

Supporting information for: Compensation of Coulomb blocking and exciton effects on current through molecular nanojunctions

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It is known [1] that for the evaluation of Eq. (5) of the paper it is essential to work in the representation of the eigenstates of the Hamiltonian $\hat{H}_{wire} + \hat{H}_{leads}$ that defines the zeroth-order time evolution. The use of other representations bears the danger of generating artifacts, which, for instance, may lead to a violation of fundamental equilibrium properties [2]. We thus face the problem of diagonalizing a matrix of order 256. This procedure may be facilitated by using the pseudospin description based on the symmetry properties of Lie group SU(2) associated with the two state problem $(1f, 2f)$; $f = e, g$. Such a “donor acceptor” system may be described by the “charge transfer” operators $b_f^+ = \hat{c}_{2f}^+ \hat{c}_{1f}$ and $b_f = \hat{c}_{1f}^+ \hat{c}_{2f}$ that describe intersite charge transfer $1 \rightarrow 2$ and $2 \rightarrow 1$, respectively, in upper and lower states of the molecular dimer. The non-diagonal part of \hat{H}_{wire} , Eq.(3) of the paper, can then be written in terms of operators b_f only

$$\hat{H}_{wire}^{(nondiag)} = - \sum_{f=g,e} \Delta_f (b_f^+ + b_f) - \hbar J (b_e^+ b_g + b_g^+ b_e) \quad (1)$$

Define also the pseudospin (Bloch) vector in the second quantization picture

$$\begin{pmatrix} r_1^f \\ r_2^f \\ r_3^f \end{pmatrix} = \begin{pmatrix} b_f^+ + b_f \\ i(b_f - b_f^+) \\ \hat{n}_{2f} - \hat{n}_{1f} \end{pmatrix}; \quad f = g, e \quad (2)$$

Its components have the following properties: (a) They satisfy the same commutation rules as Pauli matrices $\hat{\sigma}_{1,2,3}$ [3–5]; (b) the operators $\lambda_f = \hat{n}_{2f} + \hat{n}_{1f} = \sum_{m=1,2} \hat{c}_{mf}^+ \hat{c}_{mf}$, $f = e, g$ and r_i^f commute: $[r_i^f, \lambda_f] = 0$ ($i = 1, 2, 3$); (c) any linear operator of the “donor acceptor” system can be written as linear superposition of the operators $\{r_i^f\}$ and λ_f . In particular, the wire Hamiltonian can be written as

$$\begin{aligned} \hat{H}_{wire} = & \frac{1}{2} \lambda_e (\varepsilon_{1e} + \varepsilon_{2e}) + \sum_{f=g,e} \left[\frac{1}{2} r_3^f (\varepsilon_{2f} - \varepsilon_{1f}) - \Delta_f r_1^f \right] \\ & - \frac{\hbar J}{2} (r_1^e r_1^g + r_2^e r_2^g) + \frac{U}{2} (\lambda_e \lambda_g + r_3^e r_3^g) \end{aligned} \quad (3)$$

In Eq.(3) we have put, without loss of generality, $(\varepsilon_{1g} + \varepsilon_{2g})/2 = 0$. Because the operators λ_f and r_i^f commute, the total molecular populations described by operators λ_f are conserved under unitary transformations related to the diagonalization of \hat{H}_{wire} . Therefore, a total $2^4 \times 2^4$ space can be partitioned into nine smaller subspaces, i.e. the Liouvillian matrix in the required basis is block diagonal with blocks, according to the values of $[\lambda_f] = 0, 1, 2$ (see Fig.1): four one-dimensional subspaces for $[\lambda_f] = 0, 2$ for either $f = e, g$ (type I); four two-dimensional subspaces for $[\lambda_f] = 1$ and $[\lambda_{f'}] = 0, 2$ where $f \neq f'$ (type II); and one four-dimensional subspace for $[\lambda_e] = [\lambda_g] = 1$ (type III). Here we use $[\lambda_f]$ to denote the eigenvalues of matrix operator λ_f . The type I submatrix is diagonal, while four state pairs with each pair coupled by the charge transfer interaction are associated with the four 2×2 blocks of the type II subspace. The remaining four states are coupled by both the charge transfer and exciton transfer interaction and constitute the 4×4 block of subspace III. Each of these subspaces is characterized by assigning the values $([\lambda_e], [\lambda_g])$ of total populations in the ground and excited states of the two bridge sites.

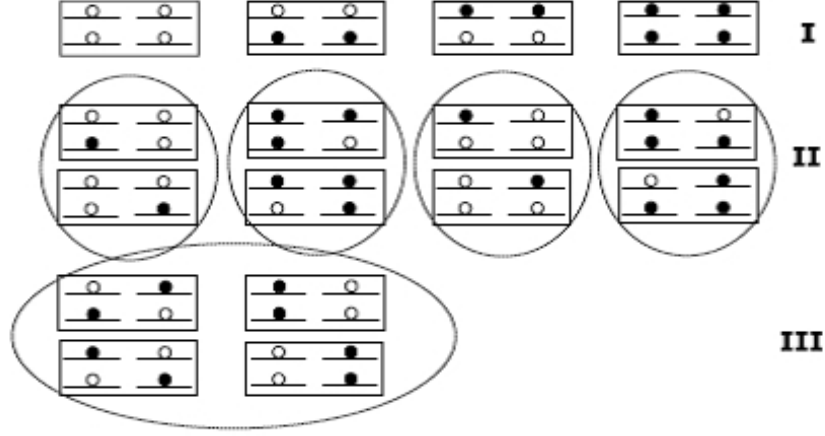


FIG. 1: A schematic display of the block structure of the wire Hamiltonian.

Using the identity

$$(r_1^f)^2 = (r_2^f)^2 = (r_3^f)^2 = \lambda_f - 2\hat{n}_{2f}\hat{n}_{1f} = \begin{cases} 0 & \text{for } [\lambda_f] = 0, 2 \\ 1 & \text{for } [\lambda_f] = 1 \end{cases}, \quad (4)$$

the wire Hamiltonian (3) can be written in the form

$$\begin{aligned} \hat{H}_{wire} = & \frac{1}{2}\lambda_e(\varepsilon_{1e} + \varepsilon_{2e}) + \frac{U}{2}(\lambda_e\lambda_g + r_3^e r_3^g) + \\ & + 0 \quad \text{For subspaces I} \\ & + \frac{1}{2}r_3^f(\varepsilon_{2f} - \varepsilon_{1f}) - \Delta_f r_1^f \quad \text{For subspaces II} \\ & + [\frac{1}{2}\sum_{f=g,e} r_3^f(\varepsilon_{2f} - \varepsilon_{1f}) - \sum_{f=g,e} \Delta_f r_1^f - \\ & - \frac{\hbar J}{2}(r_1^e r_1^g + r_2^e r_2^g)] \quad \text{For subspace III} \end{aligned} \quad (5)$$

This prediagonalization provides an important simplification of our problem. Specifically, considering for brevity a homodimer bridge with $\varepsilon_{ng} = 0$, $\varepsilon_{ne} = \varepsilon_e$, the current is given by Eq.(23) of Ref.[6]

$$\hat{I} = \frac{e}{\hbar} \Delta_e r_2^e ([\lambda_e] = 1) \quad (6)$$

for $\Delta_g = 0$. Obviously $[\lambda_e] = 1$ in Eq.(6) is another way of saying that the current in channel e exists only for the case of one of states $\{e\}$ is occupied and another one of $\{e\}$ is unoccupied. The expectation value of the current is given by $\langle I \rangle = Tr(\hat{I}\sigma_{SS})$ where σ_{SS} is the steady state solution of Eq.(5) of the paper for the reduced density matrix of the molecular bridge.

The diagonalization procedure yields the transformation between the eigenstates of the wire Hamiltonian and the states of the non-interaction molecular wire, $|n_{1g}, n_{2g}, n_{1e}, n_{2e}\rangle$ displayed in Fig.1. Denoting the column vectors of these states by $\{\Phi\}$ and $\{\chi\}$, respectively, and the transformation between them by \hat{Y} , i.e. $\{\chi\} = \hat{Y}\{\Phi\}$, we can characterize each eigenstate Φ by the corresponding subspace ($[\lambda_e], [\lambda_g]$).

In subspaces I the unitary transformation $\hat{Y}(I)$ is obviously the unity matrix. The diagonalization of the block matrices in subspaces II is similar to that carried out in Appendix A of Ref.[6]. Then using Eq.(A6) of Ref.[6], the

expectation value of the current, Eq.(6), can be written as

$$\begin{aligned} \langle I \rangle = & -\frac{2e}{\hbar} \Delta_e \text{Im} \langle b_e([\lambda_e] = 1) \rangle = \frac{2e}{\hbar} \Delta_e \text{Im} \left\{ \sum_{[\lambda_g]=0,2} \sigma_{-+}(II; [\lambda_e] = 1, [\lambda_g]) - \right. \\ & \left. - \sum_{\alpha\beta} \sigma_{\beta\alpha}(III) [\hat{Y}^+(III) \tilde{\chi}^+(III) b_e \tilde{\chi}(III) \hat{Y}(III)]_{\alpha\beta} \right\} \end{aligned} \quad (7)$$

where $\tilde{\chi}$ denotes the transpose matrix $\hat{\chi}$, and indices "+" and "-" in Eq.(7) label the eigenstates of the wire Hamiltonian in subspaces II. The diagonalization of the block matrices in subspaces III is carried out by extending the procedure described in Appendix A of Ref.[6] for $U = 0$, to the case $U \neq 0$. Doing so, one can reduce Eq.(7) to Eq.(8) of the paper.

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