How the Surrounding Water Changes the Electronic and Magnetic Properties of DNA

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We study the influence of humidity on the transport and magnetic properties of DNA within the quantum chemistry methods. Strong influence of water molecules on these properties, observed in this study, opens up opportunities for application of DNA in molecular electronics. Interaction of the nucleobases with water molecules leads to breaking of some of the π bonds and appearance of unbound π electrons. These unbound electrons contribute significantly to the charge transfer at room temperature by up to 10^3 times, but at low temperature the efficiency of charge transfer is determined by the spin interaction of two unbound electrons located on the intrastrand nucleobases. The charge exchange between the nucleobases is allowed only when the spins of unbound electrons are antiparallel. Therefore, the conductance of DNA molecule can be controlled by a magnetic field. That effect has potentials for applications in developing nanoscale spintronic devices based on the DNA molecule, where efficiency of spin interaction will be determined by the DNA sequence.

I. Introduction

The growing interest in the application of organic molecules for building nanoelectronic devices is motivated by several factors: conductance properties, self-assembly, and molecular recognition properties. Self-assembly of molecular building blocks into well-structured systems allows us to exclude physical manipulation during fabrication of nanosize devices. Moreover, the structural damages of the electrical elements can be repaired without any physical contact using the molecular recognition. Since the DNA molecules satisfy all these requirements and, moreover, have been found to conduct charge, its application to developing nanoscale molecular devices is quite promising. While pristine DNA is not a good conductor, its conductivity can be greatly enhanced by suitably changing the environment, thereby rendering it an important element for the nanobio electronics.[1]

An important finding that the overlapping of π orbitals of the stacked base pairs can create a π pathway for charge migration in DNA has over the years inspired many research groups to investigate the electronic properties of this important biomolecule.[2−12] Two independent possible directions can be discerned from various experiments, reported as yet: the charge migration in DNA[3,5,10,11,13,14] and its conductivity.[15−19] It is now more or less established that charge migration in DNA occurs through superexchange tunneling and charge hopping.[2,20,21] However, the experimental data related to DNA conductivity remain unclear: DNA molecules exhibit a wide range of behaviors, from insulator to metallic.[15−19] Only recently, this issue has received a new twist; i.e., the humidity is recognized as an important factor controlling both DNA conductivity[22−24] and DNA magnetic properties.[25,26] It has been observed that the DNA conductivity can increase exponentially by up to 10^6 times with rising humidity.[22−24] In ref 24, participation of the DNA molecule in charge transport was verified by the high resistance of the environment, which exceeds up to 100 times the resistance of DNA itself. The origin of DNA conductivity and its enhancement with humidity was not yet clearly understood. The current interpretation of this phenomena[23] rests on the change of DNA permittivity and, therefore, the DNA conductivity due to adsorption of the water molecules on the DNA skeleton.

For DNA conductivity, the electronic interaction of the nearest-neighbor base pairs is the most important issue that was extensively investigated by many research groups.[7−9,27,28] The parameters thus obtained were subsequently used for simulations of the charge transfer in DNA within different approaches, such as the tight-binding Hamiltonian,[14,29,30] the system of kinetic equations,[20,21] and the polaron model.[4,31] Interestingly, when the superexchange tunneling and hopping were taken as two main transfer mechanisms, the experimentally observed features for hole migration[5,13] were indeed reproduced by the theories. However, these models fail to explain the diverse behaviors of DNA conductivity observed in the experiments.

From our point of view, the inconsistency of theory and experiment on DNA conductivity lies with the reported theoretical approaches, where the charge transfer parameters were evaluated via the quantum-chemistry methods in a vacuum.[7−9,27,28] Moreover, most often this evaluation was performed for a single nucleobase in vacuum[8,9,28] that disregards the significant shift of the highest occupied molecular orbital (HOMO) energies due to the interstrand interaction of the nucleobases participating in the pair formation.[7,27] The discrepancy between the computed parameters and the experimental estimate is rather large. For example, the potential barrier for the charge transfer from G-C to A-T has been estimated theoretically to be ∼0.7 eV,[7,27] while the experimental value is 0.2 eV.[10] Application of the pure electrostatic model to account for the solvation effect[32,33] has shown a decrease of this potential barrier from 0.7 to ∼0.5 eV, still higher than the experimental value. Therefore, it was suspected[32] that interaction of DNA with water contributes not only to the solvation effect but also by changing the nucleobase electronic properties due to their interactions with water.

Of late, several papers have reported quantum-chemical calculations of the electronic properties of DNA surrounded by solvent molecules.[32,34,35] We have shown earlier[32] that the nucleobases link to water and interactions between them can change the symmetry of the occupied π orbitals localized on the nucleobases, which significantly shifts their orbital energies.

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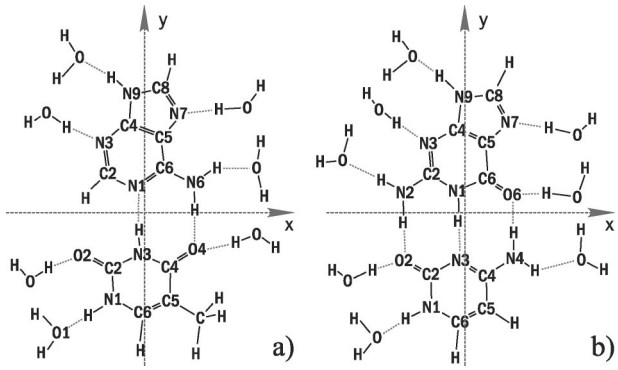

Figure 1. Crystal structures: (a) water-(A-T) and (b) water-(G-C) geometries. The water molecules are attached by hydrogen bonds to the base pairs at positions given in ref 36. These positions correspond to the location of the unshared electron pairs (*O*, *N*) or the polar covalent bonds (*N*−*H*).

Therefore, the potential barrier for hole migration from G-C to A-T pairs is decreased from 0.7 eV (dehydrated pairs) to 0.123 eV (hydrated pairs). Moreover, occurrence of unbound π electrons was found to be a reason for an increase of DNA conductivity with rising humidity.[32] The unbound π electrons result in breaking of π bonds, which occurs because of redistribution of the electron density from the π bonds toward the nitrogen atoms due to hydrogen bonding of nitrogen with water molecules. The increase of the charge transfer between two base pairs due to contribution of such unbound electrons (up to 250 times)[32] thus found is still much less than in the experiments.[22−24] We suggest that the reason for the underestimation of the humidity effect lies in the fact that the DNA geometry transformation from B to A forms with dehydration of DNA is not taken into account.

In our present work we report on our investigation of the impact of humidity on the orbital interaction and charge transfer between two base pairs if they are stacked according to the structural parameters of B-DNA and A-DNA. The aspects of the orbital interaction of the unbound electrons are considered also for an explanation of the magnetic properties of the B-DNA molecule, exhibiting the paramagnetic behavior in a magnetic field.[25,26]

II. Methods

The molecular dynamics simulations for the DNA molecule placed into the "water box" have shown that the nucleobases are able to make hydrogen bonding with the water molecules.[36] For our investigation of the electronic properties of canonical base pairs for dehydration and hydration, the optimized structures of the A-T and G-C base pairs without water molecules and the same structures connected by hydrogen bonds to the water molecules were constructed via the quantum-chemical methods. In the first stage, the geometries of the A-T and G-C base pairs were optimized in vacuum with the Jaguar program.[37] The Becke3−Lee−Yang−Parr functionals[38] and the restricted basis set with polarization and diffuse functions 6-31++G** were applied. Next, the crystal structure of the hydrated DNA base pairs were obtained by placing the water molecules close to the nucleobase atoms having the ability to make hydrogen bonding with the water molecules.[36] The positions of water molecules were optimized under the condition of frozen base pair geometries to save their planarity. The crystal structures of the hydrated (A-T) and (G-C) pairs thus obtained are shown in Figure 1.

To build the polysequences such as $(A\text{-}T)_2$ and $(G\text{-}C)_2$ and also the mixed sequences, the optimized geometries of the hydrated (A-T) and (G-C) base pairs were stacked using the parameters of B-DNA and A-DNA. The natural bond orbital (NBO) analysis[39] for these structures was performed, based on the electron density calculated with the B3LYP/6-31++G** functional, which was earlier found to be a better choice for this purpose.[40,32] The application of the Hartree−Fock (HF) method for determination of the electron density distribution provides similar results as the NBO analysis,[32] except for weaker interaction of the natural bond orbitals. The Ω_i eigenfunctions are the natural bond orbitals built within the NBO analysis based on the input atomic orbital basis set obtained from the density functional theory (DFT). The advantage of the NBO analysis is that the Pauli exclusion principle is applied not only at the inner nodes that preserve orthogonality of the two electrons in the same orbital but also at the outer nodes preserving the interatomic orthogonality. Within the NBO analysis[39] the charge transfer between the nucleobases Q_{DA} has been found as the sum of the $\Omega_i \rightarrow \Omega_j^*$ charge transfer between the donor orbital Ω_i belonging to one nucleobase to the acceptor orbital Ω_j^* on another nucleobase as

$$Q_{DA} = \sum_{i,j} Q_{i,j} = \sum_{i,j} q_i F_{i,j}^2/(\epsilon_i - \epsilon_j)^2 \qquad (1)$$

where q_i is the donor orbital occupancy, ϵ_i, ϵ_j are the orbital energies, and $F_{i,j}$ is the off-diagonal element. The charge occupancy transfer is considered for stabilizing the orbital interaction, i.e., when the second-order interaction energy $\Delta E_{i,j} = -2F_{i,j}^2/(\epsilon_i - \epsilon_j)$ is characterized by the positive sign. The electronic coupling between the nucleobases has been estimated for the natural bond orbitals set as

$$V_{DA} = \sum_{i,j} V_{i,j} = \sum_{i,j} F_{i,j}^2/(\epsilon_i - \epsilon_j) = \sum_{i,j} Q_{i,j}(\epsilon_i - \epsilon_j)/q_i \qquad (2)$$

To estimate the $\pi-\pi^*$ charge transfer in the DNA molecule, we took into account the charge exchange only between the π orbitals.

III. π-Orbital Interaction

It is well-known that charge transfer in DNA occurs due to the overlapping of the π orbitals of the nearest-neighbor nucleobases. The efficiency of charge transfer is determined by the coupling of these π orbitals and the difference of their energies. Thus, for two interacting base pairs, the transfer of a π electron between stacked nucleobases is usually attributed to the interaction of HOMO and HOMO-1 orbitals (located on purines) and HOMO-2 and HOMO-3 (located on pyrimidines). The more efficient charge transfer is expected for two molecular orbitals located on the purines.

In this section, we analyze the interaction of the HOMO and HOMO-1 orbitals in the system of two stacked base pairs. The efficiency of such interactions directly depends on the location of the base pairs relating to each other. It is known that sufficiently wet DNA is characterized by a B-form, while dehydration changes the geometry of the DNA molecule to the A-form.[41,42] The distinction of A- and B-forms lies mostly in the helical twist θ, which for A-DNA is 32° and for B-DNA is 36°, and in a dislocation of the base pairs from a helix axis Δ, which for A-DNA is 4.5 Å and for B-DNA is −1.0 Å.[41] These

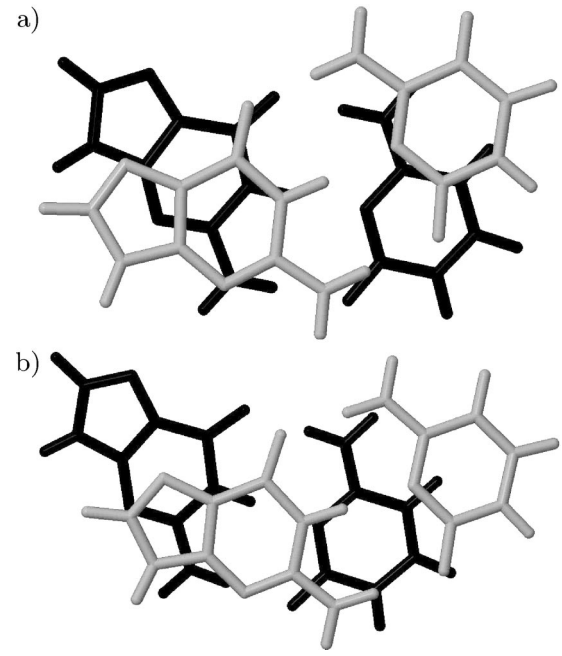

Figure 2. Geometry of the $(G\text{-}C)_2$ sequences where the base pairs stacked with parameters characterized (a) for the B-DNA molecule and (b) for the A-DNA molecule.

parameters are important to describe a location of a base pair in the system of the two stacked pairs. The rest of the parameters, such as the base pair tilt γ and axial rise per nucleotide d, which are linearly dependent on each other,[41] do not significantly change this location. The geometry of the $(G\text{-}C)_2$ sequences, where base pairs are stacked with structural parameters of B-DNA and A-DNA, are presented in Figure 2. As the nucleobases in the B-form are located on top of each other (the displacement from the helix axis Δ is close to zero), the most important contribution to the base pair interaction comes from the intrastrand part. For the A-form, the dislocation of the base pair from the helix axis causes both the intra- and interstrand charge exchange between the nucleobases.

Here we study the influence of the base pair location in a system of two stacked base pairs, such as $(A\text{-}T)_2$ and $(G\text{-}C)_2$ sequences. The shift of the π-orbital energies due to the interaction between two stacked base pairs can be determined from[43]

$$e_{\psi_1} \approx e_{\psi_1^0} - H_{12} + (e_{\psi_1^0} - H_{12})S_{12} \quad (3)$$

$$e_{\psi_2} \approx e_{\psi_2^0} + H_{12} - (e_{\psi_2^0} + H_{12})S_{12} \quad (4)$$

where $e_{\psi_{1,2}^0}$ and $e_{\psi_{1,2}}$ are the π-orbital energies respectively before interaction and after interaction, $H_{12} = \langle\psi_1|h^{\text{eff}}|\psi_2\rangle$ is the intrinsic interaction integral, h^{eff} is the effective core potential, and S_{12} is the orbital overlap.

In the system of $(A\text{-}T)_2$ and $(G\text{-}C)_2$ sequences the interaction of filled π orbitals is repulsive, and therefore, the base pairs tend to repeal each other.[43] This process is dominant when filled orbitals are orthogonalized, i.e., when the tilt angle $\gamma = 0°$ and the twist angle $\theta = 0°$. In this case, because the wave functions ψ_1 and ψ_2 are interacting in such a way that their lobes of the same sign overlap (ψ_1 and ψ_2 are orthogonal orbitals, i.e., in-phase interaction), this leads to a decrease of the charge occupancy transfer Q_{DA} between the intrastrand nucleobases and

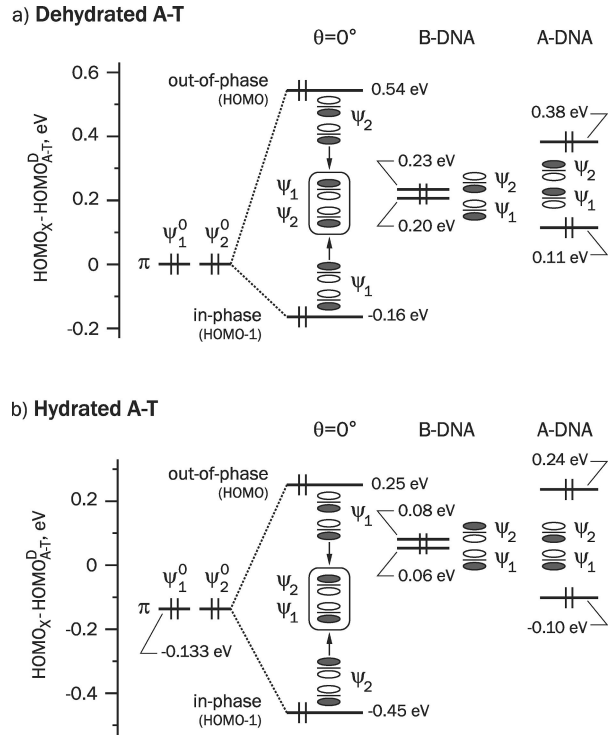

Figure 3. Shift of the HOMO and HOMO-1 energies and change of the ψ_1 and ψ_2 wave functions' symmetry due to stacking of the two dehydrated A-T pairs (a) ($e_{\psi_{1(2)}^0}$) or two hydrated A-T pairs (b) into $(A\text{-}T)_2$ sequences with different parameters: (1) two parallel base pairs ($\gamma = 0°$, $d = 3.4$ Å) stacked with twist angle of $\theta = 0°$; (2) two base pairs stacked with parameters corresponding to B-DNA ($\gamma = 0°$, $d = 3.4$ Å, $\theta = 36°$), and (3) with parameters corresponding to A-DNA ($\gamma = 10°$, $d \approx 3.0$ Å, $\theta = 32°$). All energies for the $(A\text{-}T)_2$ sequences are calculated with respect to the HOMO energy of the single dehydrated A-T pair ($e_{\psi_{1(2)}^0}$).

the Pauli repulsion becomes dominant. The result of such an interaction is a shift of the π-orbital energies e_{ψ_1} and e_{ψ_2} by H_{12}, while the contribution of the $(e_{\psi_1^0} \pm H_{12})S_{12}$ term is approximately zero. The shift of the HOMO and HOMO-1 orbital energies after perturbation is presented in Figure 3 for the $(A\text{-}T)_2$ sequence and in Figure 4 for the $(G\text{-}C)_2$ sequence. For a twist angle of 0° the ψ_i wave functions are almost equally delocalized over two purines, and the splitting of the HOMO and HOMO-1 orbitals is large $\sim 2H_{12}$.

However, in the A- and B-DNA molecule the pair bases are stacked with a helical twist, and additionally they are shifted from the helix axis. Therefore, the π-electron density of the ψ_1 and ψ_2 wave functions are shifted such that it destroys the wave function orthogonality and results in a rise of the intrastrand charge occupancy transfer Q_{DA} between the stacked base pairs. Depending on the efficiency of the charge occupancy transfer, which is determined by the orbital overlap S_{12} and symmetry of the interacting orbitals, the orbital energies e_{ψ_1} and e_{ψ_2} can be significantly shifted in comparison to the orthogonal case (see the case of $\theta = 0°$ in Figures 3 and 4). Since the π-electron clouds are shifted, the charge occupancy transfer is significant even when two orbitals ψ_1 and ψ_2 are in-phase (see dehydrated B-DNA in Figure 4a). Therefore, for the B-DNA and the A-DNA, the wave functions ψ_1 and ψ_2 are strongly localized on one nucleobase, and splitting of their HOMO and HOMO-1 orbitals is decreased relating to orthogonal case due to the contribution from the $(e_{\psi_1^0} \pm H_{12})S_{12}$ term in eqs 3 and 4. In our earlier works,[32] the humidity was found to change the electron density distribution and symmetry of the π orbitals for

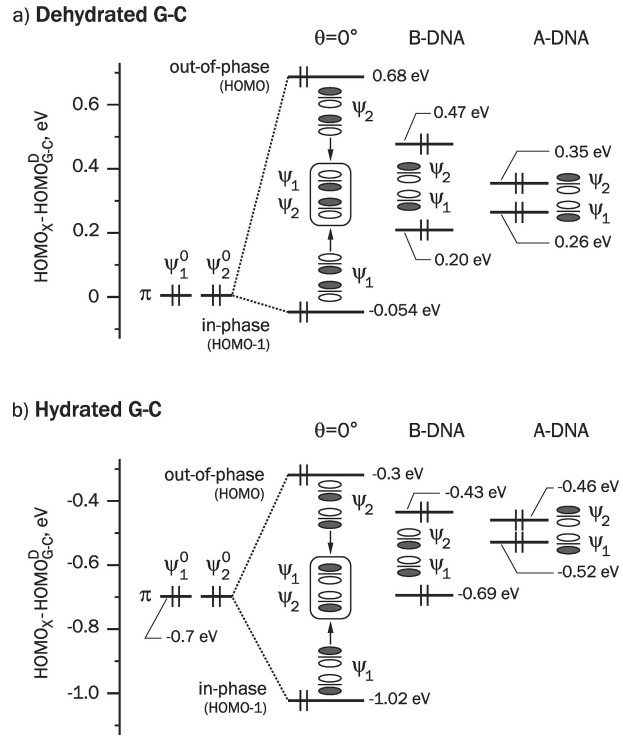

Figure 4. Shift of the HOMO and HOMO-1 energies and change of the ψ_1 and ψ_2 wave function's symmetry due to stacking of the two dehydrated G-C pairs (a) ($e^0_{\psi_{1(2)}}$) or two hydrated G-C pairs (b) into $(G\text{-}C)_2$ sequences with different parameters (for parameters see points 1−3 in caption for Figure 3). All energies for the $(G\text{-}C)_2$ sequences are calculated with respect to the HOMO energy of the single dehydrated G-C pair ($e^0_{\psi_{1(2)}}$).

the single G-C and A-T base pairs. Here, we observe that for the $(A\text{-}T)_2$ and $(G\text{-}C)_2$ sequence in the B-form hydration reverses the interaction of the ψ_1 and ψ_2 wave functions. For example, for the $(A\text{-}T)_2$ sequence, hydration changes the interaction from out-of-phase to in-phase, while for the $(G\text{-}C)_2$ sequence from in-phase to out-of-phase. For the A-DNA the humidity changes the symmetry of the ψ_1 and ψ_2 wave functions as well, but preserve the type of their interaction; i.e., the interaction of the ψ_1 and ψ_2 wave functions always remains out-of-phase for the $(A\text{-}T)_2$ sequence and in-phase for the $(G\text{-}C)_2$ sequence.

The symmetry of the ψ_1 and ψ_2 wave functions localized on purines shows an opposite behavior for the $(A\text{-}T)_2$ and $(G\text{-}C)_2$ sequences stacked with parameters of the B- and A-forms. This was found to be a result of the interaction of purines with pyrimidine within the DNA pairs. For two stacked dehydrated guanines $(G)_2$ and two stacked dehydrated adenines $(A)_2$ only out-of-phase interactions of their ψ_1 and ψ_2 wave functions corresponding to HOMO and HOMO-1 orbitals are observed for both A- and B-forms in the dehydrated case. Therefore, the stacked guanines and the adenines originally are characterized by the same symmetry of the ψ_1 and ψ_2 wave functions. Their properties are changed due to the contribution of the pyrimidine bases participating in the base pair formation. Thus, for the $(G\text{-}C)_2$ sequences, the contribution of the π-orbital symmetry from cytosine switch the interaction of the ψ_1 and ψ_2 wave functions to in-phase type, while the contribution of the π-orbital symmetry from thymine for the $(A\text{-}T)_2$ sequence do not provide such a phase reversal. Similar to the occupied orbitals, the $(A\text{-}T)_2$ and $(G\text{-}C)_2$ sequences have shown the opposite type of interaction of the lowest unoccupied molecular orbitals (LUMOs), such as LUMO and LUMO-1.

We thus conclude that the transport properties of the poly(dG)−poly(dC) and poly(dA)−poly(dT) will be quite different due to the difference of their electronic structures, namely due to different symmetry of their interacting HOMOs and LUMOs. This implies that experimentally observed[16] different properties of poly(dG)−poly(dC) and poly(dA)−poly(dT) molecules showing respectively the p-type and n-type conductance can be related to their intrinsic electronic properties.

IV. π Charge Transfer

Our next step is the quantitative characterization of the charge occupancy transfer between stacked base pairs performed with the NBO analysis for DNA of B- and A-forms with different levels of humidity. For the hydrated $(A\text{-}T)_2$ and $(G\text{-}C)_2$ sequences in the B-form, the intrastrand interaction between the stacked pairs and interaction of the nucleobases with water molecules drastically change the electron density distribution and population of the π orbitals over the base pairs. As a result, the covalent structure of the nucleobases is converted to a structure with separated charge (ionic), which has been obtained by the NBO analysis.[32] In particular, for adenine and guanine the π electron density between the *C*4 and *C*5 atoms is shifted. Therefore, instead of a double bonding to the *C*5 atom, the *C*4 atom *donates* an electron to form a double bond with the *N*9 atom, which contributes one π electron from the lone pair. Consequently, the *C*5 atom has only three bonds and carries a negative charge (one π electron not locked up to the covalent bond), while the *N*9 atom has four bonds (one missing π electron) and carries a positive charge. The charge separation occurs for the cytosine in a similar manner, where the *N*3 atom carries a negative charge and the *N*4 atom carries a positive charge. Interestingly, for the $(A\text{-}T)_2$ sequence, the adenines are converted to the ionic structure already for the dehydrated case, while thymine always has a covalent structure. The origin of this behavior is the low weighting of the covalent structure of adenine and the high weighting of thymine.[40]

The alteration of the double bond pattern due to conversion of the covalent structure to the structure with separated charges changes the orbital perturbation and the intrastrand charge occupancy transfer between the nucleobases within each base pair. Therefore, the interaction of guanine and cytosine within the hydrated G-C pair ($\gamma = 0$) is significantly increased in comparison to that for the dehydrated G-C pair. Their interstrand interactions are enhanced because of the change of the covalent structure of guanine and cytosine to the ionic structure and consequently to lowering the energy gap between their π orbitals. In the covalent structure of the dehydrated G-C pair the charge transfer ($Q_{G\to C} = 0.00043\ \bar{e}$) occurs mostly between the *N*1 lone pair (guanine) and the π^* orbital of the *N*3−*C*4 bond (cytosine), where the energy gap is $\epsilon_{N1(G)} - \epsilon_{N3-C4(C)} = 5.98$ eV. In the structure with separated charge, the charge transfer occurs mostly between the lone pair of the *N*1 atom (guanine) and unbound π electron on the *N*3 atom (cytosine). The energy gap between them is decreased to $\epsilon_{N1(G)} - \epsilon_{N3(C)} = 1.9$ eV, and the amount of charge transfer is $Q_{G\to C} = 0.0054\ \bar{e}$. The electronic coupling between guanine and cytosine is estimated to be $V_{G\to C} = 0.0065$ eV for the hydrated case against $V_{G\to C} = 0.0016$ eV for the dehydrated. Unlike in dry DNA in wet DNA the interstrand charge transfer within the G-C pair can actually make a large contribution to the DNA transport properties because of a stronger electronic coupling between guanine and cytosine and a lower energy gap between them. The enhancement of the interaction of the thymine and adenine within a A-T pair due to hydration is found to be very small.

TABLE 1: Intrastrand Charge Transfer between Guanines $G_1 \rightarrow G_2$ and Cytosines $G_1 \rightarrow G_2$ within $(G\text{-}C)_2$ Sequences under Different Conditions

	Q_{DA}, ē	Q_{AD}, ē	$Q = Q_{DA} - Q_{AD}$, ē
	$G_1 \rightarrow G_2$		
hydrated B-DNA	0.1630	0.0063	0.1567
dehydrated B-DNA	0.0030	0.0036	−0.0007
hydrated A-DNA	0.0062	0.0140	−0.0078
dehydrated A-DNA	0.0017	0.0015	0.000 17
	$C_1 \rightarrow C_2$		
hydrated B-DNA	0.0034	0.0030	0.0003
dehydrated B-DNA	0.0003	0.0010	−0.0007
hydrated A-DNA	0.0100	0.0069	0.0033
dehydrated A-DNA	0.0042	0.0046	−0.0004

TABLE 2: Intrastrand Charge Transfer between Adenines $A_1 \rightarrow A_2$ and Thymines $T_1 \rightarrow T_2$ within $(A\text{-}T)_2$ Sequences under Different Conditions

	Q_{DA}, ē	Q_{AD}, ē	$Q = Q_{DA} - Q_{AD}$, ē
	$A_1 \rightarrow A_2$		
hydrated B-DNA	0.0269	0.0052	0.0218
dehydrated B-DNA	0.0040	0.0026	0.0014
hydrated A-DNA	0.0053	0.0140	−0.0087
dehydrated A-DNA	0.0025	0.0055	−0.0030
	$T_1 \rightarrow T_2$		
hydrated B-DNA	0.0020	0.0010	0.0010
dehydrated B-DNA	0.0018	0.0011	0.0007
hydrated A-DNA	0.0056	0.0033	0.0023
dehydrated A-DNA	0.0057	0.0033	0.0024

Within the ionic structure of both guanine and adenine, the unbound π electrons are localized on the $C5$ atom. However, the participation of these π electrons in the intrastrand charge transfer within the $(G\text{-}C)_2$ and $(A\text{-}T)_2$ sequences is completely different for these purines due to the symmetry of the interacting orbitals HOMO and HOMO-1 observed in the previous section (in-phase and out-of-phase). For the $(G\text{-}C)_2$ sequence in B-form, the ψ_1 and ψ_2 wave functions are out-of-phase, and therefore, the charge transfer between two guanines is large because of the permitted direct charge exchange between the $C5$ atoms ($Q_{C5(G_1)\rightarrow C5(G_2)}$) with participation of the unbound π electrons. The overlap of these unbound electrons for the B-DNA is significant (the overlap matrix $S_{C5(G_1)\rightarrow C5(G_2)} = 0.0245$), and energy gap for transfer is rather small $\epsilon_{C5(G_1)} - \epsilon_{C5(G_2)} = 0.33$ eV. All of these provide a charge occupancy transfer from one guanine to another with participation of the unbound electrons to be $Q_{C5(G_1)\rightarrow C5(G_2)} = 0.145$ ē, which is a dominant charge transfer channel for the $(G\text{-}C)_2$ sequence. Because the unbound π electrons on the $C5$ atoms are strongly localized, their orbital overlapping is sensitive to the twist angle. Therefore, the $Q_{C5(G_1)\rightarrow C5(G_2)}$ charge transfer exists only in the confined range of twist angle from $\theta = 33°$ to $\theta = 44°$. Our computational results for the charge occupancy transfer between guanines and cytosines within the $(G\text{-}C)_2$ sequence are presented in Table 1. Dehydration of the $(G\text{-}C)_2$ sequence in B-form leads to a major decrease of the charge occupancy transfer and change of its trend as result of application of the symmetry rule (see dehydrated B-DNA in Figure 4). For the intrastrand cytosines in the $(G\text{-}C)_2$ sequences, the dominance of the $N3-C4(C_1) \rightarrow C4-N4(C_2)$ interaction in the dehydrated case is switched to the prevalence of the $N3-C4(C_1) \rightarrow N3-C4(C_2)$ interaction in the hydrated case, which significantly increases the charge transfer between the hydrated bases. However, contribution of the cytosine in the charge occupancy transfer between stacked G-C pairs is quite small and can be neglected for both B- and A-forms. For the $(G\text{-}C)_2$ sequence stacked with parameters corresponding to the A-DNA, their HOMO and HOMO-1 are in-phase which invalidates the charge transfer between natural bond orbitals created by unbound electrons and decreases substantially the whole intrastrand charge transfer between guanines. As was already mentioned above, sufficiently wet DNA is characterized by the B-form and dry DNA is of A-form, and the poly(dG)−poly(dC) conductivity with humidity is enhanced 10^3-10^6 times.[22−24] The comparison of the magnitude of $Q = Q_{DA} - Q_{AD}$ (the charge transfer Q was determined by the difference of donor−acceptor Q_{DA} and acceptor−donor Q_{AD} charge transfer), computed for the hydrated B-DNA (wet DNA) (see Table 1) and dehydrated A-DNA, is found to be $\sim 10^3$, in excellent agreement with the experimental data.[22] As was expected, the charge occupancy transfer observed between interstrand guanine and cytosine belonging to different base pairs is quite large ($Q_{G_1\rightarrow C_2} = 0.0322$ ē) for the A-form in comparison to that for the B-DNA structure ($Q_{G_1\rightarrow C_2} = 0.00136$ ē).

For adenines within the $(A\text{-}T)_2$ sequences stacked according to parameters of the B-form, the overlap of the unbound π electrons is $S_{C5(A_1)\rightarrow C5(A_2)} = -0.0265$, which is similar to that for the guanines, but ψ_1 and ψ_2 wave functions are in-phase which restricts the $C5(A_1) \rightarrow C5(A_2)$ charge transfer. However, the unbound π electrons participate in the intrastrand charge exchange with π^* orbitals on the $C4-N9(A_2)$ bond, but the efficiency is not high, $Q_{C5(A_1)\rightarrow C4-N9(A_2)} = 0.0223$ ē, because of a large energy gap $\epsilon_{C5(A_1)} - \epsilon_{C4-N9(A_2)} = 1.9$ eV. Our computational results for the $(A\text{-}T)_2$ sequences are presented in Table 2. For adenines within the hydrated $(A\text{-}T)_2$ sequences of A-form, the HOMO orbitals are out-of-phase and $C5(A_1) \rightarrow C5(A_2)$ charge transfer is permitted. However, the overlap matrix of this transfer is small, $S_{C5(A_1)\rightarrow C5(A_2)} = 0.0130$, and the magnitude of the off-diagonal element $F_{C5(A_1)\rightarrow C5(A_2)}$ is 10 times smaller than that for B-DNA. Therefore, the contribution of the charge exchange between unbound electrons in $(A\text{-}T)_2$ sequences of the A-form is less. Because thymine structure remains covalent independent of hydration, the charge transfer between thymines for the A- and B-form is slightly modified by hydration only due to a change of the $(\epsilon_i - \epsilon_j)$ energy gap. Finally, an increase of the $\pi-\pi^*$ charge transfer for the $(A\text{-}T)_2$ sequences is found to be only ~40 times due to the hydration, while the experimental value was 10^3 times.[22] This discrepancy is related to the applicability of the simulated results only for low temperature range, where orbital symmetry of the unbound electrons is preserved, i.e., when the energy required to change the orbital symmetry is $\Delta E_S \ll k_B T/q$. We estimated the magnitude of ΔE_S for adenines within the $(A\text{-}T)_2$ sequence as the difference between the $\epsilon_{C5(A_1)} - \epsilon_{C5(A_2)}$ for unbound electrons when the wave functions are out-of-phase and in-phase, which was found to be $\Delta E_S = 0.12$ eV. Therefore, already at a low temperature ($T < 100$ K) unbound π interacting electrons have enough energy to switch the wave functions from out-of-phase to in-phase, which opens up the opportunity for a direct $C5(A_1) \rightarrow C5(A_2)$ charge transfer in the $(A\text{-}T)_2$ sequences of the B-form. As a result, at room temperature the charge transfer with participation of the unbound electrons in B-DNA is possible not only for the $(G\text{-}C)_2$ sequence but also for the $(A\text{-}T)_2$ sequence. Therefore, at room temperature the hydration of DNA should provide an increase of the DNA conductance approximately as the same magnitude for the poly(dG)−poly(dC) and poly(dA)−poly(dT) chains (up to 10^3 times) because the orbital overlap of nearest-neighbor unbound electrons for stacked guanines and stacked adenines is the same ($S_{C5(G_1(A_1))\rightarrow C5(G_2(A_2))} \approx \pm 0.025$), and orbital symmetry is not preserved at room temperature.

In summary, we found that the occurrence of the unbound π electrons activated by humidity suppresses the DNA band gap from ~8.0 eV for the dehydrated DNA to ~3.0 eV for the hydrated DNA. This value of the band gap was often observed in the experiments.[44,45] Therefore, the occurrence of the unbound π electrons suppressing the band gap of wet DNA is the main factor for high B-DNA conductivity.

V. DNA Magnetism

A noninvasive means to investigate the intrinsic electronic properties of DNA was recently applied to wet and dry λ-DNA by measuring the magnetization of this molecule at different humidity levels.[25] The paramagnetic behavior of λ-DNA in the B-form was observed at low temperature, while dry A-form was shown to be diamagnetic for a wide temperature range. The solvent of distilled H_2O itself is paramagnetic due to the contribution from the O_2 molecules, but the measured magnitude of magnetization of distilled water was not large enough in comparison to that for wet λ-DNA,[26] which proves the origin of the DNA paramagnetism from the intrinsic DNA properties. The orbital motions of free electrons have been attributed to be the reason for this paramagnetic effect, while the spin contribution to paramagnetism was claimed to be unlikely. However, the interaction of nearest-neighbor unbound π electrons created by interaction of the base pairs with water molecules can be a source of spin paramagnetism because of possible pairing of the unbound electrons with parallel or antiparallel spins.

We have shown in the previous section that each DNA base pair linked to water molecules has unbound π electrons, whose interaction is not strong because of the large separation (3.4 Å). The consideration of the Pauli exclusion principle for outer nodes (interatomic orthogonality) in the NBO analysis allows us to analyze the spin state of unbound electrons. Originally, the phase of the interacting wave functions is taken from the standard calculation B3LYP/6-31++G** within the restricted basis set. If the wave functions of the HOMO and HOMO-1 orbitals obtained within the DFT method are in-phase, then the unbound electrons obtained within the NBO analysis are also in-phase (see Figures 3 and 4), i.e., paired with parallel spin. Their natural orbitals are closer in energy because of absence of exchange repulsion term K in the interaction energy of two electrons. For the two unbound electrons paired with antiparallel spins (out-of-phase interaction of HOMO wave functions) their orbital energy splitting is quite large. The energy diagram of the unbound electrons in the guanines within the $(G\text{-}C)_2$ sequence, in adenines within the $(A\text{-}T)_2$ sequence, and in cytosines within the $(G\text{-}C)_2$ sequence are presented in parts a, b, and c of Figure 5, respectively, for hydrated sequences in B- and A-forms. Two stacked cytosines are found to be source of paramagnetic behavior because their paired unbound electrons have parallel spin, while for the stacked adenines and guanines the interaction of the unbound electrons largely depends on the DNA geometry. However, the stacked adenines are also expected to contribute to the B-DNA paramagnetism.

Therefore, with regards to the diamagnetic and paramagnetic properties of DNA, dry DNA is expected to be always diamagnetic because of the absence of unbound electrons, while wet DNA should be paramagnetic and the efficiency of paramagnetism is directly dependent on the DNA sequences. The control of the spin of the unbound electrons by the magnetic field would open up real opportunities for using DNA in spintronics.[46]

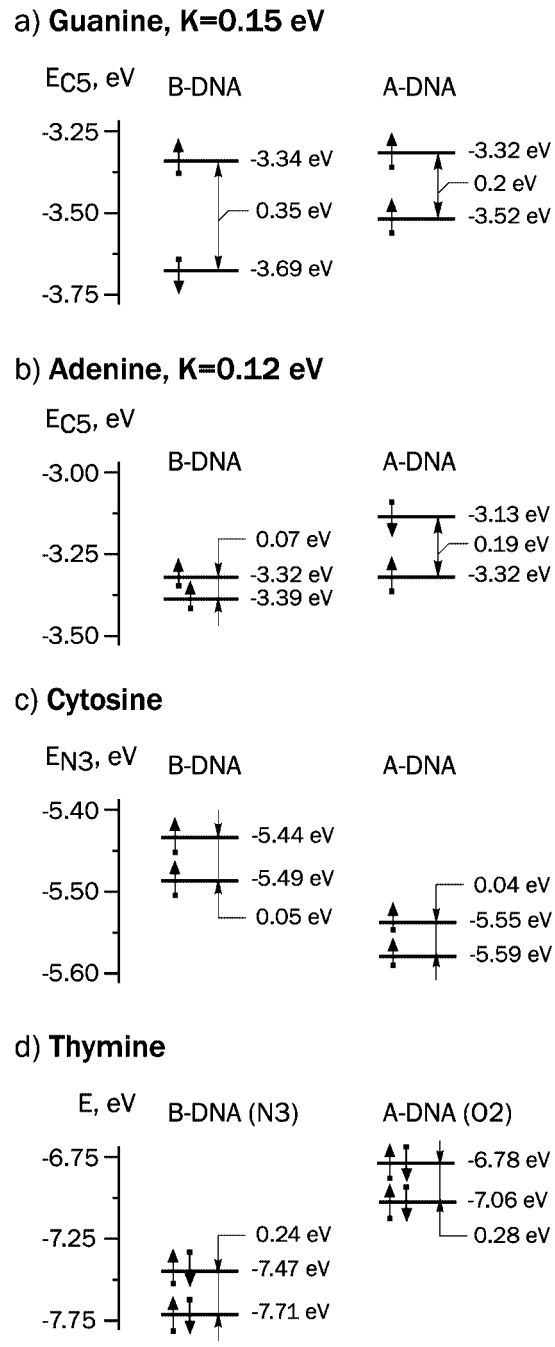

Figure 5. Energetics of the natural bond orbitals Ω_i corresponding to the valence unbound electrons formed within the nucleobases due to their interaction with water (a) for guanines within the hydrated $(G\text{-}C)_2$ sequence, (b) for adenines within the hydrated $(A\text{-}T)_2$ sequence, (c) for cytosines within the hydrated $(G\text{-}C)_2$ sequence, and (d) the highest occupied natural orbitals for thymines within the hydrated $(A\text{-}T)_2$ sequence. K is the exchange repulsion term calculated as difference of energy ΔE for paired electrons with antiparallel spins and parallel spins.

VI. Conclusion

Our findings that hydration of DNA activates the occurrence of the unbound π electrons, which can easily participate in conductance because of narrowing of the band gap to ~3.0 eV in comparison to ~8.0 eV for dehydrated DNA, allow us to characterize the DNA molecule as a narrow band gap semiconductor. The main factors enhancing the appearance of these unbound electrons are linking of the nucleobases with water molecules and intrastrand interactions between

neighboring nucleobases. The main contribution to the conductivity comes from the intrastrand transfer of unbound π electrons between purines because of quite strong overlapping of their orbitals ($S_{C5(G_1(A_1))\rightarrow C5(G_2(A_2))} \approx \pm 0.025$) and a small energy gap $\epsilon_{C5(G_1(A_1))} - \epsilon_{C5(G_2(A_2))} = 0.33$ eV. Therefore, at room temperature sufficient hydration of DNA can lead to an increase of the conductivity by up to 10^3 times, but at low temperature the conductance properties of the poly(dG)−poly(dC) and poly(dA)−poly(dT) sequences should be significantly different because of the orbital symmetry rule. As an example, because of the out-of-phase interaction of the wave function of the corresponding π unbound electrons, the conductivity of the poly(dG)−poly(dC) chain is expected to be much larger than that for the poly(dA)−poly(dT) structure, where these wave functions are in-phase. The pairing of the unbound π electrons from the nearest-neighbor intrastrand bases within the hydrated DNA chain can be with antiparallel or parallel spins, which is a source of correspondent diamagnetic and paramagnetic behavior of DNA in a magnetic field.

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