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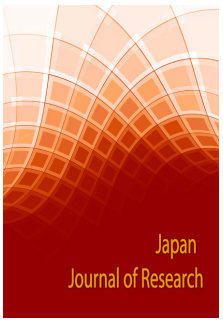

Frenkel Excitons in Helical Two-Strand DNA-Like Regular Polymers

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Abstract

Frenkel Excitons (FEs) as collectivized electronic excitations are treated using two models of helical two-strand regular polymers with B-DNA geometry. As basis excitations we consider two excitations of a pair of complementary bases, not the excitations of separate bases (due to the permanent pairing, e.g. A-T, of complementary bases and small inter-bases distance). The studied regular structures contain combination of one pair only ordered as follows: A. Complementary homopolymers, i.e. pairing of two strands each with one type of base (A or T) B. Self-complementary copolymers in which each strand is supposed to contain alternatively ordered A-T-A:... (and each step of double helix contains the pair A-T). The linear absorption and circular dichroism (CD), correspondingly the tensor of dielectric permittivity and of gyration are calculated near the frequencies of FEs, using method of Green functions at T=0 (T-temperature). Two types of FEs appear in the helices: a) two branches of FEs with transition dipole moment perpendicular to the helical axis (like strong π→π transitions) do not couple each other; b) two branches with parallel to the axis n→π* transitions dipoles are mixed and this modulates linear absorption spectra but for antiparallel DNA strands phenomenon CD in model B does not appear near n→π* maxima. Exciton spectra and their splitting (like Davydov splitting) are exposed, as well as the approximate connection between FEs of the pair and FEs of separate bases which compose the pair.*

Introduction

In the present paper we study Frenkel Excitons (FEs) as collectivized electronic excitations of the pairs of complementary bases in helical two-strand regular structures and manifestation of FEs in linear absorption spectra and in Circular Dichroism (CD). As usual the regular structures represent a first step in modelling DNA molecules with special or arbitrary sequence of the pairs of complementary bases.

The introducing of the electronic excitations of the pairs as basic is more adequate compared with the excitations of separate bases. We emphasize two main reasons: 1) the permanent pairing of the bases as A-T, C-G. Namely pairs are structural units of double helices; 2) the short inter-bases distances in pairing of complementary bases. This is connected with geometrical complementarity but with electronic complementarity also (see [1], Ch.6).

The early studies of FEs in double-stranded DNA [2, 3] are based on transfers of the base's excitations between the steps of the helix. We prefer to develop a formalism of transfers electronic excitations of the pair, e.g. A-T[4]. The strongest transitions of each of the two bases are n→π* transitions with transition dipole moment perpendicular to the helical axis in geometry of B-DNA. Correspondingly two non-degenerate excitations of the pair appear and they do not mix in regular structures even in the transfers between neighbor pairs (see below, Sect.2 and 3). This is not the case of n→π* transitions with transition dipoles parallel to the axis. The two n→π* pair's excitations with collinear transition dipoles can be mixed due to the stack coupling. We consider the lowest excited states of the pair but treating of excitations with higher energy is also possible.

Our studies of the excitonic spectra and their manifestation in linear absorption and CD include calculations of dielectric permittivity and gyration tensor (see Ref.[5]) of double helix in FEs region and are based on general theory of excitons [6-8] applying Green functions method at T=0 (T-temperature) and nearest-neighbor approximation.

The organization of the paper is the following: in Section 2 we analyze FEs in

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relatively simple model A of complementary homopolymers in which one strand contains one base only (A or T) and each step is AT-pair. The corresponding Hamiltonians for π→π* and n→π* excitations of the AT pair allow to calculate dielectric permittivity $\varepsilon_{ij}(\omega,k)$ and gyration tensor ρ. In Section 3 the analysis of FEs in model B of self-complementary co-polymers (with perfect alteration A-T-A… in each strand) includes the same treating as that of Sect.2. Section 4 represents an approximate connection between two initial points – electronic excitations of the separate bases of the pair and electronic excitation of the pair as structural unit. Section 5 is concluding.

FEs in the model of complementary homopolymers

The scheme of complementary homopolymers is shown on Fig.1. The angle of repetition of AT-pairs is φ=36º, typical for B-DNA, the step distance along helical axis is a=3.4Å.

Two electronic excitations (connected with π→π* or n→π* transitions) in two bases exist in each AT-pair with energy E1 and E2 and wave functions (Ψ_1,Ψ_2). Let the ground nonexcited state of the pair is $\Psi_0 \equiv |0\rangle$ and vectors of transition electric dipole and magnetic dipole moment are correspondingly by:

$$\vec{R}^{(1,2)} = \left\langle \Psi_{1,2} \left| \sum_m (e\vec{r_0})_m \right| \Psi_0 \right\rangle ; D_{i,j}^{(1,2)} = \left\langle \Psi_{1,2} \left| Q_{i,j}(0) \right| \Psi_0 \right\rangle \quad (1)$$

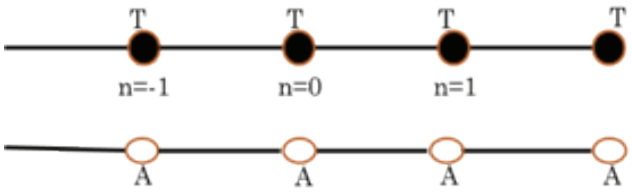

Figure 1. *Scheme of a complementary homopolymers with bases A and T, n- number of (AT)-pair in double helix*

$\vec{R}^{(1,2)}$ and $D_{i,j}^{(1,2)}$ denote transition moments for the pair n=0, sum m concern all electric charges and their positions in the same pair and $Q_{i,j}(0)$ is the sum of electric quadrupole + magnetic dipole (transition magnetic dipole moment $\vec{M}$ is antisymmetrical part of tensor $D_{i,j}^{(1,2)}$. Their quantities for the pair n, $\vec{R}^{(1,2)}$ and $D_{i,j}^{(1,2)}$ may be found using relations (see, e.g. Ref.9)

$$\vec{R}_\alpha^{(1,2)}(n) = \sum a_{\alpha\beta}^{(n)} R_\beta^{(1,2)} \; ; D_{\alpha,\beta}^{(1,2)}(n) = \sum_{\gamma,\delta} a_{\alpha,\gamma}^{(n)} a_{\beta,\delta}^{(n)} D_{\gamma,\delta}^{(n)} \quad (2)$$

where

$$\left\| a_{\alpha\beta}^{(n)} \right\| = \begin{Vmatrix} \cos(n\varphi) & -\sin(n\varphi) & 0 \\ \sin(n\varphi) & \cos(n\varphi) & 0 \\ 0 & 0 & 1 \end{Vmatrix}$$

(supposing the helical axis directed along axis $\hat{z}$ and arbitrary orthogonal axes $(\hat{x},\hat{y}) \perp \hat{z}$

In the realistic case of nondegenerate excited states, $E_1 \neq E_2$, the latent vectors of Heisenberg matrix are mutually ortogonal, but they are not collinear with transition dipole vectors $\vec{R}^{(1)}, \vec{R}^{(2)}$ which depend on symmetry of wave functions Ψ_1,Ψ_2 and Ψ_0. The symmetry and the values (E_1,E_2) of excitations of the pair is problem of quantum chemistry, certainly more complicated compared with the problem of excitations of separate bases, but it is more informative. It describes the properties of the pair of complementary bases and namely the pairs are structural units of double helix (not separate bases).

First we consider FEs with transition dipoles perpendicular to the helical axis. Their transfers between the pairs are possible only separately for FEs1 and FEs2 because in the treated regular structures the transfers in both directions of the axis $\hat{z}$ must be equivalent. The inter-pair transfers FEs1⇆FEs2 are possible only in rather exotic case of collinear vectors $\left(\vec{R}^{(1)}, \vec{R}^{(2)}\right)$. Even in the case of calculations in model of atomic transition charges [4,10] the distributions of the charges of FEs1 and FEs2 must be improbably mutually symmetrical to allow the transfers of different FEs along the helix. Thus the Hamiltonian in the nearest-neighbors approximation is the following:

$$\hat{H} = \sum_{n,i=1,2} E_i T_{in}^+ T_{in} + \sum_{nm,i=1,2} V_i T_{in}^+ T_{im} \quad (3)$$

in which T_{in} is operator of annihilation of FEs i=1,2 on pair and V_i are the transfer parameters of the same FE between the neighbor pairs. In momentum space **k** one reads:

$$\hat{H} = \sum_{k,i=1,2} \left(E_i + 2V_i \cos(ka)\right) T_{ik}^+ T_{ik} \quad (4)$$

In calculations of dielectric susceptibility tensor $\varepsilon_{\alpha\beta}(\omega, k)$ for homopolymers with parallel axes $\hat{z}$ we follow methodics described in Ref.[5,9]. One reads for the terms connected with FEs1 and FEs2:

$$\Delta\varepsilon_{\alpha\beta}(\omega,\mathbf{k}) = -A \sum_{\substack{n,m \\ i_k,j=1,2 \\ l=x,y,z}} \left[\begin{matrix} R_\alpha^{(i_k)}(n) R_\beta^{(j)}(m) \\ +ik_l \left(\begin{matrix} R_\beta^{(i_k)}(m) D_{\alpha l}^{(j)}(n) \\ -R_\alpha^{(j)}(n) D_{\beta l}^{(i_k)}(m) \end{matrix} \right) \end{matrix} \right] e^{-i\mathbf{k}\cdot(\mathbf{n}-\mathbf{m})} \left\langle 0 \left| T_{i_k n}(t) T_{jm}^+(0) \right| 0 \right\rangle. \quad (5)$$

in which A∼N/v, where N is number of the steps in helix and v is volume of one step. The last multiple in (5) is Fourier-component of the following retarded Green function:

$$G_{i,j}(n,m) = -i\theta(t) \left\langle 0 \left| T_{i,n}(t) T_{jm}^+(0) \right| 0 \right\rangle \quad (6)$$

($\theta(t)$ is step function)

According Hamiltonian (3)-(4) we need function (6) at i_1=j. The averaging of in (6) is on the ground state |0> only because if inequalities $E_1, E_2 \gg kT$ (k – Boltzman constant, T – temperature). Using usual procedure to calculate Green functions (6) and expression (2) one obtains:

$$\Delta\varepsilon_{xx} = \Delta\varepsilon_{yy} = -\left(\frac{A}{2}\right)\left\{ R^{(1)^2} G_1\left(\omega, \frac{\varphi}{a}\right) + R^{(2)^2} G_2\left(\omega, \frac{\varphi}{a}\right) \right\} \quad (7)$$

$$\Delta\varepsilon_{xy} = -\Delta\varepsilon_{yx} = ik\left(\frac{A}{2}\right)\left\{ R^{(1)^2} \frac{\partial G_1}{\partial q}\Big|_{q=\frac{\varphi}{a}} + R^{(2)^2} \frac{\partial G_2}{\partial q}\Big|_{q=\frac{\varphi}{a}} \right\} \quad (8)$$

in which

$$G_i(\omega,q) = \frac{1}{\hbar\omega - E_{i_1} - 2V_{i_1}\cos(qa)} ; i_1 = 1,2 \quad (9)$$

Tensor $\rho_{\alpha\beta}$ of gyration is connected with dielectric permittivity with relation [8,9]:

$$\varepsilon_{\alpha\beta}(\omega,k) = \varepsilon_{\alpha\beta}^{(1)}(\omega) + i\sum_{l,n_1} k_l e_{\alpha\beta n_1} \rho_{n_1 l} + O(k^2) \quad (10)$$

In this expression functions $\varepsilon_{\alpha\beta}^{(1)}(\omega)$ describe linear absorption in UV-spectra, $e_{\alpha\beta n_1}$ is Levi-Chivita unit tensor and $O(k^2)$ depends on higher power of k. Using Hamiltonian (3)-(4) one obtains:

$$\rho_{xx}^{(a)} = \rho_{yy}^{(a)} = -\left(\frac{A}{2}\right)\sum_{i=1,2}\left[R_x^{(i)} D_{zy}^{(i)} - R_y^{(i)} D_{zx}^{(i)} \right] G_i\left(\frac{\varphi}{a}\right) \quad (11a)$$

$$\rho_{xy}^{(a)} = \rho_{yx}^{(a)} = \left(\frac{A}{2}\right)\sum_{i=1,2}\left[R_x^{(i)} D_{zx}^{(i)} + R_y^{(i)} D_{zy}^{(i)} \right] G_i\left(\frac{\varphi}{a}\right) \quad (11b)$$

$$\rho_{zz}^{(s)} = A\sum_{i=1,2}\left[R_x^{(i)}D_{yz}^{(i)} - R_y^{(i)}D_{xz}^{(i)}\right]G_i\left(\frac{\varphi}{a}\right) \quad (11c)$$

Symbol (a) denotes the first part of corresponding component. The components (7), (8) and (11) describe FEs which originate from π→π* transitions. The component ρ_{zz} contains two addents: $\rho_{zz}^{(s)}$, see (11c), and dipole contribution to gyrotropy, see (8), notably (Ref. [8], [9], [11]):

$$\rho_{zz}^{(d)} = \frac{A}{2}\sum_{i=1,2}R^{(i)^2}\frac{\partial G_i}{\partial q}|_{q=\frac{\varphi}{a}} \quad \rho_{zz} = \rho_{zz}^{(d)} + \rho_{zz}^{(s)}. \quad (12)$$

The quantity $\rho_{zz}^{(d)}$ describes sigmoidal lineshapes in CD spectra.

The second part of components (11a,b) appears in calculations with parallel to helical axis ẑ components of transition dipoles which concern n→π* transitions. Then transition dipoles for the two excitations i=1,2 in each pair parallel and stacking coupling allows transitions 1⇆2. The parts of Hamiltonians of type (3)-(4) are valid also but Hamiltonians contain the terms V_5 $(T_{3,n\pm1}^{+}T_{1,n} + T_{1,n}^{+}T_{3,n\pm1})$. In k-space one reads:

$$\hat{H} = \sum_{k,i=3,4}\left\{\left(E_i + 2V_i\cos(ka)\right)T_{ik}^{+}T_{ik} + 2V_5\cos(ka)\left(T_{3k}^{+}T_{4k} + T_{4k}^{+}T_{3k}\right)\right\} \quad (13)$$

Naturally the quantities E_i, V_i are not the same as eq. (4). The excitonic spectra, corresponding to Hamiltonian (13) are the following:

$$E_z(k) = \left(\frac{1}{2}\right)\left\{\begin{matrix}E_3 + E_4 + 2(V_3 + V_4)\cos(ka) \\ \pm\sqrt{\left[E_3 - E_4 + 2(V_3 - V_4)\cos(ka)\right]^2 + 16V_5^2 cos^2(ka)}\end{matrix}\right\} \quad (14)$$

In calculations of tensors εij and ρ we need components $R_z^{(1)}, R_x^{(2)}$ of transition dipoles and each of them is the same for all values of n, see(2). By using formulas (5), (10) and (6) in calculations of Green functions one obtains at k=0, which is the case of parallel to helical axis dipoles:

$$\Delta\varepsilon_{zz} = -\frac{A}{2\Delta_z(k=0)}\left[R_z^{(1)^2}a_4(0) + R_z^{(2)^2}a_3(0) + 4V_5R_z^{(1)}R_z^{(2)}\right], \quad (15a)$$

$$\Delta_z(k=0) = a_3(0)a_1(0) - 4V_5^2;\ a_i(k) = \hbar\omega - E_i - 2V_i\cos(ka);(i=3,4) \quad (15b)$$

$$\rho_{xx}^{(b)} = \rho_{yy}^{(b)} = \frac{A}{2_z(k=0)}\left\{\begin{matrix}R_z^{(1)}\left[\left(D_{xy}^{(1)} - D_{yx}^{(1)}\right)a_4(0) + \left(D_{xy}^{(2)} - D_{yx}^{(2)}\right).2V_5\right] \\ +R_z^{(2)}\left[\left(D_{xy}^{(1)} - -D_{yx}^{(1)}\right).2V_5 + \left(D_{xy}^{(2)} - D_{yx}^{(2)}\right)a_3(0)\right]\end{matrix}\right\} \quad (16a)$$

$$\rho_{xy}^{(b)} = -\rho_{yx}^{(b)} = -\frac{A}{2_z(k=0)}\left\{\begin{matrix}R_{iiiiii}^{(1)}\left[\left(D^{(1)} + D^{(1)}\right)a_4(0) + \left(D^{(2)} + D^{(2)}\right).2V_5\right] \\ +R_{iiiiii}^{(2)}\left[\left(D^{(1)} + D^{(1)}\right).2V_5 + \left(D^{(2)} + D^{(2)}\right)a_3(0)\right]\end{matrix}\right\} \quad (16b)$$

Linear absorption spectra can be calculated as imaginary parts of expressions (7), (15) in which we replace ω→ω + iδ. Then excitonic spectra can be found as zeros of the real parts of denominators. The CD spectra represent the zeros of the real parts of denominators at the same replacement in expression

$$\rho^{(\theta)} = \rho_{xx}sin^2\theta + \rho_{zz}cos^2\theta \quad (17)$$

in which θ is the angle between helical axis and direction of light beam.

For completion we calculate functions *ε(ω)*and *ρ(ω)* in the isotropic solution of such double helices with concentration n_0 in unit volume at arbitrary orientation of the helical axis:

$$\Delta\varepsilon(\omega) = \frac{C}{3}n_0\left[2\Delta\varepsilon_{xx} + \Delta\varepsilon_{zz}\right] \quad (18a)$$

$$\rho(\omega) = \frac{C}{3}n_0\left[\rho_{zz}^{(d)} + \left(2\rho_{xx}^{(a)} + \rho_{zz}\right) + 2\rho_{xx}^{(b)}\right] \quad (18ba)$$

in which C depends on units.

The last addend in (18b) contains antisymmetrical part $D_{xy}^{(i)} - D_{yx}^{(i)}$ which is $M_z^{(i)}$ component of transition magnetic dipole moments. Correspondingly sum $2\rho_{xx}^{(a)} + \rho_{zz}^{(s)}$, see (11a,c) contains the antisymmetrical parts $D_{yz}^{(i)} - D_{zy}^{(i)}$ and $D_{xz}^{(i)} - D_{zx}^{(i)}$ which are the components M_x and (-M_y) of transition magnetic moment. So this sum can be represented as:

$$\sum_{i=1,2}AG_i\left(\frac{\varphi}{a}\right)\left[R_x^{(i)}M_x^{(i)} + R_y^{(i)}M_y^{(i)}\right]$$
$$= \sum_{i=1,2}A\left\{\begin{matrix}G_i\left(\frac{\varphi}{a}\right)\left(R_\perp^{(i)}.\vec{M}_\perp^{(i)}\right) + \\ \frac{1}{2\Delta_z(k=0)}\left[\begin{matrix}R_z^{(1)}M_z^{(1)}a_4(0) + R_z^{(2)}M_z^{(2)}a_{43}(0) \\ +2V_5(R_z^{(1)}M_z^{(2)} + R_z^{(12)}M_z^{(1)})\end{matrix}\right]\end{matrix}\right\} \quad (18c)$$

Dipole contribution to gyrotropy, expressed with $\rho_{zz}^{(d)}$, is active in isotropic solutions also.

FEs in model of self-complementary co-polymers

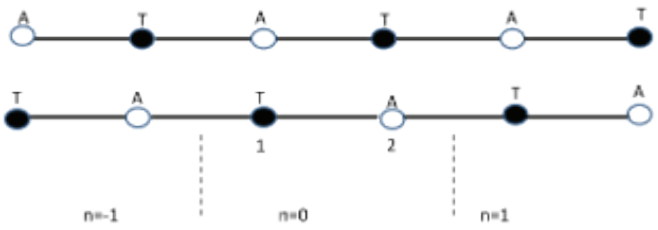

Figure 2. *Scheme of self-complementary co-polymer with bases A and T. n-number of two- pairs unit cell. (1,2)-number of the pair in each cell n*

The scheme of our model B is represented on Figure 2. The angle of rotation and the step distance are the same as model A. The unit cell contains two (AT) pairs and the distance of equivalent pairs along helical axis is 2a. The electronic excitations of each pair and their transition moments have been introduced in the previous section. We use the operators of annihilation T_{11},T_{21};$T_{12,}$ T_{22} in which the second index denotes number of the step in unit cell (Figure 2).

Treating the excitations with transition dipoles perpendicular to the helical axis ẑ we note again the absence of inter-pair coupling FEs1⇆FEs2, see the reasons in Section 2. We use as transfer parameters F_i, i=1,2, for transitions of (FE_i) between the neighbor pairs. In Hamiltonian appear the terms

$$\sum_{n,i=1,2}F_i\left\{T_{i1}^{+}(n)\left[T_{i2}(n) + T_{i2}(n\pm1)\right] + h.c\right\} \quad (19)$$

In k-space one obtains:

$$\hat{H} = \sum_{\substack{k \\ i=1,2}}\left[E_i + 2V_i\cos(k.2a)\right]\left[T_{i1}^{+}(k)T_{i1}(k) + T_{i2}^{+}(k)T_{i2}(k)\right]$$
$$+\sum_{\substack{i=1,2 \\ k}}F_i\left[T_{i1}^{+}(k)T_{i2}(k)\left(1 + e^{i2ka}\right) + h.c\right] \quad (20)$$

The excitonic spectra are splitting (Davydov),

$$W_i(k) = E_i + 2V_i\cos(k.2a) \pm 2F_i\cos(ka);i=1,2 \quad (21)$$

Using formulas (5)-(6) for model B with two pairs in unit cell we obtain after lengthy calculations taking into account that in formula (2) the arguments are [n(π+φ)] instead of [nφ]:

$$\Delta\varepsilon_{xx} = \Delta\varepsilon_{yy} = -\frac{A}{2}\sum_{i=1,2} R^{(i)^2} G_i(q)\big|_{q=\frac{\varphi}{a}} \quad (22)$$

in which $\vec{R}^{(i)}$ is transition dipole moment for excitation i=1,2 and $G_i(q)$ is corresponding Fourier component of Green function (see Appendix):

$$G_i(q) = \frac{1}{\hbar\omega - E_i - 2V_i\cos(2aq) + 2F_i\cos(aq)}; (i=1,2) \quad (23)$$

We see that only one level (21) is active in linear absorption (the level with sign "-"). Calculations of the component $\Delta\varepsilon_{xy}$, as well as the components "a" of gyration tensor ρ, give again the formulas (8) and (11) but with expressions (23) for $G_i(q)$ multiplied by 2. Now we turn to transitions n→π* with transition dipole moment parallel to the axis. One introduces again operators $S_{il}\left(S_{il}^{+}\right)$ in which first index denotes number of excitation and the second index is number of the step in unit cell. As a result of antiparallel strands of double helix the transition dipole moments of each of excitations for i=3 and i=4, being collinear have opposite directions. Thus we are interested in dipole active operators, notably:

$$Z_{in} = \frac{1}{\sqrt{2}}\left(S_{i1}(n) - S_{i2}(n)\right), i = 3,4 \quad (24)$$

(the sum $S_{i1}(n) + S_{i2}(n)$ is nonactive) with transition dipoles $R_i^{(z)} = \sqrt{2}R_i^{(z)}(0), R_i^{(z)}(0)$ is transition dipole moment at i=3 for all values of n. The coupling parameter of excitation i=3,4 between $S_{i3}^{(n)} \rightleftarrows S_{i4}^{(n)}$ is M_i. In the case of dipole coupling $M_i < 0$, due to the opposite directions of both transition dipoles. As it is in model A the common z-direction of transition dipoles ensures the coupling of FEs3 and FEs4. Hamiltonian $\hat{H}^{(z)}$ is as follows:

$$\hat{H}^{(z)} = \sum_{i=3,4;k}\left[E_i - M_i + 2V_i\cos(2ka)\right]Z_{ik}^{+}Z_{ik} + \sum_k 2V_6\cos(ka)\left[Z_{3k}^{+}Z_{4k} + Z_{4k}^{+}Z_{3k}\right] \quad (25)$$

in which V_6 is the transfer parameter between two neighbor pairs with change of excitation. Note that (in dipole coupling) parameters V_i as product of parallel vectors $R_i^{(z)}$ are positive but parameter V_6 can be positive and negative depending on $\left(R_3^{(z)}.R_4^{(z)}\right)$.

In calculations of component $\Delta\varepsilon_{zz}$ one obtains Green functions at k=0 and the following expression holds:

$$\Delta\varepsilon_{zz} = -\frac{A}{\Delta_z(0)}\left\{R_3^{(z)^2}\left[\hbar\omega - b_4(0)\right] + R_4^{(z)^2}\left[\hbar\omega - b_3(0)\right] + 4R_3^{(z)^2}R_4^{(z)^2}V_6\right\} \quad (26)$$

in which

$$b_i(0) = E_i - M_i + 2V_i\ ,\ \Delta_z(0) = \left[\hbar\omega - b_4(0)\right]\left[\hbar\omega - b_3(0)\right] - 4V_6^2 \quad (26a)$$

The result for components (b) of tensor ρ for antiparallel strands of double helix is a little surprising: these components are zero. Formulas (16) show the presence of the sums D_{xy} - D_{yx} and D_{xx} + D_{yy}. Dipole active operators (24) lead to the differences for i=3 and i=4:

$$\left(D_{xy,1}^{(i)} - D_{yx,1}^{(i)}\right) - \left(D_{xy,2}^{(i)} - D_{yx,2}^{(i)}\right) \text{ and } \left(D_{xx,1}^{(i)} + D_{yy,1}^{(i)}\right) - \left(D_{xx,2}^{(i)} + D_{yy,2}^{(i)}\right) \quad (27)$$

We apply equation (2) for the neighbor step of the helix (n=1) with argument [n(π+φ)] instead of [nφ]. One obtains that $\left(D_{xy}^{(i)} - D_{yx}^{(i)}\right)$ are the same for all values of n (and the same for $(D_{xx}^{(i)} + D_{yy}^{(i)})$. Thus differences (27) and therefore components (b) of gyration tensor ρ are zero.

Hence, in the case of regular antiparallel strands of double helix (model B) the CD does not exist. The CD signal is caused by other excitations (not n→π*).

Calculations of the tensors ε(ω) and ρ(ω) in isotropic solutions of self-complementary co-polymers give the results as formulas (18) but part $2\rho_{xx}^{(b)}$ is zero. Corresponding Green functions $G_i(q)$ are given with formula (23).

Approximate connection between excitations of the pair and of the separate complementary bases

In this section we consider the coupling of the electronic excitations of the separate bases and their connection with electronic excitations of the pair.

Let electronic excitation of the base A has excitation energy E_a and transition dipole moment $\vec{p}_a$ and correspondingly – the same quantities for base T are ET and $\vec{p}_T$. We suppose the possibility to describe the excitations of the pair as a result of coupling of the excitations of two bases with operators of annihilation (A,T). Hamiltonian of the pair is:

$$\hat{H} = E_\alpha A^{+}A + E_T T^{+}T + V_8\left(A^{+}T + T^{+}A\right) \quad (27)$$

where V8 is coupling parameter. Wave functions of mixed excited states will be linear combinations of both wave functions of excitations:

$$\Psi = \left(aA^{+} + bT^{+}\right)|0\rangle \quad (28)$$

Using traditional methods for treating the problem of mixed excitations one obtains the excitation energy levels of the pair of the bases:

$$\varepsilon^{\pm} = \frac{1}{2}\left[E_a + E_T \pm \sqrt{\left(E_a - E_T\right)^2 + 4V_8^2}\right] \quad (29)$$

Than we obtain for coefficients a and b in (28) the following expressions which correspond to values $\varepsilon^{\pm}$:

$$a_{\pm} = \frac{V_8}{\sqrt{V_8^2 + (\Delta \mp R)^2}} \quad b_{\pm} = \frac{\Delta \mp R}{\sqrt{V_8^2 + (\Delta \mp R)^2}} \quad (30)$$

where $\Delta = \frac{(E_a - E_T)}{2}$, $R = \sqrt{\Delta^2 + V_8^2}$ and $a_{\pm}^2 + b_{\pm}^2 = 1$

Transition dipole moments of the excitations (29) are correspondingly:

$$\vec{p}_{\pm} = a_{\pm}\vec{p}_a + b_{\pm}\vec{p}_T \quad (31)$$

The approximation consists in hypothesis for relatively separate excitations of the two bases supposing their weak or medial coupling.

Conclusions

In this study we use concept for Frenkel excitons as electronic excitations of the pairs of complementary bases (as it is used in preliminary communication [12]). The excitations are transferred in double helical polymers of type B-DNA. The applied methodics are well known in explorations of FEs transferred in condensed matter structures. DNA-molecule is the biggest one and the approaches for excitations in organic solids (see Ref. [7]) can be productive. Our basic concept to consider as fundamental the excitations of the pairs, not of their complementary bases (not pronounced now first) is more natural and our formalism demonstrates its advantages. Limitations of models of regular structures do not allow to describe transferred excitations in real DNA molecules with given sequences of the pairs. Nevertheless, the regular

structures can be useful as models of double helices not only treating of linear absorption and CD spectra but also describing interaction of DNA molecules with other organic structures. We emphasize on possibilities to treat more complicated models with three or more electronic excitations of the pair with close energy levels, as well as to the study vibronic spectra of double helical structures as coupling of FEs and vibrations of the pair as a whole.

Our results on FEs-spectra and of frequency dependence of linear absorption and CD spectra are applicable in interpretation of UV-spectra of double helices which is more difficult than the spectra of crystals due to the several close transitions and big width of spectral lines. We note the informativeness and different polarizations of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ spectra. The absence of optical activity and CD for $n \rightarrow \pi^*$ transitions in model B is an interesting result which may be seen even in the spectra of non-regular double helices.

Another possible direction of the studies is also regular double helical polymers with different pairs of complementary bases.

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Appendix

In Appendix we consider the scheme of calculations of component $\Delta\varepsilon_{xx}$ using Green functions method.

- By using formulas (2) and (5) one obtains in model A:

$$\Delta\varepsilon_{xx} = -A\sum_{\substack{nm \\ i=1,2}} P_x^{(i)}(n)\,P_x^{(i)}(m)\,e^{-ik(n-m)} \tag{A.1}$$

in which

$$\vec{P}_x^{(i)}(n) = R^{(i)}\cos(n\varphi+\theta)\left(T_{in}+T_{in}^{+}\right) \tag{A.2}$$

where θ is the angle between transition dipole vector *Pi (n = 0)* and axis $\widetilde{X}$

Hence

$$\Delta\varepsilon_{xx} = -A\sum_{i=1,2} R^{(i)^2}\sum_{nm,k_1}\cos(n\varphi+\theta)\cos(m\varphi+\theta)e^{-ik(n-m)a}$$

$$<0\,|\,T_{in}(t)\,T_{im}^{+}(0)\,0> \tag{A.3}$$

$$=-\left(\frac{A}{2}\right)\sum_{i=1,2} R^{(i)^2}\sum_{nm,k_1}\begin{bmatrix}\cos(n-m)\varphi \\ +\cos\left[(n+m)\varphi+2\theta\right]\end{bmatrix}e^{i(k_1-k)(n-m)a}G_{ii}(k_1)$$

see formula (6) at i=j in k-space. The addend cos(n+m)φ is vanishing and

$$\cos(n-m)\varphi = \left(1/2\right)\left[e^{i(n-m)\varphi}+e^{-i(n-m)\varphi}\right] \tag{A.4}$$

We obtain $k_1 = k \pm \varphi/a$ (A.5)

Calculations of Green function Gii(q) at Hamiltonian (4) allow to find function (9) which is even relatively q. Formulas (A.3) – (A.5) lead to expression (7) neglecting terms of order k2 and higher. Other components of tensor $\Delta\varepsilon_{\alpha\beta}$ are calculated following the same way.

Calculations in model B are more complicated since we need Green functions with operators $T_{11}(n)$, $T_{12}(n)$ for excitations i=1 and $T_{21}(n)$, $T_{22}(n)$ for i=2. Fourier components of Green functions (6) at i,j=1,2 at Hamiltonian (20) enter the systems:

$$\left[\hbar\omega - E_i - 2V_i\cos(q2a)\right]G_{11}^{(i)}(q) - F_i\left(1+e^{2iaq}\right)G_{12}^{(i)}(q) = 1$$

$$-F_i\left(1+e^{-2iaq}\right)G_{11}^{(i)}(q) + \left[\hbar\omega - E_i - 2V_i\cos(q2a)\right]G_{12}^{(i)}(q) = 0 \tag{A.6}$$

Their solutions are as follows:

$$G_{11}^{(i)}(q) = \frac{\hbar\omega - E_i - 2V_i\cos(q2a)}{Ä(q)}\ ;G_{12}^{(i)}(q) = \frac{F_i\left(1+e^{-2iaq}\right)}{Ä(q)} \tag{A.7}$$

where

$$Ä(q) = \left[\hbar\omega - E_i - 2V_i\cos(q2a)\right]^2 - 4F_i^2\cos^2(qa) \tag{A.7a}$$

Final results (23) are obtained using similar expressions as (A.1) – (A.4) for two pairs of double helix and (A.6) – (A.7) for Green functions.