First-principles study of the quasi-Fermi level splitting in ferrocene-based molecular junctions

Minsu Jeong, Jaeeun Kim, Ryong-Gyu Lee, Hyeonwoo Yeo, and Yong-Hoon Kim
Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Daejeon, 34141, Korea
e-mail: minsu.jeong@kaist.ac.kr

INTRODUCTION

While the splitting of quasi-Fermi levels (QFLs) represents a fundamental aspect in the finite-bias nonequilibrium operation of semiconductor devices [1], its atomic-level calculations remained a challenge due to the limitation in the standard approach combining density functional theory (DFT) and nonequilibrium Green's function (NEGF) formalisms. Another inherent shortcoming of the DFT-NEGF approach is its incapability of dealing with finite two-dimensional (2D) electrodes, because it requires semi-infinite electrode models. Both limitations can be overcome within the multi-scale constrained-search DFT (MS-DFT) formalism we recently developed [2,3]. In this report, we apply the MS-DFT formalism to ferrocene-based molecular junction sandwiched between metal and graphene electrodes [4,5], and analyze the transport properties of ferrocene.

MODELS & METHOD

Within the MS-DFT calculation for a semiconductor device, we assign the spatial origins of single-electron Kohn–Sham eigenstates within the junction system to the left electrode (L), channel (C), and right electrode (R) regions. Under the finite applied bias $V = (\mu_L - \mu_R)/e$, where μ_L and μ_R are the electrochemical potentials of L and R, respectively, the electrons in the C region are occupied by one group originating from L and right-traveling and the other group originating from R and left-traveling, resulting in QFL distributions within C [2].

RESULTS

In Fig.1, we modeled a ferrocene molecular junction system in contact with Au and graphene electrode. As shown in Fig.2, the junction shows the rectification operation due to the ferrocene formed an interface with graphene. Experimentally, the conductivity of junction increases/decreases depending on whether the Fe within the ferrocene undergoes reduction/oxidation, respectively [4,5]. In Fig.3 this charge transfer of Fe can be observed. Under a bias $V_{sd} = 1\,V$, Fe undergoes oxidation, resulting in low conductivity of the junction. As the bias decreases into $-1\,V$, the charge on Fe is depleted. It leads to increased conductivity in the molecular junction, so that the ferrocene junction exhibits diode operation. In Fig.4 and 5, the non-linear bias drop occurs at the gold-ferrocene and ferrocene-graphene junctions under positive and negative bias, respectively. This can be understood in terms of the hybridization of ferrocene with electrodes [3]. Under both biases, electrons are depleted from the HOMO state of ferrocene, effectively replacing the role of the gold/graphene electrode with its lower chemical potential. This depletion corresponds to the charge transfer of down/up state for $+1/-1V$ in Fig.3, respectively. At the graphene electrode under $V_{sd} = -1V$, a discrepancy arises between the electrochemical and electrostatic potential differences, with the applied electrostatic potential difference being smaller. This discrepancy is due to the quantum capacitance effect in graphene [3]. However, under positive bias, this quantum capacitance effect is absent. This occurs due to the hybridization of ferrocene with graphene, where ferrocene compensates for the lack of metallicity in graphene.

REFERENCES

[1] Shockley, W. & Read, W. T. Statistics of the Recombinations of Holes and Electrons, *Physical Review* **87**, 835-842 (1952).

[2] Lee, J., Yeo, H. & Kim, Y. H. Quasi-Fermi level splitting in nanoscale junctions from ab initio, *PNAS* **117**, 10142-10148 (2020).

[3] Kim, T. H., Lee, J., Lee, R.-G. & Kim, Y.-H. Gate- versus defect-induced voltage drop and negative differential resistance in vertical graphene heterostructures, *npj Computational Materials* **8** (2022).

[4] Jeong, H. *et al.* Redox-Induced Asymmetric Electrical Characteristics of Ferrocene-Alkanethiolate Molecular Devices on Rigid and Flexible Substrates, *Advanced Functional Materials* **24**, 2472-2480 (2013).

[5] Jia, C. *et al.* Redox Control of Charge Transport in Vertical Ferrocene Molecular Tunnel Junctions, *Chem* **6**, 1172-1182 (2020).

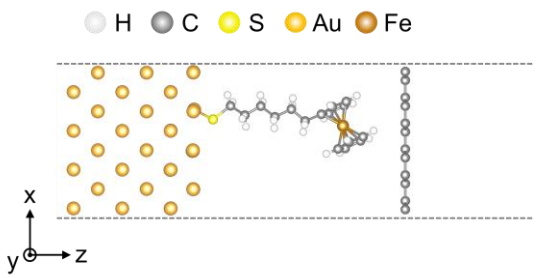

Fig. 1. Structure of ferrocenyl-alkanthiolate (ferrocene)-based molecular junction. We carried out MS-DFT calculations adopted the generalized gradient approximation PBE, double ζ-plus-polarization-level numerical atomic orbital basis sets, and the Troullier-Martins type norm-conserving pseudopotentials within the SIESTA software. The mesh cutoff of 200 Ry for the real-space integration was used. The k-point mesh was 3 x 3 x 1 Monkhorst-Pack grid.

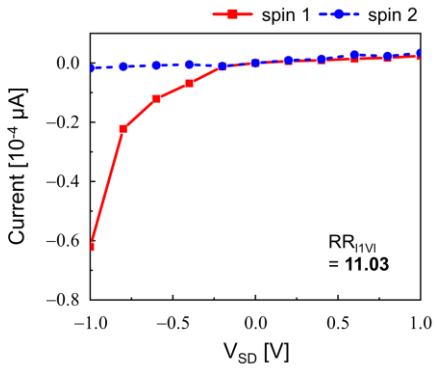

Fig. 2. The current–bias voltage (I-V) characteristics. calculated within MS-DFT. Red line with square and blue line with circles indicate the results corresponding to spin1 and spin2, respectively.

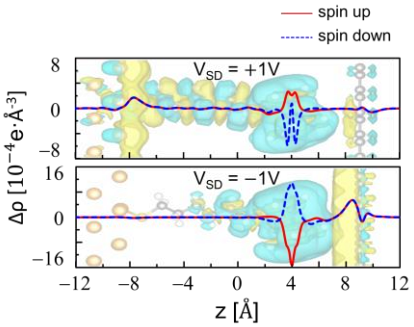

Fig. 3. The plane-averaged charge density differences or Landauer resistivity dipole $\Delta\rho$ for $V_{sd} = +1\,V$ (upper) and $V_{sd} = +1\,V$ (lower). It is defined as $\Delta\rho(r) = \rho^V(r) - \rho^0(r)$, where ρ^V and ρ^0 are the charge densities at the nonequilibrium and equilibrium conditions. Fe of the ferrocene locates at $z = 4$.

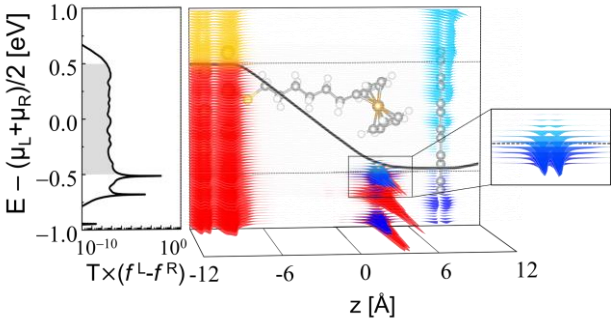

Fig. 4. Transmission, the non-equilibrium QFL profile and for $V_{sd} = +1\,V$ obtained from MS-DFT calculations. To account for the effect of the source-drain bias on electron transport, we multiply the transmission function by the bias window, $f^L - f^R$, which represents the difference in Fermi-Dirac distributions between the left and right electrodes. The red/blue color represents the electrons (occupied states, or QFL) originating from the left/right electrode, respectively. The orange and light blue color represent the unoccupied states. The red and blue peaks in the channel region (near $z = 4$) represent the states of ferrocene. The thin black dotted lines near $\pm 0.5\ eV$ indicate the chemical potential of source and drain electrode. The thick black line represents the plane-averaged bias-induced electrostatic potential change $\Delta\bar{v}_H$. It is defined as $\Delta\bar{v}_H(r) = \bar{v}_H^V(r) - \bar{v}_H^0(r)$, where $\bar{v}_H^V$ and $\bar{v}_H^0$ are the classical Hartree Coulomb potentials at the nonequilibrium and equilibrium conditions. The HOMO level is spin up/down for the -1/+1 V cases, respectively.

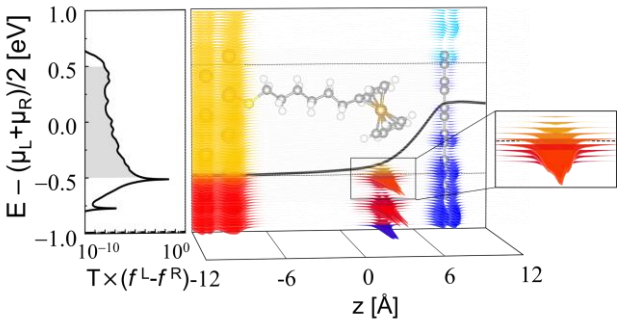

Fig. 5. Transmission, the non-equilibrium QFL profile and the plane-averaged bias-induced electrostatic potential change ΔV_H for $V_{sd} = -1\,V$ obtained from MS-DFT calculations.