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Journal of Molecular Structure (Theochem) 666–667 (2003) 1–9

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Solid state physics of biological macromolecules: the legacy of Albert Szent-Györgyi

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Abstract

A. Szent-Györgyi contributing so much to the citric acid (oxygen metabolism) cycle in which subsequent electron transfers occur in eight proteins has come to the idea already in 1941 that proteins have to be conductors. This hypothesis was first not accepted because of the too large gap and non-periodic nature of a protein chain.

With the development of the theory of disordered systems and the occurrence of high-speed computers it was possible to show that both proteins and nucleotide base stacks are good hopping semiconductors, proving the correctness of Szent-Györgyi's original idea.

Ab initio Hartree–Fock correlation corrected band structures were computed both for homopolypeptides and periodic nucleotide base stacks. On the basis of these band structures applying the intermediate exciton theory the UV spectra of different biopolymers were calculated. The results for a cytosine stack, polyglycine and polyalanine are in good agreement with experiments.

Finally, the expected further development of the quantum theory of biopolymers are discussed.

Keywords: Hopping conductivity of disordered proteins; a.c. conductivity of aperiodic nucleotide base stacks; The frequency-, water content-, temperature-dependence of the conductivity of DNA

1. Introduction

In 1937, Albert Szent-Györgyi obtained the Nobel Prize in Medicine and Physiology besides for discovering vitamin C for his seminal contributions to the establishment of the oxygen metabolism cycle (citric acid cycle, Szent-Györgyi–Krebs cycle) [1]. In his works he has demonstrated that cellular respiration is strongly accelerated by catalytic amounts of succinate, fumerate, malate or oxoloacetate and that these compounds were interconverted according to the reaction sequence succinate → fumerate → malate → oxoloacetate [1]. One should mention that Szent-Györgyi was the only Hungarian who was resident of the country (here in Szeged) when he has obtained the Prize.

In the citric acid cycle, the different reactions are catalyzed by different (altogether eight) enzymes. This means that in running around the cycle electrons have to be transferred through the eight-enzymatic proteins. This observation has led Szent-Györgyi to the hypothesis that proteins are conductors, which make possible these electron transfers [2,3].

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doi:10.1016/j.theochem.2003.08.050

Szent-Györgyi's hypothesis was for many years not accepted by the scientific community. This has had two reasons.

1. The periodic part of the proteins, the peptide group (see polyglycin) has a gap value of about 7.5 eV, which is far too large for the existence of thermal semiconduction.
2. Real proteins are non-periodic due to their different side chains and different conformations of them.

In 1941 (and also for many years after) the theory of aperiodic (disordered) chains was not worked out and no high-speed electronic computers were not available to make a calculation of the frequency-dependent hopping conductivity of disordered polymeric chains as proteins. As it will be shown in this paper the situation in the meantime has been changed completely. One can calculate the frequency-dependent hopping conductivity of proteins (and also of DNA) if one knows the sequence of the amino acids or nucleotide bases, respectively, together with the conformation of the chain. In both cases, it has turned out that at frequencies above 10^{10}–$10^{11}\,s^{-1}$ the a.c. hopping conductivity is quite large. It should be mentioned that the time scale of the elementary steps in enzymatic reactions is $\approx 10^{13}$ s, that is, the results have a large biological relevance.

In Section 2, it will be qualitatively outlined how the electronic density of states (DOS), hopping frequencies and a.c. conductivity were calculated in the case of aperiodic protein chains or nucleotide stacks. In the case of DNA (where experimental results are available) the a.c. conductivity as the function of frequency, water content and temperature is in complete agreement with the measurements.

In a subsequent point, the treatment of periodic base stacks and polypeptides will be outlined in the HF + Moeller–Plesset2 [5] level and the resulting band structures will be discussed [6]. The UV (excitonic spectrum) of biopolymers will be discussed afterwards. Finally, an outlook will be given for the developments, which can be expected in the near future.

2. The hopping conductivity of proteins and aperiodic nucleotide base stacks

The calculation of hopping conductivities was performed in four steps. First, one calculates the total electronic DOS of the disordered chains. For this, the so-called negative factor counting (NFC) method [7] was applied in its most general form [8] (taking into account also S–S-bridges in cystin residues [9]). Here and subsequently no mathematical formulations are given (because it is quite complicated and therefore they would not fit in the general scope of this Symposium Proceedings). The interested reader can find out the technical details from the ample references. Of course, the results will be given in the different figures.

Having calculated DOS, as next step one can apply the standard inverse iteration method [10] to determine the localized wave functions (Anderson localization) belonging to the physically interesting levels (the levels belonging to the upper part of the filled valence band and those belonging to the lower part of the unfilled conduction band). In this way one can treat both hole and electron hopping conduction.

As third step, the so-called hopping frequencies (primary jump rates) were computed using the simplified expression for the electron–acoustic phonon interaction given in the book of Mott and Davis [11]. In the case of proteins, the vibrations of the side chains with respect to each other are the acoustic phonons. In DNA, the motion of the stacked base pairs in the direction of the main axis of the double helix can be described by acoustic phonons. There are, of course, many other vibrations in proteins or DNA, but the above-mentioned motions correspond to the direction of the conduction in both systems.

Using a generalized form of a random walk theory developed by Lax and co-workers [12], one can calculate the frequency-dependent diffusion constant $D(\omega)$ of the electrons and holes, respectively. Substituting these into Einstein's relation

$$\sigma(\omega) = \frac{ne^2}{k_B T} D(\omega) \tag{1}$$

where n is the number of charge carriers per unit volume, k_B is the Boltzmann's constant and T is the absolute temperature. One finally obtains

the frequency-dependent complex conductivity. $\sigma(\omega)$ is also T-dependent, as one can see from Eq. (1), but $D(\omega)$ also shows a strong temperature-dependence [12]. The above sketched four-step procedure is described in detail in Ref. [13].

This procedure was first applied to native pig insulin (in its active form) at room temperature [14] (which has 51 amino acid residues and 3 disulphur bridges), taking into account its first 50 unfilled levels. Its amino acid sequence and detailed conformations are known. In Fig. 1 the $|\sigma(\omega)|$ versus ω curve is shown.

One has found that $\sigma_R(\omega)$ (σ_R is the real part of σ) and $|\sigma(\omega)|$ show a very similar ω-dependence. (The reason of this is that $\lim_{\omega\to\infty} \sigma_I(\omega) \to 0$, as it is easy to show [15].) The $\sigma(\omega)$ curve has a saturation value of $5 \times 10^{-3}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at $\omega = 10^{11}\,\mathrm{s}^{-1}$ (it should be pointed out that conductivity measurements still can be performed at such large frequencies as it was done in the case of DNA with the help of microwave techniques.)

Since there are no a.c. measurements on proteins, one can compare these results only with the hopping conductivity of amorphous glasses like chalcenogides (see for instance Fig. 15 of Ref. [11] in the frequency range of 10^4–$10^8\,\mathrm{s}^{-1}$). One finds that $|\sigma(\omega)|$ lies between those of Te_2AsSi and As_2Se_3. (The same is true for the $\sigma(\omega)$ values of hen egg white lysozyme.)

The same kind of calculation has been performed also for the inactive form of pig insulin [16]. In this case, the saturation value at $\omega = 10^{10}\,\mathrm{s}^{-1}$ is by two orders of magnitude smaller ($|\sigma(\omega)| = 10^{-4}\,\Omega^{-1} \times \mathrm{cm}^{-1}$). Since in the inactive form of pig insulin the sequence is the same, only its conformation is different, this shows that the conductivity is strongly dependent on the conformation of a protein molecule.

As mentioned before $|\sigma(\omega)|$ was also computed for hen egg white lysozyme [15], which is an enzyme with 129 amino acid residues and again 3 S–S bridges. In the active form of this protein, the saturation value of $|\sigma(\omega)|$ is $10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at $\omega = 10^{11}\,\mathrm{s}^{-1}$. In the inactive form it has a saturation value already at $\omega = 10^8\,\mathrm{s}^{-1}$ [17]. This shows again the important role of the conformation of a protein in its conduction properties. It is especially important in the case of the active sites of enzymes, which in most cases change their comformation (especially in the presence of reactants) quite easily [17]. These considerations show that in the case of enzymatic reactions charge transport hopping conductivity is very probably quite important. The investigations were extended also to the native and inhibited form of subtilisin [17]. In the latter case at $\omega = 10^{10}\,\mathrm{s}^{-1}$ $|\sigma(\omega)|$ has a saturation value of $10^{-3}\,\Omega^{-1}\,\mathrm{cm}^{-1}$, one order of magnitude larger than in its original native form ($10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$). In Table 1, $|\sigma(\omega)|$ values of the calculated proteins at $\omega = 10^{11}\,\mathrm{s}^{-1}$ and room temperature are summarized.

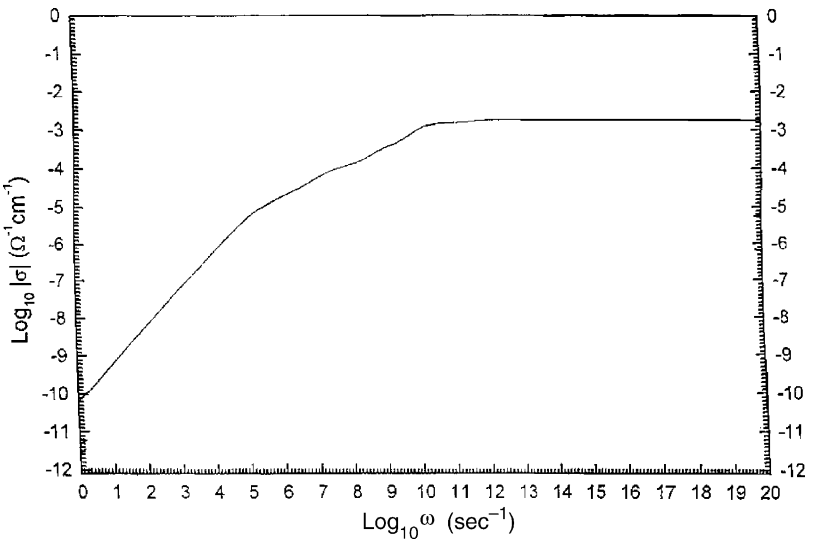

Fig. 1. $|\sigma(\omega)|$ (in $\Omega^{-1}\,\mathrm{cm}^{-1}$) – ω (in s^{-1}) curve of native pig insulin (in its active form).

Table 1
The calculated hopping conductivities of different proteins (in Ω^{-1} cm^{-1}) at $\omega = 10^{11}$ s^{-1} and $T = 298$ K

Native pig insulin	Inactive pig insulin	Active egg white lysozyme	Inactive egg white lysozyme	Native subtilisin	Inhibited subtilisin
10^{-2}	10^{-4}	10^{-4}	10^{-5}	10^{-4}	10^{-3}

All these results show that proteins have a significant hopping conductivity (in a DNA-nucleohistone complex in the nucleosomes, the negatively charged DNA molecule gives over electrons to the protein that possess some positively charged side chains) if a segment of a folded protein closes a small angle with the local effective electric field. To find out the role of electron transfer through a protein molecule one also has to take into account also the other electron transfer channels as: (1) the electronic motion coupled to the motion of protons in hydrated proteins; (2) hopping between different segments of folded proteins and (3) multi-channel tunnelling between more distant segments of the protein. Since all these mechanisms occur in many channels, to find out the overall electron transfer through a protein an appropriately modified form of the Feynman path integral formalism could be applied. This is, of course, not an easy undertaking. We can conclude anyway that Szent-Györgyi's hypothesis from 1941 [2,3] is right, proteins under certain circumstances can be quite good semiconductors. The hopping conductivity values of different proteins, which we have computed are only lower bounds because a minimal basis set was used and no correlation corrections of the electronic structure were taken into account. Namely, it can be shown that both effects increase the hopping conductivity values [18].

In a subsequent series of calculations, the hopping conductivity of aperiodic nucleotide base (pair) stacks were performed. For these investigations, the same four-step procedure was applied as in the case of proteins. The sequence of the bases and the conformation from a part of a human oncogene [19] was taken. One should mention here that according to previous calculations [20–22] on periodic polynucleotides (base stacks with super-phosphate backbone of DNA) have shown that the highest filled (n^*) and the lowest unfilled ($n^* + 1$) bands come from the base stacks and only the $n^* - 1$ and $n^* + 2$ bands, respectively, bands originate from the backbone. Therefore, the bound structure of the periodic stacks and the distributions of the physically interesting levels of the aperiodic stacks describe quite well the corresponding strands of DNA. Further, the alternating positive and negative charges on the different constituents (net negative charges on the bases, positive ones on the sugar groups, again negative one on the phosphate and positive K^+ counter-ions [20–22]) screen each other out. Therefore, the DOS histograms obtained for the aperiodic base stacks have to be quite similar to those which one would have obtained for native DNA in its B conformation [23].

In Fig. 2, we have shown the DOS [24] of a 100 base and base pairs long segment of the aperiodic stack corresponding to Ref. [19].

It is apparent that the fundamental gaps are larger than they were in the periodic cases (see for instance Refs. [4, p. 77, 25]). In Fig. 3, $\sigma(\omega)$ as a function of ω is given for a double strand with 200 levels and for a single strand applying in both cases the oncogene sequence.

At room temperature and $\omega = 10^{10}$ s^{-1} $|\sigma(\omega)| = 5 \times 10^{-1}$ Ω^{-1} cm^{-1} (which is one and a half orders of magnitude larger than in the case of native pig insulin) for the base pair sequence with 200 levels in the valence bands regions and about 10^{-5} Ω^{-1} cm^{-1} with only 100 levels in the valence bands regions. For both cases Clementi's minimal basis [26] was used.

In further computations besides Clementi's minimal basis, his double ζ one [27] was applied for a single stack of the oncogene sequence taking into account 100 levels in the valence bands regions. As one can see in Fig. 4 the saturation value of $|\sigma(\omega)|$ is $\approx 7 \times 10^{-7}$ Ω^{-1} cm^{-1} at $\omega = 10^5$ s^{-1} and $\approx 7 \times 10^{-6}$ Ω^{-1} cm^{-1} at $\omega = 10^{12}$ s^{-1} (Fig. 4).

We have corrected the double $|\sigma(\omega)| - \omega$ curves for correlation at the MP2 level [18]. For this purpose, we have introduced into the matrix elements of the different units (bases or base pairs) these corrections before the DOS calculation with the help of the NFC procedure (for the mathematical details see Ref. [28]).

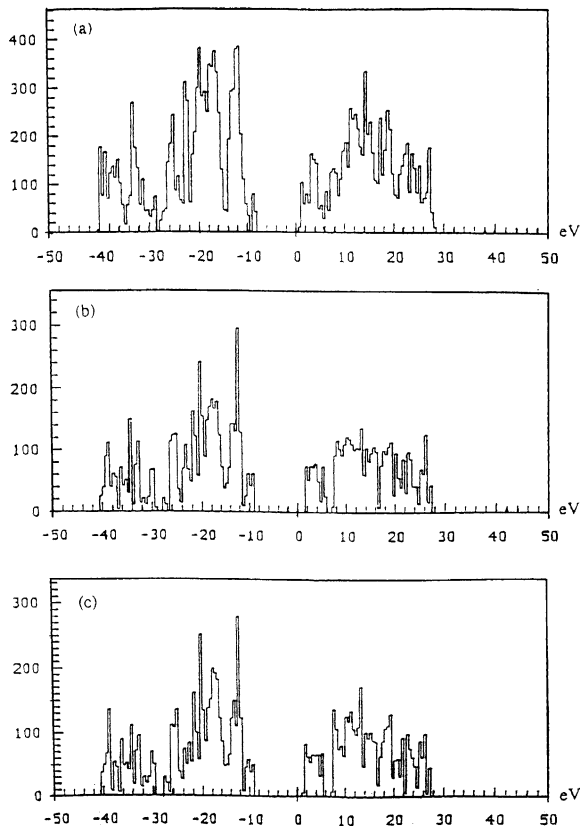

Fig. 2. The electronic density of states of a 100-base and base pair segment of the human oncogene described in Ref. [19]. (a) STO-3G basis, (b) 6-31G basis, (c) 6-31 + MP2.

As one can see from Fig. 4, the introduction of correlation has increased $|\sigma(\omega)|$ by two and a half orders at magnitude. ($|\sigma(\omega)|$ is $\approx 4 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at $\omega = 5 \times 10^{10}\ \mathrm{s}^{-1}$.) To summarize, the better basis increased $|\sigma(\omega)|$ by one and the MP2 correlation by additional 2.5 orders of magnitudes. For this reason, the former (minimal basis) $|\sigma(\omega)|$ value for a base pair stack can be considered only as a loose lower bound. (It should be around $10\ \Omega^{-1}\ \mathrm{cm}^{-1}$ if no other effects would interfere.) It should be pointed out that our results are in good agreement with a measurement of Gruener at al. [29], who have investigated the frequency-dependence of the conductivity of lambda phage DNA at room temperature by electron energy loss in a cavity resonator. They have obtained for $|\sigma(\omega)|$ $24\ \Omega^{-1}\mathrm{cm}^{-1}$ in wet DNA. They have also found that if DNA is dried, its conductivity decreases by half an order of magnitude. This result is also in qualitative agreement with our result [30], according to which for a single stack $|\sigma(\omega)| = 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ in the presence and $10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ in the absence of water [30]. This large effect of water can be explained first of all by the fact that dry DNA is not anymore in a B form and therefore the overlap of the stacked bases is smaller. (In the case of Gruener et al. their purification procedure has left still 15% water in the sample, which is enough to keep the DNA molecules in their B form.)

It should be mentioned that most recently there is a measurement on wet spun macroscopically oriented calf thymus Li-DNA in an a.c. field and at low frequencies between 20 and $10^6\mathrm{cm}^{-1}$ [31]. Combining the data of Ref. [31] with those of Ref. [29], one obtains (with some interruptions) the $|\sigma(\omega)|-\omega$ curve between 10^{-3} and 10^{15} Hz. Comparing this curve with our theoretical one (10^{-3}–$10^{20}\ \mathrm{s}^{-1}$), one finds a very good agreement in all parts of the curve where experimental results are available (with the exception of optical frequencies where the measured $\sigma(\omega)$ values refer to excited states of the base pairs). It is also very interesting to point out that our estimated $|\sigma(\omega)|$ value of $10\ \Omega^{-1}\ \mathrm{cm}^{-1}$, if one takes into account correlation, agrees also quite well with the value of Kutjnjak et al. [31]. Finally, in a further paper we have calculated the temperature-dependence of the hopping conductivity [32]. We have found that $|\sigma(\omega)|$ first decreases exponentially with T (the range $60\ \mathrm{K} \leq T \leq 360\ \mathrm{K}$ was investigated) for a base pair stack (oncogene sequence) until about 60 K (at $\omega = 10^{11}\ \mathrm{s}^{-1}$). A 60 K its value is not T-dependent anymore. This behaviour is again in good agreement with the experimental findings [29,31].

The activation energy of the conductivity (ΔE) calculated from these T-dependence shows (see Fig. 5 and Ref. [33]) that at $T = 60\ \mathrm{K}$ $\Delta E = 0.030\ \mathrm{eV}$, increases exponentially with T between 70 and 120 K. (ΔE has its maximum at 120 K, where its value is 0.159 eV.) By further increase of T it decreases not very steeply. $\Delta E = 0.114\ \mathrm{eV}$ at 310 K. This shows that at larger temperatures the dominant mechanism of conductivity is variable range hopping and below 60 K [32,33] multi-channel tunnelling (Fig. 5). Of course, further experimental and theoretical investigations are needed to find out in detail the mechanisms of a.c. conductivity in DNA.

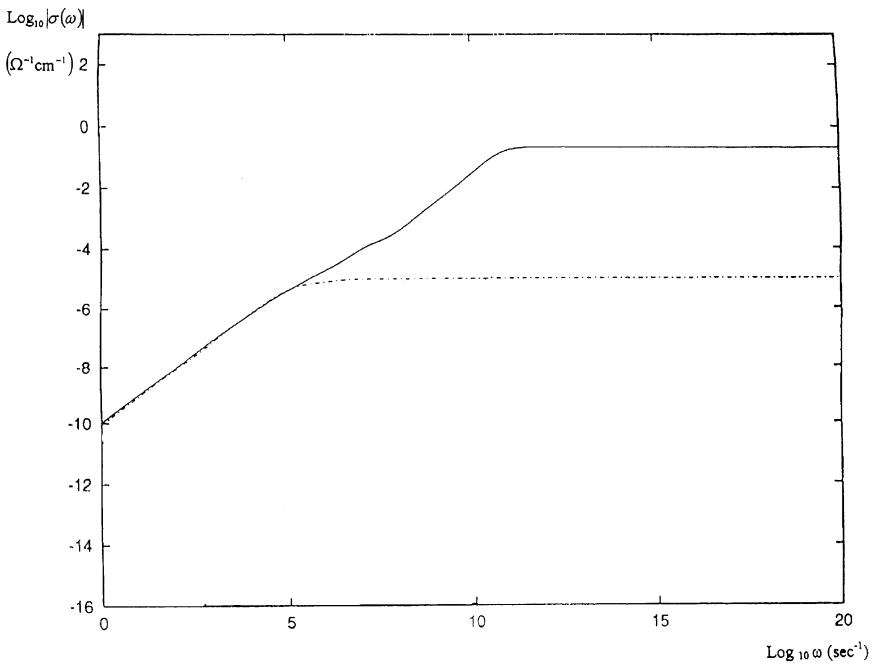

Fig. 3. $|\sigma(\omega)|$ as a function of ω ($T = 298$ K). $\omega_{sat} = 10^{10}$ s^{-1} if 200 levels were taken into account in the valence bands region (—) and $\omega_{sat} = 10^{5}$ s^{-1} if only 100 levels were considered. (–·–·–).

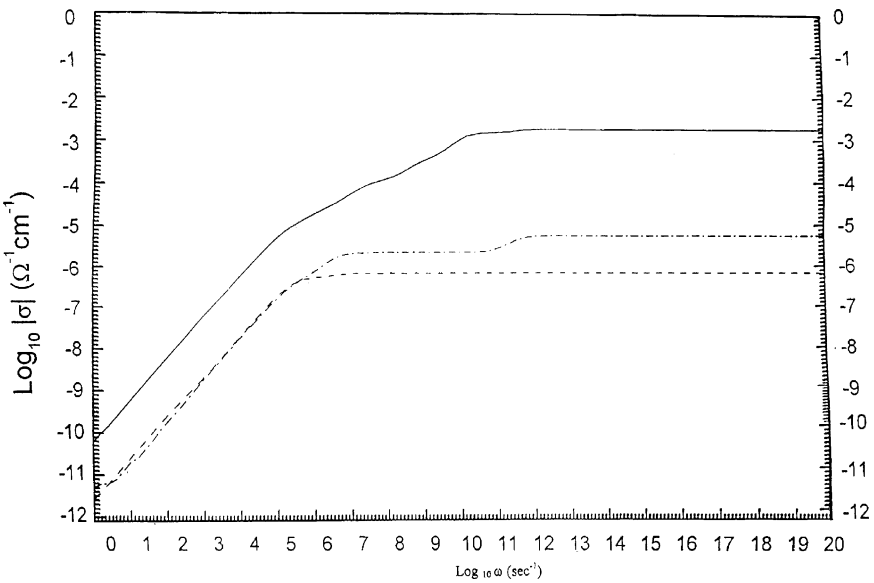

Fig. 4. The $|\sigma(\omega)|-\omega$ for a single stranded base stack (oncogene sequence) with 100 levels in the valence bands region with a minimal basis (– – –), with a double ζ one (–·–·–) and with a double ζ one and correlation (MP2) (—).

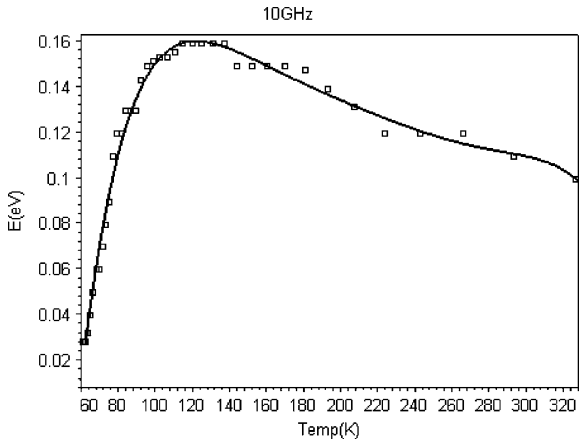

Fig. 5. The mechanism of charge transfer at different temperatures in aperiodic nucleotide base stacks [33].

3. Calculation of the band structures and spectra of periodic nucleotide base stacks and homopolypeptides

Though native proteins and DNA have a non-periodic sequence of their constituents, one can obtain more insight into their electronic structure and properties from their periodic counterparts.

If one has a 1D periodic system one can formulate the calculations of their band structures and wave functions, the crystal orbitals (CO-s), which are a linear combination of Bloch orbitals, if one takes into account their periodic symmetry. In the case of simple translation, this was done first by Löwdin [34] and in more detail (taking into account an arbitrary number of orbitals in the unit cell) by Del Re et al. and André et al., respectively, [35]. The method was extended for the case of general periodic symmetry (like helix or zip-zag operation) [36]. The latter development has made it possible to determine the band structure of homopolypeptides and of periodic nucleotide base (pair) stacks.

As next step, the band structure calculation method was worked out to take into account the major part of correlation using either many body perturbation theory in its Moeller–Plesset (MP) form [5,37] or applying the coupled cluster theory to polymers [38,39].

Both the HF and the HF + MP2 band structures were calculated for a larger number of periodic polymers. For the ones which do not play a role in biology, see Chapter 2 of Ref. [4].

For detailed calculation of the periodic nucleotide base stacks, see Ref. [25]. In this paper, the basis set-, k- and number of neighbours' dependence were investigated in detail. It was found that with a double ζ basis supplemented by a set of p functions centered at the middle plane of the stacking distance (at 3.36/2 = 1.68 Å distance from the stacked base) with 21k-points in the first Brillouin zone and with second neighbours' interactions the HF + MP2 calculation provides a rather realistic band structure with a gap value of 6.5 eV, which is close to the value estimated on the basis of the intermediate exciton spectrum of a cytosine stack [40].

There are a larger number of correlation corrected [MP2] calculations on homopolypeptides. The HF + MP2 gaps turned out to be too large [41,42], which means that one has to use a better basis set than the double ζ and probably has to apply for correlation the higher MP2 + MP3 + MP4 approximation.

In subsequent density functional theoretical calculations (DFT), 12 homopolypeptides were calculated in the LDA approximation [43] and 19 ones in the β pleated sheet form in the BLYP one [44]). In all cases the fundamental gaps were far too small. The density gradient containing BLYP calculation changed the gap only in a small amount. We expect that the B3LYP DF investigations (which are in progress) will increase the gap but probably not in the desired amount, because they contain only partly the HF exchange. Most probably one can obtain still more correct gap values if one applies a suitable form of the optimized effective potential approximation to polymers. Despite this situation, it was worthwhile to apply the different forms of the DFT to homopolypeptides because

1. it has given some insight of its electronic structure, and
2. it will be easy to change the band structure programs for calculations of the total energy per unit cell for which the BLYP and B3LYP DFT methods work quite well.

Using their correlation corrected band structures with the aid of the intermediate exciton theory [45], the UV spectra of a cytosine (C) stack [46] and that of polyglycine and polyalanine [47] were calculated applying the double ζ basis. In the case of the C stack,

the first singlet exciton band has its minimum at 4.7 eV and its width is 0.7 eV. These results agree quite well with experiments [48].

The results also show the importance to take into account charge transfer-type excitations as compared to the results of Frenkel's exciton theory (where the excitations occur within the same cell). The intensity (oscillator strength) value of the first singlet exciton band of the C stack is by 26% smaller than the corresponding monomer value. This so-called hypochromicity is well known in the spectrum in DNA. Due to the $\sum_i f_i = 1$ rule, the second theoretical exciton band shows a hyperchromicity of 12%.

In the case of a polyglycine and a polyalanine, the calculations applying a 6-31G* basis, assuming an α-helix conformation and taking into account fifth neighbours' interactions resulted in the case of a polyglycine as the lower edge of the first singlet exciton band 6.2 eV and for polyalanine the result is 6.1 eV. In both cases the band widths are ≈0.4 eV. One finds again hypochromicity in the first singlet exciton band, a hyperchromicity in the second one for both homopolypeptides. Again, one has to take into account (like in the case of the stacks) charge transfer-type excitations until 4–5th neighbours to obtain saturated results. Finally, one should point out that the small differences in the spectra of these two homopolypeptides indicate that the side chains of the amino acid residues play a minor role in the spectra of proteins (at a given conformation) which is dominated by the $\pi \rightarrow \pi^*$ transitions of the $-\underset{H}{N}-\overset{O}{C}-$ parts of the peptide groups.

4. Outlook

With the very fast development of the power of computers and that of the numerical techniques one can expect that in the next years it will be possible to perform more accurate calculations on biopolymers and their properties. As next step, we will be able to treat much better the interactions between different biopolymers that is very important for their biological functions.

One expects that one can treat simultaneously the different channels of charge transfer in biopolymer taking simultaneously into account: (1) coherent (Bloch-type conduction); (2) hopping conductivity; (3) multi-channel tunnelling (using a suitably modified Feynmann path integral or WKB formalism) and (4) electron transfer coupled to protons or ions.

One expects that before long the very important protein folding problems will be solved and in this way one will be able to better understand the mechanism of action of enzymes and other functions of proteins.

Further, one hopes that one will be able to treat with the help of quantum theory the concerted action of proteins (proteomics) and in this way one can handle theoretically the electron transfer through a chain of proteins as it happens for instance in the Szent-Györgyi-Krebs cycle.

Acknowledgements

I would like to express my deep gratitude to late Professor Albert Szent-Györgyi, whose way of thinking has inspired me very much. I am indebted very much to Professors I.G. Csizmadia and B. Penke for inviting me to the International Symposium, which has given the impetus to write this small review.

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