Current rectification by asymmetric molecules:  
An ab initio study  
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(Dated: March 23, 2022)  
We study current rectification effect in an asymmetric molecule HOOC-C₆H₄-(CH₂)ₙsandwiched between two Aluminum electrodes using an ab initio nonequilibrium Green function method. The conductance of the system decreases exponentially with the increasing number n of CH₂. The phenomenon of current rectification is observed such that a very small current appears at negative bias and a sharp negative differential resistance at a critical positive bias when n ≥ 2. The rectification effect arises from the asymmetric structure of the molecule and the molecule-electrode couplings. A significant rectification ratio of ∼38 can be achieved when n = 5.  
PACS numbers: 85.65.+h, 73.63.-b, 36.40.-c  
I. INTRODUCTION  
Electronic transport properties of single molecule junctions have gained tremendous interest in recent years, since they may have a wide variety of important applications in future electronic components such as transistors, diodes and switches. With the advantages of experimental techniques, for example, scanning tunneling microscope and mechanically controllable break junction, measurement of the current through nanoscale systems is now allowed. Some interesting behaviors, such as highly nonlinear I-V characteristics, negative differential resistance (NDR) and electric switching behavior, are observed in various systems. Meanwhile, considerable amounts of theoretical work have been performed to study transport properties of molecular devices.  
Rectification, one of the most important functions in a traditional electronic component, has also been suggested and observed in molecular devices. Some mechanisms for rectification phenomena in these devices have been suggested. The first molecular rectifier was proposed by Aviram and Ratner in 1974 using D-σ-A molecules, where D and A are, respectively, an electron donor and an electron acceptor, and σ is a covalent “sigma” bridge(insulator). In this model, the inelastic electron transfer is more favorable from A to D, rather than in the opposite direction, thus current rectification happens. However, electrical rectification was observed experimentally only recently in Langmuir-Blodgett (LB) multilayers or monolayers of the molecule C₁₆H₃₃Q-3CNQ sandwiched between metal electrodes. The underlying mechanism, which was first considered to be a possible implementation of the Aviram-Ratner mechanism, is of somewhat different D-π-A type. Although the molecule does show rectification, it behaves as an anisotropic insulator rather than a conductor because of the long alkane tail C₁₆H₃₃. In fact, the current is of order 10⁻¹⁷A/molecule for the structure Al/C₁₆H₃₃Q-3CNQ/Al and 10⁻¹⁵A/molecule for the structure Au/C₁₆H₃₃Q-3CNQ/Au in Ref. The current is too small for practical applications. To achieve effective rectification with a reasonably conductive molecule, one should avoid using molecules with long saturated groups that may lead the molecules to be prohibitively resistive. It seems attractive to use relatively short molecules with certain end groups to allow their selfassembly on a metallic electrode’s surface. In Ref. transport measure-
a much wider region than in previous investigations in Refs. 14,20. It suggests another new mechanism of molecular rectification, where a single electroactive unit is positioned asymmetrically with respect to electrodes and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are positioned asymmetrically with respect to the Fermi level. For majority of the applied voltage drops on the longer insulating barrier, the conditions for resonant tunneling through the active level are different for different directions of the applied voltages on the two opposite polarities. A maximal rectification ratio 35 is expected with longer alkane chains $n = 10$ and $m = 2$, the current magnitude is still not ideal, with order $10^{-10} A$. Recently ideal rectification has been demonstrated in diblock oligomer diode molecules and single C$_{59}$N molecules. However, the current reported is still of the unsatisfactorily order $10^{-10} A$. In this work, we perform a systematic study on the transport properties of a single molecule HOOC-C$_{6}H_{4}$-(CH$_{2}$)$_{n}$ with sulfur end to together with four surface atom layers in the left electrode and three surface atom layers in the right electrode is chosen as the central scattering region, as indicated by two vertical white lines in Fig. 1. The structure of every molecule HOOC-C$_{6}H_{4}$-(CH$_{2}$)$_{n}$ with sulfur end is optimized via Hartree-Fock approximation in ArgusLab25,26,27,28, and the energy convergence of $10^{-10}$ kcal/mol has been achieved. The molecule-lead distance is fixed to be a constant for all the systems. The distance of the H-Al (from the left terminal hydrogen atom to the surface of Al electrodes) is 1.5 Å and the S-Al is 1.0 Å.

The calculations for transmission and Current-Voltage (I-V) characteristics have been performed using a recently developed first-principles package TranSIESTA-C, which is based on the nonequilibrium Green's function (NEGF) technique. The TranSIESTA-C, as implemented in the well tested SIESTA method, is capable of fully modeling self-consistently the electrical properties of nanoscale devices, which consist of an atomic scale system coupling with two semi-infinite electrodes as shown in Fig. 1. Such a nanoscale device is divided into three parts: left and right electrodes, and a central scattering region. In fact, the central region includes a portion of the semi-infinite electrodes. The external potential bias is included in the self-consistent calculation directly. Therefore, the effects of the bias voltage on the electronic structure of the system can be fully considered. Details of the method and relevant references can be found elsewhere21,22,23,24. In our actual calculations, the con-
vergence criterion for the Hamiltonian, charge density, and band structure energy is $10^{-4}$ and the atomic cores are described by normconserving pseudopotentials.

III. RESULTS AND DISCUSSIONS

Firstly, the equilibrium conductance as a function of the number $n$ of CH$_2$ has been studied and is presented in Fig. 2. We find that the conductance decreases exponentially as the number $n$ of CH$_2$ increases. The conductance is $0.15G_0$, $0.043G_0$, $0.0043G_0$, $0.00026G_0$ if the number of CH$_2$ $n = 0, 1, 2, 3$ ($G_0 = 2e^2/h$ is the conductance quanta). The similar exponential decrease of conductance with the length has been found for carbon chains.$^{29}$

The $I$-$V$ curves are plotted in Fig. 3 (the cases $n = 4, 6$ are not shown in this work). As shown in Fig. 3, the current takes a large value of order $\mu$A both at the negative bias and at the positive bias, When $n = 0$ and 1. When $n \geq 2$, interesting phenomenon are observed. The current through the molecule structure at the negative bias is increasing slowly irrespective of the bias voltage increase, as compared to the quick increase of the current with the increasing bias voltage in the positive bias case. When the bias is positive, the current reaches its maximum value at a bias, which is different for different $n$ systems. These are typical current rectification and NDR phenomena. A significant rectification ratio $\sim 38$ is found for the molecule system with the number of CH$_2$ $n = 5$ , and the current in the negative bias side is negligibly small. We note that, for every configuration, a strong NDR can be observed as the bias is positive. The NDR in our system may find potential applications as switches.

What are the underlying mechanisms for the current rectification and NDR in our molecule system? Why the current rectification can be observed only when the number of CH$_2$ exceeds 1? To answer these two questions, one need to know detailed information of the transmission spectra of such a system. For current rectification to occur, two essential conditions should be satisfied that the transmission resonance must be reasonably sharp and exists only at one vicinity side of the Fermi energy.$^{30}$ The transmission spectra $T(E)$ are plotted in Fig. 4 for

![FIG. 4: The transmission $T$ as a function of energy $E$ for $n = 0, 1$ and 2. For comparison, the transmission for $n = 2$ is magnified by 10.](Available upon request)

![FIG. 5: (color online) The LUMO and HOMO distribution on the molecule for $n = 0, 1$ and 5 respectively: (a) LUMO for $n = 0$, (b)HOMO for $n = 0$, (c) LUMO for $n = 1$, (d)HOMO for $n = 1$, (e) LUMO for $n = 5$, and (f)HOMO for $n = 5$.](Available upon request)

![FIG. 6: Transmission spectra, $T(E, V_b)$, for the $n = 5$ case. The two crossing dotted lines indicate the bias window.](Available upon request)
n = 0, 1 and 2 cases. We can see from Fig. 4 that the resonance is rather wide for n = 0 case and has a long tail near the Fermi energy. A direct comparison reveals that the resonance in the case n = 1 is wider than that in the case n = 0, but moves toward right. However, the resonance becomes much more narrow and can be seen only at the right side of the Fermi energy for the case n = 2. The reason is that, when n = 0, the sulfur atom is directly attached to the benzene, thus the orbitals of the lone electron pair of the sulfur are overlapped with that of the π electrons of the ring, resulting in molecular orbitals distributed almost over the ring and the sulfur. Such an observation is confirmed in Fig. 5(a), where both the LUMO and HOMO extend almost over the whole molecule. Since the sulfur is directly coupled to the electrode, the molecular orbitals are broadened. In the n = 1 case, the sulfur is separated from the ring by a single insulating -CH2- group. However, the separation is not large enough to prevent elongated π orbitals of sulfur and sp3 hybridization of carbon from direct overlapping, as seen in Fig.5(b) where the LUMO and HOMO still distribute almost over the whole molecule. As a result, the electronic level is still much broadened. Things changes when n = 2. Two insulating groups move the sulfur away from the ring by 4.09Å, so that the direct overlap between the sulfur and the ring wave functions is weakened, and the LUMO and HOMO do not distribute on the left (CH2)2 (which is not shown). That’s why rectification can be observed only for n ≥ 2.

To prove clearly the origin of rectification and NDR, we take the molecule HOOC-C6H4-(CH2)n as an example. When the molecule is coupled two Al electrodes, the calculation shows that the LUMO and Homo energies are 0.394eV, −2.896eV, respectively, consistent with the indications in the transmission spectra in equilibrium in Fig. 6. We can see from Fig.5(c) that the LUMO distributes over the HOOC and the carbon atoms in benzene ring, and the HOMO mainly on the sulfur atom. The electron has an accessible LUMO near the Fermi energy only of one electrode, the left electrode in the present work. This asymmetry leads to a significant current when the applied bias is positive and a negligibly small current in the negative case.

The calculated transmission spectra T(E, Vb) are presented in Fig.6 for different applied bias voltages from −1.5V to +1.5V with an interval 0.1V and a doubled interval within [−0.6,0.6]V. The dashed line represents the transmission spectrum in equilibrium. The current is obtained using the Landauer-Büttiker formula:

\[ I = \int_{µ_L}^{µ_R} T(E, V_b) dE \]

The bias window contributing to the current integral is indicated by two dotted lines in Fig.6. The transmission resonance in equilibrium appears on the right side of the Fermi energy, and its width is narrow, about 0.13 eV. With the increase of the positive bias, the resonance moves toward the bias window and makes contributions to the current. As a result, the current increases rapidly and reaches its maximum value at the bias 1.2 V. However, when the applied bias is negative, the resonance moves far away from the Fermi energy as the bias increases, and finally is pushed out of the bias window. It results in a negligibly small current. This is a typical phenomenon of current rectification. A notable rectification ratio of 38 can be observed at the bias 1.2 V. When the positive bias continues to increase, the transmission within the bias window is degraded in magnitude and width, leading to an NDR phenomenon.

IV. CONCLUSION

A system of HOOC-C6H4-(CH2)n is studied systematically using a first principles method based on NEGF. The equilibrium conductance decreases exponentially with the increase of n. Strong rectification effect is observed when n ≥ 2 and a significant rectification of ~38 is achieved from n = 5 for bias <1.2V. Irrespective of the number of CH2, a strong NDR can be seen under positive bias. A detailed analysis on the origin of rectification is given from the distribution of the HOMO and LUMO and from the transmission spectra at various bias.

This work was supported by the NSFC under Grant No. 10404010, the Project-sponsored by SRF for ROCS, SEM, and Scientific Research Fund of Jiangxi Provincial Educational department(112[2006]), and the Talent Fund of Jiangxi Normal University.

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1 C. Zhang, M. H. Du, H. P. Cheng, X. G. Zhang, A. E. Roitberg and J. L. Krause, Phys. Rev. Lett. 92, 158301; (2004) S. J. Wind, J. Appenzeller, and Ph. Avouris, Phys. Rev. Lett. 91, 053801 (2003)

2 Jens Koch, M. E. Raikh, and Felix von Oppen, Phys. Rev. Lett. 96, 056803 (2006)

3 Young-Woo Son, Jisoon Ihm, Marvin L. Cohen, Steven G. Louie, and Hyoung Joon Choi, Phys. Rev. Lett. 95, 216602 (2005)

4 Markus Büttiker and David Sánchez, Phys. Rev. Lett. 90, 119701 (2003)

5 S. de Haan, A. Lorke, J. P. Kotthaus, W. Wegscheider, and M. Bichler, Phys. Rev. Lett. 92, 056806 (2004)

6 Michael E. Flatt and Jeff M. Byers, Phys. Rev. B 53, 10536 (1996)

7 C. T. Black, M. T. Tuominen, and M. Tinkham, Phys. Rev. B 50, 7888 (1994)

8 A. Halbritter, Sz. Csonka, G. Mihaly, E. Jurdik, O. Y. Kolesnychenko, O. I. Shklyarevskii, S. Speller, H. van Kempen, Phys. Rev. B 68, 035417 (2003)

9 E. G. Emberly and G. Kirczenow, Phys. Rev. Lett. 91, 188301 (2003)

10 A. N. Andriotis, M. Menon, D. Srivastava and L. Cher-
11 S. Roche, Phys. Rev. Lett. 91, 108101 (2003)
12 A. Aviram and M. A. Ratner, Chem. Phys. Lett. 29, 277 (1974)
13 D. E. Feldman, S. Scheidl, and V. M. Vinokur, Phys. Rev. Lett. 94, 186809
14 I. I. Oleynik, M. A. Kozhushner, V. S. Posvyanskii and L. Yu, Phys. Rev. Lett. 96, 096803 (2006)
15 A. Troisi and M. A. Ratner, Nano Lett. 44, 591 (2004)
16 R. M. Metzger, Synth. Met. 137 1499 (2003)
17 R. M. Metzger, Synth. Met. 124 107 (2001)
18 C. Krzeminski, C. Delerue, G. Allan, D. Vuillaume and R. M. Metzger, Phys. Rev. B 64 085405 (2001)
19 B. Larade and A. M. Bratkovsky, Phys. Rev. B 66 165436 (2003)
20 J. Zhao, C. G. Zeng, K. D. Wang, G. W. Wang, J. L. Yang, J. G. Hou and Q. S. Zhu, Phys. Rev. Lett. 95 045502 (2005)
21 R. M. Metzger, J. Solid State Chem. 168, 696 (2002)
22 M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B 65, 165401 (2002)
23 J. Taylor, H. Guo, and J. Wang, Phys. Rev. B 63, 245407 (2001)
24 Taylor J, Ph. D. thesis, McGill University (2000)
25 J. Linnanto, and J. K. Tommola, J. Comput. Chem. 251, 123 (2003)
26 O. Moran, L. J. V. Galietta, and O. Z. Moran, Cell. Mol. Life Sci. 62, 446 (2005)
27 D. Walter, D. Neuhauser, and R. Baer, Chem. Phys. 299, 139 (2004)
28 D. Jansone, M. Fleisher, G. Andreeva, L. Leite, J. Popelis, and E. Lukevics, Chem. Heterocycl. Comp. 39, 1584 (2003)
29 For example, see C. C. Kaun and H. Guo, Nano Lett. 3, 1521 (2003)
30 J. Taylor, M. Brandyge, and K. Stokbro, Phys. Rev. Lett. 89, 138301 (2002)