



# Negative differential resistance induced by the Jahn–Teller effect in single molecular coulomb blockade devices



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## ABSTRACT

Using valence bond theory in combination with a master equation technique, we have investigated the electron transport properties of benzene-based coulomb blockade devices. The results show that the benzene molecule undergoes a Jahn–Teller distortion when ionized, which lifts the state degeneracy. The lifted degenerate states couple differently to the left and right electrodes, leading to negative differential resistance. This type of negative differential resistance involves the Jahn–Teller effect and symmetry-breaking, which provides a way to design coulomb blockade devices with negative differential resistance behavior.

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## 1. Introduction

Single electron coulomb blockade effects in nanoscale structures (e.g. quantum dots) have been studied for the last few decades because of the potential application in three-terminal electronic devices [1–3]. Such three-terminal devices are usually called single electron transistors (SETs). Due to the large charging energy required to add a unit charge to the device, electrons are only allowed to pass through the device one by one (or a few by a few), which gives a new way of controlling and probing the behavior of single conduction electrons. Such devices have been used to manipulate single electron spin [4], and as a spectroscopic tool for revealing higher electronic excitations [1,5] and vibrational states [6,7].

Recently, SETs have been successfully scaled down to the molecular level – the single molecular SET [8–10]. The experimental success has prompted a wide range of theoretical studies on single molecular SETs, including studies on negative differential resistance (NDR) [11–19] and quantum interference effects [20,21]. The first NDR effect of SET devices was reported in 2003 [11]. In 2007, Muralidharan and Datta [12] reported a generic current blockade model for SET devices: the asymmetric coupling of some molecular states to the left and right electrode can cause the NDR effect. Two independent groups, Migliore and Nitzan [17] and Leijnse et al. [16], confirmed how charge localized in the redox state, which is essential to asymmetric coupling and will eventually lead to NDR. Leijnse also suggested how to obtain the

desired charge localization by side-group substitution. However, there are more general ways of introducing asymmetric coupling: Schultz et al. [14] carefully investigated the interplay of Jahn–Teller vibration modes and degenerate electronic states, which would lift the electronic state degeneracy and introduce two new states that couple differently to the left and right electrodes and eventually lead to NDR. Kaasbjerg and Flensberg [18] studied how the image charge effect can introduce a similar splitting effect and trigger NDR. Both studies indicate that breaking of the molecular symmetry is essential to the NDR effect. In this study, we studied the electron transport behavior of benzene-based SETs taking into consideration the symmetry-breaking effect.

## 2. Model and computational method

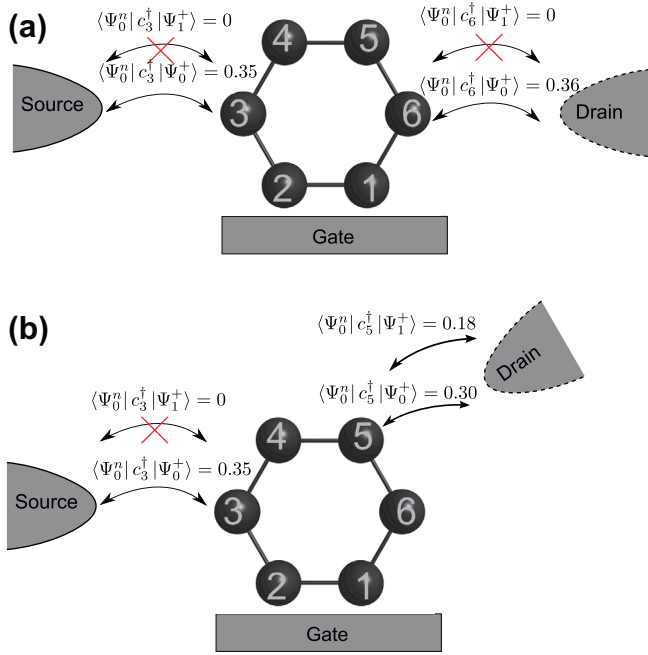
Fig. 1 shows the structures of benzene SETs with para and meta configurations: the molecule bridges the source and drain electrodes and its electrostatic energy can be adjusted by a gate electrode. The system is described by the Hamiltonian

$$H = H_M + H_{\text{lead}} + H_T, \quad (1)$$

where  $H_M$  denotes the molecular Hamiltonian. In the regime dominated by coulomb blockade, molecular-electrode coupling is sufficiently weak that the molecule can be reasonably characterized by a set of energy eigenstates  $|N, i\rangle$ . Generally,  $|N, i\rangle$  is a many-body state, where  $N$  denotes the number of electrons in the molecule and  $i$  represents the possible  $N$ -electron state. There are a number of ways to obtain the many-body molecular states, such as direct diagonalization of semi-empirical Hamiltonians [11,18], the molecular orbital configuration interaction (MO–CI) [22], and re-constructing

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**Fig. 1.** Illustration of the benzene SET in (a) para configuration and (b) meta configuration. The calculated transition matrix elements among  $\Psi_0^n$ ,  $\Psi_0^+$  and  $\Psi_1^+$  states of both configuration are provided for comparison.

from Kohn–Sham density functional theory orbitals [16]. In the present work, we chose valence bond (VB) theory [23,24] to calculate the molecular states. VB theory is a quantum chemistry *ab initio* method [25] and uses the same philosophy as molecular orbital (MO) theory: expressing the molecular state as a linear combination of Slater determinants, which are antisymmetrized products of single-body electron orbitals. Most MO-based methods use orthogonal molecular orbitals as elements of Slater determinants. In contrast, the VB method uses localized molecular orbitals (LMOs), which are not necessarily orthogonal. A general VB function for the molecular state  $|N, i\rangle$  is

$$|N, i\rangle \equiv \Psi = \sum_k c_k \Phi_k, \quad (2)$$

where  $\Phi_k$  is determined by VB configurations.

For the molecule-electrode coupling  $H_T$ , a reasonable assumption is that only the two LMOs that are closest to the electrodes have non-vanishing coupling to the continuum of electron states in the electrodes, and other coupling terms vanish due to large spatial distances. Thus,  $H_T = \sum_k (t_{mk} c_m^\dagger c_k + h.c.) + \sum_p (t_{np} c_p^\dagger c_n + h.c.)$ , where  $c_m^\dagger$ ,  $c_n^\dagger$  and  $c_k$ ,  $c_p$  are operators of the corresponding source lead and drain lead LMOs, respectively.

The leads are simply described as electron reservoirs:  $H_{\text{lead}} = \sum_k \epsilon_k c_k c_k^\dagger + \sum_p \epsilon_p c_p^\dagger c_p$ . The focus of the current work is on how the intrinsic molecular properties affect electron transport, while other effects caused by the electrodes, such as the image charge effect [18] and the band width effect, are not discussed.

The transition matrix elements between two different molecular states differing by a single electron in the presence of  $H_T$  can be obtained by lowest-order perturbation theory. Using the left electrode as an example, then electron transport

$$\Gamma_{N,i;N-1,j}^L = \gamma^L |\langle N, i | c_m^\dagger | N-1, j \rangle|^2 \quad (3)$$

and hole transport

$$\Gamma_{N,i;N+1,j}^L = \gamma^L |\langle N, i | c_m | N+1, j \rangle|^2, \quad (4)$$

where  $\gamma^L$  characterizes the coupling strength between the molecule and the left electrode. The weight of the transition matrix element

by the electrode Fermi distribution function gives the transition rate:

$$W_{N,i;N-1,j}^L = \Gamma_{N,i;N-1,j}^L [1 - n_F(E_N - E_{N-1} - \mu_L)], \quad (5)$$

and

$$W_{N,i;N+1,j}^L = \Gamma_{N,i;N+1,j}^L n_F(E_{N+1} - E_N - \mu_L), \quad (6)$$

where  $n_F$  denotes the Fermi–Dirac distribution and  $\mu_L$  is the chemical potential of the left electrode. If the bias voltage is symmetrically applied, the chemical potentials of the leads are shifted by  $\mu_L = E_f - eV_{\text{bias}}/2$  and  $\mu_R = E_f + eV_{\text{bias}}/2$ . Here, the equilibrium Fermi energy is chosen to be equal to the molecular Mulliken negativity defined as  $\mu_0 = (E^{N+1} + E^{N-1} - 2E^N)/2$ . In real experiments,  $\mu_0$  will be strongly influenced by the electrode material and dimensions.

Therefore, the rate equation of the transport process is written as

$$\dot{P}_i^N(t) = \sum_{j,\alpha} [W_{N,i;N-1,j}^\alpha P_j^{N-1} + W_{N,i;N+1,j}^\alpha P_j^{N+1} - (W_{N-1,j;N,i}^\alpha + W_{N+1,j;N,i}^\alpha) P_i^N], \quad (7)$$

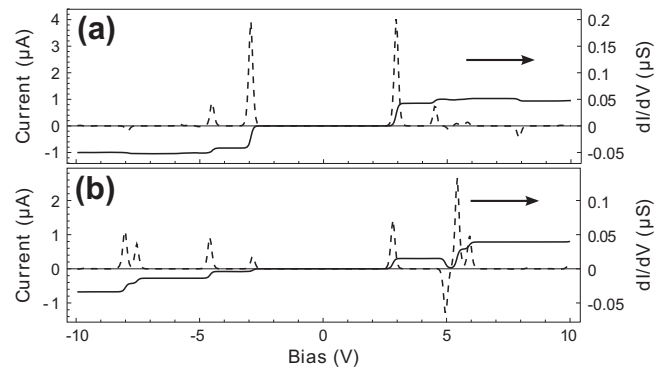
where  $P_i^N$  is the occupation probability of state  $|N, i\rangle$  and  $\alpha = L, R$ . The steady state solution (time-independent, i.e.  $\dot{P}_i^N = 0$ ) gives the measurable current in the real device operation. Along with the normalization constraint  $\sum_{N,j} P_j^N = 1$ , the steady state current is obtained by

$$I = -\frac{e}{\hbar} \sum_{N,i,j} (W_{N+1,j;N,i}^L - \Gamma_{N-1,j;N,i}^L) P_i^N. \quad (8)$$

The existence of the gate electrode only effectively modifies the molecular static potential, i.e., a substitution of  $E_N \rightarrow E_N - \beta N e V_g$ ,  $\beta$  is the gate coupling constant.

### 3. Results and discussion

Fig. 2 shows the curves of calculated current and differential conductance versus bias voltage. Each step in the  $I/V$  curve indicates the activation of one new transport channel. The figure is perfectly symmetric relative to the bias voltage in the para configuration (Fig. 1(a)), but strongly asymmetric and shows a noticeable NDR effect in the meta case (Fig. 1(b)). Asymmetry and the NDR effect are more clearly shown in the charge stability diagram (Fig. 3). From Fig. 3(b), NDR occurs in a wide range of gate voltages (0.9–3 eV) and bias voltages (1–5 eV). Furthermore, there is a negligible NDR effect in the para attached SET at sufficiently high voltages (Fig. 3(a)). For example, in the  $dI/dV$  curve at  $V_g=1$  eV the device is driven out of the coulomb blockade diamond at  $V_{\text{bias}}$  around 3 eV (also see Fig. 4(b)), and after spending a short period of



**Fig. 2.** Calculated current (solid lines) and differential conductance (dashed lines) as a function of the applied bias voltage: (a) the para configuration and (b) the meta configuration. The gate voltage is set to  $V_g = 1$  V

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