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THz and above THz electron or hole oscillations in DNA dimers and trimers

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Why study DNA electronic & charge transfer properties?

Nanotechnology:

- (self)-assembling nanocircuits

- nanodevices as a molecular wire

Biology:

- carcinogenesis and mutagenesis
  e.g. hole migration to guanine - - - direct strand breaks occur preferentially at guanines

- long-range charge transfer along DNA may be crucial for DNA damage & repair

Introduction to DNA

Charge transfer in DNA

Results for dimers

Results for trimers

Greater sequences

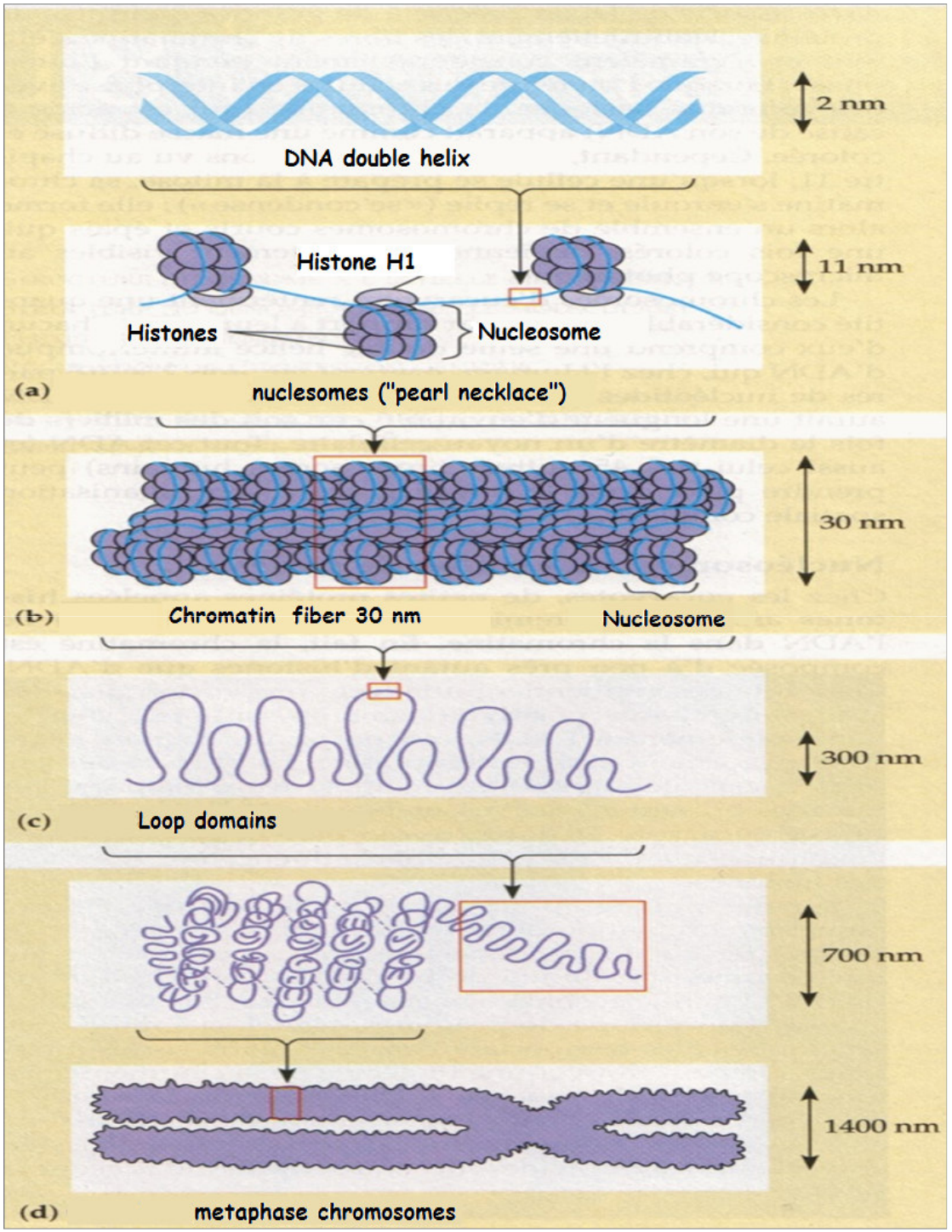
Introduction to DNA

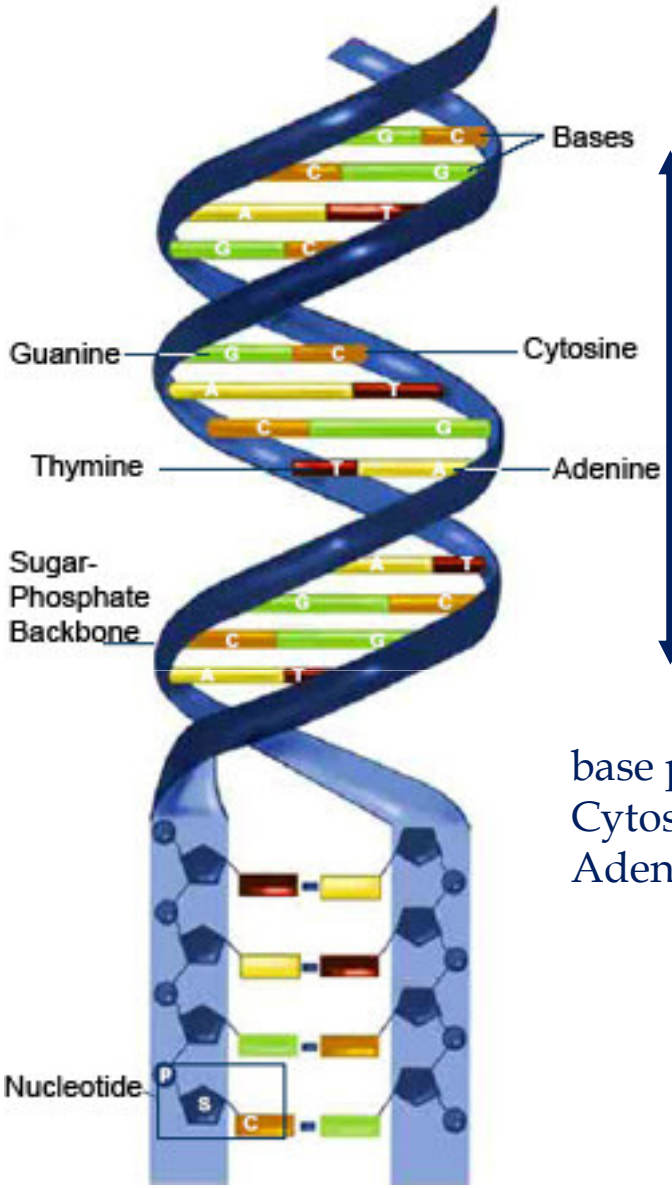
From double helix to chromosomes

Histones: proteins which package and order DNA into structural units called nucleosomes.

Chromatin: the combination of DNA, histone, and other proteins that make up chromosomes.

Metaphase chromosome: a chromosome in that stage of the cell cycle when it is most condensed and easiest to distinguish and so to study.





base pair separation
~ 3.4 Å

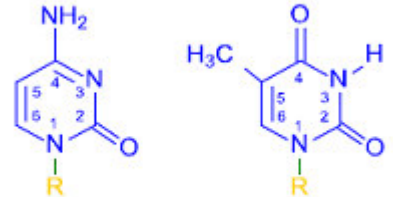
helix step ~ 34 Å

base pairs:
Cytosine <3 H bonds> Guanine
Adenine <2 H bonds> Thymine

Purines

Adenine Guanine

Pyrimidines



Cytosine Thymine

Charge transfer in DNA

From Schrödinger's equation to a Tight-Binding System of Differential Equations

Description at the base-pair level

Starting from the time-dependent Schrödinger's equation:

$$i\hbar\frac{\partial\Psi_{H/L}^{DNA}}{\partial t}=\hat{H}^{DNA}\Psi_{H/L}^{DNA}$$

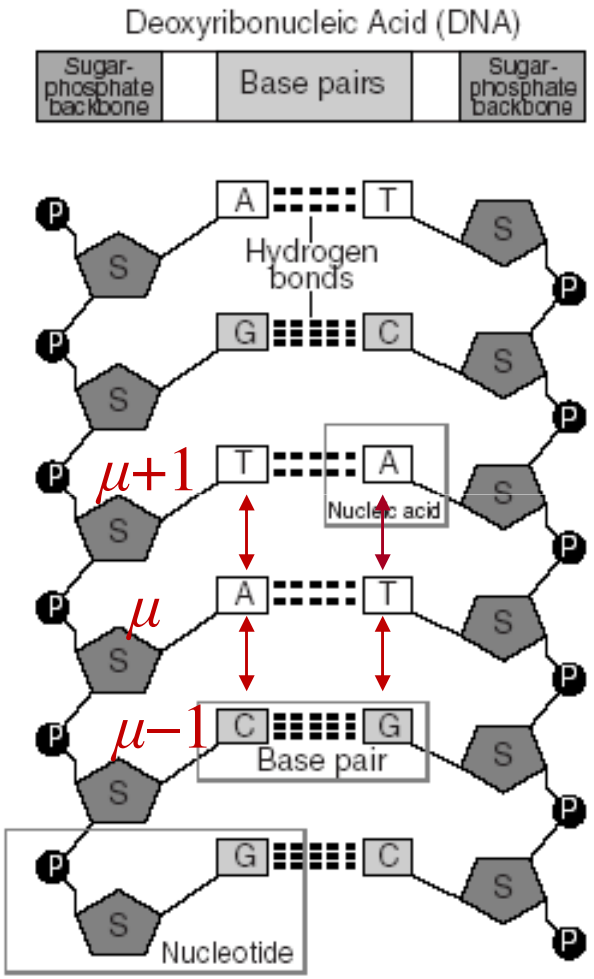
We analyze the DNA wavefunction into the bp wavefunctions:

$$\Psi_{H/L}^{DNA}(\mathbf{r},t)=\sum_{\mu}A_{\mu}(t)\Psi_{H/L}^{bp(\mu)}(\mathbf{r})$$

$|A_{\mu}(t)|^2$ probability to find the carrier at base-pair μ

we find that the time evolution of the coefficients $A_{\mu}(t)$ obeys the following system of equations:

$$i\hbar\frac{dA_{\mu}}{dt}=E_{H/L}^{bp(\mu)}A_{\mu}+t_{H/L}^{bp(\mu,\mu-1)}A_{\mu-1}+t_{H/L}^{bp(\mu,\mu+1)}A_{\mu+1}$$



$E_{H/L}^{bp}$: on-site energies of the two possible base-pairs

$t_{H/L}^{bp}$: hopping parameters for all possible combinations of successive base-pairs

HOMO and LUMO on-site energies of the base-pairs

- Calculated by various authors
- Used for the solution of the tight-binding system of equations

$$i\hbar\frac{dA_\lambda}{dt} = E_{H/L}^{bp(\lambda)}A_\lambda + t_{H/L}^{bp(\lambda;\lambda-1)}A_{\lambda-1} + t_{H/L}^{bp(\lambda;\lambda+1)}A_{\lambda+1}$$

B-DNA base-pair	A-T	G-C	reference
E_H^{bp}	-8.3	-8.0	[4]
E_L^{bp}	-4.9	-4.5	[4]
$E_{\pi-\pi^*}$	3.4	3.5	[4]
$E_H^{bp\ \text{first pr.}}$	$-$(7.8-8.2)	$-$(6.3-7.7)	[7–12]
$E_{\pi-\pi^*}^{\text{first pr.}}$	6.4	4.3-6.3	[12, 13]
$E_H^{bp\ \text{used}}$	8.3	8.0	[4]
$E_L^{bp\ \text{used}}$	-4.9	-4.5	[4]

All energies in eV

Hopping parameters between successive base-pairs

- Calculated by various authors
- Used for the solution of the tight-binding system of equations

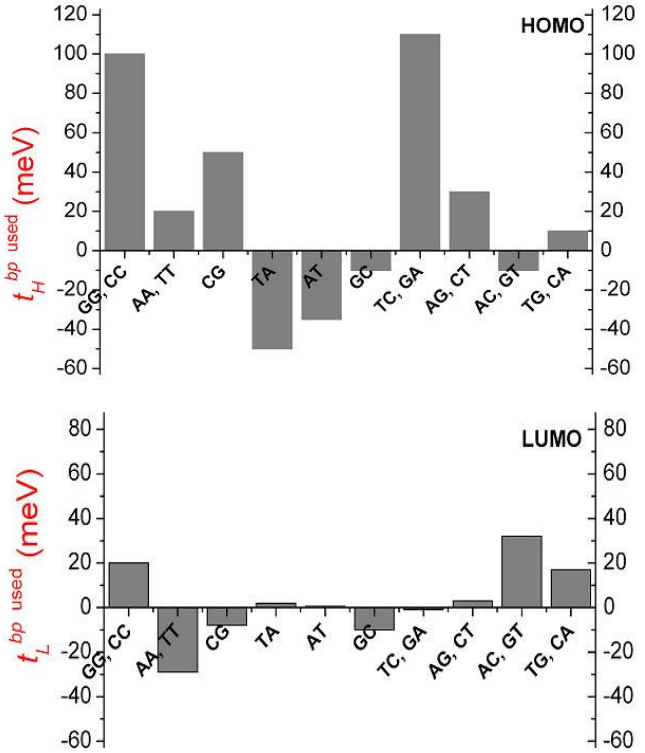
$$i\hbar\frac{dA_\lambda}{dt} = E_{H/L}^{bp(\lambda)}A_\lambda + t_{H/L}^{bp(\lambda;\lambda-1)}A_{\lambda-1} + t_{H/L}^{bp(\lambda;\lambda+1)}A_{\lambda+1}$$

- Successive base-pairs ⇔ denoted by *YX*

$$\begin{array}{lccc} & 5' & & 3' \\ \lambda & Y & - & Y_{compl} \\ \lambda' & X & - & X_{compl} \\ & 3' & & 5'\,. \end{array}$$

Base-pair sequence	t_H^{bp} [9]	$\lvert t_H^{bp}\rvert$ [19]	t_H^{bp} [8]	t_H^{bp} [20]	t_H^{bp} [21]	t_H^{bp} [22]	t_H^{bp} used	t_L^{bp} [9]	t_L^{bp} [8]	t_L^{bp} used
AA, TT	−8	26	−25	8-17	19(19)	22	20	−29	35	−29
AT	20	55			47(74)	37	−35	0.5		0.5
AG, CT	−5	25	−50		35(51)	43	30	3	35	3
AC, GT	2	26			25(38)	20	−10	32		32
TA	47	50			32(68)	52	−50	2		2
TG, CA	−4	27			11(11)	25	10	17		17
TC, GA	−79	122	−160		71(108)	60	110	−1	35	−1
GG, CC	−62	93	−140	75	72(101)	63	100	20	35	20
GC	1	22			20(32)	22	−10	−10		−10
CG	−44	78			51(84)	74	50	−8		−8

All hopping parameters in meV



General solution of the tight-binding system of equations

To solve the system:

$$i\hbar\frac{dA_\lambda}{dt} = E_{H/L}^{bp(\lambda)}A_\lambda + t_{H/L}^{bp(\lambda;\lambda-1)}A_{\lambda-1} + t_{H/L}^{bp(\lambda;\lambda+1)}A_{\lambda+1}$$

we define the vector matrix $\boldsymbol{x}(t) = \begin{bmatrix} A_1(t) \\ A_2(t) \\ \vdots \\ A_N(t) \end{bmatrix}$

Therefore:

$$\dot{\boldsymbol{x}}(t) = \widetilde{\mathcal{A}}\boldsymbol{x}(t), \quad \widetilde{\mathcal{A}} = -\frac{i}{\hbar}\begin{bmatrix} E_{H/L}^{bp(1)} & t_{H/L}^{bp(1;2)} & 0 & \cdots & 0 & 0 & 0 \\ t_{H/L}^{bp(2;1)} & E_{H/L}^{bp(2)} & t_{H/L}^{bp(2;3)} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & t_{H/L}^{bp(N-1;N-2)} & E_{H/L}^{bp(N-1)} & t_{H/L}^{bp(N-1;N)} \\ 0 & 0 & 0 & \cdots & 0 & t_{H/L}^{bp(N;N-1)} & E_{H/L}^{bp(N)} \end{bmatrix}$$

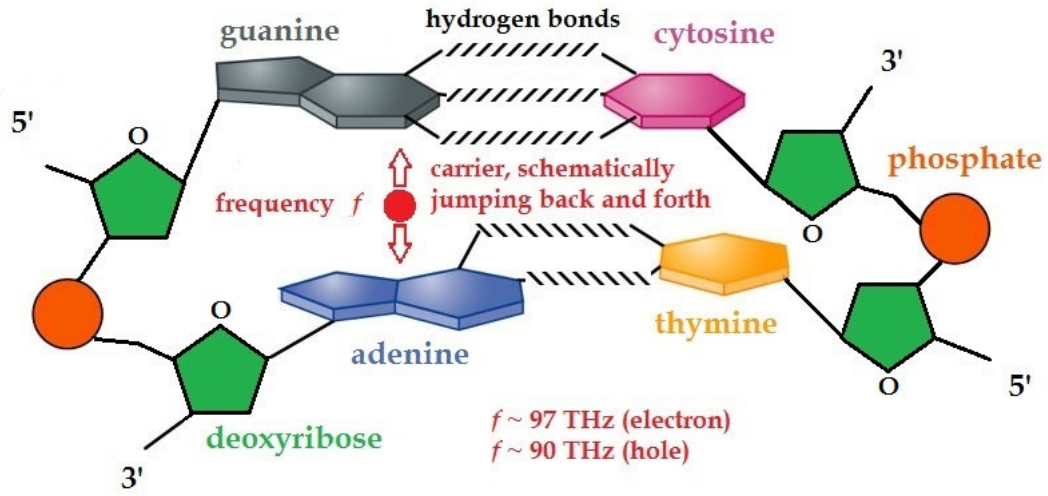
eigenvalue method, the general solution is:

$$\boldsymbol{x}(t) = \sum_{k=1}^{N} c_k \boldsymbol{v_k} e^{-\frac{i}{\hbar}\lambda_k t}$$

$\boldsymbol{v}_k$: normalized (linearly independent) eigenvectors

λ_k: eigenvalues.

Results for dimers



Dimers: solution, periods, frequencies

10 unique dimers, 6 made of identical monomers

General solution: $\vec{x}(t) = \sum_{k=1}^{2} c_k \vec{v}_k e^{-\frac{i}{\hbar}\lambda_k t}$ Initial condition: $\vec{x}(0) = \begin{bmatrix} A_1(0) \\ A_2(0) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$

Suppose $\lambda_2 \geq \lambda_1$.

It follows that:

$$f = \frac{1}{T} = \frac{\lambda_2 - \lambda_1}{h}$$

1) Dimers consisting of identical monomers (e.g. GG ≡ CC, AT):

$$f = \frac{1}{T} = \frac{2|t^{bp}|}{h}$$

(periodic carrier movement)

2) Dimers consisting of different monomers (e.g. GA ≡ TC, CT ≡ AG):

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

(periodic carrier movement)

$$\Delta^{bp} = |E^{bp1} - E^{bp2}|$$

Dimers: maximum transfer percentage, pure maximum transfer rate

Maximum transfer percentage, p: the maximum value of $|A_2(t)|^2$

$$p = \frac{(2t^{bp})^2}{(2t^{bp})^2 + (\Delta^{bp})^2}$$

1) Dimers consisting of identical monomers ($\Delta^{bp} = 0$):

$$p = 1\ (100\%)$$

2) Dimers consisting of different monomers:

$$p < 1\ (<100\%)$$

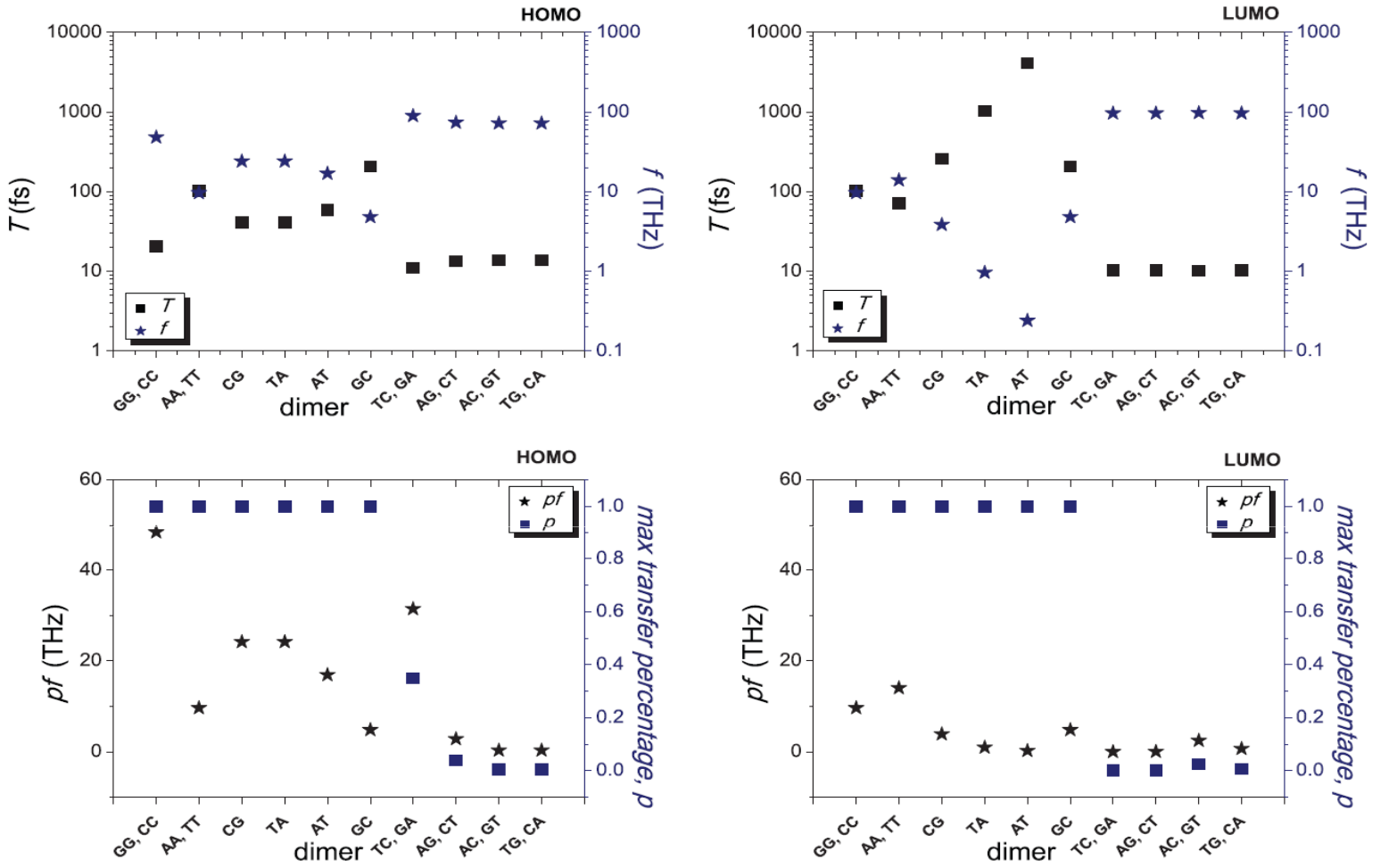
Pure maximum transfer rate: pf

$$pf = \frac{(2t^{bp})^2}{h\sqrt{(2t^{bp})^2 + (\Delta^{bp})^2}}$$

Dimers consisting of identical monomers:

$$pf = \frac{2|t^{bp}|}{h}$$

Periodic carrier transfer in base-pair dimers

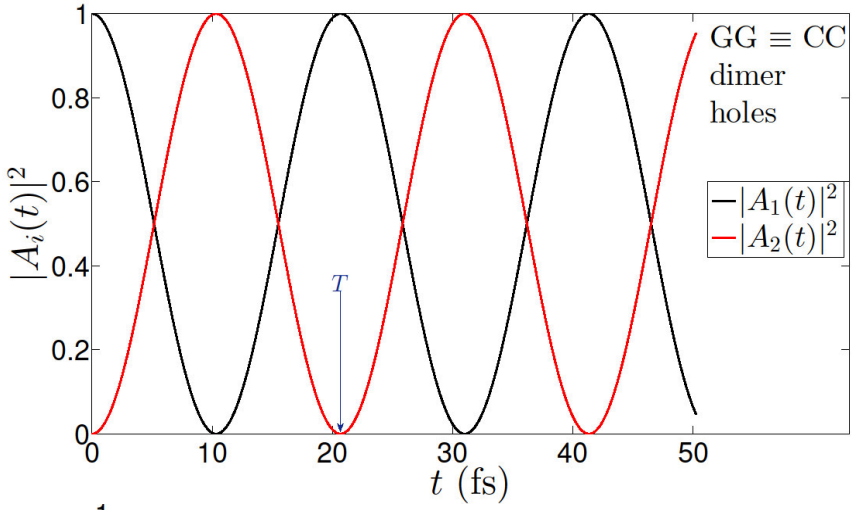


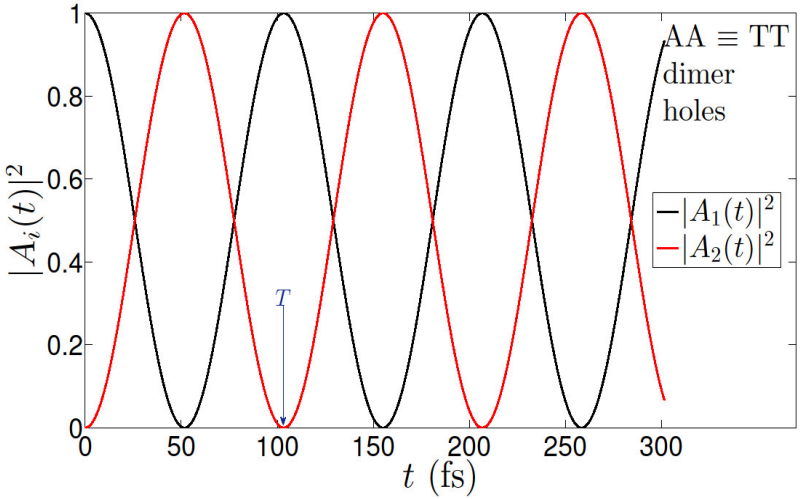
Left column: holes (HOMO) Right column: electrons (LUMO)

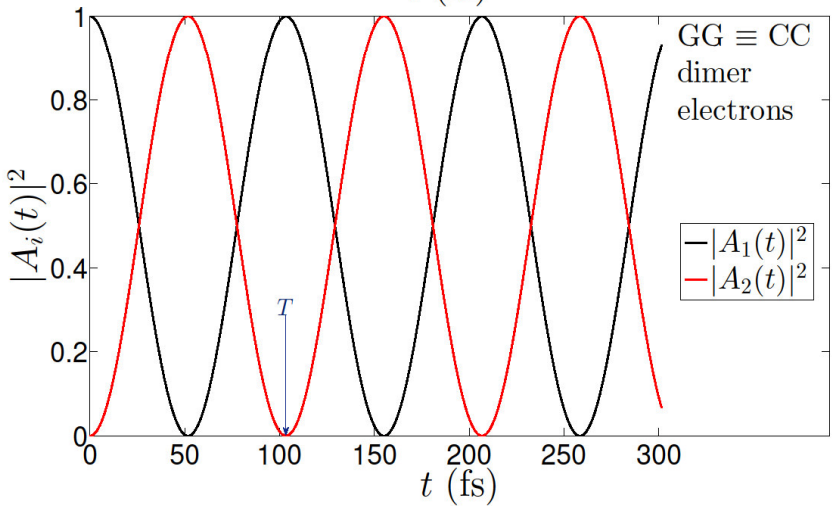
1st row: T in fs (■) , f in THz (★)

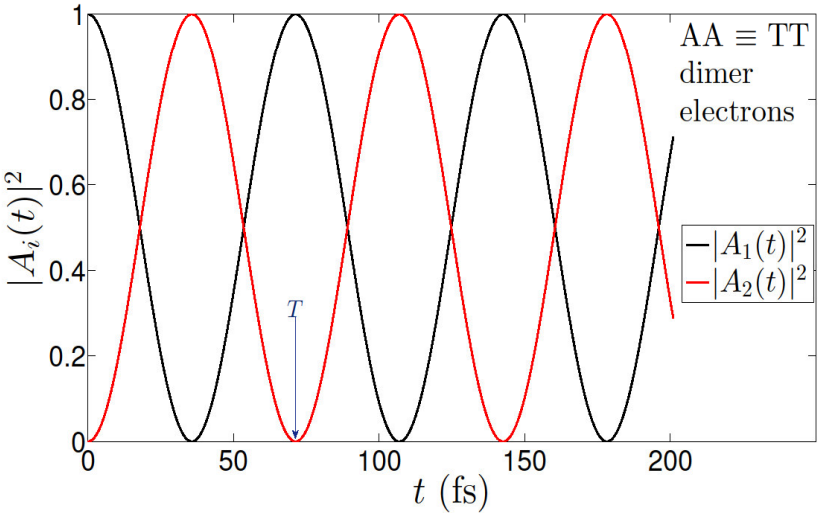
2nd row: pf in THz (★), p (■)

GG ≡ CC and AA ≡ TT dimers



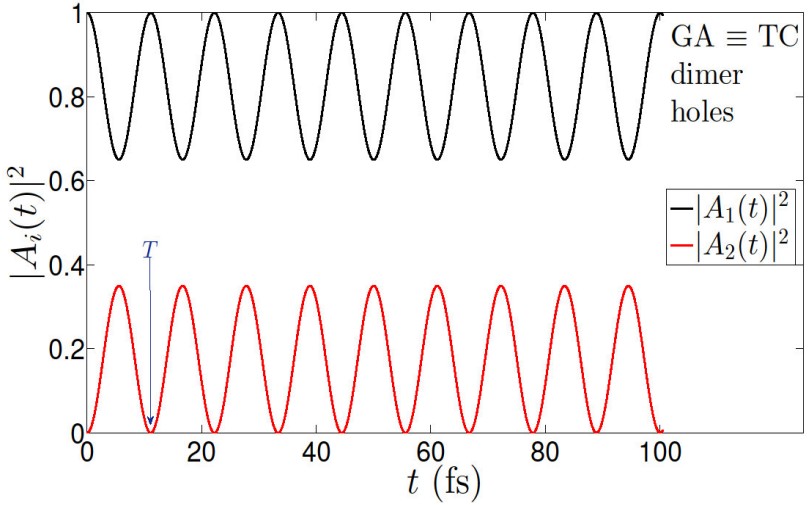


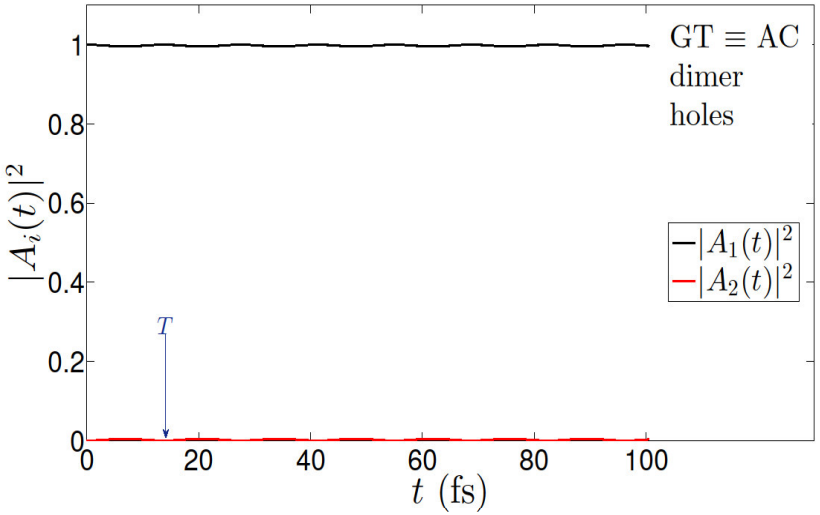


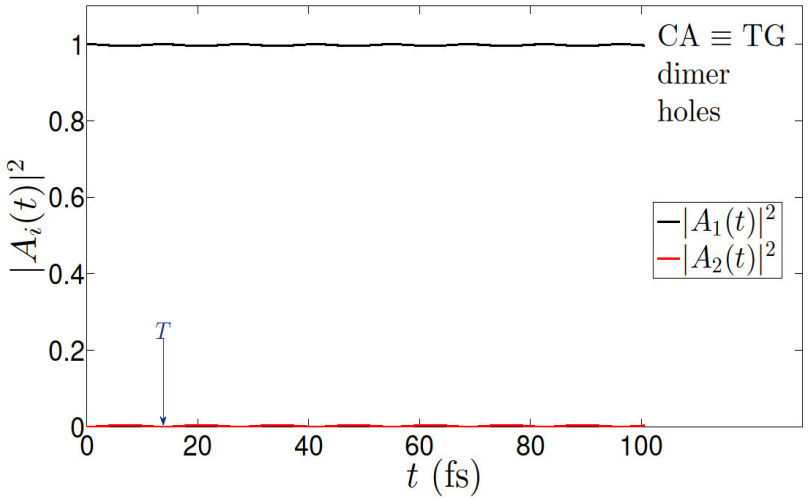


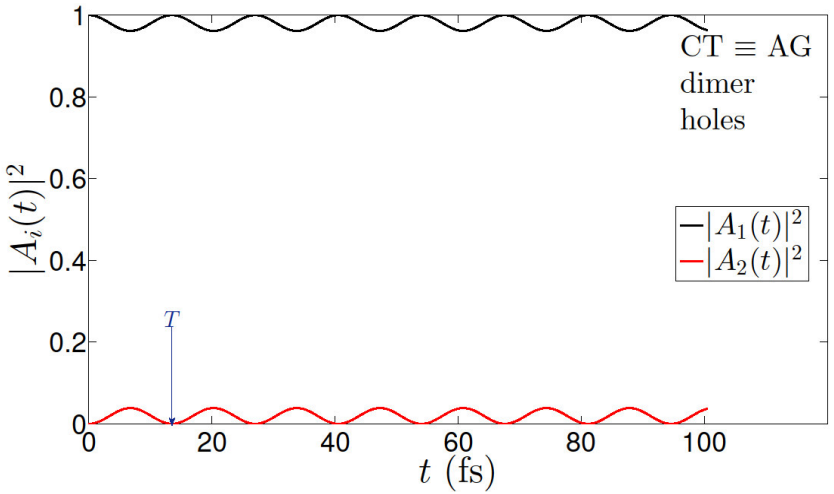
$|A_\mu(t)|^2, \mu = 1, 2$ for **hole** and **electron** transfer in GG ≡ CC and AA ≡ TT dimers. The maximum transfer percentage $p = 1$ (100%).

GA≡TC, GT≡AC, CA≡TG, and CT≡AG dimers



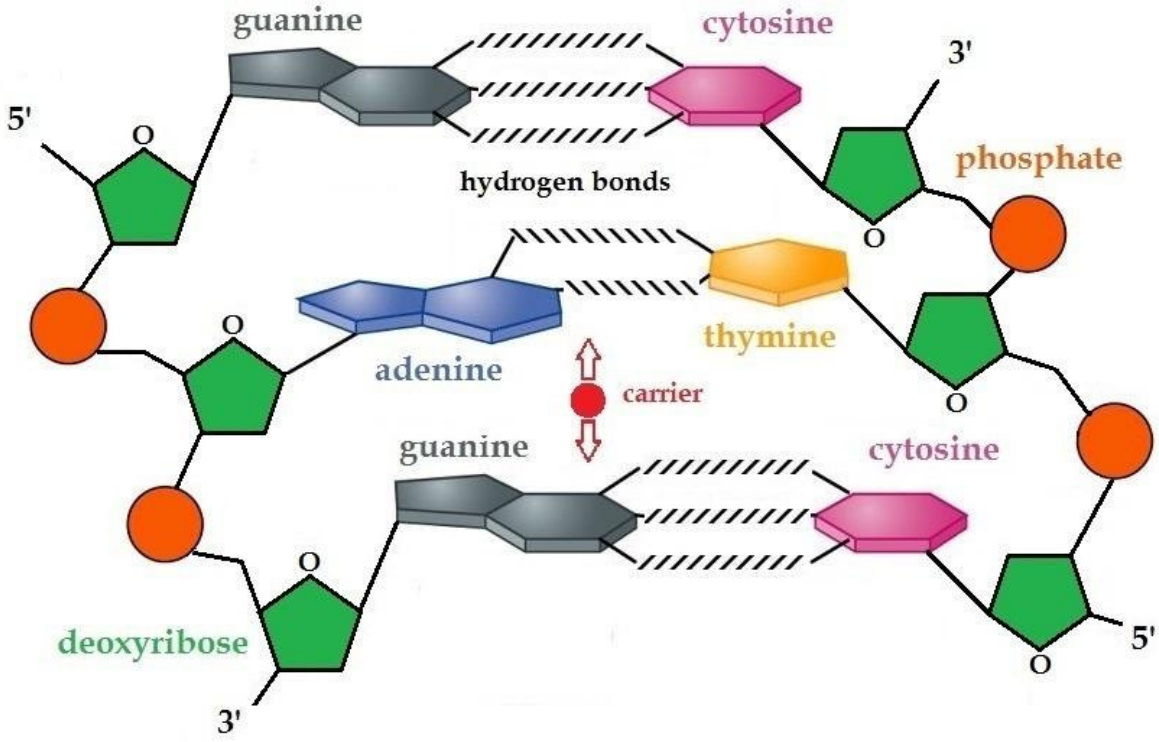






$|A_\mu(t)|^2, \mu = 1, 2$ for **hole** transfer in GA≡TC, GT≡AC, CA≡TG, and CT≡AG dimers. The maximum transfer percentage $p < 1$ (<100%).

Results for trimers



Trimers: solution, periods, frequencies

32 unique trimers, 8 made of identical monomers

General solution: $\vec{x}(t) = \sum_{k=1}^{3} c_k \vec{v}_k e^{-\frac{i}{\hbar}\lambda_k t}$ Initial condition: $\vec{x}(0) = \begin{bmatrix} A_1(0) \\ A_2(0) \\ A_3(0) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$

Suppose $\lambda_1 \leq \lambda_2 \leq \lambda_3$

It occurs that:

$$T_{21} = \frac{h}{\lambda_2 - \lambda_1}, \quad T_{32} = \frac{h}{\lambda_3 - \lambda_2}, \quad T_{31} = \frac{h}{\lambda_3 - \lambda_1}$$

Notation : $T_M = T_{M(21)} = T_{M(32)}$, $T_E = T_{E(31)}$

1) Trimers consisting of identical monomers with no crosswise purines (e.g. GGG ≡ CCC):

$$T_M = \frac{h}{t^{bp}\sqrt{2}}, \quad T_E = \frac{h}{2t^{bp}\sqrt{2}} \Rightarrow \frac{T_M}{T_E} = \frac{2}{1}$$

(periodic carrier movement)

2) Trimers consisting of identical monomers with crosswise purines (e.g. ATA ≡ TAT):

$$T_M = \frac{h}{\sqrt{t^{bp^2} + t^{bp'^2}}}, \; T_E = \frac{h}{2\sqrt{t^{bp^2} + t^{bp'^2}}} \Rightarrow \frac{T_M}{T_E} = \frac{2}{1}$$

(periodic carrier movement)

3) Trimers consisting of different monomers (e.g. GAC ≡ GTC):

$$T_{M(32)} = \frac{h}{\frac{\Delta^{bp}}{2} + \sqrt{\frac{\Delta^{bp^2}}{4} + t^{bp^2} + t^{bp'^2}}}, \; T_{E(31)} = \frac{h}{2\sqrt{\frac{\Delta^{bp^2}}{4} + t^{bp^2} + t^{bp'^2}}}, \; T_{M(21)} = \frac{h}{-\frac{\Delta^{bp}}{2} + \sqrt{\frac{\Delta^{bp^2}}{4} + t^{bp^2} + t^{bp'^2}}}$$

(carrier movement may be non periodic)

Trimers: maximum transfer percentage, pure maximum transfer rate

(defined only in periodic cases of trimers)

Maximum transfer percentage, p: the maximum value of $|A_3(t)|^2$

1) Dimers consisting of identical monomers with no crosswise purines:

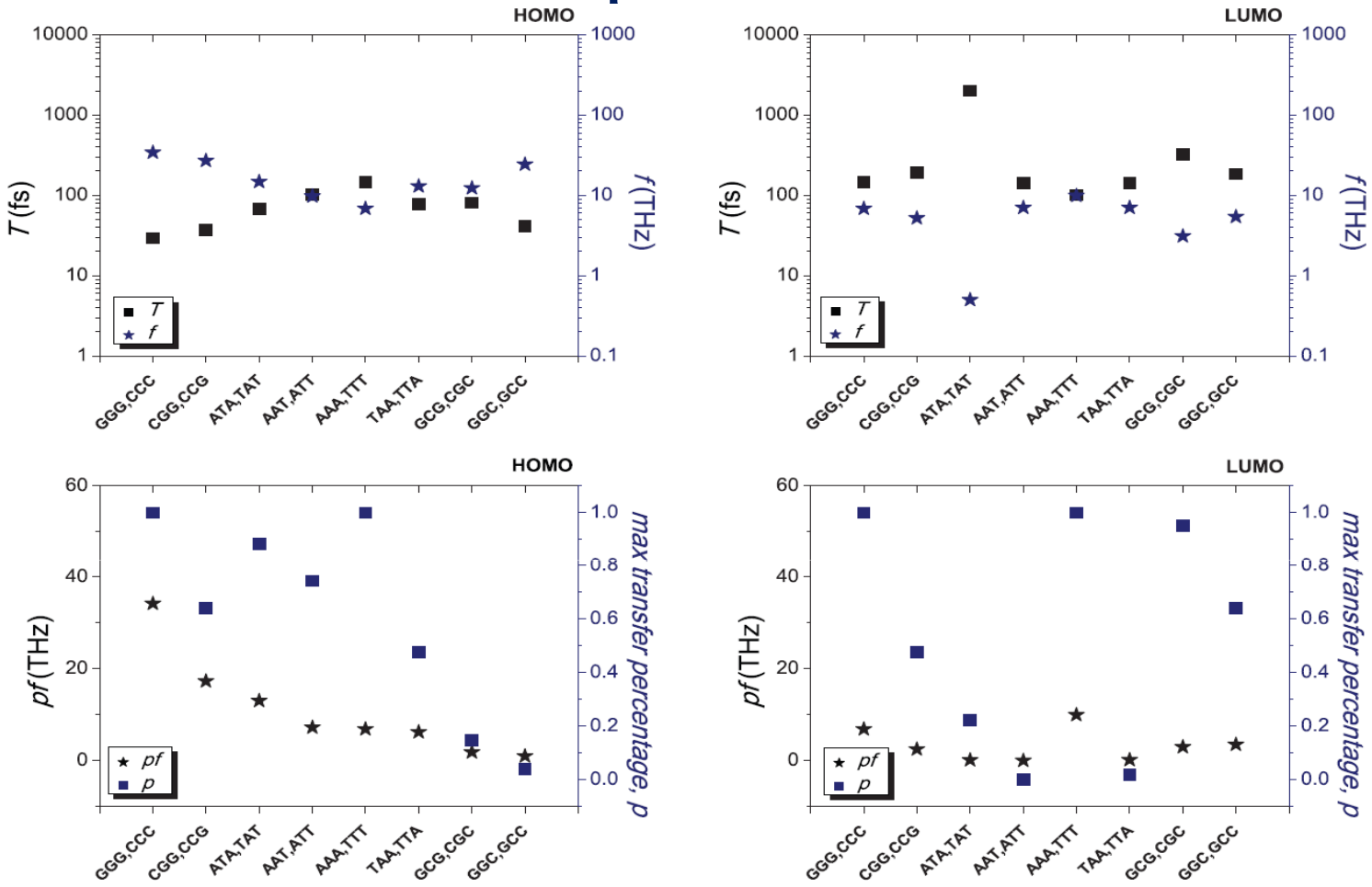
$$p = 1 \ (100\%)$$

2) Trimers consisting of identical monomers with crosswise purines:

$$p < 1 \ (<100\%)$$

Pure maximum transfer rate: pf

Periodic carrier transfer in base-pair trimers made of identical monomers



Left column: holes (HOMO) Right column: electrons (LUMO)

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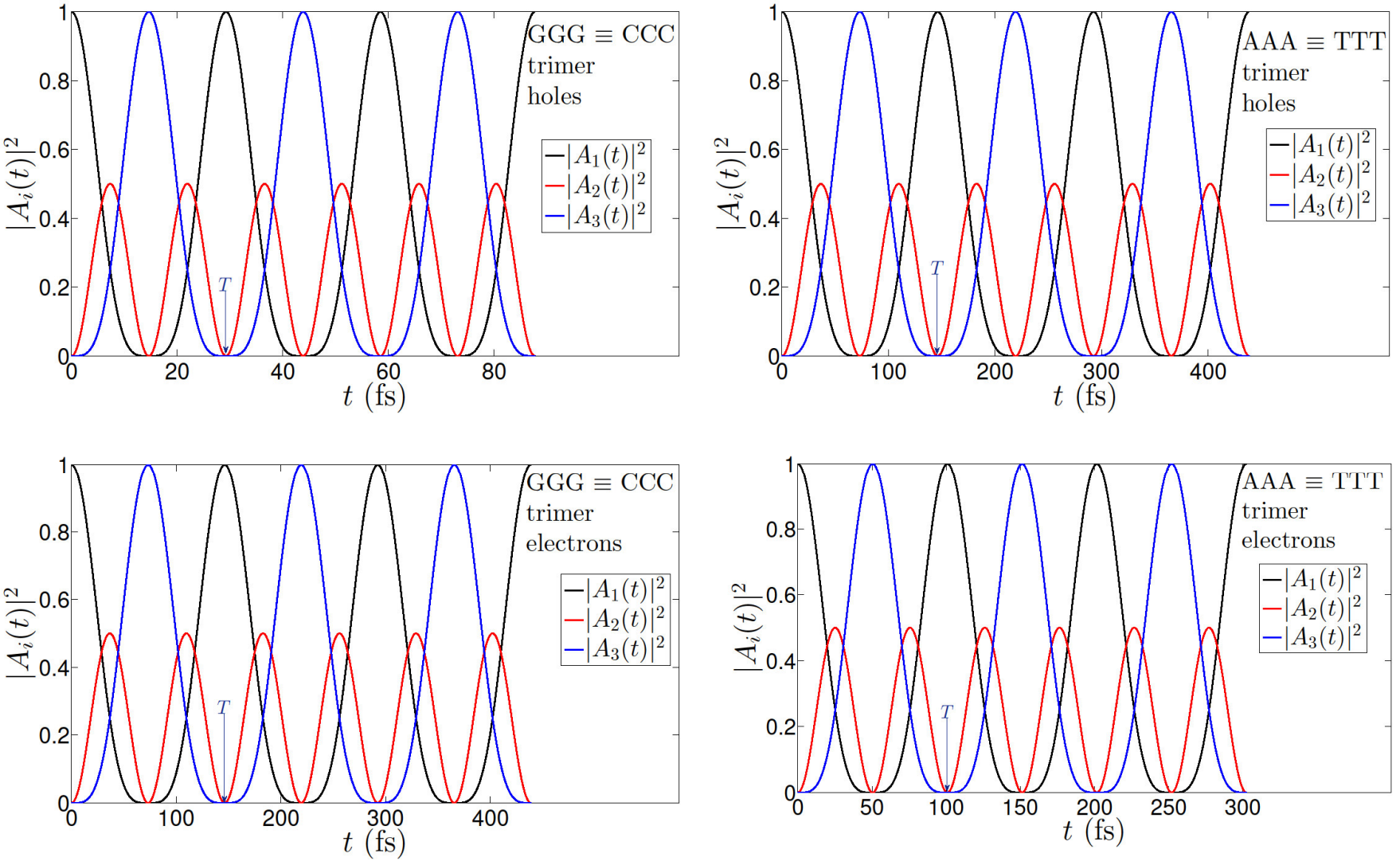
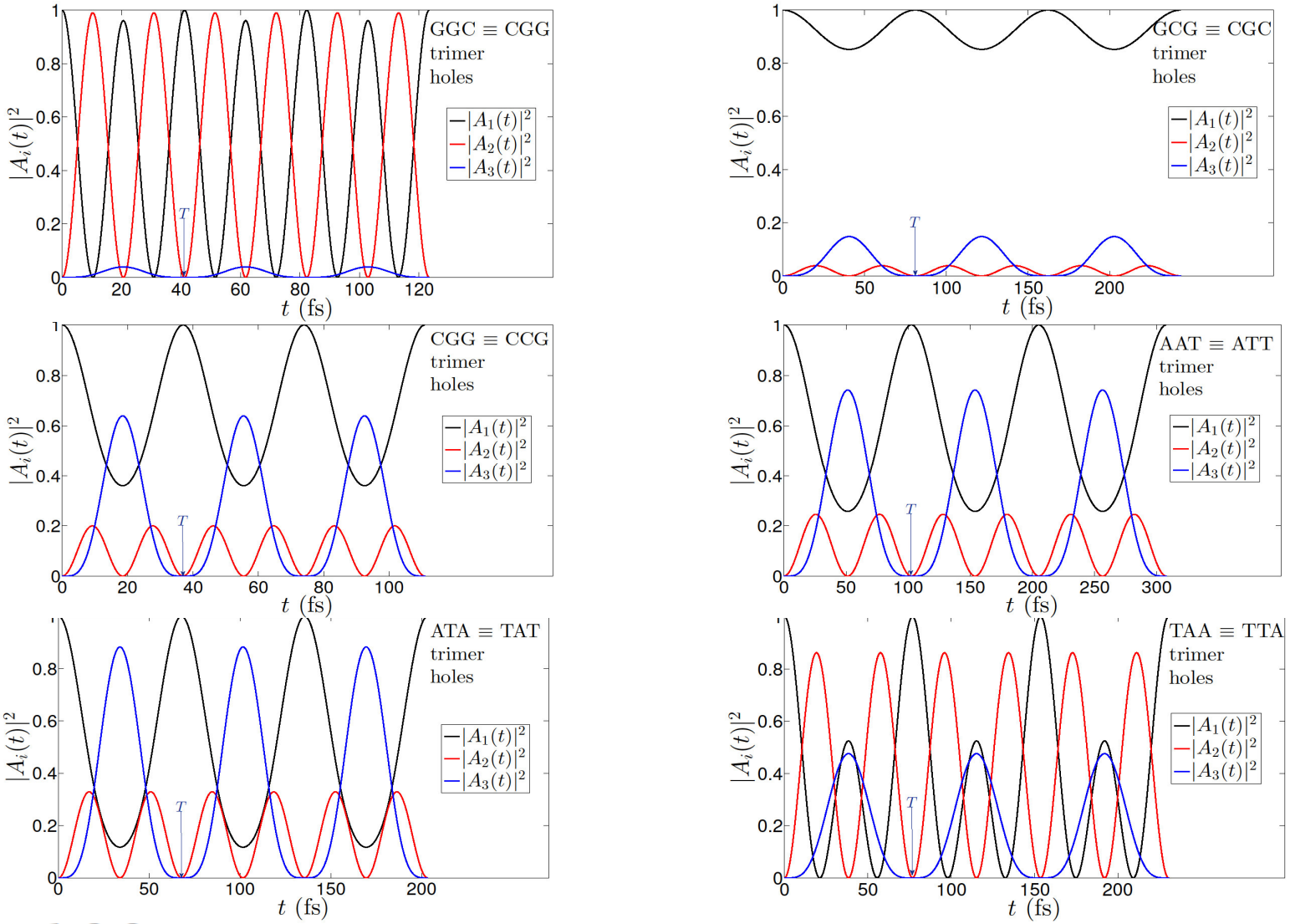
GGG ≡ CCC and AAA ≡ TTT trimers



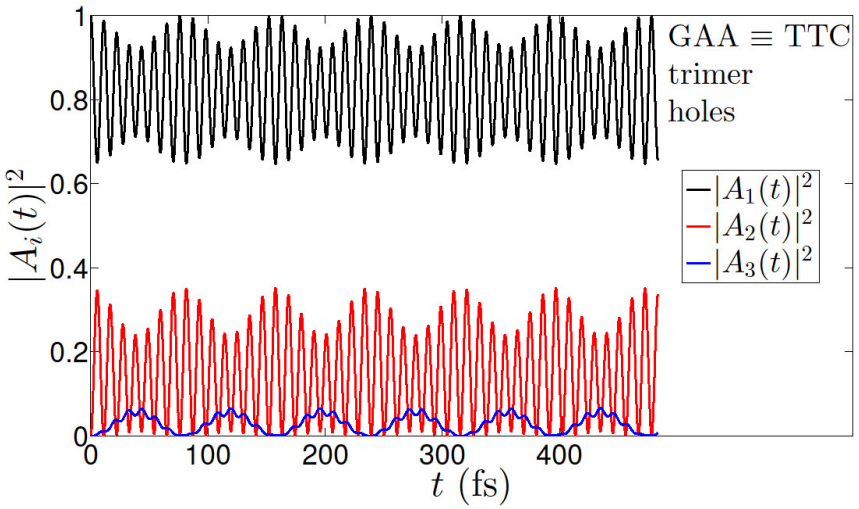
$|A_\mu(t)|^2, \mu = 1, 2, 3$ for **hole** and **electron** transfer in GGG ≡ CCC and AAA ≡ TTT trimers (no crosswise purines). The maximum transfer percentage $p = 1$ (100%).

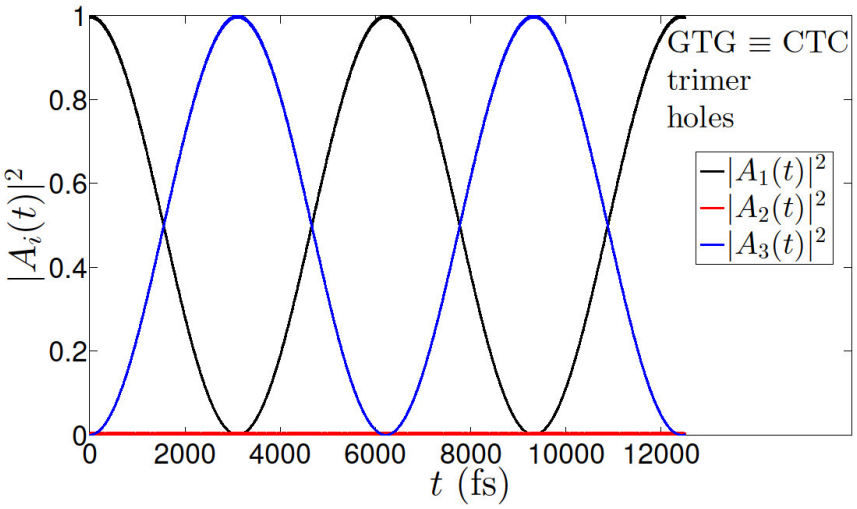
GGC ≡ GCC, GCG ≡ CGC, CGG ≡ CCG, AAT ≡ ATT, ATA ≡ TAT, and TAA ≡ TTA trimers

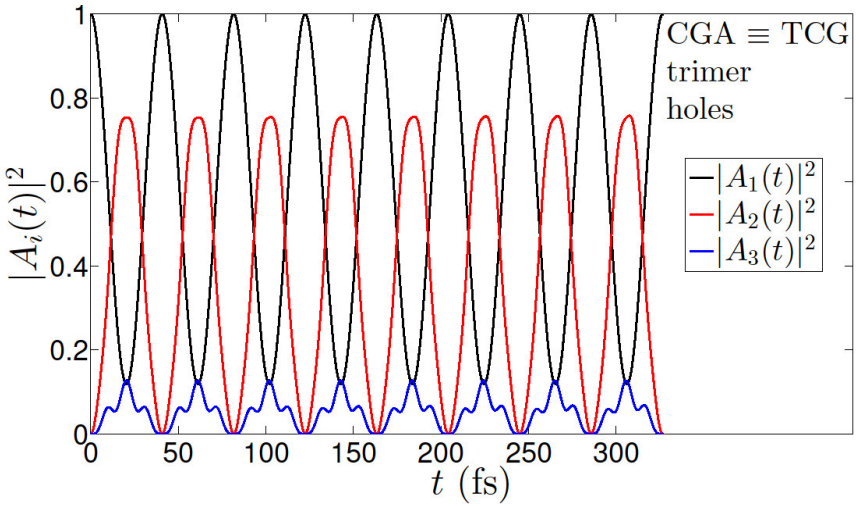


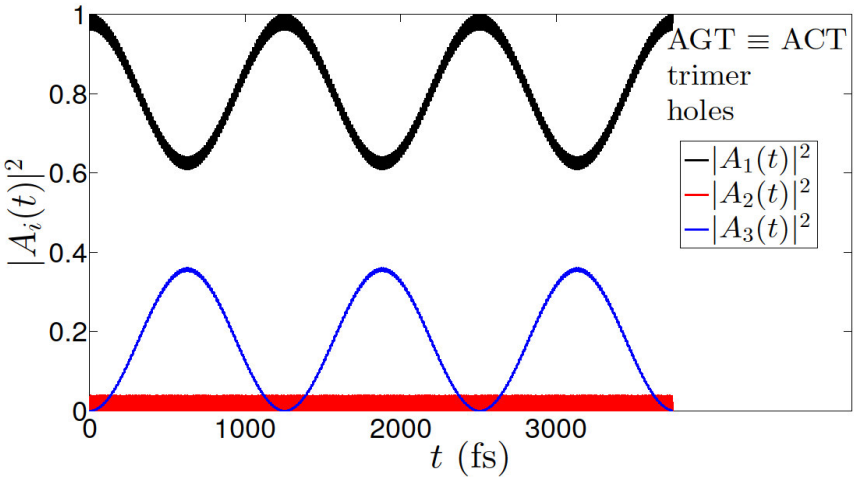
$|A_\mu(t)|^2$, $\mu = 1, 2, 3$ for **hole** transfer in GGC ≡ GCC, GCG ≡ CGC, CGG ≡ CCG, AAT ≡ ATT, ATA ≡ TAT, and TAA ≡ TTA trimers (crosswise purines). The maximum transfer percentage $p < 1$ (<100%).

GAA ≡TTC, GTG≡CAC, CGA≡TCG, and AGT≡ACT trimers



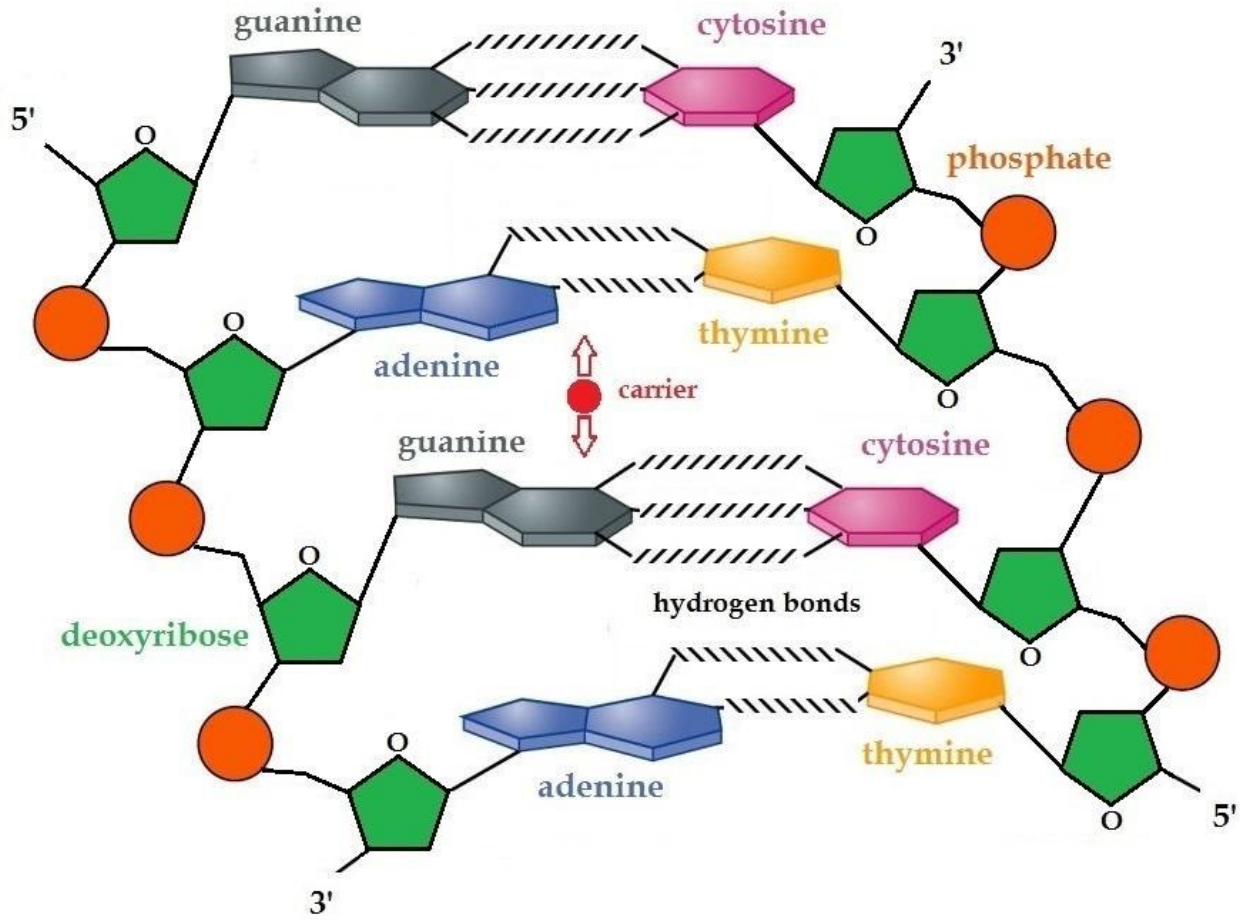






$|A_\mu(t)|^2, \mu = 1, 2, 3$ for **hole** transfer in GAA ≡TTC, GTG≡CAC, CGA≡TCG, and AGT≡ACT trimers (some examples of trimers consisting of different monomers).

Greater sequences



Tetramers

136 unique tetramers, 20 made of identical monomers

-Simplest case: GGGG ≡ CCCC and AAAA ≡ TTTT (identical monomers with no crosswise purines).

-Fractions of the periods involved in carrier movement:

$$\frac{T_{43}}{T_{41}} = \sqrt{5} + 1$$

$$\frac{T_{42}}{T_{41}} = 1 + \frac{\sqrt{5}}{5}$$

$$\frac{T_{32}}{T_{41}} = \frac{3 + \sqrt{5}}{5}$$

Even in this case, carrier movement is not periodic.

-Increasing the number of monomers above 3 periodicity is lost (generally).

Conclusions

-We can induce **charge oscillations** in **all** DNA **dimers** by adding an extra charge.

***f* ≈ 0.25–100 THz**

1) identical monomers: ***p*=1**
2) different monomers: ***p*<1**

- Carrier movement is still **periodic** in **trimers** made of **identical monomers**.

***f* ≈ 0.5–33 THz** (narrower)

1) no crosswise purines: ***p*=1**
2) crosswise purines: ***p*<1**

-Oscillations in dimers and trimers mainly in **MIR** and **FIR** range.

-**Trimers** made up of **different monomers**: periodicity depends on specific parameter values.

-Increasing the number of monomers above **three,** leads –generally – to **loss of periodicity**.

The end

Thank you !

Related Work

[1] C. Simserides, Chemical Physics **440** (2014) 31

[2] K. Lambropoulos, K. Kaklamanis, G. Georgiadis, C. Simserides, Annalen der Physik (Berlin) **526** (2014) 249

[3] L.G.D. Hawke, G. Kalosakas, C. Simserides, Eur. Phys. J. E **32** (2010) 291; ibid.**34** (2011) 118