0 V (Fig. 21) to illustrate their voltage dependence. We have also shown for PDT molecule the LDOS at energies corresponding to the peak position in the PDOS plots of the HOMO and LUMO states at bias voltage of 3.8 V (Fig. 20).

For the PDT molecule changing from zero bias (Fig. 9) to $V=1.6$ V (Fig. 19), both the peak positions in the PDOS and the electron distribution associated with the LUMO states do not change much. The HOMO energy level also does not change much, but there is a shift in charge distribution from the right end sulfur atom to the right carbon atom (not shown here). The energy of the HOMO-1 state increases with bias, leading to a decrease in the energy spacing between the HOMO and HOMO-1 states. At 1.6 V, the transmission versus energy of the PDT molecules reaches a peak at energy corresponding to the drain Fermi level at $E_F-\epsilon/2$, giving rise to the first peak in the conductance. As we increase the bias voltage further from $V=1.6$ to 3.0 V (Fig. 19), the energy levels of the HOMO and HOMO-1 states shift gradually toward the equilibrium Fermi level $E_F$, increasing the transmission coefficient there. As we further increase the bias to $V=3.8$ V (Fig. 20), the energy of the LUMO continues to decrease, but the energies of both the HOMO and HOMO-1 states move up to the metal Fermi level $E_F$, increasing the transmission coefficient there. As we further increase the bias to $V=3.8$ V, the charge distribution (the LDOS) at energies corresponding to the peak position of the LUMO state also changes, developing large weight on the end sulfur $P_Z$ and the peripheral hydrogen atoms (Fig. 20). Because the HOMO and HOMO-1 states move up to the metal Fermi level as the bias increases, the current increases more gradually than would be obtained if the bias-induced modification of molecular states is neglected (Fig. 14).

For the BPD molecule, the first peak in conductance is reached at $V=1.4$ V (Figs. 15 and 21). From zero bias to 1.4 V, the energies of the LUMO and HOMO-1 states decrease and there is a shift of charge from the right benzene to the left benzene ring. The energy of the HOMO states increases, and the shift of charge distribution is from the left benzene ring to the right benzene ring (not shown here). Compared to the PDT molecule, the bias-induced modification is stronger despite the longer molecule length, due to the stronger spatial variation of the potential profile. As we increase the bias to $V=3.0$ V (Fig. 21), the energy of the LUMO continues to decrease, but the energies of both the HOMO and HOMO-1...
states increase toward the metal Fermi level $E_F$. The transmission coefficient at both energies decreases significantly since the electrons are now more localized on the right ring. A notable change is that a second peak in the PDOS of the HOMO state develops at $E = -7.0$ eV. Examining the corresponding LDOS shows similar charge distribution to that of the HOMO-2 state with energy of $-7.15$ eV which has charge distribution on both benzene rings (not shown here) and correspondingly large transmission probability. Increasing the bias to 4.0 V (Fig. 21) further decreases the energy of the LUMO state and increase the energies of the HOMO and HOMO-1 states. At $V = 3.8$ V, the electrons shift from the right benzene ring back to the left for both the HOMO and HOMO-1 states (not shown) increasing the transmission coefficients there. Since the electrochemical potential of the left (right) electrode approaches alignment with the HOMO-2 and also the LUMO state, there is a rapid increase in the conductance as we increase the bias further toward $V = 4.0$ V (Fig. 15).

**V. DISCUSSION AND CONCLUSION**

**A. Tunneling or single-electron tunneling?**

In this work we have considered electron-electron interaction in the molecule within a self-consistent-field framework through the use of density-functional theory. Tunneling through the molecular junction is therefore a single-step coherent process equivalent to that of a noninteracting particle tunneling through an effective potential barrier determined through the self-consistent procedure detailed in Sec. II, which can be understood qualitatively through the energy mismatch between the injected electrons from the electrodes and the molecular eigenstates. This is in contrast to the phenomena of single-electron tunneling through metallic or semiconducting quantum dots separated from the electrodes by two insulating gaps, where the tunneling is a correlated two-step process mediated by the electron transfer onto the quantum dots. Such quantum dots are often characterized as "artificial molecules." The difference between these "artificial molecules" and the molecules considered in this work lies in their different coupling with the electrodes and the degree of delocalization of the electron states within the metal-molecule-metal junctions. For the devices considered here, the molecule couples strongly to at least one of the electrodes through the end group and the metallic states penetrate sufficiently deep inside the molecule (MIGS). The Coulomb blockade of tunneling is therefore washed out by quantum fluctuations of the charge on the electrodes, similar to the situation of electron tunneling through ultrasmall quantum dots with low-impedance electromagnetic environments.

This is no longer true if the molecule is physisorbed onto both electrodes and the electron states of the molecule can be considered as localized, where Coulomb Blockade phenomena has indeed been observed. A different system that combines tunneling through molecular junction with single-electron tunneling phenomena is realized using molecular-assembled nanoparticles, where the nanoparticle is connected to the electrodes through molecular bridges. Here the tunnel barrier in the conventional single-electron devices is replaced by the molecular tunnel junction, and the theory of electron transport through molecular junction described in this work can be combined with the theory of charging dynamics on the nanoparticle to provide a microscopic understanding of transport through such metal-molecule composite system. Interestingly, the scaling limit of such molecular-assembled nanoparticle system will correspond to a metal complex where a single metal atom is embedded within the molecule and connected to the electrodes through the molecular bridges. Such systems have been realized recently using transition-metal complex, where both Coulomb blockade and Kondo effect have been successfully demonstrated. It will be of great interest to extend the theory presented here to incorporate both the strong electron-electron interaction and the discrete electron states on the metal atoms such that a single theory can be used to describe all the transport regimes involved in single-molecule devices. This is a challenging topic currently under investigation.

**B. Electron transport or hole transport?**

A common practice in the literature on molecular electronics is to characterize the molecular transport as "electron transport" if the conduction is mediated by tunneling through the unoccupied molecular states, or as "hole transport" if the conduction is mediated by tunneling through the occupied molecular states, following the terminology commonly used in semiconductor/organic device and electron transfer research. Here it is important to recognize their differences. For bulk semiconductor devices, the concepts of "electron" or "hole" are associated with introducing shallow-impurity (dopant) atoms into the ideal lattice structure, which introduces electron into the (unoccupied) conduction band or removes electrons from the (filled) valence band. The "electron" or "hole" thus introduced are mobile charge carriers with delocalized wave functions. The system as a whole remains charge neutral, since the charges associated with these carriers are compensated by the impurity ions left behind. Therefore, the type of charge transport depends only on the type and amount of dopant atoms introduced, which is an equilibrium property. By contrast, for organic devices, the system is often not doped. Charge transport occurs by injecting charge carriers into the system from the electrodes. The type of transport depends on the charging state of the molecule and the nonequilibrium injection of charge carriers into the neutral system. For both cases, the type of transport is determined by the change in the occupation of electron states through doping or contact injection, independent of the nature of charge transport itself (band transport or polaron hopping).

The situation for coherent molecular transport is quite different. For the symmetric molecular devices considered here, both the total number of electrons (the charging state of the molecule) and the occupation of the individual molecular orbitals change little with the applied bias. Although a fractional amount of charge is transferred from the gold to the molecule upon electrode contact, the transferred charge is localized in the interfacial region and characterizes the
changes in the interfacial bond. The change in the occupation of molecular states is fractional and gradual, either upon contact to the electrodes at equilibrium or upon application of a finite bias voltage out of equilibrium (Fig. 17). Due to the quantum mechanical nature of the coherent tunneling transport, we cannot characterize the tunneling electron as being physically injected into the molecule and subsequently extracted out. Therefore, it is more appropriate to characterize molecular transport through the relevant resonant molecular states without associating it with specific transport types.

C. Single molecule versus molecular monolayer

The focus of the present series of work is on current transport through a single molecule in contact with two metallic electrodes. This corresponds closely to the molecular transport measurements using atomic-size break junctions, where either one or several molecules are probed. However, many molecular transport experiments are performed on molecular monolayers where thousands or tens of thousands of molecules are probed by the contacts to the electrodes. Such experiments with monolayer configuration present a quite different situation from the single molecule configuration considered here. In addition to the additional complexity of intermolecular interactions within the monolayer, the most important difference lies in the interface electrostatics. Note that the same boundary condition for the electrostatic potential across the molecular junction applies to both the single molecule configuration and the monolayer configuration: deep inside the electrodes they approach the bulk value, which can be shifted rigidly with respect to each other by the applied bias voltage. For the single molecule configuration, the transfer of charge across the metal-molecule interface is confined in a small region, whose contribution to the electrostatic potential decays to zero in regions far away from the molecule. But for the monolayer configuration, the electrostatic potential in regions far away from the molecule is the superposition of contributions from the transferred charge on a large number of molecules. To satisfy the same boundary condition of the electrostatic potential, the charge transfer per molecule in a molecular monolayer can be orders of magnitude smaller than that in the single molecule considered here. This is the situation often met in organic electronics, where a monolayer of self-assembled molecules is used to modify the work function of the metallic contacts. Similar problems have also been considered in the electron transport through metal-carbon nanotube interfaces. Here it is important to recognize the different physics of the metal-molecule interface in single-molecule devices and monolayer devices, since it may have profound effect on the device functionalities achievable using molecular materials.

D. Comparison with experiments

Although the present work focuses on the conceptual understanding of fundamental electronic processes involved in the operation of any single-molecule device rather than on explaining specific experiment, it is appropriate here to comment on the relation between the present work and the current experimental activities in molecular electronics. Perhaps the single most important discrepancy between the present calculation and experiment is the magnitude of current and conductance. This is especially true for the PDT molecule, for which the present calculation gives result two orders of magnitude larger than experiment. Other theoretical calculations using similar formalism as the present work, as well as the plane-wave based work of Di Ventra, Pantelides, and Lang have given similar results in terms of the magnitude of current and conductance. The situation is more optimistic for longer phenylene thiolate molecules (PDT molecule is the smallest of such molecules), where both experiment and theory give currents in the µA range.

Since the existing experiment on PDT molecule gives smaller conductance than the longer phenylene thiolate molecules, in contradiction to the expectation of decreasing molecular conductance with molecular length, we consider the following two factors as the likely cause of the discrepancy between theory and experiment: (1) atomic geometry of the metal-molecule interface and (2) the use of density-functional theory in computing molecular energy levels. Within the current theoretical model, the magnitude of the current/conductance is determined by the lineup of molecular level relative to the metal Fermi level as well as the broadening of the frontier molecular states, both of which are sensitive to the details of the metal-molecule interaction, especially for the small PDT molecule. The use of density-functional theory in describing the molecular electronic structure, on the other hand, is an approximation to the more rigorous quasi-particle theory and its non-equilibrium extensions, whose error generally increases with decreasing molecule size. This is reflected in the relatively large difference in the molecular levels of PDT (0.5 eV or larger) computed using different parameterization scheme within DFT. Although other possibilities including inter-molecular interaction exist, it is likely that much better agreement with experiment can be achieved using carefully characterized interface models and improved electronic structure theories.

E. Conclusion

We have presented a first-principles-based microscopic study of current transport through individual molecules. The real-space formulation allows us to establish a clear connection between the transport characteristics and the molecular electronic structure perturbed by the metal-molecule coupling and the applied bias voltage. By separating the problem into equilibrium and nonequilibrium situations, we identify the critical electronic processes for understanding the linear and nonlinear transport characteristics. At equilibrium, the critical problem is the charge transfer process upon formation of the metal-molecule-metal contact, which modifies the molecular states and determines the energy level lineup relative to the metal Fermi level. This is mainly an interface-related process and can be controlled by controlling the contact. Out of equilibrium, the central problem is the molecular
charge response and the consequent molecular screening of the applied electric field, which depends on both the molecule core and the nature of the metal-molecule contact and can be understood by viewing the molecules as “heterostructures” of chemically well-defined local groups and analyzing their electrical response to the applied bias voltage.92

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For carbon and sulfur, we use the pseudopotential and the corresponding polarized split valence basis sets of W.J. Stevens, H. Basch, and M. Krauss, J. Chem. Phys. 81, 6026 (1984); for gold, we use the pseudopotential and the valence basis sets of P.J. Hay and W.R. Wadt, ibid. 82, 270 (1985).

For the gold atoms lying on top of the semi-infinite substrate (e.g., describing the atomic-scale structure of the surface), we use the standard double-zeta basis set as described by P.J. Hay and W.R. Wadt [J. Chem. Phys. 82, 270 (1985)]. For the gold atoms on the surface of the semi-infinite substrate, we follow the standard convention in surface and solid state electronic structure calculation using molecular Gaussian-type orbital basis sets to construct a minimum valence basis set by removing the most diffuse Gaussian primitive. A minimum-valence basis set may also be formed including the most diffuse component [H. Basch (unpublished)], however, we find this leads to convergence problem and overcharging of the “extended molecule” with charge overflow onto the substrate atoms without affecting the molecule significantly. For further information regarding the basis set usage for surface and bulk calculations, see the series of work related to the CRYSTAL95 package (V. Saunders, R. Dove, C. Roetti, M. Causa, N. Harrison, R. Orlando, and C.M. Zicovich-Wilson, University of Torino, Torino, 1998, e.g., Y. Noel, C.M. Zicovich-Wilson, B. Civaleri, Ph. D’Arco, and R. Dove, Phys. Rev. B 65, 014111 (2001); A. Kokaly and M. Causa, J. Phys.: Condens. Matter 11, 7463 (1999).


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81. A simple estimate can be given in the limit of an ideal (infinitesimal) two-dimensional molecular monolayer. We assume the molecule-metal distance is 3 Å and each molecule occupies a surface area of 10 Å² on average. Replacing the charge distribution of the two-dimensional monolayer by an uniform charge sheet, a charge transfer of 0.02 per molecule is enough to give an electrostatic potential drop of 2.5 V across the metal-monolayer junction.

82. D. Jans (private communication).


89. Since our emphasis in this work is in conceptual issues, we have not tried testing or optimizing the more technical aspects of the modeling work such as the choice of the exchange-correlation functionals and the optimum molecular basis sets. For example, the calculations reported in this work were performed using a quite restricted basis set for the metal atoms on the surface of the semi-infinite substrate. The metal atoms belonging to atomic-scale structures on top of the substrate and the molecule itself
are treated using much better basis sets as in standard molecular calculations. The description of the metallic substrate may not be adequate. And obtaining a better balance in the basis set description between the substrate atoms and the molecule is a difficult and important issue for further improving the accuracy of the modeling of molecular-scale devices within the NEGF formalism. Such refinement may be needed for obtaining quantitative agreement with specific transport measurement. In particular, the calculated charger transfer from the gold surface to sulfur may be different depending on the basis sets (plane waves or extended gaussian basis sets) as well as the surface models (semi-infinite crystal, cluster or supercell geometry) chosen.