

Driven Liouville von Neumann Approach for Time-Dependent Electronic Transport Calculations in a Non-Orthogonal Basis-Set Representation

Supporting Information

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Transmittance Probability

In Fig. 2f of the main text we have presented the transmittance probability of the gold/benzene-dithiol/gold and gold/pyridine-dithiol/gold junctions in the vicinity of the Fermi level and some representative molecular orbital isosurfaces. For completeness, we plot in Fig. S1a the transmittance probability through the two junctions in an energy range of ± 0.5 eV around the Fermi energy, corresponding to the full transport window opened by the applied bias voltage of $V_b = 1.0$ V. The transmittance patterns of the two systems are found to be similar throughout the transport window, apart from a narrow region near the Fermi energy, where the benzene dithiol junction presents two nearly fully opened conducting channels as discussed in the main text. A larger set of molecular orbital isosurfaces, corresponding to extended molecule eigenstates located in the vicinity of the Fermi energy, is presented in Fig. S1b.

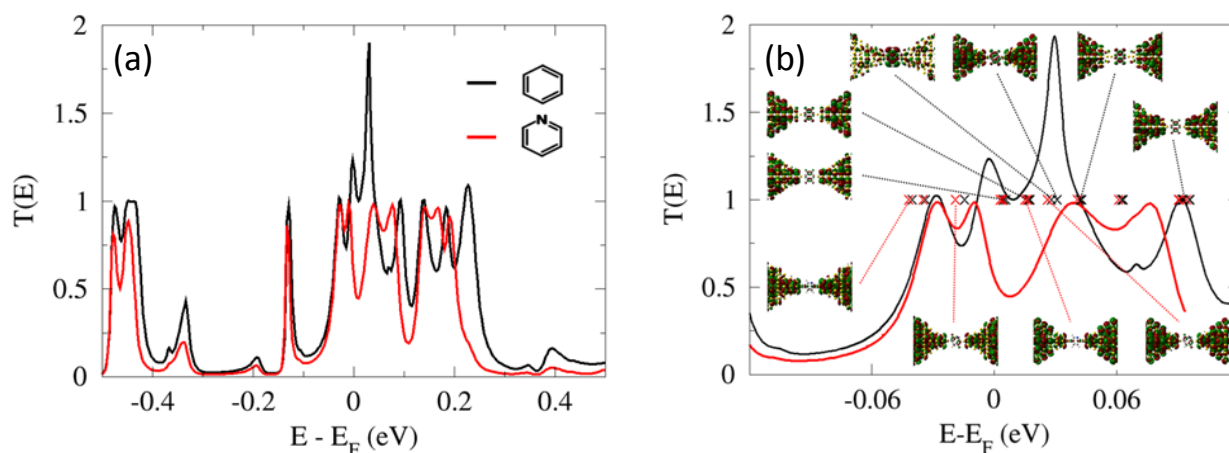


Figure S1: (a) Transmittance probability of the gold/benzene-dithiol/gold (black) and gold/pyridine-dithiol/gold (red) junctions in the full Fermi transport window obtained at a bias voltage of $V_b = 1.0$ V. Here, the origin of the energy axis is set to the center of the HOMO-LUMO energy gap of the entire (finite) system. (b) Zoom-in on the transmittance probability in the vicinity of the Fermi energy, along with some molecular orbital isosurfaces of the extended molecule (using an isosurface value of 0.0075 atomic units), for orbitals that bridge the two leads and can support current.

Electron Density Variations

The difference between the transport characteristics of the two junctions considered above is also manifested in their time-dependent electron density variations. In Figs. S2 and S3 we plot the electron density differences with respect to the ground state electron density of the benzene dithiol and pyridine dithiol systems, respectively, at different time frames during the simulation. During the initial dynamics the left (right) lead section of the extended molecule experiences an increase (reduction) in its electron density due to its coupling to the high (low) chemical potential lead. Following this initial dynamics the benzene dithiol system that shows higher currents also exhibits a large density increase in the molecular region itself whereas the density variations on the pyridine ring are significantly smaller. As the systems approach steady-state the density variations stabilize and remain unchanged.

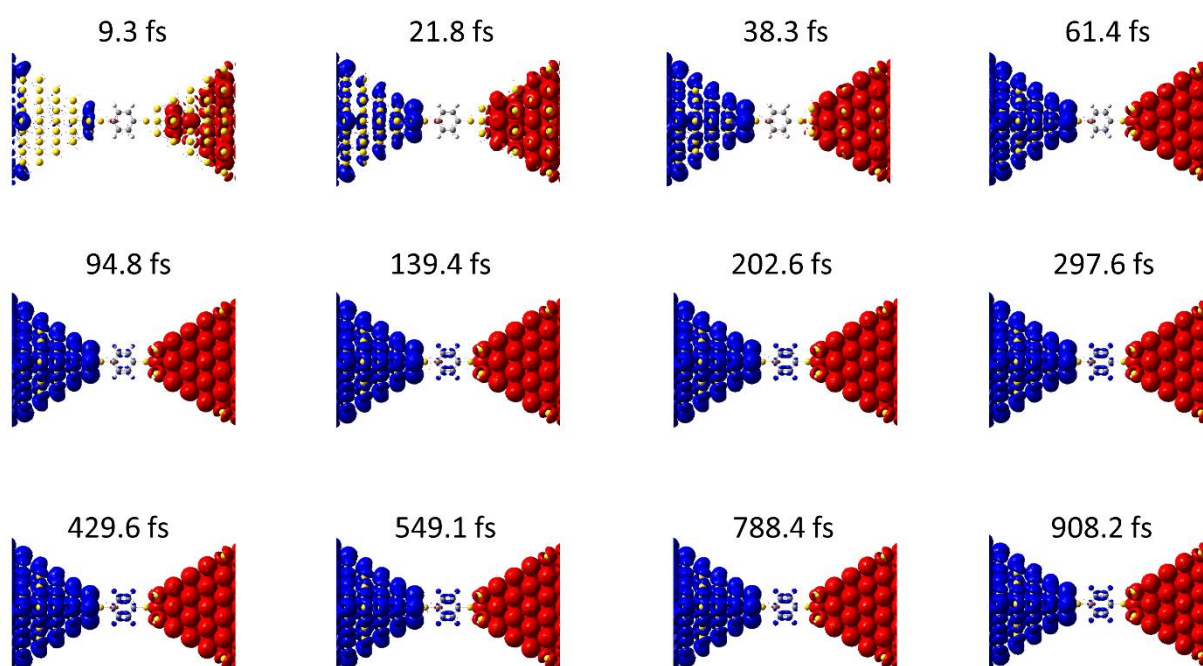


Figure S2: Electron density variations with respect to the ground state density of the gold/benzene-dithiol/gold junction at various simulation times. Blue and red isosurfaces represent density increase and decrease, respectively. The isovalue used is 0.0035 atomic units.

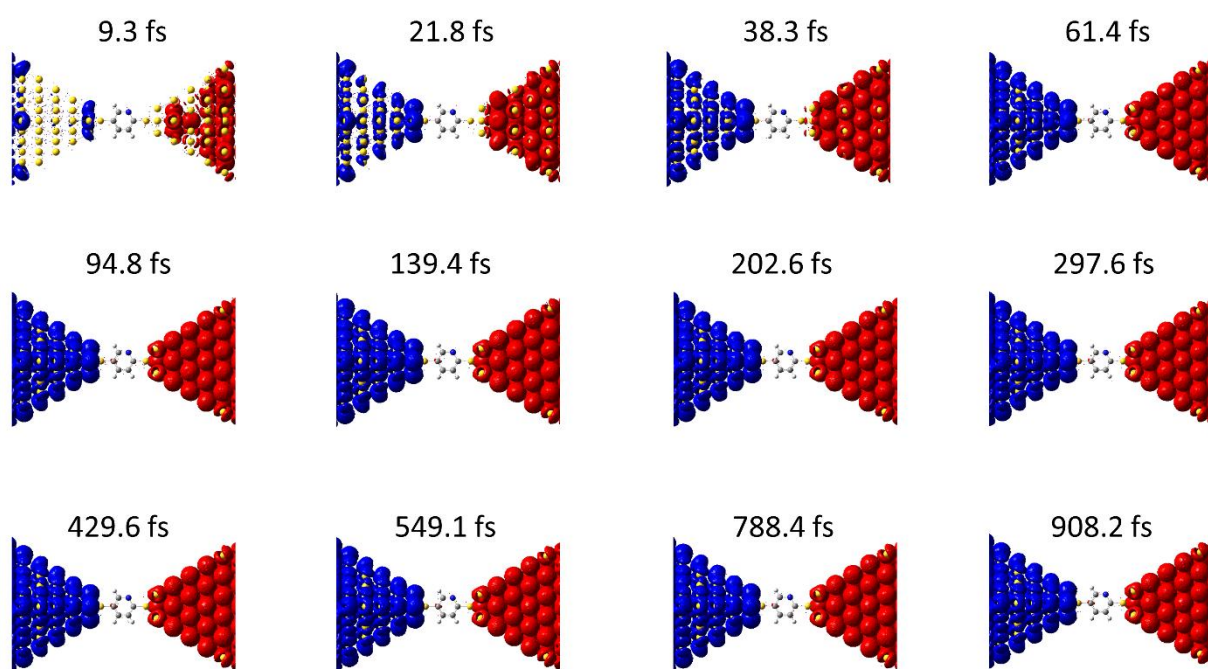


Figure S3: Electron density variations with respect to the ground state density of the gold/pyridine-dithiol/gold junction at various simulation times. Blue and red isosurfaces represent density increase and decrease, respectively. The isovalue used is 0.0035 atomic units.

Effect of Lead-Molecule Coupling on the Steady-State Occupations

In Fig. 3 of the main text we have demonstrated how the effective coupling to the low and high chemical potential leads dictates the steady-state occupations of four extended molecule single-particle states. It was shown that as the coupling favors the (lower) higher chemical potential lead the state occupation (decreases) increases. To show that this effect is of a general nature we plot in Fig. S4 the steady-state occupations of all extended molecule states within the Fermi transport window as a function of the ratio of their coupling to the left (higher chemical potential) and right (lower chemical potential) leads. A general trend, where the state occupation increases with the ratio between the coupling to the higher and lower chemical potential leads, is indeed observed. When the coupling is symmetric (a ratio of 1, see inset) the state occupations are typically ~ 0.5 .

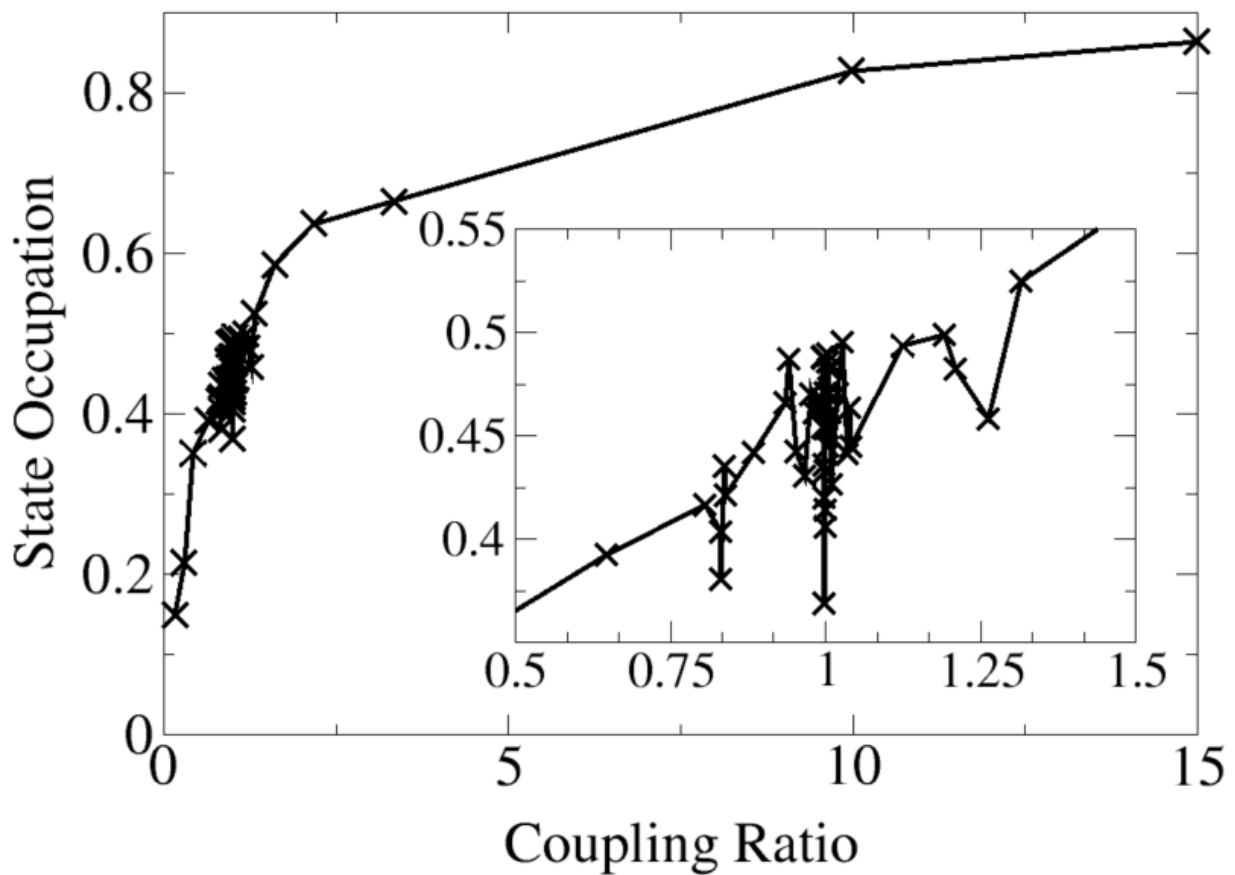


Figure S4: Steady-state occupations of the single-particle extended molecule states within the Fermi transport region, as a function of the ratio between the effective coupling to the left (high chemical potential) and right (low chemical potential) leads. Inset: Zoom-in on the region close to symmetric coupling.