

Supporting Information for
Small Heterocyclic Molecule as Multistate Transistor : A
Quantum Many-body Approach

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I. MODEL AND METHODS

Theoretical modelling of the weakly coupled devices exhibits that coherent non-equilibrium Green's function (NEGF)^{1,2} formalism coupled with self-consistent field (SCF) approach is not adequate to reproduce experimental findings even at the qualitative level. Unlike in the case of strongly coupled systems, the charging energies of molecules in these devices are much higher than the electrode coupling and plays a vital role in carrier transport^{3,4}. To describe the molecular transport in these systems the quantum master/rate equation approach has been widely used^{5,6}. This formalism efficiently describes electron transport through many-body eigenstates of molecular systems. Since charging energy is much higher than the molecule/dot electrode coupling, in the weak coupling limit, we do not explicitly consider the electrode or its coupling with the molecule/dot device, in the kinetic equation method.

Using this approach, Hettler et. al. have demonstrated the large NDC behaviour in weakly coupled benzene-based molecular junctions⁷. They proposed that under a finite bias, the radiative relaxation of electrons populate a particular many-body state which blocks the transport of current, resulting in the NDC behaviour. Darau et al. revisited the same system with the generalised master equation approach, where a strong interference effect appears to be the reason for the observed NDC behaviour⁸.

Apart from molecules, donor-acceptor QDs have also been investigated thoroughly for their various non-linear transport characteristics in weak coupling regime. Muralidharan et al have demonstrated the criterion to find NDC in these double QDs in terms of transition rates for populating and depopulating the transport-active many-body states⁴. Song et al have observed rectification in I-V characteristics for weakly coupled spatially separated donor-acceptor systems⁹. The difference in coupling strengths of these sites to the electrodes results in the rectification effect in these molecular junctions. Parida et al have used kinetic equation approach to investigate transport characteristics in donor-acceptor double QD systems¹⁰. They propose that the increased population of the non-conductive triplet state with an increase in bias voltage and consequent reduction in the current transport leads to a prominent NDC feature.

In our present study, a heterocyclic benzene i.e. $B_2C_2N_2H_6$ is weakly coupled to the metallic electrodes on either side. Thus, the molecular junction is effective in the Coulomb

blockade regime. Here, B, C and N sites act as acceptor, bridge and donor (from the electron point of view), respectively due to their intrinsic chemical nature. This molecule can efficiently be modelled as two identical donor-bridge-acceptor half-rings (B-C-N), connected to each other in an end-on manner by covalent bonds. We construct the interacting isolated molecular Hamiltonian considering only the localised $2p_z$ orbitals of B, C and N atoms^{7,8} since the σ orbitals are at a much higher energy scale, as followed in earlier works.

To compute the transport properties in the sequential tunnelling limit, we diagonalize the Hubbard Hamiltonian, H . Diagonalization of H provides many-body eigenstates $|s\rangle$ with the corresponding eigenenergies, E_s . We compute the occupation probabilities P_s , through the master equation approach, in the steady state of the system. The transition rate, $W_{s'\rightarrow s}$, from the many-body state, s' of the molecule with N electrons to a state s with $(N - 1)$ or $(N + 1)$ electrons, is calculated up to linear order in Γ , where Γ is the bare electron tunnelling rate between the molecule and the left/right electrode. Using the Fermi's golden rule the transition rate can be written as follows,

$$W_{s'\rightarrow s}^{L+} = \Gamma f_L(E_s - E'_s) \sum_{\sigma} | \langle s | a_{1\sigma}^{\dagger} | s' \rangle |^2$$

$$W_{s'\rightarrow s}^{R+} = \Gamma f_R(E_s - E'_s) \sum_{\sigma} | \langle s | a_{N\sigma}^{\dagger} | s' \rangle |^2 \quad (1)$$

The corresponding equation for $W_{s\rightarrow s'}^{L-}$ and $W_{s\rightarrow s'}^{R-}$ are formulated by replacing $f_{L,R}(E_s - E'_s)$ by $(1 - f_{L,R}(E_s - E'_s))$, where $f_{L/R}$ is the Fermi function for left/right electrode. Here, $+/-$ represents the creation/annihilation of an electron inside the molecule due to electron movement from/to left (L) or right (R) electrodes. $C_{1\sigma}^{\dagger}$ and $C_{N\sigma}^{\dagger}$ are the creation operators for electrons with spin, σ , at the 1^{st} and N^{th} lattice sites, respectively. We also have assumed that the creation and annihilation happens only at the sites which are directly connected to the electrodes. The total transition rate is obtained as, $W_{s\rightarrow s'} = W_{s\rightarrow s'}^{L+} + W_{s\rightarrow s'}^{R+} + W_{s\rightarrow s'}^{L-} + W_{s\rightarrow s'}^{R-}$. Now, the non-equilibrium probability, P_s , of occurrence of each many-body state, s , can be represented by the rate equation,

$$\dot{P}_s = \sum_{s'} (W_{s' \rightarrow s} P_{s'} - W_{s \rightarrow s'} P_s). \quad (2)$$

At the steady state, the population of the different many-body states (P_s) can be found by solving the above rate equation (Eq. (2)). Thus, the Eq. (2) becomes

$$\dot{P}_s = \sum_{s'} (W_{s' \rightarrow s} P_{s'} - W_{s \rightarrow s'} P_s) = 0. \quad (3)$$

Eq. (3) can be written in an expanded form that results in a homogeneous linear system ($AX=0$) of the size of the many-body space. Since $AX = 0$ can not be solved, we make use of $\sum_s P_s = 1$ to eliminate one row/column, thus reformulating the eigenvector problem into an inhomogeneous linear system ($AX=B$), which can be solved using well-known linear algebraic methods¹¹. Thereafter, the current in the left and right electrodes is calculated by the following formula,

$$I_\alpha = \frac{e}{\hbar} \sum_{s,s'} (W_{s' \rightarrow s}^{\alpha+} P_{s'} - W_{s \rightarrow s'}^{\alpha-} P_s) \quad (4)$$

where $\alpha = L/R$. Note that at steady state, the current at two terminals is same, i.e. $I_L(t) = I_R(t) = I(t)$.

In presence of magnetic field t_{ij} modifies as $t_{ij} e^{\frac{2\pi i \delta \phi}{\phi_0}}$, where $\phi_0 = h/e$ is the quantum of magnetic flux, and $\delta \phi$ is the Peierl's phase given by,

$$\delta \phi = \int_i^j \mathbf{A} \cdot d\mathbf{l}, \quad (5)$$

where \mathbf{A} is the vector potential created by the perpendicular B-field, $\mathbf{B} = (0, |\mathbf{B}\mathbf{x}|, 0)$. Magnetic flux, ϕ , corresponding to this magnetic field is $\phi = \mathbf{B} \cdot \mathbf{A}_s$, where A_s is the area of the hexagonal ring i.e. $3\sqrt{3}a^2/2$ with a as the bond length.

To optimize the molecule on top of gold electrode, we have used density functional theory based simulations as implemented in Vienna Ab Initio Simulation Package (VASP).^{12,13} The projected augmented wave (PAW) method has been considered with a plane-wave basis set of cut-off energy 500 eV.¹⁴ For exchange-correlation interactions, we use the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional (PBE) form.¹⁵

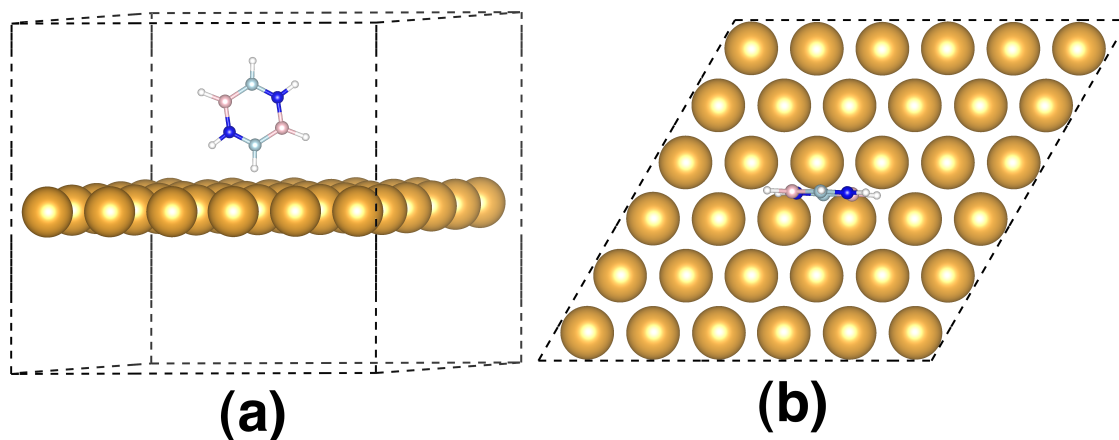


Figure S 1. (a) Side-view and (b) top-view of the optimized structure of $B_2C_2N_2H_6$ molecule on top of the (111) surface of the gold electrode. The molecule remain chemically intact and bonded to the metal surface.

Keeping the electrode positions fixed, the molecular geometry on top of gold was relaxed till all the interatomic forces become less than $0.01 \text{ eV } \text{\AA}^{-1}$. Binding energy of molecule on gold surface has been calculated by subtracting total energies of isolated metal surface and molecule from electrode+molecule system. The DFT-D3 method as described by Grimme¹⁶ and a $5 \times 5 \times 1$ Γ -centered Monkhorst-Pack¹⁷ mesh were used for this simulation. A vacuum of at least 10 \AA in non-periodic direction (that is perpendicular to the metal electrode) had been considered to mitigate spurious interactions between periodic images of the system.

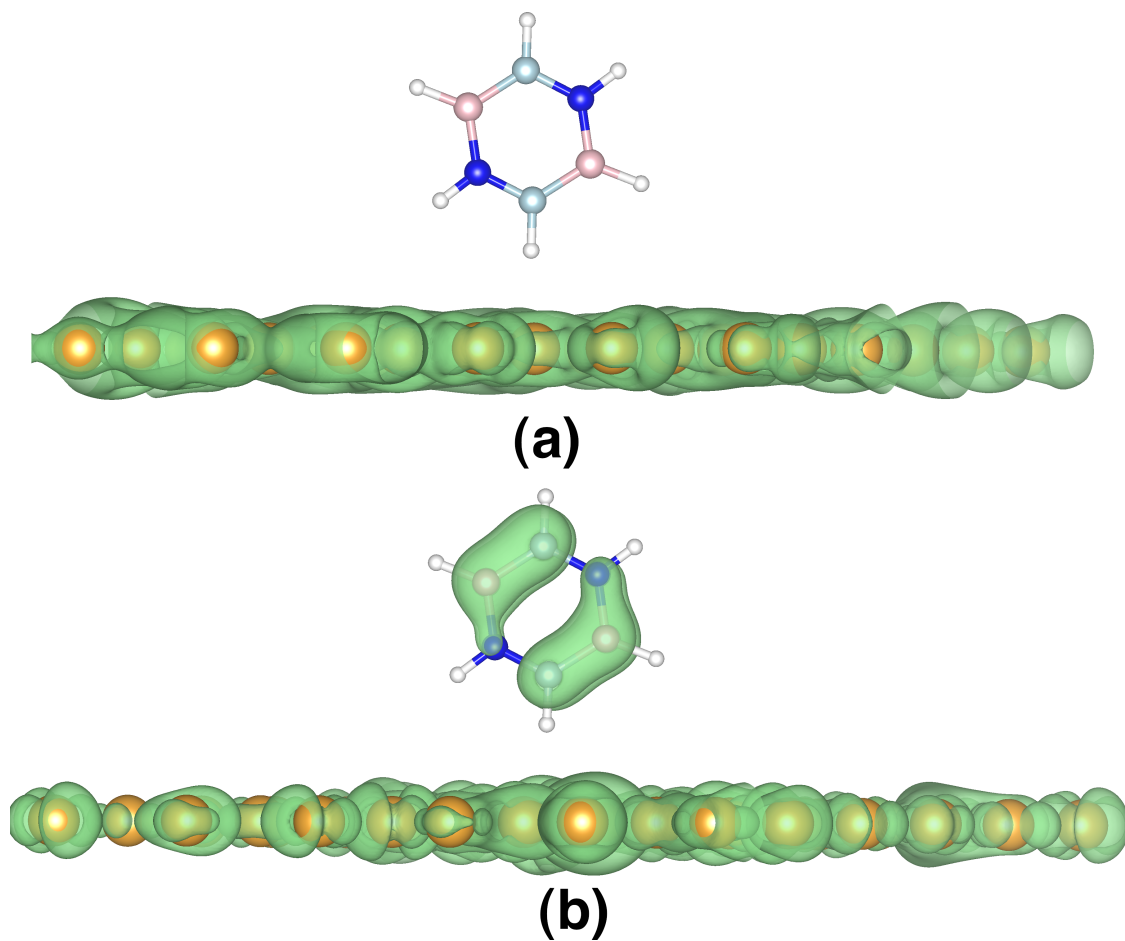


Figure S 2. The single-particle charge densities of electrode-molecule system. The charge densities for (a) conduction band edge states and (b) valence band edge states. The charge densities on $B_2C_2N_2H_6$ and electrode are not overlapped due to weak coupling and electron transport can happen only through sequential hopping mechanism. The charge densities have been calculated by self-consistent field DFT simulations using optimized geometry of electrode-molecule system.

To make weakly coupled molecular bridge between electrodes, the cyclic $B_2C_2N_2H_6$ molecule can be attached to the electrodes in different conformations. Fig. S2 shows the conformations considered in this study.

Note that, as the calculations are in weak coupling limit, electrodes can be connected through weakly interacting anchoring groups or through a long thiol chain.^{18,19} These approaches make the molecular site-electrode coupling negligible.

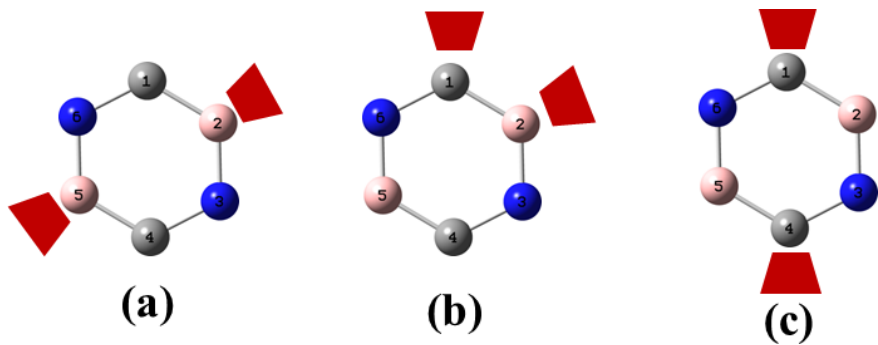


Figure S 3. (a-c) Few representative conformations of electrode- $B_2C_2N_2H_6$ molecule. The electrodes can be attached in different positions of the molecule. Following the representation used in the Fig 2 of the main text, (a) para B-B (b) ortho C-B (c) para C-C. Red blocks are the loosely attached electrodes to the molecule.

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