Current-voltage characteristics of molecular conductors: two versus three terminal

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Abstract—This paper addresses the question of whether a “rigid molecule” (one which does not deform in an external field) used as the conducting channel in a standard three-terminal MOSFET configuration can offer any performance advantage relative to a standard silicon MOSFET. A self-consistent solution of coupled quantum transport and Poisson’s equations shows that even for extremely small channel lengths (about 1 nm), a “well-tempered” molecular FET demands much the same electrostatic considerations as a “well-tempered” conventional MOSFET. In other words, we show that just as in a conventional MOSFET, the gate oxide thickness needs to be much smaller than the channel length (length of the molecule) for the gate control to be effective. Furthermore, we show that a rigid molecule with metallic source and drain contacts has a temperature independent subthreshold slope much larger than 60 mV/decade, because the metal-induced gap states in the channel prevent it from turning off abruptly. However, this disadvantage can be overcome by using semiconductor contacts because of their band-limited nature.

Keywords—Molecular electronics, MOSFETs, electrostatic analysis, quantum transport, Non-equilibrium Green’s function (NEGF) formalism.

I. INTRODUCTION

MOLECULES are promising candidates as future electronic devices because of their small size, chemical tunability and self-assembly features. Several experimental molecular devices have recently been demonstrated (for a review of the experimental work see [1]). These include two terminal devices where the conductance of a molecule coupled to two contacts shows interesting features such as a conductance gap [2], asymmetry [3] and switching [4]. Molecular devices where a third terminal produces a negative differential resistance [5], or suppresses the two terminal current [6] have been theoretically studied, but most of the work on modeling the current-voltage (IV) characteristics of molecular conductors has focused on two-terminal devices (see, for example, [1], [7], [5], [8], [9] and references therein).

The purpose of this paper is to analyze a three-terminal molecular device assuming that the molecule behaves essentially like a rigid solid. Unlike solids, molecules are capable of deforming in an external field and it may be possible to take advantage of such conformational effects to design transistors with superior characteristics. However, in this paper we do not consider this possibility and simply address the question of whether a “rigid molecule” used as the conducting channel in a standard three-terminal MOSFET configuration can offer any performance advantage relative to a standard silicon MOSFET.

Although rigorous ab initio models are available in the literature [8], [10], [11], [12], they normally do not account for the three-terminal electrostatics that is central to the operation of transistors. For this reason we have used a simple model Hamiltonian whose parameters have been calibrated by comparing with ab initio models. We believe that a simple model Hamiltonian with rigorous electrostatics is preferable to an ab initio Hamiltonian with simplified electrostatics since the essential physics of a rigid molecular FET lies in its electrostatics.

The role of electrostatic considerations in the design of conventional silicon MOSFETs (with channel lengths ranging from 10 nm and above) is well understood. For the gate to have good control of the channel conductivity, the gate insulator thickness has to be much smaller than the channel length. Also, for a given channel length and gate insulator thickness, a double gated structure is superior to a single gated one, simply by virtue of having two gates as opposed to one. If a molecule is used as the channel in a standard three-terminal MOSFET configuration, the effective channel length is very small - about 1 nm. Would similar electrostatic considerations apply for such small channel lengths? In this paper we answer this question in the affirmative. Specifically we will show that:

- The only advantage gained by using a molecular conductor for an FET channel is due to the reduced dielectric constant of the molecular environment. To get good gate control with a single gate the gate oxide thickness needs to be less than 10% of the channel (molecule) length, whereas in conventional MOSFETs the gate oxide thickness needs to be less than 3% of the channel length [13]. With a double gated structure, the respective percentages are 60% and 20% [14].
- Relatively poor subthreshold characteristics (a temperature independent subthreshold slope much larger than 60 mV/decade) are obtained even with good gate control, if metallic contacts (like gold) are used, because the metal-induced gap states in the channel preclude it from turning off abruptly.
to doped silicon source and drain contacts, however, show a
off abruptly. Preliminary results with a molecule coupled
Hartree-Fock or the Density Functional theory may be used
is not included in this study.

Fig. 1

(a) Schematic of a Phenyl Dithiol molecule coupled to gold
source and drain contacts. A third (gate) terminal
modulates conductance of the molecule. The phenyl ring is
shown in the plane of the paper for clarity. In the actual
simulation the phenyl ring is perpendicular to the plane of
the paper, “facing” the gate electrode. (b) The molecule is
described by a Hamiltonian $H$ and a self-consistent
potential $U_{SC}$. The effect of the large contacts is
described using self-energy matrices $\Sigma_{1,2}$. Scattering
processes may be described using another self-energy matrix
$\Sigma_p$. The source and drain contacts are identified by their
respective Fermi levels $\mu_1$ and $\mu_2$. Given $H$, $U_{SC}$, $\Sigma_{1,2,p}$ and
$\mu_{1,2}$ the Non-Equilibrium Green’s Function (NEGF)
formalism has clear prescriptions to obtain the density
matrix from which the electron density and current may be
calculated. At equilibrium (zero drain bias) $\mu_1 = \mu_2 = E_f$,
where $E_f$ is the common equilibrium Fermi level of the
contact-molecule-contact system. When a drain bias $V_{DS}$ is
applied the source and drain Fermi levels separate by an
amount equal to $\nu q V_{DS}$ ($q$: electronic charge) and a current
flows. This non-equilibrium situation may be modeled by
self-consistently solving the coupled NEGF-Poisson’s
equations as shown in (c). The word “Poisson’s” is in quotes
as a reminder that more sophisticated theories like the
Hartree-Fock or the Density Functional theory may be used
to obtain $U_{SC}$.

A schematic figure of a molecule coupled to gold contacts
(source and drain) is shown in Fig. 1a. As an example we
use the Phenyl Dithiol (PDT) molecule which consists of
a phenyl ring with thiol (-SH) end groups. A gate terminal
modulates the conductance of the molecule. We use a
simple model Hamiltonian $H$ to describe the molecule
(Fig. 1b). The effect of the source and drain contacts is
taken into account using self-energy functions $\Sigma_1$ and $\Sigma_2$
[14]. Scattering processes may be described using another
self-energy matrix $\Sigma_p$. However, in this paper we focus on
coherent or ballistic transport ($\Sigma_p = 0$). The source and
drain contacts are identified with their respective Fermi levels
$\mu_1$ and $\mu_2$. Our simulation consists of iteratively solving
a set of coupled equations (Fig. 1c) - the Non-Equilibrium
Green’s Function (NEGF) formalism [16], [17] equations
for the density matrix $\rho$ and the Poisson’s equation for the
self-consistent potential $U_{SC}$. Given $H$, $U_{SC}$, $\Sigma_1$, $\Sigma_2$, $\mu_1$ and
$\mu_2$ the NEGF formalism has clear prescriptions to obtain
the density matrix $\rho$ from which the electron density
and the current may be calculated. Once the electron density
is calculated we solve the Poisson’s equation to obtain
the self-consistent potential $U_{SC}$. The solution procedure
thus consists of two iterative steps:

- **Step 1:** calculate $\rho$ given $U_{SC}$ using NEGF
- **Step 2:** calculate $U_{SC}$ given $\rho$ using Poisson’s equation

The above two steps are repeated till neither $U_{SC}$ nor $\rho$
changes from iteration to iteration. It is worth noting that
the self-consistent potential obtained by solving Poisson’s
equation (Eq. (1)) may be augmented by an appropriate
exchange-correlation potential that accounts for many elec-
tron effects using schemes like Hartree-Fock (HF) or Den-
sity Functional Theory (DFT) [18]. In this paper we do not
consider the exchange-correlation effects.

### II. Theory

A. Step 1: To obtain $\rho$ from $U_{SC}$

The central issue in non-equilibrium statistical mechanics is to
determine the density matrix $\rho$; once it is known, all
quantities of interest (electron density, current etc.) can

1 The authors are aware of one experimental claim (J.H. Schön et
al., Nature 413, page 713, 2001) reporting superior molecular FET
with a single gated geometry. This claim, however, has been strongly
questioned (see article by R.F. Service in Science 298, page 31, 2002).
Comparison of the simple $\pi$ orbital based model with an ab initio model (density functional theory with atomic orbital basis set) for the PDT molecule. The energy levels can be divided into two sets: occupied levels (analogous to the valence band) and unoccupied levels (analogous to the conduction band). The energy gap (analogous to the bandgap) is the energy difference between the highest occupied molecular orbital (HOMO) level (analogous to the top of the valence band) and the lowest unoccupied molecular orbital (LUMO) level (analogous to the bottom of the conduction band). The simple $\pi$ model agrees very well with the ab initio calculation in both the energy gap (middle) and HOMO and LUMO wavefunctions (left and right). The energy levels obtained from the simple model were equally shifted in energy so as to make the HOMO level coincide with the ab initio HOMO level.

be calculated. A good introductory discussion of the concept of density matrix may be found in [17]. To obtain the density matrix $\rho$ from the self-consistent potential $U_{SC}$ using the NEGF formalism, we need to know the Hamiltonian $H$, the contact self-energy matrices $\Sigma_{1,2}$ and the contact Fermi levels $\mu_{1,2}$. In this section we describe how we obtain these quantities, and then present a brief outline of the NEGF equations.

**Hamiltonian**: We use a simple basis consisting of one $p_z$ (or $\pi$) orbital on each carbon and sulfur atom. It is well known that the PDT molecule has $\pi$ conjugation - a cloud of $\pi$ electrons above and below the plane of the molecule that dictate the transport properties of the molecule [13]. The on-site energies of our $p_z$ orbitals correspond to the energies of valence atomic $p_z$ orbitals of sulfur and carbon (apart from a constant shift of all levels which is allowed as it does not affect the wavefunctions). The carbon-carbon interaction energy is 2.5 eV which is widely used to describe carbon nanotubes [2]. The sulfur-carbon coupling of 1.5 eV is empirically determined to obtain a good fit to the ab initio energy levels obtained using the commercially available quantum chemistry software Gaussian ‘98 [2] (Fig. 3).

Our model is very similar to the well established $p_z$ orbital based Hückel theory used by many quantum chemists. Although we use a simple model Hamiltonian to describe the molecule, we believe that the essential qualitative physics and chemistry of the molecule is captured. This is because both the molecular energy levels and the wavefunctions closely resemble those calculated from a much more sophisticated ab initio theory (Fig. 3).

**Self-energy**: Self-energy formally arises out of partitioning the molecule-contact system into a molecular subsystem and a contact subsystem. The contact self-energy $\Sigma$ is calculated knowing the contact surface Green’s function $g$ and the coupling between the molecule and contact $\tau$. For a molecule coupled to two contacts (source and drain) the molecular Green’s function at an energy $E$ is then written as [14] ($I$: identity matrix, $H$: molecular Hamiltonian, $U_{SC}$: self-consistent potential):

$$G = [E I - H - U_{SC} - \Sigma_1 - \Sigma_2]^{-1}$$  \hspace{1cm} (1)

where the contact self-energy matrices are

$$\Sigma_{1,2} = \tau_{1,2} g_{1,2} \tau_{1,2}^\dagger$$  \hspace{1cm} (2)

We model the gold FCC (111) contacts using one $s$-type orbital on each gold atom. The coupling matrix element between neighboring $s$ orbitals is taken to be $-4.3 \text{ eV}$ - this gives correct surface density of states (DOS) of 0.07 / (eV - atom) for the gold (111) surface [22]. The site energy for each $s$ orbital is assumed to be $-8.74 \text{ eV}$ in order to get the correct gold Fermi level of $-5.1 \text{ eV}$. The surface Green’s function $g$ is calculated using a recursive technique explained in detail in [23]. The contact-molecule coupling $\tau$ is determined by the geometry of the contact-molecule bond. It is believed [24] that when a thiol-terminated molecule like Phenyl Dithiol is brought close to a gold substrate, the sulfur bonds with three gold atoms arranged in an equilateral triangle. For a good contact extended Hückel theory predicts a coupling matrix element of about $2 \text{ eV}$ between the sulfur $p_z$ orbital and the three gold
s orbitals. However to simulate the bad contacts typically observed in experiments we reduce the coupling by a factor of five (this factor is also treated as a parameter, and our results do not change qualitatively for a range of values of this parameter).

Unlike the Hamiltonian, the self-energy matrices are non-Hermitian. The anti-Hermitian part of the self-energy, also known as the broadening function:

\[ \Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^\dagger) \]  

is related to the lifetime of an electron in a molecular eigenstate. Thus upon coupling to contacts, the molecular density of states (Fig. 2) looks like a set of broadened peaks.

**Where is the Fermi energy?** When a molecule is coupled to contacts there is some charge transfer between the molecule and the contacts, and the contact-molecule-contact system attains equilibrium with one Fermi level \( E_f \). A good question to ask is where \( E_f \) lies relative to the molecular energy levels. The answer is not clear yet, the position of \( E_f \) seems to depend on what contact model one uses. A jellium model for the contacts predicts that \( E_f \) is closer to the LUMO level for PDT whereas an extended Hückel theory based model predicts that \( E_f \) is closer to the HOMO level (see Fig. 2 and the related caption for a description of HOMO and LUMO levels). Our ab initio model seems to suggest that for gold contacts, \( E_f \) (\( \sim -5.1 \) eV) lies a few hundred millivolts above the PDT HOMO. In this paper we will use \( E_f = -5.1 \) eV and set the molecular HOMO level (obtained from the \( \pi \) model) equal to the ab initio HOMO level (\( \sim -5.4 \) eV) (see Figs. 2, 3). Once the location of the equilibrium Fermi energy \( E_f \) is known, we can obtain the source and drain Fermi levels \( \mu_1 \) and \( \mu_2 \) under non-equilibrium conditions (non-zero \( V_{DS} \)): \( \mu_1 = E_f \) and \( \mu_2 = E_f - qV_{DS} \).

**NEGF equations:** Given \( H, \Sigma_{1,2}, \) contact Fermi energies \( \mu_{1,2} \) and the self-consistent potential \( U_{SC} \), NEGF has clear prescriptions to obtain the density matrix \( \rho \). The density matrix can be expressed as an energy integral over the correlation function \(-iG^<(E)\), which can be viewed as an energy-resolved density matrix:

\[ \rho = \int dE [-iG^<(E)/2\pi] \]  

The correlation function is obtained from the Green’s function \( G \) (eq. 3) and the broadening functions \( \Gamma_{1,2} \) (eq. 3):

\[ -iG^< = G(f_1 \Gamma_1 + f_2 \Gamma_2)G^\dagger \]  

where \( f_{1,2}(E) \) are the Fermi functions with electrochemical potentials \( \mu_{1,2} \):

\[ f_{1,2}(E) = \left(1 + \exp \left[ \frac{E - \mu_{1,2}}{k_B T} \right] \right)^{-1} \]  

The density matrix so obtained can be used to calculate the electron density \( n(\vec{r}) \) in real space using the eigenvectors of the Hamiltonian \( \Psi_\alpha(\vec{r}) \) expressed in real space:

\[ n(\vec{r}) = \sum_{\alpha,\beta} \Psi_\alpha(\vec{r})\Psi_\beta^\dagger(\vec{r})\rho_{\alpha\beta} \]  

The total number of electrons \( N \) may be obtained from the density matrix as:

\[ N = \text{trace}(\rho) \]  

The density matrix may also be used to obtain the terminal current \( I \). For coherent transport, we can simplify the calculation of the current by using the transmission formalism where the transmission function \( \Gamma G^\dagger \) is used to calculate the terminal current:

\[ I = (2q/h) \int_{-\infty}^{\infty} dE T(E) (f_1(E) - f_2(E)) \]  

**B. Step 2: To obtain \( U_{SC} \) from \( \rho \)**

The Poisson’s equation relates the real space potential distribution \( U(\vec{r}) \) in a system to the charge density \( n(\vec{r}) \). We assume a nominal charge density \( n_0(\vec{r}) \) obtained by solving the NEGF equations with \( U(\vec{r}) = 0 \) (at \( V_{GS} = V_{DS} = 0 \)). The Poisson’s equation is then solved for the change in the charge density \( n(\vec{r}) - n_0(\vec{r}) \) from the nominal value \( n_0 \) :

\[ \nabla \cdot (\epsilon \nabla U(\vec{r})) = -q^2 (n(\vec{r}) - n_0(\vec{r})) \]  

The Poisson (or Hartree) potential \( U \) may be augmented by an appropriate exchange-correlation potential \( U_{xc} \). In this paper, we do not take into account the exchange-correlation effects \( U_{xc} = 0 \). We have two schemes to solve the Poisson’s equation: (1) simple Capacitance Model and (2) rigorous numerical solution over a 2D grid in real space.

**Capacitance Model:** We use a simplified picture of the molecule as a quantum dot with some nominal total charge \( N_0 \) (at \( V_{GS} = V_{DS} = 0 \)) and some average potential \( U \) arising because of the change \( N - N_0 \) in this nominal charge due to the applied bias. Thus \( U, N_0 \) and \( N \) are numbers and not matrices. The total charge \( N \) can be calculated from the NEGF density matrix using Eq. 3 \( U \) is the solution to the Poisson’s equation, and may be written as the sum of two terms: (1) A Laplace (or homogeneous) solution \( U_L \) with zero charge on the molecule but with applied bias and (2) A particular (or inhomogeneous) solution \( U_P \) with zero bias but with charge present on the molecule. Thus \( U = U_L + U_P \). \( U_L \) is easily written down in terms of the capacitative couplings \( C_{MS}, C_{MD} \) and \( C_{MG} \) of the molecule (Fig. 4) with the source, drain and gate respectively:

\[ U_L = \beta(-qV_{GS}) + \frac{1 - \beta}{2}(-qV_{DS}) \]  

where \( \beta \) the potential distribution corresponding to the nominal charge density (when no drain or gate bias is applied) is included in the calculation of the molecular Hamiltonian.
C is closer to the molecule, then because the center of the molecule is equidistant from the source and drain. With C procedure also yields the potential in the region occupied by the molecule and carrying the gate control is. Gate control is ideal when absence of a gate (β = 0), as is evident from eq. (12) (also see Fig. 6c,d and the related caption).

\[ \beta = \frac{C_{MG}}{C_{MS} + C_{MD} + C_{MG}} \]  

(13)
is a parameter (0 < β < 1) and is a measure of how good the gate control is. Gate control is ideal when C_{MG} is very large as compared to C_{MS} and C_{MD}. In this case, β = 1 and the Laplace solution U_L = −qV_{GS} is essentially tied to the gate. An estimate of gate control may be obtained from the numerical grid solution explained below by plotting β as a function of gate oxide thickness (Fig. 8).

The particular solution U_p may be written in terms of a charging energy U_0 as:

\[ U_p = U_0(N - N_0) \]  

(14)
The charging energy is treated as a parameter, and may be estimated as follows. The capacitance of a sphere of radius R is 4πεR. If we distribute a charge of one electron on this sphere, the potential of the sphere is q/4πεR. For R = 1 nm the value of this potential is about 1.4 eV. Thus we use a charging energy U_0 ∼ 1 eV. U_0 is the charging energy per electron per molecule and may also be estimated from the numerical grid solution by finding the average potential in the region occupied by the molecule and carrying one electronic charge distributed equally. This numerical procedure also yields U_0 ∼ 1 eV and is used to estimate the charging energy while comparing the capacitance model with the numerical grid solution (see Fig. 3 and the related caption).

With the simple capacitance model just described, the Poisson’s solution U is just a number. The self-consistent potential that adds to the \( p_z \) Hamiltonian (see Eq. [3]) is then calculated as \( U_{SC} = U_{I} \), where \( I \) is the identity matrix of the same size as that of the Hamiltonian.

**Numerical solution:** We use a 2D real space grid to solve the discretized Poisson’s equation for the geometry shown in Fig. 4. The applied gate, source and drain voltages provide the boundary conditions. We use a dielectric constant of 3.9 for silicon dioxide and 2 for the self-assembled monolayer (SAM) [26].

The correct procedure to obtain the real space charge density \( n(\vec{r}) \) (see Eq. [1]) from the \( p_z \) orbital space density matrix \( \rho \) is to make use of Eq. [4]. However, we simplify the calculation of \( n(\vec{r}) \) by observing that a carbon or sulfur p_z orbital has a spread of about five to six Bohr radii (1 Bohr radius \( a_B = 0.529 \) Å). For each atomic site \( \alpha \) we distribute a charge equal to \( \rho_{\alpha\alpha} \) equally in a cube with side \( \sim 10a_B \) centered at site \( \alpha \).

The solution to Poisson’s equation yields the real space potential distribution. However, the self-consistent potential \( U_{SC} \) that needs to be added to the Hamiltonian (Eq. [1]) is in the \( p_z \) orbital space. We assume that \( U_{SC} \) is a diagonal matrix with each diagonal entry as the value of the real space solution U at the appropriate atomic position. For example, the diagonal entry in \( U_{SC} \) corresponding to the sulfur based \( p_z \) orbital would be equal to \( U(\vec{r}_S) \) where \( \vec{r}_S \) is the position vector of the sulfur atom.

### III. Results

The self-consistent procedure (Fig. 4) is done with the two types of Poisson solutions discussed above. The simple capacitance model is fast while the 2D numerical solution is slow but more accurate. The capacitance model has two parameters, namely \( \beta \) which is a measure of the gate control, and \( U_0 \) which is the charging energy. These parameters can be extracted using the 2D numerical solution. We will first present results with the capacitance model by assuming ideal gate control, or \( \beta = 1 \). This ideal case is useful to explain the current saturation mechanism. We will then compare the results obtained from the capacitance model with those obtained from the numerical solution, and show that the two match reasonably well.

#### A. Ideal gate control, on state

Fig. 5 shows the molecular IV characteristic obtained by self-consistently solving the coupled NEG - capacitance model Poisson’s equations. We contrast the IV for ideal gate control (\( \beta = 1 \), Fig. 5a,b) with that for no gate control (\( \beta = 0 \), Fig. 5c,d). For each case, we have shown the IV for positive as well as negative drain voltage. We observe the following:

- With ideal gate control the IV is asymmetric with respect to the drain bias. For positive drain bias, we see very little gate modulation of the current. For negative drain bias we see current saturation and good gate modulation - the IV looks like that of a MOSFET.
- With no gate control the IV is symmetric with respect to the drain bias. There is no gate modulation.

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3 We have assumed that \( C_{MS} = C_{MD} \) in eq. 13, which is reasonable because the center of the molecule is equidistant from the source and drain contacts in our model (see Fig. 1). In general, if the source (drain) is closer to the molecule, then \( C_{MS} \) (\( C_{MD} \)) will be bigger. With \( C_{MS} = C_{MD} \), the molecular Laplace potential is \( V_{DS}/2 \) in the absence of a gate (\( \beta = 0 \)), as is evident from eq. 12 (also see Fig. 6c,d and the related caption).
Three terminal molecular drain current vs. drain to source voltage characteristic with (a) Ideal gate control ($\beta = 1$), negative drain bias, (b) Ideal gate control, positive drain bias, (c) No gate control ($\beta = 0$), negative drain bias and (d) no gate control, positive drain bias. With ideal gate control the IV is asymmetric with respect to drain bias. Good saturation and gate modulation is seen for negative drain bias but not for positive drain bias. With no gate control the IV is symmetric with respect to drain bias. For an explanation of the underlying mechanism for each of these IV curves, see Fig. 6.

These features of the IV characteristic may be understood as follows (Fig. 2). Let us first consider the ideal gate case. Since the gate is held at a fixed potential with respect to the source, the molecular DOS does not shift relative to the source Fermi level $\mu_1$ as the drain bias is changed $\mu$. For negative drain bias (Fig. 2a), the drain Fermi level $\mu_2$ moves up (towards the LUMO) with respect to the molecular DOS. Since the drain current depends on the DOS lying between the source and drain Fermi levels, the current saturates for increasing negative drain bias because the tail of the DOS dies out as the drain Fermi level moves towards the LUMO. If the gate bias is now made more negative, the molecular levels shift up relative to the source Fermi level, thereby bringing in more DOS in the energy range between $\mu_1$ and $\mu_2$ (referred to as the $\mu_1$-$\mu_2$ window from now on), and the current increases. Thus we get current saturation and gate modulation.

For positive drain bias (Fig. 2b), $\mu_2$ moves down (towards the HOMO) with respect to the molecular DOS. The current increases with positive drain bias because more and more DOS is coming inside the $\mu_1$-$\mu_2$ window as $\mu_2$ moves towards the HOMO peak. Once $\mu_2$ crosses the HOMO peak, the current levels off. This is the resonant tunneling mechanism. If the gate bias is now made more negative, no appreciable change is made in the DOS inside the $\mu_1$-$\mu_2$ window, and the maximum current remains almost independent of the gate bias.

Now let us contrast this with the case where no gate is present. In this case, due to the applied drain bias $V_{DS}$, the molecular DOS floats up by roughly $-qV_{DS}/2$ with respect to the source Fermi level. For either negative (Fig. 2c) or positive (Fig. 2d) drain bias, the current flow mechanism is resonant tunneling. Since the equilibrium Fermi energy lies closer to the HOMO, for negative drain bias $\mu_1$ crosses HOMO while for positive drain bias $\mu_2$ crosses HOMO. No gate modulation is seen as expected, and the current is symmetric with respect to drain bias.

Gate induced current saturation mechanism: Assuming that the gate is very close to the molecule (ideal gate control, $\beta = 1$), the gate holds the molecular DOS fixed relative to the source Fermi level $\mu_1$ because the gate is held at a fixed potential with respect to the source. When a negative drain bias is applied (top left), the drain Fermi level $\mu_2$ moves up relative to the molecular DOS. Since the DOS dies out in the gap, for sufficiently high drain bias, no more DOS comes in the $\mu_1$-$\mu_2$ window and the current saturates. When a positive drain bias is applied (top right), $\mu_2$ moves down relative to DOS and eventually crosses the HOMO. The IV is thus asymmetric. If the gate is far away (no gate control, $\beta = 0$), the DOS lies roughly halfway between the source and drain Fermi levels. In this case, for negative drain bias (bottom left), $\mu_1$ crosses HOMO while for positive drain bias (bottom right) $\mu_2$ crosses HOMO. No gate modulation is seen as expected, and the current is symmetric with respect to drain bias.

This is true as long as the charging energy $U_0 \sim 1$ eV, which is typically the case. For high charging energies the particular solution $U_P$ can dominate the Laplace solution $U_L$ (see eqs. 12, 14 and related discussion), thereby reducing gate control.
The HOMO peak thus moves away from the LUMO. As the gate voltage is made more positive, the molecular DOS as explained below.

Temperature independent - the subthreshold slope of the molecular FET is temperature independent and only depends on the molecular DOS as explained below.

The poor subthreshold slope may be understood as follows. As the gate voltage is made more positive, the molecular DOS shifts down with respect to the \( \mu_1 - \mu_2 \) window. The HOMO peak thus moves away from the \( \mu_1 - \mu_2 \) window, and fewer states are available to carry the current. The rate at which the current decreases with increasing positive gate bias thus depends on the rate at which the tail of the DOS in the HOMO-LUMO gap dies away with increasing energy (Fig. 3). Typically we find that the tail of the DOS dies away at the rate of several hundred milli-electron-volts of energy per decade, and this slow fall in the DOS determines the subthreshold slope. The slow fall in the molecular DOS may be attributed to the metal-induced gap (MIG) states - the gold source and drain contacts have a sizeable DOS near the Fermi energy, and are separated only by a few angstroms \( ^5 \). Since the molecule is assumed to be rigid, the molecular DOS has no temperature dependence and hence neither does the subthreshold slope. Thus the molecular FET with a rigid molecule acting as the channel is a very poor switching device even with ideal gate control.

C. Estimate of Gate Control

The 2D numerical Poisson’s solution may be used to estimate the gate control as follows. From Eq. (12) we see that

\[
\beta = -\frac{1}{q} \frac{\partial U_L}{\partial V_{GS}} \bigg|_{V_{DS}}
\]

Thus \( \beta \) may be estimated from the numerical solution by slightly changing \( V_{GS} \) (keeping \( V_{DS} \) constant) and calculating how much the Laplace’s solution changes over the region occupied by the molecule. A plot of \( \beta \) calculated using this method as a function of the gate oxide thickness \( T_{ox} \) is shown in Fig. 8.

Knowing that the channel length (length of the PDT molecule) is about 1 \( \text{nm} \), it is evident from Fig. 8 that in order to get good gate control \( (\beta > 0.8) \) the gate oxide thickness has to be about one tenth of the channel length, or about 1 \( \text{Å} \)!

We have used 3.9 and 2 as the dielectric constants for silicon dioxide and the self-assembled monolayer (SAM) respectively. For a double gated geometry, good gate control can be obtained with more realistic oxide thicknesses \( (~ 7 \text{ Å}) \), as expected simply because two gates can better control the channel than one.

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\( ^5 \) For ballistic silicon MOSFETs, due to the band-limited nature of the doped silicon source/drain contacts, the MIG DOS is negligible. The subthreshold slope at a finite temperature is thus determined by the rate at which the difference in the source and drain Fermi function tails falls as a function of energy. This rate depends on the temperature, and the subthreshold slope is thus proportional to \( k_B T/q \) \((\approx 60 \text{ mV} \text{ at room temperature})\) for ballistic Si MOSFETs \[12\]. Preliminary results for a molecular FET with doped silicon source and drain contacts do show a subthreshold slope proportional to \( k_B T/q \); we are currently investigating this effect.
molecular environment (=2) is about 6 times smaller than that of silicon (=11.7) \cite{28}.

Fig. 5c also shows \( \beta \) as a function of \( t_{ox} \) calculated using the 2D numerical Laplace’s solution over a double gated molecular FET structure. In this case, we find that to get good gate control, we need \( L_{ch}/t_{ox} \sim 1.6 \). Thus a double gated structure is superior to a single gated one for a given \( L_{ch} \) and \( t_{ox} \), as is also expected for conventional silicon MOSFETs. The reason for this is simply that two gates can better control the channel than one.

D. Comparison: Capacitance model vs. Numerical Poisson’s solution

Fig. 8 compares the IV characteristic obtained by solving the self-consistent NEGF-Poisson’s equations with the numerical Poisson’s solution and the capacitance model. The parameters \( \beta \) and \( U_0 \) for the capacitance model were extracted from the numerical solution. We see a reasonable agreement between the two solutions despite the simplifications made in the capacitance model (the capacitance model assumes a flat potential profile in the region occupied by the molecule, which may not be true, especially at high bias) . For \( t_{ox} = 1.5 \) nm (Fig. 8h) there is very little gate modulation and no saturation as expected. In this case \( \beta = 0.28 \) (Fig. 8) and the IV resembles that shown in Fig. 8 more than the one in Fig. 8a. Also seen in Fig. 9 are the results for \( t_{ox} = 1 \) Å. For this case \( \beta = 0.82 \) and we observe reasonable saturation and gate control. For realistic oxide thicknesses, however, we expect to observe an IV like the one shown in Fig. 8a. We have also calculated the IV characteristics with a double gated geometry (not shown here), and as expected from Fig. 8, saturating IVs can be obtained for more realistic oxide thicknesses (\( \sim 7 \) Å).

IV. Conclusion

We have presented simulation results for a three terminal molecular device with a rigid molecule acting as the channel in a standard MOSFET configuration. The NEGF equations for quantum transport are self-consistently solved with the Poisson’s equation. We conclude the following:

1. The current-voltage (IV) characteristics of molecular conductors are strongly influenced by the electrostatics, just like conventional semiconductors. With good gate control, the IV characteristics will saturate for one polarity of the drain bias and increase monotonically if the polarity is reversed. By contrast two-terminal symmetric molecules typically show symmetric IV characteristics.

2. The only advantage gained by using a molecular conductor for an FET channel is due to the reduced dielectric constant of the molecular environment. To get good gate control with a single gate the gate oxide thickness needs to be less than 10% of the channel (molecule) length, whereas in conventional MOSFETs the gate oxide thickness needs to be less than 3% of the channel length. With a double gated structure, the respective percentages are 60% and 20%.

3. Relatively poor subthreshold characteristics (a temperature independent subthreshold slope much larger than 60 mV/decade) are obtained even with good gate control, if metallic contacts (like gold) are used, because the metal-induced gap states in the channel preclude it from turning off abruptly. Preliminary results with a molecule coupled to doped silicon source and drain contacts, however, show a temperature dependent subthreshold slope (\( \sim k_B T/q \)). We believe this is due to the band-limited nature of the silicon contacts, and we are currently investigating this effect.

4. Overall this study suggests that superior saturation and subthreshold characteristics in a molecular FET can only arise from novel physics beyond that included in our model.
Further work on molecular transistors should try to exploit the additional degrees of freedom afforded by the “soft” (as opposed to rigid) nature of molecular conductors.

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