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HSSH-model of Hole transfer in DNA

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Abstract. A method based on a selfconsistent solution of a quantum-mechanical system with temperature fluctuations described by Langevin equations is developed to calculate the charge carrier mobility in DNA. To model the charge transfer in DNA, a combined Holstein – SSH Hamiltonian is considered. As an example the hole mobility is calculated at room temperature for synthetic poly (G)/poly (C) duplex with regard to main structural fluctuations.

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To date, numerous experiments have demonstrated with certainty that a charge can travel in DNA over rather a long distance [1–9]. This fact opens up comparatively unusual possibilities for microelectronics and nanotechnology where DNA molecules can be used as molecular wires and molecular devices of novel types [10]. In this respect, reliable approaches are required which would enable one to calculate conducting properties of DNA wires. To our knowledge, any experimental data on the value of the mobility of electrons and holes in DNA are presently lacking. All available information on charge transfer in DNA is concerned with relative rates of transfer reactions, rather than with the charge mobility [5–7].

Since direct measurements of the charge mobility in DNA have not been realized, the hole mobility has been estimated theoretically in a poly (G)/poly (C) fragment ((G) denotes guanine, (C) cytosine) [11,12]. It is analyzed in [12] how the hole mobility is influenced by static and structurally-dynamical disorder in the nucleotide chain, while the work [11] deals with the influence of dynamical (caused by the charge motion) and temperature (due to temperature fluctuations) disorder.

Since the value of mobility in a homogeneous chain is determined by its structural fluctuations, theoretical calculations should include, if possible, all the main degrees of freedom of the molecule which lead to structural changes influencing the hole transfer.

In this work we present the results of calculations of the hole mobility at room temperature for synthetic poly (G)/poly (C) duplex with due regard to the main structural fluctuations in DNA affecting the states of a hole.

In [11] we found a contribution into the mobility of displacements u_n of the bases from their equilibrium positions along the direction of hydrogen bonds that connect two bases in a pair. In [13] it was shown that structural changes caused by such displacements change the energy of a hole at each site of a nucleotide chain.

Two other important degrees of freedom leading to structural changes are relative base pair displacements along the stack $(q_{n+1} - q_n)$ and the relative twist angles $(\theta_{n+1} - \theta_n)$ [14,15]. Since these degrees of freedom are not independent they can be taken into account by introducing the dependence of the matrix elements of the transition on $(q_{n+1} - q_n)$ with effective coupling constant ν' [15].

Note, that while relative base pair displacements modulate the matrix elements, displacements along hydrogen bonds modulate the hole energy at each nucleotide pair [11–17]. Changes in the hole energy at the sites can be considered by introducing an efficient constant for the coupling of a hole with intrasite displacements α' much as the efficient coupling constant ν' was introduced.

In modeling the process of transfer we consider the nucleotide sequence as a system of sites in which each site corresponds to a base pair. The combined Holstein – Su – Schrieffer – Heeger (HSSH) Hamiltonian $\mathcal{H}$ of a charge transfer along a homogeneous chain of sites has

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the form [11,13] and [14,15]:

$$\begin{aligned}
\mathcal{H} &= H_h + T_{K1} + U_{P1} + T_{K2} + U_{P2},\\
H_h &= \sum_i \alpha_i\, a_i^+ a_i + \sum_i \nu_{i,i+1}(a_i^+ a_{i+1} + a_{i+1}^+ a_i)\\
T_{K1} &= \sum_i M\,\dot{u}_i^2/2, \quad U_{P1} = \sum_i K u_i^2/2,\\
T_{K2} &= \sum_i m\,\dot{q}_i^2/2, \quad U_{P2} = \sum_i I\,(q_{i+1}-q_i)^2/2, \qquad (1)
\end{aligned}$$

where

$$\begin{aligned}
\alpha_i &= \alpha' u_i, \qquad (2)\\
\nu_{i,i+1} &= \nu^0_{i,i+1} + \nu'(q_{i+1} - q_i).
\end{aligned}$$

Here H_h is the Hamiltonian of a hole, a_i^+, a_i are the operators of hole creation and annihilation at the ith site, α_i is the energy of a hole at the ith site, $\nu_{i,j}$ are matrix elements of the transition from the ith site to the jth one. T_{K1} and U_{P1} are the kinetic and potential energies for displacements along H-bounds; T_{K2} and U_{P2} are the kinetic and potential energies for displacements along the chain axes; m, M are appropriate effective masses corresponding to base pair oscillations along the axis and in the perpendicular direction; K and I are appropriate effective elastic constants.

It is assumed in (2) that the energy of a hole at the sites α_i and the matrix elements of the hole transfer $\nu_{i,i+1}$ are linear functions of the site displacements u_i and q_i from their equilibrium positions, $i = 1,\ldots,N$, N is the number of sites in the chain.

Assuming $\nu'_{i,i+1} = 0$ in the HSSH Hamiltonian $\mathcal{H}$ we get the Holstein Hamiltonian [18], which was studied in [11,13,19,20] as applied to DNA. On putting $\alpha'_i = 0$ in the HSSH Hamiltonian we obtain the SSH Hamiltonian [21], which was considered in [14,15] as applied to DNA.

We choose the wave function of a hole $|\Psi\rangle$ in the form: $|\Psi\rangle = \sum_{n=1}^N b_n|n\rangle$, where b_n is the amplitude of the probability of a hole occurrence at the nth site, and derive from Hamiltonian (1) the following motion equations of the HSSH model:

$$\begin{aligned}
i\,\hbar\dot{b}_n &= \alpha'_n u_n b_n + [\nu^0_{n,n+1} + \nu'(q_{n+1} - q_n)]\, b_{n+1}\\
&\quad + [\nu^0_{n,n-1} + \nu'(q_n - q_{n-1})]\, b_{n-1}, \qquad (3)\\
M\ddot{u}_n &= -K u_n - \Gamma\dot{u}_n - \alpha'|b_n|^2 + A_n(t),\\
m\ddot{q}_n &= I(q_{n+1} + q_{n-1} - 2q_n) - \gamma\dot{q}_n\\
&\quad + \nu'(b_n^* b_{n+1} + b_{n+1}^* b_n)\\
&\quad - \nu'(b_{n-1}^* b_n + b_n^* b_{n-1}) + A'_n(t). \qquad (4)
\end{aligned}$$

Equations (3) are the Schrödinger equations for the probability amplitudes. To take into account the processes of dissipation, classical motion equations (4) are modified in such a way as to add the terms $\Gamma\dot{u}_n$ and $\gamma\dot{q}_n$; Γ and γ are the friction coefficients. The random forces $A_n(t)$ and $A'_n(t)$ with the following statistical characteristics:

$$\begin{aligned}
&\langle A_n(t)\rangle = 0, \quad \langle A_n(t)A_m(t+t')\rangle = 2k_B T\,\Gamma\delta_{nm}\delta(t')\\
&\langle A'_n(t)\rangle = 0, \quad \langle A'_n(t)A'_m(t+t')\rangle = 2k_B T\,\gamma\delta_{nm}\delta(t') \qquad (5)
\end{aligned}$$

are included in (4) to model the temperature fluctuations, where T [K] is the temperature, so the site motion is described by the Langevin equation.

The values of microscopic parameters for a hole transfer in DNA have not been agreed upon community yet. We take the matrix elements $\nu_{n,n+1}$ from quantum-chemical calculations [22]: for the case of poly (G)/poly (C) chain $\nu^0_{n,n+1} = \nu_{GG} = 0.084$ eV (another set of electronic matrix elements is reported in [23]). In this chain a hole travels along guanine bases whose oxidation potential is lower than that of cytosine nucleotides [6]. For the effective coupling constant ν' we choose the same value as in [15]: $\nu'_{GG} = 0.4$ eV/Å, accordingly for $\alpha' = 0.13$ eV/Å, we take the value from [11] (the value 1.3×10^{-4} eV/Å instead of correct value 0.13 eV/Å was mistakenly figured in [11]). Notice that the value of α' close to ours was used in [13] to explain the experiments by Giese et al. [5]. In many works concerned with modeling DNA dynamics the frequencies of nucleotide pair oscillations ω, Ω are assumed to lie in the picoseconds range [11,16,17]. In this work we put $\omega = \sqrt{K/M} = 10^{12}$ s^{-1} [11] and $\Omega = \sqrt{I/m} = 3.7 \times 10^{12}$ s^{-1} [15], and consider different friction coefficients γ, Γ.

The effective half-mass of a base pair takes into account the atomic constituents of a nucleotide and a backbone as well as the primary hydration shell which is tightly bound to the base. The size of primary shell depends on the hydration degree and is of order of 10–20 water molecules per nucleotide [24–26]. In the calculations we put the values of effective mass M and m to be equal: $M = m = 10^{-21}$ g.

For numerical integration of adequate dimensionless Cauchy system we used the scheme of [27].

In the calculations, the normalizing condition was fulfilled with calculation accuracy $|\sum |b_n|^2 - 1| < 0.001$. The initial conditions for the displacements and site velocities were taken from the equilibrium distribution at given temperature. At the initial moment, the charge was assumed to be localized in the middle of the chain consisting of 499 sites (at the 250th site).

We considered three situations: Holstein model, SSH model and HSSH one, with different values of friction coefficients. For each case we calculated 500 realizations at the prescribed temperature $T = 300$ K. The coefficients $b_n(t)$ thus found were used to calculate the mean-square hole displacement $X^2(t) = \langle\Psi(t)|n^2a^2|\Psi(t)\rangle = \sum_n |b_n(t)|^2 n^2 a^2$, where a is the distance between neighboring sites ($a \approx 3.4$ Å). For the sequences considered, the hole mobility μ was calculated by the Kubo formula [28]:

$$\mu = -\frac{ea^2}{2k_B T}\lim_{\varepsilon\to 0}\varepsilon^2\int_0^\infty \langle X^2(t)\rangle e^{-\varepsilon t}dt, \qquad (6)$$

where e is the electron charge, $\langle X^2(t)\rangle$ is the square of the hole displacement along the chain of sites avareged by realizations.

With the parameter values mentioned above, the results obtained are the following.

For the Holstein Hamiltonian ($\nu' = 0$, $\alpha' = 0.13$ eV/Å): at the friction coefficient $\Gamma = 1 \times 10^{-10}$ g/s we estimated $\mu \approx 3.05$ cm^2/V s; at $\Gamma = 6 \times 10^{-10}$ g/s the value $\mu \approx 2.87$ cm^2/V s (the improved value of [11]); at $\Gamma = 8 \times 10^{-9}$ g/s (damping vibrations of sites) $\mu \approx 1.79$ cm^2/V s.

For the SSH Hamiltonian ($\alpha' = 0$, $\nu' = 0,4$ eV/Å): at the friction coefficient $\gamma = 1 \times 10^{-10}$ g/s μ was found to be ≈ 2.54 cm^2/V s; at $\gamma = 6 \times 10^{-10}$ g/s we have $\mu \approx 2.44$ cm^2/V s; at $\gamma = 8 \times 10^{-9}$ g/s we estimated $\mu \approx 1.82$ cm^2/V s.

For the HSSH Hamiltonian ($\nu' = 0,4$ eV/Å, $\alpha' = 0,13$ eV/Å and $\Gamma = 6 \times 10^{-10}$ g/s): at $\gamma = 1 \times 10^{-10}$ g/s we obtain $\mu \approx 1.04$ cm^2/V s; at $\gamma = 6 \times 10^{-10}$ g/s μ was estimated ≈ 1.02 cm^2/V s; at $\gamma = 8 \times 10^{-9}$ g/s we have $\mu \approx 0.74$ cm^2/V s.

The results obtained suggest that in all approaches the mobility decreases as the friction coefficient grows. Theoretically, one would expect the mobility to be minimum when Γ, $\gamma \to \infty$. In this case, the equilibrium Maxwell–Boltzmann distribution is established in the system of sites and a hole moves in the most disordered media. In the opposite case of $\Gamma, \gamma \to 0$ the establishing of the Maxwell–Boltzmann distribution requires infinite long time and can not be formed during the process of the hole transfer through the nucleotide chain. In this extreme case the mobility will exceed its value in the limit $\Gamma, \gamma \to \infty$.

So, the contribution of structural fluctuations leading to changes in the value of the matrix element has appeared to be considerable.

To our knowledge, this is the first calculation of the mobility in the SSH model as applied to DNA (in [14,15] the SSH model was used to calculate the energy characteristics in the steady state).

Note that the approach developed can be used to calculate the mobility in regular nucleotide sequences of any type. In this case one might expect that the mobility is greatly influenced by insertions of non-guanine nucleotides between neighboring guanine bases whose oxidation potential is higher than that of guanine. Varying the type of nucleotides and the length of the insertions one could vary mobility in rather a wide range.

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References

1. C.J. Murphy, M.R. Arkin, Y. Jenkins, N.D. Ghatlia, S. Bossman, N.J. Turro, J.K. Barton, Science **262**, 1025 (1993)
2. S.O. Kelley, J.K. Barton, Science **283**, 375 (1999)
3. A. Harriman, Angew. Chem. **111**, 996 (1999)
4. F.P. Lewis, Y. Zhang, X. Liu, N. Xu, R.I. Lestinger, J. Phys. Chem. B **103**, 2570 (1999)
5. E. Meggers, M.E. Michel-Beyerle, B.J. Giese, J. Am. Chem. Soc. **120**, 12950 (1998)
6. F.D. Lewis, Y. Wu, J. Photochemistry and Photobiology **2**, 1 (2001)
7. G.B. Schuster, Acc. Chem. Res. **33**, 253 (2000)
8. H.W. Fink, C. Schönenberger, Nature **398**, 407 (1999)
9. D. Porath, A. Bezryadin, S. de Vries, C. Dekker, Nature **403**, 635 (2000)
10. C. Dekker, M.A. Ratner, Phys. World **14**, 29 (2001)
11. V.D. Lakhno, N.S. Fialko, JETP Lett. **78**, 336 (2003)
12. F.C. Grozema, L.D.A. Siebbeles, Y.A. Berlin, M.A. Ratner, CHEMPHYSCHEM **6**, 536 (2002)
13. V.D. Lakhno, in *Metal-Ligand Interactions*, edited by N. Russo et al. (Kluver Academic Publishers, 2003), p. 571
14. E.M. Conwell, S.V. Rakhmanova, PNAS **57**, 4556 (2000)
15. D.M. Basko, E.M. Conwell, Phys. Rev. E **65**, 061902-1 (2002)
16. F.C. Grozema, Y.A. Berlin, L.D.A. Siebbeles, J. Am. Chem. Soc. **122**, 10903 (2000)
17. F.C. Grozema, Y.A. Berlin, L.D.A. Siebbeles, Int. J. Quant. Chem. **75**, 1009 (1999)
18. T. Holstein, Ann. Phys. **8**, 325 (1959)
19. N.S. Fialko, V.D. Lakhno, Phys. Lett. A **278**, 108 (2000)
20. N.S. Fialko, V.D. Lakhno, Regular & Chaotic Dynamics **7** (3), 299 (2002)
21. W.P. Su, J.R. Schrieffer, A.J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979)
22. A.A. Voityuk, N. Rösch, M. Bixon, J. Jortner, J. Phys. Chem. **104**, 9740 (2000)
23. A. Troisi, G. Orlandi, Chem. Phys. Lett. **344**, 509 (2001)
24. V. Lisy, P. Miskovsky, P. Schreiber, J. Biomol. Struct. Dyn. **13**, 707 (1996)
25. H. Urabe, Y. Sugawara, M. Ataka, A. Rupprecht, Biophys. J. **74**, 1533 (1998)
26. J.A. McCommon, S.C. Harvery, *Dynamics of Proteins and Nucleic Acids* (Cambridge University Press, Cambridge, 1987)
27. H.S. Greenside, E. Helfand, The Bell System Tech. J. **60**, 1927 (1981)
28. J. Dyre, T.D. Schroder, Rev. Mod. Phys. **72**, 873 (2000)