Simulated Quantum Computation of non-equilibrium charge transport in a cyclic molecule

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Квантовое уравнение Линдблада для оператора плотности применяется для изучения транспорта электронов через молекулярное соединение, включающее в себя петлевую компоненту с двумя путями для электронной проводимости. Рассматривается концепция квантовой интерференции с целью проверки, может ли это явление влиять на электрический ток в режиме сильно неравновесного состояния системы. Показано существование двух режимов протекания электрического тока с возникновением и без возникновения кругового тока в бензольном кольце в зависимости от величины связи (параметра перескока J) между молекулой и электродами. Решения уравнения Линдблада находятся с использованием открытого для пользователей программного кода LindbladMPO, моделирующего элементы квантового алгоритма на классическом компьютере.

Lindblad master equation (LME) for the density operator is applied to examine electron transport through a molecular junction with a ring component having two pathways for an electron propagation. Here the concept of quantum interference is addressed to check whether this phenomenon may influence the electric current in a far-from-equilibrium regime. The existence of two modes of electric current flow with and without the occurrence of a circular current in the benzene ring is shown, depending on the value of coupling (hopping parameter J) between the molecule and electrodes. LME is solved with the use of the open-source program code LindbladMPO that simulate elements of quantum algorithm on a classical computer.

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Introduction

Charge transport in a single molecule suggests a smallest scale for functional electronic devices. On this scale peculiar properties are seen due to quantum interference (QI) effects in molecules whose rings branches provide several pathways for charge transport [1]. A paradigmatic case is a benzene molecule connected to two metallic nano-electrodes in different ways - either in the para (PC) or the meta (MC) configuration, Fig. 1. A good electrical conductance in PC is in contrast with its low value in MC, as shown in [2],

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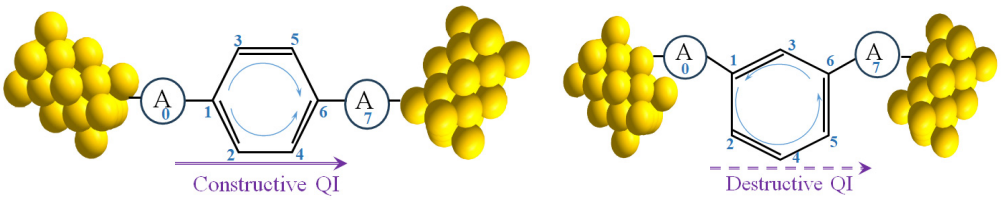


(a) (b)

Fig. 1. Schematic view on electron transport through benzene molecule coupled to metal electrodes via anchor (A) atoms in (a) para (PC) and (b) meta (MC) configurations; the atomic positions in the molecular junction are indicated by numbers.

which is in accord with the idea of a constructive and distractive interference of single-electron wave functions either in PC or MC, respectively.

This observation is well established experimentally in a weak nonequilibrium regime [2], when the voltage difference V between the left and right electrodes is not large, which can be described by the Landauer formula [1] integrating the transmission coefficient $T(E)$ in a narrow energy window $E_{\rm F} - \frac{eV}{2} < E < E_{\rm F} + \frac{eV}{2}$ around the Fermi energy $E_{\rm F}$ of electrodes. A dynamical approach based on the equation of motion for the density operator $\hat{\rho}(t)$ describing a benzene molecule that is dissipatively coupled to electrodes have been also developed [3] in a weak nonequilibrium regime. The expected steady-state *circular* electrical current within the benzene ring in the meta configuration was confirmed theoretically in [3], which is thought to be a bright feature of a destructive QI manifestation, Fig. 1b.

To check whether effects of QI can also be observed in a far-from-equilibrium regime of electron current in a molecular junction, in our work we also develop the dynamical approach by solving the Lindblad master equation for $\hat{\rho}(t)$. The underlying fermionic model is first formulated in the qubit representation, which facilitates using a quantum simulator - a software program [4] that implicates a quantum circuit, but runs on a classical computer.

I. Model and computational method

We focus on the time evolution of an electric current passing via the atomic $\pi-$ orbitals of the molecular junction schematically shown in Fig. 1. Here, six sites, $j = 1, \ldots, 6$, are for the benzene carbons, while $j = 0$ and $j = 7$ denote the orbitals of two anchor (A) atoms that are dissipatively coupled to electrodes, either in PC or MC.

The effective tight-binding model for the eight- orbital molecular junction is first rewritten in the qubit representation by mapping the the spinless creation/ annihilation Fermi operators onto the Pauli ones, $\sigma_j^\alpha, (\alpha = x, y, z)$, together with $\sigma_j^\pm = \sigma_j^x \pm i\sigma_j^y$. Then the tight-binding Hamiltonian takes the following form:

$$H = \sum_{\langle ij \rangle} J_{ij} \left(\sigma_i^x \sigma_j^x + \sigma_i^y \sigma_j^y \right), \tag{1}$$

where the electron's hopping parameters J_{ij} are for the bonds $\langle ij \rangle$ of the nearest neighbour atoms only. Hopping within the benzene bonds $\langle ij \rangle$, $(i, j = 1, \ldots, 6)$, is taken the same, $J_{ij} = J$, while for coupling between the anchor's and benzene's orbitals the following two parameters settings are chosen: (I) $J_{01} = J_{67} = J$ and (II) $J_{01} = J_{67} = J/8$.

Metallic electrodes act on the molecular system by injecting and absorbing electrons via the anchor atoms. Responsible for these processes in the Lindblad master equation (LME):

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{\imath}{\hbar}\left[H, \hat{\rho}\right] + D[\hat{\rho}] \tag{2}$$

the dissipative term $D[\hat{\rho}]$ is involved in a special form:

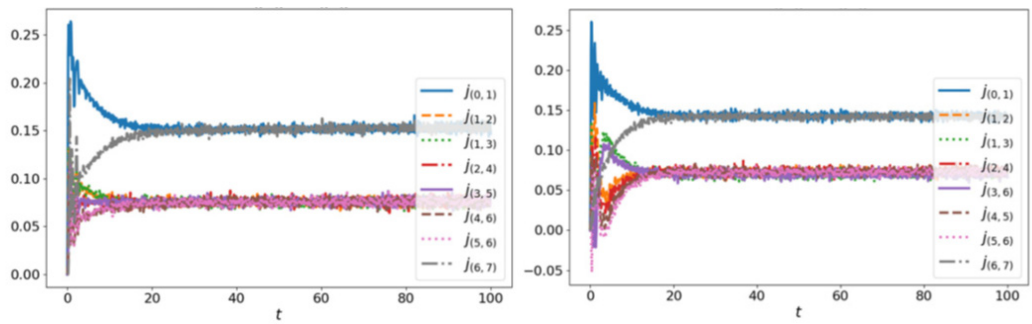
$$D[\hat{\rho}] = g_0 \left(\sigma_0^- \hat{\rho} \sigma_0^+ - \frac{1}{2}\left\{\sigma_0^+ \sigma_0^-, \hat{\rho}\right\} \right) + g_7 \left(\sigma_7^+ \hat{\rho} \sigma_7^- - \frac{1}{2}\left\{\sigma_7^- \sigma_7^+, \hat{\rho}\right\} \right) \tag{3}$$

which drives the molecular current in a far-from-equilibrium regime. In particular, this regime occurs if the bias voltage eV between electrodes is large compared to a characteristic energy difference $|\varepsilon_m - \varepsilon_n|$ in the molecular orbital spectrum. The rates of electrons injection $\sim g_0$ into the molecule from the left electrode and their extraction $\sim g_7$ to the right electrode are equal, $g_0 = g_7 = g$. Formalism employed here is similar to that in Ref.[5] except for the inverse, but fully equivalent mapping of the creation (annihilation) spinless fermion operators into the Pauli matrix describing qubit state flipping, i.e., $c_j^+ \to \sigma_j^-$ $(c_j^- \to \sigma_j^+)$. A correspondence between the far-from-equilibrium regime and a choice of Lindblad operators (3), together with the physical meaning of the coupling constant g, are also discussed in Ref.[5] in great detail. At $t = 0$, the initial occupancy of the valence $\pi-$ orbitals is taken to be zero, and thus many-particle effects on the electron transport are minimized. After solving the LME, the electric bound currents $j_{\langle i,j \rangle}(t)$ are found as $j_{\langle i,j \rangle}(t) = J_{ij}\mathrm{Sp}\left[\hat{\rho(t)}\left(\sigma_i^y \sigma_j^x - \sigma_i^x \sigma_j^y\right)\right]$, with a special attention to the incoming $j_{\langle 0,1 \rangle}$ and outgoing $j_{\langle 6,7 \rangle}$ currents, as well as to the internal currents $j_{\langle i,j \rangle}$ along the benzene bonds. We exploited an open-source solver for LME based on the matrix product operators [4].

II. Results and discussion

The calculated time evolution of electrical current along all bonds in the molecular junction is shown in Fig. 2 for the I-st parameters setting and in Fig. 3 for the II-nd setting. Throughout the calculations, parameters J and g are kept fixed such that in Fig. 2 and 3.

From Fig. 2 we deduce that for both configurations, PC and MC, the calculated time evolution of molecular currents is nearly the same even quantitatively and any QI effects distinguishing the two configurations are not observed. Therefore, this behaviour can be classified as a classical one. The argument in favor of this conclusion is as follows. Two quantities, $J_{01}/\hbar$ and



(a) (b)

Fig. 2. . Long-time evolution of electric currents $j_{\langle i,j\rangle}(t)$ along bonds $\langle i,j\rangle$ including the incoming $j_{\langle 0,1\rangle}$, outcoming $j_{\langle 6,7\rangle}$ current for PC (a) and MC (b); parameter setting (I) is taken for both configurations. Units of time and current are taken to be $\Delta t \simeq 0.33$ fs and $\Delta j \simeq 50$ μA, respectively.

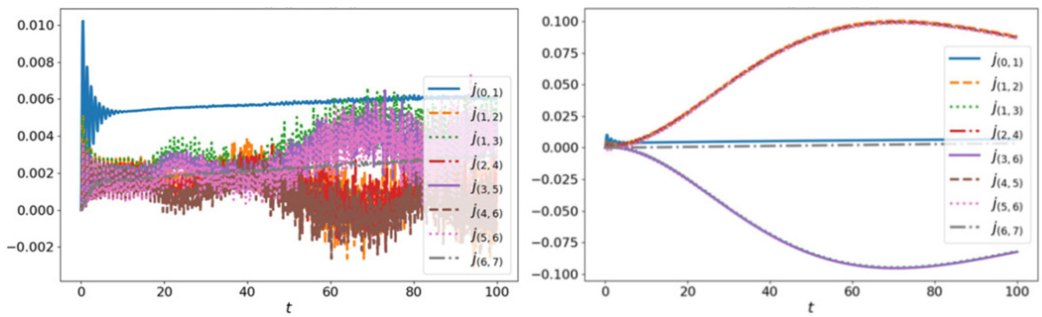
$J_{67}/\hbar$, meaning rates of the electron injection into and extraction out of the benzene molecule, should be compared to the frequency $J/\hbar$ of interatomic electron hopping within the benzene molecule. For the I-st setting one has $J_{01} = J_{67} = J$, and rates of an electron exchange are as high as the frequency $J/\hbar$. This fast dynamics prevents an incoming electron from forming any quasi-stationary wave state corresponding to a molecular electron orbital. In such a incoherent state QI effects are excluded.

To test this assumption, we reduce the dynamic coupling between the molecule and electrodes by taking the II-nd setting $J_{01} = J_{67} = J/8$. Now, after injection an incoming electron lives in the molecular junction for a longer time, thus enabling to form coherent extended molecular orbitals. Consequently, QI effects are expected to persist, which explains considerable difference in time evolution of currents for PC (Fig. 3a) and MC (Fig. 3b). We pay attention to the different scales chosen for electrical currents, which explains the enhanced current fluctuations on the intramolecular bonds seen in Fig. 3a, but not in Fig. 3b.

Complementary argument in favor of the destructive QI effect is the *circular* current existing within the benzene's ring in the meta configuration. Actually, a current in the right/positive direction (the upper branch in Fig. 3b) flows over the longer pathway and the opposite/negative current (the lower branch there) flows over the shorter pathway of the molecule. According to Ref.[6], a *circular* electrical microcurrent within ring's substructures of conductive molecular junctions cannot be understood without invoking the concept of quantum coherence.

III. Conclusion

Based on the Lindblad master equation, computations of the electric molecular current in the far-from-equilibrium regime have shown that keeping the rates of dissipation processes (electron's injection and absorption) $g_0 = g_7$ =const and varying the effective coupling between the molecular



(a) (b)

Fig. 3. Long-time evolution of electric currents $j_{\langle i,j \rangle}$; parameter setting (II) is taken for both configurations. Units of time and current are taken to be $\Delta t \simeq 0.33$ fs and $\Delta j \simeq 50$ μA, respectively.

system and the reservoir (controlled by hopping rates $J_{01} = J_{67}$) a dramatic change of the time evolution behavior occurs, from a classical to the one indicating a strong influence of quantum interference effects. In particular, analysis of the presented results allows us to predict for complex molecular junctions containing ring's substructures like the benzene molecule that a *circular* electric current can be induced within the ring under a certain voltage regime compatible with far-from-equilibrium state of the system.

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