PREVIOUS STEPS IN UNDERSTANDING THE MECHANISM OF ELECTRON TRANSFER THROUGH DNA

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Reason

Daily problems:

- Reach limit in miniaturization of solid-state electronic device
- Have the desire to achieve competitive technologies that would not have the same excessive specific heat, accompanying any computational work

Why is DNA a good candidate as transistor:

- Small size
- Width band of realizing its electric property

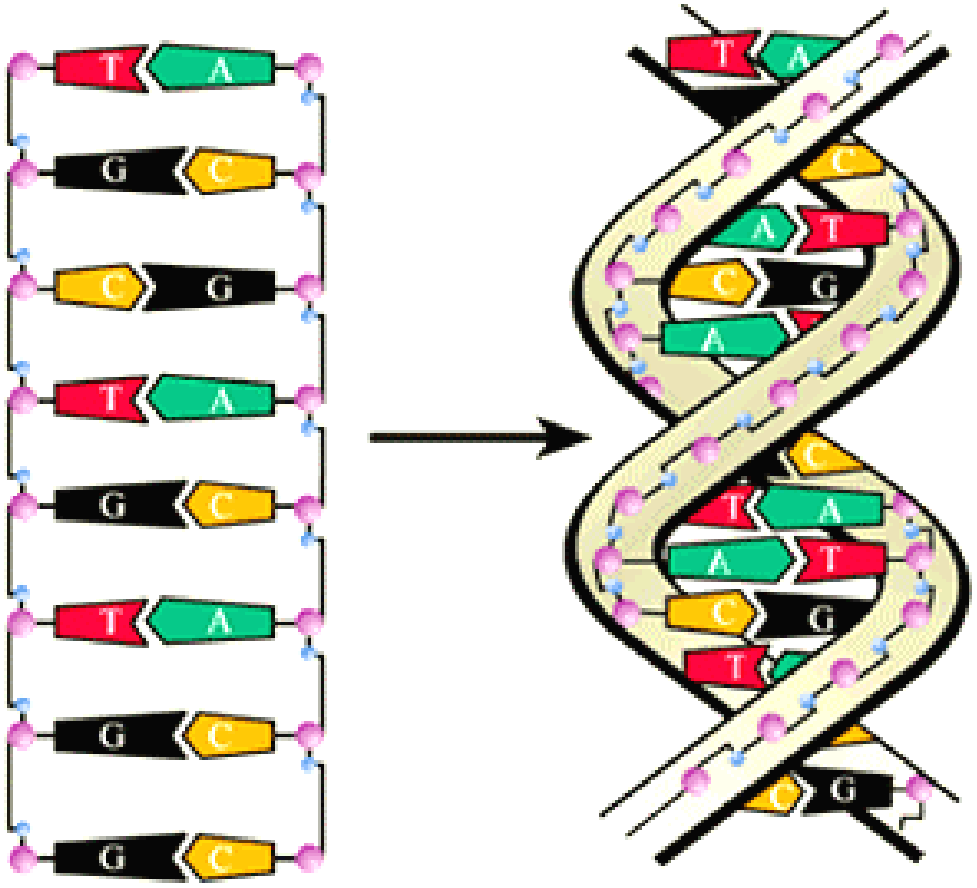
The problem that arose:

- There is no universal theory of explaining the mechanism of charge transfer through DNA

Our goals:

1. To go over previous existing theories and experimental works
2. To find out any correlations between circumstances and electric property of DNA
3. To write down existing calculated and predicted values of electric characteristics of nucleobases
4. To sum up previous steps of studying DNA
5. To come up with own idea of explanation of mechanism of charge migration through DNA, based on past experience
6. To build up mathematic model of electron transfer through acids chain and further to do experiments and check if they are satisfying with each other.

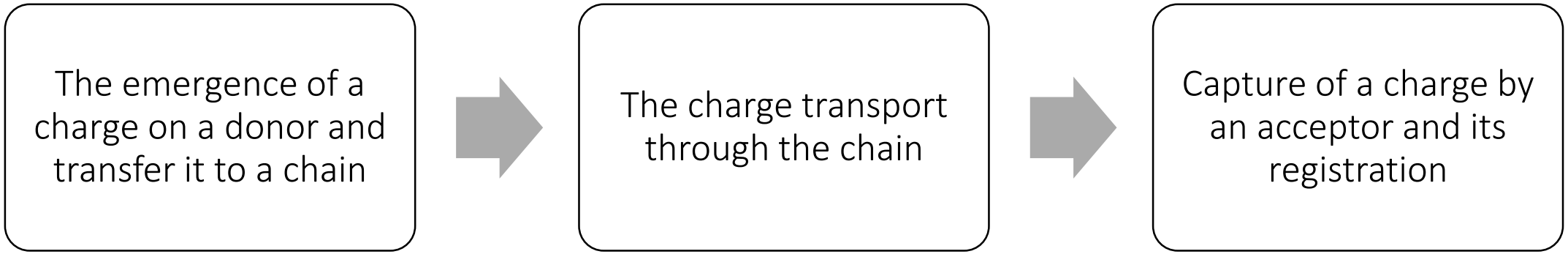
DNA



The overlapping of electronic π-systems leads to a good electronic exchange interaction, as well as to the stability of the entire system. It is this electronic configuration of the DNA molecule that allows us to assume that the charge transfer occurs over π-conjugate bases (Chen & Tao, 2009), (Luo & Frisbie, 2010).

DNA can be considered as a semiconductor with a wide forbidden band, but many experiments indicate that this biological molecule has a wide range of conductivity values: from the insulator to the induced superconductor (4 K; (Kasumov, Klinov, Roche, Guron, Bouchiat, 2004)).

Stages of charge transfer along the DNA chain



This figure shows the main steps that determine the transfer of charge along the DNA chain. Each of these stages can have a significant influence on the further dynamics of the process of charge migration along the nucleotide chain, i.e. each stage can be a limiting factor.

Experimental research methods

Object of study

Methods

Donor

- What it does: serves to inject a charge into the circuit
- Requirements:
  - Good interaction with DNA bases
  - Initiation of the transfer should occur with good quantum yield and serve as a good detector of this process
  - It should not chemically interact with DNA either in the main or in the excited state
- Examples:
  - Metal Complexes
  - The dye methylene blue
  - Bromo-uracil

Chain of DNA

- Synthetically created
- Has a random nucleotide composition

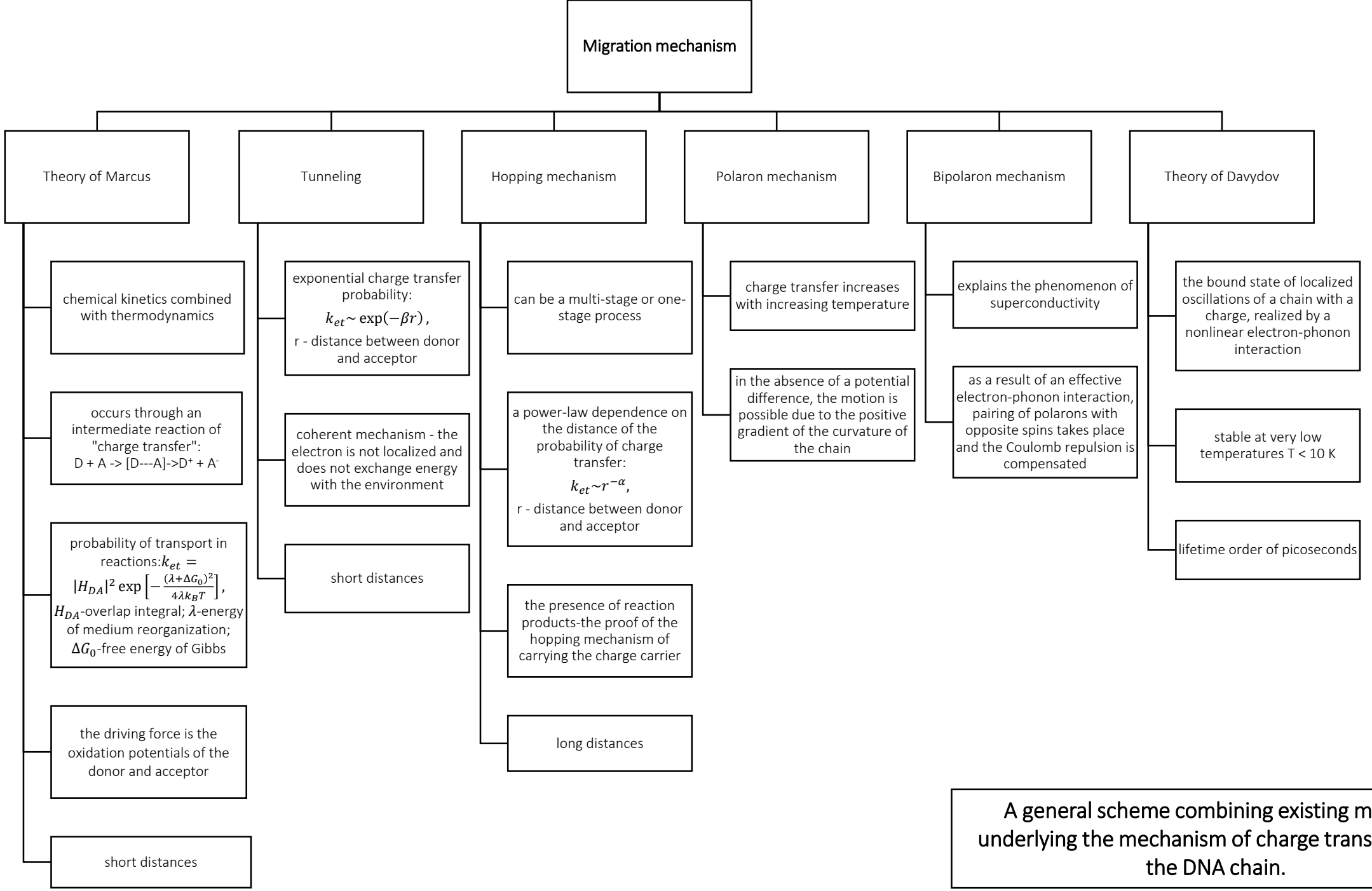
Acceptor

- What it does: registers the incoming charge
- Requirements:
  - From the absorption / excitation spectra
  - Due to chemical oxidation-reduction reactions
  - Good interaction with DNA bases
  - Initiation of the transfer should occur with good quantum yield and serve as a good detector of this process
  - It should not chemically interact with DNA either in the main or in the excited state
- Examples:
  - Metal Complexes
  - The dye methylene blue
  - Cyclopropyl- and bromo-substituted DNA bases

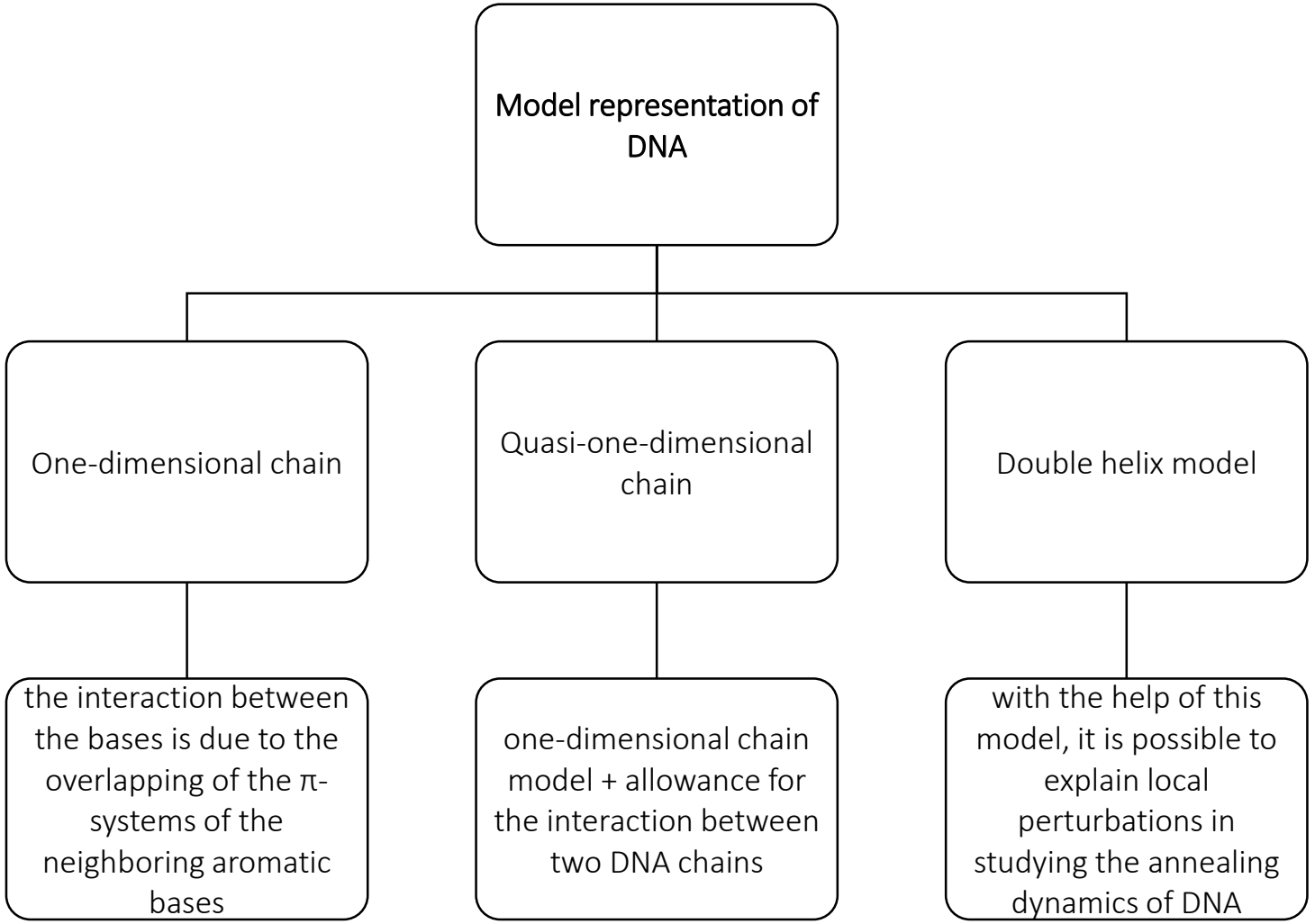
Methods

- Pulse
  - The charge is generated by the absorption of a quantum of light
  - A constant source of charges is used
- Stationary
- Modified method of scanning tunneling microscopy
- Atomic force microscopy

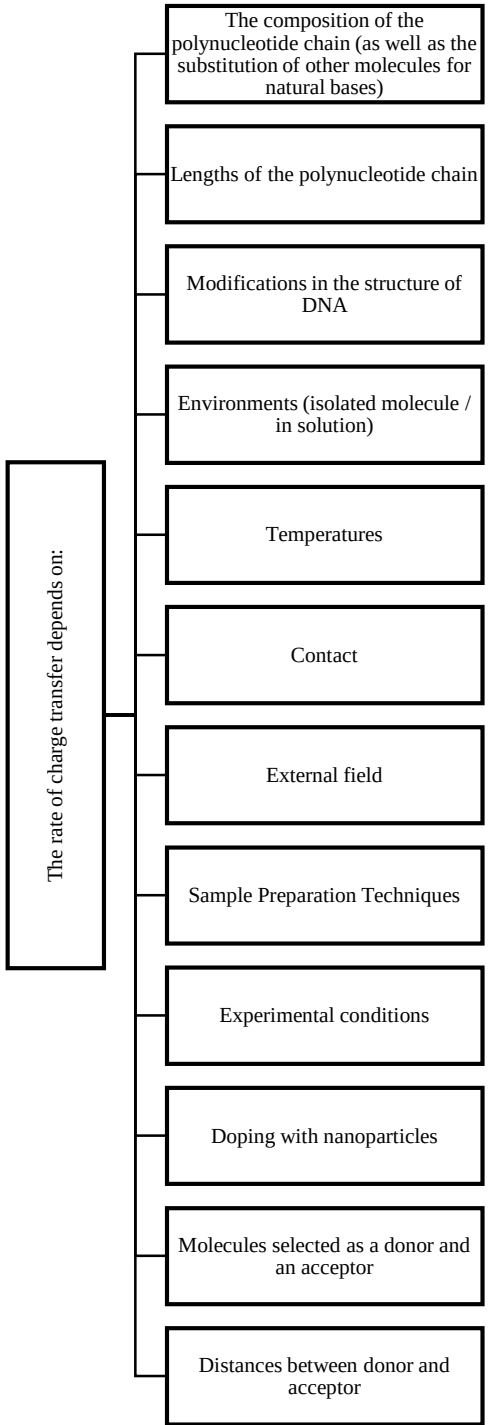
The general idea of setting up experiments from research objects with the requirements presented to them is presented schematically, to the physical methods of detecting the process of charge migration.



A general scheme combining existing models, underlying the mechanism of charge transfer along the DNA chain.



Existing models for examining the DNA molecule. Each model is characterized by its own set of degrees of freedom for the molecule: in the equations of motion within a single model, intermolecular interactions between DNA strings, degrees of freedom, responsible for rotations, shifts, displacements of the polynucleotide chain itself.



The main parameters affecting the rate of charge transfer

TR - transfer rate,
CT - charge transport,
HT - hole transport

This table stores some results regarding theme of charge migration through DNA

Table 2. Experimental values

Investigated system	Value of parameter	Paper
Hairpin = Chromophore + 2 complementary DNA segments	-direct TR constant:$5\times10^{7}s^{-1}$ -reverse TR constant:$5\times10^{6}s^{-1}$	(Frederick D.L. et al., 2000)
Short fragments of DNA in the form of a hairpin	-TR $\sim 10^{9}s^{-1}$ -TR= $1.2ns^{-1}$ in (Blaustein, Lewis, Burin, 2010), where mechanism is tunneling	(Daublain et al., 2009) (Blaustein et al., 2010) (Conron, Thazhathveetil, Wasielewski, Burin, Lewis, 2010)
$G(A)_5G \rightarrow G(zA)_5G$	-replacing leads to $\uparrow of\ TR$ by an amount$>10^{3}s^{-1}$	(Kawai, Kodera, Osakada, Majima, 2009)
$(zA)_n$	-k_{CT} : $4.2\times10^{10}s^{-1}$ -for $(G)_n$: $4.3\times10^{9}s^{-1}$	(Thazhathveetil, Trifonov, Wasielewski, Lewis, 2011)
poly-(dA)-poly-(dT) poly-(dG)-poly-(dC)	-resistance at room temperature for: poly-(dA)-poly-(dT)=100 MΩ poly-(dG)-poly-(dC)=1.3 MΩ	(Yoo et al., 2001)
Aq-DNA u-DNA	-quantum resistance for: Aq-DNA = $4.0\ \pm0.2\times10^{-4}G_0$, u-DNA = $14\ \pm1\times10^{-4}G_0$, where $G_0 = 7.748\times10^{-5}S$	(Xiang et al., 2017)
GATGGG GATGTGGG GTTGGG GTTGTTGGG GTTGTTGTTGTTGGG	-$k_{CT,rel}\ of\ HT = 3.20$ -$k_{CT,rel}\ of\ HT = 3.40$ -$k_{CT,rel}\ of\ HT = 8.90$ -$k_{CT,rel}\ of\ HT = 2.80$ -$k_{CT,rel}\ of\ HT = 0.88$	(Meggers, Michel-Beyerle, et al.,1998) (Bernd Giese, Wessely, Lindemann,Meggers, Michel-beyerle, 1999)

Our mathematical model

$$H = H_F + \frac{1}{2}\sum_n \alpha'_n \left(\frac{p_{zn}^2}{m_n} + K_n z_n^2\right) + \sum_n \frac{e^2\mu_n^2}{6(4\pi\varepsilon_0)^2 k_B T(z_n^2 + u_n^2)^2} + \sum_n eEz\delta(z - z_n) + U_M$$

$$H_F = H_{cl} + \langle\Psi|H_q|\Psi\rangle = \frac{1}{2}\sum_n \alpha'_n \left(\frac{p_n^2}{m_n} + K_n u_n^2\right) + \langle\Psi|H_q|\Psi\rangle \text{ [*]}$$

$$H_q = \sum_{n=1}^{N} \alpha_n |n\rangle\langle n| + \sum_{n\neq k} \nu_{nk} |n\rangle\langle k| + \sum_{n=1}^{N} \alpha'_n u_n |n\rangle\langle n|$$

$$U_M(z_n) = D_n(1 - e^{-a_n z_n})^2$$

$$|\Psi\rangle = \sum_n b_n(\tilde{t})|n\rangle$$

$b_n(\tilde{t})$- probability of detection of charge on the n-th site,

m_n- mass of the n-th site,

K_n- constant of elasticity,

α_n- charge energy on the n-th site,

α'_n- the charge-coupling constant with the displacement of the n-th section from the equilibrium position

$U_M(z_n)$ - Morse potential

Further goals:

- To keep on going over published works regarding similar theme
- To make calculations based on our derived mathematical model
- To do experiments
- To satisfy experimental results with model’s prediction

Thank you for your attention!

Nucleotide	Topological area: (A^2)	The average size of a molecule (A)	μ (dipole moment) (D)	The potential of oxidation (eV) *acetonitrile solvent
Timin (T)	58,2	4,305	3,975	1,9
Cytosine (C)	67,5	4,636	5,684	1,9
Adenine (A)	80,5	5,06	2,492	1,69
Guanine (G)	96,2	5,535	5,450	1,24

Nucleotide pairs	The exchange integral (eV)	Nucleotide pairs	The exchange integral (eV)
GG	0,084	TG	0,085
GA	0,089	TA	0,086
GT	0,137	TT	0,158
GC	0,110	TC	0,076
AG	0,049	CG	0,042
AA	0,030	CA	0,029
AT	0,105	CT	0,1
AC	0,061	CC	0,041

Characteristics of nucleotides

Falloff parameter and its limitation:

$$k_{CT}(R) = k_0 \exp(-\beta R)$$

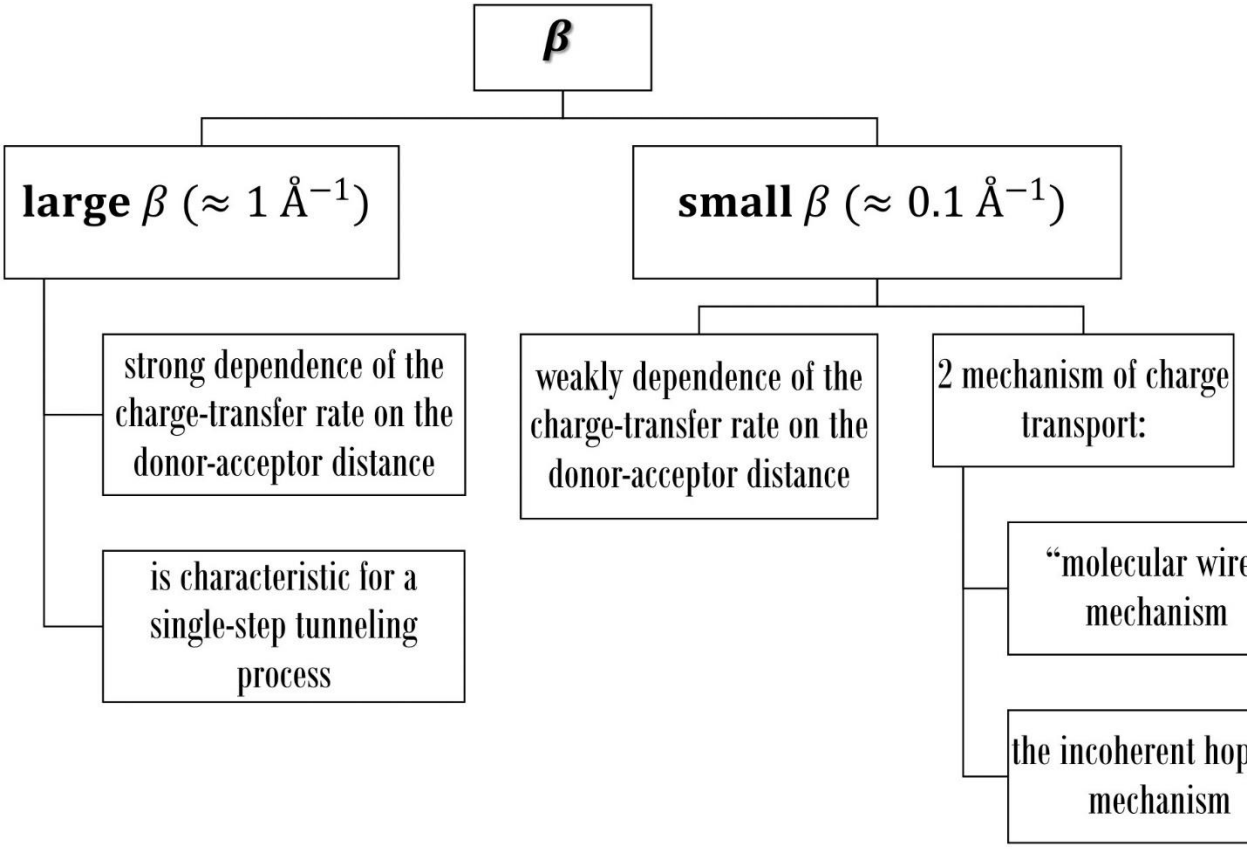
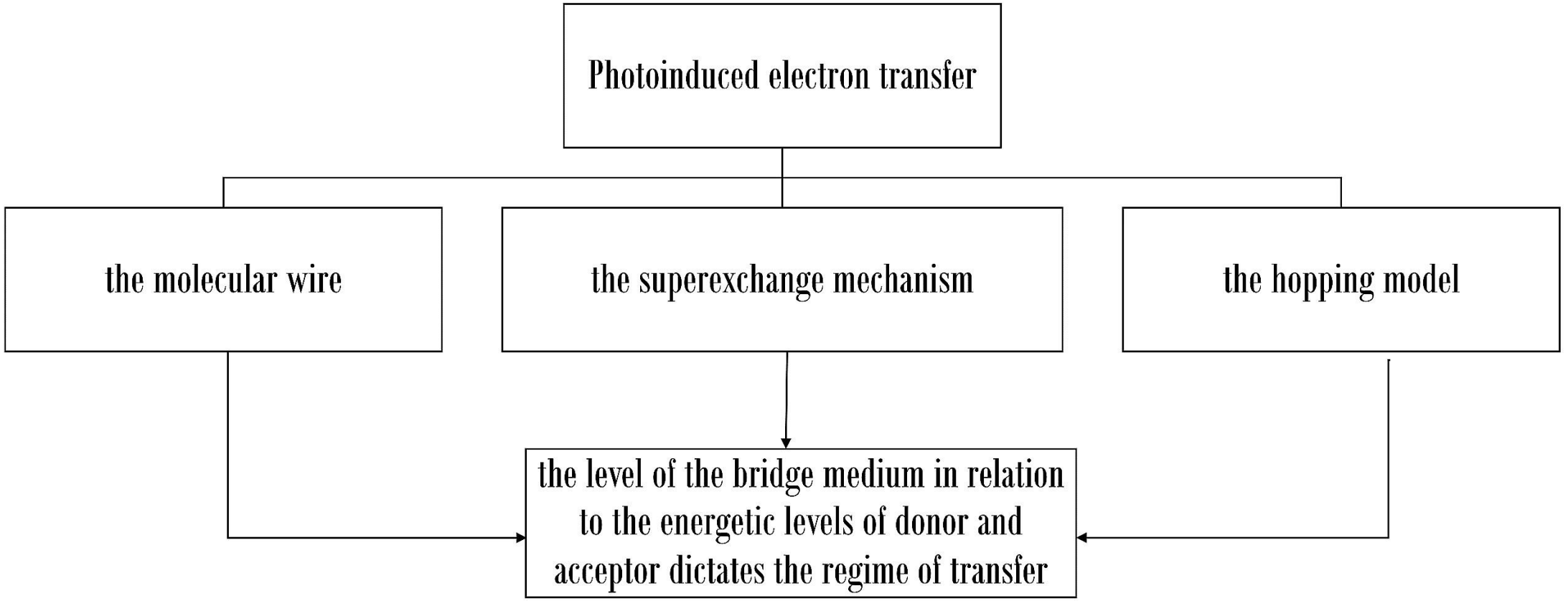


Table 1. Experimental parameters of β

β value, Å^{-1}	Paper
0.2	(Kelley SO, 1999)
1.0	(Messer et al., 2000)
-0.017 ±0.004	(Ly, Sanii, Schuster, 1999)
1.4	(Tanaka, 1998)
0.7	(Lewis et al., 1999)
0.07	(Giese, Wessely, Lindemann, Meggers, Michel-beyerle, 1999)

Principal mechanisms of photoinduced electron transfer



(Wagenknecht, 2006)

Principal mechanisms of photoinduced electron transfer

Mechanism/differences	the molecular wire	the super exchange mechanism	the hopping model
the molecular wire	• the bridge states are energetically comparable to the level of the donor • the electron can be injected into the bridge • the electron is localized within the bridge and moves incoherently to the acceptor	----------	• the electron is not delocalized within the bridge during the electron hopping
the super exchange mechanism	----------	• the bridge states lie above the level of the donor. • the electron is transferred in one coherent jump and is never localized within the bridge • it can be expected that the electron transfer rate of the latter process is highly distance-dependent.	• the electron hopping represents a multi- step process consisting of charge injection, charge transport and charge trapping
the hopping model	• the electron is not delocalized within the bridge during the electron hopping	• the electron hopping represents a multi- step process consisting of charge injection, charge transport and charge trapping	• if the bridge state of the electron transfer medium is energetically comparable to the photoexcited donor

(Wagenknecht, 2006)