

Asymmetry in negative differential resistance driven by electron–electron interactions in two-site molecular devices

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We demonstrate that Coulomb interactions within the Hartree–Fock approximation can induce a strong asymmetry in the negative differential resistance of a two-site resonant molecular device. This sharp cutoff at high voltage is generic and independent of the detailed single-particle electronic structure of the system. The intersite coupling between distinct molecular subunits controls a transition from staircase to resonant current–voltage characteristics. These studies clarify the relationship between weak screening and strong nonlinearity. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413499]

Molecular electronics, which exploits the nonlinear switching behavior of individual molecules, affords the possibility of ultrasmall electronic devices that circumvent lithographic limits, in addition to providing an interesting regime for fundamental physics.^{1,2} With fabrication techniques^{3,4} and the observation of strongly nonlinear transistor-like^{3,5} and switching⁶ behaviors, this field has become a strong candidate for fundamental advances in electronics. Molecular devices afford a wide variety of chemical compositions which can tune electronic hopping rates, on-site energies, level spacings, electron–phonon interactions, and Coulomb interactions.

Here, we identify a mechanism for modulating negative differential resistance (NDR): the two-site resonance across a molecular element exhibits a strong intrinsic asymmetry in the current peak due to Coulomb interactions. We show how a molecular wire transitions between different regimes of electron transport depending on the strength of intersite coupling. At moderate coupling, the system shows the familiar eigenvalue staircase current-voltage ($I-V$).^{7,8} At weaker intersite coupling, the energy levels of each site shift self-consistently under the influence of the external voltage; the system then exhibits resonant transport at the intramolecular degeneracy. The resonance is independent of the detailed electronic structure of the electrodes, such as the band-edge effects of conventional resonant devices.⁹

We decompose the molecular part of the device into subunits which are strongly coupled internally, such as aromatic rings in a molecular wire or individual quantum wells in a solid state device. These subunits are then coupled via weaker electron hopping through high(er) potential barriers (for example, disruptions in the π bonding between rings). The Hamiltonian contains terms describing the device, the contact reservoir, and the interaction between them: $H_{\text{tot}} = H_{\text{wire}} + H_{\text{contact}} + H_{\text{wc}}$. H_{wire} includes an electron hopping integral parameterized by t and the one-particle energies $\epsilon_{i\sigma}$ of sites $i (= 1, 2)$ with spins σ (measured from the chemical potential of the electrodes at zero bias). The Coulomb inter-

action is described via an on-site repulsion of strength U_i . H_{wire} then reads

$$H_{\text{wire}} = -t \sum_{i\sigma} (c_{i\sigma}^\dagger c_{i+1\sigma} + \text{h.c.}) + \sum_{i\sigma} \epsilon_{i\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow}. \quad (1)$$

The finite bias influences the on-site energy through changes in the charge distribution on both the molecule itself and the adjacent electrodes. A full description of the electrode charges requires explicit treatment of the shape and electronic structure of the electrodes, which is beyond the scope of this work (but has been treated theoretically in *ab initio*^{5,10} and model⁸ calculations). Here, we focus on the physics of charge redistribution within the molecule. We treat the Coulomb interaction by incorporating Hartree contributions to the *bare* level $\epsilon_{i\sigma}$. The effective molecular level $\epsilon_{i\sigma}^H$ is then given as

$$\epsilon_{i\sigma}^H = \epsilon_{i\sigma} + U_i \langle n_{i-\sigma} \rangle, \quad (2)$$

with self-consistent occupation numbers $\langle n_{i\sigma} \rangle$. This accounts for nonequilibrium current-induced polarization. Molecular electronic structures under finite bias can be very different from those of isolated molecules. An isolated molecule adjusts its levels in an external electric field by polarizing with higher charge density at low-energy sites. However, when the molecule makes contact to metallic leads, these accumulated charges leak and the external field is more weakly screened. We parametrize $\epsilon_{i\sigma}$ as⁷

$$\epsilon_{i\sigma} = \epsilon_{i\sigma}^0 - \frac{1}{2} eV, \quad (3)$$

where V is the applied voltage and $\epsilon_{i\sigma}^0$ is the equilibrium one-particle energy at zero bias. This particular parameterization provides conceptual transparency; our essential conclusions can be generalized well beyond this approximation, including treatments that incorporate the electric field induced by the electrodes.⁸

The contact reservoir Hamiltonian is taken as a featureless continuum of noninteracting conduction states: $H_{\text{contact}}^{L/R} = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}}^{L/R} n_{\mathbf{k}\sigma}$, where $\epsilon_{\mathbf{k}}^{L/R}$ are the eigenstates of the contacts shifted by the external voltage, i.e., $\epsilon_{\mathbf{k}}^{L/R} = \epsilon_{\mathbf{k}} - eV_{L/R}$ with

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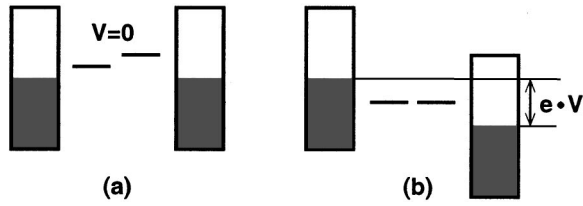


FIG. 1. Energy scheme for molecular levels and electrodes. (a) Molecular levels at zero bias; (b) For weak intersite coupling, the intramolecular bias can drive the molecular levels to degeneracy.

$V_L=0$ and $V_R=V$ (L/R =left-/right-hand side). The coupling Hamiltonian between the wire and contacts is $H_{wc}^{L/R} = g(c_{1/2\sigma}^\dagger c_{L/R\sigma} + \text{h.c.})$, where $c_{L/R\sigma}$ is the annihilation operator of the contact point for the L/R leads and g is the coupling strength. We consider a local density of states in the contact which is flat over an energy $[-D, D]$ and zero otherwise. We choose a bandwidth large enough ($D=5$). (This simple form is actually a strength of the method, as it shows that the resulting sharp structure is intrinsic to the device, and does not depend on band cutoffs in the contacts.)

The Keldysh formalism¹¹ can describe nonequilibrium transport with the Coulomb repulsion incorporated up to a finite order in U . A first order approximation significantly simplifies the nonequilibrium Green function equation, yet captures the essential physics, as discussed next. The contacts are described via a contact self-energy, $\Sigma_C(\omega)$, which not only broadens the molecular levels but also maintains nonequilibrium by setting different chemical potentials on the left- and right-hand side electrodes. The retarded Green function, $\mathbf{G}^r(\epsilon)$, is given by an 2×2 matrix Dyson equation, $[\mathbf{G}^r(\omega)]^{-1} = \omega - \mathbf{H}_w^H - \Sigma_C(\omega)$, where $[\Sigma_C(\omega)]_{mn} = \delta_{1n}\delta_{1m}\Sigma_L(\omega) + \delta_{2n}\delta_{2m}\Sigma_R(\omega)$ with $\Sigma_{L/R}(\omega) = g^2 \int d\epsilon N_{L/R}(\epsilon)/(\omega - \epsilon + i\eta)$ with an infinitesimal η and $N_{L/R}(\epsilon)$ the densities of states of the electrodes. The advanced Green function $\mathbf{G}^a(\omega)$ is similarly defined. In \mathbf{H}_w^H , the Coulomb terms are incorporated into the on-site energy, $\epsilon_{i\sigma}^H$ [See Eq. (2)], with a self-consistently chosen occupation number $\langle n_{i\sigma} \rangle$. $\langle n_{i\sigma} \rangle$ can be computed from

$$\langle n_{i\sigma} \rangle = \langle c_{i\sigma}^\dagger c_{i\sigma} \rangle = -i \int \frac{d\omega}{2\pi} G_{ii}^<(\omega), \quad (4)$$

with $[\mathbf{G}^<(\omega)]_{ij} = i \langle c_{i\sigma}^\dagger(\omega) c_{j\sigma}(0) \rangle$, which is computed from $\mathbf{G}^<(\omega) = i \mathbf{G}^r(\omega) \mathbf{f}(\omega) \mathbf{\Gamma}(\omega) \mathbf{G}^a(\omega)$ with the (frequency-independent) line-broadening functions of both electrodes $\Gamma_{L/R}(\omega) \equiv \pi g^2 N_{L/R}(\omega)$ and $[\mathbf{f}(\omega)]_{nm} = \delta_{1n}\delta_{1m}f(\omega - eV_L) + \delta_{2n}\delta_{2m}f(\omega - eV_R)$ with the Fermi-Dirac function $f(\omega)$. We limit our results to the nonmagnetic case, $\langle n_{i-\sigma} \rangle = \langle n_{i\sigma} \rangle$. The current is computed as¹²

$$I = \frac{2e}{h} \int d\omega [f(\omega) - f(\omega - eV)] \text{Tr}\{\mathbf{G}^a \mathbf{\Gamma}_R \mathbf{G}^r \mathbf{\Gamma}_L\}. \quad (5)$$

We apply a positive voltage (i.e., lower energy) to the right-hand side electrode and consider $\epsilon_{1\sigma}^0 < \epsilon_{2\sigma}^0$ [see Fig. 1(a)]. The asymmetry in the on-site energy could come from chemical composition, asymmetric contacts, etc. For simplicity, we consider only a two-site system, but the same physics can apply to multisite systems with resonant subunits.

The site energies at zero bias are set at relatively generic values of $\epsilon_{1\sigma}^0=0.5$ and $\epsilon_{2\sigma}^0=1.0$. ($\epsilon_{2\sigma}^0=1.0$ is the unit of

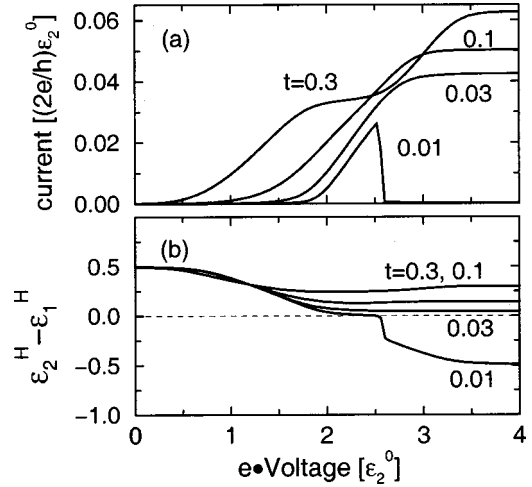


FIG. 2. (a) I - V curves for various intersite hopping integrals t . On-site energies (ϵ_i^0) at zero bias are set as $\epsilon_1^0=0.5$ and $\epsilon_2^0=1.0$ (unit energy). On-site Coulomb interaction strength U_i and the molecule-wire coupling strength Γ_i are set to 1.0 and 0.013, respectively, for all $i(=1,2)$. For a moderate hopping integral ($t=0.3$), the I - V curve shows a familiar staircase behavior. At a smaller hopping integral, comparable to the line broadening ($t=0.01$), the I - V curve changes drastically to reveal a strongly asymmetric NDR. (b) The intersite level spacing $\epsilon_{2\sigma}^H - \epsilon_{1\sigma}^H$. For moderate hopping integrals, the intermolecular voltage drop converges to finite values due to efficient screening. As the hopping integral decreases, the intersite screening becomes ineffective and eventually allows a sharp level crossing.

energy, on the order of an eV.) Here, we set the Coulomb interaction strength U_i to 1.0, which is an accessible regime for molecular-scale devices. The molecule-contact coupling strength is taken to be weak; $\Gamma_i=0.013$ (for $i=1,2$). The temperature is set at $T=0.05$; the main results are not particularly sensitive to temperature.

The abrupt transition in electron transport as a function of intersite coupling is illustrated in Fig. 2(a). At moderate intersite hopping ($t=0.3$), the system shows the well-known eigenvalue staircase.^{7,8} The lower step corresponds to the molecular bonding state opening up a conduction channel, while the second step is the antibonding state. With finite bias, the left-hand side (right-hand side) electrode acts as electron donor (acceptor), which leads to charge polarization and an intersite voltage drop via the Hartree contribution. However, the moderate intersite hopping is strong enough to nearly screen out this nonequilibrium effect, as seen in the converged level splitting $\epsilon_{2\sigma}^H - \epsilon_{1\sigma}^H$ in Fig. 2(b). Therefore, the electronic levels of the subunits are driven in unison by the external bias.⁷ Many molecular electronic devices with relatively weak nonlinearity apparently fall into this well-screened regime.

As the hopping integral (or bonding/antibonding level splitting) decreases, the double step merges into a single step. When the hopping integral drops to values comparable to the line broadening, the electron transport changes dramatically. The I - V characteristic ceases to be a conventional staircase and develops an asymmetric NDR. The critical difference here is that the energy levels of the two subunits cross, due to the weak screening of the intramolecular voltage drop, and this level splitting shifts through an energy range larger than the intersite hopping integral [Fig. 1(b)]. (In a limiting-case thought experiment, one can imagine that the molecular wire is cleaved in half, each section remaining

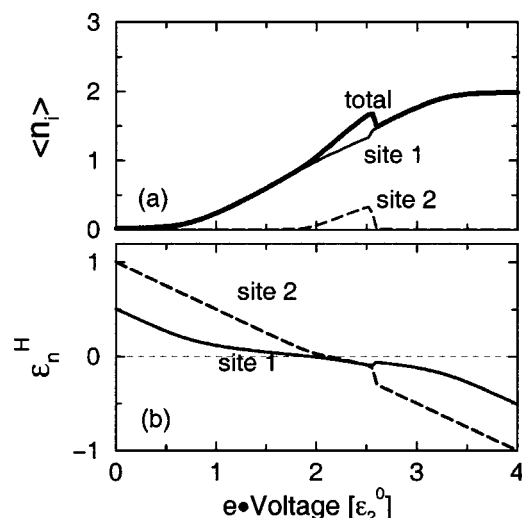


FIG. 3. (a) Occupation numbers (spin summed), $\langle n_i \rangle$, for weak intersite coupling ($t=0.01$) at the parameter regime of Fig. 2. Around resonance ($\epsilon_{2\sigma}^H = \epsilon_{1\sigma}^H$), the molecular wave function becomes more delocalized and the $\langle n_i \rangle$ approach each other. (b) The Hartree energy levels $\epsilon_{i\sigma}^H$ ($i=1,2$). $\epsilon_{i\sigma}^H$ cross with a sharp cusp at high voltage. The thin dashed line is the chemical potential of the left-hand side electrode.

connected to only one electrode. Then, the electrode voltage would directly control the energy levels of each molecular subunit.)

Electron–electron interactions here create strong asymmetry in the NDR peak. When the two sublevels fall into resonance, the electron wave function delocalizes and spreads more evenly across the whole molecule. As shown in Fig. 3(a) the resonance has a negative (positive) contribution to the occupation number for site 1 (2). Since the electron–electron interaction also tends to even out the electron charge, it can also help lock the system into the resonance. As the voltage approaches the resonance from below, the site 1 (2) gets electron depleted (filled); the Coulomb interaction then pushes the energy levels closer to resonance [see Fig. 3(b)]. In contrast, just above resonance, site 1 (2) is electron filled (depleted) and the electron–electron interaction exacerbates the deviation from resonance, producing a sudden cutoff in the current. This nonlinear I – V behavior is accompanied by strong hysteresis,¹³ which might be exploitable for device applications such as persistent information storage. The data shown here correspond to increasing the bias voltage slowly from zero.

Within the Hartree approximation, one can obtain analytical expressions for the current in terms of model parameters; these expressions then provide a simple intuitive picture of the phenomena. For example, the maximum current at the resonance ($\epsilon_{2\sigma}^H = \epsilon_{1\sigma}^H$) is approximately $(e^2/\hbar)[\Gamma_L\Gamma_R/(\Gamma_L+\Gamma_R)][t^2/(\Gamma_L\Gamma_R+t^2)]$. As can be seen from the term $t^2/(\Gamma_L\Gamma_R+t^2)$, when the molecule–lead coupling exceeds the intersite coupling ($\Gamma_{L/R} \gg t$), the NDR diminishes, since the bonding/antibonding splitting becomes smaller than the linewidth and destructive interference between the conduction channels suppresses the current. In the opposite limit, when the molecule–lead coupling is very weak ($\Gamma_{L/R} \ll t$), most of the voltage drop occurs at the contacts and the reso-

nant NDR also disappears.¹⁴ The resonant NDR is strongest when the intersite hopping integral is comparable to the line broadening of the molecular levels. These general observations could help guide future searches for interesting nonlinear transport behavior in small molecules.

It is interesting to consider the relation between the phenomena described here [i.e., Fig. 2(a) at $t \sim 0.01$] and the NDR observed in functionalized polyphenylene between gold electrodes³ and tunneling between two C_{60} molecules.⁴ In particular, the sharpness of the experimental curves in Chen *et al.*³ suggests that: (1) only one or two molecular levels are involved, (2) the molecule–contact coupling is weak so as to maintain sharp molecular levels (here we define “contact” broadly to include e.g. any subunits of the molecule that are strongly coupled to the contact and weakly coupled to the remainder of the molecular) and (3) the relatively featureless density of states of the gold electrode does not contribute directly to the nonlinear device function. Within the two-site resonance mechanism, the magnitude of the current at resonance is controlled mostly by the strength of the molecule–lead contacts;⁵ the conductance is then well below $2e^2/h$ in the relevant operating regime, which is consistent with experiment. In addition, the sharp cutoff at higher voltages seen experimentally is consistent with the model discussed here. However, we emphasize that the exact cause of the experimental NDR is not yet known. In the two- C_{60} tunneling device, it would be interesting to examine how the NDR evolves with intersite hopping strength by controlling the inter- C_{60} distance, perhaps through polymerization.

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¹⁴ Depending on the size of the intersite voltage drop induced by the electrode charges, intersite level splitting is possible and the operating range of the NDR could widen into the regime $\Gamma_{L/R} < t$.