



The effect of water environment on the hopping conductivity of an aperiodic nucleotide base stack

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Abstract

We have used the matrix block negative factor counting method to calculate the density of states of an aperiodic single stack of DNA (a part of a human oncogene), consisting of 100 nucleotide bases in the DNA B conformation. The nearest water molecules were taken into account in the calculation. The work refers to the valence bands region of the stacks.

Consequently the inverse iteration method was used to determine the Anderson localization of the physically interesting wave functions. The hopping frequencies between the units were determined from these. They have been used as input in a random walk theory.

According to the results obtained, the real part and the absolute value of the complex hopping conductivity gets saturated at the frequency of 10^{12} s^{-1} . Its value lies at $\sim 10^{-4} \Omega^{-1} \text{ cm}^{-1}$, which is by two orders of magnitude larger than the one obtained previously in the absence of water ($\sim 10^{-6} \Omega^{-1} \text{ cm}^{-1}$). Different reasons for this rather large effect of water are discussed (e.g. basis set improvement by bases set superposition, the effect of the water dipoles). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In several recent papers, the electronic density of states [1] and the hopping conductivity of aperiodic single and double stranded nucleotide base stacks have been calculated at room temperature [2,3]. The results have given a complex

hopping conductivity $\sigma(\omega)$ at $(\omega = 10^{10} \text{ s}^{-1}) 1 \Omega^{-1} \text{ cm}^{-1}$ in the double stranded and $\sim 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ in the single stranded molecule. The calculations have not taken into account the water environment of DNA explicitly, but since the DNA B form (which is stable only over a rather large relative humidity), was used for the computations, the water molecules surrounding DNA were considered implicitly.

Most recently, Grüner et al. [4] have measured the conductivity of native λ phage DNA extracted from *E. coli* by determining the loss in a hole resonator at 12 and 100 GHz. They have found that at 12 GHz in a buffer, the value of the real part is $\sigma = 2.4 \Omega^{-1} \text{ cm}^{-1}$ in excellent agreement with our theoretical result. They have also measured the conductivity of the so-called dry DNA at room temperature. These DNA samples were purified according to standard procedures. Of the total weight of the samples, 85% was DNA and 15% of it was water and

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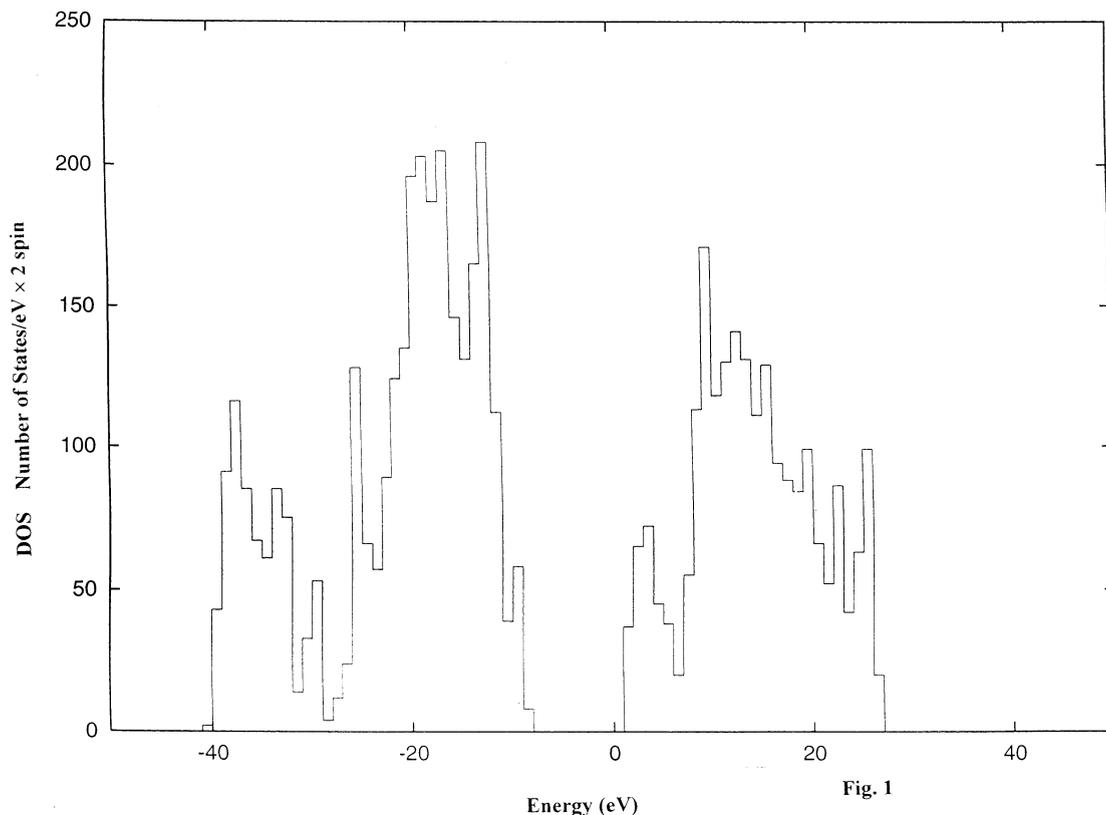


Fig. 1. The electronic density of states of the conduction and valence band regions of a single strand segment of a part of a human oncogene in the presence of water.

residual counterions [4]. Thus, the remaining water molecules were enough to keep the DNA sample in its B form. At 12 GHz it is smaller by about a half order of magnitude (in $\Omega^{-1} \text{ cm}^{-1}$ units), than that in buffer.

In this paper we would like to present theoretical results of the effect of the water on the hopping conductivity of a single aperiodic stack of 100 bases with the sequence of a part of human oncogene [5] (sequence 1 in Ref. [3]).

As was discussed in Ref. [3] the electronic structure of a free aperiodic base stack is in very good approximation, the same as that of the same stack in DNA.

The calculations, as in Ref. [3] were done in four steps:

1. The electronic density of states in the valence bands and conduction bands regions were computed with the help of the matrix block negative factor counting (NFC) method [6–9].
2. The Anderson localization of the individual levels (which can be determined using the step length in the DOS histogram) has been calculated with the help of the standard inverse iteration method [10].
3. The hopping frequencies between the energy levels belonging to the localized orbitals were calculated with the help of the simple expressions given by Mott and

Davis [11]. This contains as factors, the frequency of the acoustic phonon (10^{12} s^{-1}) corresponding to the vibration of the molecules in the stack with respect to each other, the overlap integral between the two localized orbitals belonging to neighboring molecules and finally a Boltzmann factor (see Eq. (2) in Ref. [3]). Ref. [3] also contains an expression (Eq. (3)) that takes into account explicitly the electron–phonon interaction integrals. However, it was not applied in this calculation.

4. The calculated hopping frequencies were used as input for the generalized random-walk theory of Odagaki and Lax [12–14].

The method of considering the effect of water molecules is described in Section 2.

2. Computational details

The addition of water to the pure aperiodic base stack was done as follows with the help of the ‘Insight II’ program of Biosym [15]:

1. A box was filled with liquid water (randomly oriented water molecules).

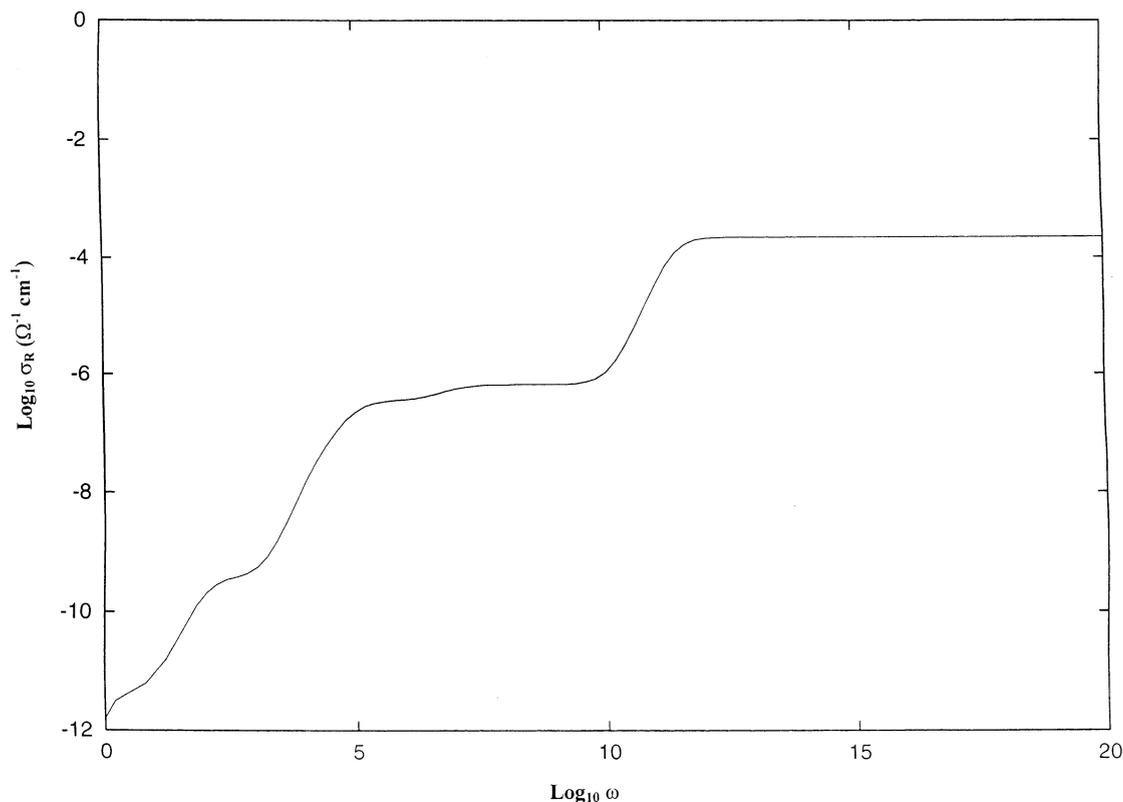


Fig. 2. The real part of the hopping conductivity of a single DNA stack with the 100 units part of a human oncogene sequence in the presence of water.

2. A full double helix DNA (together with sugar and phosphate parts) was introduced into the box, and the water molecules that overlapped with the DNA molecule were deleted.
3. The water molecules, which would overlap of the second strand and the sugar–phosphate part of the first strand, were also deleted.
4. To each base of the stack of n atoms water molecule(s) which had the smallest water oxygen (O_w) distance to any atom of the base were assigned.

$$d(w, b) = \min(d1, d2, \dots, di, \dots, dn) \tag{1}$$

$$di = \text{dist}(O_w, Ai) \tag{2}$$

where Ai is the i th atom of the base.

Since the distribution and the orientation of the water molecules are random, it is possible that different than 1 (0, 2 or 3) water molecule is nearer to any atom of a base than to the atoms of the others. In our case of a stack with 100 bases, no water molecule was found nearest to a particular base 13 times, 50 times 1 water molecule was nearest to a given base. This occurred 29 times with 2 water mole-

cules and 8 times with three. Totally 131 water molecules were taken into account.

For the NFC procedure we have used the overlapping dimer approximation for the Fock and overlap matrix of the whole stack (it has been shown that this causes very little error [16]. This means that in a stack ABCDCBA... one takes the dimers as AB, BC, CC, CD, DB, BA etc. and calculates the SCF Fock matrix blocks for instance for AB as

$$\begin{pmatrix} \underline{F}_A & \underline{F}^{AB} \\ \underline{F}_{AB}^{tr} & \underline{F}_B \end{pmatrix} C_i = \epsilon_i \begin{pmatrix} \underline{S}_A & \underline{S}_{AB} \\ \underline{S}_{AB}^{tr} & \underline{S}_B \end{pmatrix} C_i \tag{3}$$

where tr refers to the transpose of the matrices. (Since the unit B occurs both in the first and second dimer we have taken the algebraic mean value for it in both dimers). From the ab initio Fock- and overlap matrix blocks obtained in this way we have constructed the Fock- and overlap matrices of the whole stack on which we have performed the NFC [8] procedure.

In the case of water molecules near the stacks, we have constructed the dimers by allowing the water molecules to interact with the bases. These interactions were taken into account with the help of the supermolecule approach, that is

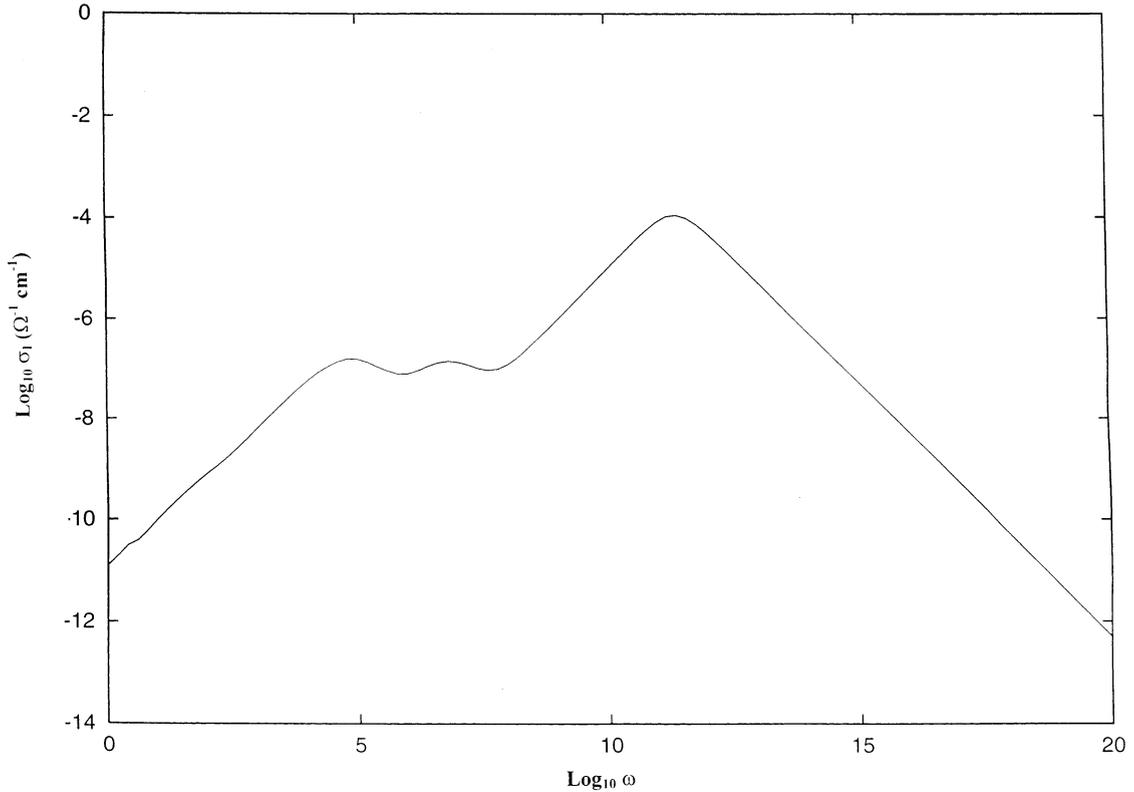


Fig. 3. The imaginary part of same quantity under the same conditions.

the bases and the near-lying water molecules have common MOs. Of course in this way the matrix blocks in Eqs. (3) and (4), respectively, become larger. This means that in the case of the starting sequence of the oncogene C₂T₂C₂G₁A₁G₁..., for instance, the Fock matrices of the dimers appear as:

$$\begin{pmatrix} \underline{E}_{C(w2)} & \underline{E}_{C(w2)-T(w2)} \\ \underline{E}_{C(w2)-T(w2)}^{tr} & \underline{E}_{T(w2)} \end{pmatrix}, \begin{pmatrix} \underline{E}_{T(w2)} & \underline{E}_{T(w2)-C(w2)} \\ \underline{E}_{T(w2)-C(w2)}^{tr} & \underline{E}_{C(w2)} \end{pmatrix},$$

$$\begin{pmatrix} \underline{E}_{C(w2)} & \underline{E}_{C(w2)-G(w1)} \\ \underline{E}_{C(w2)-G(w1)}^{tr} & \underline{E}_{G(w1)} \end{pmatrix}, \begin{pmatrix} \underline{E}_{G(w1)} & \underline{E}_{G(w1)-A(w1)} \\ \underline{E}_{G(w1)-A(w1)}^{tr} & \underline{E}_{A(w1)} \end{pmatrix} \quad (4)$$

In Eq. (4) for instance $F_{C(w2)T(w2)}$ indicates the matrix block for the interaction of C with 2 water (w) molecules with T with 2 water molecules.

Solving Eq. (3) with the matrix k Eq. (4), the Fock matrix of the whole stack with water molecules was constructed from these modified dimers. After that the NFC procedure was performed in the usual way and the whole calculation of the hopping conductivity was executed as in the consecutive steps described in Ref. [3] and in Section 1 of this paper.

It should be mentioned that the water structure is in reality different around DNA than in the bulk liquid. However, as

this does not strongly affect the density of states (DOS) of the system, it may not have a large influence on the hopping conductivity either.

The calculations were performed using the DNA B geometry [17] and Clementi's basis set [18].

3. Results and discussion

In Fig. 1 the density of states of the 100 bases long human oncogene segment is shown. Comparing this to Fig. 2b of [1] it is observed that the two DOS histograms are rather similar. The widths and positions of the conduction and valence bands regions, respectively, are practically the same and therefore the fundamental gap. The intensities of the DOS peaks are in some cases somewhat larger without water, than with the water molecules.

In Figs. 2–4 the $Re\sigma(\omega)$, $Im\sigma(\omega)$ and $|\sigma(\omega)|$ of a single stranded region of the human oncogene is shown in its valence bands region.

Looking at these figures it is remarkable that the $Re\sigma(\omega)$ (Fig. 2) and $|\sigma(\omega)|$ (Fig. 4) become saturated only at $\omega = 10^{12} s^{-1}$, while the corresponding $|\sigma(\omega)|$ curve without water (see Fig. 3 of Ref. [3]) is saturated already at $\omega = 10^6 s^{-1}$. At the same time if [3] one takes into account the correlation, the curve saturates only at $\omega = 10^{11} s^{-1}$. The

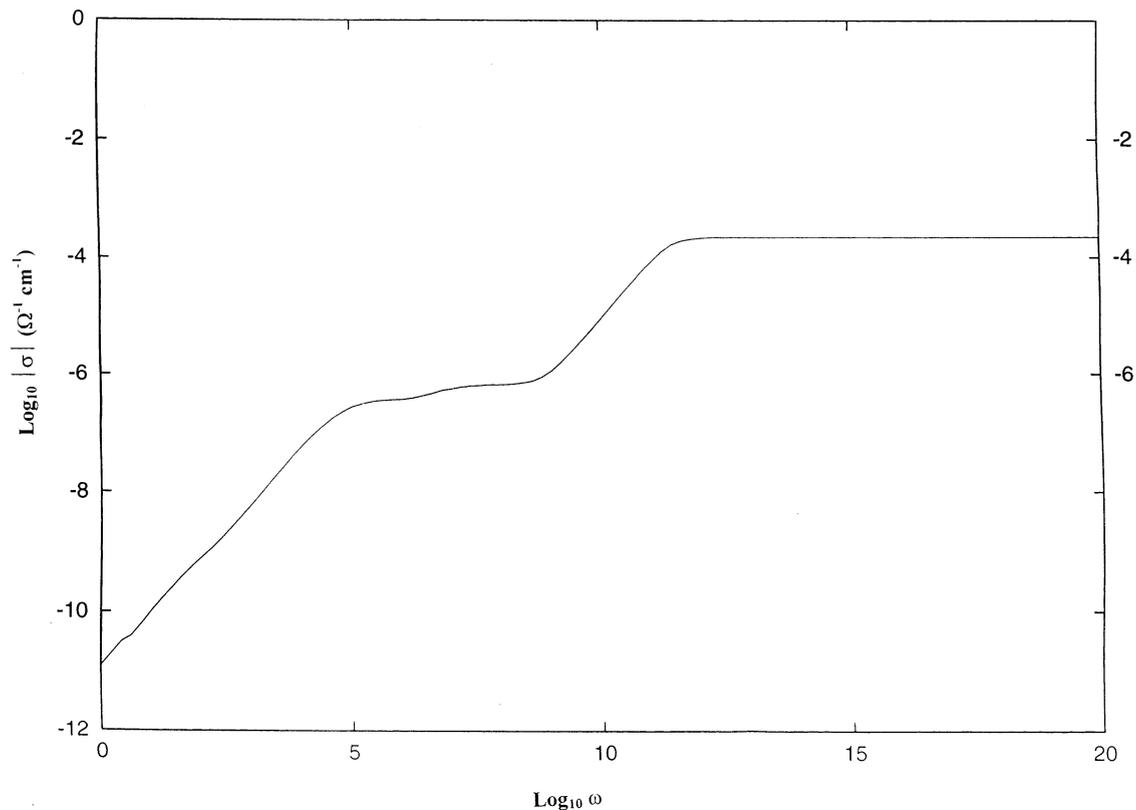


Fig. 4. $|\sigma(\omega)|$ under the same conditions.

same is true for the $|\sigma(\omega)|$ curve of a base stack (see Ref. [3], Fig. 1).

The saturation value of $Re\sigma(\omega)$ and $|\sigma(\omega)|$ lies at several times $10^{-6} \Omega^{-1} \text{cm}^{-1}$. The corresponding curve without water reaches its plateau (at least in the minimal basis case) at $10^{-6} \Omega^{-1} \text{cm}^{-1}$, though if one uses a double ζ basis and corrects the electronic structure of the dimers for correlation with an MP2 self energy in the inverse Dyson equation it becomes $\sim 5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ [3].

One should emphasize that all measurements (also that of the so-called ‘dry DNA’ with 15% water and ion content [4]) and the calculations were performed on DNA B (by keeping the stack artificially in this conformation). Therefore the large water effect which we have found has nothing to do with a conformation change of DNA. (This is also indicated by the small difference of the $|\sigma(\omega)|$ value in the cases of buffer and ‘dry’ DNA, respectively). Theoretically the reason for the increase of the hopping conductivity when water molecules and bases interact, could be basis set superposition effects. $|\sigma(\omega)|$ is by an order of magnitude larger if one uses a double ζ instead of a minimal basis; see Fig. 3 of Ref. [3]). This reduces the discrepancy in water effects between experiment (4) and theory. Furthermore, since the water structures were somewhat different in the experiment and in the calculations causing different electric

fields (due to their different water dipole moment distributions) at the bases of a single stack and a double stack, respectively, the remaining difference could be caused by this effect.

4. Concluding remarks

To perform a really good calculation on the band structure and conductivity of DNA one should first perform correlation corrected dimer calculations including the sugar-phosphate parts and construct a correlation corrected Fock matrix \tilde{F} for them. In this calculation also water molecules should be taken into account as described earlier. Their distribution, however, will not be uniform and the water structure around DNA calculated by Clementi [19] should be used. Only hopping conductivity differences in the absence and presence of water could give a final answer on the effect of water.

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