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Electronic conduction in a model three-terminal molecular transistor

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Abstract
The electronic conduction of a novel, three-terminal molecular architecture, analogous to a heterojunction bipolar transistor, is studied. In this architecture, two diode arms consisting of donor–acceptor molecular wires fuse through a ring, while a gate modulating wire is a π-conjugated wire. The calculated results show the enhancement or depletion mode of a transistor on applying a gate field along the positive or negative direction. A small gate field is required to switch on the current in the proposed architecture. The changes in the electronic conduction can be attributed to the intrinsic dipolar molecular architecture in terms of the evolution of molecular wavefunctions, specifically the one associated with the terphenyl group of the modulating wire in the presence of the gate field.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

With the past four decades of continued miniaturization of the complementary metal-oxide-semiconductor (CMOS) transistors, the density of active devices in integrated circuits has essentially followed the so-called Moore's law [1], according to which the number of components per integrated function doubles every 18 months. According to the International Technology Roadmap for Semiconductors (ITRS) the CMOS technology will reach a 18 nm node with 7 nm physical gate-length in a field-effect transistor (FET) by 2018 [2]. Further miniaturization of the CMOS feature size will likely face a roadblock due to the fundamental physical limits on the device size imposed by the laws of quantum mechanics obeyed by matter at nanometer-scale. Such an anticipated end of the Moore's curve [1], combined with recent advancements in instrumentation and experimental techniques to probe materials at molecular and nano-scale have attracted a great deal of attention in emerging research materials [2], such as organic and bio-molecules as active device elements. In a single molecule, electronic charge can be modulated either by electrical field or by chemical effects, thereby opening up the possibility of their use as active elements in electronic devices. For example, a two-terminal molecular architecture consisting of a donor (D)–bridge (B)–acceptor (A) can show a significant rectification in current (I) under the applied bias voltage (V). Experimentally, many prototypes have been demonstrated using single molecules in electronic devices [3–9] since the first theoretical study of a unimolecular diode by Aviram and Ratner [10].

The most challenging and difficult goal of molecular-scale electronics has been the realization of a three-terminal molecular transistor, which can switch current across two arms by an external electric field modulation through the third arm of a single molecule. Switching effects in architectures consisting of hybrid molecular diodes, where tunnel current through the molecule is modulated by chemical gating, has been demonstrated recently [11], although the underlying theory is not yet established.

There have also been reports of three-terminal devices using C_{60} fullerene molecules [12, 13], carbon nanotubes [14, 15], organic self-assembled monolayers [16], organic molecules such as benzene-1,4-dithiolate [17, 18], and transition metal coordination complex [19], in which the source–drain current is controlled by voltage through a physical electrode in contact with the molecule.

In this paper, we report the results of a first-principle quantum mechanical study of a novel, three-terminal

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architecture which is analogous to the heterojunction bipolar transistor (HJBT). In this architecture, two diode arms consisting of donor–acceptor molecular wires fuse through a ring and a base or modulating wire is a π-conjugated wire. We note that it has recently been demonstrated that substitution by electron donating (D) or electron withdrawing (A) groups can effectively tune the electronic behavior of organic molecules and either lead to a simple shift of the electron transmission or to a more complex resonance effect [20]. In the present study, we explore the possible means of combining both D and A substitutions to control the functionality of the molecular transistor. The design of this unimolecular transistor further allows us to have a strong electrostatic coupling between the molecule and the gate, but a relatively weak coupling between the molecule and the source/drain electrode which is highly desirable in a three-terminal transistor architecture.

The diode characteristics of a DBA wire was focus of our recent study [21] where the intrinsic dipole of the molecule was shown to determine its diode-like behavior. The larger the polarization of the system under an applied field, the more effective the electrical rectification. The essence of the design of the proposed unimolecular transistor is to utilize the flexibility of molecular engineering to modify the electronic conducting channels (i.e. orbitals) of the molecular system and to magnify their response under an applied gate potential. There are three unique features in the proposed three-terminal architecture: (i) paring of p- and n-type functional units in a single molecule to introduce frontier orbitals for electron transport; (ii) unipolarity along the gate direction ensuring a strong coupling to the gate; and (iii) base molecule intervention in the evolution of molecular orbital wave characters to enhance electron transmission.

In the following section, we will give details of the three-terminal transistor and the method used for calculations of electrical characteristics of the device. The current (I) versus bias voltage (V) curves obtained under the gate voltage (V_g) are given in section 3.1. The results are discussed in terms of the transmission functions in section 3.2–3.3 and summary of the paper is given in section 4.

2. Computational details

The model three-terminal molecular transistor, shown in figure 1, consists of two diode units ABD and DBA where the donor (D) and acceptor (A) moieties are derived from 1,3-diaminobenzene and 1,2,4,5-tetracyanobenzene, respectively. A π-conjugated phenyl ring was used as the bridge (B) between the two diode structures, ABD and DBA. The bridging phenyl ring (B) is also covalently bonded to the π-conjugated terphenyl molecule, referred to here as the interconnect (IC), which essentially serves as the molecular gate. Thus the three-terminal transistor is modeled in analogy with the HJBT, architecture inherited from the microelectronic device designs of transistors. The molecule is symmetric along the source–drain direction (having a zero dipole component), while asymmetric in the gate direction (with a large dipole component). Our model architecture is likely to translate the internal conducting states with respect to the pseudo-Fermi level of the system [22]. The application of a gate voltage (V_g) across the IC arm is expected to influence the electronic energy levels of the system and thus the current response of the transistor across the source (emitter) and drain (collector) arms.

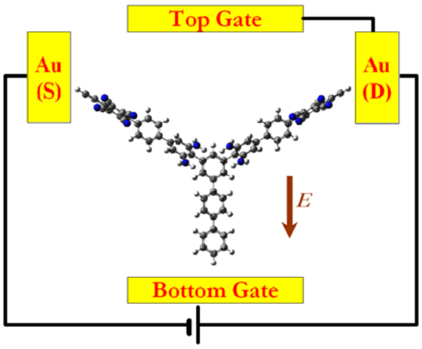

Figure 1. Schematic illustration of the setup of a unimolecular transistor ABD-IC-DBA in measurement. C atoms are in gray spheres, N atoms in blue (dark gray) spheres, H atoms in small white spheres, and Au electrodes in yellow (light gray) slabs. In this setup, a positive bias is applied upon the source (S) and the drain (D) termini, where the drain has a higher potential. A top-and-bottom double gate is applied generating a uniform positive gate field E pointing downward in the same direction as that of the intrinsic dipole moment of the entire molecule.

The commonly used gold is taken to be source and drain electrodes. In order to eliminate the interfacial effects introduced by thiol groups, we used the C≡CH group as contacts to both termini. The molecule is considered to be coupled capacitively to the top and the bottom gates and the leakage current from the gates is considered to be negligibly small. The positive and negative gate fields are defined with respect to the direction of the dipole moment of the molecule. Thus a positive field is parallel to the dipole moment while a negative field has the opposite direction. Direction of a positive gate field pointing downwards is shown in figure 1.

The electron transport calculations were performed in two steps. The first step was an electronic-structure calculation on the extended molecular complex instead of ‘an isolated molecule’. It was performed in the framework of the density functional theory (DFT) with B3LYP functional form [23, 24] and the LanL2DZ basis set [25]. The extended molecular complex is the core scattering region of the molecular transport system, composed of the molecule and atomic-scale gold contacts in the form of atomic chains coupled to the source and drain electrodes. The geometrical configuration of the molecular complex obtained at the zero field was used for all the calculations, assuming that the external electric filed employed does not significantly distort the molecular configuration.

An external electric field is applied in simulation of the applied gate potential. The correspondence between the electric field and the gate potential is listed in table 1 assuming a linear electrostatic potential drop and a distance of about 32 Å between the top-and-bottom plate gates. The change in the total charge of the molecule is found to be negligible in the gate range considered here since the molecule electrochemical

Table 1. The extended molecular complex under a series of applied gate fields: total energy, dipole moment, and energy of the HOMO level (due to the D moiety) with respect to the pseudo-Fermi level $\Delta(\varepsilon_D - E_F)$. The separation between the top-and-bottom gates in the device architecture is taken to be 32 Å.

Field (10^8 V m^{-1})	Gate potential* (V)	Energy (Hartree)	Dipole (Debye)	$\Delta(\varepsilon_D - E_F)$ (eV)
−9.25	−3	−3733.596 496	0.43	−0.88
−6.17	−2	−3733.596 802	2.16	−0.76
−3.08	−1	−3733.597 518	3.90	−0.65
0.00	0	−3733.598 644	5.64	−0.53
3.08	1	−3733.600 182	7.39	−0.41
6.17	2	−3733.602 135	9.15	−0.30
9.25	3	−3733.604 504	10.92	−0.18

potential remains confined in an energy range where the molecule has a very low density of states (DOS). The effect of the capacitance due to the charge redistribution under a non-zero gate field is taken into account via a self-consistent calculation. The Fock matrix F and overlap matrix S (corresponding to a non-orthogonal set of wavefunctions) from the Kohn–Sham solution of the extended molecule electronic-structure calculation for each gate potential were then used for electron transport calculations based on the Green's function-based Landauer–Büttiker formalism [26–28]. Therefore, the Stark effect due to the electric field inside the molecule induced by the applied gate potential is included explicitly in the calculation.

The tunneling current (I) as a function of the applied bias (V) in such a device can be expressed as

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} \mathrm{d}E\, T^{V_g}(E, V)[f(E-\mu_1) - f(E-\mu_2)] \quad (1)$$

where μ_1 and μ_2 are the electrochemical potentials in the source and drain electrodes under an external bias V, $f(E)$ is the Fermi–Dirac distribution function. For instance, a positive bias lowers the electrochemical potential at the drain by eV

$$\mu_1 - \mu_2 = eV \quad (2)$$

and gives rise to different Fermi–Dirac distribution functions at the source and the drain

$$f(E-\mu_1) = \frac{1}{e^{\frac{E-\mu_1}{k_B T}} + 1}$$
$$f(E-\mu_2) = \frac{1}{e^{\frac{E-\mu_2}{k_B T}} + 1} \quad (3)$$

which is the driving force for generating the source–drain current, I. $T^{V_g}(E, V)$ is the electron transmission function at a gate potential of V_g. The transmission function, T^{V_g}, is a measure of the strength of electron transmission through the various allowed channels, which in the present case are the participating one-electron molecular levels coupled to the metallic reservoirs (emitter/source and collector/drain). It is assumed here, that the molecule is in contact with metals at two ends, referred to as the left and right. $T^{V_g}(E, V)$ can be calculated from a knowledge of the corresponding molecular energy levels and their coupling to the metallic contacts under a gate potential of V_g by

$$T^{V_g}(E, V) = \mathrm{Tr}\left[\Gamma_L^{V_g}(E, V) G^{V_g}(E, V) \Gamma_R^{V_g}(E, V) G^{V_g +}(E, V)\right] \quad (4)$$

where, the trace runs over all the orbitals and $\Gamma_{L(R)}^{V_g}$ are twice the imaginary part of the self-energy matrices $\sum_{L(R)}^{V_g}$ [29, 30]. In this way, the contact resistance is explicitly included.

It is important to note here that one treats the source–drain and gate voltages separately by representing them as double perturbations, i.e. the total Hamiltonian of the system in the presence of the external electric fields due to V_d and V_g is represented as,

$$H^T = H^0 + H' + H'' \quad (5)$$

where H^0 is the Hamiltonian in the absence of external perturbations, and H' and H'' represent perturbations due to applied V_d and V_g, respectively.

3. Results and discussion

3.1. Tunneling current—enhancement/depletion gating effect

Unlike the conventional CMOS transistor, a unimolecular transistor consists of a single molecule integrated between source, drain and gate. In this architecture, the effect of an applied field (potential difference) between the source and the drain acts as a perturbation to polarize the charge distribution and mix one-electron energy levels. The effect of an additional perturbation along the gate terminal is, therefore, to simply add to the perturbation due to the many body effects. Of course, the overall change in the spatial distribution of the electron charge and energy levels depends on the direction of the additional perturbation. In the present case, for example, the perturbation due to the electric field along the gate terminal is symmetric with respect to source and drain, but asymmetric in the gate direction. Thus, the effect of the perturbation, especially in low-field regime, due to the source–drain bias on the electronic structure is symmetrical and less important for affecting electron transport than the effect of the gate potential. Therefore, in the low-bias regime as considered here, the change in the molecular spectra with respect to the source–drain bias is ignored [31, 32].

The variation of the current as a function of the applied source–drain voltage is calculated at a gate field ranging from −9.25 to 9.25 (10^8 V m^{-1}). Taking the top-to-bottom gate distance to be ∼32 Å, the maximum gate potential (V_g) considered here is about 3 V. The calculated current (I) versus drain voltage (V_d) curves under various gate potentials are plotted in figure 2. It is interesting to note that for a low V_d (<1.4 V) and without a gate field ($V_g = 0$), the current is calculated to be negligibly small. However, as the bias (V_d) increases, the current (I) tends to increase dramatically due to the resonant tunneling. An enhancement in current is observed for the positive gating as shown in figure 2, but depletion in current for the negative gating (not shown in figure 2).

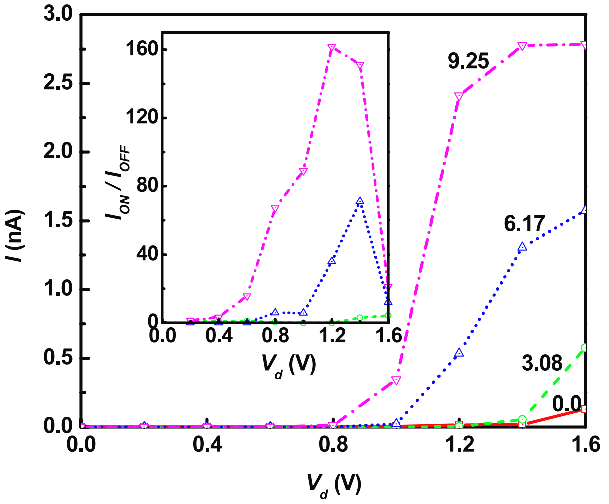

Figure 2. I–V_d curves for the molecular system under an applied positive gate field (labeled in the figure next to each curve in unit of 10^8 V m^{-1}) in the range of 0.0–9.25 × 10^8 V m^{-1}. The calculated modulation factors (the current ratios I_{ON}/I_{OFF}) are also plotted in the inset for each field.

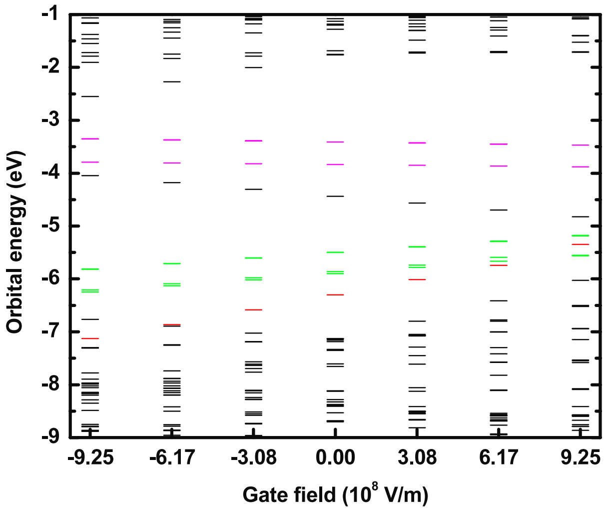

Figure 3. Evolution of molecular spectra of the Au_2-ABD-IC-DBA-Au_2 extended molecule under a series of applied gate field. The highest occupied orbitals due to the donor group (D) are in green (light gray); the lowest unoccupied orbitals due to the acceptor group (A) are in magenta (gray); the highest occupied orbital due to the IC unit is in red (dark gray).

Under positive gate fields, we find a gap showing a Coulomb blockage region, and then a sudden increase in the I–V_d curves. The current gets saturated when the V_d is further increased. The observed Coulomb blockade is due to the weak coupling (no chemical bonding) between the molecule and the electrodes, where the molecule essentially behaves as an isolated quantum dot. The sudden increase and saturation of the current arises due to the resonant tunneling of molecular one-electron energy levels. More details on the specific molecular orbitals of the system are discussed in the following sections.

We observe that increasing the gate electric field (E_g) from 0 to 9.25 × 10^8 V m^{-1} switches the molecule from a non-conducting state (OFF) to a conducting state (ON). The modulation of current (the ON/OFF ratio, defined as the current ratio with/without a gate field) also increases dramatically with an increase in the gate potential (V_g), as shown in the inset of figure 2. The I_{ON}/I_{OFF} value reaches a maximum of about 70 for an applied gate field of 6.17 × 10^8 V m^{-1} ($V_g \approx 2$ V) and 160 for a gate field of 9.25 × 10^8 V m^{-1} ($V_g \approx 3$ V) at $V_d \approx 1.4$ V. The gate electric field value of 3.08 × 10^8 V m^{-1} ($V_g \approx 1$ V) does not appear to be sufficient to switch the molecule from the OFF to the ON state. These values are significant for a transistor working in an enhancement mode. Under negative fields, the total current is reduced, suggesting a depletion working mode for the device.

3.2. Molecular orbital energy shift—polarization effect

It is instructive to analyze and establish the electronic-structure mechanism of the current switching observed in our calculations on the model single-molecule transistor. It was noted in our previous study [22] that the intrinsic dipole moment and the induced polarization of the molecule due to the applied external perturbation plays an important role on quantum transport in molecular systems. Therefore, it is useful to examine the relationship of dipole moment, polarization, and energy-level mixing with the switching behavior noted in our model transistor. We note that the model system has a zero dipole moment along the source–drain direction due to symmetry. However, the polarity along the gate direction, produces a permanent dipole moment along the z direction, which ensures the strong electrostatic coupling between the molecule and the gate terminal. Furthermore, the presence of two acceptor–donor moieties bonded in a quasi-linear chain in the architecture enhances its polarizability.

In order to gain further insight, we list in table 1 the total energy and change in the electronic structure in terms of the dipole moment under a varying gate field. As can be seen from the table, the dipole moment in this molecule varies significantly and almost linearly with the external electric field. The positive field enhances the dipole moment and lowers the energy of the system, while the negative field reduces the dipole moment and increases the total energy.

The evolution of molecular orbital eigenvalue spectra with applied gate potential is plotted in figure 3. The molecular orbitals due to the donor (D) group on the HOMO side and the acceptor (A) group on the LUMO side are the frontier orbitals near the pseudo-Fermi level, E_F. We note that the D–A orbital gap narrows with a positive field (enhancement mode) and opens up under a negative field (depletion mode). It should be mentioned that the pure metallic orbitals from Au in the near-E_F region (LUMO and LUMO + 1, which are 2-fold degenerate) do not contribute to the conductance of the molecule.

In the low-bias regime considered, contribution to the molecular conductance mainly comes from the D orbitals (from the HOMO side), because the A orbitals are far above the Fermi level. The polarization effect induced by the positive gate potential moves the HOMO energy levels upward

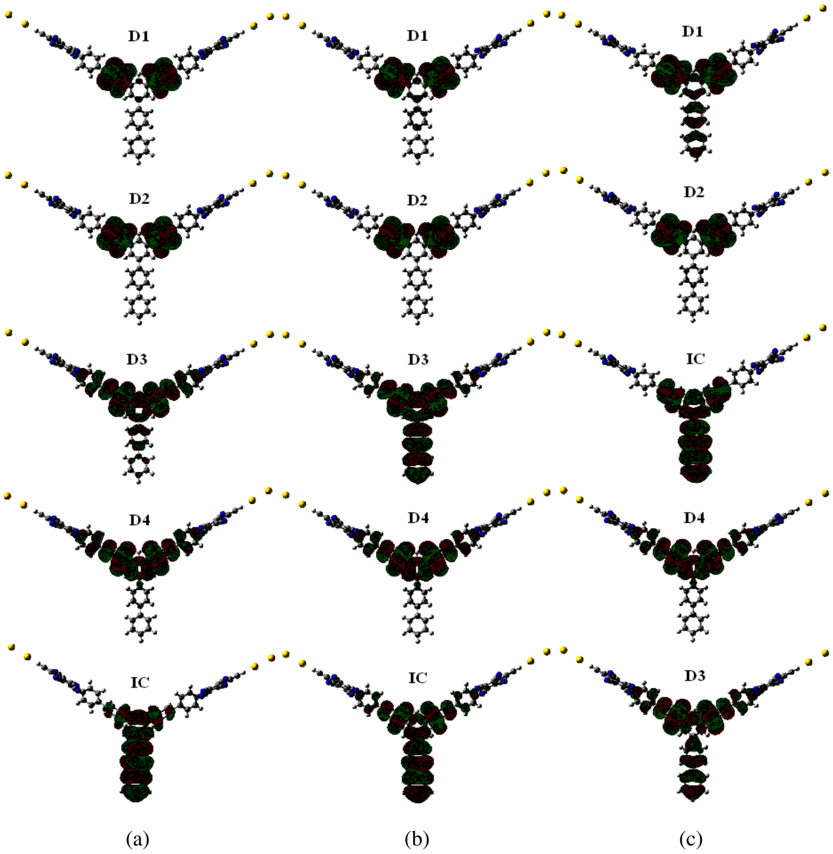

Figure 4. Evolution of molecular orbitals of the Au_2-ABD-IC-DBA-Au_2 extended molecule under a series of applied gate field: (a) 0.0 V m^{-1}, (b) 6.17×10^8 V m^{-1} and (c) 9.25×10^8 V m^{-1}. The highest occupied orbitals mostly due to the donor group (D) at a zero field are labeled in sequence of D1, D2, D3 and D4. The highest occupied orbital due to the IC unit is labeled as IC.

(table 1), bringing it closer to the pseudo-Fermi level relative to the cases when no or smaller gate potentials are applied. This partially accounts for the switching effect calculated in the I–V_d curve upon the application of a positive gate potential. Conversely, the application of a negative gate potential moves the molecular energy levels lower and away from the pseudo-Fermi level, thus increasing the value of V_d required for reaching the molecular resonant states. Thereby a suppression of current is observed for all negative gate fields.

3.3. Evolution of molecular orbital wave characters—base molecule intervention effect

Analysis of the molecular orbitals reveals a significant evolution of the wavefunctions with the varying gate field in the range considered, as shown in figure 4. The IC (terphenyl) orbital near E_F (highlighted in red in figure 3) lies below the four highest occupied donor (D) orbitals labeled as D1, D2, D3, and D4, respectively, at zero gate field. The IC orbital moves further down as the magnitude of the negative field increases, but floats up when a positive field is applied, thereby mixing significantly with the D orbitals, especially the antisymmetric wavefunctions D1 and D3, at a field of 6.17×10^8 V m^{-1}. However, at a field of 9.25×10^8 V m^{-1}, the IC orbital lies above the second pair of the D orbitals (D3 and D4).

The transmission peaks due to the second pair of D orbitals (D3 and D4) appear to make the most contribution to the electron conduction (figure 5), and correspond to the steep increase in current. On the other hand, the peaks due to the first pair of D orbitals (D1 and D2) are rather small because of their association with the strong localization of the molecular wavefunctions.

A relatively strong transmission peak appears at −0.6 eV due to a large mixing between IC and D3 orbitals at a gate field of 6.17×10^8 V m^{-1}, suggesting that the terphenyl unit enclosed in the molecule acts more than just a passive capacitor electrostatically coupling the molecule to the gate. Its intrinsic character plays an active role in the enhancement gating of the three-terminal molecular transistor considered.

It is obvious that the IC orbital has a strong influence on the wavefunctions of the D orbitals which determine the electron transmission property of the model molecular transistor. In general, the electric field along the IC chain direction seems to mix the IC orbital wavefunction with the D wavefunctions and also moves its energy above the lowest D orbital. This introduces additional delocalization of the wavefunction of the frontier orbitals, thus enhancing the current and lowering the switching voltage. It should also be noted that a strong terphenyl-ring character may also work as an electron trap due to its highly delocalized character, thus reducing the magnitude of current as can be seen from the small

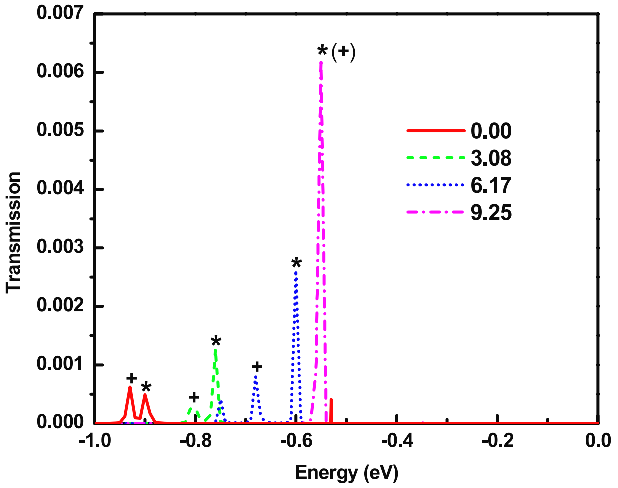

Figure 5. Transmission functions for the ABD-IC-DBA molecular system under a series of applied gate field (labeled in the figure in unit of 10^8 V m^{-1}). The transmission peaks due to the second pair of the highest occupied D orbitals D3 and D4 are labeled by $*$ and $+$, respectively. The pseudo-Fermi level is aligned to zero.

transmission peak in figure 5 which is associated with the IC orbital.

4. Summary

In summary, we have proposed a single-molecule model to realize the enhancement/depletion mode of a three-terminal transistor by applying a gate field along the positive/negative direction. A small gate field is required to switch on the current, with the ON/OFF ratio reaching 160 at $V_g \approx 3$ V and $V_d \approx 1.4$ V. The asymmetric spatial structure leads to a sensitive coupling to electric field produced by the applied gate potential. The source–drain current is affected not only by the magnitude, but also by the direction, or the sign of the gate potential. A positive gate field enhances the current, while a negative field reduces it. The evolution of wavefunctions, specifically the one associated with the terphenyl group in the presence of the gate-coupling as well as the shift in molecular orbital energies appear to contribute to the enhancement of the source–drain current in the three-terminal transistor considered. The present study establishes an electronic-structure mechanism for current switching in a model single-molecule transistor. Although the model structure is analogous to a solid-state HBJT, the orbital mixing and shift in levels modulated by the gate field, acting as a second perturbation to the overall perturbed wavefunction, appear to be generally applicable to single-molecule molecular transistors. Thus the present study provides a physical foundation in terms of the molecular architecture and electronic structure to design, synthesize and realize single-molecule three-terminal transistors. It would be interesting and useful to examine the proposed mechanism by experimental measurements on real systems.

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References

[1] Moore G E 1965 *Electronics* **38** 114
[2] *International Technology Roadmap for Semiconductors* 2007 http://www.itrs.net/reports.html (web access on Oct. 16, 2008)
[3] Martin A S, Sambles J R and Ashwell G J 1993 *Phys. Rev. Lett.* **70** 218
[4] Bumm L A, Arnold J J, Cygan M T, Dunbar T D, Burgin T P, Jones L II, Allara D L, Tour J M and Weiss P S 1996 *Science* **271** 1705
[5] Metzger R M *et al* 1997 *J. Am. Chem. Soc.* **119** 10455
[6] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 *Science* **278** 252
[7] Chen J, Reed M A, Rawlett A M and Tour J M 1999 *Science* **286** 1550
[8] Piva P G, Dilabio G A, Pitters J L, Zikovsky J, Rezeq M, Dogel S, Hofer W A and Wolkow R A 2005 *Nature* **435** 658
[9] Kumar M J 2007 *Recent Patents Nanotechnol.* **1** 51 and references therein
[10] Aviram A and Ratner M A 1974 *Chem. Phys. Lett.* **29** 277
[11] Jäckel F, Watson M D, Mllen K and Rabe J P 2004 *Phys. Rev. Lett.* **92** 188303
[12] Park H, Park J, Lim A K L, Anderson E H, Alivisatos A P and McEuen P L 2000 *Nature* **407** 57
[13] Yu L H and Natelson D 2004 *Nanotechnology* **15** S517
[14] Tans S J, Verschueren A R M and Dekker C 1998 *Nature* **393** 49
[15] Martel R, Schmidt T, Shea H R, Hertel T and Avouris Ph 1998 *Appl. Phys. Lett.* **73** 2447
[16] Luo K, Chae D-H and Yao Z 2007 *Nanotechnology* **18** 465203
[17] Di Ventra M, Pantelides S T and Lang N D 2000 *Appl. Phys. Lett.* **76** 3448
[18] Rashkeev S N, Di Ventra M and Pantelides S T 2002 *Phys. Rev.* B **66** 033301
[19] Yu L H, Keane Z K, Ciszek J W, Cheng L, Tour J M, Baruah T, Pederson M R and Natelson D 2005 *Phys. Rev. Lett.* **95** 256803
[20] Perrine T M, Smith R G, Marsh C and Dunietz B D 2008 *J. Chem. Phys.* **128** 154706
[21] He H, Pandey R and Karna S P 2008 Asymmetric currents in a donor (D)–bridge (B)–acceptor (A) single molecule—revisit of the Aviram–Ratner diode arXiv:0809.3268
[22] Lang N D and Solomon P M 2005 *Nano Lett.* **5** 921
[23] Becke A D 1993 *J. Chem. Phys.* **98** 5648
[24] Lee C, Yang W and Parr R G 1998 *Phys. Rev.* B **37** 785
[25] Frisch M J *et al* 2003 *GAUSSIAN03* (Pittsburgh, PA: Gaussian)
[26] Landauer R 1989 *J. Phys.: Condens. Matter* **1** 8099
[27] Büttiker M 1986 *Phys. Rev. Lett.* **57** 1761
[28] Datta S 1995 *Electronic Transport Properties in Mesoscopic Systems* (Cambridge: Cambridge University Press)
[29] Tian W, Datta S, Hong S, Reifenberger R, Henderson J I and Kubiak C P 1998 *J. Chem. Phys.* **109** 2874
[30] He H, Pandey R and Karna S P 2007 *Chem. Phys. Lett.* **439** 110
[31] Heurich J, Cuevas J C, Wenzel W and Schön G 2002 *Phys. Rev. Lett.* **88** 256803
[32] He H, Pandey R, Pati R and Karna S P 2006 *Phys. Rev.* B **73** 195311