Quantum interference effects on charge transport in molecular electronic junctions



Introduction

The study of charge transfer in organic molecules is important for > development of theoretical biology and medicine;

- - understanding the mechanisms of DNA replication, transcription and repair (mutagenesis and carcinogenesis);
- > development of modern microelectronics;
 - nanobioelectronics, which uses the conductive properties of DNA and other organic molecules in new microelectronic devices.

Ouantum interference effect occurring in molecules through which a charge can travel via multiple pathways can be the basis for new unconventional design principles in molecule scale electronics. The example chosen is that of charge transport from donor to an acceptor through a benzene molecule in either the ortho, meta, and para configuration.

Charge transport in DNA

We consider the following model applicable to describe charge transfer in DNA, namely: an excess charge embedded in DNA, an electron or a hole, moves as a quantum particle along the system of electronic π -orbitals belonging to nitrogen and carbon atoms of nucleotide bases.



Fig.1. The overlapping π -orbitals of the carbon and nitrogen atoms of nitrogenous bases form the "paths" of charge movement through DNA.

The quantum model of Skurtis and Nitzan [1] is structurally represented as a donor-bridgeacceptor: D-B-A. Here, the donor center D, on which the additional charge is initially localized, corresponds to the guanine-cytosine base pair (G-C), is attached to the $(A-T)_N$ bridge of N adenine-thymine base pairs, which is connected to the acceptor A that is the $(G-C)_3$ cluster.



Fig. 2. Energy level diagram of the Skurtis-Nitzan model. D (A) are the states of the hole on the donor (acceptor), $|\varphi_n\rangle(n=1+N)$ is the state of the hole on the *n*-th (A-T)-pair of the bridge.

A hole moves along effective sites: n=0 and n=N+1 correspond to the donor and acceptor centers, and n = 1, 2, ..., N- to the same base pairs of the bridge $(A-T)_{N}$. On each *n*-th pair of bases, including D and A centers, only the localized ground state $|\varphi_n\rangle$ of the hole with the lowest energy \mathcal{E}_n is taken into account: $|\varphi_n\rangle(n=1 \div N)$ is the state of the hole on the *n*-th (A-T)-pair of the bridge. Within the Skurtis and Nitzan model the Hamiltonian takes the tight-binding form:

$$\mathbf{H} = \sum_{n=1}^{N+1} [\mathcal{E}_n \mid \varphi_n \rangle \langle \varphi_n \mid + V_{n,n+1}(\mid \varphi_n \rangle \langle \varphi_{n+1} \mid + \mid \varphi_{n+1} \rangle \langle \varphi_n \mid)]$$

Model parameters:

- \mathcal{E}_D , \mathcal{E}_A donor (D) and acceptor (A) energy levels; the imaginary parts of \mathcal{E}_A takes into account the decay at acceptor:
- . E_R - energy levels for the n-th pair $(A-T)_n$ of the $(A-T)_N$ fragment,
- $V_{0,1} = V$ and $V_{N,N+1} = V$ the hopping amplitudes donor-bridge and bridge-acceptor; together

with $V_{n,n+1} = V_B$ within the bridge, their values are taken from the literature.

One solves the time-dependent Schrödinger equation: $i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$ with the initial condition $|\Psi(t=0)\rangle = \varphi_0 = |D\rangle$. Then the evolution of the wave function for t > 0 is described by the solution of the Schrödinger equation: $|\Psi(t)\rangle = \exp(-iHt/\hbar) |D\rangle$. Probability of detecting the add-charge on an acceptor (donor) is: $P_A(t) = |\langle A | \Psi(t) \rangle|^2 (P_D(t) = |\langle D | \Psi(t) \rangle|^2).$ The dimensionless transfer rate determined in the experiment is calculated by $R = \frac{\gamma_A}{\gamma_D} \cdot \frac{W_A}{W_D}$

where $W_A = \int_0^{\infty} P_A(t) dt$ ($W_D = \int_0^{\infty} P_D(t) dt$) - integral probabilities of finding add-charge on the acceptor (donor).

Calculation scheme:

- 1. The choice of basis $\{ | \varphi_n \rangle \}$, where the vector $| \varphi_n \rangle$ of the state of charge, localized at the site n=0.1.2...N+1
- 2. Calculation of eigenfunctions $|\psi_j\rangle$ and eigenvalues $(E_j i\Gamma_j)$ of the Hamiltonian \hat{H} : $H |\psi_j\rangle \equiv (E_j - i\Gamma_j) |\psi_j\rangle$
- 3. Decomposition of a vector $|\Psi(t=0)\rangle = |D\rangle$ into a superposition in terms of $|\psi_j\rangle |\Psi(0)\rangle = \sum_{j=1}^{N+1} a_j |\psi_j\rangle$

4. Solution of the Schrödinger equation: $|\Psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\Psi(0)\rangle = \sum_{k=1}^{k+1} a_k e^{-i(k_k - i\Gamma_k)t/\hbar} |\Psi_k\rangle$

5. Calculation of transition amplitudes: $\langle D | \Psi(t) \rangle$, $\langle A | \Psi(t) \rangle$ integral transition probabilities W_4 ,

 W_D and dimensionless transfer rate R.

Results

Results of model calculations in comparison with Experimental Data [Giese et al., Nature. 2001. V.412. P.318]



Fig. 3. The rate of charge transfer R(N) from donor to acceptor depending on the length N the intermediate fragment $(A-T)_{N^2}$

The change in the transfer rate R(N)dependence from fast at $N \le 3$ to slow at N > 3 indicates different charge transfer mechanisms: tunneling in the short $(N \le 3)$ and hopping in the long (N > 3) $(A-T)_N$ fragments.

Charge transport in cyclic organic molecules

To study quantum interference effects in a donor - molecular bridge - acceptor system in different configurations, characteristics of a charge transport through the benzene molecule are calculated.



Fig.4. a) A benzene molecule with an acceptor bound to it in the ortho, meta, or para configuration; b) p_{-} -orbitals on the carbon atoms in the benzene ring, on the donor and on the acceptor, with two possible "spatial" paths between the donor and the acceptor

The p_z – orbital atomic basis $(\varphi_n, \{\varphi_n\}, \varphi_n)$ is used where n = 1, ..., 6 are for the eigenstates of the benzene molecule. In this basis the tight-binding Hamiltonian is written as:

 $\hat{H} = \varepsilon_D \left| D \right\rangle \left\langle D \right| + \sum_{n=1}^{\infty} \varepsilon_n \left| n \right\rangle \left\langle n \right| + \left(\varepsilon_A + i \frac{\pi}{\tau} \right) \left| A \right\rangle \left\langle A \right| + \sum_{n=1}^{\infty} t_{Dn} \left(\left| D \right\rangle \left\langle n \right| + h.c. \right) + \sum_{n=1}^{\infty} t_{An}^{(\zeta)} \left(\left| A \right\rangle \left\langle n \right| + h.c. \right) \right\rangle$

Here we choose $\varepsilon_D = \varepsilon_A = 0$, while the molecular eigenvalues ε_n and hopping parameters t_{Dn} , $t_{An}^{(\xi)}$ are given in the Table.

The complex part $i\hbar/\tau$ ($\tau \approx 1 \text{fs}$) of the acceptor energy ensures that the charge is irreversibly trapped when it arrives at the acceptor.

To find the wavefunction of a charge $\psi(t) = c_D(t)\varphi_D + \sum_{n=0}^{\infty} c_n(t)\varphi_n + c_A(t)\varphi_A$ the time-dependent Schrödinger equation is solved with the initial condition

 $c_D(0) = 1$, $c_n(0) = c_A(0) = 0$

This determines the survival probability:

 $P(t) = |c_D(t)|^2 + \sum_{n=1}^{6} |c_n(t)|^2 + |c_A(t)|^2$

that the charge remains in the system at time t. Results of the numerical solutions for P(t) with an acceptor in different configurations (Fig. 3) and conclusions are presented in the next section.

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n	\mathcal{E}_n	t _{Dn}	$t_{An}^{(para)}$	$t_{An}^{(ortho)}$	$t_{An}^{(meta)}$			
1	-6.8	$\frac{J_0}{\sqrt{6}}$	$\frac{J_0}{\sqrt{6}}$	$\frac{J_0}{\sqrt{6}}$	$\frac{J_0}{\sqrt{6}}$			
2	6.8	$\frac{J_0}{\sqrt{6}}$	$-\frac{J_0}{\sqrt{6}}$	$-\frac{J_0}{\sqrt{6}}$	$\frac{J_0}{\sqrt{6}}$			
3	-3.4	$\frac{J_0}{\sqrt{3}}$	$-\frac{J_0}{\sqrt{3}}$	$\frac{J_0}{2\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$			
4	3.4	$\frac{J_0}{\sqrt{3}}$	$\frac{J_0}{\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$			
5	-3.4	0	0	$-\frac{J_0}{2}$	$-\frac{J_0}{2}$			
6	3.4	0	0	$-\frac{J_0}{2}$	$\frac{J_0}{2}$			

Results

Fig. 5. Decay of the survival probability for a charge in the system donor- benzene molecule acceptor in an ortho (orange), meta (green) and para (blue) configuration.

In each configuration, there are two possible spatial pathways for a charge travelling from the donor to the acceptor. The charge wavefunction at the acceptor site interfere constructively (para, ortho) or destructively (meta), which correspond to a good or bad charge conductivity through the molecular bridge. These effects can be taken into account and may be used in the functional way in the design of the molecular electronic devices

References

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Table. Parameters of the tight-

				√3	√3	2-43	243
		4	3.4	$\frac{J_0}{\sqrt{3}}$	$\frac{J_0}{\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$	$-\frac{J_0}{2\sqrt{3}}$
		5	-3.4	0	0	$-\frac{J_0}{2}$	$-\frac{J_0}{2}$
		6	3.4	0	0	$-\frac{J_0}{2}$	$\frac{J_0}{2}$
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