Computational chemistry for molecular electronics

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Abstract

We present a synergetic effort of a group of theorists to characterize a molecular electronics device through a multiscale modeling approach. We combine electronic-structure calculations with molecular dynamics and Monte Carlo simulations to predict the structure of self-assembled molecular monolayers on a metal surface. We also develop a novel insight into molecular conductance, with a particular resolution of its fundamental channels, which stresses the importance of a complete molecular structure description of all components of the system, including the leads, the molecule, and their contacts. Both molecular dynamics and electron transport simulations imply that knowledge of detailed molecular structure and system geometry are critical for successful comparison with carefully performed experiments. We illustrate our findings with benzenedithiolate molecules in contact with gold.

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1. An introduction to the science of molecular electronics

The continuing fabrication of solid-state electronic devices that obey Moore’s law is reaching fundamental and physical limitations, and becoming extremely expensive. Alternatives such as self-assembled molecular-based electronic systems composed of many single-molecule devices may provide a way to construct future computers with ultra dense, ultra fast molecular-sized components [1]. Molecular-scale devices offer several advantages over conventional technology including miniaturization that will allow the scaling of component size to the ultimate level of atoms and molecules. Potential benefits include dramatically increased computational speed and lower fabrication costs.

However, the path to single-molecule electronic devices (or, more simply, molecular electronics), which began with the theoretical prediction over 25 years ago that such devices were possible [2] has been characterized by a significant disconnect between theory [3,4] and experiment [5]. One example involves the conductance of the benzenedithiolate...
molecule between two gold electrodes where theory overpredicts the experimental measurement by three orders of magnitude.

Our work focuses on developing a multiscale modeling approach to molecular electronic devices. We combine electronic structure calculations to determine the nature of the metal–molecule interaction and to calculate conductance with atomistic molecular dynamics and Monte Carlo simulations to predict the structure of self-assembled monolayers (SAMs) composed of the molecules, the resulting configuration of the molecule within the SAM, and its conductance. We focus on the Au-1,4 benzenedithiolate (BDT) system, the same system studied previously theoretically [4] and experimentally [5]; however, the methods employed are general and applicable to other metal–molecule systems.

As part of this work, we develop new insights into conductance [6] and demonstrate that the structure of the SAM is largely dominated by excluded volume interactions between the adsorbed molecules [7,8]. It quickly became clear to us, as it has to others, that the theoretical prediction for conductance in this system can be changed by orders of magnitude depending on the metal–molecule coupling.

Consistent with our own observations, it is now emerging that the key to understanding experimental measurements in this field is characterizing the metal–molecule contact [9]. Recent careful experiments by Cui et al. [10] with a two-component SAM of alkanethiols (ATs) and gold contacts demonstrate that there is a clear difference (by at least two orders of magnitude) between conduction in an idealized system as visualized in Fig. 1 (in which each sulfur is chemically bonded to the gold contact) and analyzed theoretically, and the situation where only one sulfur is chemically bonded to the contact (and the other is simply in close proximity, termed a non-bonded contact). The experimental setup in the earlier BDT conductance measurement does not assure that both ends of the BDT molecule are chemically bonded to each gold surface [5]. The assumption in Cui et al.’s experimental work is that the limit to conductance is the AT molecule. Another possibility is that the gold cluster may be conductance limiting, and in fact this assumption underlies experimental methods to measure the conductance of gold clusters [11–14].

As the above example demonstrates, the characterization of molecular electronics requires a coupled effort between theorists who are able to generate sophisticated numerical models and simulations of the molecules in question, and experimentalists who carefully control the chemical environment in which molecular-electronic devices are manufactured. In this paper, which is written by a collection of theorists, we will demonstrate the techniques currently available for theoretical investigations of SAMs and devices made from them. Thus, this paper focuses on the theoretical and computational tools necessary to interpret the experimental situation for understanding molecular scale conductance in materials that could be
used in future nanoscale devices. We organize our thoughts in the following manner. We first discuss in Section 2 various computational tools and programs that we have used in order to obtain our scientific understanding. We also briefly discuss the pros and cons of using density functional theory. One of our major efforts involved developing an ab initio method for calculating conduction within a single molecule in the presence of leads. We present this work in Section 3. Self-assembly has also been a major component of our research and results will be presented in Section 4. Section 5 contains our conclusions and a look forward.

2. Computational chemistry for molecular electronic systems

The solution of the non-relativistic many-body Schrödinger equation in the Born–Oppenheimer (BO) approximation [15] is the basic problem of the science of molecular-scale electronics and of theoretical quantum chemistry, in general. The resulting Schrödinger equation describes the motion of electrons in a field of fixed nuclei and it is solved by treating the nuclear coordinates as external parameters. One can formulate a complete solution of the quantum many-body problem in terms of the correlated many-body wave function. However, one is typically unable to solve the full problem for all but quite small systems, and approximations are required. This is the case in molecular electronics, as even the smallest realistic systems of interest require extended levels of approximations. The need to accurately represent molecular structures and their interfaces with their environment (e.g., physically realistic electrodes, molecular packing in self-assembled monolayers, and chemisorption and physisorption of nearby molecules) greatly increases the computational complexity of quantitative descriptions of charge-transport phenomena in molecular systems as compared with semiconductor structures [16].

A common way to deal with the many-body problem is through a mean-field approximation (MF). The MF approximations are most accurate for ground-state or equilibrium configurations. The Hartree–Fock (HF) approximation [17] includes the exchange interaction exactly, but omits electron–electron correlation. Density-functional theory [18,19], another MF theory, is a formally exact, single-electron theory for many-body systems, with the total energy being determined by the Kohn variational principle [20,21]. As in other MF theories, electrons move independently in a potential produced by all electrons and ions, $U(r) = U_e(\vec{r}) + U_a(\vec{r}) + U_{XC}(\vec{r})$ where $\vec{r}$ is the position coordinate of the active electron, $U_e(\vec{r})$ is the potential due to ions, $U_a(\vec{r})$ is the electrostatic potential due to the other electrons (i.e., the Hartree potential), and $U_{XC}(\vec{r})$, includes all exchange and correlation effects. The fundamental theorem of DFT [20] states that the total ground-state energy of a system, $E = E(\rho(\vec{r}))$, is a functional of the particle (charge) density $\rho(\vec{r})$. The Kohn–Sham method [21] is based on the same theorem and its corollary that enables one to minimize the total energy by varying over all densities containing $N$ electrons. This leads to single-electron equations, with $U_{XC} = \delta E_{XC}(\rho)/\delta \rho$, were $E_{XC}$ is the exchange-correlation functional. Having $\rho$ defined in terms of single-particle electron states $\rho = \sum_{i=1}^{N} |\psi_i(r)|^2$, one may construct a self-consistent solution assuming $E_{XC}(\rho)$ is known. However, $E_{XC}$ is, in principle, unknown, and must be approximated.

At present, the exchange-correlation functionals have only been determined numerically for a few simple model systems and, thus most density-functional calculations use semi-empirical expressions for $E_{XC}$, obtained for a characteristic group of molecules by calibration to more advanced methods of computational chemistry, or by comparison with experimental data. The approximate functionals are calibrated for various groups of organic (e.g., hydrocarbons), or inorganic (e.g., metals) molecules [22]. Very limited attention has been given to the construction and calibration of functionals for the hybrid organic–inorganic materials typical of molecular electronics. In the work reviewed here, we consider the local-density-approximation (LDA) with Slater exchange [23] and Vosko–Wilk–Nusair (VWN-V) correlation functionals [24], and PBE0 [25], a hybrid, parameter-free approximation for exchange-correlation combining a generalized gradient functional.
(LDA-GGA) with a predefined amount of exact exchange. For easier reference in the text, these are labeled in Table 1.

The DFT approach to the quantum many-body problem has the advantage of being sufficiently accurate to treat many problems of interest as a result of the inclusion of electron correlation and exchange effects, while being as simple computationally as the Hartree scheme. Other approaches for the many-body problem that can be more accurate than DFT include a hierarchy of methods of increasing complexity: many-body perturbation theory (e.g., MP2), configuration interaction (CI) methods, and coupled-cluster techniques (CC) [17]. These systematic quantum chemistry methods can provide highly accurate results for small systems. However, for realistic systems of interest in molecular electronics, the required computational effort scales very poorly and is not practical.

An additional approximation present in all quantum-mechanical calculations and necessary for all methods, is the truncation of the basis set to finite size. A related issue concerns the number of active (or valance) electrons allotted for a given atom, and the replacement of the, relatively inactive, core electrons by effective core potentials (ECP) [26], or pseudo-potentials [27]. In our calculations reported here, we use all-electron basis sets: 3-21G Split Valence Basis [28] and the 6-311G Valence Triple Zeta Basis [29]. For the large Au atom, we also use basis sets of two sizes [30]. The small shape consistent Gaussian basis set CRENBS ECP is for use with averaged relativistic, large-core ECPs replacing 68 core electrons, while the large shape consistent Gaussian basis set CRENBL ECP is for use with averaged relativistic, small-core ECPs replacing 60 core electrons. The detailed specifications of the basis sets and their combinations (labeled A and B), applied in all our calculations reported here, are shown in Table 2.

With the understanding of their short-comings, we employ DFT methods as implemented in the NWChem package [22] to compute atomic and molecular interaction potentials for use in molecular dynamics simulations and to construct the Hamiltonian matrix to be used in calculations of electron transport in molecules. This choice is necessitated by practical concerns: DFT is the only approach currently capable of achieving sound physical results for large systems in a computationally efficient manner. This has been demonstrated in both chemical and solid-state physics, and is currently being exercised at the intersection of these disciplines in molecular electronics. In our discussion, we will highlight examples where the choice of exchange-correlation functional and/or basis set make a quantitative difference in the computed result. It is our hope and expectation that, by focusing on the technical, quantitative features of DFT calculations, our contribution here will motivate the development of improved

Table 1
Exchange-correlation (XC) DFT functionals used in calculations, as defined in text

<table>
<thead>
<tr>
<th>XC functionals</th>
<th>Label A</th>
<th>Label B</th>
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</thead>
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<td>PBE0</td>
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</table>

Table 2
Gaussian basis sets used in characterization of BDT, Au–leads and BDT–Au junctions for transport calculations as well as in calculation of BDT–Au interaction energies for MD simulations of the BDT SAM on gold substrate

<table>
<thead>
<tr>
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<th>C</th>
<th>H</th>
<th>Au</th>
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<td>3-21G</td>
<td>3-21G</td>
<td>3-21G</td>
<td>ECP CRENBS</td>
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<tr>
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<td>All</td>
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<td>19</td>
</tr>
</tbody>
</table>
methods for the quantum many-body problem inherent in the science of molecular electronics.

All computational chemistry calculations referred in this text were done on the ORNL IBM SP4 parallel computer, which has 27 nodes, each possessing 32 processors, or on IBM SP3 parallel computer with 184 four processors nodes.

3. Calculation of tunneling conductance through a molecule

Our approach to calculate the tunneling conductance of a molecular device is based on a Green’s function formulation. In this section we will discuss our method within the context of a simple molecular circuit, which consists of a single molecule connected to two electrodes or leads. Although multiple molecules can in principle be treated as a large composite molecule, the problem of more than two leads, while interesting and extremely useful, will be too cumbersome for our presentation and will not be considered here. A second simplifying assumption is that the electrons move in perfect coherence, “elastically”, throughout the device. The electron is scattered by a stationary, spatially varying potential, situated between two infinite electron reservoirs represented by the two electrodes, in what is termed a “ballistic” process. And finally, we also assume nearly thermodynamic equilibrium and a very small voltage drop across the device, the so-called linear-response regime. This assumption allows us to use the electronic structure from the DFT calculations for the ground state of the device to calculate the transport properties without the need to treat the transport problem and the electronic structure simultaneous in a self-consistent procedure, thus greatly simplifying the calculation. Despite the name “linear-response theory”, such an approach has led to qualitatively correct current-voltage characteristics up to a few volts [31], which apparently are non-linear transport properties. Of course there also exists fully self-consistent non-linear approaches [4,32] which are outside the scope of our paper.

The physical motivation and detailed derivation of our approach is given in Ref. [6]. In this paper, we will focus on the implementation of the algorithm and numerical considerations. We employ the Landauer [33] conductance formula which expresses the conductance of a sample in terms of the total transmission probability, $\mathcal{T}$, of an electron incident on a sample that is connected to two semi-finite ideal leads (so called two-terminal formula) [34],

$$\sigma = \frac{2e^2}{h} \mathcal{T},$$

(1)

where the factor of 2 is due to the electron spin degeneracy in the considered channels. The particular approach we use to evaluate the $\mathcal{T}$ is formulated in terms of the Green’s functions of the molecule and the self-energies of the leads, known as the Caroli’s formula [35],

$$\mathcal{T} = \text{Tr}[\Gamma_L G_M^+ \Gamma_R G_M^-],$$

(2)

where $G_M$ is the Green’s function of the molecule,

$$\Gamma_{\{L,R\}} = i\left[\Sigma^+_{\{L,R\}} - \Sigma^-_{\{L,R\}}\right]$$

(3)

and where the self-energy terms $\Sigma_{\{L,R\}}$ are due to coupling of the semi-infinite leads on the left, $L$, and on the right, $R$, respectively, with the molecule. The ± signs denote the retarded (+) or advanced (−) Green’s functions, both for the self-energies as well as for the Green’s functions in the formula.

One question regarding the Caroli formula that has been overlooked by some of previous works, is its applicability, without modification, when basis functions are non-orthogonal, as is common in quantum chemistry applications. In studying quantum systems that are composed out of atomic building blocks, it is customary to solve the problem by expressing the electron’s wave function in terms of atomic orbitals on the various atoms. These orbitals are not usually orthogonal to each other, and therefore, the overlap matrix cannot be normalized to a unit matrix. For example, when calculating the Green’s function, instead of using $G = (EI - H)^{-1}$ where $I$ is a unit matrix and $H$ is the Hamiltonian, we need to use $G = (ES - H)^{-1}$ where $S$ is the overlap matrix. If we were dealing with a closed system, then an orthogonal representation can be obtained easily by diagonalizing the matrix $S$. However, this is impractical for an
open system, which includes two semi-infinite leads and both matrices $S$ and $H$ have infinite dimensions. Even if one can diagonalize $S$ for such a system, the resulting Hamiltonian would necessarily lose its tight-binding characteristics making the approach unattainable.

If we rewrite the Green’s function in the form $G = [E - (1 - S)E - H]^{-1}$ and treat the sum $(1 - S)E + H$ as an effective Hamiltonian, then it would appear that the Caroli formula can be applied to this Hamiltonian with no modification. However, there is a complication in distinguishing between the advanced and the retarded solutions as it is necessary to introduce a small imaginary part to the energy parameter in the Green’s function. Because the Gaussian basis is not orthogonal, so the $(1 - S)E$ term contains off-diagonal elements which, when evaluated at a complex energy, makes the effective Hamiltonian non-Hermitian. This breaks the causality of the Green’s functions and may introduce unphysical negative transmission probability contributions in the Caroli formula. The effect of non-analyticity of the Green’s function can often be subtle. It sometimes switches the left-going and right-going Bloch eigenstates, causing a negative contribution to the tunneling current from that particular state, while giving the correct contributions from all other states. At energy values where there is only a single conduction channel, the error can be more obvious, in the form of negative current at a few energy points. Noting that the only purpose of introducing a small imaginary part of the energy is to separate the advanced and the retarded solutions, and that it should be sufficiently small so that the actual size of the imaginary part of the energy does not affect the numerical solution, we introduce a complex energy only in the diagonal elements, while keeping the energy in the off-diagonal term, $(1 - S)E$, real. This ensures the proper causality and extends the validity of the Caroli formula to non-orthogonal basis representations. In particular, this guarantees the proper signs of the imaginary parts of the self-energies $\Sigma^{\pm}_{(L,R)}$.

Another problem in solving for the building blocks of the problem in an atomic orbital basis is that the boundary conditions for such a solution, presumed with the localized features of the basis, are those for a closed quantum system, having only bound states. It would seem that such a solution would not be appropriate for treating the transport problem for a molecule connected to a circuit with two leads, which is a typical scattering problem. The Hamiltonian for the open system can be approximately obtained from closed boundary quantum chemistry calculations in the following manner. For a lead-molecule-lead system, we assume that each lead is periodic along the direction of the current which we take to be in the $z$-direction and has a finite cross section perpendicular to this direction. We call each periodic unit of the lead a layer, which may consist of any number of atoms and may also be divided into sublayers. We assume that the matrix elements of the Hamiltonian are all zero except between elements within the same layer or neighboring layers. Thus the Hamiltonian takes a layered TB form of tri-diagonal block matrix. In what follows the subscripts $L$ and $R$ denotes the left and right semi-infinite leads, respectively, and the subscript $C$ denotes the molecule block which actually contains the molecule and one layer of the gold lead on each side.

The matrix elements are extracted from two (or three when two leads are different) separate quantum chemistry calculations. The blocks for the left lead, for example, $H_{L00}$ and $H_{L01} = H_{L10}^T$; in the case of a gold nanowire are obtained from a calculation of a gold cluster containing four equal layers. The block-diagonal part of the Hamiltonian corresponding to one of the middle layers is taken as $H_{L00}$, and the hopping terms between the two middle layers are the corresponding elements of $H_{L01}$ and $H_{L10}$. Analogous techniques are used to construct the right-hand side lead. To construct $H_{CC}$, $H_{CL} = H_{LC}^T$, and $H_{CR} = H_{RC}^T$, a separate quantum chemistry calculation was done for a cluster containing the molecule plus two additional gold layers on either side (four gold layers total). The diagonal block of the Hamiltonian with the two outside gold layers removed is $H_{CC}$, while the hopping terms between this block and the two outside gold layers are the corresponding elements of $H_{CL}$, $H_{LC}$, $H_{CR}$, and $H_{RC}$. When the molecule region $C$ is removed and the right lead is made to
be the continuation of the right lead, we get an infinite perfect wire.

Once the Hamiltonian is defined, our approach can be specified by the following steps: first, the calculation of the Green’s functions for infinite and semi-infinite leads; second, the calculation of the self-energies in the sample (molecule region), due to the coupling to the leads; third, the calculation of the transmission through the sample, and its decomposition into contributions from individual Bloch states (channels) in the leads; and, finally calculation of the 1–U characteristics and the conductance of the system. Throughout the text we illustrate our approach with the example of gold leads and benzene-dithiolate molecule (BDT).

3.1. Green’s function and self-energy of perfect leads

We consider an infinite perfect lead. Dropping the indices L and R, the non-zero subblocks of the Hamiltonian, i.e., $H_{00}$, $H_{01}$ and $H_{10}$, and the corresponding overlap matrices, i.e., $S_{00}$, $S_{01}$, and $S_{10}$, have dimensions $N \times N$, $N$ being the total number of orbitals within each layer of the lead. We define matrices $M(E) = ES_{00} - H_{00}$ and $h(E) = ES_{01} - H_{01}$, and write the equation of motion for a wavefunction $u$ as,

$$M(E)u_0 - h(E)u_1 - h^\dagger(E^*)u_{-1} = 0,$$

where $u_i, i = -1, 0, 1$, are the vectors containing the $N$ components of $u$ corresponding to three neighboring layers, labeled here with subscripts $-1, 0,$ and $1$ respectively. Due to the translation symmetry of the system, the wavefunction must satisfy the conditions $u_0 = \exp(ikd)u_{-1}$, and $u_1 = \exp(ikd)u_0$, where $k$ is the Bloch wavevector and $d$ is the period in z-direction. Eliminating $u_1$ from the Eq. (4), we obtain a $2 \times 2$ block equation,

$$\begin{pmatrix} 0 & 1 \\ h(E) & -M(E) \end{pmatrix} \begin{pmatrix} u_{-1} \\ u_0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -h^\dagger(E^*) \end{pmatrix} \begin{pmatrix} u_{-1} \\ u_0 \end{pmatrix} \lambda,$$

where $1$ and $0$ denote unit and zero matrices of order $N \times N$, and $\lambda = \exp(ikd)$. For a given $E$ this defines a generalized eigenvalue problem in $\lambda$, which is the basis for our method of calculating the Green’s function.

As an example, we construct a lead as an infinite nanowire made of layers of gold, where each layer contains two sublayers, of 7 and 3 atoms, corresponding to the Au(111) lattice. Fig. 1 shows the two layers, on each side of the BDT molecule, each of them containing two sublayers (7 and 3 atoms). To construct the TB model for the wire within the Gaussian DFT approach to compute Kohn–Sham orbitals, we use functional A (Table 1) and CRENBS ECP Gaussian basis (Section 2), which gives $N = 100$ functions per layer, determining the dimensionality $N$ of the matrices $H_{00}$, $H_{01}$, and $S_{00}, S_{01}$ for the lead. This provides both overlap ($S$) and Hamiltonian ($H$) matrices. The diagonalization of Eq. (5) for each $\theta = kd$ yields the band structure $E_n(k)$ of the gold nanowire, shown in Fig. 2. The bands in the considered energy range are made of either $p_z$ orbitals or of a mixture of $s$ and $p$ orbitals (dominantly $s$). For example, as indicated by the horizontal lines in the figure, there is only one band, $p_z$, at $E = -0.2$ Hartrees denoted by “1”, three bands, “1”, “3” and “4”, at $E = -0.19$ Hartrees, a gap between $-0.16$ and $-0.15$ Hartrees and, so on.

To investigate the influence of the choice of the DFT functionals on the transport properties, we perform the calculations with both A and B exchange-correlation functionals (Table 1). While the discussion and intermediate results in Figs. 1–4...
are shown for the functional A, the comparison of the results obtained with both functionals A and B will be given in the $I–V$ characteristics of Fig. 5.

Before we proceed to the Green’s functions, we note that not all solutions of Eq. (5) represent the real eigenstates, or Bloch states, of the system. At each energy, there are a finite number of Bloch states, often only one or two, as can be seen from Fig. 2. On the other hand, Eq. (5) should give $2N$ eigenvalues, twice as the number of basis functions within each layer and independent of the number of Bloch states at this energy. For real $E$ the Bloch states correspond to the $\lambda_i$s on the unitary circle, i.e., $|\lambda_i| = 1$. Other solutions are called evanescent states. When $|\lambda_i| > 1$, the corresponding $u_i$ decays to the right, and will be called a right-going evanescent wave, which we denote them with $\lambda_{i>}$. Similarly, when $|\lambda_i| < 1$, the corresponding $u_i$ decays to the left, and will be called a left-going evanescent wave, which we denote by $\lambda_{i<}$. There are $N$ pairs of $\lambda_{i>}$ and $\lambda_{i<}$, and each pair is related by $\lambda_{i>}\lambda_{i<} = 1$. For the particular Gaussian basis used in our calculation, there are exactly 100 of them inside the unitary circle, and 100 outside, and the Bloch eigenstates are characterized by $|\lambda_i| = 1$ for real $E$. By introducing an infinitesimal imaginary part $\eta$ to the energy, these $\lambda_i$s are moved slightly off the unitary circle, thus their directions of travel can be determined. Although the diagonalization of Eq. (5) yields $2N$ eigenvalues for each $E$, we show in Fig. 3 only $N = 100$ eigenvalues, those inside the unitary circle for $E = -0.19$ Hartrees, with $\eta = 10^{-10}$. From the
figure it is obvious that for $E = -0.19$ Hartrees, there are only three $\lambda^b_k$ on the unit circle. In each case the number of $\lambda_k$ corresponds to the number of bands at a relevant energy, and these numbers are associated with the well known integer conductance of an infinite perfect lead. As might be expected, to each $\lambda_k$ corresponds a $\lambda^b_k$ just outside the unitary circle. In general, for sufficiently small values of $\eta$, all $\lambda_k$ which correspond to evanescent states appear either in complex conjugated pairs or on the real axis. As the number of basis functions per layer, $N$, increases, and if basis is convergent, the additional “evanescent” eigenvalues converge either to zero or to infinity. Cumulation of $\lambda_S$ to a narrow region around $|\lambda| = 0$ is visible in Fig. 3. Here we have used real $(1 - S)E$ as discussed earlier, and its impact is to prevent a switching of the Bloch states which are inside and infinitesimally close to the unit circle $|\lambda| = 1$ with their counterparts outside the unit circle.

Using superscripts ± to label eigenstates for $E^+$ and $E^-$, respectively, where ± signs indicate that the energy argument contains an infinitesimal imaginary part, $E_k = E \pm \eta$, with $\eta > 0$, $\eta \to 0$, we now can define the diagonal square matrices $\Lambda^±_k$ ($\Lambda^±_S$), whose $i$th diagonal element is the complex number $\lambda^±_k$ ($\lambda^±_S = 1/\lambda^±_S$), and the corresponding eigenvector matrices $U^±_k$ ($U^±_S$), whose $i$th column is the $a_0$ block of the $i$th eigenvector of Eq. (5). The Bloch states, whose $\lambda_S$ are on the unitary circle for real $E$, are resolved to be inside or outside the unitary circle by using an infinitesimal imaginary part of the energy.

By defining two additional $N \times N$ matrices, $\alpha^± = U^±_S \Lambda^±_S (U^±_S)^{-1}$ and $\beta^± = U^±_S (\Lambda^±_S)^{-1} (U^±_S)^{-1} = U^±_S \Lambda^±_S (U^±_S)^{-1}$, it is shown in [6] that the site-diagonal elements of the Green’s function in the real space, $G^{\infty}_0(E^\pm)$, for the infinite wire, can be obtained in form,

$$g_0^± \equiv G^{\infty}_0(E^\pm) = \{h^± [(\alpha^±)^{-1} - \beta^±]\}^{-1}$$

and similarly for the nearest-neighbor block of the Green’s function, $g^±_1 \equiv G^{\infty}_1(E^\pm) = \alpha^± g^±_0$, where shorter notations $g_0$ and $g_1$ are introduced for $G^{\infty}_0$ and $G^{\infty}_1$, respectively. Both $G^{\infty}_0(E^\pm)$ and $G^{\infty}_1(E^\pm)$ are square matrices of dimension $N$.

A pair of semi-infinite wires can be constructed from an infinite wire by removing the coupling between layers $i$ and $i + 1$, creating a left semi-infinite wire (labeled by L) with a surface layer on $i$, and a right semi-infinite wire (labeled by R) with a surface layer on $i + 1$. Using the notations $g^L_i$ and $g^R_i$ to represent the Green’s functions $G^{(L)}_i$ for the left lead and $G^{(R)}_{i+1}$ for the right lead, respectively, one can express $g^L_i$ and $g^R_i$ in terms of the matrices $\alpha$ and $\beta$, and obtain the very simple expressions, $g^L_i = \alpha^+ (h^r)^{-1} = (h^-)^{-1} (\alpha^-)^+$ and $g^R_i = \beta^+ (h^-)^{-1} = (h^+)^{-1} (\beta^-)^+$, which yield the self-energies of the “left” and “right” semi-infinite wires in the form

$$\Sigma^L_i \equiv (h^-)^+ g^L_i h^+ = (h^-)^+ \alpha^+ = (\alpha^-)^+ h^+,$$  

$$\Sigma^R_i \equiv h^+ g^R_i (h^-)^+ = h^+ \beta^+ = (\beta^-)^+ h^-.$$  

The Green’s functions and the self-energies for $E^-\infty$ are obtained by the Hermitian conjugate of the above equations.

### 3.2. Decomposition of the conductance into channels

Now we consider the conductance of a molecule that is connected on both ends with two semi-infinite perfect leads, labeled by L and R, respectively. We use a subscript C to label the Green’s function for the atoms in the molecule. The molecule here is defined to contain the atoms that make up the molecular tunneling junction such as a BDT, and any part of the lead whose potential is changed by the presence of the molecule (and thus cannot be part of a perfect lead). The Green’s function for the molecule that is embedded between two perfect leads, is given in terms of the Hamiltonian matrix of the molecule, and the self-energies due to the coupling with two semi-infinite leads. The self-energies are $\Sigma^C_{LC} = (h^C_{LC})^+ g^C_{LC} (h^C_{LC})$, and $\Sigma^C_{CR} = (h^C_{CR})^+ g^C_{CR} (h^C_{CR})$. The Green’s functions of the semi-infinite leads, $g^{±}_{L,R}$, are given by the equivalent of equations for $g^L_i$ and $g^R_i$, as defined by the geometry, shape, crystal structure and chemical composition of the L and R leads, which are not necessarily the same here. The Green’s function for the molecule connected to both leads is

$$G^C_i = (M^C_i - \Sigma^C_{LC} - \Sigma^C_{CR})^{-1},$$
where $M_C$ is the matrix containing the elements of the Hamiltonian and the overlap integrals for the orbitals within the molecule C in the presence of the leads, and the dimension of all matrices in Eq. (9) is $N_C$, the number of basis functions used to define the molecule.

By this point we already have everything we need to use the Caroli formula, Eq. (2), with $G_C^\pm$ and the corresponding $T$ computed from the self-energies $\Sigma_{LC}^\pm$ and $\Sigma_{CR}^\pm$. However, in order to find the decomposed contributions from individual Bloch channels, we need to be able to use the $\Gamma_{(L,R)}$ for the perfect leads. To accomplish this, we include in the “molecule” one additional layer of the perfect leads on each side of the molecule. This defines a larger “molecule” consisting of three parts, the left layer, $\ell$, that is identical to the layers in the left lead, the molecule, C, and the right layer, $r$, that is identical to the layers in the right lead. The TB couplings between the leads and the layers $\ell$ and $r$ are $h_\ell$ and $h_R$, respectively. In addition, we assume that layers $\ell$ and $r$ do not couple to each other directly. Of course, in general the layers of the two leads, L and R, can be structurally and geometrically different, and so layers $\ell$ and $r$ can be different. Using these definitions, we decouple the transmission probability into

\[ T = \sum_{mn} p_{mn} q_{nm}, \quad (10) \]

where $p_{mn}$ and $q_{nm}$ are the elements of the $N \times N$ matrices $p$ and $q$,

\[ p = (\lambda_\ell^+)^L(U_{\ell}^+)^{-1} (h_\ell^+)^{-1} h_{LC}^+ G_C^+ \Gamma_R^+ (U_{\ell}^+)^R \quad (11) \]

and

\[ q = (\lambda_R^+)^R(U_{\ell}^+)^{-1} (h_R^+)^{-1} (h_{CR}^+)^L G_C^+ \Gamma_L^+ (U_{\ell}^+)^L \quad (12) \]

and where $G_C^+$ is an $N_C \times N$ matrix representing the propagator from the molecule to layer $r$, and $G_C$ is similarly the propagator from the molecule to layer $\ell$. Eqs. (11) and (12) show explicitly that the indices, $m$ and $n$, count the eigenstates $\lambda_\ell \lambda_R$ and $\lambda_\ell \lambda_R$, respectively, including both Bloch and evanescent states. The conductance is now in principle decomposed into contributions from different Bloch eigenstates and evanescent states, including all possible cross terms between these states.

3.3. Numerical example

In our numerical example, a nanodevice is constructed of a BDT molecule between two gold semi-infinite leads, as in Fig. 1. As in Section 3.2, the lead is made of a nanowire, with an asymmetric layer of 10 atoms. In this example, the BDT molecule is positioned between two top-sublayers of the leads, at distance of 11.32 Å. The sulphur atoms are symmetrically placed at minimum potential energy distance of 2.54 Å from the central Au atom. The distance of the sublayers of the gold lead are 2.356 Å. The BDT atoms in the DFT calculations were defined by the basis B of Table 2.

We note that removal of the BDT from the system would not (even by shifting the leads) yield an infinite lead: The left and right leads both have the same surface (top sublayer) and thus the interface between the two leads would be a stacking fault. The whole system possesses the mirror symmetry. The consequences of the symmetry are $h_\ell^T = h_R$, $(U_{\ell}^+)^L = (U_{\ell}^+)^R$ which obviously leads to $g_\ell^T = g_R^T$ and $\Sigma_{LC}^T = \Sigma_{CR}^T h_\ell^T = h_R$. With these symmetry relations in mind, application of Eqs. (10)–(12) leads again to a tremendous simplification. Thus,

\[ T = \sum_{n,m = 1, N(E)} T_{nm}, \quad (13) \]

where $v$ is a total number of Bloch states at the energy, $E$, under consideration. This number is, for the case considered here, the same for the left and right leads. So, rather than 10,000 terms in the considered case one has one term surviving in transmission at $E = -0.20$ Hartrees (1→1), nine terms surviving at $E = -0.18$ Hartrees (1,2,3→1,2,3). The total transmission function of the molecule $F$ is shown in Fig. 4, as well as the leading $T_{nm}$ terms that constitute the total transmission.

Apparent asymmetry in the transmission probabilities ($T_{12} \neq T_{31}$, for example) highlights the difference between a realistic TB Hamiltonian, in which the left-going and right-going Bloch states can be quite different, and may couple to different states in the molecule and model TB Hamiltonians used in the past, which assumed symmetry between left-going and right-going states. We have
shown [6] that the total transmission into the Bloch states \( m \), \( T_m = \sum_{n=1,1} T_{nm} \), and the total transmission \( T_n = \sum_{m=1,1} T_{nm} \) scattered from the various Bloch states \( n \) as functions of energy \( E \) significantly differ from each other. The difference in the two results comes from the asymmetry in \( T_{nm} \) transmission components.

We also constructed the molecule \( \mathcal{F} \) by adding two and three pairs of gold layers on each side of the BDT molecule. Both the total transmission and the decomposition into the partial contributions remain unchanged with respect to the number of gold layers added.

### 3.4. I–V characteristics of the molecule

Because we are calculating transport properties using a Hamiltonian derived from an ab initio calculation rather than directly through an ab initio self-consistent non-equilibrium method, we need to ensure that the Fermi energy at which the transport coefficients are calculated is placed correctly with respect to the bandstructure of the system as obtained from our Hamiltonian. We determine the Fermi energy by counting the number of electrons per unit cell within either electrode, and requiring that number equal the number of states below the Fermi energy. Once the Fermi energy is determined, we also place a constraint on total number of electrons in the electrode-molecule-electrode assembly so that the entire system is neutral, by placing a constant shift in the part of the Hamiltonian corresponding to the molecule region. The calculations of the number electrons per unit cell in the leads as well as the total number of electrons are accomplished with the standard contour integration technique, where one integrates the imaginary part of the Green’s function over a complex energy contour. Deep core states are counted with a simple diagonalization.

In Fig. 5 we show the \( I–V \) curves calculated with our code. Although our code cannot include the effect of bias voltage self-consistently, we have approximated the bias effect in the following way. The energy parameter in the matrix elements of \( E\mathcal{S} - \mathcal{H} \) for the left and right electrodes were changed to \( E - eV/2 \) and \( E + eV/2 \), respectively, where \( V \) is the bias voltage. The energy parameter for the molecule region remains at \( E \). The Fermi energy \( E_F \) remains the same for all biases, but the shift of the potential in the molecule region is readjusted at zero bias to ensure the total charge neutrality. This shift in the molecule region is maintained at the same value as the bias is changed. The transmission probability, \( T(E) \), is calculated as a function of \( E \) using the Caroli formula within the energy window of \( E_F - eV/2 \) and \( E_F + eV/2 \) where \( E_F \) is the Fermi energy. Finally the total current is evaluated by the integral

\[
I = \frac{e}{\hbar} \int_{E_F - eV/2}^{E_F + eV/2} T(E, V) \, dE. \tag{14}
\]

Three \( I–V \) curves are plotted, for various Fermi energies and the DFT exchange-correlation functionals. It is evident that a very small change in the Fermi energy in the lead can cause more than an order of magnitude change in the conductance, so can a change in the exchange functional. The consequences of the choice of the DFT functionals and need for their “tuning” to the cases of metallic lead–organic molecule systems, typical in molecular electronics is further highlighted in the next Section.

### 4. Molecular dynamics simulations of self-assembled monolayers of benzenedithiolate molecules on the Au(1 1 1) surface

It has become clear that the electron transport properties of metal–molecule–metal junctions strongly depend on the molecular conformations [4,36,37], the temperature [4] and the nature of contact between the organic molecules and electrodes [9,10,38]. At the quantum level, significant progress has been made in the framework of density functional theory (DFT) to calculate metal–single molecule–metal conductance [4,39–41]. However, in both of the key experimental measurements to date [5,10] the organic molecule whose conductance is measured has been part of a self-assembled monolayer (SAM)––either a one-component or two-component SAM. Additionally, it is likely that any manufacturable molecular
electronics device will be produced by self-assembly. Since the conformation of a molecule within a SAM is quite different from that of an isolated molecule on the same surface, it is important to determine the structure of the SAM and the conformation of the molecule of interest within the SAM to use as input to a DFT calculation of electron transport in the molecule.

For this purpose, we have developed a classical molecular simulation of a SAM of benzenedithiolate (BDT) molecules on the (1 1 1) surface of Au. Ultimately, we anticipate that the molecular simulation will be part of an iterative scheme in which the structure of the BDT within a SAM is initially calculated using classical molecular simulation; DFT is then used to optimize the structure of the molecule within the external field of the SAM and in the presence of two electrodes at non-zero voltage; the non-zero voltage will create a large electric field which will cause charge redistribution within the BDT molecule, and hence change its interactions with its neighbors; we will then calculate the conductance of the molecule using DFT methods. We then re-perform the classical molecular simulation to re-equilibrate the SAM, and continue iteratively until convergence is achieved. Beyond this iterative scheme, we also anticipate using a hybrid approach in which the BDT molecule connected to two leads (and perhaps its nearest neighbors in the SAM) are treated by ab initio molecular dynamics and the remainder of the system treated classically. Such an approach removes the need for an iterative scheme; however, it is expected to be computationally very intensive and to require developments in methodology to accommodate the interface between the region treated by ab initio methods and the region treated by classical molecular dynamics. Examples of such hybrid schemes currently exist but for much simpler problems, such as crack propagation [42]. At the current stage of this overall simulation strategy, we have been developing the classical force fields needed to simulate a BDT SAM on a single Au(1 1 1) surface and performing preliminary simulations. Before describing the development of the force fields and our simulations, we begin with some comments about our expectations from these simulations.

The structure of a BDT molecule within a BDT SAM is, a priori, expected to be different from an isolated BDT molecule on the same surface, since a fully occupied SAM will result in significant steric constraints on the possible conformations of the molecule. This is clear from many past experimental and simulation studies of SAMs of alkanethiols and other molecules [43]. In early unpublished work [44], we explored the degree to which steric interactions alone determine the structure of a SAM of benzene thiol (BT) molecules using fairly simple models for the BT–BT and for the BT–Au interaction based on existing models in the literature. We expect that a SAM on a single Au(1 1 1) surface of BT will have similar characteristics to a SAM of BDT on the same surface. Using Gibbs ensemble Monte Carlo [45,46], we studied the self-assembly of a condensed phase of BT molecules permitted to adsorb only on the bonding sites of the Au(1 1 1) surface. Monte Carlo moves enabled BT molecules to move from on site to another, as well as to adopt different orientations of the benzene ring with respect to the Au surface. Despite the simplicity of this model, we obtain the resulting condensed phase, shown in Fig. 6. This condensed phase is essentially has a small number of defects (vacant sites) and, when analyzed statistically over a long Monte Carlo simulation, this condensed phase is found to have the same structure as that measured experimentally by Wan et al. [47], namely a well-ordered \((\sqrt{13} \times \sqrt{13})R13.9^\circ\) herringbone structure.
in which 25% of the BT adsorbates are bound to top sites, 75% are bound to bridge sites, and none are bound to hollow sites. Note from Fig. 6 that there are only a few defects on the herringbone structure. A similar structure for a BT SAM on Au(1 1 1) was found using the CHARMM force field [48].

Since we obtained this structure from a relatively simple model, it is clear that many of the global characteristics of the BDT SAM structure will be determined primarily from steric (i.e., excluded volume) interactions. However, the details of the SAM structure, and the conformation of an individual BDT molecule within a SAM, will require a much more sophisticated simulation. In considering the simulation of SAMs of BDT molecules on the Au(1 1 1) surface, several issues arise, namely, the force field to be used for BDT–BDT interactions, the force field to be used for BDT–Au interactions, and the simulation algorithms to be employed. We have addressed each of the issues in the Subsection 4.1 through 4.3 below. Representative results are given in Subsection 4.4. The MD simulation code was developed in-house as a hybrid of several MD simulation codes originally developed independently by Keffer, Leng and Cummings.

4.1. BDT–BDT interactions

To define the BDT–BDT interaction energy (where the BDT molecules is shown in Fig. 7) requires several components: in essence we have used the universal force field (UFF) [49,50] with one modification, namely that partial charges, derived from ab initio DFT calculations, have been used in the interaction. The UFF force field is a popular choice for materials simulations since it is defined for all of the elements of the periodic table. It breaks down the interactions between molecules and within molecules to interactions between atoms.

4.1.1. Intramolecular interactions

First, it should be pointed out that between any pair of atoms in the same molecule separated by more than two bonds we compute an interaction energy based on the same atom-atom potential used for intermolecular interactions (see following paragraph). Thus, for example, the carbon atom labeled C3 in Fig. 7(a) has a Lennard-Jones plus Coulombic interaction with the carbon atom labeled C6, which is the same as the intermolecular interaction between a C3 carbon in one molecule and a C6 carbon in a distinct molecule. This is a convention adopted in the UFF that is typical of
many force fields used for molecular simulation. Second, within the classification scheme used by UFF, the atom types for the C, H, and S atoms in a BDT molecule are C_R (resonant carbon), H_, and S_3+2 (tetrahedral sulfur with +2 oxidation state). Between any bonded pair of atoms I and J, there is a bond stretching potential

\[ E_R = \frac{1}{2} k_{IJ} (r - r_{IJ})^2, \quad (15) \]

where the equilibrium bond length \( r_{IJ} \) is assumed to be the sum of atom type specific single bond radii, plus a bond order correction and an electron negativity correction. Expressions for the UFF parameters for the bond-stretching interactions are available [49,50]: the explicit values for BDT molecules are tabulated by Leng et al. [8]. Between any three bonded atoms I–J–K (I bonded to J, J bonded to K, making an angle \( \theta \) at the atom center \( J \)), there is a bond-angle bending potential, and for every set of four bonded atoms I–J–K–L (I bonded to J, J bonded to K, K bonded to L, with the dihedral angle \( \phi \) defined as the angle between the plane defined by the three atom centers I, J, K and the plane passing through the three atom centers J, K, L), there is a torsional interaction. Finally, when an atom is bonded to exactly three other atoms, an inversion potential maintains the geometry of the tertiary bond. In the BDT molecule, the inversion potential acts at each of the six C atoms, and favors the planarity of the benzene ring. Explicit expressions for each of these potentials and the force constants are given in [8].

### 4.1.2. Intermolecular interactions

In UFF, the van der Waals contribution to all of the atom–atom pair potentials are given by the Lennard-Jones form

\[ E_{vdw} = D_{IJ} \left[ \left( \frac{x_{IJ}}{r} \right)^{12} - \left( \frac{x_{IJ}}{r} \right)^6 \right], \quad (16) \]

where \( D_{IJ} \) is the well depth in kcal/mol and \( x_{IJ} \), the position of the minimum of the potential, is the van der Waals bond length in \( \text{Å} \). Expression for determining the van der Waals parameters \( D_{IJ} \) and \( x_{IJ} \) for like species atoms are given by Rappé and coworkers [49,50]: explicit values for the BDT molecule are tabulated by Leng et al. [8]. For unlike species, the Lorentz–Berthelot combining rules,

\[ x_{IJ} = \frac{1}{2} (x_I + x_J), \quad D_{IJ} = \sqrt{D_ID_J} \quad (17) \]

are used. The partial charges used for the atoms in the BDT molecules are determined from ab initio calculations of the BDT–Au interaction, discussed in the next subsection.

### 4.2. BDT–Au interactions

Characterization of the interaction between alkanethiols, particularly methanethiolate, on Au(1 1 1) has received a great deal of interest in the literature, focusing on the relative favorability of the various adsorption sites on the gold substrate [51–55]. We have performed extensive ab initio density functional theory (DFT) calculations of the BDT–Au interactions. It is beyond the scope of the present paper to describe these calculations in detail; the interested reader is referred to descriptions given elsewhere [7,8].

The ab initio DFT calculations were performed on a single BDT molecule at three possible adsorption sites on the Au(1 1 1) surface: top (in which the S is bonded to a single Au atom), bridge (in which it is bonded at the midpoint of two Au atoms) and hollow (in which it is bonded at the center of three Au surface atoms in an FCC or HCP arrangement). The energies of many possible conformations of the BDT molecule (varied by distance from surface, orientation with respect to the surface and to the plane of the benzene ring) were computed. All calculations were performed using the NWChem DFT for molecules package. In turn, the obtained quantum-mechanical potentials were fitted to functional forms to characterize the various force fields. For example, at the top site, we fitted the Au–BDT interaction due to the Au–S stretching to a harmonic form (similar to Eq. (15)), as well as characterizing bond bending and torsional potentials involving the Au site. For the other sites, a fictitious center of force (called SC, for site center) was used as the site involved in bond stretching, bond angle and torsional interactions. In view of the discussion in Section 2 concerning the inherent uncertainty of the quantum chemistry calculations for the meso-size systems of the metal–organic combinations, we
performed the set of the DFT calculations, for three different quantum-chemistry models, given in Table 3 and denoted QMC1 through QMC3. The models differ in size of Gaussian bases used as well as in choice of the exchange-correlation functionals. Thus, QMC1 (A,A) and QMC2 (B,A) cases test the convergence with respect to the basis size, while QMC2 (B,A) and QMC3 (B,B) show the sensitivity of the MD results to the choice of the DFT functionals. Partial charges for each model chemistry were calculated using the Mulliken population analysis.

The BDT–Au interaction potentials and partial charges were adopted for extensive molecular dynamics simulations. Of particular interest is the degree to which differences in the BDT–Au interactions give rise to significant differences in the structure of the BDT SAM. We use formulations for the BDT–Au interaction similar to those in the UFF. For example, when BDT molecule is on the top site of gold (1 1 1) surface (see Fig. 7(c)), the bond stretching, bond angle bending, and bond torsion correspond to Au–S8, Au–S8-C4, and Au–S8-C4-C3 (Au–S8-C4-C5 is also considered by dividing the force constant by a factor of two). For BDT molecules adsorbed on the bridge and the threefold hollow sites, we introduce a pseudo-atom that represents the geometric site center (SC) of the bridge or hollow sites. The bond stretching, bond angle bending, and bond torsion in the on-bridge case correspond to SC–S8, SC–S8-C4, and SC–S8-C4-C3 (SC–S8-C4-C5) (see Fig. 7(d)). There is a second bond torsion introduced: Au–SC–S8–C4. This term determines the bending direction of BDT molecules relative to the orientation of Au sites. Interactions of BDT molecules with all the other non-bonded Au atoms are treated as van der Waals interactions, as discussed in Subsection 4.1.

The functional forms of the BDT–Au potentials and values for the force constants are given elsewhere [7,8].

4.3. Molecular simulation algorithms

Now that all of the necessary force fields have been specified, we are able to perform molecular dynamics (MD) and Monte Carlo (MC) simulations of BDT SAMs on Au(111). Based on our preliminary calculations, for our initial simulations we have not simulated self-assembly directly, but have assumed that we have a fully populated (defect-free) SAM, and then performed MD on the resulting SAM. As shown in Fig. 8, the MD simulation box consists of the unit cell along the x- and y'-directions (where y' is the local skew axis) replicated five times along each of these directions. This is a two-dimensionally rhombic box containing 100 BDT molecules on Au (1 1 1) surface. The geometric parameters of the unit cell are \( a = b = \sqrt{13}a_\text{Au} = 10.38 \, \text{Å}, \) and \( \theta = 60^\circ \). The gold substrate is composed of three layers of static Au atoms with each layer containing 325 atoms. In Fig. 8, only the top layer of gold atoms and adsorbed sulfur atoms are shown, with four BDT molecules (one on the top site and the other three on the bridge sites) and 13 top-layer Au atoms in each unit cell. Periodic boundary conditions are implemented in the x and the skew y'-directions. Owing to the stiffness of the molecule (the benzene

![Fig. 8. The rhombic simulation box of BDT–Au system. The inset parallelogram shows a unit cell. Open circle: gold atoms; solid circle: sulfur atoms. Three kinds of bridge sites, marked by 0°, 60°, and 120° lines are also shown in the figure.](image-url)
ring remains close to planar at all times) as well as the small molecular weight of the hydrogens compared to the other atoms in the simulation, we have developed a two-level multi-time-step MD algorithm, known as a double r-RESPA (reversible reference system propagator algorithm) scheme [56]. The derivation of this algorithm, based on a Trotter decomposition of the Liouville operator, is provided elsewhere [8]. Compared to a naive implementation of MD, in which the time step would be reduced to capture accurately the fastest motion, our implementation of the double r-RESPA is 20 times faster. In addition, we have to take into account the long range Coulombic forces. Details of this are provided elsewhere [8]; to summarize, for efficiency we use three-dimensional Ewald sums with a correction term for the plane-wise summation of forces. This is known as the EW3DC method [58], and it is considerably more efficient than a two-dimensional Ewald sum method.

4.4. MD simulation results

In this section, we report some representative MD simulation results. Fig. 9 shows a snapshot of the simulation, confirming visually the herringbone structure we expect to see based on the earlier preliminary simulation results and scattering experiments of BT on Au(1 1 1) [47]. In the top panel of Fig. 10, we exhibit the normalized distributions of Au–S bond stretching for the top and bridge sites and for the two basis sets, QMC1 and QMC2. The results of QMC3 for stretching and bending on the top site are also shown in the figure. The deviations of the QMC3 from the QMC2 distribution is due to the different DFT functionals, and these are at least comparable to those inflicted by the unconverged basis of smaller size (QMC1). Our research indicates that these deviations could be even larger for the bridge site, but this require further studies and will be shown in detail elsewhere [7].

There is a substantial difference between the issues of convergence with a choice of basis and with a choice of the DFT functionals. While the former case can be controlled self-consistently by increasing the size of basis, the quality of the functionals for each considered case can be judged only by comparison with experiment. Thus, the QMC2 results are consistent with prior MD calculations [48] on similar molecules interacting with the Au(1 1 1) surface and these would be our best "guess". In principle, the scattering of the MD results due to various DFT functionals represents the inherent uncertainty of the theory, and decreasing of this uncertainty imposes a new challenge for the more accurate force field determination. This is a cross-cutting problem in the nano-system modeling (as also shown in Fig. 5 for transport calculations of Section 3), and needs to be properly addressed through improvement of the computational quantum chemistry methods for treatment of the meso-size molecular systems.

Fig. 9. The packing structure of BDT monolayer on Au(1 1 1) surface. (a) Stick representation. The structure exhibits a herringbone pattern clearly visible along approximately 120° direction. (b) Atoms shown in space-filled mode based on van der Waals radii. Bright yellow: S; deep yellow: Au, grey: C; white: H.
While it is currently difficult to apply more advanced methods than mean-field approaches (as discussed in Section 2), adequate attention should be paid to development of the DFT functionals

Fig. 10. The normalized distributions of Au–S bond stretching (a, b), bending (c, d) and torsion (e, f). The dashed lines are the normalized Boltzmann distributions solely determined by the corresponding potentials. The characters "l", "s", and "p" represent results from large B, (QMC2), small A, (QMC1), basis sets with functional A, and from large basis, B, (QMC3), with functional B, in the DFT calculations of the potentials. Data averaged over 120,000\(\Delta t\) with \(\Delta t = 0.1fs\). (a, c, e) top site, (b, d, f) bridge site.
which are appropriate for the metal–organic molecule combinations present in considered systems.

The Boltzmann factors for the corresponding potentials are also shown. There are several observations to make concerning these results. First, the basis set size has considerably impact on the location and breadth of the peak in the distribution; second, the impact of intermolecular forces is not very great on these distributions, since the measured distributions do not deviate to a large degree from the Boltzmann factors. This is not unexpected, as bond potentials are typically large in magnitude and typically constrain bond lengths quite severely; however, we do note there is evidence in all cases of the BDT molecule being shifted slightly away from the surface. For the bond bending and torsion distributions, shown in the middle and bottom panels of Fig. 10, the impact of intermolecular forces is greater than on the bond stretch. We now consider the global molecular orientations, which can be described by three angles (see Fig. 7(b)): the tilt angle from the Au (1 1 1) surface normal, $\theta_g$; the azimuthal angle $\chi$, which defines the tilt direction of BDT molecules relative to the $x$-axis; and the twist angle $\psi_g$, which defines the rotation of benzene ring around the BDT molecular axis (which is 0° when the surface normal ($z$-axis) and benzene ring are in the same plane, i.e., in-plane tilting). These global geometric parameter distributions are shown in Fig. 11. It can be seen clearly that while the local bonding geometry may depend on the basis set, the global

![Fig. 11](image-url)
molecular orientations do not depend significantly on them. The peak differences in probability distributions are well within 15%. Both basis sets A and B give a tilt angle around 26°, which is comparable to that of BT molecules on Au(1 1 1) surface [47], and is also comparable to that of alkylthiols on Au(1 1 1) surface [57]. The azimuthal angle distribution has two peaks at χ = 0° and 60°, corresponding to the two tilt directions in the herringbone structure of BDT molecules. These two tilt directions, in fact, are basically along the two bridge Au directions of 0° and 60°, which can be also seen in Fig. 9(a). The twist angles, ψg, predicted from the two basis sets are approximately 95° (out-of-plane tilting), which is also comparable to that in experiment for BT molecules on Au(1 1 1) surface [47]. These ψg distributions are much similar to those local torsion distributions in Fig. 10 due to the rigidity of benzene rings in BDT molecules.

5. Conclusions

We focused in this paper on three basic themes necessary for implementing theoretical studies of molecular-electronics devices. We discussed the need for computing the structure of a single BDT and its surrounding environment on the same quantum-mechanical footing. We mainly employed the Gaussian basis DFT to affect this type of calculation. We also developed a tight-binding approach to study the conduction through the BDT molecule, as found that surface properties significantly affect the conductance. We found that the conduction results are significantly sensitive to both the lead Fermi energy and a choice of the DFT exchange-correlation functionals.

The preliminary molecular simulation results presented in this paper of benzenedithiolate (BDT) self-assembled monolayer on Au(1 1 1) surface demonstrate the feasibility of large-scale modeling of molecular electronics devices. Since accurate predictions of binding property at molecule–metal interface and molecular configuration are important to the further conductance and electron transport calculations, the developments of accurate force fields and highly efficient computational tools are crucial. Using the universal force field (UFF) [49,50], combined with BDT–Au bonding potentials developed from ab initio calculations [7], and appropriate molecular dynamics strategies [8], the structure of BDT molecules on gold surface were predicted and found to be consistent with those of experimental measurements for BT molecules on Au(1 1 1) surfaces. Further experiments are needed on BDT SAMs on Au(1 1 1) to confirm the MD predictions described in this paper. Perhaps the most interesting result from the MD simulations to date is that overall global structure is converging much faster with the basis size of the DFT calculations than the details of the structure. Still, a special care is indicated for choice of the DFT functionals, which effect might be more difficult to control even for the global structural properties.

The multi-scale modeling assumes close mutual interaction between the MD simulations and transport calculations. Although we have not yet achieved this level of synergism between MD and transport calculations, this remains our long-term goal. In our work to date, reviewed in this paper, we have attempted to highlight some of the solutions and shed light on some of the problems that need to be resolved before the transport, MD and quantum chemistry modeling may merge into a consistent “iterative scheme”.

While global properties are very important for our understanding of SAMS, controlling the details will likely influence our future ability to use SAMs for computational devices. Suppose one wants a device with one-billion switches. Those switches may, in some calculations, need to perform tasks simultaneously. Such a collective task would be less efficient if the fluctuations from the average desired behavior are large. Understanding how to control the fluctuations will almost certainly require investigations of the detailed molecular structure and true multi-scale modeling will become necessary. For example, MD simulations in regions of SAM where fluctuations are small may need to be coupled to time-dependent DFT simulations in regions where fluctuations are large. Such marriages of the classical and quantum mechanical will require major breakthroughs in our modeling capabilities. We may also need to
address the role that quantum mechanics plays beyond the DFT level. In this paper, we confined the discussions to DFT calculations. Yet, DFT is limited to a description of ground-state properties. How to self-consistently include excited states into the conduction problem? This question will require significant research in the future.

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