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Origin of Negative Differential Resistance in a Strongly Coupled Single Molecule-Metal Junction Device

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A new mechanism is proposed to explain the origin of negative differential resistance (NDR) in a strongly coupled single molecule-metal junction. A first-principles quantum transport calculation in a Ferripyridine linker molecule sandwiched between a pair of gold electrodes is presented. Upon increasing the applied bias, it is found that a new *phase* in the broken symmetry wave function of the molecule emerges from the mixing of occupied and unoccupied molecular orbitals. As a consequence, a nonlinear change in the coupling between the molecule and the lead is evolved resulting in NDR. This model can be used to explain NDR in other classes of metal-molecule junction devices.

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The controlled transport of electrons in metal-molecule junctions has been an active field of research for the past decade [1], with an aim to find a possible solution to the miniaturization impasse that the semiconductor industry is currently facing. Researchers have already demonstrated conduction, rectification, and switching in metal-molecule junction devices [2–4]. Among all of these, the demonstration of a single-molecule switch with a negative differential resistance (NDR) feature [2] has drawn considerable attention in recent years. The NDR feature is described by an increase followed by a decrease in current (I) with the steady increase in applied bias (V). Since its realization [2], various groups have been working on this problem to unravel the *true* mechanism of NDR in a molecular junction, the understanding of which would revolutionize the field of molecular electronics [1]. Different mechanisms have been proposed to explain the observed NDR [2,5–7] in metal-molecule junctions. For example, in a *weakly coupled* junction, it is argued [5,8,9] that the narrow density of states (DOS) feature of the tip apex atom is responsible for the NDR. But in contrast it has been recently proposed [6] that the local orbital symmetry matching between the tip and the molecule is the cause of the observed NDR. In another example [2], the bias induced charging and conformational change of the molecule is suggested as a viable mechanism for inducing NDR. However, it should be noted that controversy still remains concerning whether the conformational change arising from the rotation of the ligand group [10] or from the rotation of the molecular group [11–13] within the molecular backbone is responsible for the observed NDR. Another possible model for NDR based on polaron formation was also proposed very recently [14]. Based on a simple mean-field theory it is suggested [14] that NDR is possible if the bias induced polaron formation shifts the energy level away from the window between the chemical potentials of the leads.

It can be seen from the above review that none of the mechanisms proposed thus far have stressed the importance of bias induced change in coupling between the molecule and lead. Bias induced relaxation of the molecular eigenstates will affect the coupling between the molecule and lead, which would have a measurable effect in altering the I - V feature. Furthermore, it is still controversial whether NDR is intrinsic to the molecule or junction dependent. Here, we propose a new consistent and unified model to explain the origin of NDR in a strongly coupled metal-molecule junction. It is found that a new *phase* in the broken symmetry wave function of the molecule arising from the mixing of occupied and unoccupied molecular orbitals upon increasing applied bias leading to a nonlinear change in the coupling between the molecule and lead is responsible for the observed NDR. Our calculation further reveals that, even in the presence of a symmetric junction at the molecule-lead local interface, the asymmetric channel coupling upon applied bias originating from the structural asymmetry within the molecule can produce an asymmetric I - V characteristic.

We have used a self-consistent *many body* approach to investigate the quantum transport properties of a Ferripyridine (FETP) linker molecule sandwiched between two gold electrodes (Fig. 1). The selection of an FETP molecule is prompted by the recent interest in organometallic molecules [15] in molecular electronics. Furthermore, an organometallic molecule exhibiting NDR behavior has been demonstrated very recently [6]. The electric field effect for each applied bias [16] is explicitly included in our calculation within a many body framework. The nonequilibrium Green function approach is used to calculate the quantum transport. Our calculation reveals asymmetry and NDR features with peak (I_p) to valley (I_v) current ratio (PVR) of 2.7 at both positive and negative bias. Even though the magnitude of calculated current differs between the positive and negative bias range, the

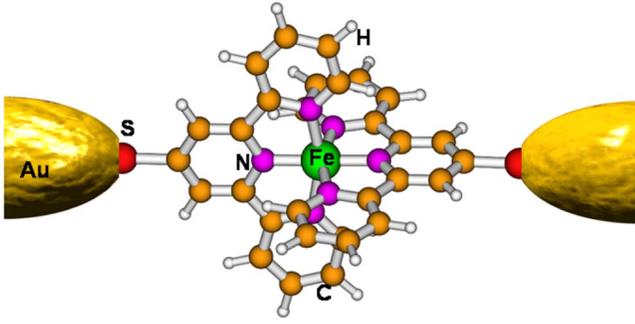


FIG. 1 (color online). Schematic of the strongly coupled single molecule (FETP)-gold junction.

$\frac{I_p}{I_v}$ remains about the same for both positive and negative bias.

In our calculation, we have used a real space approach in which the many body wave function is expanded in terms of a finite set of Gaussian atomic orbitals [17]. This allows us to partition the *open* molecular device structure into two regions of interest. The first is the *true* device region, which includes an optimized FETP sandwiched between two gold clusters of three atoms each, taken from the Au (111) surface with a terminal S atom at the threefold hollow fcc site [18] of the gold with S-Au distance of 2.45 Å. The second part is essentially the semi-infinite contact region, which is assumed to be unperturbed by the molecular adsorption. As exact exchange with dynamical correlation plays a key role in determining accurate energy spectra in density functional theory, and consequently the *I-V*, we have used *a posteriori* Becke's three parameter hybrid density functional approach (B3LYP) [17,19] for our calculation. The Los Alamos double zeta effective core potential basis set (LANL2DZ) [17], which includes the scalar relativistic effect, is used for the calculation of the nonequilibrium electronic structure. The nonequilibrium Hamiltonian $H(\varepsilon)$ of the true device region is calculated as [20] $H(\varepsilon) = H(0) + \vec{\varepsilon} \cdot \sum_i \vec{r}(i)$, where $H(0)$ is the equilibrium many body Hamiltonian; $\vec{\varepsilon}$ is the applied dipole electric field, and $\vec{r}(i)$ is the coordinate of the electron i . This approach allows us to explicitly obtain the true nonequilibrium energy spectra including the Stark shift. It should be noted that the convergence thresholds for energy, maximum, and root mean square electron density are set at 10^{-6} , 10^{-6} , and 10^{-8} a.u., respectively, to ensure tight convergence during the self-consistent calculation. Subsequently, we constructed the nonequilibrium Green function as $G(\varepsilon) = [E \times S - H_{\text{mol}}(\varepsilon) - \Sigma_l(\varepsilon) - \Sigma_r(\varepsilon)]^{-1}$, where $H_{\text{mol}}(\varepsilon)$ is the orthogonalized field dependent Kohn-Sham molecular Hamiltonian matrix obtained by suitable partitioning of $H(\varepsilon)$, E is the injection energy of the tunneling electron, and S is the identity matrix. $\Sigma_{l,r}(\varepsilon)$ are the self-energy functions [21,22] calculated from the bias dependent coupling matrices and the Green function of the Au lead. The latter is approximated from the 6s-band DOS at the Fermi energy of bulk Au [23] and kept fixed for

all bias points. The current in the molecular junction is calculated as [21,22] $I = \frac{2e}{h} \int_{\mu_1}^{\mu_2} T(E, V) [f(E, \mu_2) - f(E, \mu_1)] dE$, where $\mu_{1,2} = E_f \mp eV/2$; E_f is the equilibrium Fermi energy (-4.69 eV), f is the Fermi distribution function, $T(E, V)$ is the bias dependent transmission function [21,22], obtained from nonequilibrium G and Σ 's.

First we comment on our calculated *I-V* characteristic presented in Fig. 2. The current is symmetric for voltages up to $+0.4$ and -0.4 V. As the bias increases, the asymmetry takes over and the magnitude of current increases until it reaches a peak current of $-125.36 \mu\text{A}$ at -3.417 V and $142.496 \mu\text{A}$ at 3.484 V. Increasing the applied bias further on both the positive and negative bias range, the magnitude of current decreases and reaches a valley current of $-45.78 \mu\text{A}$ at -5.36 V and $51.69 \mu\text{A}$ at 5.36 V, revealing a clear NDR pattern. The PVRs in currents are found to be 2.74 and 2.76 on the negative and positive bias range, respectively. To corroborate the NDR patterns in *I-V*, we calculated the conductance dI/dV , which is plotted in Fig. 2. The negative values of the conductance in the positive and negative bias range clearly confirm the two peaks. In addition, we found another small negative value for conductance at -2.91 V. Examining the *I-V* curve, we found from -2.8 to -3.0 V, the current is almost constant with a very small $0.1 \mu\text{A}$ spike at -2.88 V. Since the bias range considered in this study is quite high, we included the incoherent scattering effect (ISE) due to electron-phonon (*e-ph*) coupling self-consistently within Büttiker's approach [21,24,25] and recalculated the current at -2.88 V as well as for the bias points around it. We found the small spike of $0.1 \mu\text{A}$ at -2.88 V disappeared. Inclusion of *e-ph* coupling at bias points -3.417 and -5.36 V gives I_p and I_v as -120.17 and $-52.21 \mu\text{A}$ with PVR of 2.30. The PVR value is found to be 2.34 for the positive bias range with the inclusion of ISE. Inclusion of ISE is found to reduce the current, but does not shift the peak or the valley position of the current. It is worthwhile to note that, when the explicit field dependent term is not included in $H(\varepsilon)$, the *I-V*

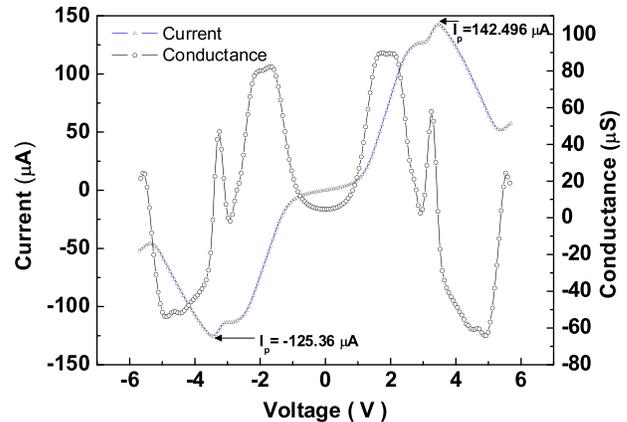


FIG. 2 (color online). Calculated current and conductance as a function of applied bias. I_p refers to the peak value for current.

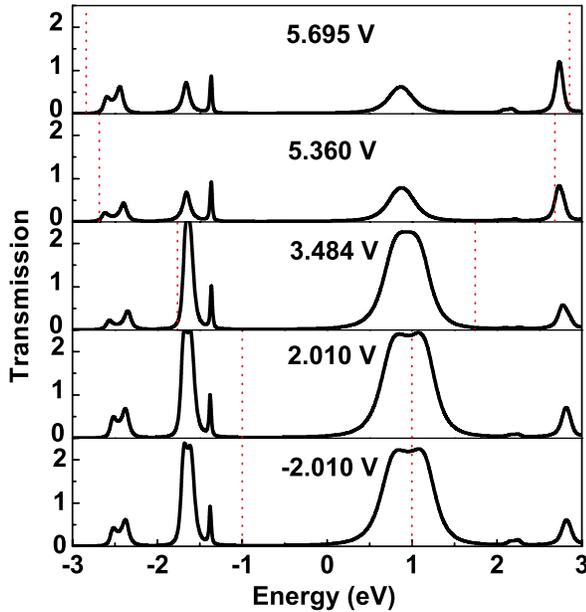


FIG. 3 (color online). Bias dependent transmission as a function of injection energy E . Fermi energy is set to zero in the energy scale; dotted lines in each panel represent the chemical potential window.

results do not reveal asymmetry or NDR effect, suggesting the importance of the self-consistent electric field dependent screening in inducing NDR.

To understand the origin of the asymmetry and NDR, we have calculated the $T(E, V)$ (Fig. 3) as a function of injection energy. For brevity, we have considered only five bias points. The higher current in the positive bias range ($80.42 \mu\text{A}$ at 2.01 V) than in the negative bias ($-74.69 \mu\text{A}$ at -2.01 V) can be understood by comparing the $T(E, V)$ for -2.01 and 2.01 V . The higher transmission around $\sim 1 \text{ eV}$ for 2.01 V (within the chemical potential window) as compared to -2.01 V explains the higher current at 2.01 V . Analysis of eigenvalues of the $H_{\text{mol}}(\epsilon)$,

and the DOS calculated from $G(\epsilon)$, suggest that the lowest unoccupied molecular orbital (LUMO) and LUMO + 1 (Fig. 4) contribute to the current at 2.01 and -2.01 V . No change in the eigenvalue spectrum of $H_{\text{mol}}(\epsilon)$ is found between 2.01 and -2.01 V . This suggests that the asymmetric channel coupling arising from the structural asymmetry within the molecule (dihedral angle between the terpyridine rings is 91.67°) is responsible for the asymmetry in I - V . Increasing the bias from 2.01 to 3.484 V (peak position), we found a decrease in the contribution of LUMO and LUMO + 1 due to a decrease in the transmission peak height at $\sim 1 \text{ eV}$. But, as the chemical potential window increases, the highest occupied molecular orbital (HOMO) and HOMO - 1 contribute to the transmission at $\sim -1.4 \text{ eV}$ and HOMO - 2 at $\sim -1.6 \text{ eV}$ resulting in a higher net transmission and current. Increasing the bias from 3.484 to 5.36 V (valley position), we found the contribution of LUMO and LUMO + 1 to transmission decreases significantly, as well as the contribution from HOMO and HOMO - 1, and HOMO - 2. This explains why we see less current at 5.36 V compared to 3.484 V , despite the contribution of additional channels HOMO - 3 ($\sim -2.3 \text{ eV}$) and HOMO - 4 ($\sim -2.5 \text{ eV}$) to transmission due to the increase in the chemical potential window. Increasing the bias to 5.695 V , we found the contribution of LUMO and LUMO + 1 decreases by a very small amount, but the contribution of additional channels LUMO + 2, LUMO + 3 ($\sim 2.1 \text{ eV}$), and LUMO + 4 ($\sim 2.8 \text{ eV}$) to transmission increases. Additionally, the contribution to transmission from HOMO - 3 and HOMO - 4 also increases, leading to a higher current at 5.695 V compared to 5.36 V . Another very interesting feature is noted from the comparison of the transmission in the three upper panels of Fig. 3. As the bias increases, the contribution to transmission from the orbital near the Fermi energy decreases, but the contribution from the orbital away from the Fermi energy increases. This clearly suggests that the frontier orbitals and the

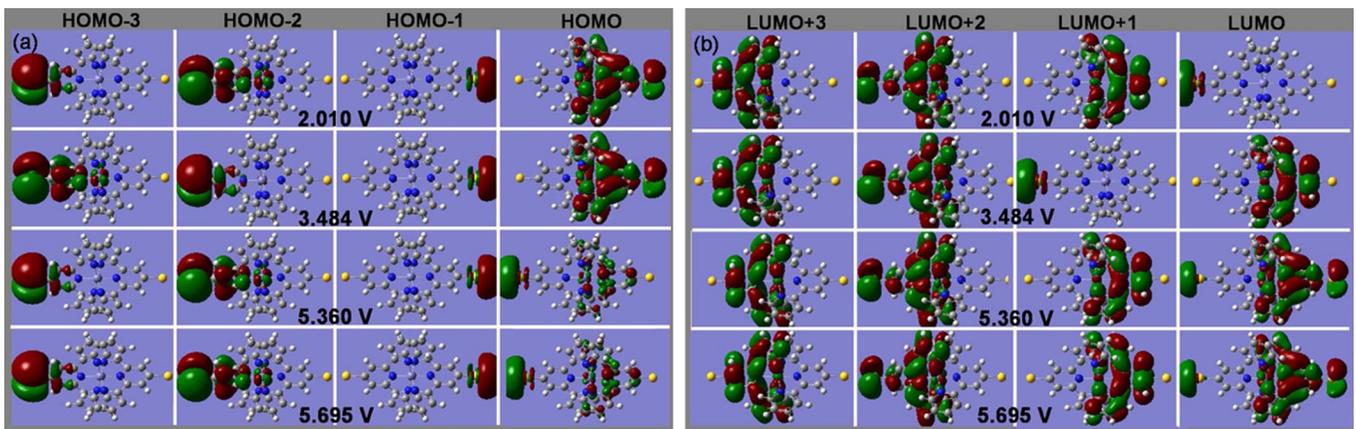


FIG. 4 (color online). (a) Occupied molecular orbital under applied bias: from right to left (column wise) the orbitals are HOMO, HOMO - 1, HOMO - 2, and HOMO - 3. (b) Unoccupied molecular orbitals under applied bias: from right to left (column wise) the orbitals are LUMO, LUMO + 1, LUMO + 2, and LUMO + 3. Bias changes row wise. Notation: dark gray (red) corresponds to negative lobe, and light gray (green) corresponds to the positive lobe.

orbitals away from the Fermi energy respond differently to the applied bias.

Thus the question arises, What is the cause for this nonmonotonic feature in the net transmission which gives rise to the NDR effect? Does NDR have a molecular origin or is it junction dependent? To answer these subtle questions, the eigenvalue spectrum of $H_{\text{mol}}(\epsilon)$ is analyzed near the Fermi energy. Though some small shift in energy levels bringing LUMO and LUMO + 1 closer are found with the increase of bias from 3.484 to 5.36 V, no shift in energy levels away from the window of chemical potential is observed that would explain NDR. But comparing the eigenvalue spectrum of $H_{\text{mol}}(\epsilon)$ and the DOS obtained from $G(\epsilon)$, a strong bias dependent energy level broadening is observed due to the coupling of the molecule with the lead. Thus the question again arises, Why does the broadening effect change significantly from the peak to the valley position? The energy level broadening depends strongly on the coupling of molecular eigenstates with the lead. Hence we analyzed the response of the molecular orbitals to the electric field (Fig. 4). First, between 2.01 and -2.01 V only a *phase* reversal of the molecular eigenstate is found. Second, as the bias increases (Fig. 4) from 3.484 to 5.36 V, a new phase in the broken symmetry wave function of the molecule [22] emerges because of the strong mixing of the HOMO and LUMO + 1 at 3.484 V to give LUMO at 5.36 V. It is important to note that the new broken symmetry phase appears spontaneously after 3.484 V (starting from 3.551 V). This significant change upon increasing bias is expected to have a sensitive effect on the coupling between the molecule and the lead. To confirm this hypothesis, we recalculated the current at 5.36 V using coupling matrices extracted at 3.484 V. The calculated current is found to be $62.63 \mu\text{A}$, which is higher than the original valley current. Similar calculation at 5.695 V using the bias dependent coupling matrices extracted from the self-consistent calculation at 5.360 V gives a lower current of $50.05 \mu\text{A}$ than the original valley current, suggesting a weaker coupling at the valley position than at 3.484 and 5.695 V. Thus, unambiguously, we have confirmed that the nonlinear change in coupling arising from a bias dependent transition in the broken symmetry phase of the molecular eigenstate is responsible for NDR.

In summary, using an exhaustive first-principles approach, we have identified the origin of NDR in a strongly coupled single-molecular junction. Our calculation in an FETP molecule-metal junction reveals asymmetry and strong NDR features in the I - V , with high PVR of ~ 2.7 . The origin of the asymmetry in current between the positive and negative bias range is ascribed to the asymmetric channel coupling at the junction. The high PVR suggests that this switching device could potentially be used as an active component in a new generation molecular electronic circuit. Most important, we found that the bias dependent transition in the broken symmetry phase of the molecular wave function leading to a nonlinear change in the cou-

pling between the molecule and lead is the root cause of NDR. This mechanism can be used to explain NDR in other classes of metal-molecule junction devices.

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