The electronic structure of the four nucleotide bases in DNA, of their stacks, and of their homopolynucleotides in the absence and presence of water

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Using the *ab initio* Hartree-Fock crystal orbital method in its linear combination of atomic orbital form, the energy band structure of the four homo-DNA-base stacks and those of poly(adenilic acid), polythymidine, and polycytidine were calculated both in the absence and presence of their surrounding water molecules. For these computations Clementi's double ζ basis set was applied. To facilitate the interpretation of the results, the calculations were supplemented by the calculations of the six narrow bands above the conduction band of poly(guanilic acid) with water. Further, the sugar-phosphate chain as well as the water structures around poly(adenilic acid) and polythymidine, respectively, were computed. Three important features have emerged from these calculations. (1) The nonbase-type or water-type bands in the fundamental gap are all close to the corresponding conduction bands. (2) The very broad conduction band (1.70 eV) of the guanine stack is split off to seven narrow bands in the case of poly(guanilic acid) (both without and with water) showing that in the energy range of the originally guanine-stack-type conduction band, states belonging to the sugar, to PO_4^-, to Na^+, and to water mix with the guanine-type states. (3) It is apparent that at the homopolynucleotides with water in three cases the valence bands are very similar (polycytidine, because it has a very narrow valence band, does not fall into this category). We have supplemented these calculations by the computation of correlation effects on the band structures of the base stacks by solving the inverse Dyson equation in its diagonal approximation taken for the self-energy the MP2 many body perturbation theory expression. In all cases the too large fundamental gap decreased by 2–3 eV. In most cases the widths of the valence and conduction bands, respectively, decreased (but not in all cases). This unusual behavior is most probably due to the rather large complexity of the systems. From all this emerges the following picture for the charge transport in DNA: There is a possibility in short segments of the DNA helix of a Bloch-type conduction of holes through the nucleotide base stacks of DNA combined with hopping (and in a lesser degree with tunneling). The motivation of this large scale computation was that recently in Zürich (ETH) they have performed high resolution x-ray diffraction experiments on the structure of the nucleosomes. The 8 nucleohistones in them are wrapped around by a DNA superhelix of 147 base pairs in the DNA B form. The most recent investigations have shown that between the DNA superhelix (mostly from its PO_4^- groups) there is a charge transfer to the positively charged side chains (first of all arginines and lysines) of the histones at 120 sites of the superhelix. This would cause a hole conduction in DNA and an electronic one in the proteins. © *2008 American Institute of Physics*.
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INTRODUCTION

Recently there is a very large development in the determination (using high resolution x-ray diffraction) of the structure of nucleosomes [both of the histone proteins[1] and of DNA (Ref. 2) in it] as well as in modeling chromatins and most recently an x-ray investigation of a tetranucleosome[3] was published. Their structures obtained make very probable that due to charge transfer (CT) between DNA and the histones there is a hole conduction in DNA and an electronic one in the proteins (for more details and references see below). This is the reason why we have started a detailed investigation of the electronic structure of DNA and are planning to do the same for proteins.

In a previous paper[4] the band structure of poly(guanilic acid) in the presence of water was described. In the present work we also present the Hartree-Fock (HF) band structures of the other three homopolynucleotides in the presence of water, poly(adenilic acid), polythymidine, and polycytidine, respectively.

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To understand better these band structures we have also calculated the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the four nucleotide bases occurring in DNA and the band structures of their stacks in a Watson-Crick-type single helix. We have also repeated these stack calculations taking into account correlation in the MP2 level. Further, we have also computed the bands of the four homopolynucleotides in the absence and presence of water. Finally, we also present the band structures of a sugar-phosphate chain and of the water "chains" in the cases of poly(adenilic acid) and polythymidine.

Since in the band structure of polythymidine (with H_2O) the conduction band and in the case of polycytidine (again with water) the valence band are very narrow (with widths smaller than 0.1 eV) there cannot occur Bloch-type conduction by electrons in polythymidine and the same type of conduction by holes in polycytidine.

The main reason of these very narrow bands in the homopolynucleotides containing pyrimidine-type bases (thymine or cytosine) is that their spatial overlap and with it the overlap of the π orbitals is much smaller in a stack because they contain only one six-membered ring. On the other hand the overlap of the wave functions in a stack in the case of the purine-type bases (adenine and guanine) is much larger because they contain besides six-membered rings also five-membered ones.[5]

To see better the occurrence of these very narrow bands we have analyzed four bands above the conduction band of polythymidine and one band below the valence band of polycytidine looking at the eigenvectors belonging to their band edges. It has turned out that—in contrary to poly(guanilic acid) and poly(adenilic acid) (containing one of the purine-type bases) cases—there is a much larger mixing of the states not belonging to a base (sugar, PO_4^-, Na^+, water-type states). We shall return to this problem in more detail at the Results and Discussion.

It should be pointed out that we have performed these quite extensive calculations—as it was discussed already in our previous paper[4]—because in the past ten years detailed high resolution x-ray investigations have been performed on the nucleosomes[1–3] (both on their protein parts which contain 8 nucleohistones[1] and on its DNA B superhelix containing 147 nucleotide base pairs[2]). In the nucleosomes the DNA superhelix is wrapped around the histone molecules. The structure is held together first of all by the CT through H bonds of the positive side chains (arginine and lysine) of the histones and the PO_4^- groups of DNA. There are also other interactions between the other negative sites of the nucleotide bases and the positive sites (for instance, dipoles) of the histones.

The detailed data given in Ref. 1 indicate that the number of CTs between DNA and histones in a nucleosome can be estimated to be roughly at 120 sites[6] of the DNA superhelix.

The occurrence of this CT in a nucleosome causes a hole current in DNA and an electronic one in the histones.

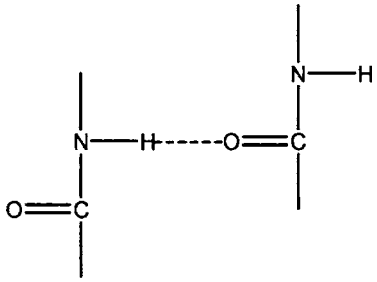
The authors of Ref. 1 also point out that if by some external disturbances (binding of foreign molecules to DNA, radiations, etc.) the mutual positions of the negative groups in DNA and the positive ones in the histones can change in such a way that the charge transfer between them occurs in much lesser degree.

In that case the hole and electron conductivities, respectively, can diminish strongly, so they become insulators. If this happens the DNA superhelix will move away from the histones and therefore the genetic information contained in it becomes readable. This causes a large perturbation of the self-regulation of the cell via the well known biochemical mechanisms.[5,7]

One should mention that more recently Schalch *et al.* have determined by x ray the structure of a four nucleosome system at 0.9 Å resolution.[3] The structure, which they have obtained, fits into the chromatin fiber model (two stacks of nucleosomes starting in opposite directions) which they have constructed previously.[8]

These very important developments in the determination of the structure of the nucleosomes and modeling of chromatins have given us the impetus to perform the very large scale DNA calculations described below. We intend to develop from these band structures a theory of charge transport in DNA. This will be a combination of hole hopping (sometimes tunneling) and for some short segments Bloch-type hole conduction.

We plan to perform a similar theoretical development for electron transport in proteins. In the latter case the electron transport can occur through the infinite crystal orbitals



which are perpendicular to the main chain in the case of α helices (in the nucleohistones). At the same time a hopping conduction can occur along the aperiodic main chains. It should be mentioned that the idea of infinite crystal orbitals perpendicular to the main chains of proteins originates from Coulson who, however, never published this, but told to several of his acquaintances.[9] The first protein band structure calculations were based on this model.[10–12]

METHODS

The calculations mentioned in the Introduction were performed with the help of the *ab initio* HF crystal orbital (CO) method in its linear combination of atomic orbital (LCAO) form.[13–15] The method allows an arbitrary number of basis functions in the unit cell and a general periodicity (for instance, helix operation in DNA B: translation +simultaneous rotation both of the nuclei and the basis functions in the plane perpendicular to the long axis of the double helix).[16] Only in this way was possible to calculate infinite (or very long) polymers with a helical or zigzag structure. For the details, see our very recent publication in Journal of Chemical Physics in 2007 (Ref. 4) and a detailed review of

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the CO method.[17] It should be mentioned that even the latest revision of the GAUSSIAN package[18] does not contain in their polymer programs the case of general periodicity.

We have applied again Clementi's double ζ basis set.[19] In this way the numbers of basis functions were 479 (poly(adenilic acid) with water), 443 (both for polythymidine and poly(guanilic acid)), and 389 (polycytidine). This means that to obtain the LCAO coefficients matrices of this rank had to be diagonalized. Since we have used 20 different k values in the half of the first Brillouin zone these high order matrices had to be diagonalized 20 times. The 20 different k values are sufficient, because in a previous HF calculation of the base stacks the results in the case of 30 and 20 k values, respectively, were the same.[20] In both cases in the iterations of the charge-bond order matrices (which corresponds to the density matrix in the LCAO case) the integrals were calculated numerically with the aid of the Gauss-Legendre method. In the case of the Coulomb integrals we had taken them into account, until the distance between two centers was smaller than 30 Å unless an integral had a value smaller than 10^{-6} a.u. For the rest of the Coulomb interactions we have applied a multipole expansion.[21,22] In the case of the exchange integrals we have kept only those which have two orbitals with their centers apart smaller than 30 Å. It should be mentioned that in large gap systems (like the nucleotide base stacks) the exchange integrals decay quite quickly, while they decay much more slowly if the gap is small (small gap semiconductors, etc.).

Though we have kept only two-electron Coulomb integrals larger or equal than 10^{-6} a.u. (checks with 10^{-8} a.u. accuracy have hardly changed the band structure), the handling of the large number of integrals was a formidable task which required rather large CPU times on the Athlon X2 6400 (2.0 Gbyte core memory and 3.2 GHz speed in Erlangen) and on the Intel P4 computer (1.0 Gbyte core memory and 2.8 GHz speed in Szeged).

For the determination of the water structure around the homopolynucleotides we have applied the same procedure as in our recent previous paper.[4] For starting geometry for a triple base pair with sugar, phosphate, and Na^+ we have used again the SYBYL program.[23] (This program uses 3.36 Å as stacking distance and 36° as rotation angle for DNA B. The geometries of the single bases and of the sugar-phosphate backbone were taken from Ref. 24. Originally 263 H_2O molecules were placed randomly around this system, followed by an optimization of the geometry of this system using molecular mechanics (Amber force field included in GAUSSIAN 03.[18]) After that successive elimination of the upper and lower nucleotide pairs together with the water molecules belonging to them, of the H_2O molecules on the outer part of the cylindrical mantle, and finally elimination of the complementary nucleotide together with its water molecules was executed (for instance, in the case of poly(adenilic acid) the thymidine nucleotide with its water molecules). The Na^+ ions after this procedure could be located in all cases in the plane determined by the P atom and the two O atoms, which do not take part in the sugar-PO_4^- chain.

After this briefly described procedure written in more detail in Ref. 4 there are 16 H_2O molecules around A, 14 around T, 13 (see Ref. 4) around G, and 11 around C. The electronic structures of these water molecules were explicitly taken into account in the band structure calculations of the three additional homopolynucleotides using the same basis set.

To have an idea of the effect of correlation on the band structures we have solved the inverse Dyson equation

$$\omega_l = \varepsilon_l^{\mathrm{HF}} + [\Sigma(\omega_l)]_{l,l} \tag{1}$$

in the diagonal approximation following Liegener's suggestion.[25] Here ω_I is the quasiparticle energy, $\varepsilon_I^{\mathrm{HF}}$ the corresponding HF energy, and $[\Sigma(\omega_I)]_{I,I}$ (the capital indices mean here and thereafter a given state and k value: $I=i,k$) the diagonal I,I element of the self-energy matrix at the quasiparticle energy ω_I (for the derivation of this equation from the Dyson equation see Ref. 17, p. 204).

For $[\Sigma(\omega_I)]_{I,I}$ we have applied the MP2 expression[26]

$$[\Sigma(\omega_l^{\mathrm{MP2}})]_{l,l} = \lim_{\eta\to 0}\left[\sum_{\substack{j\in \mathrm{occ}\\ A,B\in \mathrm{unocc}}} \frac{V_{IJAB}(2V^*_{IJAB} - V^*_{IJBA})}{\omega_I + \varepsilon_J^{\mathrm{HF}} - \varepsilon_A^{\mathrm{HF}} - \varepsilon_B^{\mathrm{HF}} + i\eta} + \sum_{\substack{J\in \mathrm{unocc}\\ A,B\in \mathrm{occ}}} \frac{V_{IJAB}(2V^*_{IJAB} - V^*_{IJBA})}{\omega_l + \varepsilon_J^{\mathrm{HF}} - \varepsilon_A^{\mathrm{HF}} - \varepsilon_B^{\mathrm{HF}} - i\eta}\right], \tag{2}$$

where

$$V_{IJAB} = \langle \varphi_l(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)|\varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2)\rangle \tag{3}$$

is the usual two-electron integral, where, for instance, $\varphi_I(\mathbf{r}_1)$ in its LCAO form

$$\varphi_l(\mathbf{r}_1) = \frac{1}{(2N+1)^{1/2}} \sum_{q=-N}^{N}\sum_{t=1}^{m} \exp\left[\frac{2\pi i k q}{2N+1}\right] \times d(k)_{l,t}\chi_t\{\hat{S}^{-q}[\mathbf{r}_1 - (\mathbf{R}^{t_A})]\}. \tag{4}$$

Here A is the nucleus on which the basis function χ_t is centered, and the $d(k)_{l,t}$'s are the LCAO coefficients. The operator $\hat{S}^q = \hat{D}(q\alpha) + q\boldsymbol{\tau}$, where $\hat{D}(q\alpha)$ rotates the argument of the basis function χ_t by the angle $q\alpha$ and $\boldsymbol{\tau}$ is the elementary translation.

This means that in the case of a helix one has to go from one unit to the next by a translation and rotation of the nuclei and one has to rotate simultaneously those basis functions which have nonzero components perpendicular to the helix axis by the angle of $q\alpha$. For further details see Refs. 4, 17, 27, and 28.

One should notice that this formalism is the *ab initio* and generalized form of Toyozawa's electronic polaron model.[29]

Iterating between Eqs. (1) and (2) one obtains the self-consistent-field quasiparticle energies.

We have applied this formalism to the four nucleotide base stacks using for them the same geometries as in the case of HF.

In Figs. 1–3 we show the chemical structure of the unit cells of the three homopolynucleotides in the presence of water. The unit cell of poly(guanilic acid) with water was shown in Fig. 1 of Ref. 4.

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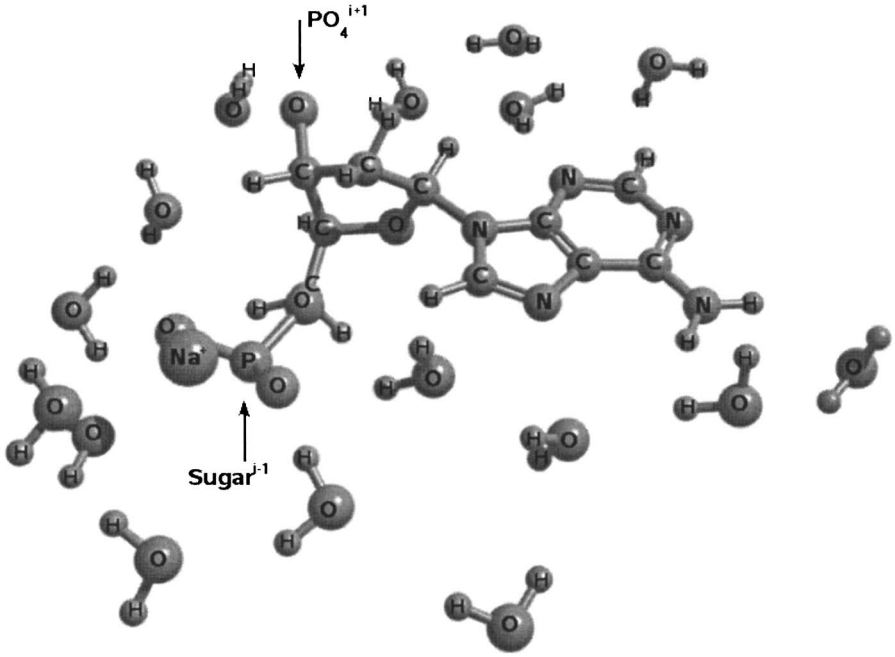

FIG. 1. The unit cell of poly(adenilic acid) together with the water structure around it (16 H_2O molecules) and the position of the Na^+ ion.

RESULTS AND DISCUSSION

In Table I we present the highest occupied energy levels and the lowest unoccupied ones of the four nucleotide bases. Further we show the valence and conduction bands formed from them in a stack of single stranded DNA B.

Looking at Table I one can observe that the highest filled energy levels are close to each other (within 1.0 eV, with the exception of the highest filled level of thymine at –9.86 eV). The energy differences of these levels are about 0.5 eV both for the two purine-type and pyrimidine-type bases, respectively. The lowest unfilled levels are very close to each other in the case of G and A and within 0.4 eV for C and T. Generally the highest filled levels of the purine-type bases are situated lower than those of the pyrimidine-type ones. One finds the same situation at the lowest unoccupied levels. The gaps between the two levels are quite similar (they are very close for pyrimidine bases: 12.02 and 12.13 eV, respectively, but about 0.5 eV apart from each other in the case of purine-type bases; the gap of G is the smallest: 11.78 eV). In Table I we have also included the differences of the electrochemically determined electron-affinities[30] and ionization potentials.[31–34]

In the case of a C stack we have also calculated the gap at the HF+MP2 level with a double ξ+polarization function basis, and with adding to it the so called ghost basis functions.[20] (The ghost basis functions mean that one puts in

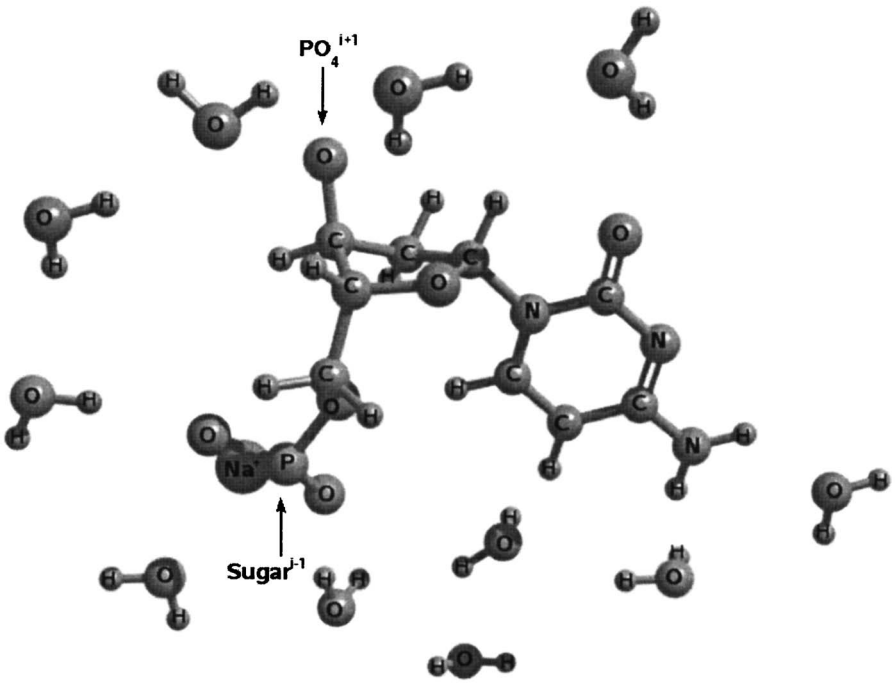

FIG. 2. The unit cell of polycytidine together with the water structure around it (11 H_2O molecules) and the position of the Na^+ ion.

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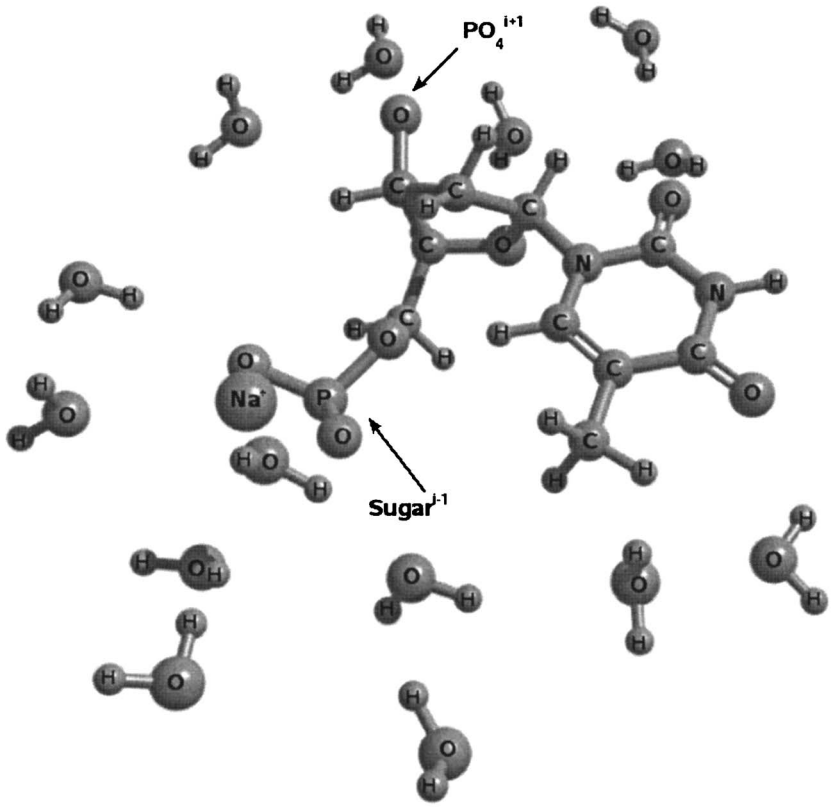

FIG. 3. The unit cell of polythymidine together with the water structure around it (14 H_2O molecules) and the position of the Na^+ ion.

the middle of the stacking distance a "ghost molecule" with no nuclear charges, but basis functions centered on the "ghost nuclei" in the same way as in the case of real molecules). According to our experience this procedure strongly decreases the still too large gap and in the case of a C stack brings it near to the experimental value.[20]

Turning to the Watson-Crick-type stacks of the four nucleotide bases one can observe that the valence bands are shifted in all cases upward by about 0.5 eV and their widths are over 0.20 eV (in the case of the T stack 0.50 eV). The only exception is that of the C stack, which has only a width of 0.06 eV (we shall see that this behavior also remains in the case of polycytidine both in the absence and presence of water).

The lower limits of the conduction bands are generally higher by 0.1–0.6 eV with the exception of the G stack which has an unusually large conduction band width (1.70 eV). One should mention that in a completely different HF CO calculation with a different polymer program and slightly different geometry the width of the conduction band of a guanine stack was also extraordinarily large (1.39 eV).[20]

The band widths of the conduction bands of an A stack and of a C stack (0.22 and 0.47 eV, respectively) are in the usual range. On the other hand the width of the conduction band of the T stack is only 0.10 eV. The width of this decreases further if the sugar and phosphate chain is coupled with the T stack both in the absence and presence of water (see Tables II and III below).

The very large width of the conduction band in a guanine stack one can try to interpret in the following way. (1) The overlap of two purine-type bases (as mentioned before) is always essentially larger than that of two pyrimidine-type

TABLE I. The physically interesting energy levels of guanine, adenine, cytosine, and thymine monomers and the band structures of their stacks (in eV). For the single bases the difference of the experimental electron affinities and ionization potentials is also given. In the case of the C stack for HF+MP2 also results with an extended basis (double ξ+polarization functions+"ghost" orbitals were applied).

		E_{valence}	$E_{\text{conduction}}$	Gap
G mon.		−8.58	3.20	11.78[a]
	u.l.[b]	−7.82	4.11	10.23[c]
G stack	l.l.[d]	−8.16	2.41	7.20[e]
	w.[f]	0.36	1.70	
A mon.		−9.12	3.22	12.34[a]
	u.l.	−8.49	3.71	11.98[c]
A stack	l.l.	−8.70	3.49	6.87[e]
	w.	0.21	0.22	
C mon.		−9.37	2.65	12.02[a]
	u.l.	−8.71	3.26	11.57[c]
C stack	l.l.	−8.77	2.80	7.41[e]
	w.	0.06	0.47	6.60[g]
T mon.		−9.86	2.27	12.13[a]
	u.l.	−9.40	2.46	11.76[c]
T stack	l.l.	−9.90	2.36	7.41[e]
	w.	0.50	0.10	

[a]HOMO-LUMO energy difference of the monomer.
[b]u.l.=upper limit.
[c]The HF gap.
[d]l.l.=lower limit.
[e]Difference between the experimental electron affinity[30] and ionization potential. [31–34]
[f]w.=band width.
[g]HF+MP2 case with extended basis set [double ξ+polarization functions +ghost orbitals at the half of the stacking distance (see text and Ref. 20)].

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TABLE II. The physically interesting bands of poly(guanilic acid), poly(adenilic acid), polycytidine, and polythymidine in the absence of water (in eV).

		$E_{valence}$	$E_{conduction}$	Gap
Poly(guanilic acid)	u.l.[a]	−6.45	3.81	
	l.l.[b]	−6.81	3.54	9.99
	w.[c]	0.36	0.27	
Poly(adenilic acid)	u.l.	−7.61	4.59	
	l.l.	−7.80	4.45	12.06
	w.	0.19	0.14	
Polycytidine	u.l.	−7.97	3.66	
	l.l.	−8.05	3.35	11.32
	w	0.08	0.31	
Polythymidine	u.l.	−8.42	3.27	
	l.l.	−8.93	3.22	11.64
	w.	0.51	0.05	

[a]u.l.=upper limit.
[b]l.l.=lower limit.
[c]w.=band width.

ones (see Ref. 5). (2) In the case of two overlapping guanine molecules the NH_2 groups and the N atoms in the six-membered rings besides the C=O group belonging to the two bases get quite close to each other. The analysis of the corresponding eigenvectors also indicates this. In the case of the two O atoms which are also geometrically quite close, we have vanishingly small eigenvector components and therefore they cannot cause this very large band broadening.

The gaps are generally by 0.3–0.4 eV smaller than the HOMO-LUMO energy level differences. The broad band of the G stack, however, decreases by 1.5 eV.

In Table II the conduction and the valence bands of the four homopolynucleotides are shown (in the absence of water).

Comparing the band edges with those of the corresponding stacks one observes that the presence of the deoxyribose, the PO_4^- group, and the Na^+ ion pushes the valence bands upward by 0.7–1.0 eV. The same happens with the conduction bands (shifts of 0.9–1.0 eV). The band widths of the valence bands remain about the same (see again the small value of 0.08 eV for polycytidine), and the conduction bands become narrower. In the case of poly(guanilic acid) by ~1.0 eV. The very narrow conduction band of the T stack still becomes narrower, 0.05 eV, by admixture to the eigenvector belonging to this conduction band, components from the sugar, PO_4^-, and Na^+ ions. The fundamental gaps going from the base stacks to the homopolynucleotides hardly change. The k values at the band edges are still mostly at $k=0$ or π/a, but the occurrence of deviations from these values is more frequent.

In Tables III–V the main features of the band structures of poly(adenilic acid), polycytidine, and polythymidine, respectively, in the presence of water are presented (the corresponding table for poly(guanilic acid) can be found in Ref. 4).

In Figs. 4–6 the same band structures are shown in a diagrammatic way (for the corresponding figure for poly(guanilic acid) see again Ref. 4).

Looking at the tables and figures one can observe that going from the base stacks to the polynucleotides (without water; Table II and Fig. 4) (1) the valence bands and with the exception of poly(guanilic acid) the conduction bands are also shifted upward by about 1 eV. (2) The widths of the valence bands are hardly changed, but the conduction bands

TABLE III. The physically interesting bands of poly(adenilic acid) in the presence of water. In the first column the role of the bands is indicated; in the next three one of the positions of their upper limits (u.l.) and of their lower limits (l.l.) is given with the corresponding k values and the band widths (w.). In the last column the origins of the bands are indicated (all in eV).

Conduction band[a]	u.l.	6.15	Dominantly adenine type
	l.l.	6.04	
	w.	0.11	
11th unocc. nonadenine-type band	u.l.	6.05	Dominantly P[b] type
	l.l.	5.75	
	w.	0.30	
1st unocc. nonadenine-type band	u.l.	1.35	Dominantly Na^+ and P types with some W[c]
	l.l.	0.86	contributions
	w.	0.49	
Valence band	u.l.	−6.30	Dominantly adenine type
	l.l.	−6.51	
	w.	0.21	
Highest occ. nonadenine-type band	u.l.	−10.33	Dominantly W type with
	l.l.	−10.37	some S[d], P, and adenine contributions
	w.	0.04	

[a]The fundamental gap is 12.34 eV.
[b]P=phosphate.
[c]W=water.
[d]S=sugar.

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TABLE IV. The physically interesting bands of polycytidine in the presence of water. In the first column the role of the bands is indicated; in the next three one of the positions of their upper limits (u.l.) and of their lower limits (l.l.) is given with the corresponding k values and the band widths (w.). In the last column the origins of the bands are indicated (all in eV).

Conduction band[a]	u.l.	4.02	Dominantly cytosine type
	l.l.	3.62	
	w.	0.40	
Sixth unocc.noncytosine-type band	u.l.	3.49	Dominantly Na^+ and P[b] types with some W[c] and S[d] contributions
	l.l.	3.36	
	w.	0.13	
First unocc.noncytosine-type band	u.l.	0.25	Dominantly Na^+ and P types
	l.l.	−0.35	
	w.	0.60	
Valence band	u.l.	−7.80	Dominantly cytosine type
	l.l.	−7.85	
	w.	0.05	
Valence band-1	u.l.	−8.60	Dominantly cytosine type with some S contributions
	l.l.	−8.94	
	w.	0.34	
Highest occ. noncytosine-type band	u.l.	−11.46	Dominantly S type with some cytosine contributions
	l.l.	−11.50	
	w.	0.04	

[a]The fundamental gap is 11.42 eV.
[b]P=phosphate.
[c]W=water.
[d]S=sugar.

become essentially narrower (in the case of polythymidine it decreases from 0.10 to 0.05). (3) The values of the fundamental gaps hardly change again with the exception of poly(guanilic acid). (4) The cases when the edges do not lie at the limits of the half Brillouin zone (0 or π/a) due to the more complicated unit cells are twice so frequent at the polynucleotides than at the base stacks.

The conduction band width of the G stack (1.70 eV) decreases very strongly in the case of poly(guanilic acid) (0.27 eV). This can be understood on the basis of the data given in Table VI. The originally only purely guanine-type states in the stack are strongly mixed with sugar-phosphate and Na^+-type states in poly(guanilic acid) in the absence of water. The six bands in an ~2 eV range over the upper limit of the conduction band partially overlap or are quite close to each other in poly(guanilic acid) (in the G stack nearly all bands overlap). In the case of poly(guanilic acid) in the presence of water the situation is very similar (Fig. 7).

Turning to the problem of the very narrow band of the cytosine stack and polycytidine in the absence and presence of water one can observe that with increasing complexity of the system this band width either remains unchanged or decreases further (0.07, 0.07, 0.05 eV). This means that no coherent hole conduction can take place in polycytidine.

There is a similar situation with the band width of the conduction band of polythymidine (0.10 eV for a T stack, 0.05 eV for polythymidine in the absence of water, and 0.11 eV in its presence; compare Tables I–III). Once again we have to conclude that even in the case of a periodic thymine sequence one cannot obtain coherent electronic conduction (only hopping) even in the case of n doping.

Comparing the electronic structure of the four polynucleotides in the absence and presence of water (Tables II and III and Figs. 4–6 as well as Table I and Fig. 3 in Ref. 4) one finds that their electronic structures are rather similar. The only difference is that in the latter case states coming from the water molecules are also mixed with the states of the naked polynucleotides.

The positions of the valence bands of the two purine-type homopolynucleotides differ by about 1.4 eV and those of the conduction bands by about 1.1 eV. However, the fundamental gap values are somewhat different 9.99 eV in the case of absence and 10.66 eV in the presence of water for poly(guanilic acid).[4] (The corresponding numbers are 12.06 and 12.34 eV, respectively, for poly(adenilic acid)).

It is interesting to notice that the upper limits of the valence band of polythymidine in the presence of water (−6.74 eV) are quite close to the corresponding quantity in the case of poly(guanilic acid) [−6.81 eV (Ref. 4)] both at $k=\pi/a$.

It should be mentioned that we have also computed the band structures of the "water chains" around poly(adenilic acid) and polythymidine (see Table VII). In both cases the corresponding valence bands lie quite deep (−11.4 and −12.0 eV) and have narrow widths (0.11 and 0.12 eV, respectively). On the other hand their conduction bands (be-

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TABLE V. The physically interesting bands of polythymidine in the presence of water. In the first column the role of the bands is indicated; in the next three one of the positions of their upper limits (u.l.) and of their lower limits (l.l.) is given with the corresponding k values and the band widths (w.). In the last column the origins of the bands are indicated (all in eV).

12th unocc. thymine-type band	u.l.	5.99	Dominantly thymine type with some P[b] and W[c] contributions
	l.l.	5.77	
	w.	0.22	
Conduction band	u.l.	4.84	Dominantly thymine type with some S[d] contributions
	l.l.	4.80	
	w.	0.04	
7th unocc. nonthymine-type band	u.l.	4.74	Dominantly Na^+ type with some P, S, and W contributions
	l.l.	4.60	
	w.	0.14	
1st unocc. nonthymine-type band	u.l.	1.89	Dominantly Na^+ and P types with some W contributions
	l.l.	1.25	
	w.	0.64	
Valence band	u.l.	−6.74	Dominantly thymine type
	l.l.	−7.29	
	w.	0.55	
Highest occ. nonthymine-typeband	u.l.	−9.77	Dominantly S type with some thymine contributions
	l.l.	−9.80	
	w.	0.03	

[a]The fundamental gap is 11.54 eV.
[b]P=phosphate.
[c]W=water.
[d]S=sugar.

tween 1.8 and 2.8 eV) are not so far from the corresponding bands of the homopolynucleotides (between 3.0 and 4.5 eV, see Table II). Therefore it is quite understandable that when they surround those, there is a mixing of water states and states belonging to the polynucleotides in the case of the conduction bands.

The band structure of the sugar-phosphate backbone (see again Table VII) with a very narrow valence band between −10.65 and −10.74 eV obviously does not play any role in the case of the valence bands of the homopolynucleotides. On the other hand their broader conduction band between 0.6 and 1.1 eV can play a role at the conduction band of a T stack (2.5–2.4 eV) and this may cause the further narrowing of this conduction band from 0.10 to 0.05 eV. Further the lower limit of the very broad conduction band of the G stack (1.70 eV, see Table I) at 2.41 eV could share states with the sugar-phosphate chain which can lead to the splitting up to several bands of this very broad band, as one can see in Table II.

Finally, to see the effect of correlation on the band structure of these kinds of systems, we have calculated the base stacks at the HF+MP2 level. After performing the HF calculation, we have computed the diagonal elements of the self-energy at the MP2 level and have solved with it the inverse Dyson equation (the formalism, see above). Keeping Clementi's double ξ basis, the same number (20 k points) and geometry, we have obtained the results shown in Table VIII.

Comparing the data given in Tables I and VIII we can find that even this low-level correlation calculation decreases the too large HF gap values substantially (in the case of G from 10.23 to 8.35 eV, for A from 11.98 to 8.60 eV, for C from 11.51 to 8.54 eV, and finally for T from 11.76 to 9.08 eV) at least by 2.0 eV. The band widths show more random behavior: in G the very broad HF conduction band (1.70 eV) decreases to 1.00 eV, while its valence band width decreases only in a small amount. Interestingly enough both the valence and conduction bands of A become about double as broad as in the HF case. One should emphasize here that the rule of thumb that correlation also narrows the bands is established only on the basis of calculations of simple systems, but not in the case of more complicated ones and there is no general justification of this rule. The general behavior of the band widths in the case of the pyrimidine bases (C and T) remains more or less the same; only the very narrow valence band width of the C stack is nearly doubled (from 0.06 to 0.11 eV). However, the latter value is still not large enough to allow Bloch-type conduction in a C stack.

The decrease of the gaps is due as usual to the upward shifting of the valence bands and the downward shifting of the conduction bands. One should observe the about 1 eV upward shift of the upper edge of the valence band of the G stack, which is in accordance with the experiment that the p doping in DNA happens first of all at the G sites.

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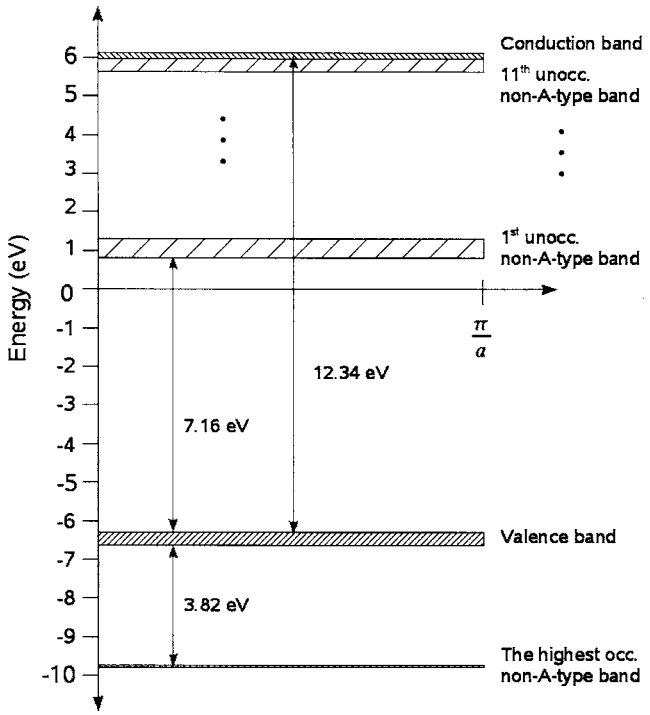

FIG. 4. The positions of the valence and conduction bands together with 11 unfilled *nonadenine-type* bands in the gap and the highest lying filled nonadenine-type band in poly(adenilic acid) in the presence of water.

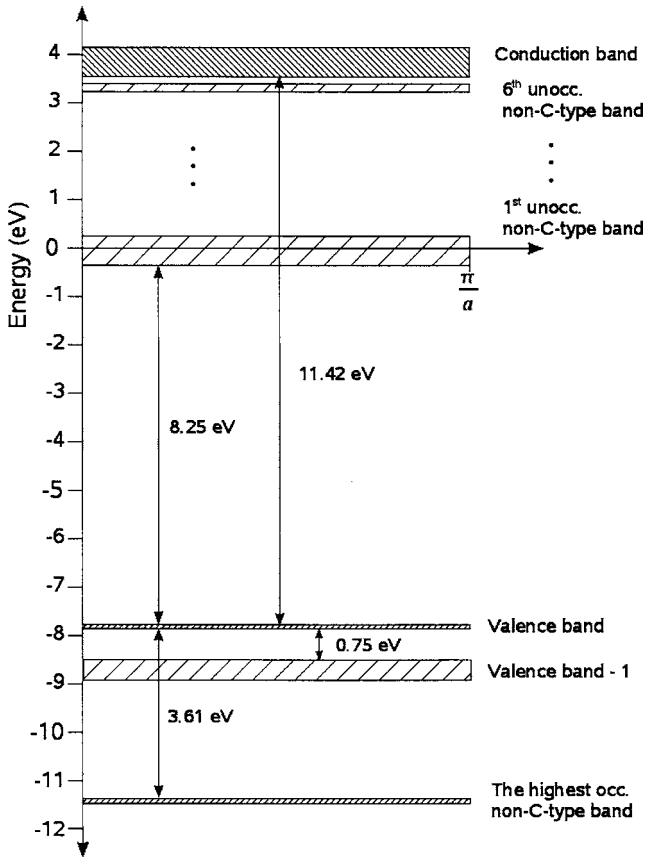

FIG. 5. The positions of the valence and conduction bands together with six unfilled *noncytosine-type* bands in the gap and the highest lying filled noncytosine-type band in polycytidine in the presence of water.

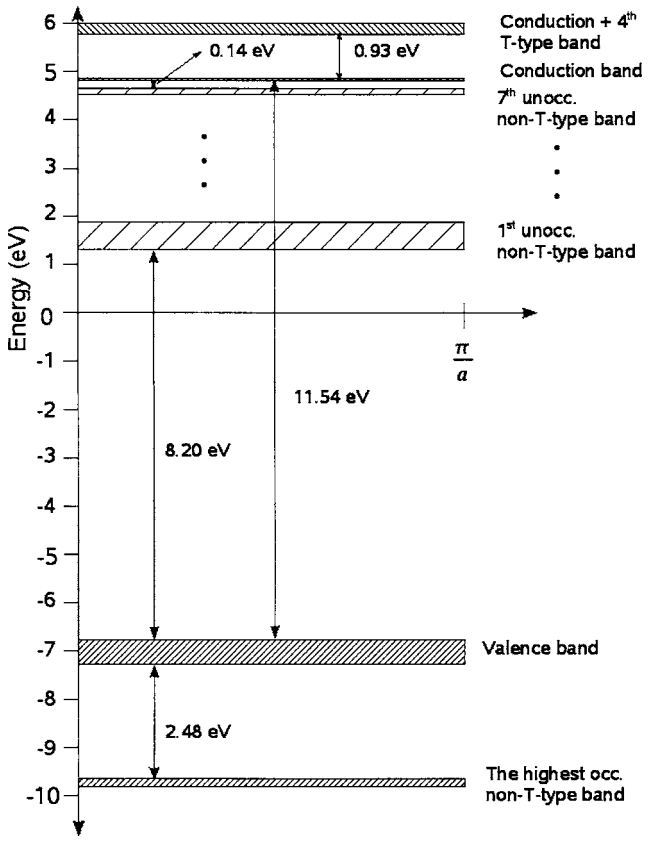

FIG. 6. The positions of the valence and conduction bands together with seven unfilled *nonthymine-type* bands in the gap and the highest lying filled nonthymine-type band in polythymidine in the presence of water.

There are a large number of theoretical calculations on DNA constituents,[35–37] on the interactions of the bases in a base stack,[38–40] and in a base pair.[39–43] Further there are calculations on their spectra,[43,44] on the effects of ion bindings to the base tautomers,[37] on intercalating in DNA olygomers,[45] and on the stability of the base pairs in organic solvents[46] first of all from Zendlova *et al.*

Shukla *et al.* performed similar investigations on DNA constituents like the conformation of a G-C base pair in a vibrationally excited state,[47] on the stacking energies in B- and A-DNA,[48] on the interactions of stacked bases in electronically excited state,[49] and on electron detachment in H-bonded amino acid side chain-G complexes.[50] The problem of the planarity of the nucleotide bases was investigated by the Carr-Parinello method.[51]

In a large work, Starikov[52] among other properties of DNA gives a detailed discussion of the stability of Hartree-Fock solution for a nucleotide in the presence of water environment. He concludes that in the presence of strong outside fields caused by the dipoles of the water molecules and the K^+ ions one should use instead of conventional HF theory the time-dependent HF equations to obtain stationary solutions. In a later work he uses the Kubo formalism in Green's function representation[53,54] to investigate the charge transport in DNA under several circumstances.[55] For these calculations he has applied the extended Hückel method which makes his results somewhat questionable.

In a subsequent paper[56] Starikov has investigated

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TABLE VI. The development of the guanine-type conduction band (comparison of the bands of a guanine stack and poly(guanilic acid) in the absence and presence of water). The table also shows the six unfilled bands in an ≈2 eV range above the conduction band (all in eV).

Bands		G stack		Poly(guanilic acid) in absence of water	Poly(guanilic acid) in presence of water	
Conduction band+6	u.l.[a]	6.66	5.77	Dominantly S[c] and G[d] with some P[e] and Na^+	5.78	Dominantly Na^+, W,[f] of P, and G
	l.l.[b]	6.06	5.55		5.37	
	w.[g]	0.60	0.22		0.41	
Conduction band+5	u.l.	6.01	5.57	Dominantly P and G with some S and Na^+	5.35	Dominantly Na^+ and W with some P and G
	l.l.	5.49	5.27		5.25	
	w.	0.52	0.30		0.10	
Conduction band+4	u.l.	5.57	5.43	Dominantly S and G with some P and Na^+	5.26	Dominantly Na^+ and W with some P and S
	l.l.	4.80	5.14		5.09	
	w.	0.77	0.29		0.17	
Conduction band+3	u.l.	4.81	5.28	Dominantly Na^+ with some P and S	5.15	Dominantly Na^+ and W with some P
	l.l.	4.29	4.51		4.91	
	w.	0.52	0.77		0.24	
Conduction band+2	u.l.	4.54	4.94	Dominantly Na^+ and P with some S	4.96	Dominantly G with some S
	l.l.	4.07	4.09		4.81	
	w.	0.47	0.85		0.15	
Conduction band+1	u.l.	4.53	4.46	Dominantly Na^+ and P with some S	4.78	Dominantly Na^+ and P
	l.l.	3.82	3.83		4.12	
	w.	0.71	0.63		0.66	
Conduction band	u.l.	4.11	3.81	Dominantly G	4.43	Dominantly G
	l.l.	2.41	3.54		3.84	
	w.	1.70	0.27		0.59	

[a]u.l.=upper limit.
[b]l.l.=lower limit.
[c]S=sugar.
[d]G=guanine.
[e]P=phosphate.
[f]W=water.
[g]w.=band width.

systematically the coupling of the 12 conformational modes in B-DNA trimers and tetramers using a tight binding Hamiltonian.[56] The work seems to be interesting, but the application of tight binding Hamiltonians makes—as always—the results questionable. Further he has performed density functional theory (DFT) and *ab initio* HF calculations on two stacked C molecules,[57] has shown that the presence of O_2 molecules increases the hole conductivity on poly(G-C) oligomers using a semiempirical (PM3) method,[58] and investigated the effect of base sequence on nucleotide base pair dimers in their excited states using both *ab initio* and semiempirical HF methods.[59]

Starikov has performed the only really solid state physical calculations of an infinite three dimensional poly(dA)-poly(dT) fiber (though only in the tight binding approximation). His results indicate that the actual DNA fibers are disordered systems. He has shown that the irregularities in the DNA conformation are much more important for the electronic properties of DNA (causing strong localization) than the aperiodicity of the base sequences in the single double helices.[60]

There is no consent on the mechanism of the charge transport in organic crystals generally and in DNA particularly. Contrary to authors who think (as we do) that in native DNA there is a mixture of variable range hopping and electronic polaron-type coherent conduction in shorter segments of the DNA strands, some people think that at higher temperatures (like at room temperature) the effects of large thermal fluctuations on the intermolecular transfer integrals destroy the band structure as the electronic states become localized. Troisi and Orlandi have demonstrated this in an one dimensional semiclassical model.[61]

Unge and Stafström[62] have come to the same results using the transfer matrix method in the case of DNA sequences if they contain many A-T base pairs. In a poly(G-C) sequence the localized states which they have obtained (es-

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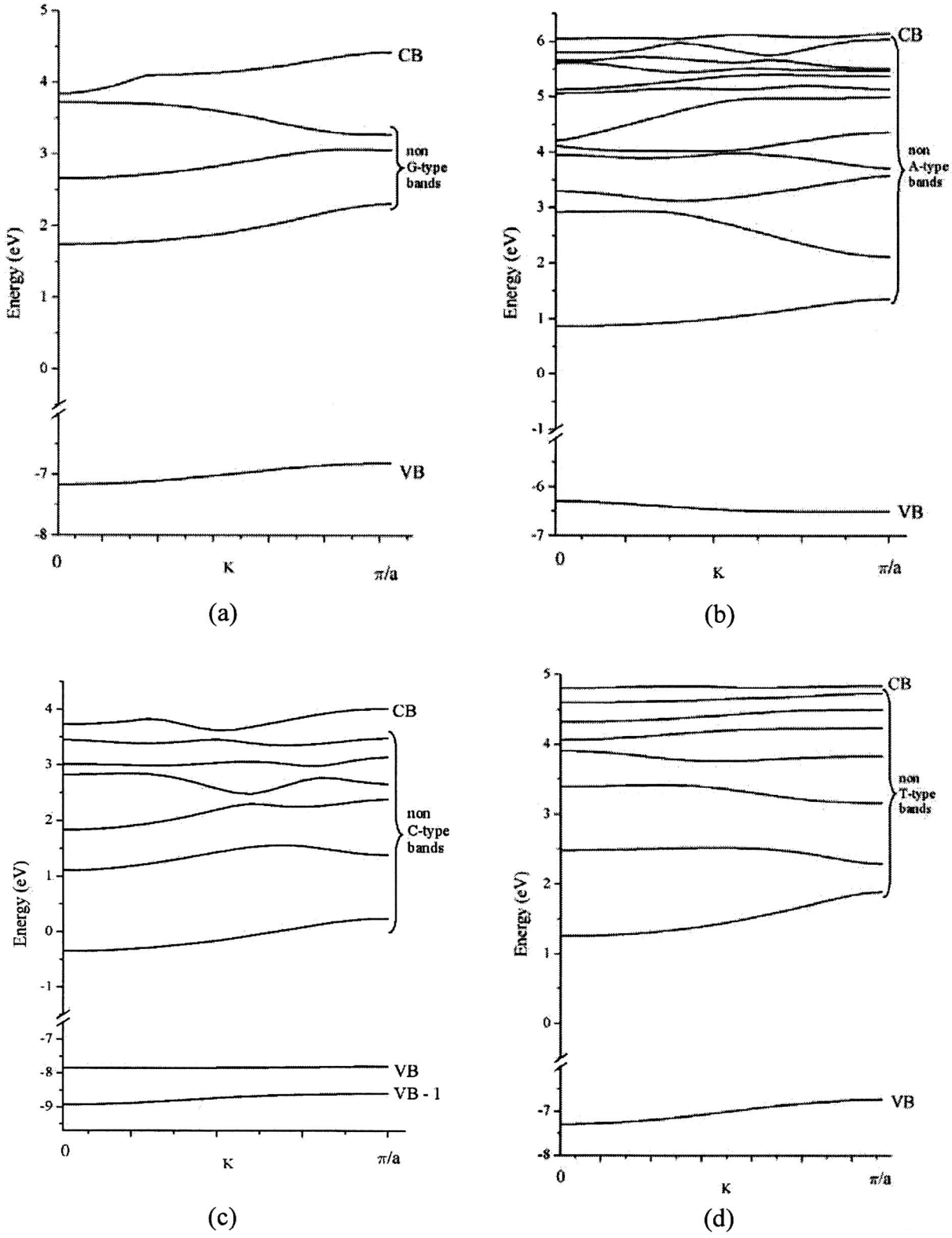

FIG. 7. The dispersion curves of the physically interesting bands of the four homonucleotides: (a) poly(guanilic acid), (b) poly(adenilic acid), (c) polycytidine, and (d) polythymidine.

pecially the G-type states) are rather extended (large localization lengths). One should point out, however, that the measurements of charge transport on native DNA have shown a transport of injected charges up to 200 Å, ≈60 base pairs (see below). One should also take into account that in tetracyanoquinone (TCNQ) and tetrathiofulvalene (TTF) stacks with a stacking similar to DNA B there is a strong charge transport.

In their paper Taniguchi and Kawai[63] have performed a DFT calculation to a ten base pairs long stack of DNA-B and

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TABLE VII. The physically interesting bands of sugar-phosphate backbone and of the water strucutres in cases of poly(adenilic acid) and polythymidine systems (in eV).

		E_{val}	E_{cond}	Gap
Sugar-PO_4^-	u.l.[a]	−10.65	1.12	
	l.l.[b]	−10.74	0.60	11.25
	w.[c]	0.09	0.52	
Water around poly(adenilic acid)	u.l.[a]	−11.36	2.26	
	l.l.[b]	−11.47	1.82	13.18
	w.[c]	0.11	0.44	
Water around polythymidine	u.l.	−12.05	2.81	
	l.l.	−12.07	2.21	14.26
	w.	0.02	0.60	

[a]u.l.=upper limit.
[b]l.l.=lower limit.
[c]w.=band width.

TABLE VIII. The valence and conduction bands of the four nucleotide base stacks calculated with the aid of HF+MP2 methods (in eV).

G stack	Conduction band		
	u.l.	2.45	
	l.l.	1.45	
	Width	1.00	
	Valence band		Gap=8.25
	u.l.	−6.80	
	l.l.	−7.11	
	Width	0.31	
A stack	Conduction band		
	u.l.	2.50	
	l.l.	2.08	
	Width	0.42	
	Valence band		Gap=8.60
	u.l.	−7.18	
	l.l.	−7.66	
	Width	0.48	
C stack	Conduction band		
	u.l.	1.89	
	l.l.	1.56	
	Width	0.33	
	Valence band		Gap=8.54
	u.l.	−6.98	
	l.l.	−7.09	
	Width	0.11	
T stack	Conduction band		
	u.l.	1.24	
	l.l.	1.12	
	Width	0.12	
	Valence band		Gap=9.08
	u.l.	−7.96	
	l.l.	−8.43	
	Width	0.47	

-A obtaining approximate band structures. One should point out, however, that the DFT methods (with the exception of the hybrid ones like B3LYP) give always too small band gaps and band widths.

It is a general problem by all attempts to calculate the band structures of helical base stacks that in the GAUSSIAN program package only simple translation and no simultaneous translation and rotation of the nuclei and the basis functions (helix operation) is incorporated. Therefore, the authors cannot perform a real solid state physical band structure calculation of a large helix (they have to take ten bases or base pairs as unit cell with the existing programs if they use only the translation symmetry).

Yu and Song[64] taking a λ phage sequence, which is completely disordered, performed a variable range hopping calculation for a DNA double helix. For the calculation, they have used Mott's expression for the hopping probability.[65] For this type of calculations, the determination of the transfer integrals between the different sites[66,67] may turn out to be very useful. Taking into account also thermal fluctuations, they have obtained strongly localized wave functions with a short localization length. Their temperature dependence of the localization agrees quite well with that of the conductivity in the λ phage.

Several authors[68,69] argue, based on a Hubbard-type model, that the sugar-phosphate backbone plays an important role in the charge transfer between the bases in the base pairs and this has an important role in the conduction properties of polynucleotides.

Some authors point out that a DNA double helix has no rigid structure and therefore dynamic effects can play an important role, especially in the hole transfer in DNA.[70,71] Other authors have drawn the attention to the long range correlation effects in the charge transport in aperiodic DNA.[72,73]

As one can see, a large number of papers are dealing with the mechanism of charge transport in DNA. Since, however, there are only parametrized or model Hamiltonian calculations even for a static single infinite polynucleotide in the presence of water and counterions, we could not find any data, which we could compare with the results of our first principles band structure calculations.

The first dc conductivity measurements on native DNA were performed back in 1962 by Eley and Spivey.[74] From the temperature dependence of the specific conductivity, they have found for the activation energy of conductivity 4.8 eV. This value lies not very far from our HF+MP2 gap value calculated by the extended basis set for a C stack (6.6 eV). x-ray absorption and soft x-ray emission spectroscopic measurements have provided for the HOMO-LUMO gap of the single bases: 4.7 eV (A), 5.2 eV (T), 2.6 eV (G), and 3.6 eV (C).[75]

In a paper Bixon and Jortner[76] have measured the electric current and conductivity for a single DNA double helix. At high voltages and sufficiently long chains, they have found a voltage independent conductivity. They have interpreted their results by a hopping model.

In an earlier paper Porath *et al.*[77] have performed a two point dc measurement of a 10.4 nm (≈30 base pairs) long poly(G-C) double helix. In their theoretical analysis, they conclude that at least in such a comparatively shorter distance the charge transfer is mediated by energy bands. In a

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subsequent paper[78] they have also investigated the dc conductivity of DNA besides short periodic sequences in bundles and networks. For the DNA double helix they have found using a DFT method again a band-type conduction (though the bands consist of near lying levels of localized wave functions).

Xu *et al.*[79] have performed dc conductance measurements on eight or more G-C pairs in the presence of aqueous buffer. They have found that the conductivity increases with the poly(G-C) segments and is inversely proportional to the length of the poly(A-T) sequences. They were able to exclude an ionic contribution to the conductance.

Hwang *et al.*[80] measured the electronic transport of 60 base pairs long periodic poly(G-C) DNA double helix. Using a tight binding Hamiltonian they have obtained 3.0 eV for the gap which seems somewhat too small.

You *et al.*[81] measured dc conductivity on poly(A-T) and poly(G-C). They interpret their results as small phonon polaron hopping. The poly(G-C) samples had the length 1700–2900 nm (5000–8600 base pairs) and the poly(A-T) samples 500–1500 nm. They have found that poly(A-T) acts as a *n*-type and poly(G-C) as a *p*-type semiconductor.

Cohen *et al.*[82] have shown (in many reproducible ways) that in 26 base pair long aperiodic DNA double helices there is a coherent (band-type) conduction.

Finally one should mention that O'Neil and Barton (see, for instance, Ref. 83) in numerous chemical experiments have shown that if they dope aperiodic DNA double helices with electron acceptors (oxidation of DNA) like rhodium complexes, there occurs a charge transport of holes at ~200 Å (about 60 base pairs) away.

One can see that there is also no consent on the interpretation of dc conductivity measurements on periodic and aperiodic DNA (coherent Bloch-type conduction, variable range hopping, small phonon polaron hopping, etc.). What one can conclude from all the above described experiments is that there is a charge transport in a DNA double helix. The hole conduction in G-C rich segment is dominant and if there is conduction through A-T rich segment this certainly happens via a hopping mechanism [and occasionally, if for instance, an A-T base pair is inserted into a poly(G-C)-type sequence by tunneling].

The seemingly contradictory theoretical and experimental results about the electronic structure and charge transport properties of DNA are caused mainly by two factors. (1) Native DNA consists of a double helix with an aperiodic sequence, sugar-phosphate side chains, and water as well as ions surrounding it. This very complex system is not rigid, but the different constituents of DNA move relative to each other. (2) Further both the theoretical and experimental works have been performed with the aid of quite different theoretical methods and experimental techniques, respectively. This way, these investigations have been performed on different systems with the aid of different methods. In this situation, it is no wonder that in many cases the results are different.

CONCLUSION

From the rather large material presented for periodic DNA structures (base stacks, homopolynucleotides in the absence and presence of water) we can come to the following conclusions: (1) Though native DNA is aperiodic, there are several facts that indicate "pseudoperiodicity" of the DNA sequences. As it is well known there are segments of several (sometimes a few tens of base pairs) which are the same. (2) Surprisingly enough, it has turned out that the valence bands of poly(guanilic acid),[4] of poly(adenilic acid), and of polythymidine are very similar (all in the presence of water). The upper limits of these bands lie at −6.81, −6.30, and −6.74 eV, respectively, while their physically less interesting lower limits are at −7.17, −6.51, and −7.29 eV. Only polycytidine with its very narrow valence band does not fit into this picture. (3) The G-C and A-T base pairs are quite similar (both consist of a purine- and a pyrimidine-type base and each has 24 π electrons if we take into account the hyperconjugation of the methyl group of thymine). (4) The H_2O-type or non-nucleotide base-type bands in the gap are all in the neighborhood of the conduction bands so they cannot produce holes in the valence bands. Therefore if CT occurs between DNA and proteins this will cause hole conduction through the base stacks. (5) One can observe the rather large effect of the sugar-phosphate side chains and of Na^+ ions as well as of water on the band structure of the base stacks. They cause a mixture of their states with the base-type ones. This can be observed first of all in the case of the very broad conduction band of a G stack (1.70 eV). They split it up to a much narrower conduction band and into six further narrow bands in the same energy region. Most of them partially overlap and some are very near to each other.

To work out a theory of charge transport in DNA one has to build up a combination of Bloch-type conduction in short segments with hopping and more rarely tunneling. In this way the mobility and the conductivity, respectively, will be sequence dependent.

If still larger computational power will become available one could repeat the same kind of computations described here for a DNA double helix.

ACKNOWLEDGMENTS

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