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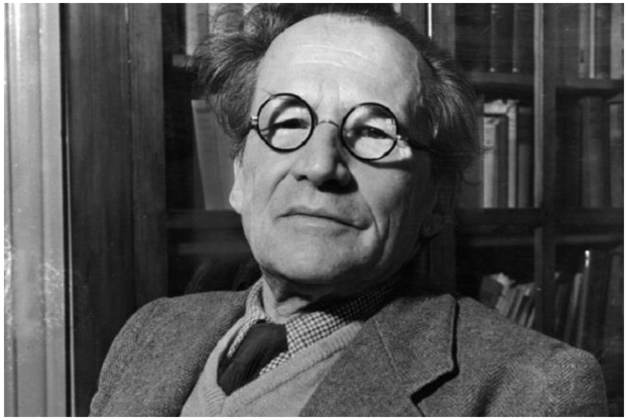
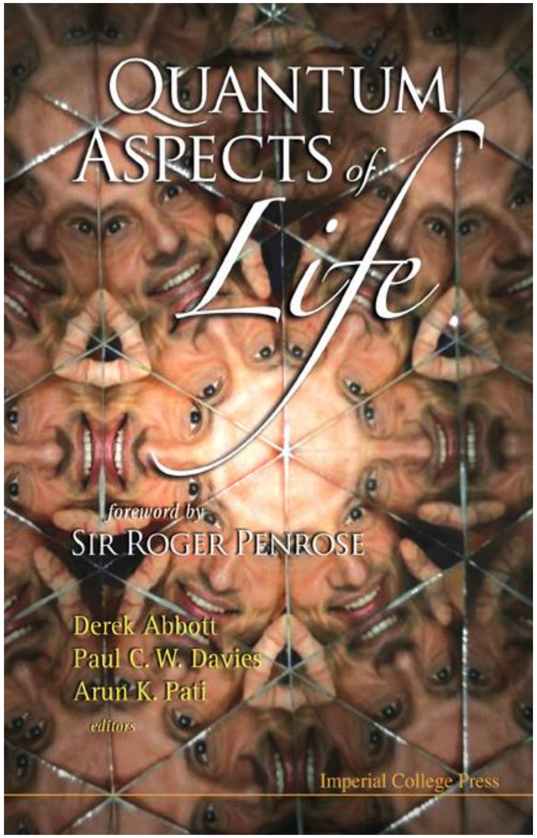
Quantum dynamics of a hole migration through DNA

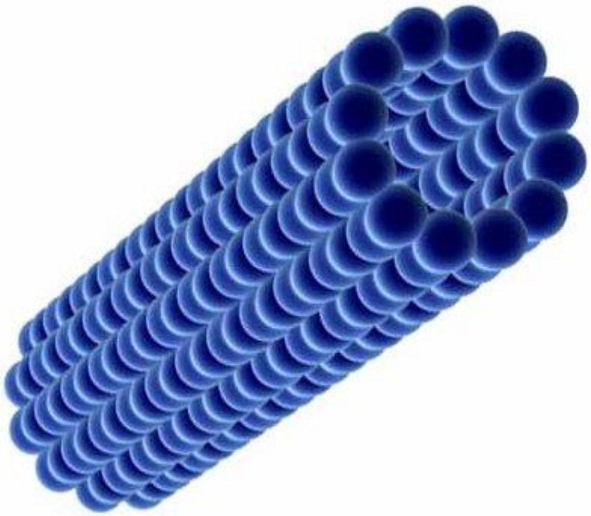
Dubna, 2017

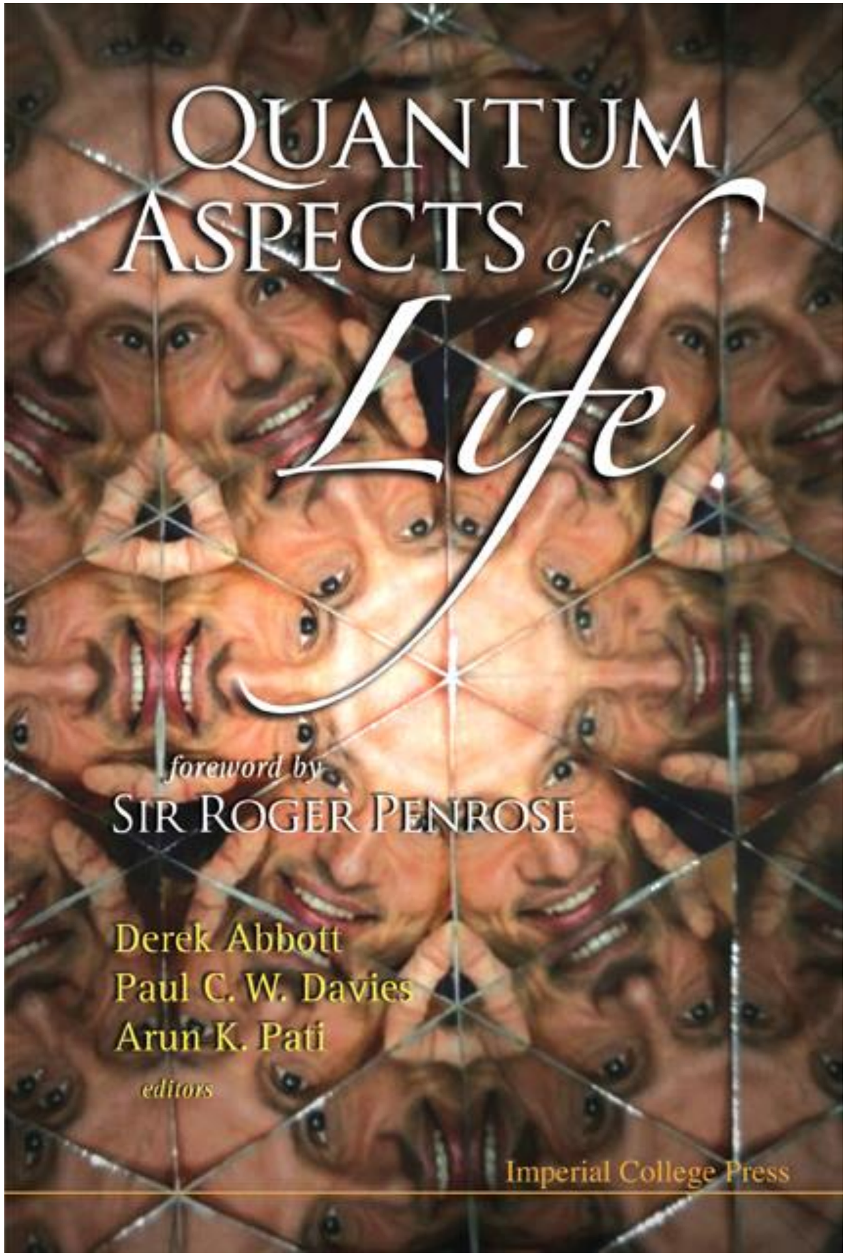


In his book “What is Life?” Erwin Schroedinger suggested a quantum basis for living systems, concluding that life’s essential framework was in “aperiodic lattices”. Schroedinger description applies to DNA, and also to cytoskeletal protein assemblies such as microtubules.



Source:A Quantum Origin of Life? Imperial College Press,
57 Shelton Street Covent Garden London WC2H 9HE, 2008.
D. Abbot, P.C.W. Davies, A.K. Pati (Eds.),
Foreword by Sir Roger Penrose.





QUANTUM ASPECTS *of* *Life*

foreword by
SIR ROGER PENROSE

Derek Abbott
Paul C. W. Davies
Arun K. Pati
editors

Imperial College Press

The principal question that arises here is as follows: are quantum effects able to considerably influence biological systems functioning?

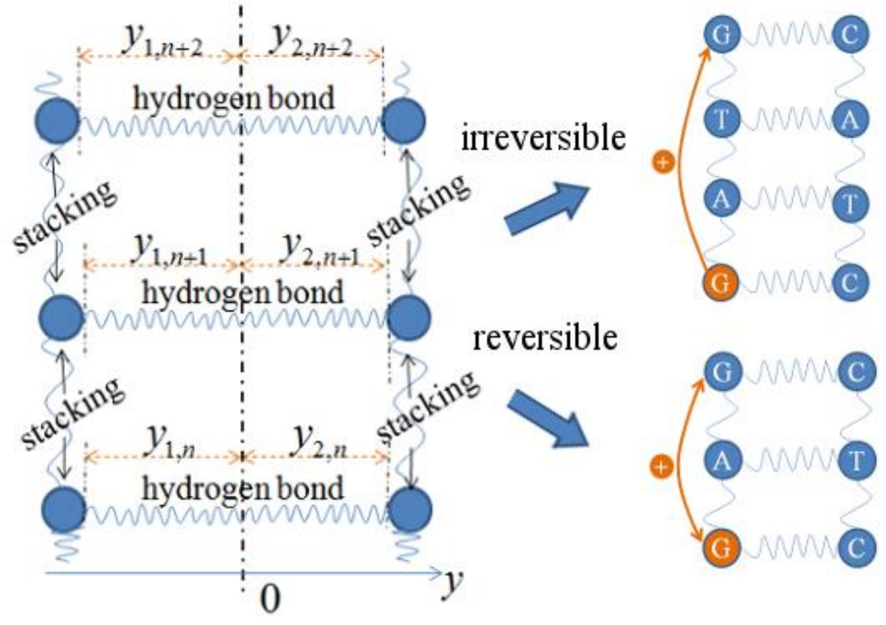
The process of charge transport through a DNA molecule via a hole transfer followed by quantum tunneling is an example of quantum effect in biosystems.

It has been found that a charge migration along DNA chain can present two opposite processes: a charge transport is reversible as in the experiments of Lewis et al.

F.D. Lewis, X. Zuo, J. Liu, R.T. Hayes, M.R. Wasielewski, Dynamics of inter- and intrastrand hole transport in DNA hairpins, J. Am. Chem. Soc. 124 (2002) 4568–4569.

On the other hand, a charge transport could be an irreversible process in the experiments of Giese et al.

B. Giese, E.Meggers, S.Wessely,M. Spormann, A. Biland, DNA as a supramolecule for long-distance charge transport, Chimia 54 (2000) 547–551.



Different approach modeling a charge transfer dynamics through DNA were suggested, among which there were:

polaronic transport - B.B. Schimidt, M.H. Hettler, G. Schon, Nonequilibrium polaron hopping transport through DNA, Phys. Rev. B 77 (2008) 165337–165344,

soliton-like solution –S.W.Englander, N.R.Kallenbach, A.J. Heeger, J.A.Krumhansl, A.Litwin, Nature of the open state in long polynucleotide double helices: possibility of soliton excitations. Proc. Natl. Acad. Sci. USA 77 (1980) 7222-7226.

superexange and multistep hoping - F.C. Grozema, S. Tonzani, Y.A. Berlin, G.C. Schatz, L.D.A. Siebbels, M.A. Ratner, Effect of structural dynamics on charge transfer in DNA hairpins, J. Am. Chem. Soc. 130 (2008) 5157–5166.

N.S. Fialko, V.D. Lakhno, Nonlinear dynamics of excitations in DNA, Phys. Lett. A 278 (2000) 108–112.

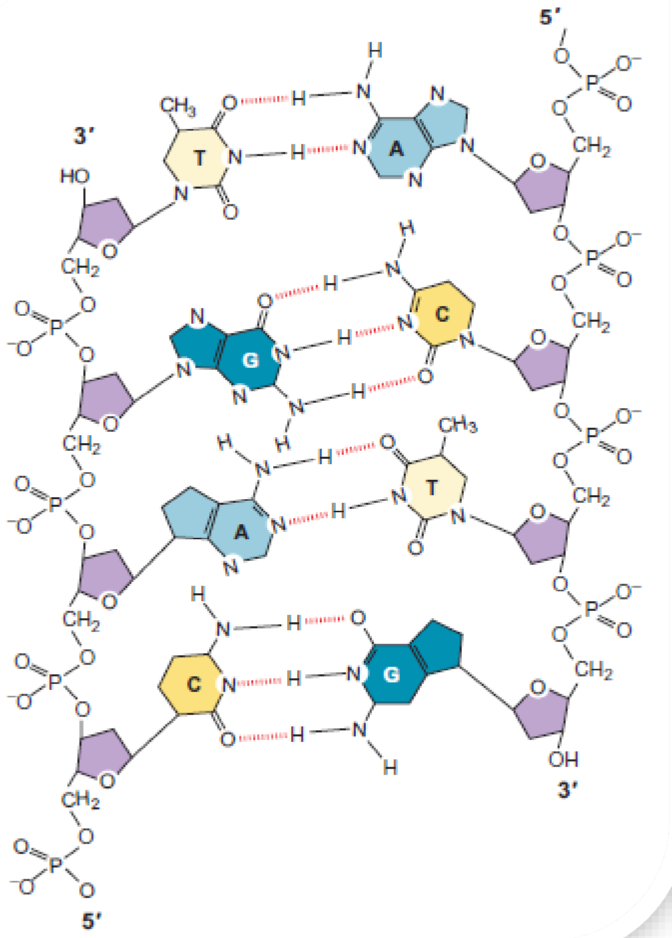
As has been shown, a positive charge transport through a DNA may be followed by quantum tunneling being about $\gtrsim$ 1 ps. This demonstrates the DNA capability of supporting a quantum superposition, being determined by time scales of different processes in biomolecules and their solutions.

S.E. Shirmovsky, D.L. Boyda, Study of DNA conducting properties: reversible and irreversible evolution, Biophys. Chem 180–181 (2013) 95–101.

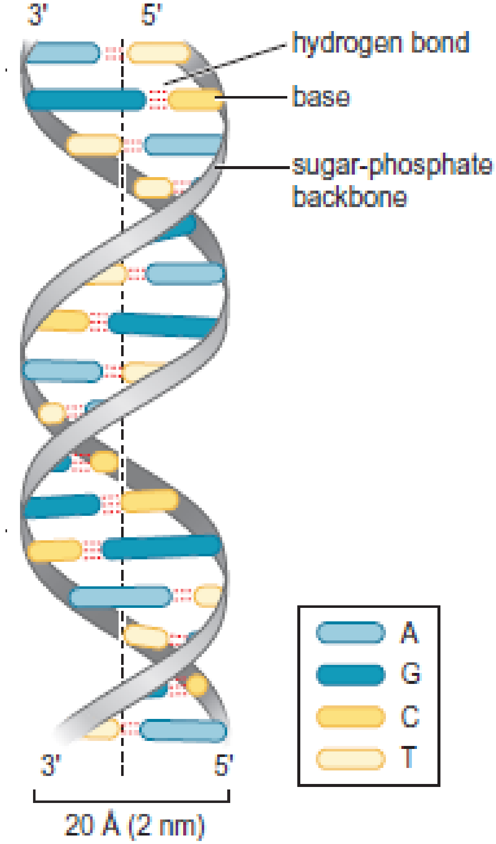
O.V. Belov, D.L. Boyda, I. Plantec, S.E. Shirmovsky, Simulation of the chargemigration in DNA under irradiation with heavy ions, Biomed. Mater. Eng 26 (2015) S1937–S1944.

S.Eh. Shirmovsky, Quantum dynamics of a hole migration through DNA: A single strand DNA model, Biophysical Chemistry 217 (2016) 42-57.

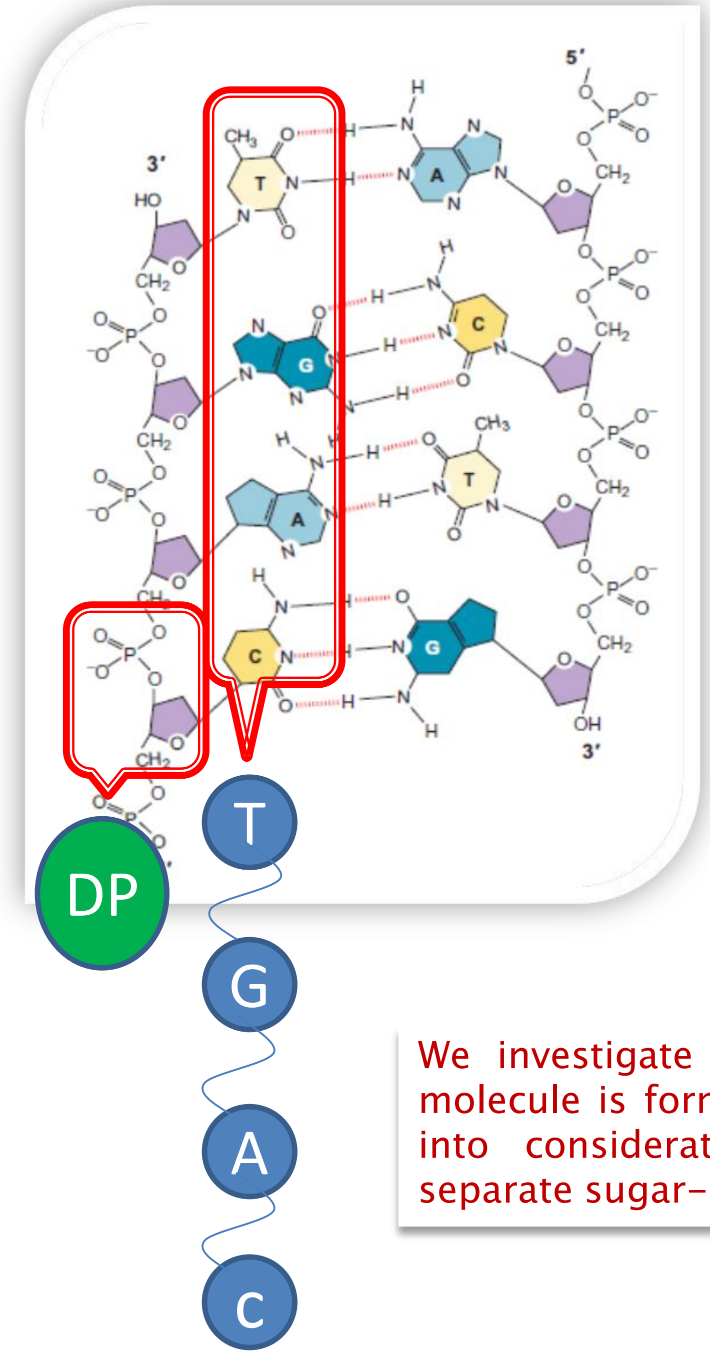
DNA in brief

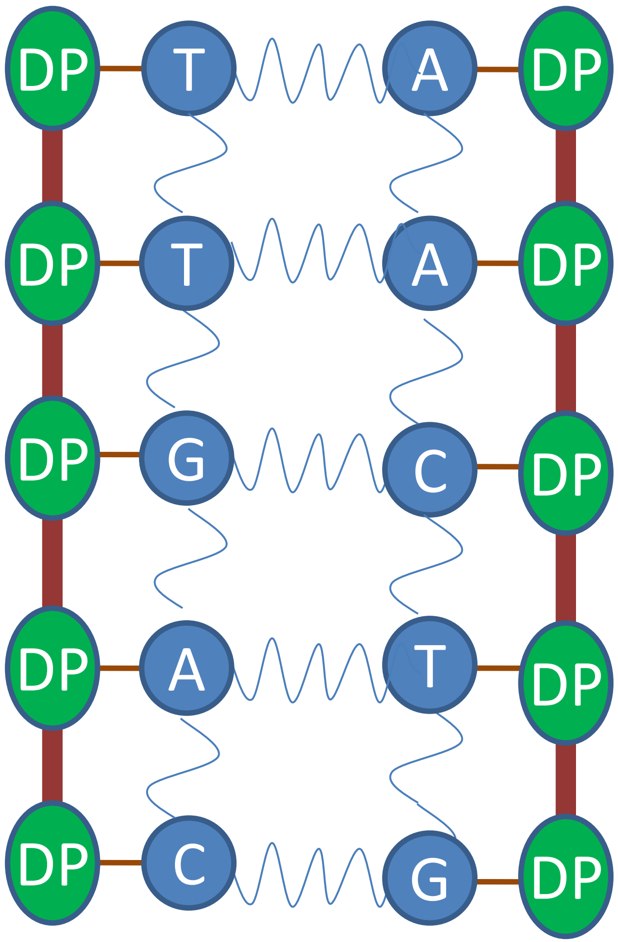


Source: Adapted from Dickerson R.E. 1983. Scientific American 249: 94. Illustration, Irving Geis. Image from Irving Geis Collection/Howard Hughes Medical Institution.

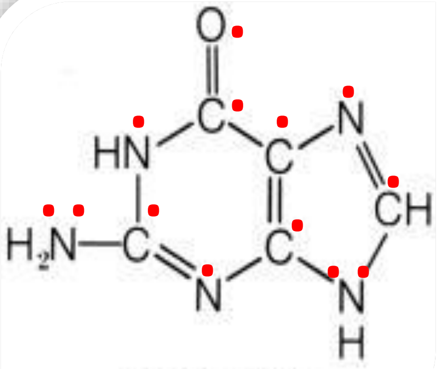


DNA is of quasiregular chemical structure. Its regular part is composed of strictly alternating sugar and phosphate groups while its irregular part is composed by bases.

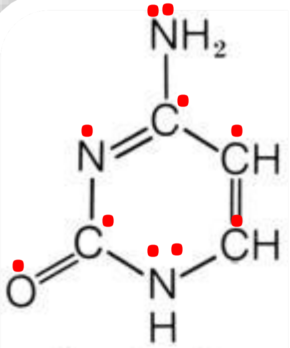




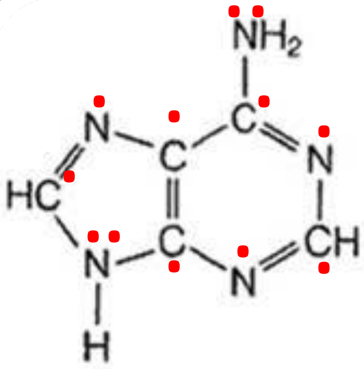
We investigate the hole- DNA Interaction. The fact that a DNA molecule is formed by a sugars phosphate group an bases is taken into consideration. The model clearly determined position of separate sugar-phosphate group and DNA bases.



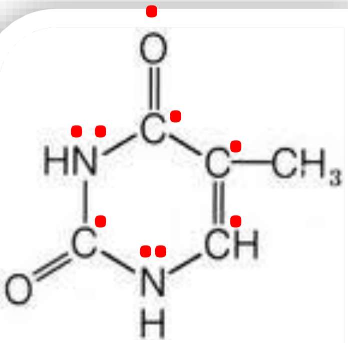
Guanine (G)



Cytosine (C)

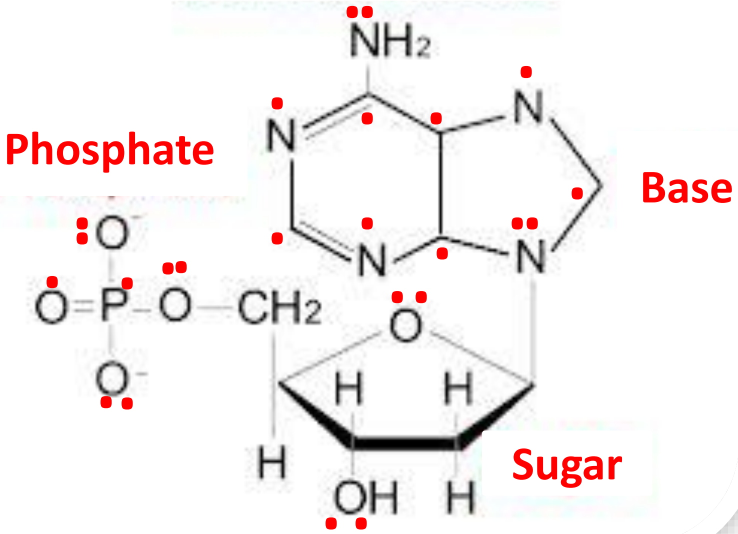


Adenine (A)



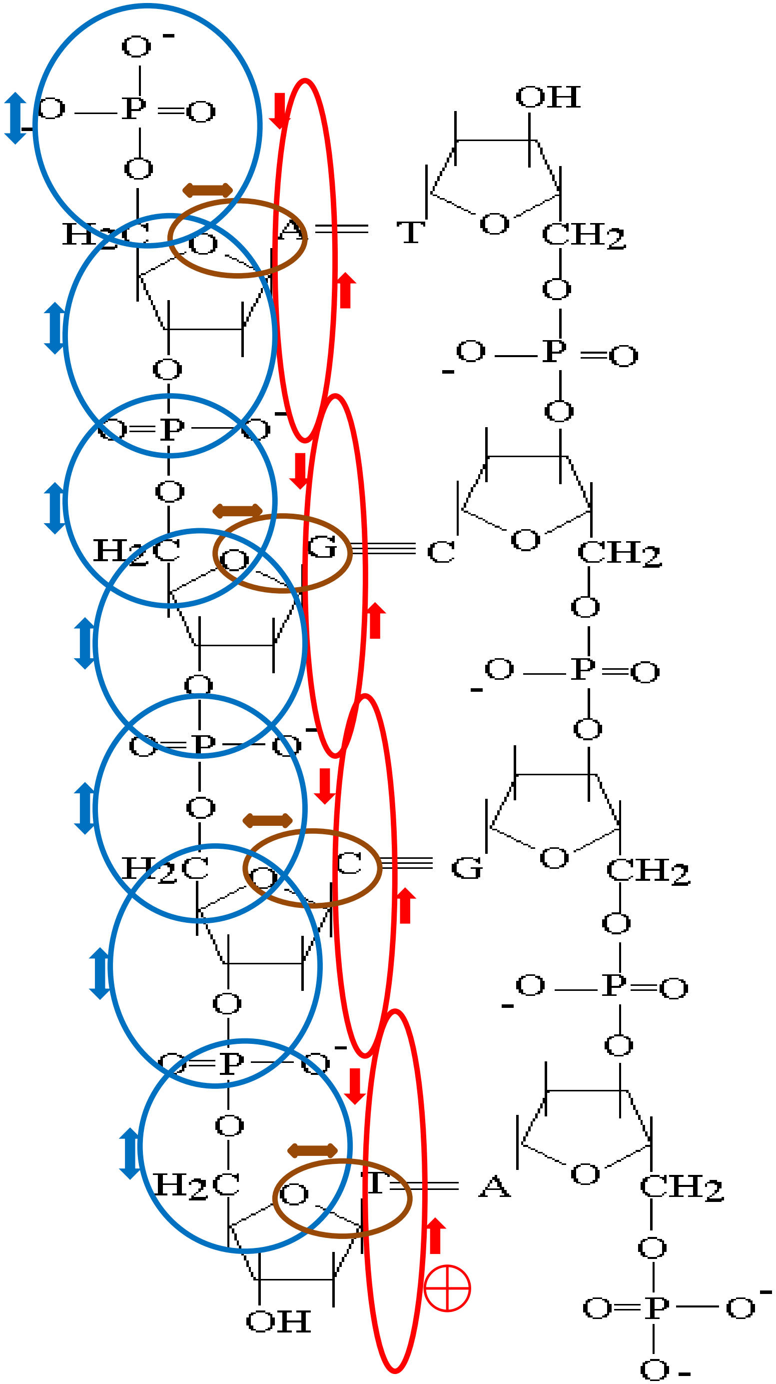
Thymine (T)

Nucleotide



12 π-electrons and 10 π-orbitals in the A molecule;
14 π-electrons and 11 π-orbitals in the G molecule;
10 π-electrons and 8 π-orbitals in the C molecule;
10 π-electrons and 8 π-orbitals in the T molecule.
In the sugar-phosphate, there are 7 orbitals with 12 electrons.

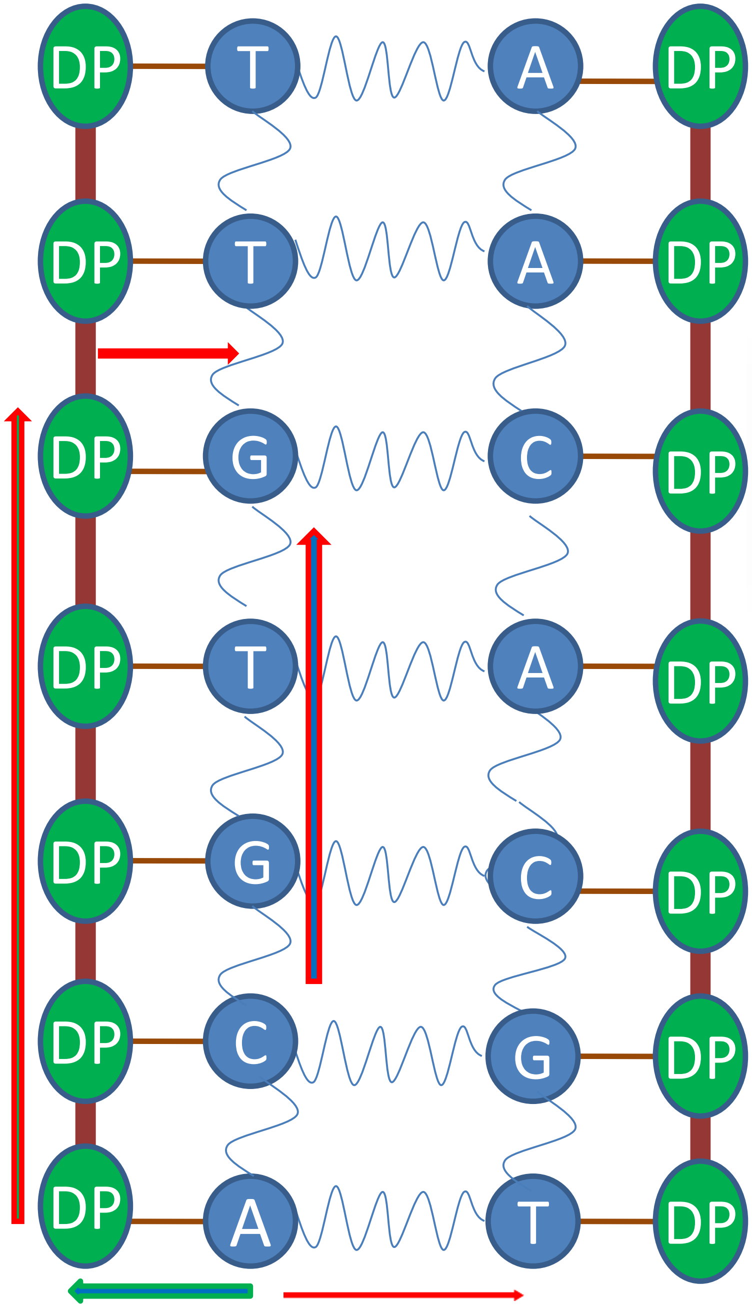
K. Iguchi, π-Electrons in a single strand of DNA: a phenomenological approach international, Int. J. Mod. Phys. B 18 (2004) 1845–1910.



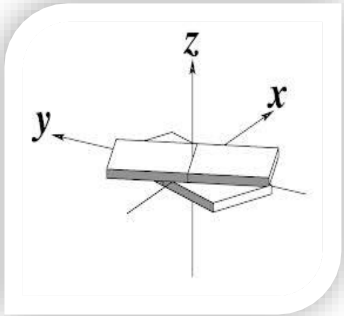
At present, an assumption that quantum effects in biosystems may be connected with arranged quantum processes in electron π clouds inside biomolecules is quite justified. Thus, the distribution of – π electron clouds in DNA sets the stage for a quantum process which directs and controls the dynamics of DNA-charge interaction.

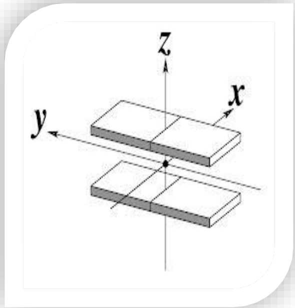
The distribution of a π -electron clouds create various periodical or aperiodical structures in DNA, which results in a possible charge transferring from one structure to another while the hole tunneling.

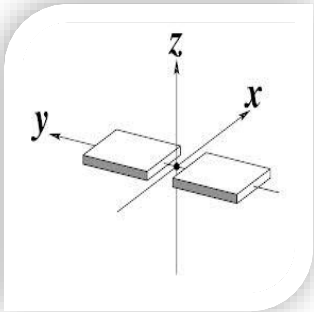
$$\hat{H} = \sum_{a} E_a |\varphi_a >< \varphi_a| + \sum_{a,a'} V_{a,a'} |\varphi_a >< \varphi_{a'}|$$



A DNA is a flexible system. The following DNA fluctuations are possible: a twist, a rise, a stretch and other.



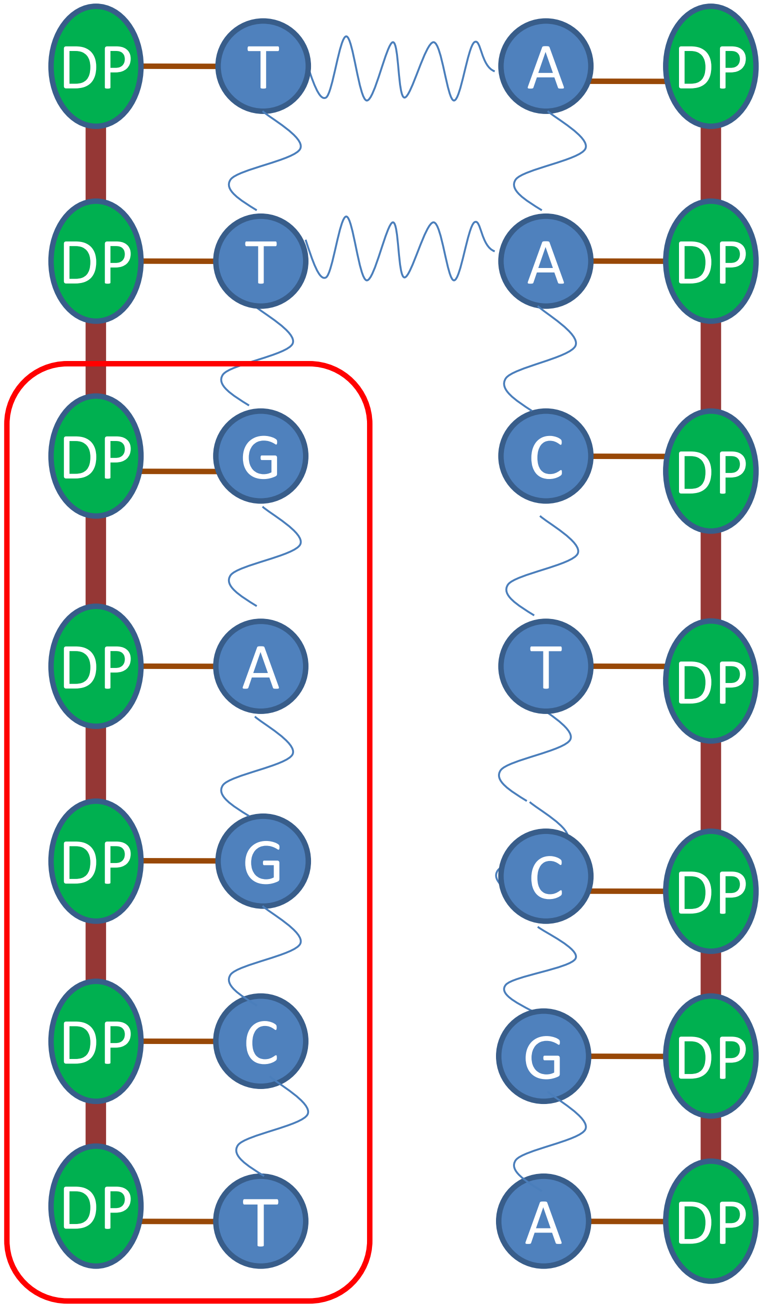




That is why the probability of the charge tunneling is largely determined by how far from each other π clouds are in DNA. In a number of cases, interaction between adjacent base pair and sugar-phosphate backbone may provide an efficient pathway for a charge transfer along DNA.

$$\boldsymbol{E_a = E_a^0 + f_E(\Delta Y)}$$

$$\boldsymbol{V_{i,j} = V_{i,j}^0 + f_v(\Delta Y)}$$

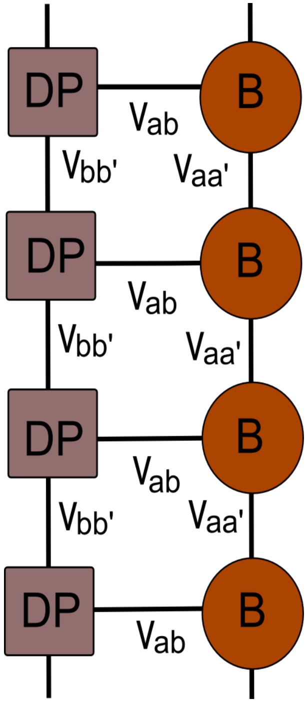


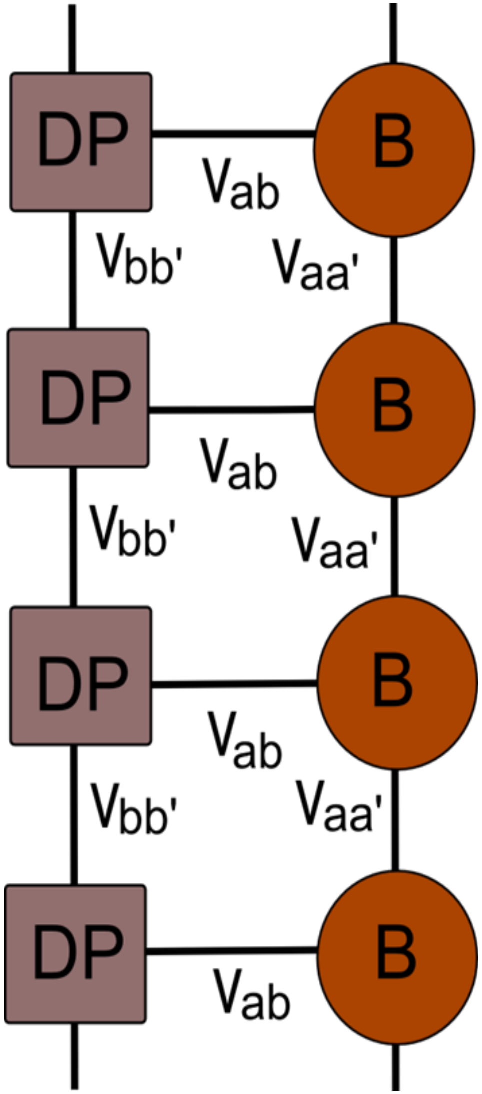
We consider quantum dynamics of a hole migration through DNA: A single strand DNA model. In this case hydrogen bonds between the bases break; the two strands unwind and separate.

A possibility of a positive charge-hole migration along the single strand is considered

It has been demonstrated that charge delocalization occour along the backbone chain I.S. Hiromi, S. Tetsuhiro, Attosecond electron delocalization in the conduction band through the phosphate backbone of genomic DNA, Phys. Rev. Lett 99 (2007) 228102.

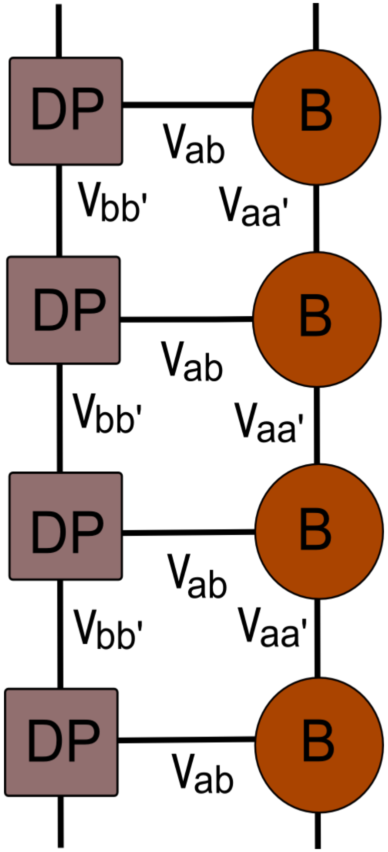
Sugar-phosphate backbone influence on the process of a hole migration through DNA has not yet been adequately investigated either theoretically or experimentally.





$$H = \sum_{a} M_a \frac{Y_a^2}{2} + \sum_{b} M_b \frac{Y_b^2}{2} + \sum_{a} k_{v,a} \frac{(Y_a - Y_{a-1})^2}{2} + \sum_{b} k_{v,b} \frac{(Y_b - Y_{b-1})^2}{2} + \sum_{a,b} k_h \frac{(Y_a - Y_b + l)^2}{2}$$

$$\hat{H} = \sum_{a} E_a |\varphi_a >< \varphi_a| + \sum_{b} E_b |\varphi_b >< \varphi_b| + \sum_{a,a'} V_{a,a'} |\varphi_a >< \varphi_{a'}| + \sum_{b,b'} V_{b,b'} |\varphi_b >< \varphi_{b'}| + \sum_{a,b} V_{a,b} |\varphi_a >< \varphi_b| + \sum_{b,a} V_{b,a} |\varphi_b >< \varphi_a|$$



$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

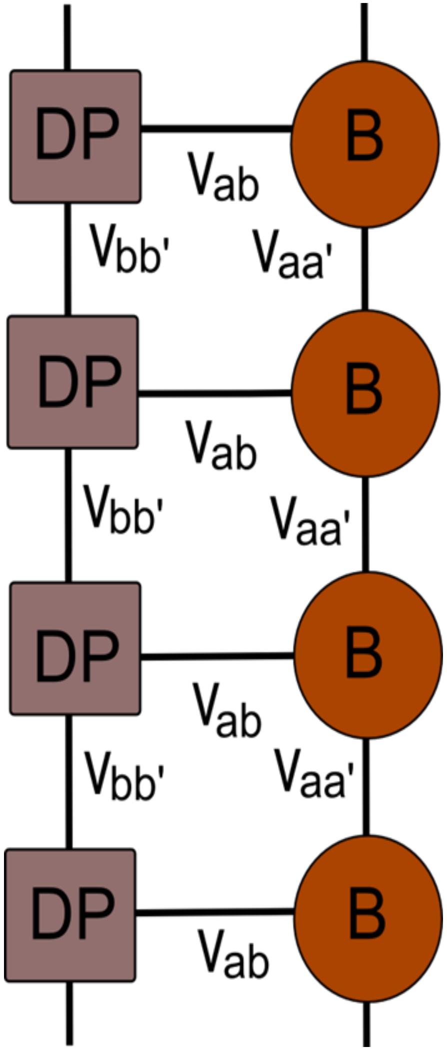
$$\hat{H} = \sum_a E_a\,|\varphi_a >< \varphi_a| + \sum_b E_b\,|\varphi_b >< \varphi_b| + \sum_{a,a'} V_{a,a'}\,|\varphi_a >< \varphi_{a'}| + \sum_{b,b'} V_{b,b'}\,|\varphi_b >< \varphi_{b'}| + \sum_{a,b} V_{a,b}\,|\varphi_a >< \varphi_b| + \sum_{b,a} V_{b,a}\,|\varphi_b >< \varphi_a|$$

$$\psi = \sum_a A_a(t)\,|\varphi_a > + \sum_b B_b(t)|\varphi_b >$$

$$i\hbar\frac{\partial A_a}{\partial t} = E_a A_a + \sum_{a'} V_{a,a'}\,A_{a'} + \sum_{a'} V_{a,b}\,B_b$$

$$i\hbar\frac{\partial B_b}{\partial t} = E_b B_b + \sum_{b'} V_{b,b'}\,B_{b'} + \sum_{a} V_{b,a}\,A_a$$

The coefficients A_a(t), B_b(t) depend on time, while its squared module determines the probability of the hole location at time t on an a–base or b–sugar–phosphate group.

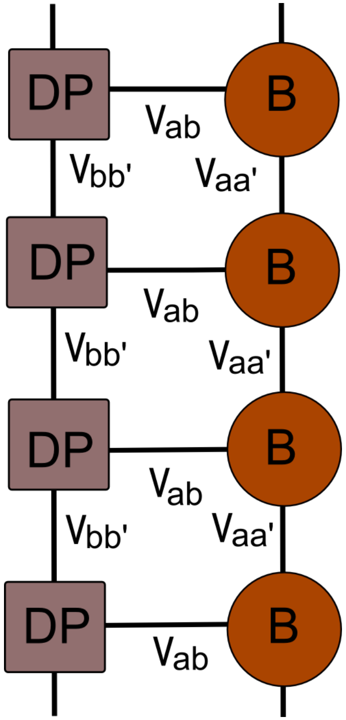


$$
\begin{aligned}
\hat{H} = {} & \sum_{b} E_a |\varphi_a >< \varphi_a| + \sum_{b} E_b |\varphi_b >< \varphi_b| \\
& + \sum_{a,a'} V_{a,a'} |\varphi_a >< \varphi_{a'}| + \sum_{b,b'} V_{b,b'} |\varphi_b >< \varphi_{b'}| \\
& + \sum_{a,b} V_{a,b} |\varphi_a >< \varphi_b| + \sum_{b,a} V_{b,a} |\varphi_b >< \varphi_a|
\end{aligned}
$$

$$E_{a,b} = E^0_{a,b} + \lambda_{a,b} \Delta Y$$

$$E^0_G < E^0_A < E^0_C < E^0_T$$

The environment influence responsible for the charge transfer in DNA leads to the ionization energy oscillations, which has a crucial impact on the DNA strands energy profile.



$$i\hbar\frac{\partial A_a}{\partial t} = E_a^0 A_a + \sum_{a'} V_{a,a'} A_{a'} + \sum_{a'} V_{a,b} B_b \boxed{+ \lambda_a A_a \Delta Y}$$

$$i\hbar\frac{\partial B_b}{\partial t} = E_b^0 B_b + \sum_{b'} V_{b,b'} B_{b'} + \sum_{a} V_{b,a} A_a \boxed{+ \lambda_b B_b \Delta Y}$$

$$M_a\frac{\partial^2 Y_a}{\partial t^2} = -\frac{\partial H_s}{\partial Y_a} - \gamma\frac{\partial Y_a}{\partial t} \qquad E_{a,b} = E_{a,b}^0 + \lambda_{a,b}\Delta Y$$

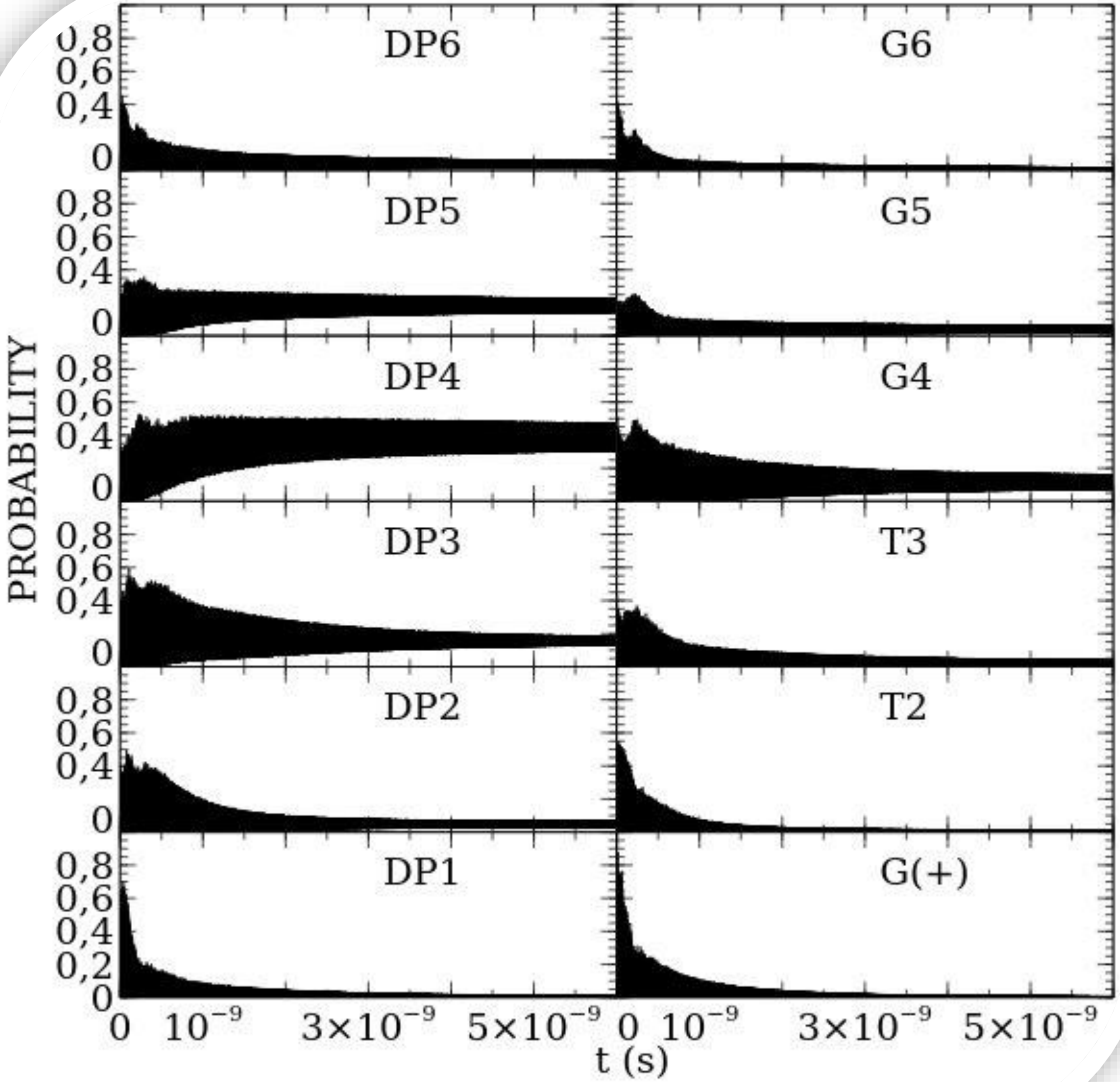
$$M_b\frac{\partial^2 Y_b}{\partial t^2} = -\frac{\partial H_s}{\partial Y_b} - \gamma\frac{\partial Y_b}{\partial t} \qquad H_s = H + < \psi|\hat{H}|\psi >$$

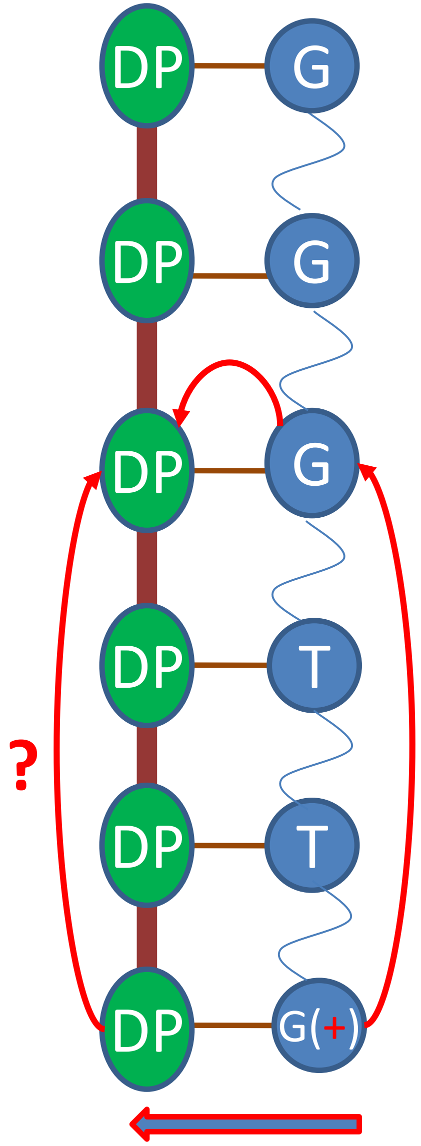
The system determines the dynamics of irreversible DNA-hole interaction.

The system of differential equations was solved using the Runge-Kutta methot. In detail the method is described in publications:

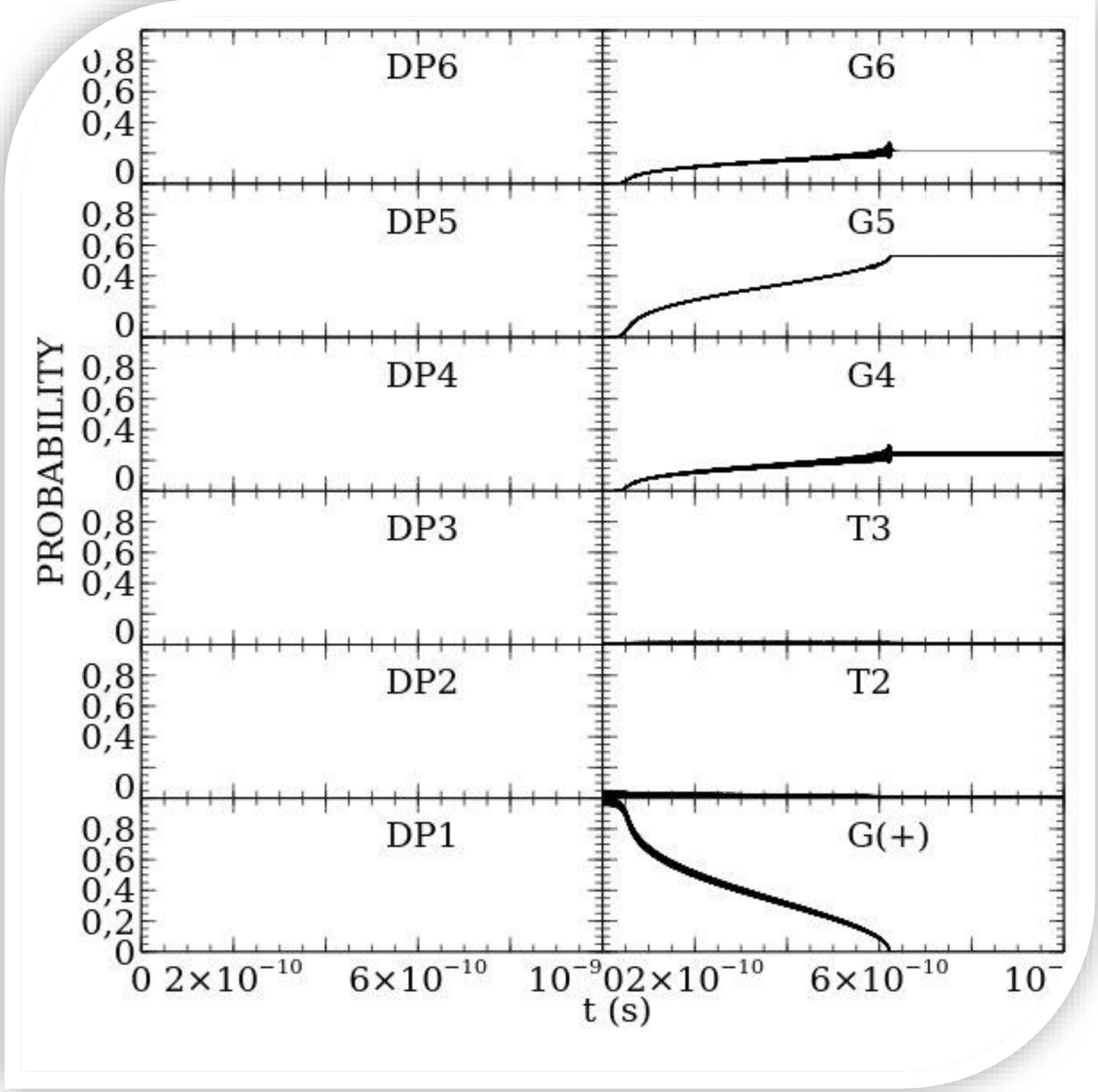
E. Fehlberg, Low-order classical Runge-Kutta formulas with strepsize control, NASA TR R-315.

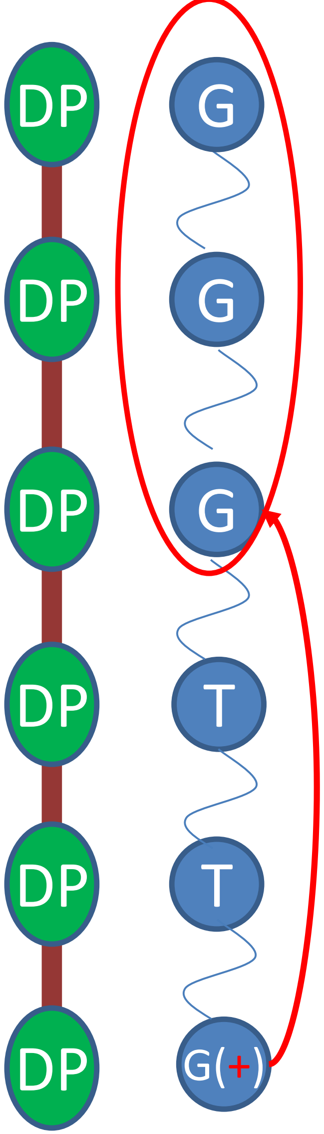
L.F. Shampine, H.A. Watts, S.Davenport, Solving non-stiff ordinary differential equations-the state of the art, Sandia Laboratories report SAND75-0182, SIAM REVIEW, 18 (1976), N3< 376-411.



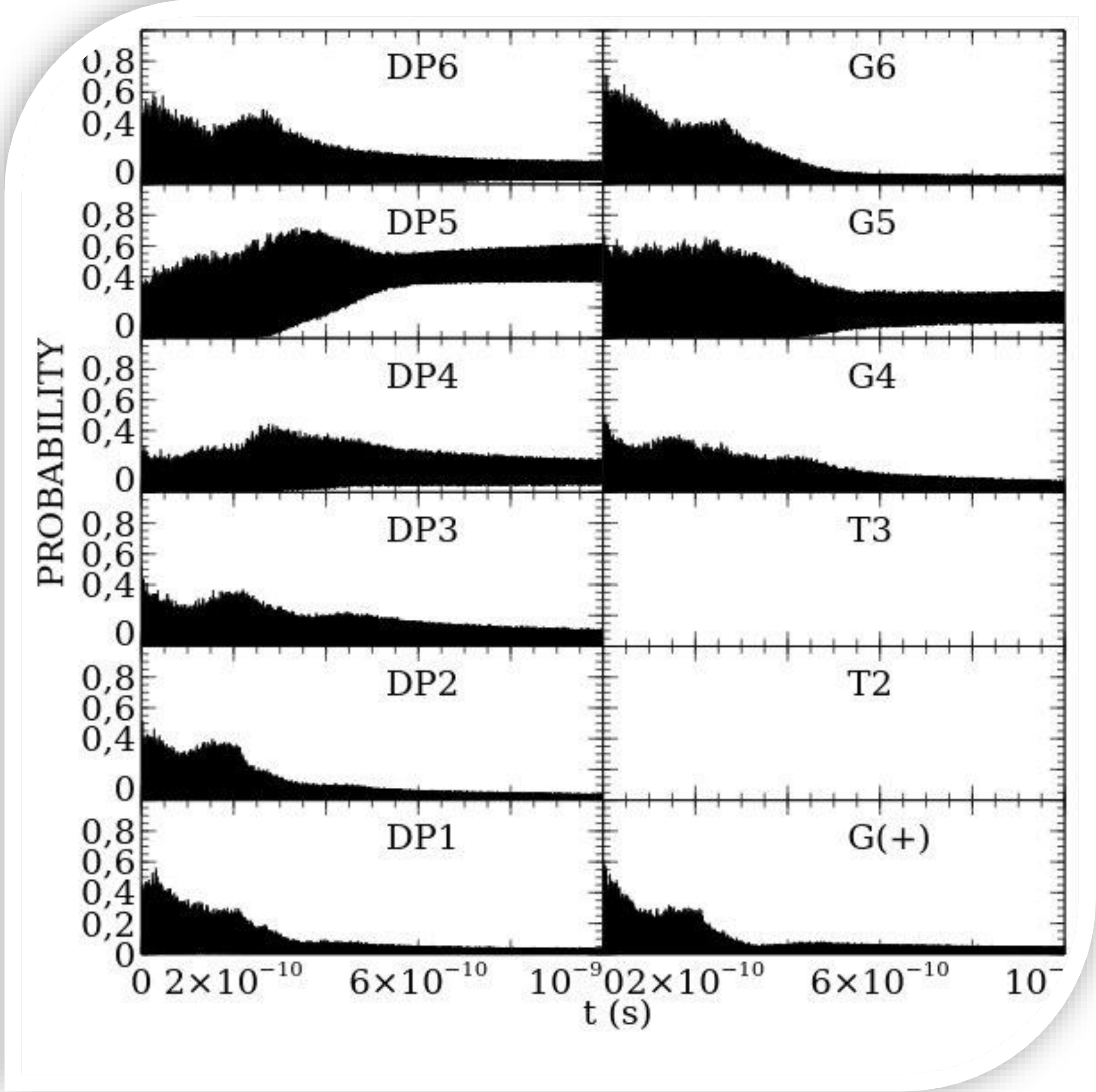


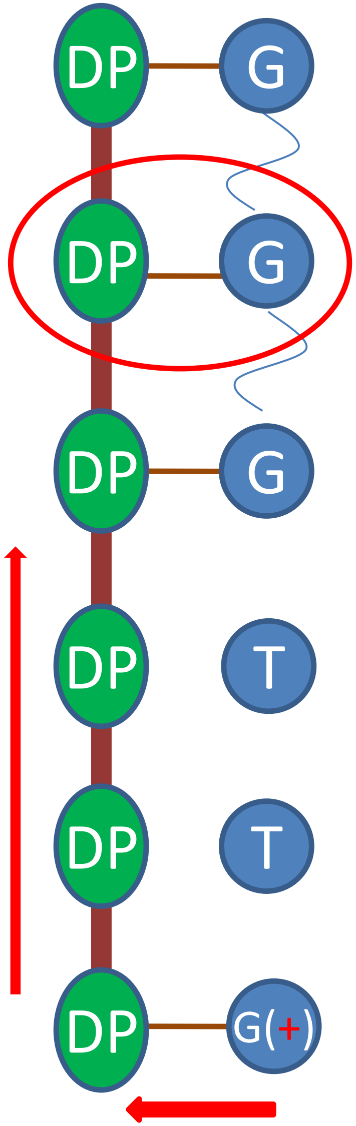
Note that since a thymines ionization potential is higher than a guanines, they present a possible barrier for the hole migratation. Thus, the hole migration occurs by means of thymines tunneling, the probability of hole localization on which is extremely low.



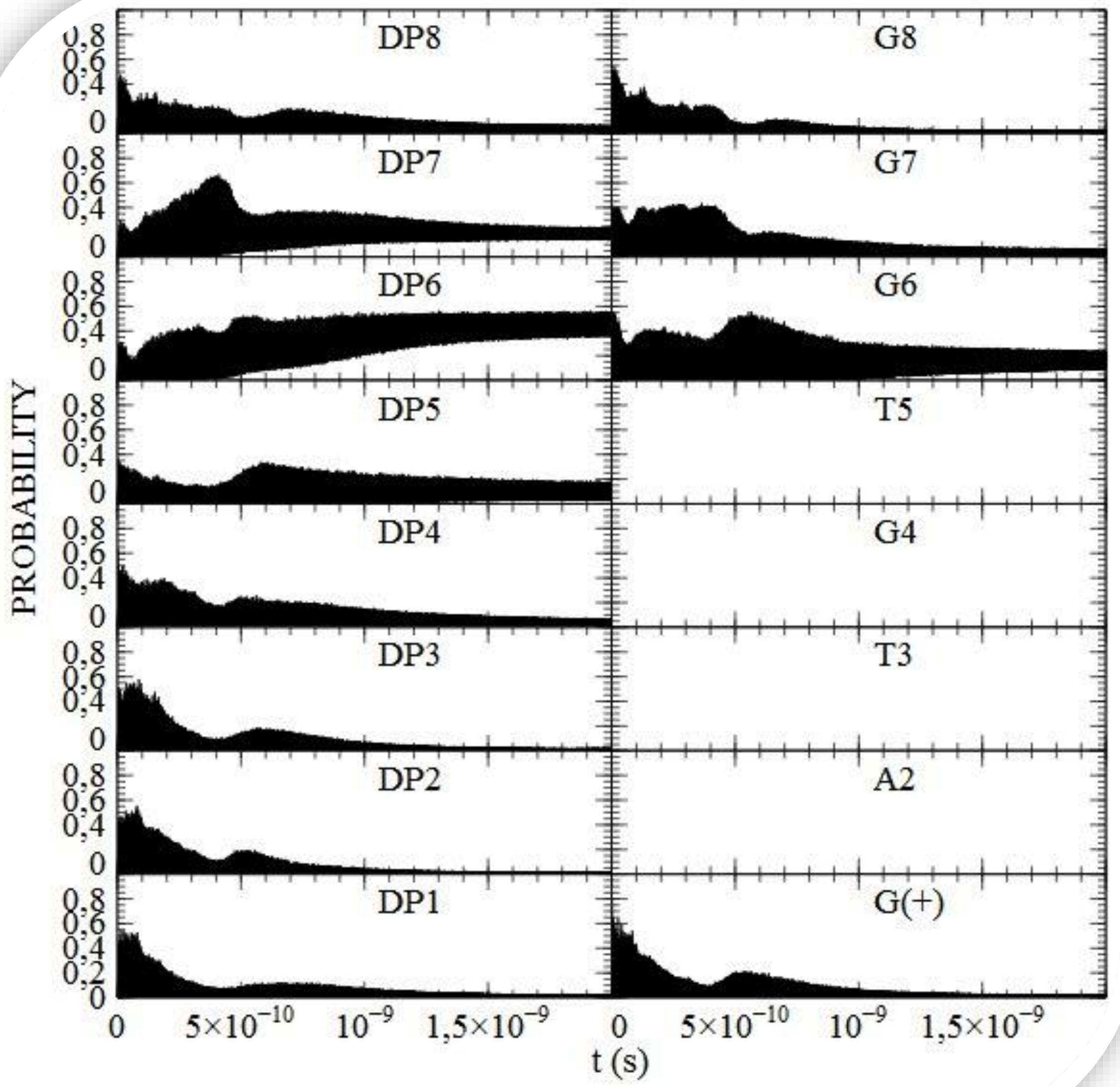


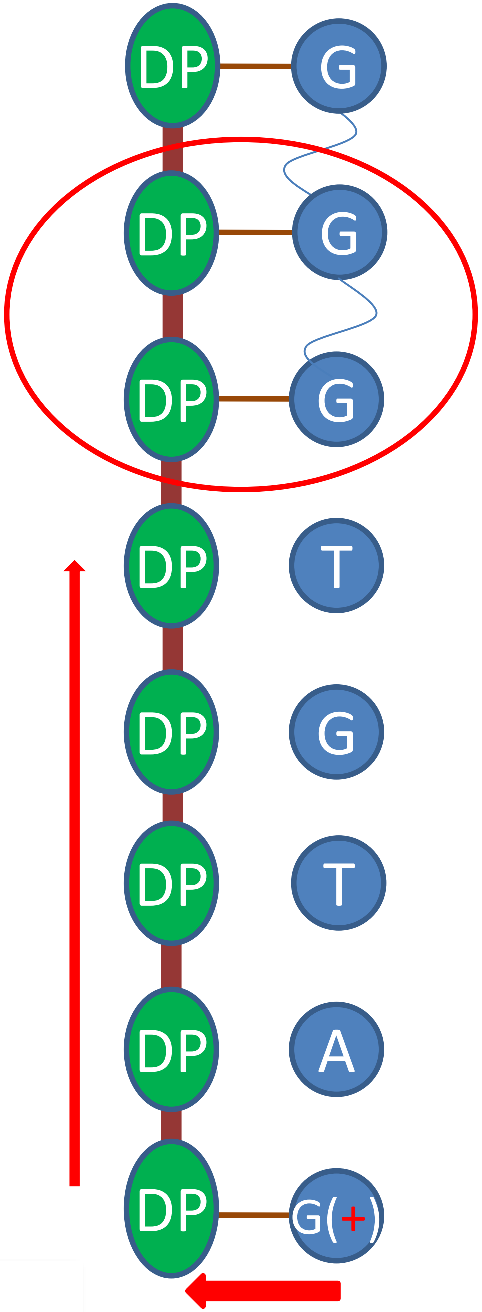
The hole migration occur only through the bases. The hole hops from the guanine to GGG unit, bypassing thymines. In this case, the result demonstrates an irreversible tunnel effect. We have a one-step hole transfer via a superexchange mechanism.



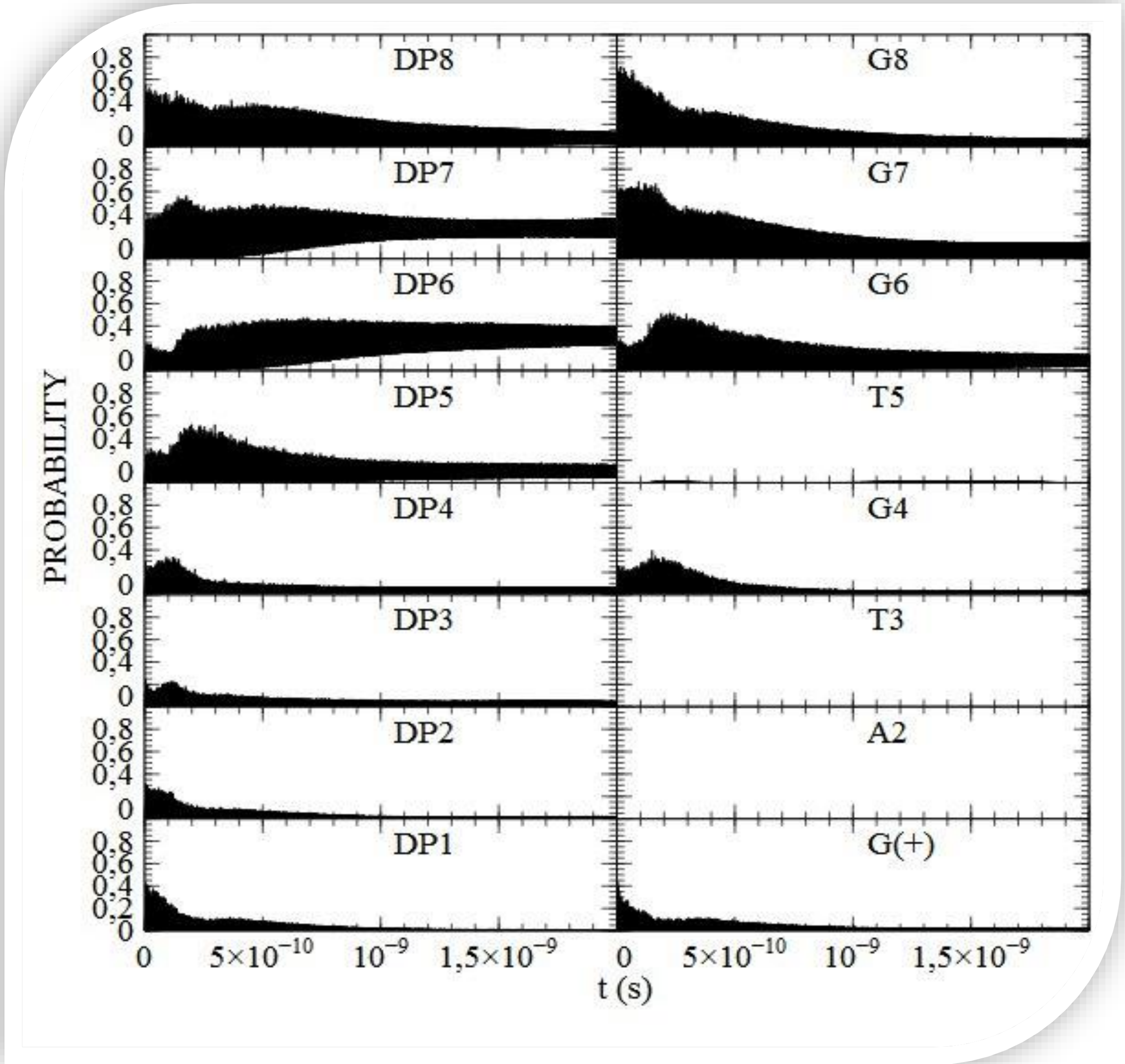


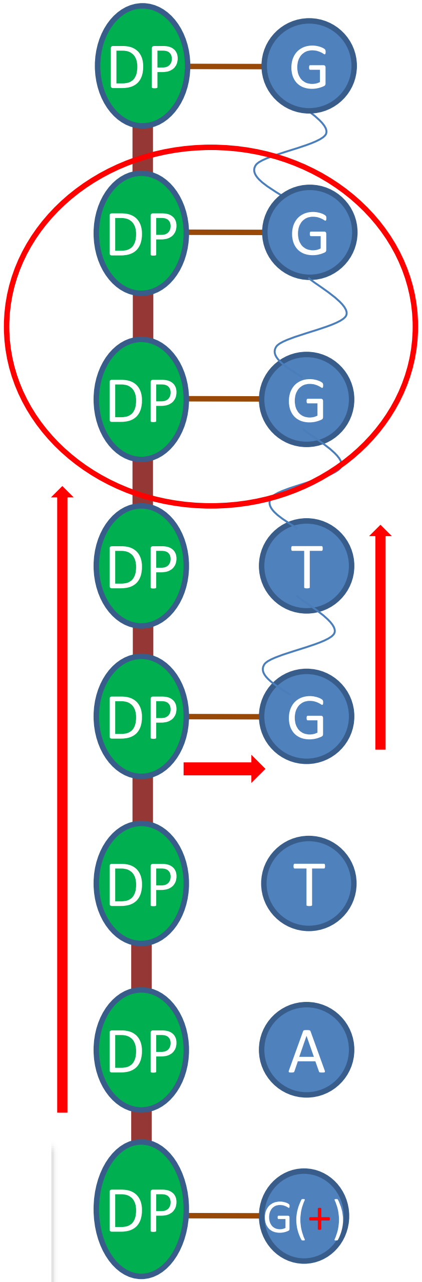
The charge migrates from G(+) , with the probability of its location on sugar-phosphate complex. Sugar-phosphate backbone acts as a conductor allowing the hole to migrate from the fist guanine through the DNA strand.



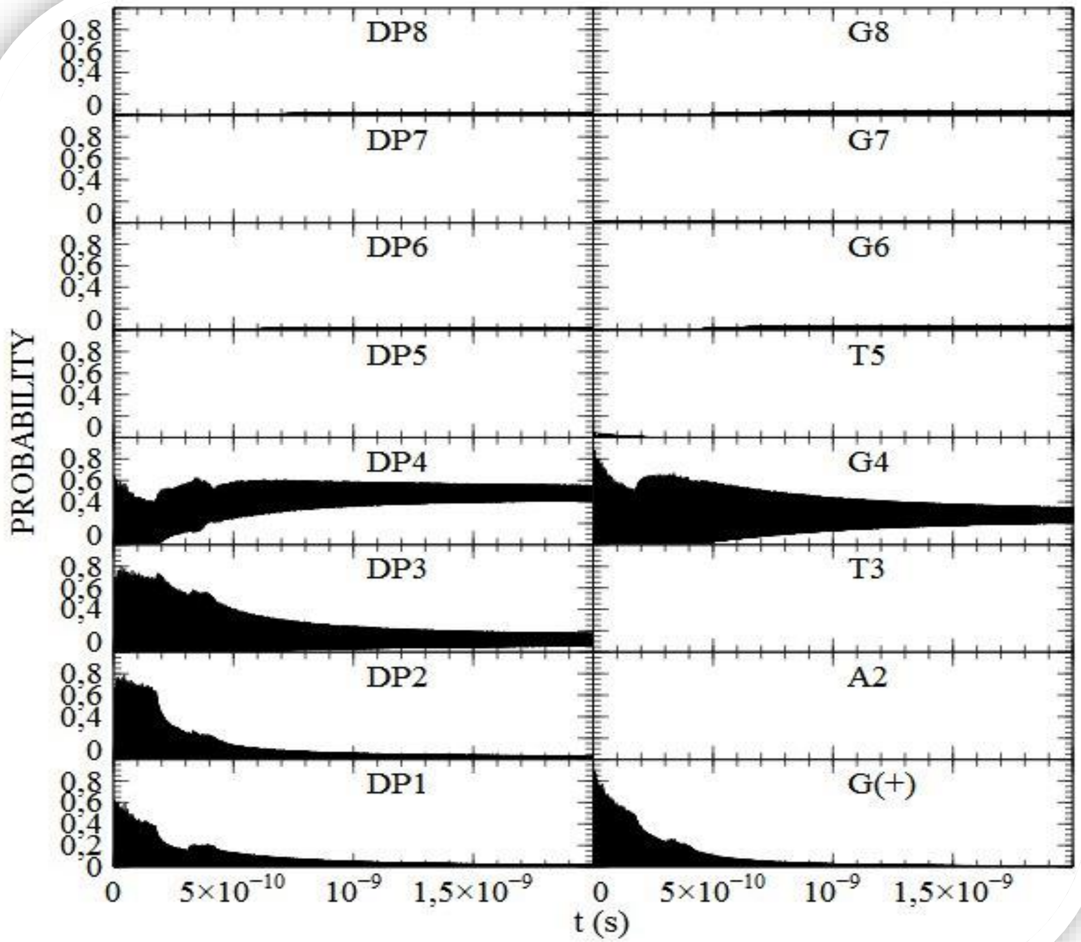


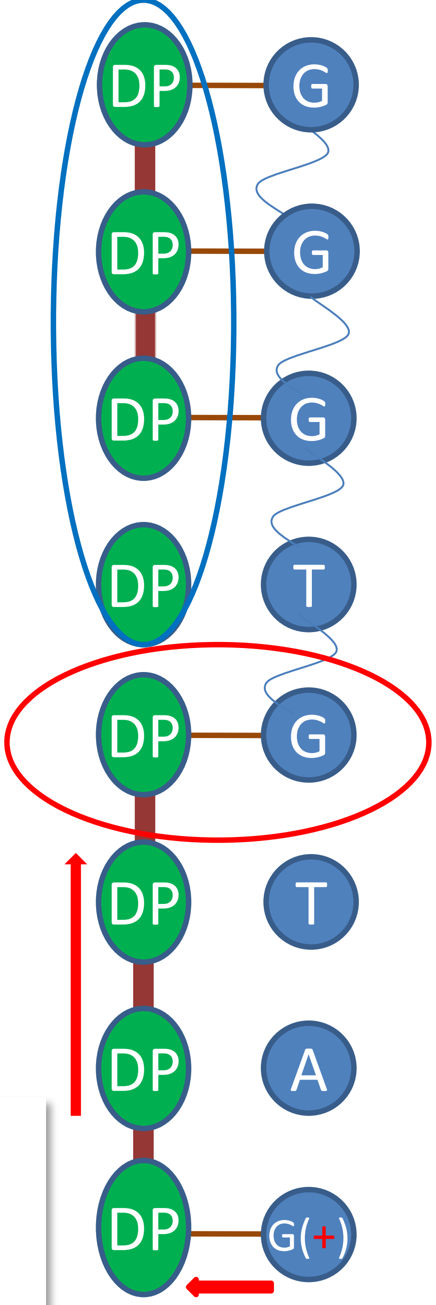
In this case, the sugar-phosphate backbone acts as conductor.
The charge localization on the DP – complex increases considerable.



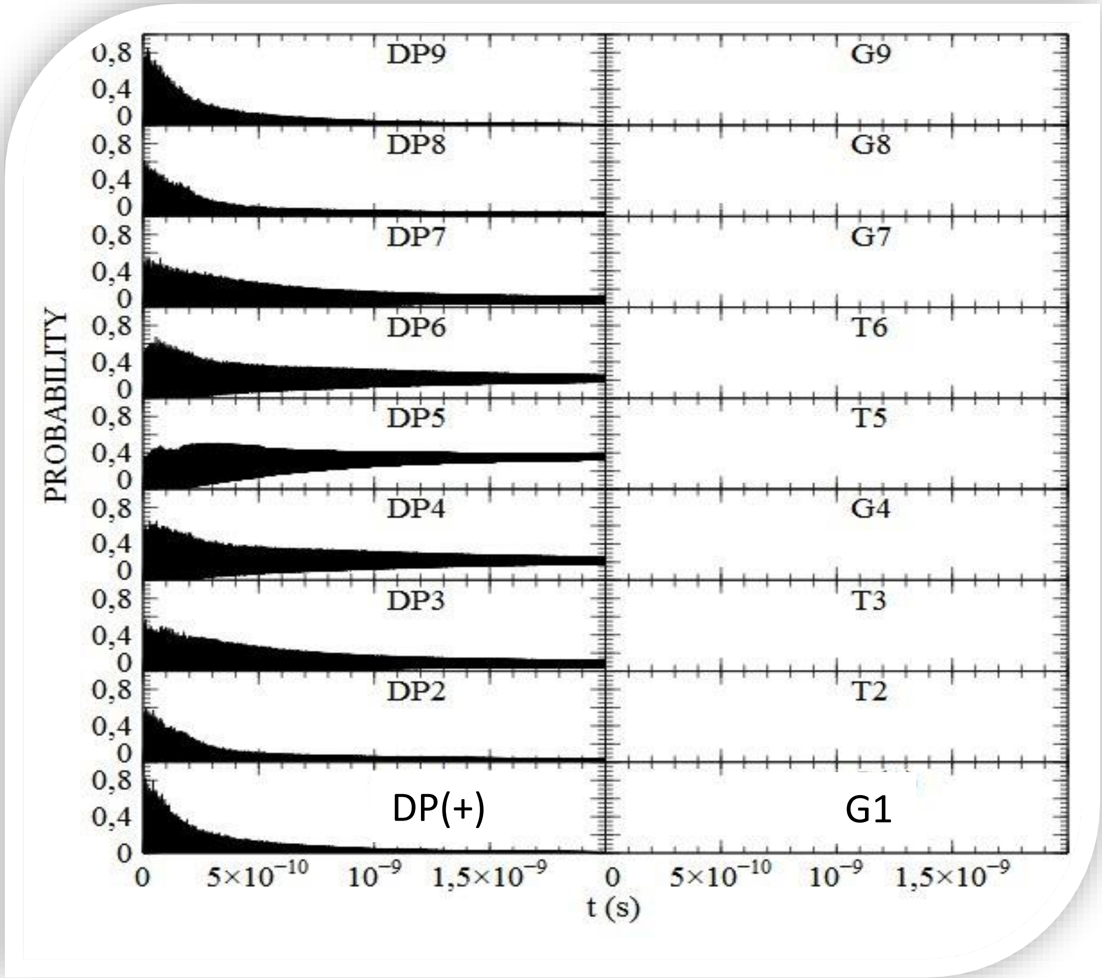


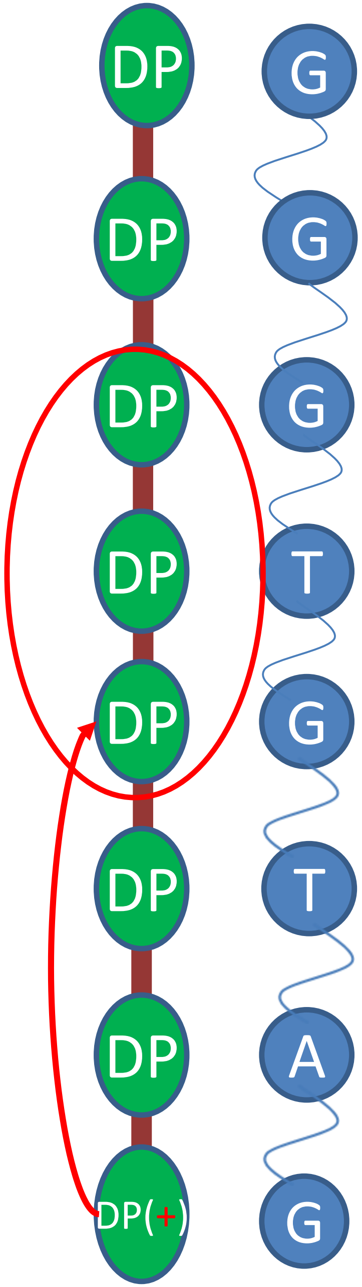
It is assumed that DNA geometry is such that the hole, migrating from the fist guanine through the DP-complex may locate on the second intermediate guanine G4 for a very short period of time; than it finally localized on the DP DP- GG unit.





Here transfer between DP4, DP5, DP6, units is prohibited. Thus, the DP sequence proved to be cleft. In this case, the sequence of first four DP complexes acts as a conductor, enabling the charge to migrate through the DNA.





It should be noted. If the strand is considered as an isolated one from the environment, the charge migration is unlikely to occur since the ionization energies E_b^0=11.13 eV of each unit is the same. However, the environment changes the strand energetic profile, thus enabling the charge to migrate.

The above considered model results in the following conclusions:

1. The hole migration is a quantum phenomenon. The tunnel effect, owing to which the hole migrates through the chain bypassing the bases with a high ionization potential, influences the process of its migration considerably.
2. The sugar-phosphate backbone possesses conducting properties affecting the hole migration process through the DNA strand.
3. The hole transfer mechanisms depend on the base energies fluctuations and is dynamic in character. Moreover the DNA dynamics as well as the environment/solvent factors are crucial for determining the nature of the hole migration.
4. The fast DNA and environment fluctuations lead to dramatic fluctuations of the charge transfer parameters, thereby facilitating (or not facilitating) the transfer.

Model parameters

E_b^0= 10.83 eV – 11.44 eV for the sugar-phosphate backbone.

DP-Na$(H_2O)_3$ E_b^0= 11.13 eV.

A.O. Colson, B. Besler, M.D. Sevilla, Ab initio molecular orbital calculations on DNA radical ions. 3. Ionization potentials and ionization sites in components of the DNA sugar phosphate backbone, J. Phys. Chem 97 (1993) 8 092–8097.

It was shown that introducing a sodium counterion in the system with the use of water molecules around the sodium ion significantly affected the ionization potential of the sugar-phosphate backbone.

E_a^0=8.00-12.40 eV for the bases.

E_G^0=11.09 eV, E_A^0=11.55 eV, E_C^0=11.98 eV, E_T^0=12.33 eV.

E. Caueet, M. Valiev, J.H. Weare, Vertical ionization potentials of nucleobases in a fully solvated DNA environment, J. Phys. Chem. B 114 (2010) 5886–5894.

The negative phosphate groups of the DNA double helix and positive counterions induce a long-range molecular structure of the solvent creating, in the center of the DNA helix, an electric potential noticeably amplified. This potential shifts the ionization energies threshold of DNA bases by approximately 3.2–3.3 eV relative to the gas phase.

D.M. Close, Calculation of the ionization potentials of the DNA bases in aqueousmedium, J. Phys. Chem. A 108 (2004) 10376–10379.

C.E. Crespo-Hernandez, R. Arce, Y. Ishikawa, L. Gorb, J. Leszczynski, D.M. Close, Ab initio ionization energy thresholds of DNA and RNA bases in gas phase and in aqueous solution, J. Phys. Chem. A 108 (2004) 6373–6377.

Matrix elements for hole transfer $V_{a,a'}$ between nucleobase pairs 5’-3’ in DNA was taken from the paper

A.A. Voityuk, N. Rosch, M. Bixon, J. Jortner, Electronic couplings for charge transfer and transport in DNA,
J. Phys. Chem 104 (2000) 9740–9745.

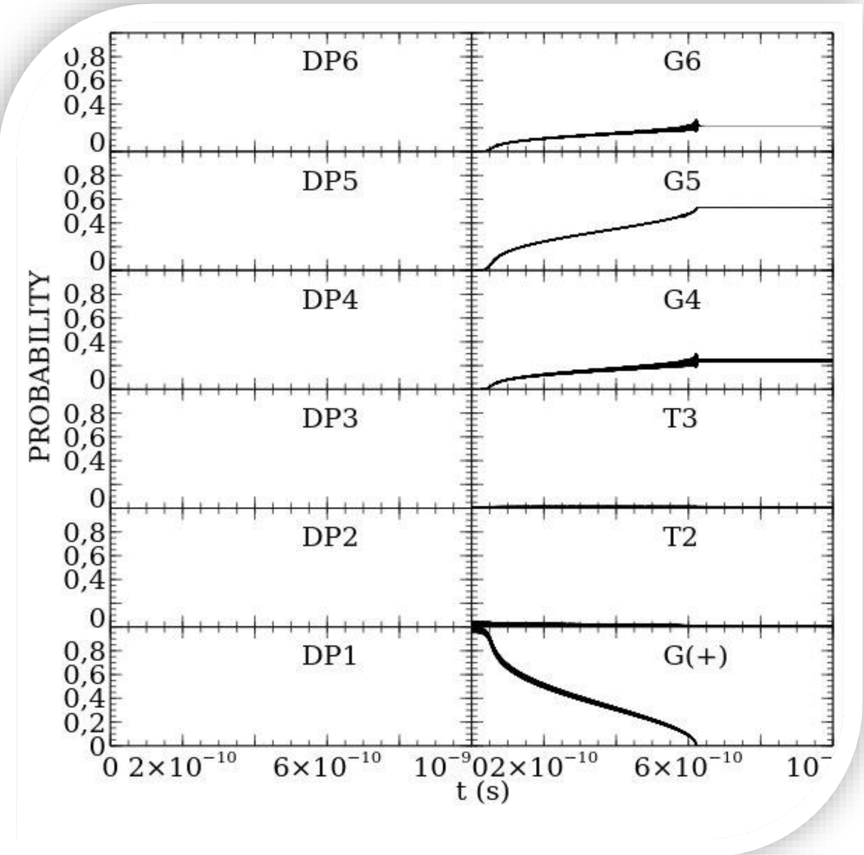
Matrix elements for a hole transfer $V_{a,b}$ between nucleobases and sugar-phosphate complexes were determined in accordance with the work

K. Iguchi, π-Electrons in a single strand of DNA: a phenomenological approach international, Int. J. Mod. Phys. B 18 (2004) 1845–1910.

It was highlighted that the charge migration between them strongly depends on the geometry of a DNA single strand. So, if the distance between the base and the sugar is far apart, we can think that hopping is not possible. Hence, it was assumed that the values $V_{a,b}$ may amount to $0 \leq V_{a,b} \leq 1.5$ eV.

Matrix elements for a hole transfer between sugar-phosphate complexes $V_{b,b'}$ were determined from inecuality $0 \leq V_{b,b'} \leq 1.5$ eV. The inequality underlines that matrix element values strongly depend on DNA geometry.

Damping coefficient γ in the model corresponds to water viscosity at a temperature of t = 37 °C.



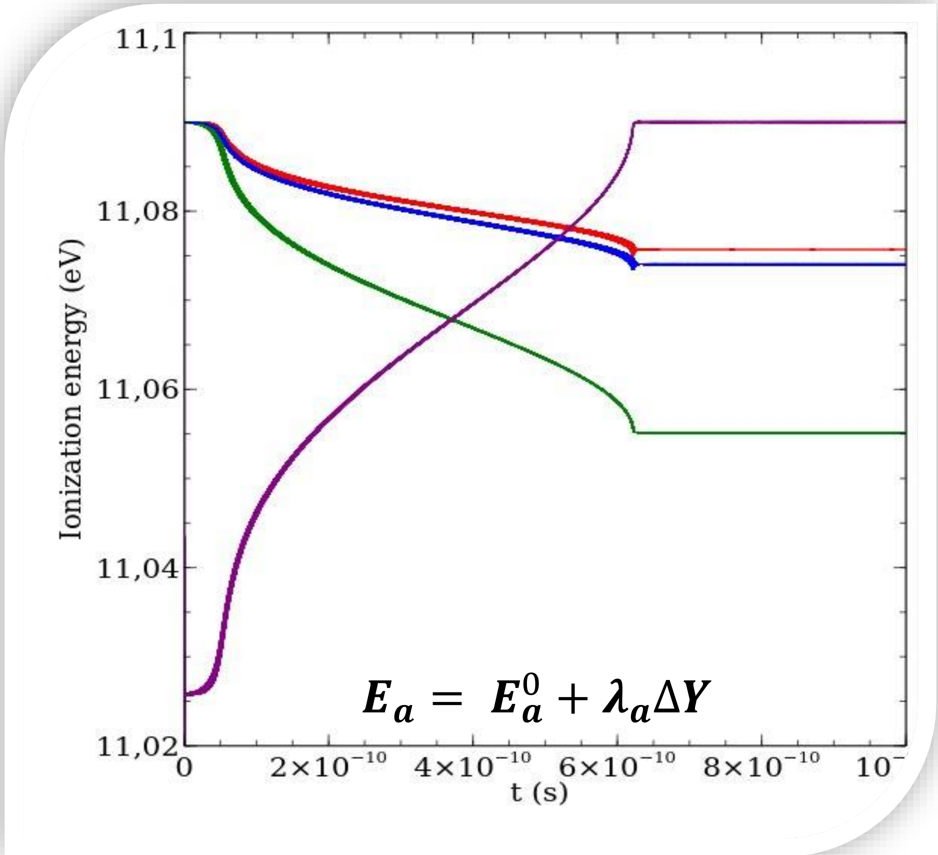
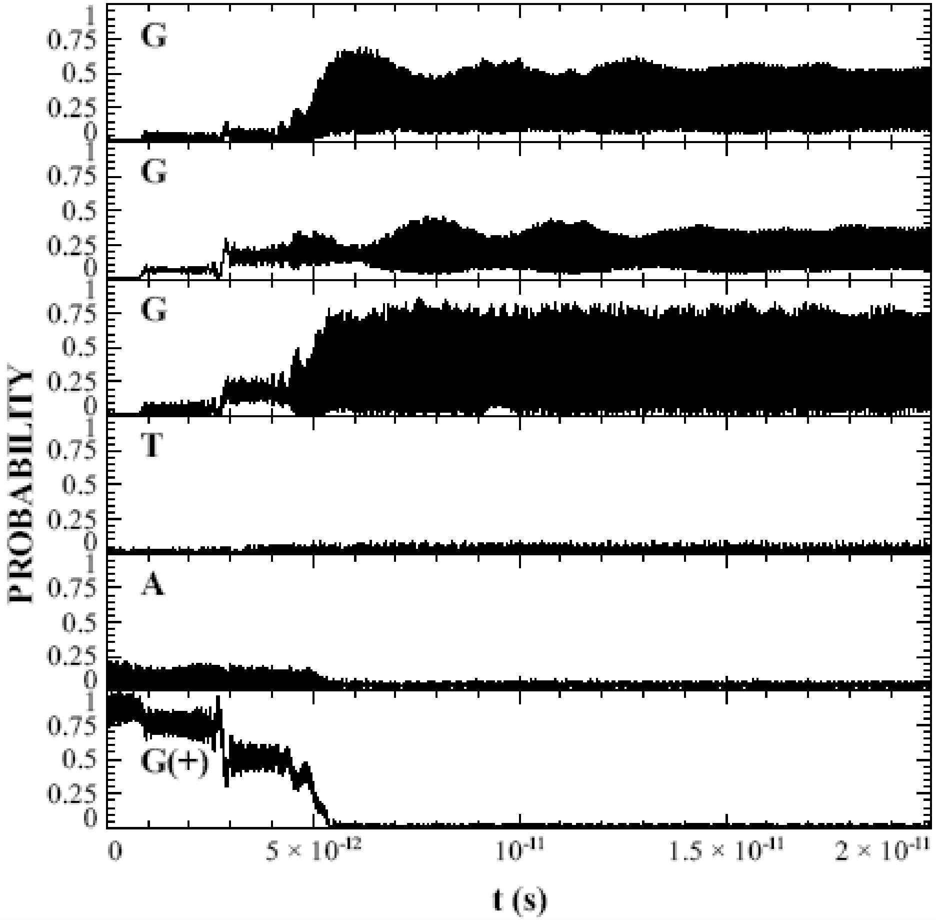
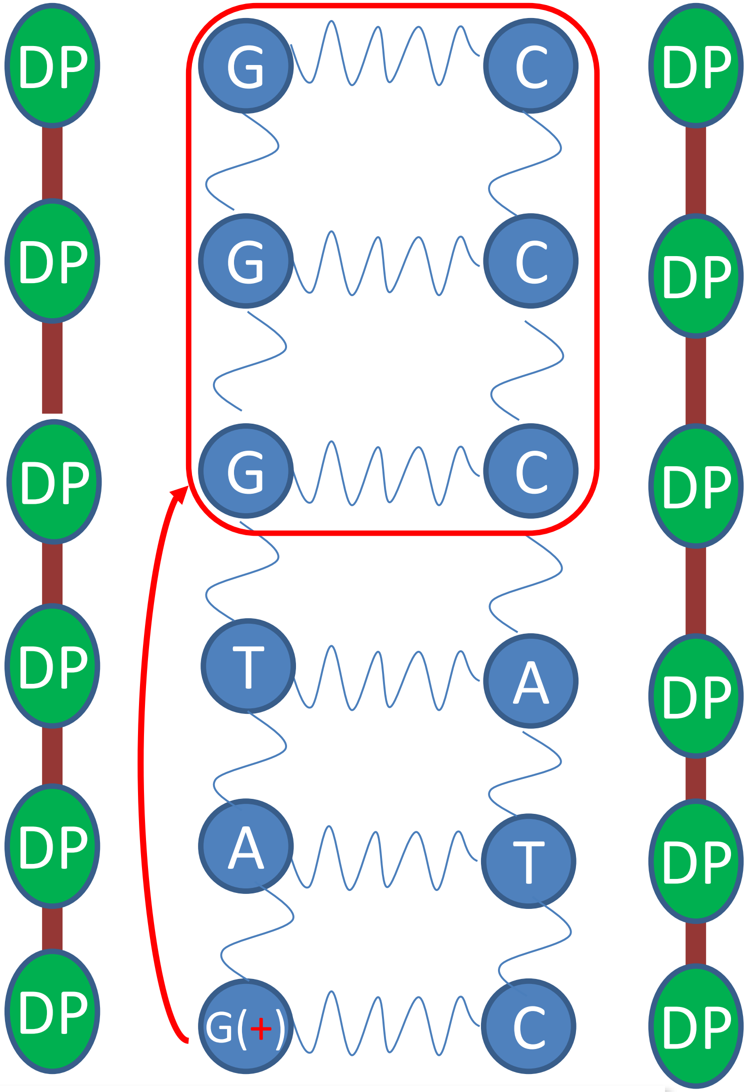


Fig. 15. Ionization energy, G(+)TTGGG sequence, base limit: G(+)- purple, G4 - blue, G5 -green, G6 - red.

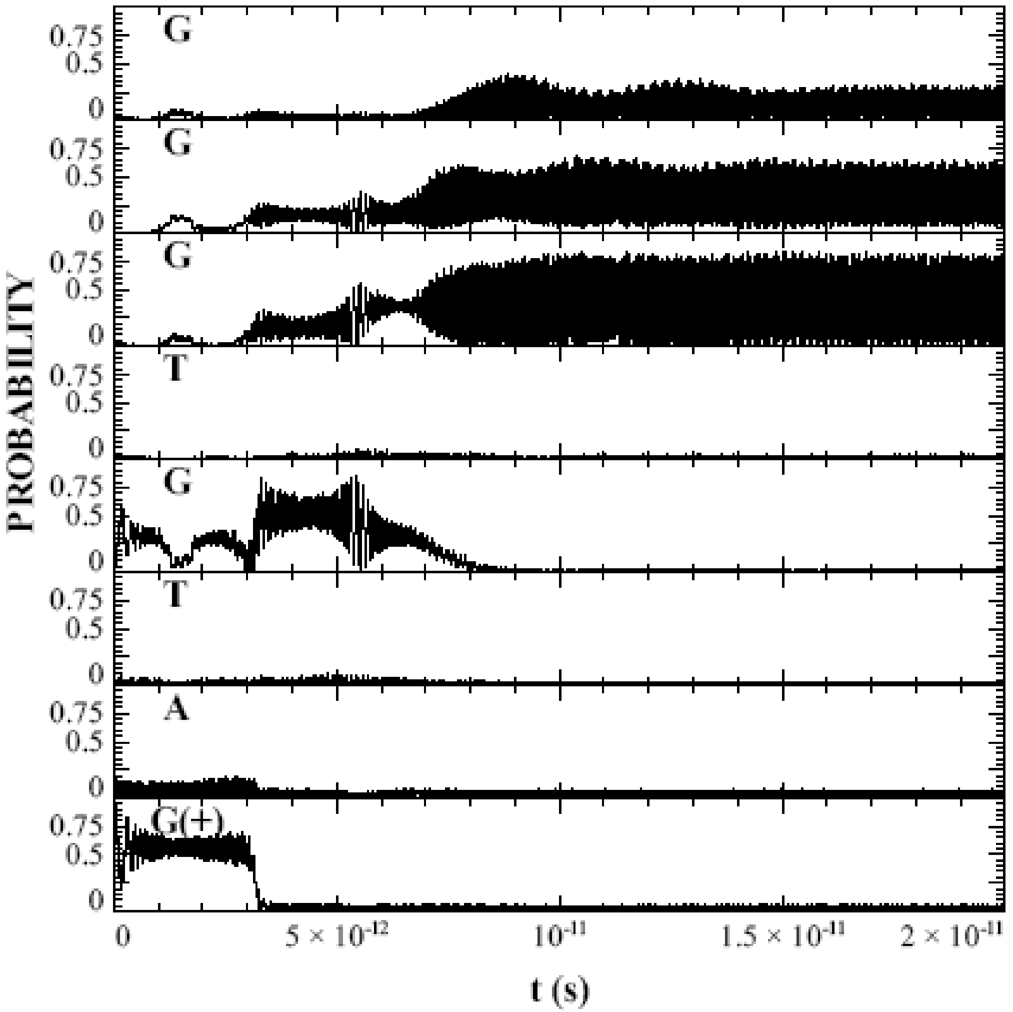
The hole located on the first G(+)-DP pair leads to its deformation. As a result,the G (+) guanine energy decreases (the purple line). Then, after a very short period of time G (+) ionization energy increases. As for the rest three bases, their ionization energies decrease in the course of time, thus creating favorable conditions for the hole migration .

Further, the charge migrates from the base G(+)-DP pair, with its deformation gradually decreasing, approaching zero. A comparison between figures shows that the hole migration is highly probable on the base whose ionization energy is minimum:G5 (the green line).

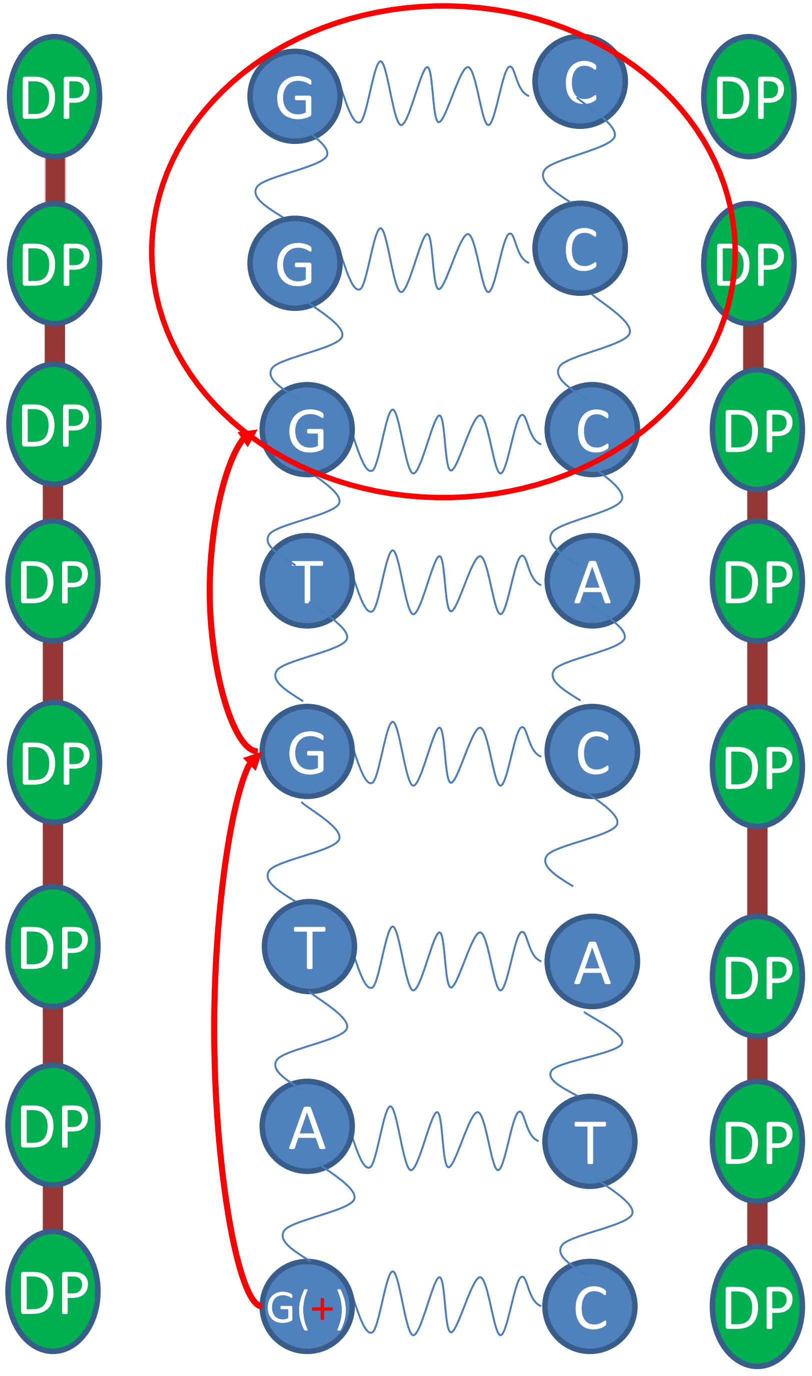




In this case, the probability of the hole location on the fist guanine falls considerably whereas the one of its location on the second, third, and fourth guanine rises. The probabilities of the charge location on the adenine and thymine are very low. In this case result demonstrates irreversible hole dynamics. We have a one-step hole transfer via a superexchange mechanism.



In this case the hole migrates to the GGG unit, bypassing the last adenine and thymine. Here, we deal with a hopping mechanism.



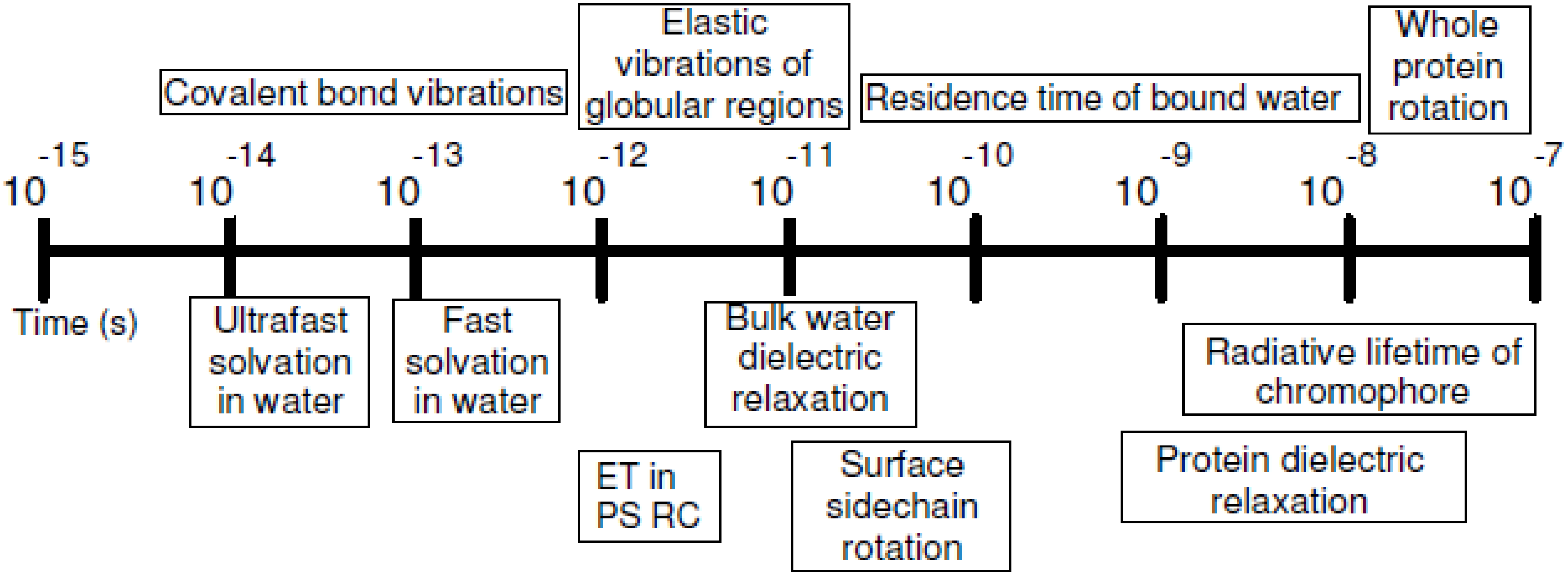


Fig. 5.1. Schematic representation of the time scales of various processes in biomolecules, proteins and solutions. ET stands for electron transfer, PS RC for photosynthetic reaction centre. See Table 5.1 for specific numbers.

Table 5.1. Timescales for various processes in biomolecules and solutions. The radiative lifetime of a chromophore is order of magnitudes longer than all other timescales, except perhaps protein dielectric relaxation. MD refers to results from molecular dynamics simulations. Of particular relevance to this work is the separation of timescales, $\tau_s \ll \tau_b \ll \tau_p$ (compare Fig. 5.1).

Process	Timescale	Ref.
Radiative lifetime	10 ns	[van Holde *et al.* (1998)]
Bulk water dielectric relaxation	8 ps	[Afsar and Hasted (1978)]
Protein dielectric relaxation (MD), $\tau_{D,p}$	1-10 ns	[Loffler *et al.* (1997); Boresch *et al.* (2000)]
Ultrafast solvation in water	10's fs	[Lang *et al.* (1999)]
Fast solvation in water, τ_s	100's fs	[Lang *et al.* (1999)]
Solvation due to bound water, τ_b	5-50 ps	[Peon *et al.* (2002)]
Solvation due to protein, τ_p	1-10 ns	[Sen *et al.* (2003)]
Covalent bond vibrations	10-100 fs	[van Holde *et al.* (1998)]
Elastic vibrations of globular regions	1-10 ps	[van Holde *et al.* (1998)]
Rotation of surface sidechains	10-100 ps	[van Holde *et al.* (1998)]
Reorientation of whole protein	4-15 ns	[Boresch *et al.* (2000)]

Experimental dates

- The idea of DNA having conducting properties has already been discussed for quite a while and proved in many experimental papers:

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Experiment

Meggers E., Michel-Beyerle M.E., Giese B. // J. Am. Chem. Soc. 1998. Vol. 120. P. 12950-12955