Effects of molecular motion on charge transfer/transport through DNA duplexes with and without base pair mismatch

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We investigate the influence of molecular motion on DNA conductance and charge transfer in the ballistic transport regime. We evaluate the conductance/charge transfer properties for ensembles of conformations representative of the molecular fluctuations in an explicit all atom representation. We generate such ensembles by classical molecular dynamics (MD) and investigate the influence of conformational change on the charge transfer properties of the system. Using this approach, we can qualitatively explain the influence of base pair mismatches on DNA electrical properties.

Keywords: DNA; Charge transport; Base mismatch; Molecular dynamics

1. Introduction

The problem of DNA charge transfer/transport is one of the important and lively debated topics (for the recent comprehensive reviews, see for example, [1,2]), since it excites a considerable interest not only in the biomedical [3], but also in the nanotechnology [4] community.

Studies of DNA conductance in the last decades have led to a bewildering array of interesting, but often still seemingly contradictory results. Many factors influence DNA conductance, including the difficulties to characterize environmental effects, such as solvation, the presence of counter-ions and the coupling to the thermal bath. In order to unravel the most contradictory aspects of the electrical properties of DNA, theoretical investigations must account for the non-trivial influence of DNA intramolecular dynamics on the detailed physico-chemical mechanisms of DNA charge transfer/transport (see for example, [5]). Due to a large number of interdependent degrees of freedom in DNA polymers and the broad, nearly continuous range of characteristic time scales in DNA molecular dynamics (MD), the exact influence of the dynamic modes is not yet fully clear. Such an information would be indispensable to fully characterize and rationally regulate DNA charge transfer/transport propensities by altering DNA molecular-dynamical properties via the base sequence or environmental modulation.

One of the fruitful theoretical approaches in tackling the above row of problems can be to combine classical molecular-dynamical simulations with quantum-chemical techniques to systematically study changes in DNA electronic structure due to intramolecular modi of these biopolymers. In the literature, there are already several examples of successful studies using such a kind of approach [6 9].

In the present communication, we would like to further extend the above technique, by combining classical molecular-dynamical simulations with a method to compute ballistic conductance of DNA duplexes in their explicit all-atom representation [10]. We compute the ballistic conductance independently for a number of snapshots collected along the MD trajectory. The results of these "snapshot evaluations" are used as a representative sample to estimate expectation values (probability-weighed averages) of DNA conductance for a range of energies around the Fermi level. The resulting energy spectrum of dynamically averaged conductance can thus be better comparable to the relevant experimental data taken at room temperature, than the analogous ballistic conduction spectrum calculated for a rigid molecular

structure at zero temperature. Here, we present the details of our method and demonstrate that its application to DNA duplexes with and without base-pair mismatch helps to qualitatively explain the experimental data on the peculiarities of charge transfer in such systems.

2. DNA duplexes under study

In the present work, the following DNA pentadecanucleotide duplexes have been studied:

(a) The conventional DNA duplex d(5′-AGTACAGTC-ATCGCG-3′), charge transfer properties of which were experimentally studied in the work [11]. From here on, we denote this molecule as 15BP;
(b) the same duplex, but with the AC mismatch at its 4th position from the 5′-end, also studied in the work [11]. From here on, we denote this molecule as 15BP-AC; and
(c) the same duplex, but with the GA mismatch at its 7th position from the 5′-end, also studied in the work [11]. From here on, we denote this molecule as 15BP-GA.

For the above DNA duplex family, the amount of the charge transferred through the DNA duplex has been found to decrease up to one third when comparing the perfectly matched oligonucleotide to that containing the A C mismatch. On the other hand, it is only slightly changed when comparing the perfectly matched oligonucleotide to that containing the G A mismatch [11]. In our previous publication [10], we have found that such an experimentally observable trend cannot be explained solely in terms of calculated ballistic charge transport through the relevant "rigid" equilibrium DNA structures. Among other possible influences, the MD of the underlying systems may be relevant to explain the experimental observations. We have therefore developed an approach to estimate the influence of conformational change on the electric properties in the present investigation.

For this purpose, we have generated representative conformation ensembles of each of the three above-mentioned duplexes. The initial DNA structures with and without base-pair mismatch were first constructed by using the molecular modeling software HyperChem [12] in accord with the standard B-form double-strand DNA. After putting them into spherical water hulls with the radius of 16.5 18.0 Å (containing 28 Na^+ counterions as to fully compensate the DNA negative charge), we minimized the energy of these hydrated complexes using the TINKER software package [13]. Here, the AMBER [14] and TIP3P [15] force fields were employed for DNA and water molecules, respectively. After the structural optimization and subsequent thermal equilibration, MD simulations by the modified Beeman algorithm have been performed for each of the three DNA duplexes under study for 100 ps with the time step of 1 fs. The temperature was maintained at 300 K by the Berendsen weak-coupling thermostat, where the coupling parameter was set equal to 0.1 ps. We thus collected a number of snapshots along all the three MD trajectories (specifically, 33 shapshots with 3 ps intervals for each of the three DNA duplexes in question), which represent different feasible deformations of the DNA structure. Each of the resulting deformed DNA structures has been subject to the conductance calculations (only DNA themselves, stripped of all other ingredients, were subject to the conductivity calculations) using the method presented below. Here, we take only 33 MD snapshots, since we use them as a random sample in the further statistical analysis of DNA conductance and the minimum reasonable size of a random sample ought to amount between 30 and 100 (for a detailed and general discussion on this issue see, for example, [16]).

It should be noted that our present approach is not taking into account any effect of the explicit counterion water surrounding of DNA on its conductivity. This means that here, we have not considered a possibility of populating positively charged states of DNA (with respect to its "ground" polyanionic state) due to their stabilization by the counterion water environment. We are aware that the latter aspect should be accounted for, especially when analyzing the results of electrochemical experiments, but this would go beyond the scope of our present communication.

3. Computation of DNA ballistic conductivity

The method we use to estimate DNA conductance of every MD snaphot has been discussed in detail elsewhere [10], so that we will present here only a succinct outline of the algorithm used. Like in our previous publication [10], we use extended Hückel Hamiltonian to describe electronic structure of DNA and electrodes.

(a) We divide the given DNA duplex into nucleotide pairs (in our algorithm, they could be the conventional Watson Crick or mismatched ones; the sequence of the pairs can be arbitrary);
(b) the leftmost and rightmost nucleotide pairs are covalently attached to sulfur atoms. In the present work, we assume that each sulfur atom establishes a single covalent bond to the pertinent deoxyribose O3′-atom (the S O3′ bond length is 1.74 Å, the C3′ O3′ S bond angle is 109.5°, the C4′ C3′ O3′ S torsion angle is 180°). It should be noted that this "C O S Au" way of attaching molecules to electrodes has not been embodied in any experimental study, to the best of our knowledge. Among other possibilities, there are usually some aliphatic bridges of the $(CH_2)_n$ shape between O and S. In the present theoretical study, we would like to exclude the effects of the bridges in question, in order to get more intensive DNA transmission spectra. Since our study is comparative, the omission of the bridges

between O and S should not drastically affect the final results;

(c) each of the above-mentioned sulfur atoms is in turn attached to a fragment of the gold {111} surface represented by a triangle of Au atoms, so that all the three S Au distances are 2.53 Å, whereas the Au Au bond lengths in the triangle are 2.885 Å. Our computer program automatically determines how the Au triangles should be placed with respect to the DNA duplex involved. Specifically, the approximation to the double-helical axis is evaluated first, in that the differences between the X, Y and Z coordinates of the proximal sulfur atoms are estimated. The axis with the greatest difference is then declared to be the axis of interest, so that the Au triangles are finally attached perpendicularly with respect to this axis. Some preliminary work, using a clever molecular viewer software, is still necessary to orientate the DNA duplex in the correct way;

(d) both Au triangles are firmly attached to ideal electrodes, so that the latter ones can have maximum of 27 modes, that is, three times the number valence electrons of Au atom;

(e) we assume that the potential V due to a voltage bias applied to both electrodes has a very simple stepwise distribution, that is, the potential is zero in the left lead up to the left Au triangle, whereas it is shifted by an electric potential energy of eV in all the nucleotide pairs, as well as in the right Au triangle together with the right lead. Although it is well-known that a distribution of the potential V within any capacitor should obey a smooth linear function [17], our approximation still ought to work reasonably well for long thin molecules and sufficiently low (near zero) voltage biases [10,18,19];

(f) the above assumption on the electric potential distribution ensures that the knowledge of the charge flux in the contact between the left Au triangle and its neighboring nucleotide base-pair would be enough to estimate the total current through the whole system. This is why, we need only Green functions of the left Au triangle and its neighboring nucleotide base-pair for our estimations;

(g) the above conclusion dictates the choice of the Green function calculation. We start from the right end by obtaining the self-energy of the ideal right-side lead (for a more detailed discussion on the self-energy of the ideal leads see [17]). This self-energy is used as an input to the Dyson equation, which is then iterated from the right-side Au triangle up to the leftmost nucleotide pair, together with the analytical calculation of the self-energy of the ideal left-side lead. The latter self-energy corrects the Hamiltonian of the left-side Au triangle, whereas the Hamiltonian of the leftmost nucleotide is corrected by the self-energy of the resting nucleotide pairs together with the whole right-side electrode. Finally, the total Green function of the system is calculated using both of these corrected Hamiltonians forming a block matrix; and

(h) apart from the above Green function, to use the Kubo formula, we need also the matrix representation of the charge velocity operator. In our non-orthogonal basis representation, this operator is also a special block matrix including matrix elements for interaction between the left-side Au triangle and the leftmost nucleotide pair. The resulting conductance corresponds to zero temperature, since no phonon scattering is taken into account here (for more detailed discussions on this topic, see [10] and the relevant references therein).

The conductance calculated with the above algorithm is naturally represented as the number of "channels" open within DNA duplexes for the charge transport (for more elaboration on these "channels" see for example, [20]), or in other words, the number of the transmitted "conductivity quanta" (e^2/h, where e is the charge of electron and h is Planck constant). Thus, to estimate DNA transmittance, one would simply need to divide this number of "channels"/"quanta" by the maximum number of modes in the electrodes.

4. Influence of DNA molecular dynamics on its conduction

In order to estimate the ballistic conductance spectra of MD snapshots, we rely upon the Born Oppenheimer approximation, bearing in mind that characteristic times of DNA charge transfer/transport (usually, in femtosecond range) are much shorter than those of DNA intramolecular dynamics (generally, in pico- to millisecond range). From such a physical viewpoint, we may view the latter just as "scatterers" generally capable of changing energy, amplitude and phase of a charged quantum particle during its propagation through DNA duplexes. In accordance with this idea, we have estimated ballistic conductance spectra (in the energy range between 3.0 and 3.0 eV around the Fermi level) for each of the 33 MD snapshots in every DNA duplex under study (that is, 99 MD snaphots in total), to investigate the influence of all the manifold of diverse scattering processes with pico- to nanosecond characteristic times on the conductance spectra of the mismatched and unmismatched DNA duplexes involved.

Thus, we assume first that the DNA ballistic conductance values at every energy for each of the MD snapshots under study are just random observations, since a huge number of DNA degrees of freedom can in principle contribute to the conductance spectra. Any *a priori* rigorous evaluation of probability distribution functions for these random observations is hardly possible due to the complexity of the system, so that we may only estimate a frequency of occurrence for each of the possible conductance values at every energy of interest, by constructing the pertinent histograms on the basis of the data from the MD snapshots involved. The latter frequency is a very rough estimate for the probability

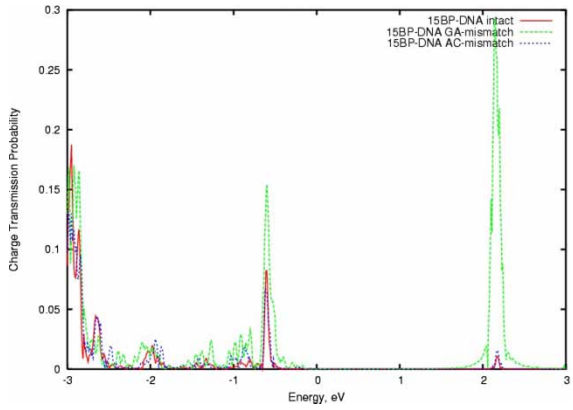

Figure 1. Comparison of 15BP, 15BP AC and 15BP GA transmittance spectra in [−3.0, 3.0 eV] Fermi energy range.

of the conductance value to occur, in presence of the explicit molecular-dynamical deformations of DNA structures. With such probabilities in hand, it is now straightforward to estimate the expectation values for the conductances in the whole energy range of interest, or in other words, their probability-weighted mean values. Plotting the latter expectation values versus energy, we estimate the dynamically averaged conductivity spectrum for each of the three DNA duplexes in question. The latter plots have also been smoothed using the conventional Sawitzki Golay procedure.

5. Results

Figure 1 gives the (3.0 + 3.0 eV)-transmittance spectrum of 15BP-AC and 15BP-GA, in comparison with that of 15-BP.

In the conduction band region, there is a single feature near +2.0 eV, which exhibits an order of magnitude higher transmission probability for excess electrons when propagating through 15BP-GA as compared to 15BP-AC and 15-BP.

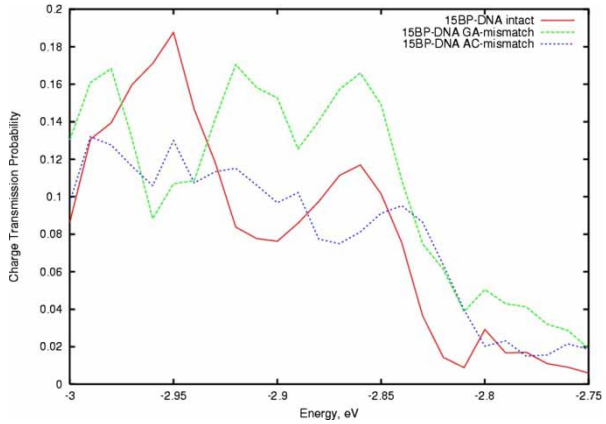

Figure 2. Comparison of 15BP, 15BP AC and 15BP GA transmittance spectra in [−3.0, −2.75 eV] Fermi energy range.

The transmittance spectra in the valence band region are much richer, in that two noticeable transmission peaks show up here, near 0.6 and 3.0 eV. In the 0.6 eV energy region, there is again a considerable dominance of the 15BP-GA peak over those of 15BP-AC and 15-BP, but the situation in the 3.0 eV energy region is more complicated. Figure 2 shows the 15-BP, 15BP-AC and 15BP-GA transmittance spectra in the latter region in more detail. It is clearly seen that whereas the above-mentioned dominance of the the 15BP-GA transmission is preserved up to approximately 2.95 eV, in the relatively narrow (3.00 2.95 eV) energy region, the 15-BP transmission probability is 1.5 times as high as that of 15BP-AC and only 1.1 as high as that of 15BP-GA.

6. Discussion

It is of considerable interest to compare our theoretical findings with the experimentally observed electrochemical trends [11]. In the latter work, a systematic investigation of electrochemical response by a number of redox-active cationic compounds in the presence of the mismatched and unmismatched DNA pentadecamer duplexes covalently attached to a gold-disk electrode has been carried out. The attachment of these redox-active cations to DNA is non-covalent (DNA intercalation or groove binding). In simplified terms, the main idea of that experimental study was to electrochemically reduce (or in other words, to add an electron to) some organic or metal-organic cations by withdrawing one electron from DNA duplexes to produce a positively charged hole in the latter, after applying some voltage to the system. The resulting hole is then more or less effectively propagating along the DNA and this propagation process has been found [11] to be appreciably influenced by various base-pair mismatches.

Remarkably, the charge transmittance trends theoretically derived here among the mismatched and unmismatched DNA duplexes (see figures 1 and 2) can be (at least, qualitatively) comparable with the experimental ones in only one energy region, namely between 3.00 and 2.75 eV. In all other energy ranges under study, there is a clear dominance of the 15BP-GA transmission peaks over the 15BP-AC and 15-BP ones, which is actually not observed in experiments [11]. To explain such a finding, we ought to consider the balance among the work function of the gold electrode (where DNA is covalently attached), ionisation potential of the DNA duplexes themselves, as well as the electron affinity of the redox-active cation non-covalently attached to DNA.

Indeed, the work function of the gold bulk/surface should lie in the 4.0 5.0 eV range [21,22], which is very close to the typical ionisation potential range of DNA duplexes [23,24]. Thus, applying the voltage in the voltammetric set-up of the work [11] ought to regulate the balance between the DNA ionisation potential and the electron affinity of the redox-active cation non-covalently attached to DNA. As the work [11] shows, voltages in the

(0.6 1 V) range are enough to reconcile the energy gap between the DNA and the redox-active cations.

Now, the question arises here as to why no true DNA conductivity has been observed in the work [11]. Would the both electrodes in the experimental set-up [11] be made of gold and the DNA duplexes be covalently attached to the both of them, the conditions for the resonance among the both electrodes and DNA could be satisfied, so that even an ohmic response might be observed when applying voltage, like in the work [3]. Meanwhile, in the experiments in question [11], the auxiliary electrode was made of platinum. From the literature, it is known that whereas the ionisation potential/work function of Pt should be very high [25], the electron affinity of Pt clusters noticeably decreases with the cluster size, unlike in Au clusters (see for example, [26,27] and references therein). This is why, any resonant tunneling of charged particles throughout the "gold DNA redox-active-cation-platinum" system studied in the work [11] cannot be anticipated and therefore, in the voltammetric assay of the work [11] charges ought to "commute" solely between the redox-active cation and the gold electrode via the high-energy (3 eV) transmission channel within the DNA duplexes.

Which mechanisms can be at work when choosing a particular charge transmission channel for the DNA charge transfer ? There is one important aspect of the work [11] which should be mentioned to this end. Specifically, the difference in charge transfer propensities between the 15BP-AC and 15-BP duplexes turns out to be noticeably dependent on the DNA binding mode, as can be seen in the table 2 of the work [11]: Intercalative drug cations are more or less capable of underscoring the difference between 15BP-AC and 15-BP, whereas the groove-binding agent $Ru(NH_3)_5Cl^{2+}$ is not. Thus, the less is the overlap among the π-electron-systems of the DNA base-pairs and redox-active cation, the less significant the difference between 15BP-AC and 15-BP. This enables us to assign the high-energy (3.00 eV) hole transmission channel to the overlapping π-orbitals within the hydrophobic core of the stacked DNA base-pairs, whereas the low-energy (0.6 eV) hole transmission channel may perhaps be assigned to some other groups with overlapping orbitals, possibly in the DNA grooves. It is extremely tempting to draw the latter tentative conclusion, since the low-energy channel exhibits no noticeable difference between 15BP-AC and 15-BP (see figure 1), and this is exactly what is observed [11] for the electrochemical response of the groove-binding agent $Ru(NH_3)_5Cl^{2+}$.

The last, but not the least, it should be noted that, due to a very restricted size of the random sample, the results presented and discussed in the present communication bear preliminary and purely qualitative character. A more detailed study based upon significantly larger random sample size is underway in our laboratories. Finally, a significant feature of the experimental set-ups employed in the works [3,11] should also be pointed out: The both measurement cycles were performed in water solutions, whereas our present calculations deal with "*in vacuo*" situations (all the solvent was removed). Meanwhile, there is a report in the most recent literature [28] which underlines a possible significance of explicit counterions and water of hydration for DNA electric properties. In principle, our approach allows inclusion of an arbitrary number of explicit solvent molecules into the system under study, such computations for the mismatched and unmismatched DNA duplexes studied in [11] and here are also currently underway in our laboratories and the pertinent results will be reported elsewhere.

7. Conclusion

Here, we have presented a theoretical method to estimate intramolecular dynamics effects on macromolecular conductivity. An application of this approach to elucidating electrical properties of mismatched and perfectly paired DNA duplexes has revealed one transmission channel in the conduction band region, as well as two transmission channels in the low (0.6 eV) and high (3.0 eV) energy range of the valence band region. A detailed comparison with the relevant experimental data enables us to tentatively assign the latter two transmission channels to some overlapping molecular orbitals in the DNA helical grooves and in the hydrophobic core of the stacked DNA base pairs, respectively.

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