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
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:

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

We analyze the DNA wavefunction into the bp wavefunctions:

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

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

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

\[ i\hbar \frac{dA_\lambda}{dt} = \left( E^{bp(\lambda)}_{H/L} \right) A_\lambda + t^{bp(\lambda;\lambda-1)}_{H/L} A_{\lambda-1} + t^{bp(\lambda;\lambda+1)}_{H/L} A_{\lambda+1} \]

<table>
<thead>
<tr>
<th>B-DNA base-pair</th>
<th>A-T</th>
<th>G-C</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^{bp}_H )</td>
<td>-8.3</td>
<td>-8.0</td>
<td>[4]</td>
</tr>
<tr>
<td>( E^{bp}_L )</td>
<td>-4.9</td>
<td>-4.5</td>
<td>[4]</td>
</tr>
<tr>
<td>( E_{\pi-\pi^*} )</td>
<td>3.4</td>
<td>3.5</td>
<td>[4]</td>
</tr>
<tr>
<td>( E^{bp} ) first pr.</td>
<td>-(7.8-8.2)</td>
<td>-(6.3-7.7)</td>
<td>[7–12]</td>
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<td>6.4</td>
<td>4.3-6.3</td>
<td>[12, 13]</td>
</tr>
<tr>
<td>( E^{bp \text{ used}}_H )</td>
<td>8.3</td>
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<td>[4]</td>
</tr>
</tbody>
</table>

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

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

- Successive base-pairs \( \Leftrightarrow \) denoted by \( YX \) \{ \lambda \quad Y \quad Y_{compl} \}
  \quad \lambda' \quad X \quad X_{compl} \quad 3' \quad 5' \quad 3'

| Base-pair sequence | \( t_{H}^{bp} \) [9] | \( |t_{H}^{bp}| \) [19] | \( t_{H}^{bp} \) [8] | \( t_{L}^{bp} \) [20] | \( t_{H}^{bp} \) [21] | \( t_{L}^{bp} \) used | \( t_{H}^{bp} \) [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                 | 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

\[ \mathbf{x}(t) = \begin{bmatrix} A_1(t) \\ A_2(t) \\ \vdots \\ A_N(t) \end{bmatrix} \]

Therefore:

\[ \dot{\mathbf{x}}(t) = \tilde{\mathbf{A}} \mathbf{x}(t), \quad \tilde{\mathbf{A}} = -\frac{i}{\hbar} \begin{bmatrix} E_{H/L}^{bp(1)} & t_{H/L}^{bp(1; 2)} & 0 & \cdots & 0 & 0 & 0 \\ t_{H/L}^{bp(2; 1)} & E_{H/L}^{bp(2)} & t_{H/L}^{bp(2; 3)} & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & E_{H/L}^{bp(N-1; N-2)} & t_{H/L}^{bp(N-1; N-1)} & \cdots & t_{H/L}^{bp(N-1; N)} \\ 0 & 0 & 0 & \cdots & t_{H/L}^{bp(N; N-1)} & E_{H/L}^{bp(N)} & \cdots & E_{H/L}^{bp(N)} \end{bmatrix} \]

eigenvalue method, the general solution is:

\[ \mathbf{x}(t) = \sum_{k=1}^{N} c_k \mathbf{v}_k e^{-\frac{i}{\hbar} \lambda_k t} \]

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

\( \lambda_k \): eigenvalues.
Results for dimers

- guanine
- cytosine
- adenine
- thymine

Hydrogen bonds

Carrier, schematically jumping back and forth

Frequency $f$

$\sim 97$ THz (electron)

$\sim 90$ THz (hole)
Dimers: solution, periods, frequencies

10 unique dimers, 6 made of identical monomers

General solution: \[ \ddot{x}(t) = \sum_{k=1}^{2} c_k \dot{y}_k e^{-\frac{\lambda_k t}{T}} \quad \text{Initial condition:} \quad \ddot{x}(0) = \begin{bmatrix} A_1(0) \\ A_2(0) \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \]

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):

\[ f = \frac{1}{T} = \frac{2|\theta_{bp}|}{h} \quad \text{(periodic carrier movement)} \]

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

\[ f = \frac{1}{T} = \frac{\sqrt{(2\theta_{bp})^2 + (\Delta_{bp})^2}}{h} \quad \text{(periodic carrier movement)} \]

\[ \Delta_{bp} = |E^{bp1} - E^{bp2}| \]
**Dimers: maximum transfer percentage, pure maximum transfer rate**

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

\[
p = \frac{(2tbp)^2}{(2tbp)^2 + (\Delta bp)^2}
\]

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: \( pf \)**

\[
pf = \frac{2|t_{bp}|}{h}\sqrt{\frac{(2t_{bp})^2}{(2t_{bp})^2 + (\Delta_{bp})^2}}
\]

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%).
$|A_\mu(t)|^2$, $\mu = 1, 2$ for hole transfer in GA≡TC, GT≡AC, CA≡TG, and CT≡AG dimers. The maximum transfer percentage $p < 1$ (less than 100%).
Results for trimers
Trimers: solution, periods, frequencies

32 unique trimers, 8 made of identical monomers

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

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

It occurs that:

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

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 $\equiv$ CCC):

$\begin{bmatrix} T_M = \frac{h}{t_b p \sqrt{2}} \\ T_E = \frac{h}{2 t_b p \sqrt{2}} \Rightarrow \frac{T_M}{T_E} = \frac{2}{1} \end{bmatrix}$  
(periodic carrier movement)

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

$\begin{bmatrix} T_M = \frac{h}{\sqrt{t_b p^2 + t_b p^2}} \\ T_E = \frac{h}{2 \sqrt{t_b p^2 + t_b p^2}} \Rightarrow \frac{T_M}{T_E} = \frac{2}{1} \end{bmatrix}$  
(periodic carrier movement)

3) Trimers consisting of different monomers (e.g. GAC $\equiv$ GTC):

$\begin{bmatrix} T_{M(32)} = \frac{h}{\Delta_{\text{hy}}^2 + \frac{\Delta_{\text{hy}}^2}{4} + t_b p^2 + t_b p^2} \\ T_{E(31)} = \frac{h}{2 \sqrt{\Delta_{\text{hy}}^2} + t_b p^2 + t_b p^2} \\ T_{M(21)} = \frac{h}{-\Delta_{\text{hy}}^2 + \sqrt{\Delta_{\text{hy}}^2} + t_b p^2 + t_b p^2} \end{bmatrix}$
(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)

1st row: \( T \) in fs (■), \( f \) in THz (★)
2nd row: \( pf \) in THz (★), \( p \) (■)
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%).
|A_μ(t)|^2, \ μ = 1, 2, 3 for hole transfer in GGC \equiv GCC, GCG \equiv CGC, CGG \equiv CCG, AAT \equiv ATT, ATA \equiv TAT, and TAA \equiv TTA trimers (crosswise purines). The maximum transfer percentage \ p < 1 (<100%).
GAA $\equiv$ TTC, GTG $\equiv$ CAC, CGA $\equiv$ TCG, and AGT $\equiv$ ACT trimers

$|A_\mu(t)|^2$, $\mu = 1, 2, 3$ for hole transfer in GAA $\equiv$ TTC, GTG $\equiv$ CAC, CGA $\equiv$ TCG, and AGT $\equiv$ 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.

\[ f \approx 0.25–100 \text{ THz} \]

1) identical monomers: \( p=1 \)
2) different monomers: \( p<1 \)

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

\[ f \approx 0.5–33 \text{ THz} \] (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

