# Model calculation of the specific hole conductivities of three homopolynucleotides, poly(guanilic acid), poly(adenilic acid) and polythymidine in the presence of water and Na$^+$ ions

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## ABSTRACT

The work presented here is the last step of our research plan to compute the band structure, the mobilities and finally the conductivities of simple, single-stranded DNA models, infinite homopolynucleotides. We have calculated the d.c. specific conductivities of three crystalline, rigid homopolynucleotides: poly(guanilic acid), poly(adenilic acid) and polythymidine in the presence of water and ions using a combined quantum chemical and solid state physical method (Hartree–Fock crystal orbital theory). The obtained specific conductivities are around $10^2$ $\Omega^{-1}$ cm$^{-1}$. The results are compared to the available experimental values. The reliability of our method and the influence of static and dynamic disorder are also discussed. These results can pave the way to future computations, where the structural and dynamical disorder will gradually be introduced (of course in this case an appropriate form of hopping model has to be used).

## 1. Introduction

Over the last decades extensive research has been carried out on the conduction in DNA using experimental and computational methods of biomolecular science. The growing interest originates from the possible role that DNA plays–besides being the carrier of genetic information–as a building block in molecular electronic devices as well as from the function of DNA's conductivity in oxidative stress related processes and repair mechanisms [1].

The dry DNA molecule most probably acts as a large band gap semiconductor which can conduct only after charge carriers are generated in it using either physical or chemical methods. Our goal was to investigate charge transport in DNA in a special environment, in the nucleosome, where the charge carriers appearing in DNA originate from the charge transfer between DNA and nucleohistone proteins. DNA in a nucleosome is wrapped around eight histone proteins and its PO$_4^-$ groups form salt-bridges

with the positively charged amino acid residues (e.g. Lysine$^+$ (Lys$^+$) or Arginine$^+$ (Arg$^+$)) of the nucleohistones. External disturbances can break the DNA-nucleohistone contact [2] and weaken the charge transfer between them. These influences the conductivity of DNA which is most probably in connection with the initiation of cancer.

Recent experiments and theoretical investigations has shown that the short-range electron transfer in DNA (up to 2–3 bases) can be characterized as coherent tunneling [3,4], while the long-range conduction can be described as a hopping process [5–9]. The conduction is strongly influenced by the structural flexibility [10–15] and environmental conditions [16,17].

The first studies on the electronic structure of DNA supposed the strict helical symmetry of the system and used a band-like description (crystal orbital (CO) theory). They could successfully interpret several important features of DNA (see [18] and references therein). In this solid state physical model both the flexibility of DNA (the deviation from the perfect helical symmetry) and also the fluctuating interactions with the environment are neglected. However, cumulated experimental results raised the question of the applicability of this approach. Artacho et al. [19] calculated the bandwidths using periodic boundary conditions

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and compared them with the energy fluctuations of vibrational or aperiodic base-sequence origin. They found that the energy fluctuations are larger than the bandwidths, which makes the coherent transport of electrons in DNA impossible. The same conclusion was drawn by Ortmann et al. [20] for guanine crystals at room-temperature. This implies that our method cannot be applied directly to long-range electron transfer at room temperature in DNA. However, at low temperatures in vacuum, for a DNA fixed on a surface, the band-like description of a perfectly symmetric chain can be the appropriate approximation. At larger temperatures this high degree of symmetry can only be considered as a limiting case where the effects of static and dynamic disorder are completely neglected. This approach may also help to identify the consequences of these disturbances on a polymer. The main advantage of our approach is that (due to the symmetry constraint involved) it can account for the properties of extended, fixed homopolynucleotides and it is not restricted to a short sequence.

The work presented here is the last step of our research plan to compute the band structure, the mobilities and the conductivities of simple, single-stranded DNA models, like infinite homopolynucleotides.

In a previous paper [21] we calculated the hole mobilities of homopolynucleotides (poly(guanilic acid), poly(adenilic acid) and polythimidine) in the presence of water and ions (for their chemical formulae see [21]) at 180 K and 300 K using the deformation potential approximation [22–24]. For these computations we used the Hartree–Fock (HF) crystal orbital (CO) method [25] in its general form which can treat combined symmetry (like a helix operation) at going from one unit cell to the subsequent one [26]. Since the valence band of polycytidine was very narrow (0.05 eV [27]) we only considered the three other homopolynucleotides having valence band widths between 0.20 and 0.30 eV [27,28]. Our goal was to contribute to a better understanding of the interaction of DNA molecules with proteins in nucleosomes and to consider the possible role of charge transfer in cancer initiation.

As the next step we are going to do the same calculation for chemically periodic double stranded DNA. We believe that the experiences obtained from these calculations may help to develop an appropriate hopping theory of charge transport in disordered (native) DNA.

## 2. Methods

In this paper we have calculated the conductivity of the homopolynucleotides for a single fiber of unit cell length, of one cm length and the specific conductivity (1 cm$^3$ material) using the following simple formulas:

$$\sigma_h^{fiber} = e \cdot n_h \cdot \mu_h \tag{1}$$

$$\sigma_h^{unit\ cell} = \frac{\sigma_h^{fiber}}{l} = \frac{e \cdot n_h \cdot \mu_h}{l} \tag{2}$$

$$\sigma_h = \frac{\sigma_h^{fiber}}{q} = \frac{e \cdot n_h \cdot \mu_h}{q}. \tag{3}$$

In our case the unit cell length is $3.32 \cdot 10^{-8}$ cm, and the cross section of a single DNA helix is $\pi r^2 = \pi \cdot 10^{-14}$ cm$^2$. Furthermore, $n_h$ is the concentration of the holes obtained from the transferred charge from the $PO_4^-$ groups of the homopolynucleotides to the positive Lys$^+$ or Arg$^+$ side chains of a polypeptide.

Since in the nucleosomes there is a large number of these side chains in the polypeptides and there are other positive sites in them (on the basis of X-ray diffraction experiments on the nucleosomes the number of positive sites which can form hydrogen (H) bonds with the $PO_4^-$ groups of DNA is 120 in

one nucleosome which contains a 147 base pairs long DNA B superhelix [29–31]).

To find out the amount of charge transferred from DNA to the protein chain we carried out detailed investigations. We have found that the charge transfer (C.T.) from DNA (per unit cell) to lysine or arginine is 0.40/base and 0.30/base, respectively, if we take into account the already mentioned factor of $\frac{120}{147}$ and the fact that the calculations refer to a single DNA helix [32,33].

Since in most cases the position of the Fermi level is known, the concentration of the charge carriers (in our case positive holes) is calculated from the formula

$$n_h = \frac{L}{2\pi} e^{-(\epsilon_{v,u}-\epsilon_F)/k_B T} \frac{\sqrt{\pi m_h^* k_B T}}{\hbar \sqrt{2}}. \tag{4}$$

Here, $\epsilon_F$ is the Fermi level, $\epsilon_{v,u}$ is the upper edge of the valence band, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $m_h^*$ is the effective electronic mass at the upper limit of the valence band. To determine the specific conductivity we have to use $L = 1$. In our case, since we know the number of free charge carriers per unit cell, instead of the more complicated equation (4) (for which the Fermi level has to be determined from the free charge carriers per unit cell using the dispersion curve of the band) we can simply divide $q_h^{eff} = 0.035e$, the number of free charge carriers (holes) in the unit cell, by the length of the repeat unit ($l = 3.32$ Å). At room temperature the Fermi level is, in our case, very close to the band edge and therefore, the exponential factor is very close to one (as our detailed calculations have shown). Thus, we can write

$$n_h = \frac{q_h^{eff}}{l} = \frac{0.035}{3.32 \cdot 10^{-8}\ \text{cm}} = 1.05 \cdot 10^6\ \text{cm}^{-1}. \tag{5}$$

Substituting this value and the corresponding effective mobility value in $\frac{cm^2}{V \cdot s}$ units (see [21]) together with the value of the elementary charge (in C) into Eqs. (1)–(3) we obtain the d.c. conductivity of a single fiber of one cm length ($\sigma_h^{fiber}$). Dividing $\sigma_h^{fiber}$ by $l$ we obtain $\sigma_h^{unit\ cell}$ (see Eq. (2). Dividing $\sigma_h^{fiber}$ (Eq. (1)) by the cross section $q$ of the DNA helix (a DNA B helix has a diameter ~20 Å) we obtain the specific conductivities in $\Omega^{-1}$ cm$^{-1}$ units.

However, if we wished to calculate $\sigma_h$ of a homopolynucleotide at a different temperature our simplified procedure would not work and we would have to return to Eq. (3).

## 3. Results

Taking the effective mobilities at 300 K (see Table III of [21]) (it should be mentioned that from biological point of view their conductivity at 180 K is uninteresting) of the homopolynucleotides we have multiplied them by $n_h = \frac{0.035}{3.32 \cdot 10^{-8}} = 1.05 \cdot 10^6$ cm$^{-1}$. This way in the case of poly(guanilic acid) [for the sake of brevity we denote here and afterward a nucleotide by the chemical symbol of the corresponding nucleotide base with a tilde on its top: e.g. poly ($\tilde{G}$)]. With $\mu_{eff}^{300} = 153.05 \frac{cm^2}{V \cdot s}$ we obtain for the conductivity of a single fiber of unit cell length

$$\sigma_{poly(\tilde{G})}^{fiber} = 1.602 \cdot 10^{-19} \cdot 1.05 \cdot 10^6 \cdot 1.53 \cdot 10^2$$

$$= 2.59 \cdot 10^{-11}\ \Omega^{-1}\ \text{cm}. \tag{6}$$

Dividing this by the length of the unit cell, $l = 3.32 \cdot 10^{-8}$ cm the conductivity of a single fiber of one cm length is obtained:

$$\sigma_{poly(\tilde{G})}^{unit\ cell} = \frac{\sigma_{poly(\tilde{G})}^{fiber}}{l} = \frac{2.59 \cdot 10^{-11}}{3.32 \cdot 10^{-8}} = 7.80 \cdot 10^{-4}\ \Omega^{-1}. \tag{7}$$

**Table 1**

The d.c. conductivity of a single fiber of one cm length ($\sigma^{fiber}$), of a unit cell length ($\sigma^{unit\,cell}$) and the specific conductivity ($\sigma$) of poly(guanilic acid), poly(adenilic acid) and polythymidine at 300 K.

|  | Poly(guanilic acid) | Poly(adenilic acid) | Polythymidine |
|---|---|---|---|
| $\sigma^{fiber}$ ($\Omega^{-1}$ cm) | $2.59 \cdot 10^{-11}$ | $3.06 \cdot 10^{-12}$ | $3.53 \cdot 10^{-12}$ |
| $\sigma^{unit\,cell}$ ($\Omega^{-1}$) | $7.80 \cdot 10^{-4}$ | $9.22 \cdot 10^{-5}$ | $1.06 \cdot 10^{-4}$ |
| $\sigma$ ($\Omega^{-1}$ cm$^{-1}$) | $8.21 \cdot 10^{2}$ | $0.97 \cdot 10^{2}$ | $1.12 \cdot 10^{2}$ |

Finally, dividing $\sigma^{fiber}_{\tilde{G}}$ by the cross section of the DNA helix, one has the specific conductivity of poly(guanilic acid) at 300 K

$$\sigma_{poly(\tilde{G})} = \frac{\sigma^{fiber}_{poly(\tilde{G})}}{q} = \frac{2.59 \cdot 10^{-11}}{3.14 \cdot 10^{-14}} = 8.21 \cdot 10^{2} \, \Omega^{-1} \, cm^{-1}. \quad (8)$$

Repeating the same calculation for poly(adenilic acid) and polythymidine on the basis of Eqs. (1) and (2) and using the mobility data given in Table III of Reference [21], we obtain the conductivities given in Table 1.

## 4. Discussion

It can be seen from Table 1 that the specific conductivities for all the three investigated systems are rather large, $\sim 10^2 \, \Omega^{-1} \, cm^{-1}$ (especially for poly(guanilic acid)) comparing it to the intrinsic semiconductors (e.g. $\sigma_{Si} \approx 10^{-5} \, \Omega^{-1} \, cm^{-1}$) but several orders of magnitude smaller than in case of metals (e.g. $\sigma_{Ag} \approx 6 \cdot 10^5 \, \Omega^{-1} \, cm^{-1}$). They are comparable to the conductivity of a doped semiconductor.

In order to be able to compare our results to the experimental ones in the followings we cite the papers of Porath's group [34–37] which carried out electric current measurements both on chemically periodic (poly($\tilde{G}$)–poly($\tilde{C}$) [34,37]) or non-periodic double stranded [35,36] as well as single stranded [36] DNA. They found a semiconductor-like behavior of the investigated double helices independently of the experimental method used. However, single stranded DNA measured in monolayers using conductive atomic force microscopy showed no conduction (most probably because of its high flexibility). In their first papers (e.g. [34]) Porath et al. mentioned the coherent band type conduction as a possible mechanism which was questioned later [38].

The direct comparison of our results to the experimental ones for the single stranded DNA (which does not conduct) would not be relevant, because the flexibility, which destroys the conduction in this case, is not taken into account in our method. On the other hand the geometry of our model is identical to the poly($\tilde{G}$) part of a double stranded DNA with strict helical symmetry. In addition, the conduction in poly($\tilde{G}$)–poly($\tilde{C}$) is dominated by the guanines. Therefore this way the comparison of our results to the poly($\tilde{G}$)–poly($\tilde{C}$) is more plausible than to a single stranded DNA with a complex sequence.

Using the almost linear part of the current–voltage curve published by Porath et al. in Nature [34] we have calculated the conductivity of the double stranded poly($\tilde{G}$)–poly($\tilde{C}$) in the absence of water. The measured conductance of the unit cell of a single fiber is $7.89 \cdot 10^{-8} \, \Omega^{-1}$, while our result for single stranded poly($\tilde{G}$) is $7.80 \cdot 10^{-4} \, \Omega^{-1}$. Our calculated value is much larger than the experimental one because our model describes a coherent, band-like- and not hopping conduction, and the conductivity is characteristically larger in the former case.

We would like to point out that the band-like conduction obtained from our model originates directly from the strict geometrical constraint (perfect helical symmetry) involved in the theory. The relaxation of this constraint would result in flat bands (as it was pointed out computationally by Artacho et al. [19])

excluding the possibility of the band-like conduction. According to experimental evidence the structural and environmental disorder indeed destroys the symmetry and in this way the long-range coherence in DNA. Therefore, most authors do not describe the charge transport in native DNA with the band model presented above but with the help of some form of hopping theory (for representative examples of this approach see Refs. [5,4,6–9]). The results of these hopping calculations are, however, different depending on the form of the model applied.

It is worth mentioning that the applied experimental technique (two-point measurement) may also cause some errors which could be reduced using a more realistic, but in the case of DNA only with great difficulty implementable four-point measurement. The latter is often used in solid state physics.

## 5. Conclusion

We have calculated (using the previously computed mobilities of the homopolynucleotides) the d.c. specific conductivities of three homopolynucleotides: poly(guanilic acid), poly(adenilic acid) and polythymidine in the presence of water and ions. We used a coherent, band-like conduction model (based on Hartree–Fock crystal orbital theory) which provided conductivities several orders of magnitude larger than the experimental ones. The main reason for the difference is that according to experimental evidence the long-range charge transport in DNA is most probably a hopping process and not a band-like conduction. We would like to mention here that several models exist for the description of this process but none of them seems to be conclusive.

We would also like to emphasize that in spite of the afore-mentioned problems the band-like description predicted some basic features of the DNA conduction correctly. Namely, (a) guanine has the highest filled energy band among the investigated systems (b) the existence of hole-type conduction in poly($\tilde{G}$), (c) poly($\tilde{G}$) has the largest calculated conductivity, (d) at all calculated cases the non-base-type bands, (which are very narrow) are close to the conduction bands. Therefore, conduction in DNA cannot take place by n-doping.

These findings indicate that the problem of charge transport in DNA is very complex, and can be influenced by several factors. Certainly, it will take some time until a final understanding emerges. The importance of understanding how DNA regulates an eucaryotic cell on the fundamental level makes even a large effort worthwhile.

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