Breakdown voltage and linear temperature drift in a single-molecule junction

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Abstract: Using first-principles calculations based on density functional theory combined with the non-equilibrium Green’s function approach, the transport behaviors of a single-molecule junction formed by benzenedithiol connected to gold electrodes are investigated. The breakdown voltage for the model of benzenedithiol plus gold electrodes is 0.7 V, which is close to the experimental value. A linear response between the conductance and temperature (known as linear temperature drift) is found in the molecular device, which indicates that it could be used to maintain the stability of molecular circuits. Meanwhile, input and output with the same accuracies would be useful for designing multi-level circuits, which would be used to improve the resolution ratio in analog-to-digital converters. The present findings indicate that benzenedithiol-based single-molecule junctions would be promising functional units for molecular sensors.

Keywords: conductivity behavior; linear temperature drift; breakdown voltage

1. Introduction

Because of the potential applications in electronic devices, the properties of single molecules connected to macroscopic electrodes have been studied intensively [1–11], and this research field—known as molecular electronics [12]—is one of the most exciting. The use of individual molecules as functional units in electronic devices has been reported for decades [1,10,11,13–22]. However, although molecular-scale currents have been reported in some molecular junction systems [8,23–27], considerable challenges remain in fabricating molecular devices with high yield, room-temperature operability, and low energy consumption [12].

Single-molecule transport behavior is very important for the further development of molecular electronics, and transport behaviors that depend on temperature and bias voltage are useful for distinguishing among conduction mechanisms [12,28,29]. The relationships between molecular conductance and (i) temperature and (ii) bias voltage have been investigated [8,10–12,15,20,26,30–32], and the molecular conduction mechanism has been classified into two distinct categories, i.e., tunneling and thermal activation. As the formulas for the conduction mechanism show, the former is not temperature dependent, while the electrical responses of the latter are [12,33]. The relationship between conductance and temperature is yet to be determined, and to investigate it and the breakdown voltage, we have built device models based on benzenedithiol (BDT). In this work, the transport behaviors are calculated using first-principles calculations based on density functional theory (DFT) and the non-equilibrium Green’s function (NEGF) approach as implemented in the NanoDCAL software.
The results of our investigations are close to the experimental results when the breakdown voltage is introduced into the BDT [36,37]. In addition, we find a linear response between the conductance and temperature (known as linear temperature drift (LTD) [38]) around room temperature. In molecular circuits, this LTD could reduce the errors of signal modulation [39] and so could be used to control the stability of the circuits. Meanwhile, because the input and output signals are both linear, the output signal would be as accurate as the input signal. In electronic measurements, the input signal could be amplified and processed as the output signal; this could avoid nonlinear processing and amplifying and could be used to improve the resolution ratio of analog-to-digital converters (ADCs) [40]. Our findings suggest that BDT-based single-molecule junctions could be used as thermo-sensitive units in molecular sensors.

2. Methods and Models

In the numerical calculations, the double-zeta polarized atomic orbital basis is selected for calculating all physical quantities, and the Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) is used for the exchange and correlation functional [41]. The atomic core electrons are described by Troullier–Martins pseudopotentials [42], and the valence electrons are fully treated. The kinetic cutoff energy is set as 80 Hartree, and self-consistent calculations are considered to have converged when every element of the density matrix is less than $10^{-4}$ Hartree. In the linear response regime, the conductance ($G$) is obtained from the Landauer formula $G = G_0 T(E_F)$, where $T$ is the transmission coefficient, $E_F$ is the Fermi energy, and $G_0 = 2e^2/h$ is the quantum conductance [43].

![Figure 1. Model containing left electrode, right electrode, and central/scattering region.](image)

The device model has three parts: (i) the central scattering region, (ii) the left electrode, and (iii) the right electrode (Figure 1). The central scattering region—which is modeled with DFT within the NEGF framework—includes a few layers of each electrode and is illustrated by the green box in Figure 1. Because sulfur binds strongly with noble metals [44], gold (Au) is selected for the electrodes. Some research has shown that a single BDT molecule connected with Au atoms along the [100] or [111] direction could form high or low conductance, respectively [44,45], so we select Au [100] for connecting the single BDT molecule in our model. In this work, the electrodes are quasi-one-dimensional Au wires with $3 \times 3$ cross section, composed of periodic units repeating along the [100] direction. The repeating sub-unit consists of seven layers that alternate between containing four and five Au atoms. In addition, the left and right electrodes are identical and extend to infinity in the left and right directions, respectively, and having the same left and right electrodes results in symmetric buffer layers on the left and right sides of the central region; see Figure 1 for details. The buffer regions allow for a smooth transition from the electronic density and potential in the periodic electrodes to those in the molecule [42]. The Au crystal lattice constant is used so that the buffer layers act as continuations of the electrodes. The buffer region includes four layers of the electrodes attached to the
adatoms of the BDT. During the calculations, the coordinates of the atoms in the electrodes are fixed as the Au lattice constant 4.078 Å, and we select the Au–S bond length as 2.20 Å [17,46].

3. Results and Discussion

To investigate the breakdown voltage, we calculated the current with the bias voltages for the above structures. The current versus the bias voltage (at 300 K) is presented in Figure 2, which shows that (i) the current increases with increasing bias voltage, which is consistent with the experimental results when the bias voltage is less than 0.7 V [36,37], and (ii) the current fluctuates when the bias voltage exceeds 0.7 V. This behavior is explained as (i) the current would increase with the bias voltage when the bias voltage is small [37], and (ii) the current is inconsistent with the experimental results when the bias voltage exceeds 0.7 V in our calculation because it does not consider that there is a breakdown voltage between the two electrodes when the bias voltage is sufficiently high as implemented in the NanoDCAL software [47]. Nevertheless, the experimental results show that the current increases sharply when the bias voltage is increased to 1.0 V; this behavior is explained as the nonlinear response between the current and bias voltage in a dominant position [36,37]. Therefore, we reason that the breakdown voltage of our model is 1.0 V, and we use this method to obtain a bias voltage that is lower than the experimental result. Therefore, we expect the bias voltage to affect other physical properties when we use this model to study those properties.

![Figure 2. Current versus bias voltage.](image)

The relationship for conductance versus temperature (Figure 3) indicates that the conductance decreases with increasing temperature. These results show the conductance depends on both bias voltage and temperature. Therefore, the main conduction mechanism for the BDT system should be the thermally activated one [12], which includes thermionic emission and hopping conduction [12,33]. The current density \( J(V,T) \) corresponding to the thermionic emission is expressed as [12]

\[
J \propto T^2 \exp \left( -\frac{\Phi - q\sqrt{qV/4\pi d}}{kT} \right)
\]

where \( J \) is the current density, \( T \) is the temperature, \( \Phi \) is the effective barrier, \( q \) is the electron charge, \( V \)
is the bias voltage, \( \varepsilon \) is the dielectric constant, and \( k \) is the Boltzmann constant.

**Figure 3.** Conductance versus temperature.

When the temperature is held constant, \( J(V,T) \) for thermionic emission becomes [33]

\[
J \propto \exp(\sqrt{V}) \quad (2)
\]

It is well known that the current \( I \) satisfies \( I = JS = VG \), where \( S \) is the effective cross section and \( V \) is the bias voltage. As the devices are fabricated, the effective barrier, electron charge, dielectric constant, and Boltzmann constant are constants. When the temperature is held constant, the relationship between the conductance and the bias voltage for thermionic emission simplifies to

\[
G \propto \frac{S \exp(\sqrt{V})}{V}
\]

The above equations indicate that the main conduction mechanism for the BDT system is thermionic emission. It is well known that the current density does not increase monotonically with increasing bias voltage, which is mainly because of the breakdown voltage that exists in any device. To understand how the bias voltage affects the thermionic emission, we discuss the relationship among the bias voltage, the current density, and the conductance in the case of thermionic emission. Equation (1) shows that the current density increases with increasing bias voltage at constant temperature, which is consistent with the experimental results of Najarian et al. [48]. Furthermore, neither Equation (1) nor Equation (2) can explain how the current density changes with the thickness of the molecular layer [48], the latter being a typical characteristic parameter that is determined by the device. The value of the breakdown voltage for a molecular device is related to the molecular length [48] and the elements in the molecule [33]. If the molecule is fabricated into a device, then the effective section, the molecular length, and the proportion of elements are constants, and the device has inherent fundamental attributes that determine the breakdown voltage [48,49]. Figures 1 and 2 show that the current fluctuates when the bias voltage exceeds 0.7 V, which indicates that the breakdown voltage is \( \sim 0.7 \) V in our model [37].

To find the relationship between conductance and temperature, the bias voltage is held constant, as are the effective barrier height, the electron charge, the Boltzmann constant, and the dielectric constant. Based on Equation (1), we obtain the formula as a partial differential equation, i.e.,
\[
\frac{\partial G}{\partial T} \approx (2T + a) \exp(-a/T)
\] (3),

where \( a = -q\sqrt{4\pi\varepsilon d/k} \) is a constant. In molecular junctions, the barrier width corresponds to the molecular length, and the barrier height can be approximated by the energy offset between the electrode Fermi level and the nearest molecular orbital [50]. The ratio of curvatures between two different temperatures is given as

\[
\eta = \frac{\frac{\partial G}{\partial T}}{|T_1|} = \frac{2T_1 + a}{2T_2 + a} \exp\left[\frac{a(T_1 - T_2)}{T_1 T_2}\right]
\] (4).

Based on experimental results [51], under zero bias voltage and at around room temperature, we obtain \( \eta \approx 1 \), which indicates that the conductance–temperature (C-T) curvature is constant, thereby suggesting a linear response between conductance and temperature. Therefore, we regard the C-T relationships as being approximately linear, i.e., \( G = -\sigma T \), where \( \sigma \) is a constant that represents the slope. From experimental results [2], we estimate \( \sigma \) as being of the order of \( 10^{-10} \), which is the same order of magnitude as our calculated result.

During the circuit design and fabrication, the LTD must be considered, and to gain insight into thermionic emission, we investigate the C-T relationship, which for a single-molecule junction based on BDT is presented in Figure 3. This shows that at around room temperature, the conductance decreases linearly with increasing temperature under low bias voltage, and this linear C-T relationship results in input–output (I-O) with the same accuracies [52]. This property is important for assuring the equivalent precision of I-O in multilevel signal systems and could be used to improve the resolution ratio in ADCs and the precision of sensors [53,54]. In ADCs, the resolution ratio is important for ensuring that digital circuits can provide clear photographs and videos. Furthermore, the linearity of the C-T relationship agrees well with the energy-saving principle.

4. Conclusions

Using the DFT–NEGF approach, the conductance for a BDT molecule with Au junctions was investigated. The transmission indicated that the breakdown voltage is ~0.7 V, which is lower than that in experiments, and the main conduction mechanism is thermionic emission. Also, LTD was found in the molecular device, indicating that I-O would have the same accuracies; this shows that a BDT molecule with Au junctions could be used to improve the resolution ratio in ADCs. The present findings indicate that BDT-based single-molecule junctions would be promising functional units in molecular sensors and multi-level circuits.

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