THz Oscillations in DNA Monomers, Dimers and Trimers

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Abstract— We call *monomer* a B-DNA base-pair and study electron or hole oscillations in *monomers*, *dimers* and *trimers*. We employ two Tight Binding (TB) approaches: (I) at the base-pair level, using the on-site energies of the base-pairs and the hopping parameters between successive base-pairs and (II) at the single-base level, using the on-site energies of the bases and the hopping parameters between neighboring bases. With (II), for monomers, we predict oscillations with frequency $f \approx 50$–$550\,\mathrm{THz}$. With (I), for dimers, we predict oscillations with $f \approx 0.25$–$100\,\mathrm{THz}$, for trimers made of identical monomers $f \approx 0.5$–$33\,\mathrm{THz}$. In other cases, the oscillations may be not strictly periodic, but Fourier analysis shows similar frequency content. For dimers, we compare approaches (I) and (II). Finally, we present calculations with (III) Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) for the adenine-thymine (A-T) and the guanine-cytosine (G-C) base-pairs. It seems that a non conventional source or receiver of electromagnetic radiation with f from fractions to THz to just below PHz could be envisaged.

1. INTRODUCTIONCARRIER

oscillations within "molecular" systems have been sporadically presented in the literature. Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) [1] simulations predicted oscillations ($\approx$ 0.1-10 PHz) within p-nitroaniline and FTC chromophore [2], zinc porphyrin, green fluorescent protein chromophores and adenine-thymine base-pair [3]. In a simplified single-stranded helix of 101 bases, a collinear uniform electric field induces THz Bloch oscillations [4]. Single and multiple charge transfer within a typical DNA dimer in connection to a bosonic bath, where each base-pair is a single site, has been studied [5], too.

Here we call *monomer* a B-DNA base-pair and study carrier oscillations in *monomers, dimers and trimers*. We assume that isolation of a few consecutive B-DNA base-pairs is possible, e.g. by connecting at the boundaries moieties with very small transfer integrals with our segment. We employ two Tight-Binding (TB) approaches: (I) at the base-pair level using the on-site energies of the base-pairs and the hopping parameters between successive base-pairs [6, 7] and (II) at the single-base level using the on-site energies of the bases and the hopping parameters between neighboring bases. The TB parameters can be found in Refs. [6–9]. We solve the system of (I) N or (II) $2N$ coupled differential equations to determine the spatiotemporal evolution of an extra carrier (electron or hole) along a N base-pair DNA segment. Carriers move either between the HOMOs or between the LUMOs of the relevant sites [(I) base-pairs, (II) bases]. The resulting oscillations are $\approx$ in the THz domain, a region of intense research [10]. We also perform calculations with (III) RT-TDDFT for the adenine-thymine (A-T) and the guanine-cytosine (G-C) base-pairs. In Section 2 we outline our TB [(I) and (II)] and RT-TDDFT [(III)] approaches. Our results for monomers, dimers and trimers are presented in Sections 3, 4 and 5, respectively. In Section 6 we state our conclusions.

2. THREE APPROACHESACCORDING

to TB approach (I) [description at the base-pair level] the HOMO or LUMO wave function of a given DNA segment, made of N base-pairs, $\Psi_{DNA}(\mathbf{r},t)$, is considered as a linear combination of the base-pair wave functions $\Psi^{\mu}_{bp}(\mathbf{r})$ with time-dependent coefficients

$$\Psi_{DNA}(\mathbf{r},t) = \sum_{\mu=1}^{N} A_{\mu}(t)\ \Psi^{\mu}_{bp}(\mathbf{r}). \tag{1}$$

$|A_{\mu}(t)|^2$ gives the probability of finding the carrier (hole for HOMO, electron for LUMO) at base-pair μ. The time evolution of the coefficients $A_{\mu}(t)$ obeys the system of equations [8]

$$i\hbar\frac{dA_{\mu}}{dt} = E^{\mu}A_{\mu} + t^{\mu,\mu-1}A_{\mu-1} + t^{\mu,\mu+1}A_{\mu+1}, \tag{2}$$

where $E^{\mu}, \mu = 1, 2, \ldots N$ are the HOMO or LUMO on-site energies of the base-pairs, and $t^{\mu,\mu'}$ are the HOMO or LUMO hopping integrals between two nearest neighboring base-pairs.

According to TB approach (II) [description at the single-base level] $\Psi_{DNA}(\mathbf{r}, t)$ is derived from the single-base wave functions, according to the expression

$$\Psi_{DNA}(\mathbf{r}) = \sum_{\mu=1}^{N} [A_{\mu}(t)\Psi_{b}^{\mu,1}(\mathbf{r}) + B_{\mu}(t)\Psi_{b}^{\mu,2}(\mathbf{r})] \tag{3}$$

where $\Psi_{b}^{\mu,i}, i = 1, 2$ and $\mu = 1, 2, \ldots N$, is the wave function of the base at the μ-th base-pair and in the i-th strand. $|A_{\mu}(t)|^2$, $|B_{\mu}(t)|^2$ give the probability to find the carrier at the base of strand 1 and 2, respectively, of the μ-th base-pair. In this case, the system of equations is [8]

$$i\hbar\frac{dA_{\mu}}{dt} = E^{\mu,1}A_{\mu} + t^{\mu,1;\mu,2}B_{\mu} + t^{\mu,1;\mu-1,1}A_{\mu-1} + t^{\mu,1;\mu+1,1}A_{\mu+1} + t^{\mu,1;\mu-1,2}B_{\mu-1} + t^{\mu,1;\mu+1,2}B_{\mu+1}, \tag{4}$$

$$i\hbar\frac{dB_{\mu}}{dt} = E^{\mu,2}B_{\mu} + t^{\mu,2;\mu,1}A_{\mu} + t^{\mu,2;\mu-1,2}B_{\mu-1} + t^{\mu,2;\mu+1,2}B_{\mu+1} + t^{\mu,2;\mu-1,1}A_{\mu-1} + t^{\mu,2;\mu+1,1}A_{\mu+1}. \tag{5}$$

$E^{\mu,i}$ are the HOMO or LUMO on-site energies of the base at the μ-th base-pair and in the i-th strand, and $t^{\mu,i;\mu',i'}$ are the HOMO or LUMO hopping parameters between neighboring bases, i.e., between (a) two successive bases in the same strand, (b) complementary bases that define a base-pair, and (c) diagonally located bases of successive base-pairs. To determine the temporal and spatial evolution of electrons or holes along a N base-pair DNA segment, we solve the system of (I) N or (II) $2N$ coupled differential equations with the eigenvalue method [6, 7, 11].

RT-TDDFT is a DFT-based approach for the explicit propagation of the coupled effective single-particle time-dependent Kohn-Sham (TDKS) equations in time. Real-time simulations can be used to compute not only spectroscopic properties (e.g., absorption spectra), but also the time and space-resolved electronic response to arbitrary external fields. Within NWChem computational chemistry package [1], the calculation starts with the computation of the ground state single-particle reduced density matrix $\mathbf{P}$, whose time evolution is governed by the von Neumann equation (in atomic units)

$$i\frac{\partial \mathbf{P}}{\partial t} = [\mathbf{F}(t), \mathbf{P}(t)]. \tag{6}$$

$\mathbf{F}$ is the time-dependent Fock matrix. The Magnus propagator with a two-step predictor-corrector scheme for the Fock matrix is used for the integration of Eq. (6), which is stable and conserves the density matrix idempotency. At the end of each time step the resulting time-dependent observables (e.g., fragment charge, dipole moment) are computed from the calculated density matrix.

3. MONOMERSWE

used Approach (II), supposing that initially we place the carrier at one of the bases. We can prove that an extra hole or electron oscillates between the bases with frequencies (or periods)

$$f = \frac{1}{T} = \frac{\sqrt{(2t)^2 + \Delta^2}}{h}. \tag{7}$$

t is the hopping integral between the complementary bases and Δ is the energy gap between the on-site energies of the complementary bases. Our results for A-T and G-C, both for holes and electrons, are shown in Fig. 1, with parameters from Ref. [8] ("HKS parametrization") and from Ref. [9] ("MA parametrization"'). For HKS parametrization, $f \approx 50$–$200\,\mathrm{THz}$ ($T \approx 5$–$20\,\mathrm{fs}$), for MA parametrization, $f \approx 250$–$550\,\mathrm{THz}$ ($T \approx 2$–$4\,\mathrm{fs}$). These ranges correspond to wavelength $\lambda \approx 545\,\mathrm{nm}$–$6000\,\mathrm{nm}$, i.e., from visible to near-infrared and mid-infrared. The maximum transfer percentage p [$\max(|B_1(t)|^2)$ for initial conditions $A_1(0) = 1, B_1(0) = 0$] is very small in all cases: the carrier is not very likely to be transferred between the monomer bases. The pure maximum transfer rate pf is also very small in all cases.

We also performed semi-ab initio simulations [12]. Initially, for each (neutral) base-pair, we optimized geometry with Cs symmetry constraint at BNL ($\mu = 0.3$)/6-31G* level of theory. Then, we obtained the initial state through a Constrained DFT calculation [13], with the constraint of an extra carrier at a specific base. Finally, RT-TDDFT computed the time evolution from this initial

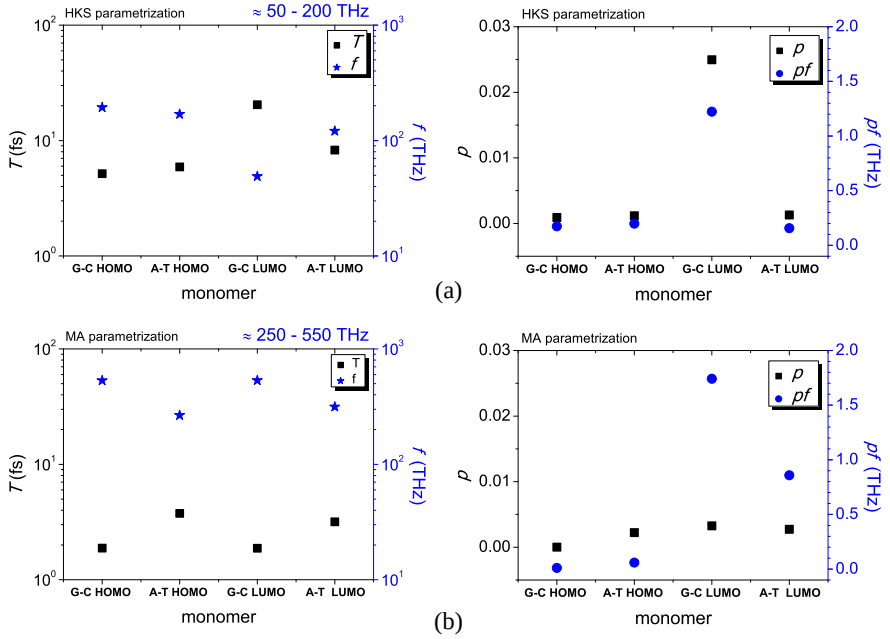

Figure 1: Charge oscillations in A-T and G-C according to the single-base approach (II). (a) TB parameters from Ref. [8] (HKS parametrization). (b) TB parameters from Ref. [9] (MA parametrization).

state, for $t = 1500$ a.u., of fragment charge and total (base-pair) dipole moment at each direction. We extracted oscillation frequencies by FFT analysis from the component of dipole moment parallel to the inter-base axis. Preliminary results indicate one or two major frequencies in the THz range (25–70 THz, 175–740 THz) and one narrow band at the PHz range (2.5–3.5 PHz). THz oscillations are generally predominant, with the exception of G-C monomer when the extra electron (hole) is initially placed on Cytosine (Guanine). The ultrafast oscillations in the PHz range appear to be slightly above the absorption peak of the neutral A-T base pair [3].

4. DIMERSLET

us denote by X_{compl} (Y_{compl}) the complementary base of $X(Y)$. The notation YX means that the bases Y and X of two successive base-pairs are located at the same strand in the direction $5' - 3'$. X-X_{compl} is the one base-pair and Y-Y_{compl} is the other base-pair, separated and twisted by 3.4 Å and 36°, respectively, relatively to the first base-pair. Y and X can be either guanine (G), adenine (A), cytosine (C), or thymine (T).

With approach (I) we proved that the carrier movement in all dimers is strictly periodic [6, 7, 11] and the frequencies (or periods) are given by Eq. (7), where, now t is the hopping integral between the base-pairs and Δ is the energy gap between the on-site energies of the base-pairs. Using the TB parameters from Ref. [6], we found that $f \approx 0.25$–100 THz ($T \approx 10$–4000 fs). The maximum transfer percentage $p = 1$ for dimers made of identical monomers; $p < 1$ for dimers made of different monomers. Using approach (II), one cannot strictly determine periodicity in the carrier movement between the four bases. Hence, f, T, p, and pf cannot be defined, but Fourier analysis shows similar frequency content in the THz domain. Approaches (I) and (II) allow us to determine the mean probability to find the carrier at a site [base-pair for (I), base for (II)]. Specifically: (a) Carrier transfer is large in dimers made of identical monomers; it is very small in dimers made of different monomers. (b) For dimers made of identical monomers, if purines are crosswise to purines, the carrier changes strand (from strand 1 to strand 2 or vice versa), while if purines are on the same strand, the carrier is transferred through the strand it was initially placed at. (c) For dimers made of different monomers, the carrier is transferred (albeit in small percentage) through the strand it was initially placed at. A comparison between the mean probabilities found with approaches (I) and (II) is shown in Fig. 2, using the HKS parametrization [8]. Single and multiple charge transfer within a typical DNA dimer in connection to a bosonic bath, where each base-pair is approximated by a single site, as in our TB approach (I), has been studied in Ref. [5]. In the subspace of single charge transfer between base-pairs the authors obtain a period slightly greater than 10 fs, having used a "typical hopping matrix element" 0.2 eV. If we use our Eq. (7), with $t = 0.2$ eV for

the "typical hopping matrix element" and identical dimers, i.e., difference of the on-site energies $\Delta = 0$, we obtain a period $T \approx 10.34$ fs in accordance with the dotted line in Fig. 4 of Ref. [5].

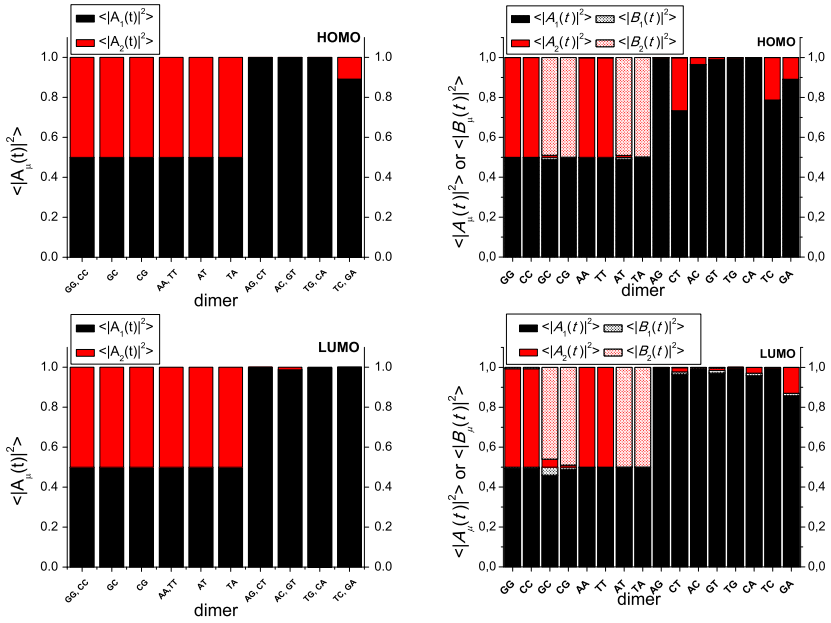

Figure 2: The mean probabilities to find an extra carrier [hole (1st row) or electron (2nd row)] at each site of a DNA dimer, as determined with (I) the base-pair approach (left column) and (II) the single-base approach (right column). For (I), the carrier is initially placed at the 1st monomer, while, for (II), it is initially placed at the base of the 1st monomer that belongs to the 1st strand. We used the HKS parametrization [8].

5. TRIMERSUSING

approach (I), we proved [6, 7] that for trimers made of identical monomers an extra carrier oscillates periodically, according to the expression

$$f = \frac{1}{T} = \frac{\sqrt{t^2 + t'^2}}{h}, \tag{8}$$

where t, t' are the hopping integrals between the base-pairs. For such trimers, when all purines are on the same strand, $t = t'$. Using the TB parameters from Ref. [6], we find that the frequencies of these oscillations are in the range $f \approx 0.5$–33 THz ($T \approx 30$–2000 fs) [7], which is narrower than for dimers. For 0 times crosswise purines, the maximum transfer percentage $p = 1$, while for 1 or 2 times crosswise purines $p < 1$ [6, 7]. For trimers made of different monomers, no periodicity can be determined, since the frequencies depend on the specific parameter values used. Hence, carrier movement may be non-periodic [6, 7]. Generally, increasing the number of monomers above three, the system becomes more complex and periodicity is lost [7]; even in the simplest cases, e.g., tetramers made of identical monomers with all the purines on the same strand, there is no periodicity [11]. Approach (II) does not allow one to strictly determine any periodicity, hence T, f, p, and pf cannot be defined. However, Fourier analysis shows similar frequency content.

6. CONCLUSIONWITH

TB approach (II), we predicted electron or hole oscillations in DNA monomers with $f \approx 50$–550 THz ($T \approx 2$–20 fs), i.e., $\lambda \approx 0.545$ μm–6 μm, from visible to near- and mid-infrared. For monomers the maximum transfer percentage p and the pure maximum transfer rate pf between the bases are very small. With TB approach (I), we predicted electron or hole oscillations in DNA dimers with $f \approx 0.25$–100 THz ($T \approx 10$–4000 fs), i.e., $\lambda \approx 3$–1200 μm, in the mid- and far-infrared. For dimers made of identical monomers $p = 1$, but for dimers made of different monomers $p < 1$. With approach (II), the carrier oscillations are not strictly periodic but the frequency content is similar to that predicted with approach (I). For the mean probabilities to find the carrier at a particular site, the two approaches give similar, complementary results. For trimers made of identical monomers the

carrier oscillates periodically with $f \approx 0.5$–$33\,\mathrm{THz}$ ($T \approx 30$–$2000\,\mathrm{fs}$) for 0 times crosswise purines $p = 1$, for 1 or 2 times crosswise purines $p < 1$. For trimers made of different monomers the carrier movement may be non-periodic but the frequency content is similar. Finally, calculations based on (III) RT-TDDFT for DNA monomers indicate one or two major frequencies in the THz range (25–70 THz, 175–740 THz) and one narrow band at the PHz range (2.5–3.5 PHz).

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