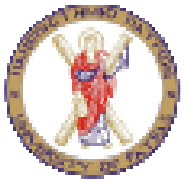
19 March 2011

Tight binding parameters for charge transport along DNA

L. G. D. Hawke[1,&], G. Kalosakas[1], **C. Simserides**[2,3]

[1] Materials Science Department, University of Patras, Patras, Greece
[2] Institute of Materials Science, NCSR Demokritos, Athens, Greece
[3] Physics Department, University of Athens, Athens, Greece

[&] *Presently at School of Physics & Astronomy, University of Leeds, U.K.*



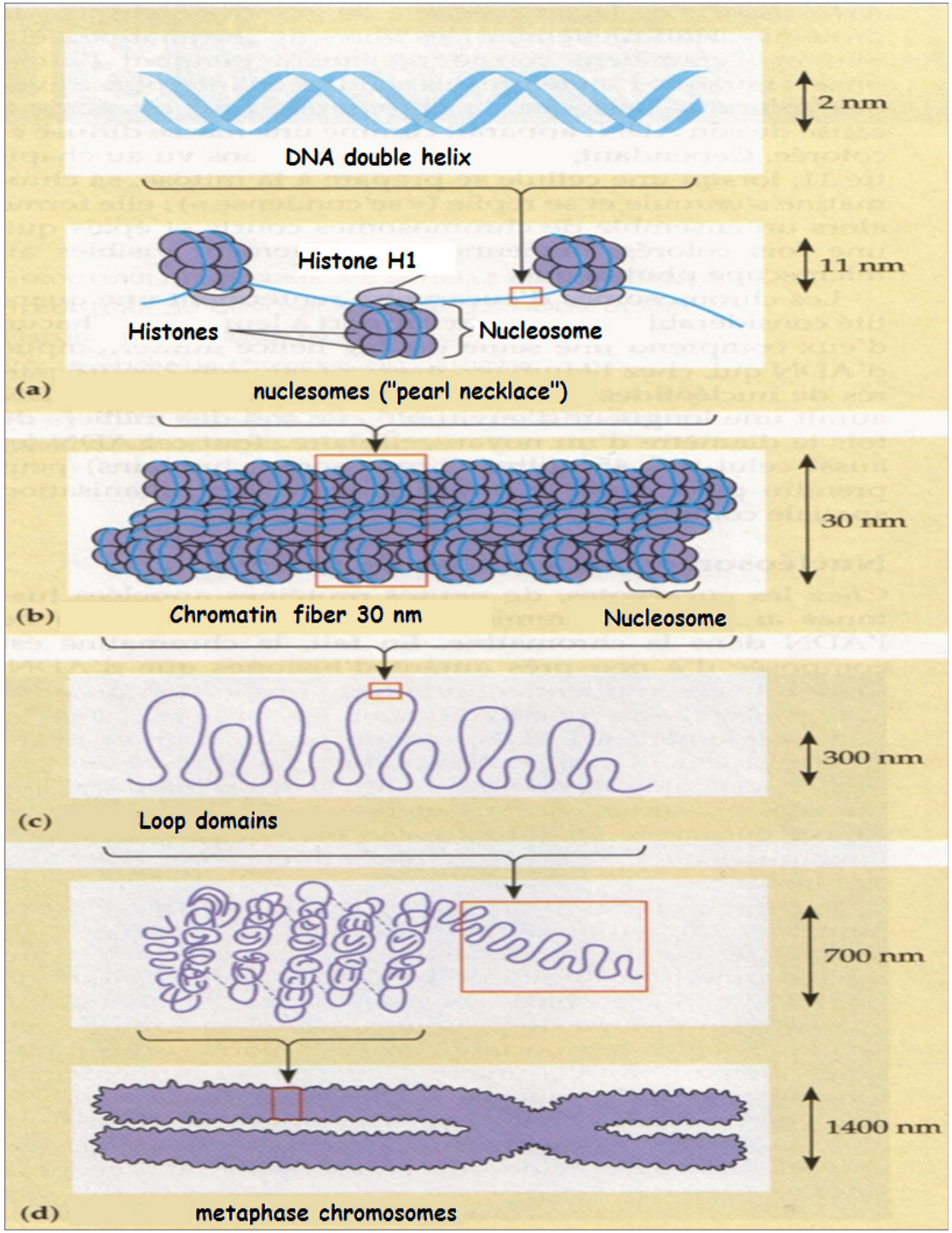
C. Carathéodory
Grant C155 Univ. Patras

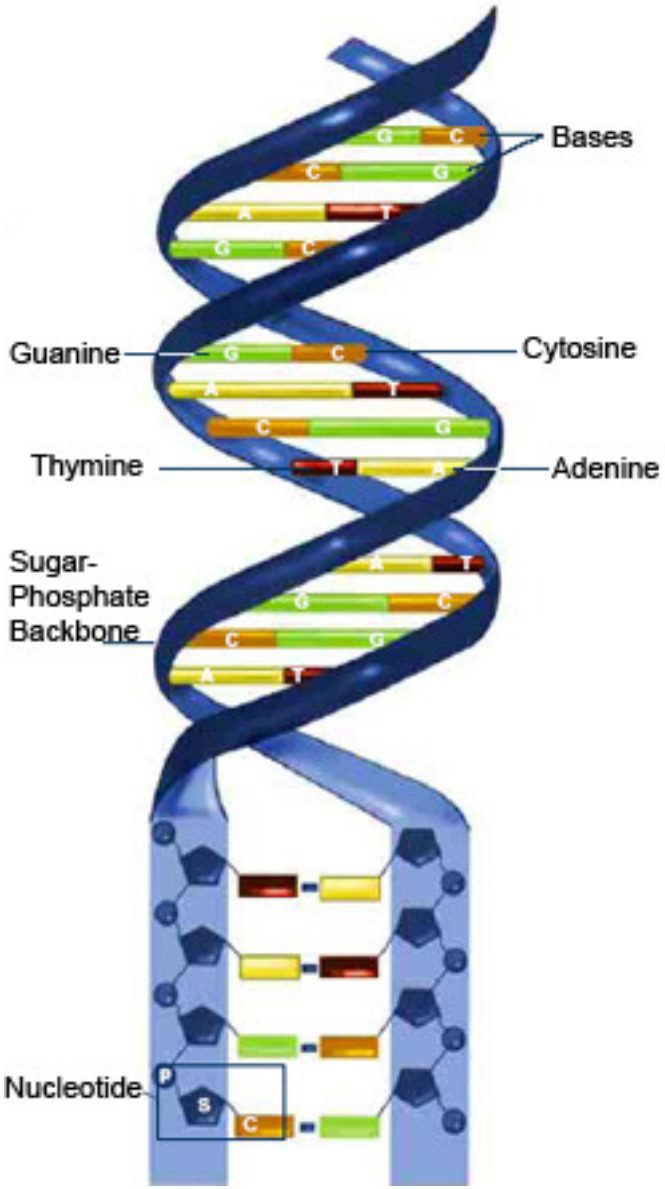
From double helix to chromosomes

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

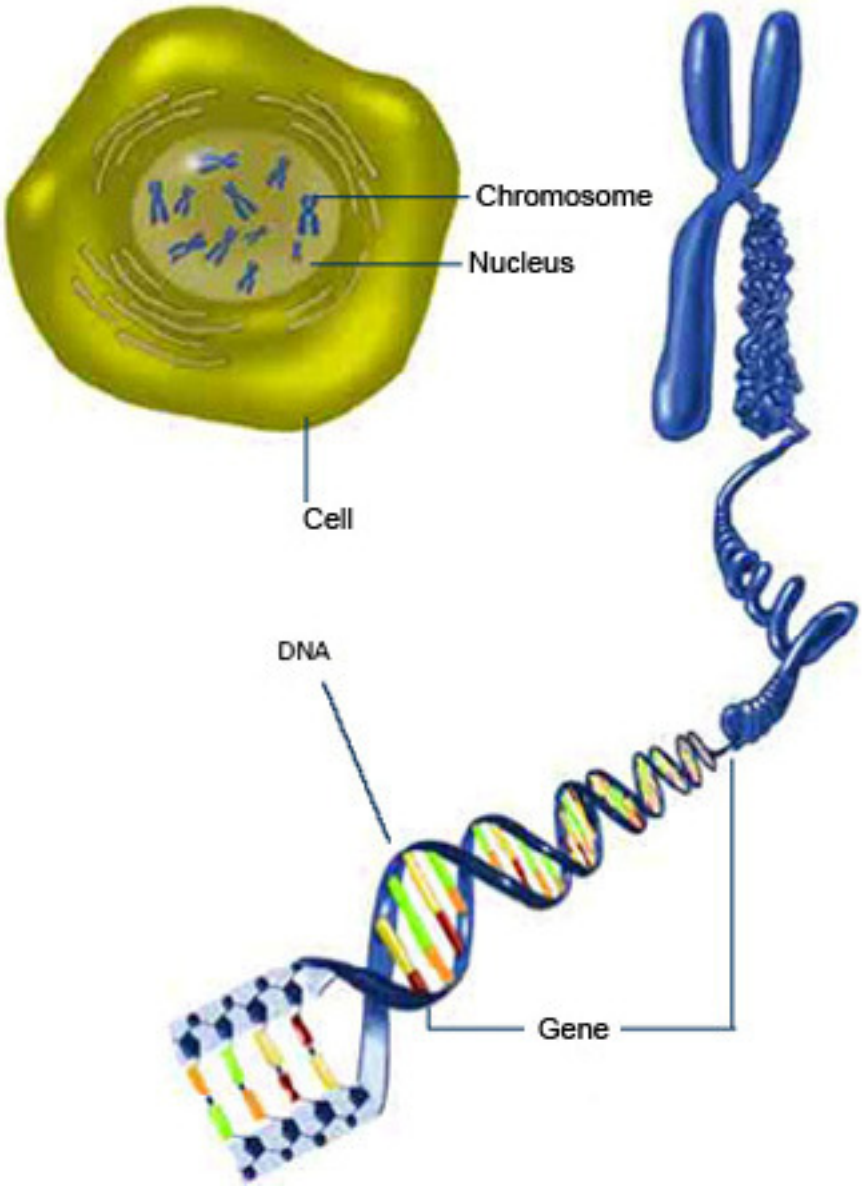
Chromatin: the combination of DNA, histone, and other proteins that make up chromosomes.

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



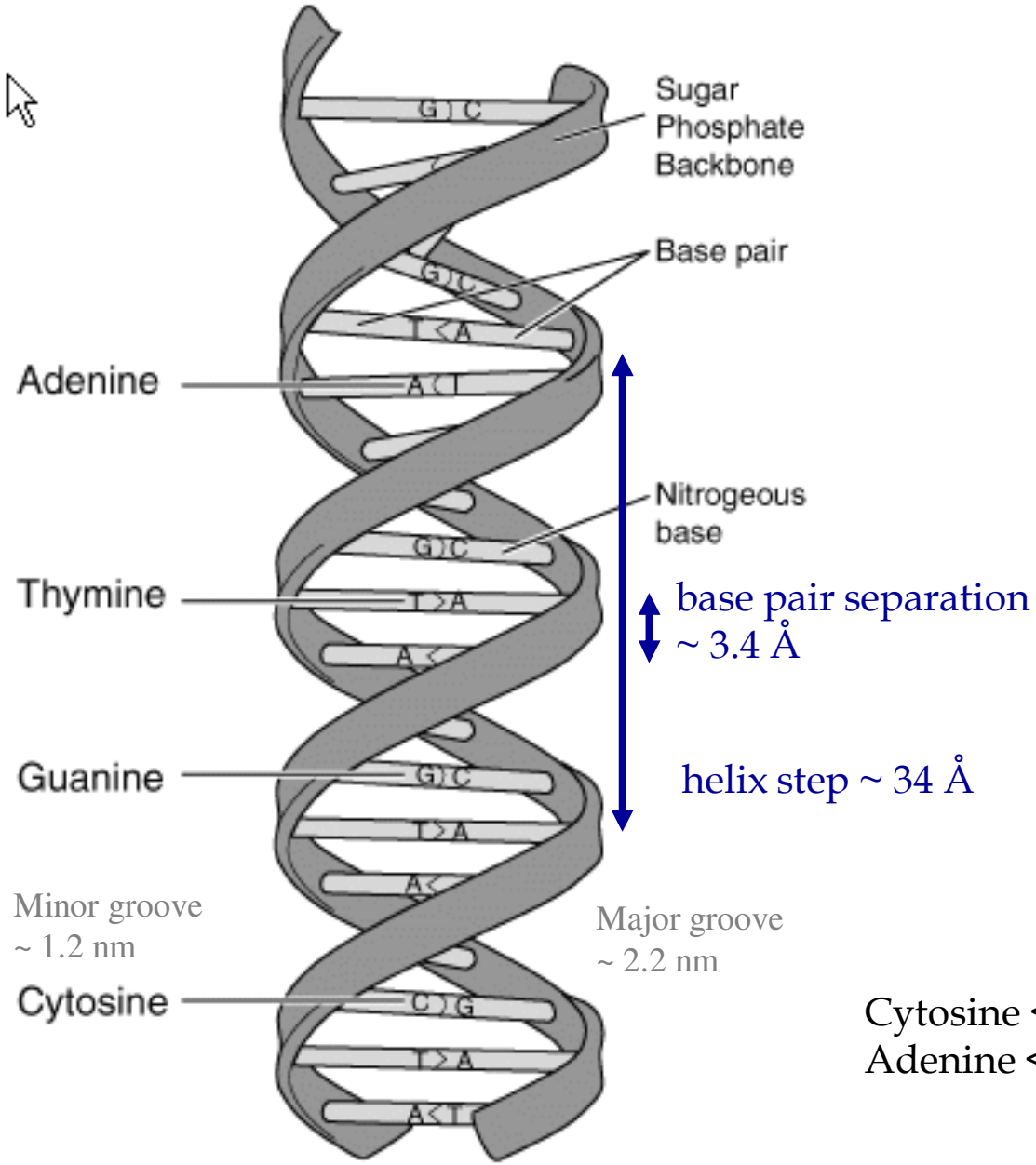


DNA: 2 long, twisted chains made up of nucleotides.
Nucleotide: base, sugar (deoxyribose), phosphate
Bases: adenine (A), thymine (T), cytosine (C), guanine (G)

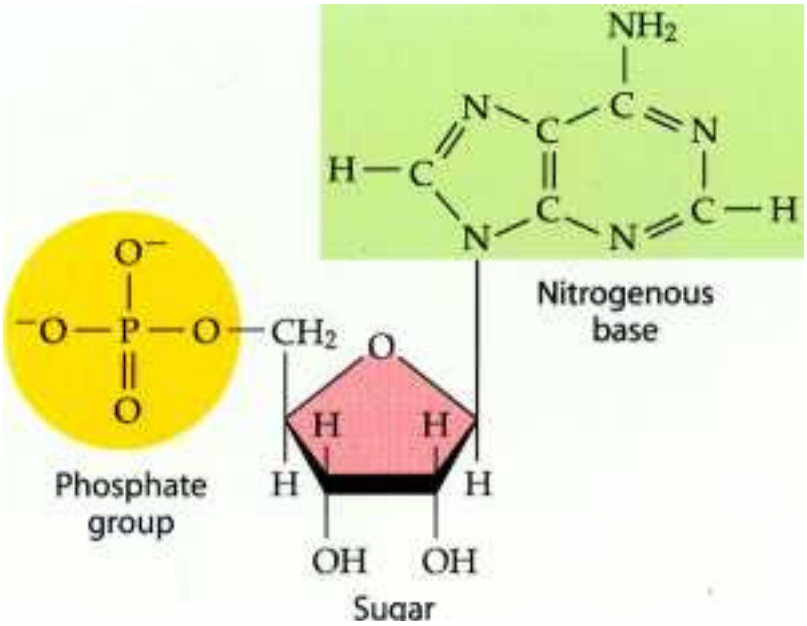


The long, stringy DNA that makes up genes is spooled within chromosomes inside the nucleus of a cell. (Note that a gene would actually be a much longer stretch of DNA than what is shown here.)

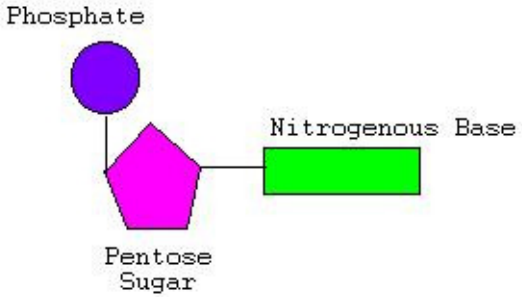
deoxyribose nucleic acid

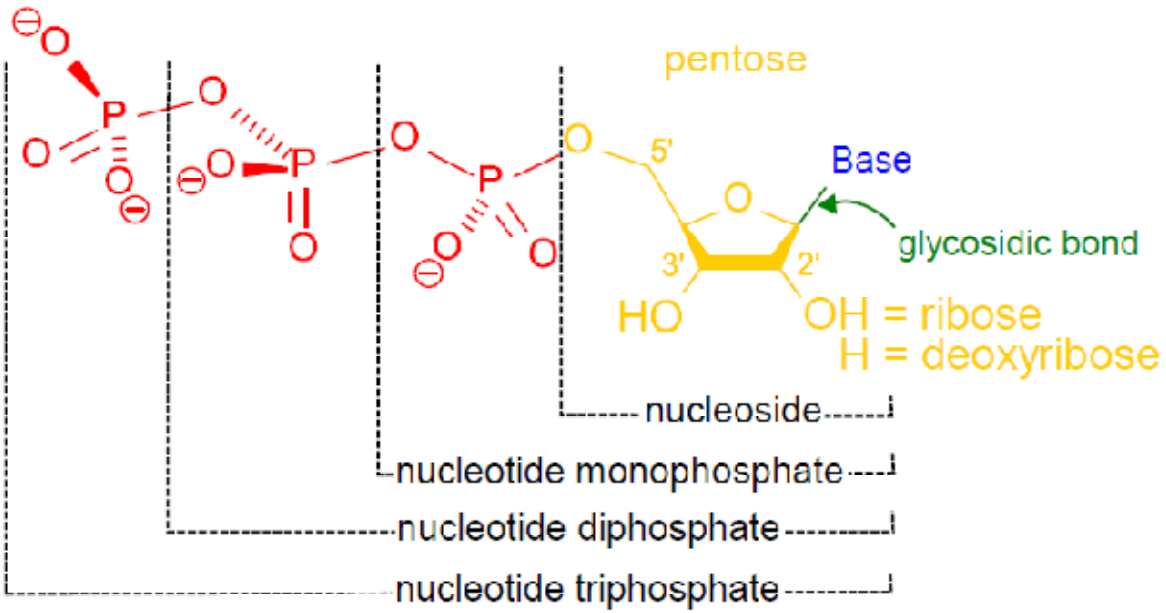


Cytosine <3 H bonds> Guanine
Adenine <2 H bonds> Thymine

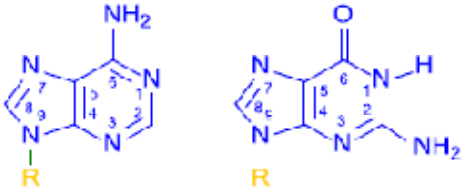


nucleotide

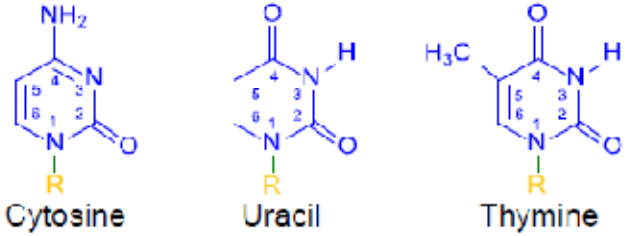




Purines



Pyrimidines



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 the DNA double helix
  may be crucial for DNA damage and repair

"How much" does DNA conduct? Experiments cover a wide range of behavior:

* insulator * semiconductor * metallic-like * Polarons vs. gap!

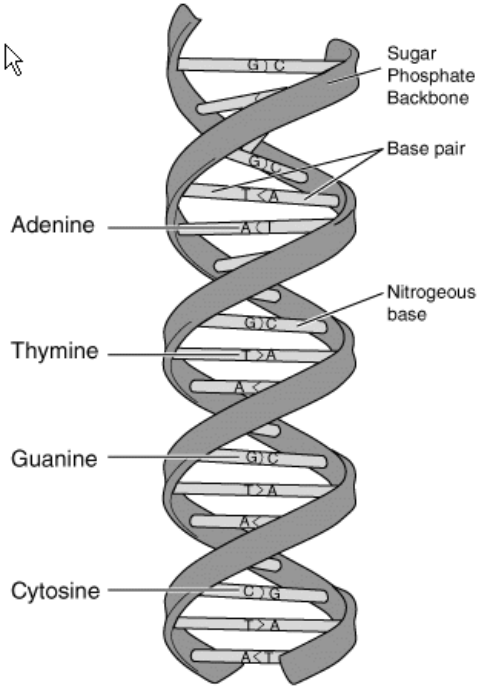
Conductivity deviations due to external factors:

- ❑ the type of substrate
- ❑ the distance between the electrodes
- ❑ the contact material
- ❑ …

and intrinsic characteristics:

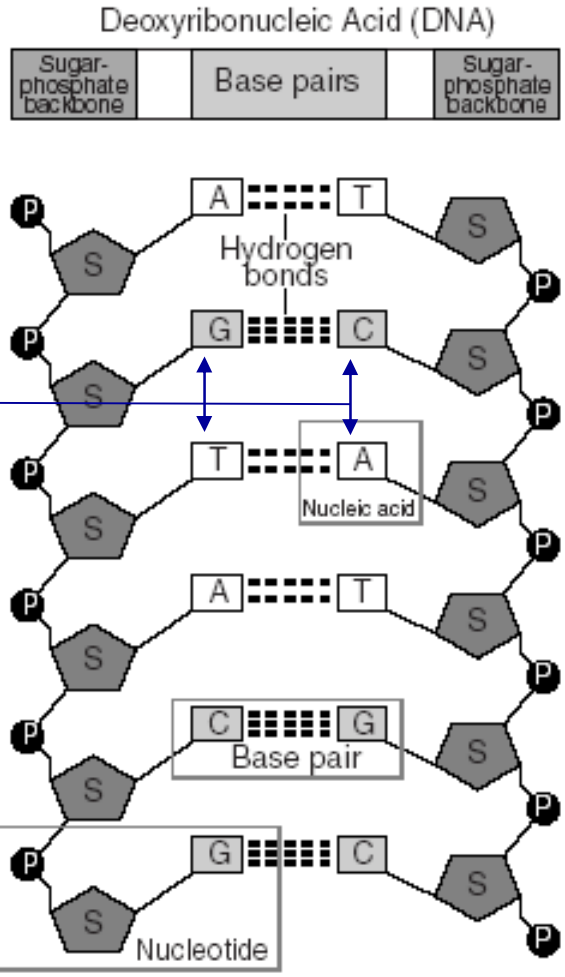
- ❑ local chemical environment due to solution used in preparation
- ❑ the hydrogen bonding
- ❑ the degree of stretching
- ❑ …

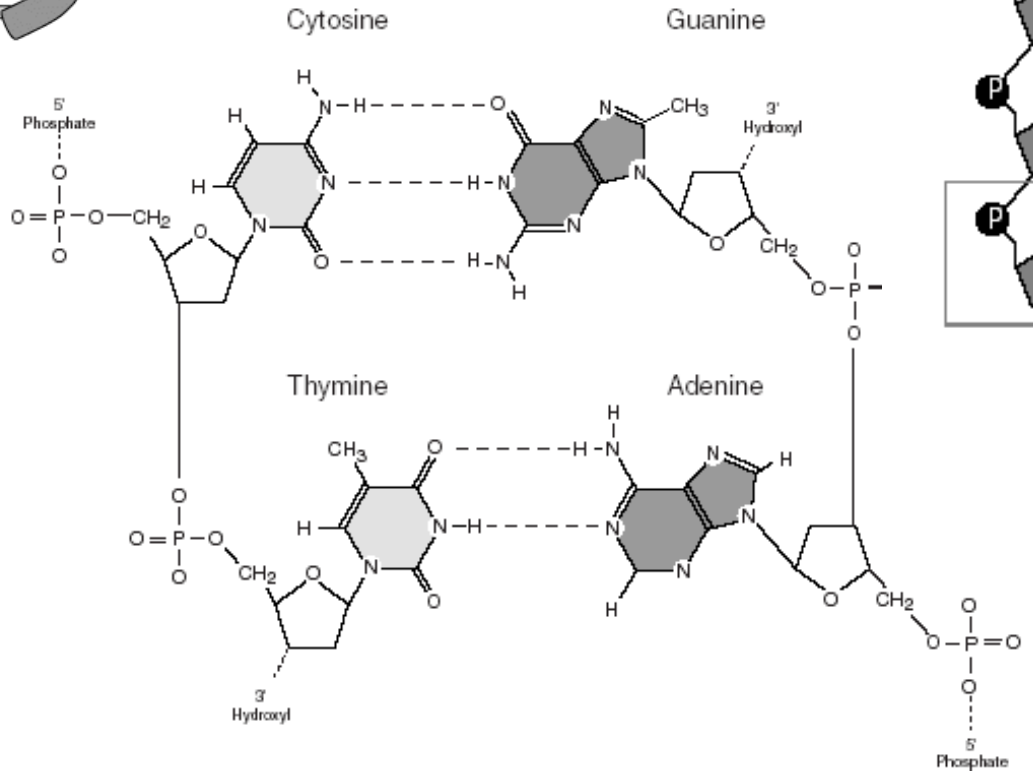
DNA



overlap of π molecular orbitals (made up by p_z atomic orbitals).

No covalent bond here.





A. π molecular structure of planar organic molecules
$\supset$ DNA bases: adenine (A), thymine (T), guanine (G), cytosine(C)

Linear Combination of Atomic Orbitals (LCAO): p_z electrons + novel parametrization
occupied molecular orbitals (π)
unoccupied molecular orbitals (π^*)

Highest Occupied Molecular Orbital (HOMO) used by holes
Lowest Unoccupied Molecular Orbital (LUMO) used by electrons
HOMO-LUMO gap (π-π^*)

B. HOMO and LUMO of base-pairs (A-T, G-C)
Linear Combination of Molecular Orbitals

C. Tight-binding hopping parameters
1. Description at the base-pair level
2. Description at the single-base level

Relevant Publications
L. G. D. Hawke, G. Kalosakas, C. Simserides, Eur. Phys. J. E **32**, 291 (2010)
L. G. D. Hawke, G. Kalosakas, C. Simserides, Mol. Phys. **107**, 1755 (2009)
L. G. D. Hawke, C. Simserides, G. Kalosakas, Mater. Sci. Eng. B **165**, 266 (2009)

A. π molecular structure of planar organic molecules

sp^2 hybridization
LCAO with p_z atomic orbitals
π, π^* molecular orbitals

$$\Psi^b(\mathbf{r}) = \sum_{i=1}^{N} c_i p_z^i(\mathbf{r})$$

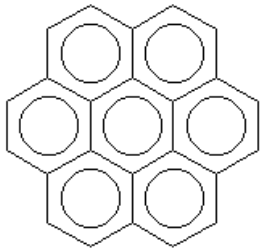
$$H^b\Psi^b(\mathbf{r}) = E^b\Psi^b(\mathbf{r})$$

$$\int p_z^{j^*}(\vec{r})\, p_z^i(\vec{r})\, d^3r = \delta_{ji}$$

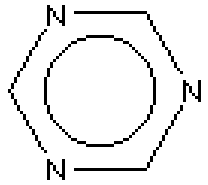
$$\sum_{i=1}^{N}[(H_{ji}^b - E^b\delta_{ji})c_i] = 0, \quad j = 1, 2, \ldots, N$$

For the diagonalization we need H_{ij}.

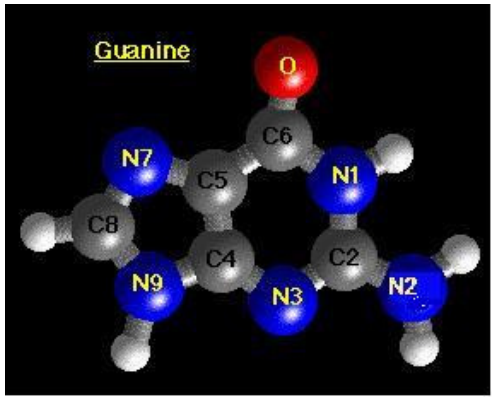
$$H_{ji}^b = \int d^3r\; p_z^{j\,\star}(\mathbf{r})\; H^b\; p_z^i(\mathbf{r})$$



coronene



1,3,5-triazine



Diagonal matrix elements, H_{ii}:

$$\varepsilon_C = -6.7 \text{ eV} \qquad \varepsilon_O = -11.8 \text{ eV}$$

$$\varepsilon_{N_2} = -7.9 \text{ eV} \qquad \varepsilon_{N_3} = -10.9 \text{ eV}$$

Non-diagonal matrix elements,
atoms not sp^2-bonded, $H_{ij} = 0$.

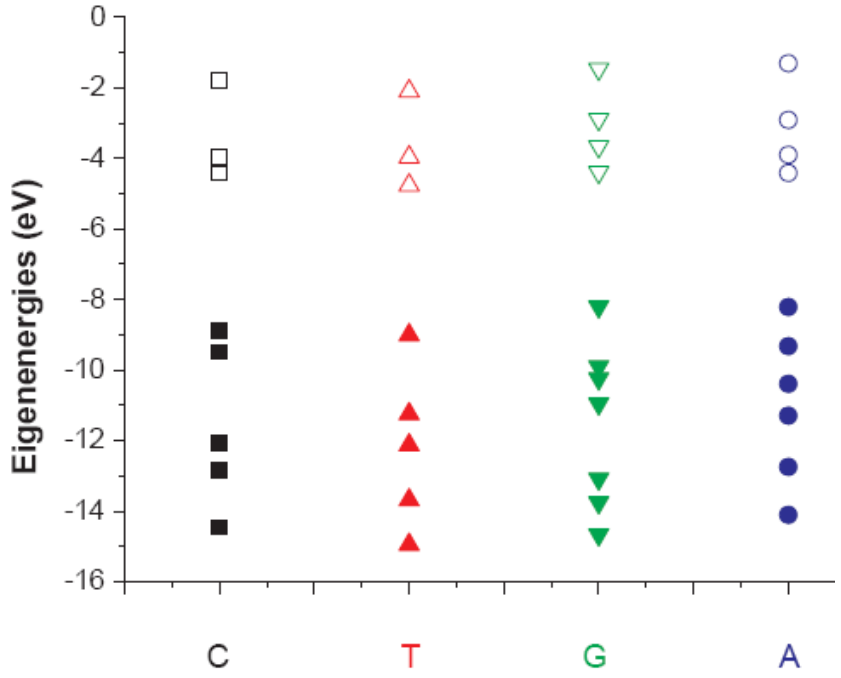
Non-diagonal neighboring matrix elements,
atoms sp^2-bonded, Harrison's expression:

$$H_{ij} = V_{pp\pi} = -0.63\frac{\hbar^2}{m d_{ij}^2}$$

Diagonalizing → N molecular orbitals and their energies

Successively fill them by 2 electrons each, until to accommodate all available p_z electrons.

results for DNA bases



all energies in eV

DNA base	Adenine	Thymine	Guanine	Cytosine
atoms in π bonds	10	8	11	8
p_z electrons	12	10	14	10
$E_H^{b\ (isol.)}$	−8.2	−9.0	−8.2	−8.9
$E_L^{b\ (isol.)}$	−4.4	−4.8	−4.4	−4.4
$E_{\pi-\pi^*}$	3.8	4.2	3.8	4.5
$IE^{\rm exp}$	8.4-8.5	9.0-9.2	8.2-8.3	8.9
$E_{\pi-\pi^*}^{\rm exp}$	4.5-4.8	4.6-4.7	4.3-4.5	4.5-4.7
$IE^{\rm first\ pr.}$	8.2-8.6	9.1-9.7	7.8-8.3	8.9-9.4
$E_{\pi-\pi^*}^{\rm first\ pr.}$	4.5-5.3	4.9-5.3	4.4-5.3	4.2-4.7
E_H^b (in B-DNA)	−8.3	−9.0	−8.0	−8.8
E_L^b (in B-DNA)	−4.4	−4.9	−4.5	−4.3

B. HOMO and LUMO of B-DNA base-pairs (A-T, G-C)

Linear Combination of Molecular Orbitals

$$\Psi^{bp}_{H/L}(\mathbf{r}) = \mathcal{C}_1\ \Psi^{b(1)}_{H/L}(\mathbf{r})\ +\ \mathcal{C}_2\ \Psi^{b(2)}_{H/L}(\mathbf{r})$$

$$H^{bp}\ \Psi^{bp}_{H/L}(\mathbf{r})\ =\ E^{bp}_{H/L}\ \Psi^{bp}_{H/L}(\mathbf{r})$$ . . . we must solve:

$$\begin{aligned} E^{b(1)}_{H/L}\,\mathcal{C}_1\ + t_{H/L}\,\mathcal{C}_2\ &= E^{bp}_{H/L}\,\mathcal{C}_1 \\ t^{\star}_{H/L}\,\mathcal{C}_1\ + E^{b(2)}_{H/L}\,\mathcal{C}_2\ &= E^{bp}_{H/L}\,\mathcal{C}_2 \end{aligned}$$

$$\int d^3r\ \Psi^{b(m)\,\star}_{H/L}\ H^{bp}\ \Psi^{b(m)}_{H/L} \approx \int d^3r\ \Psi^{b(m)\,\star}_{H/L}\ H^{b}\ \Psi^{b(m)}_{H/L} = E^{b(m)}_{H/L},\ \text{for}\ m{=}1\ \text{or}\ 2$$

$t_{H/L} = \int d^3r\ \Psi^{b(1)\,\star}_{H/L}\ H^{bp}\ \Psi^{b(2)}_{H/L}$ overlap integral, the hopping parameter for hole (H) / electron (L) transfer between the two bases of the base-pair

$$t_{H/L} = \sum_{i=1}^{N_1}\sum_{j=1}^{N_2} c^{H/L\,\star}_{i(1)}\ c^{H/L}_{j(2)}\ V_{ij}$$

$t_{H/L}=t^{*}_{H/L}$

$$V_{ij} = \int d^3r\ p_z^{i(1)\,\star}(\mathbf{r})\ H^{bp}\ p_z^{j(2)}(\mathbf{r})$$

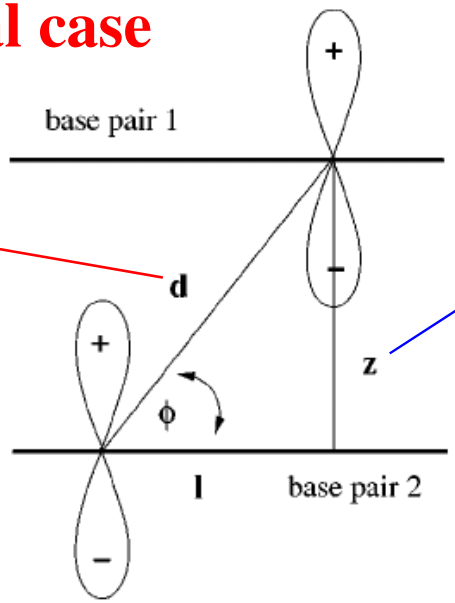
overlap integral, the hopping parameter between p_z orbitals belonging to different bases of the base pair

equivalently

$$\Psi^{bp}_{H/L}(\mathbf{r}) = \sum_{i=1}^{N} C_i^{H/L}\, p_z^i(\mathbf{r})$$

V_{ij} are given by the Slater-Koster expression $V_{ij} = V_{pp\sigma} \sin^2\phi + V_{pp\pi} \cos^2\phi$

Sketch for the general case



the distance between the two orbitals

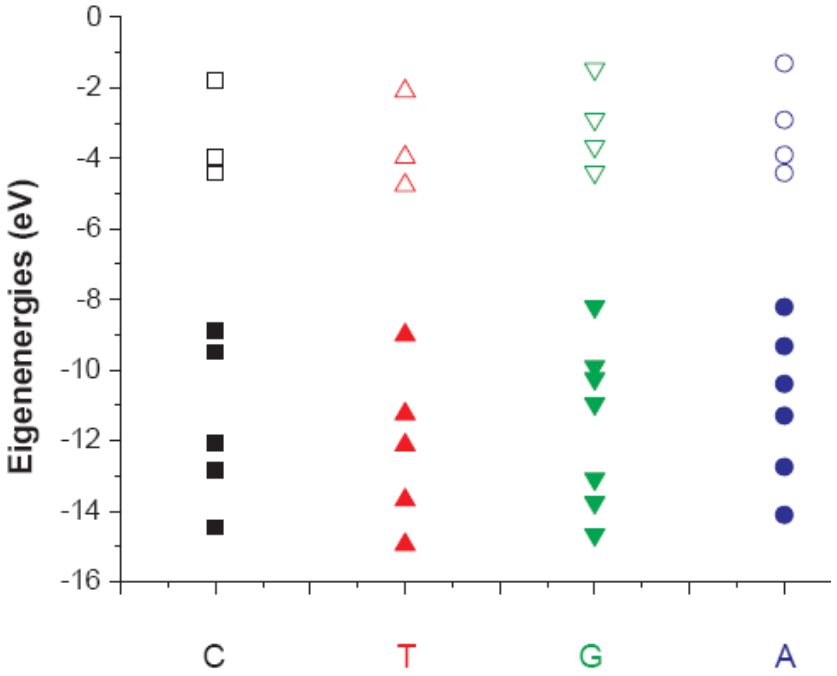
the separation between successive base-pairs

$V_{pp\pi}$ and $V_{pp\sigma}$ for interatomic distances of the order of covalent bonds e.g. $V_{pp\pi} = -0.63\frac{\hbar^2}{md^2}$

$V_{pp\pi}$ and $V_{pp\sigma}$ for greater distances e.g. $V_{pp\pi} = Ae^{-\beta(d-d_0)}$

For the intra-base-pair hopping parameters $\varphi = 0$ and only $V_{pp\pi}$ survives.

results for DNA bases



all energies in eV

DNA base	Adenine	Thymine	Guanine	Cytosine
atoms in π bonds	10	8	11	8
p_z electrons	12	10	14	10
$E_H^{b\ (isol.)}$	−8.2	−9.0	−8.2	−8.9
$E_L^{b\ (isol.)}$	−4.4	−4.8	−4.4	−4.4
$E_{\pi-\pi^*}$	3.8	4.2	3.8	4.5
$IE^{\rm exp}$	8.4-8.5	9.0-9.2	8.2-8.3	8.9
$E_{\pi-\pi^*}^{\rm exp}$	4.5-4.8	4.6-4.7	4.3-4.5	4.5-4.7
$IE^{\rm first\ pr.}$	8.2-8.6	9.1-9.7	7.8-8.3	8.9-9.4
$E_{\pi-\pi^*}^{\rm first\ pr.}$	4.5-5.3	4.9-5.3	4.4-5.3	4.2-4.7
E_H^b (in B-DNA)	−8.3	−9.0	−8.0	−8.8
E_L^b (in B-DNA)	−4.4	−4.9	−4.5	−4.3

results for B-DNA base-pairs

all energies in eV

B-DNA base-pair	A-T	G-C
E_H^{bp}	−8.3	−8.0
E_L^{bp}	−4.9	−4.5
$E_{\pi-\pi^*}$	3.4	3.5
$E_H^{bp\ \rm first\ pr.}$	−(7.8-8.2)	−(6.3-7.7)
$E_{\pi-\pi^*}^{\rm first\ pr.}$	6.4	4.3-6.3

intra-base-pair hopping parameters

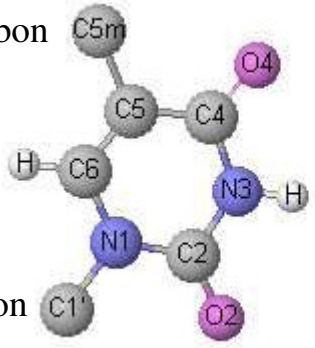
Base-pair	t_H^b	t_H^b [86]	t_L^b	t_L^b [86]
A-T	-12	26	-9	34
G-C	-12	5	16	63

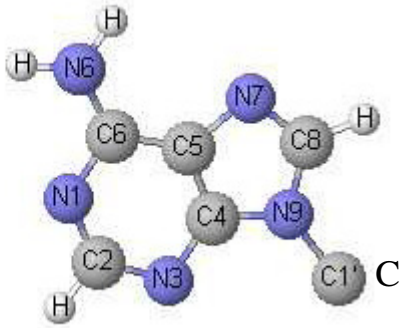
all hopping parameters in meV

Geometrical structure and atomic occupation probabilities A, T, A-T

C5m thymine's methyl carbon

thymine



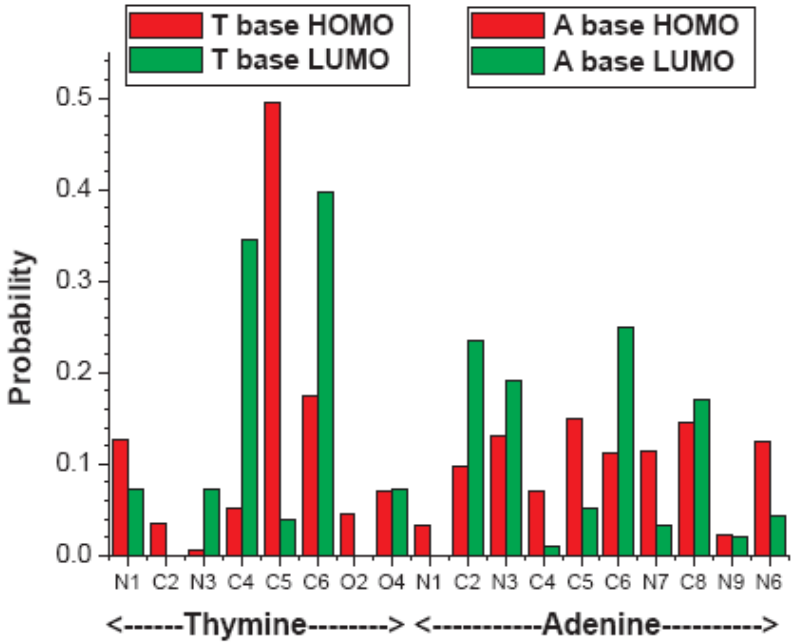


adenine

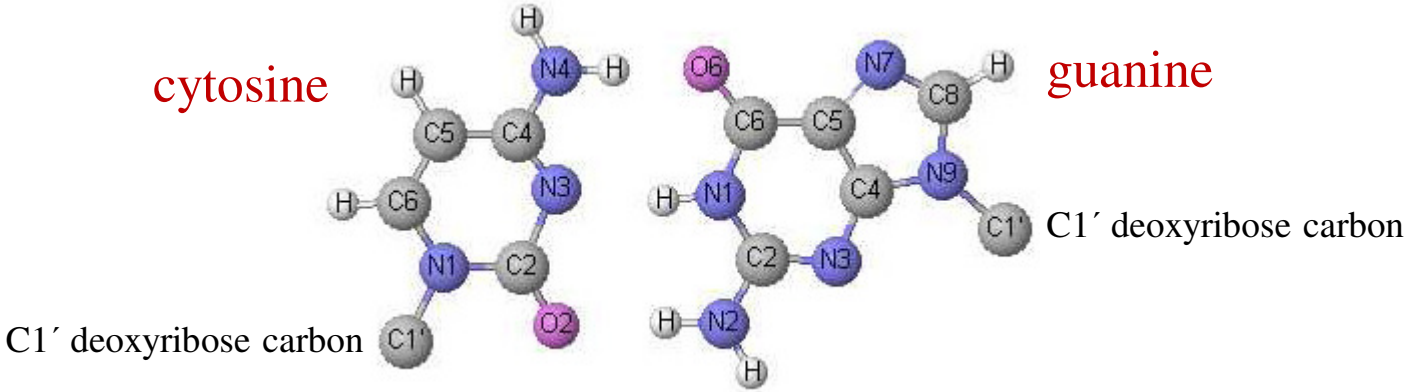
C1´ deoxyribose carbon

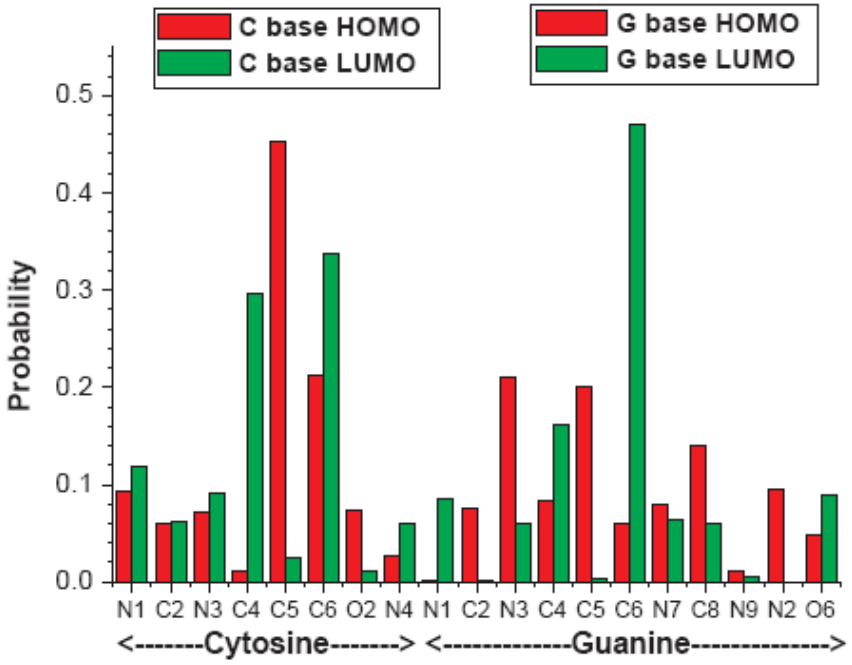
C1´ deoxyribose carbon

within an A-T base-pair



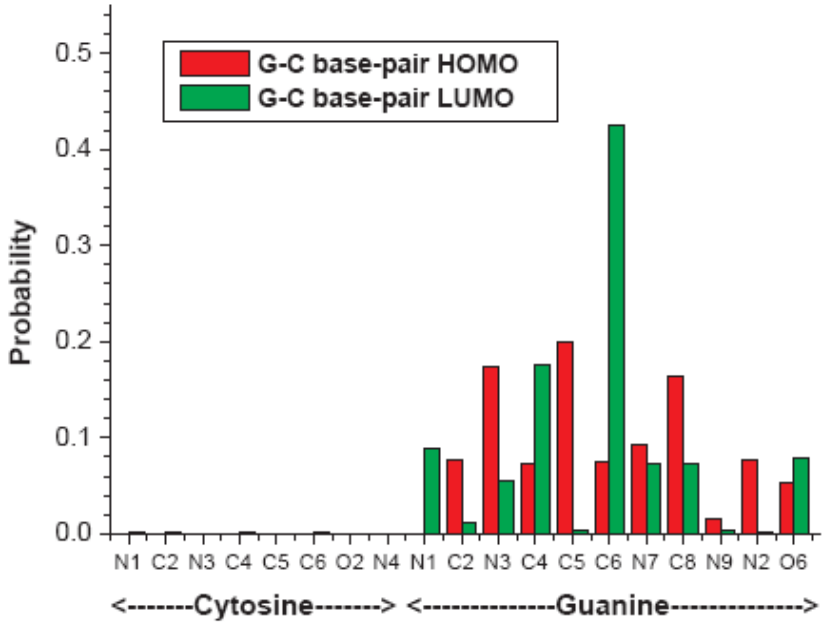
Geometrical structure and atomic occupation propabilites G, C, G-C





$|c_i|^2$

HOMO & LUMO wavefunctions of isolated C and G bases



$|C_i|^2$

HOMO & LUMO wavefunctions of G-C base-pair

C. Tight-binding hopping parameters

1. Description at the base-pair level

Aim: calculate all tight binding parameters for charge transfer along B-DNA

Assume: holes (. . . HOMOs) or electrons (. . . LUMOs) can be transferred via the overlap of the π-molecular orbitals of the stacked base-pairs

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

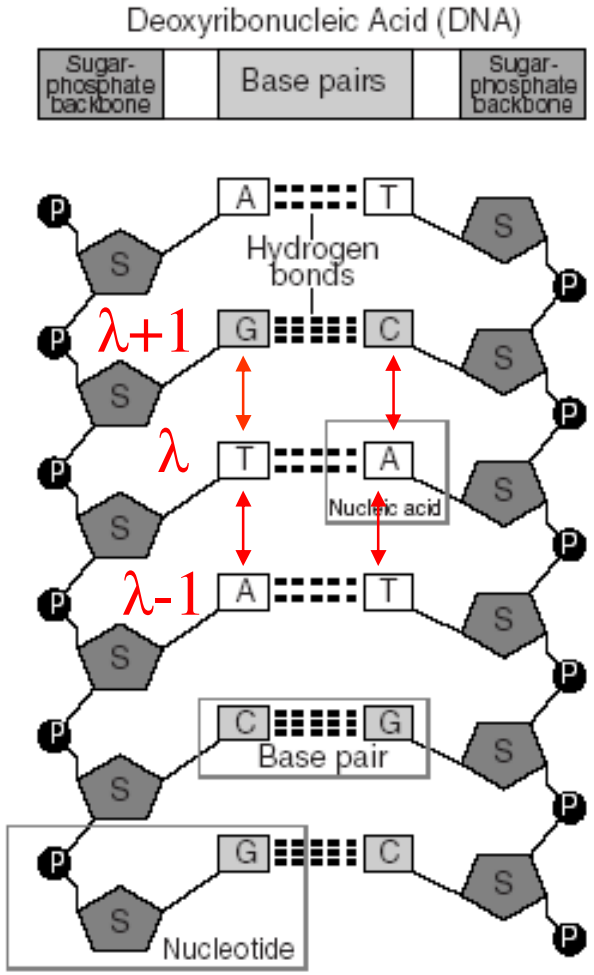
Description at the base-pair level

time dependent wavefunction of the whole DNA

λ^{th} base-pair's HOMO/LUMO wavefunction

The time evolution of the coefficients $A_{\lambda}(t)$ obeys the following system of equations:

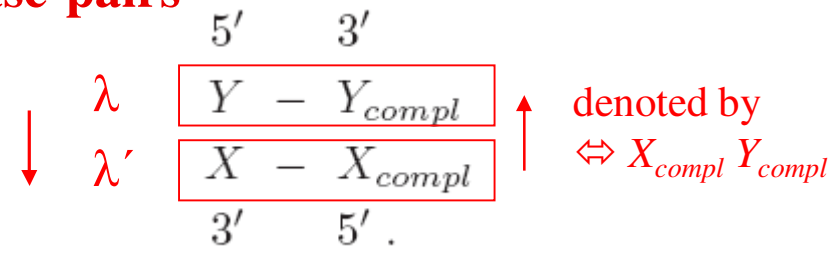
$$i\hbar\frac{dA_{\lambda}}{dt} = E_{H/L}^{bp(\lambda)}A_{\lambda} + t_{H/L}^{bp(\lambda;\lambda-1)}A_{\lambda-1} + t_{H/L}^{bp(\lambda;\lambda+1)}A_{\lambda+1}$$



hopping parameters between successive base-pairs

$$t_{H/L}^{bp(\lambda;\lambda')} = \sum_{i=1}^{N_\lambda} \sum_{j=1}^{N_{\lambda'}} C_{i(\lambda)}^{H/L\,\star}\, C_{j(\lambda')}^{H/L}\, V_{ij}$$

denoted by $\Leftrightarrow YX$



denoted by $\Leftrightarrow X_{compl}\, Y_{compl}$

Base-pair sequence	t_H^{bp}	$\lvert t_H^{bp}\rvert$ [83]	t_H^{bp} [84]	t_H^{bp} [4]	t_L^{bp}	t_L^{bp} [84]	t_L^{bp} [4]
AA, TT	-8	26	-70	≈ -25	-29	105	≈ 35
AT	20	50			0.5		
AG, CT	-5	122	-71	≈ -50	3	112	≈ 35
AC, GT	2	27			32		
TA	47	55			2		
TG, CA	-4	26			17		
TC, GA	-79	25	-187	≈ -160	-1	47	≈ 35
GG, CC	-62	93	-141	≈ -140	20	53	≈ 35
GC	1	78			-10		
CG	-44	22			-8		

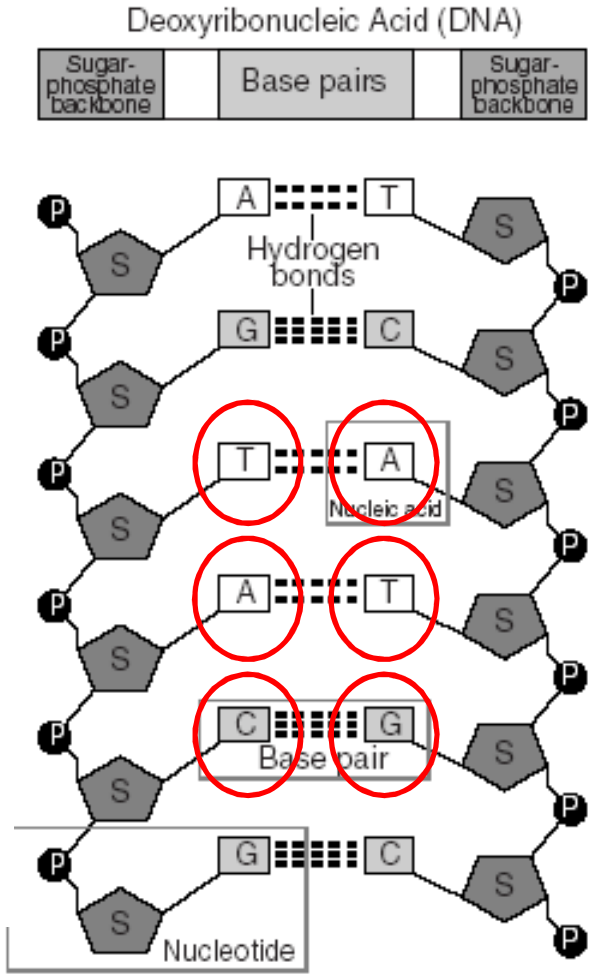
all hopping parameters in meV

C. Tight-binding hopping parameters

2. Description at the single-base level

$$\Psi_{\mathrm{H/L}}^{\mathrm{DNA}}(\mathbf{r},t)=\sum_{\lambda}\left[A_{\lambda}(t)\Psi_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1)}(\mathbf{r})+B_{\lambda}(t)\Psi_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2)}(\mathbf{r})\right]$$

$$\begin{aligned}
i\hbar\frac{\mathrm{d}A_{\lambda}}{\mathrm{d}t} &= E_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1)}\,A_{\lambda}+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1;\lambda,2)}\,B_{\lambda}+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1;\lambda-1,1)}\,A_{\lambda-1}\\
&\quad+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1;\lambda+1,1)}\,A_{\lambda+1}+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1;\lambda-1,2)}\,B_{\lambda-1}\\
&\quad+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,1;\lambda+1,2)}\,B_{\lambda+1},\\
i\hbar\frac{\mathrm{d}B_{\lambda}}{\mathrm{d}t} &= E_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2)}\,B_{\lambda}+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2;\lambda,1)}\,A_{\lambda}+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2;\lambda-1,2)}\,B_{\lambda-1}\\
&\quad+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2;\lambda+1,2)}\,B_{\lambda+1}+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2;\lambda-1,1)}\,A_{\lambda-1}\\
&\quad+t_{\mathrm{H/L}}^{\mathrm{b}(\lambda,2;\lambda+1,1)}\,A_{\lambda+1}.
\end{aligned}$$



C. Tight-binding hopping parameters

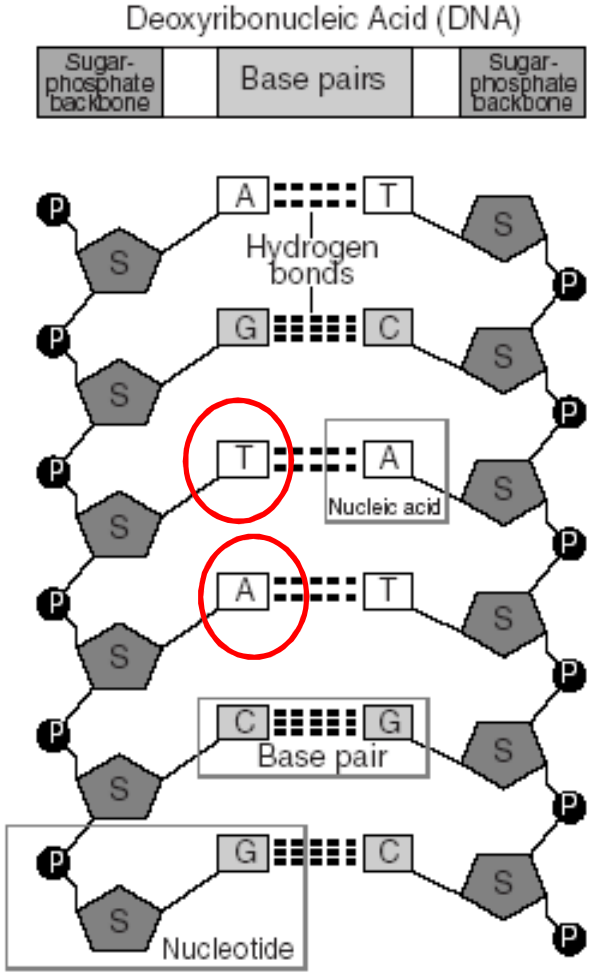
2. Description at the single-base level

(2a) successive bases in the same strand

$$t_{H/L} = \sum_{i=1}^{N_1} \sum_{i=1}^{N_2} c_{i(1)}^{H/L\,\star}\, c_{j(2)}^{H/L}\, V_{ij}$$

$$\begin{matrix} 5' & & 3' \\ Y & - & Y_{compl} \\ X & - & X_{compl} \end{matrix}$$

Base sequence	t_H^b	$\lvert t_H^b \rvert$ [87]	$\lvert t_H^b \rvert$ [85]	t_H^b [88]	$\lvert t_H^b \rvert$ [89]	t_H^b [86]	t_L^b	t_L^b [86]
AA	-8	30	4	-4	8	21	16	25
AT	68	105		-63	28		7	
AG	-5	49	44	-10	37		1	
AC	68	61		42	30		-3	
TA	26	86		-31	64		-7	
TT	-117	158		72	93	-98	-30	-23
TG	28	85	61	18	70		-17	
TC	-86	76		-28	52		22	
GA	-79	89	36	-77	52		30	
GT	73	137	81	141	49		-32	
GG	-62	84	51	53	61	-114	20	20
GC	80	110		-114	57		43	
CA	5	29		-2	5		-12	
CT	-107	100		-55	33		63	
CG	-1	42		9	31		15	
CC	-66	41		22	26	-21	-47	-60



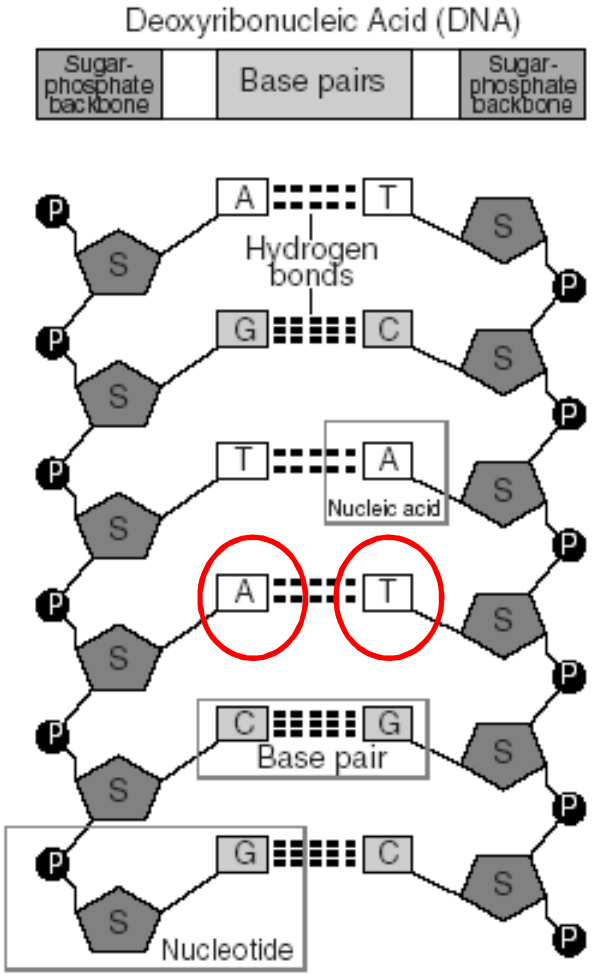
all hopping parameters in meV

(2b) complementary bases within a base-pair,

intra-base-pair hopping parameters

Base-pair	t_H^b	t_H^b [86]	t_L^b	t_L^b [86]
A-T	-12	26	-9	34
G-C	-12	5	16	63

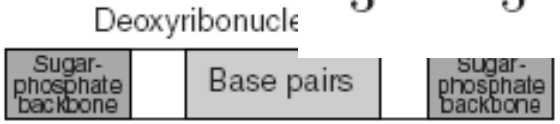
all hopping parameters in meV



(2c) diagonally located bases in opposite strands of successive base-pairs

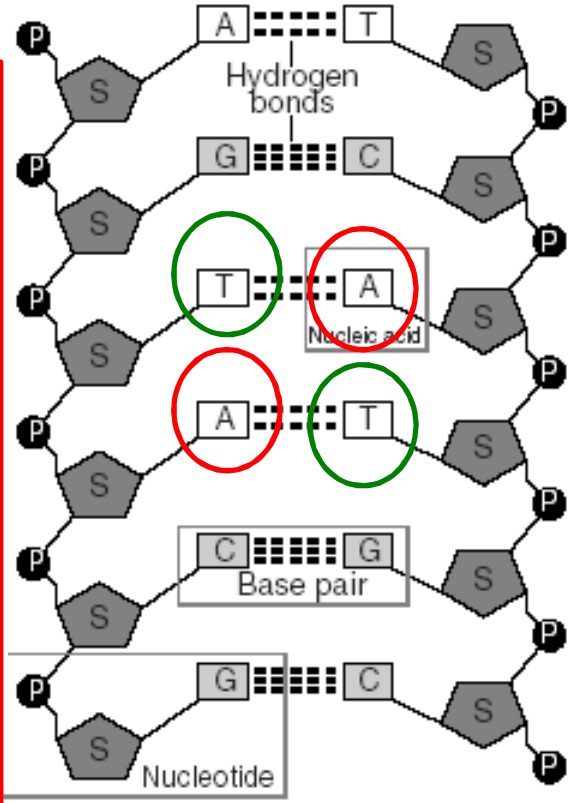
$$t_{H/L} = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} c_{i(1)}^{H/L\,\star}\, c_{j(2)}^{H/L}\, V_{ij}$$

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



Base sequence	t_H^b	t_H^b [88]	$\lvert t_H^b \rvert$ [86]	t_L^b	t_L^b [86]
AA	48	49		29	
AT, TA	-3	-7	9	3	-13
AG, GA	-3	-11		-6	
AC, CA	-5	17		-3	
TT	0.5	6		0.2	
TG, GT	5	-14		2	
TC, CT	0.5	4		-0.2	
GG	-44	-32		-5	
GC, CG	4	22	48	-4	-15
CC	1	10		0.3	

all hopping parameters in meV



Base sequence	t_H^b	t_H^b [88]	$\lvert t_H^b \rvert$ [87]	t_H^b [86]	t_L^b	t_L^b [86]
AA	2	31	31-35		6	
AT, TA	9	7	16-20	-11	2	-10
AG, GA	4	-13	19-24		3	
AC, CA	5	-1			-2	
TT	4	1	3-4		2	
TG, GT	5	-9			3	
TC, CT	2	0.3			-2	
GG	3	12	19		-2	
GC, CG	4	2		-8	-3	-12
CC	1	1	1		2	

all hopping parameters in meV

Conclusions

All tight-binding parameters for charge transfer along B-DNA

- π electronic structure of A, T, C, G by LCAO with a novel parametrization

- HOMO and LUMO of B-DNA A-T, G-C by LCMO

- took into account the slight deformation of bases within the base-pairs of B-DNA (compared to the isolated bases)
A-T: HOMO in A, LUMO in T,
G-C: HOMO in G, LUMO in G.

- HOMO energy of bases: deviation < 0.3 eV from experiment
(G, C: coincide T: 0-0.2 eV A: 0.2-0.3 eV)

- 1st π-π* transition of bases: deviations from experiment:
C:0-0.2 eV T:0.4-0.5 eV, G:0.5-0.7 eV A:0.7-1.0 eV

- compared with other theoretical results from first principles calculations

& Conclusions

- hopping parameters (electrons, holes) between
(1) succesive base-pairs
(2) neighboring bases
    (2a) successive bases in the same strand,
    (2b) complementary bases within a base-pair,
    (2c) diagonally located bases in opposite strands of successive base-pairs

- ~ hopping parameters for holes (HOMOs) > for electrons (LUMOs)
  => probably hole transport more favorable

-**temporal** and **spatial** evolution of electron or hole along DNA
can now be examined in experimentally relevant time and length scales

hole/electron **transmission coefficients** and **conductivities**
can be calculated for any DNA segment

The end

Thank you

References

scales. Important measurable quantities like hole/electron transmission coefficients and conductivities can be calculated for any DNA segment (of whatever base sequence) under consideration, since there are well-established techniques to compute such a quantities from tight-binding models. Furthermore, relative reaction rates for charge transfer between donors and acceptors within DNA segments can be calculated and compared with relevant experiments.

We acknowledge useful discussions with N. Lathiotakis and support from the C. Carathéodory program C155 of University of Patras.

References

1. C. Dekker, M. Ratner, Phys. World, August 2001 issue, 29 (2001).
2. K. Keren, M. Krueger, R. Gilad, G. Ben-Yoseph, U. Sivan, E. Braun, Science **297**, 72 (2002).
3. N.C. Seeman, Nature **421**, 427 (2003).
4. R.G. Endres, D.L. Cox, R.R.P. Singh, Rev. Mod. Phys. **76**, 195 (2004).
5. C.J. Burrows, J.G. Muller, Chem. Rev. **98**, 1109 (1998).
6. J. Cadet, in *DNA Adducts: Identification and Significance*, edited by K. Hemminki, A. Dipple, D.E.F. Shiker, F.F. Kadlubar, D. Segerback, H. Bartsch (IARC, Lyon, 1994).
7. P.J. Dandliker, R.E. Holmlin, J.K. Barton, Science **275**, 1465 (1997).
8. S.R. Rajski, B.A. Jackson, J.K. Barton, Mutation Res. **447**, 49 (2000).
9. Y. Zhang, R.H. Austin, J. Kraeft, E.C. Cox, N.P. Ong, Phys. Rev. Lett. **89**, 198102 (2002).
10. A.J. Storm, J. van Noort, S. de Vries, C. Dekker, Appl. Phys. Lett. **79**, 3881 (2001).
11. P.J. de Pablo, F. Moreno-Herrero, J. Colchero, J. Gómez Herrero, P. Herrero, A.M. Baró, P. Ordejón, J.M. Soler, E. Artacho, Phys. Rev. Lett. **85**, 4992 (2000).
12. K.-H. Yoo, D.H. Ha, J.-O. Lee, J.W. Park, Jinhee Kim, J.J. Kim, H.-Y. Lee, T. Kawai, Han Yong Choi, Phys. Rev. Lett. **87**, 198102 (2001).
13. L. Cai, H. Tabata, T. Kawai, Appl. Phys. Lett. **77**, 3105 (2000).
14. H.W. Fink, C. Schonenberger, Nature **398**, 407 (1999).
15. P. Tran, B. Alavi, G. Gruner, Phys. Rev. Lett. **85**, 1564 (2000).
16. Z. Kutnjak, C. Filipič, R. Podgornik, L. Nordenskiöld, N. Korolev, Phys. Rev. Lett. **90**, 098101 (2003).
17. J.B. MacNaughton, A. Moewes, J.S. Lee, S.D. Wettig, H.-B. Kraatz, L.Z. Ouyang, W.Y. Ching, E.Z. Kurmaev, J. Phys. Chem. B **110**, 15742 (2006).
18. S.S. Mallajosyula, A. Datta, S.K. Pati, Synth. Met. **155**, 398 (2005).
19. P. Maragakis, R.L. Barnett, E. Kaxiras, M. Elstner, T. Frauenheim, Phys. Rev. B **66**, 241104 (2002).
20. A. Rakitin, P. Aich, C. Papadopoulos, Yu. Kobzar, A.S. Vedeneev, J.S. Lee, J.M. Xu, Phys. Rev. Lett. **86**, 3670 (2001).
21. M. Fuentes-Cabrera, B.G. Sumpter, J.C. Wells, J. Phys. Chem. B **109**, 21135 (2005).
22. M. Fuentes-Cabrera, B.G. Sumpter, P. Lipkowski, J.C. Wells, J. Phys. Chem. B **110**, 6379 (2006).
23. M. Fuentes-Cabrera, X. Zhao, P.C. Kent, B.G. Sumpter, J. Phys. Chem. B **111**, 9057 (2007).
24. M.R. Arkin, E.D.A. Stemp, R.E. Holmlin, J.K. Barton, A. Hörmann, E.J.C. Olson, P.F. Barbara, Science **273**, 475 (1996).
25. D.B. Hall, R.E. Holmlin, J.K. Barton, Nature **382**, 731 (1996).
26. D. Porath, A. Bezryadin, S. de Vries, C. Dekker, Nature **403**, 635 (2000).
27. Ch. Adesi, S. Walch, M.P. Anantram, Phys. Rev. B **67**, 081405(R) (2003).
28. Ch. Adesi, M.P. Anantram, Appl. Phys. Lett. **82**, 2353 (2003).
29. S.V. Rakhmanova, E.M. Conwell, J. Phys. Chem. B **105**, 2056 (2001).
30. W. Zhang, A.O. Govorov, S.E. Ulloa, Phys. Rev. B **66**, 060303 (2002).
31. S. Komineas, G. Kalosakas, A.R. Bishop, Phys. Rev. E **65**, 061905 (2002).
32. P. Maniadis, G. Kalosakas, K.Ø. Rasmussen, A.R. Bishop, Phys. Rev. B **68**, 174304 (2003).
33. M.R. Singh, J. Biomater. Sci. Polym. Edn. **15**, 1533 (2004).
34. G.P. Triberis, C. Simserides, V.C. Karavolas, J. Phys.: Condens. Matter **17**, 2681 (2005).
35. G.P. Triberis, M. Dimakogianni, J. Phys.: Condens. Matter **21**, 035114 (2009).
36. Y.-J. Ye, R.-S. Chen, A. Martinez, P. Otto, J. Ladik, Solid State Commun. **112**, 139 (1999).
37. P.T. Henderson, D. Jones, G. Hampikian, Y. Kan, G.B. Schuster, Proc. Natl. Acad. Sci. U.S.A. **96**, 8353 (1999).
38. R. Bruinsma, G. Grüner, M.R. D'Orsogna, J. Rudnick, Phys. Rev. Lett. **85**, 4393 (2000).
39. G. Kalosakas, K.Ø. Rasmussen, A.R. Bishop, J. Chem. Phys. **118**, 3731 (2003).
40. G. Kalosakas, K.Ø. Rasmussen, A.R. Bishop, Synth. Met. **141**, 93 (2004).
41. F.C. Grozema, S. Tonzani, Y.A. Berlin, G.C. Schatz, L.D.A. Siebbeles, M.A. Ratner, J. Am. Chem. Soc. **130**, 5157 (2008).
42. P.B. Woiczikowski, T. Kubar, R. Gutierrez, R.A. Caetano, G. Cuniberti, M. Elstner, J. Chem. Phys. **130**, 215104 (2009).
43. E. Meggers, M.E. Michel-Beyerle, B. Giese, J. Am. Chem. Soc. **120**, 12950 (1998).
44. B. Giese, Acc. Chem. Res. **33**, 631 (2000).
45. Y.A. Berlin, A.L. Burin, M.A. Ratner, J. Phys. Chem. A **104**, 443 (2000).
46. Y.A. Berlin, A.L. Burin, M.A. Ratner, J. Am. Chem. Soc. **123**, 260 (2001).
47. Z.G. Yu, X. Song, Phys. Rev. Lett. **86**, 6018 (2001).
48. D. Hennig, Eur. Phys. J. B **30**, 211 (2002).
49. D. Hennig, E.B. Starikov, J.F.R. Archilla, F. Palmero, J. Biol. Phys. **30**, 227 (2004).
50. G. Kalosakas, K.L. Ngai, S. Flach, Phys. Rev. E **71**, 061901 (2005).
51. P. Maniadis, G. Kalosakas, K.Ø. Rasmussen, A.R. Bishop, Phys. Rev. E **72**, 021912 (2005).
52. E. Diaz, R.P.A. Lima, F. Dominguez-Adame, Phys. Rev. B **78**, 134303 (2008).

References

53. L.G.D. Hawke, G. Kalosakas, C. Simserides, Mol. Phys. **107**, 1755 (2009).
54. L.G.D. Hawke, C. Simserides, G. Kalosakas, Mater. Sci. Eng. B **165**, 266 (2009).
55. W.A. Harrison, *Electronic Structure and the Properties of Solids*, 2nd edition (Dover, New York, 1989); *Elementary Electronic Structure* (World Scientific, 1999).
56. J.C. Slater, G.F. Koster, Phys. Rev. **94**, 1498 (1954).
57. M. Menon, R.E. Allen, Phys. Rev. B **38**, 6196 (1988).
58. N. Lathiotakis, A.N. Andriotis, Solid State Commun. **87**, 871 (1993).
59. M. Menon, J. Connolly, N. Lathiotakis, A. Andriotis, Phys. Rev. B **50**, 8903 (1994).
60. N. Rosch, A.A. Voityuk, Top. Curr. Chem. **237**, 37 (2004).
61. `http://chemistry.gsu.edu/Glactone/PDB/pdb.html`.
62. N.S. Hush, A.S. Cheung, Chem. Phys. Lett. **34**, 11 (1975).
63. G. Lauer, W. Schafer, A. Schweig, Tetrahedron Lett. **45**, 3939 (1975).
64. D. Dougherty, K. Wittel, J. Meeks, S.P. McGlynn, J. Am. Chem. Soc. **98**, 3815 (1976).
65. J. Lin, C. Yu, S. Peng, I. Akiyama, K. Li, L.K. Lee, P.R. LeBreton, J. Am. Chem. Soc. **102**, 4627 (1980).
66. J. Lin, C. Yu, S. Peng, I. Akiyama, K. Li, L.K. Lee, P.R. LeBreton, J. Phys. Chem. **84**, 1006 (1980).
67. S. Urano, X. Yang, P. R. LeBreton, J. Mol. Sruct. **214**, 315 (1989).
68. D. Voet, W.B. Gratzer, R.A. Cox, P. Doty, Biopolymers **1**, 193 (1963).
69. L.B. Clark, G.G. Peschel, I. Tinoco Jr., J. Phys. Chem. **69**, 3615 (1965).
70. D.W. Miles, R.K. Robins, H. Eyring, Proc. Natl. Acad. Sci. U.S.A. **57**, 1139 (1967).
71. T. Yamada, H. Fukutome, Biopolymers **6**, 43 (1968).
72. W. Voelter, R. Records, E. Bunnenberg, C. Djerassi, J. Am. Chem. Soc. **90**, 6163 (1968).
73. A.F. Fucaloro, L.S. Forster, J. Am. Chem. Soc. **93**, 6443 (1971).
74. W.C. Brunner, M.F. Maestre, Biopolymers **14**, 555 (1975).
75. C.A. Sprecher, W.C. Johnson, Biopolymers **16**, 2243 (1977).
76. K. Raksanyi, I. Foldvary, J. Fidy, L. Kittler, Biopolymers **17**, 887 (1978).
77. Y. Matsuoka, B. Norden, J. Phys. Chem. **86**, 1378 (1982).
78. F. Zaloudek, J.S. Novros, L.B. Clark, J. Am. Chem. Soc. **107**, 7344 (1985).
79. L.B. Clark, J. Phys. Chem. **94**, 2873 (1990).
80. A. Holmen, A. Broo, B. Albinsson, B. Norden, J. Am. Chem. Soc. **119**, 12240 (1997).
81. A.O. Colson, B. Besler, D.M. Close, M.D. Sevilla, J. Phys. Chem. **96**, 661 (1992).
82. H. Sugiyama, I. Saito, J. Am. Chem. Soc. **118**, 7063 (1996).
83. M. Hutter, T. Clark, J. Am. Chem. Soc. **118**, 7574 (1996).
84. M.P. Fülscher, B.O. Roos, J. Am. Chem. Soc. **117**, 2089 (1995).
85. J. Lorentzon, M.P. Fülscher, B.O. Roos, J. Am. Chem. Soc. **117**, 9265 (1995).
86. M.P. Fülscher, L. Serrano-Andres, B.O. Roos, J. Am. Chem. Soc. **119**, 6168 (1997).
87. M.K. Shukla, P.C. Mishra, Chem. Phys. **240**, 319 (1999).
88. B. Mennucci, A. Toniolo, J. Tomasi, J. Phys. Chem. A. **105**, 4749 (2001).
89. X. Li, Z. Cai, M.D. Sevilla, J. Phys. Chem. B **105**, 10115 (2001).
90. X. Li, Z. Cai, M.D. Sevilla, J. Phys. Chem. A **106**, 9345 (2002).
91. A.L. Sobolewski, W. Domcke, Eur. Phys. J. D **20**, 369 (2002).
92. N. Ismail, L. Blancafort, M. Olivucci, B. Kohler, M.A. Robb, J. Am. Chem. Soc. **124**, 6818 (2002).
93. M.K. Shukla, J. Leszczynski, J. Phys. Chem. A. **106**, 11338 (2002).
94. M.K. Shukla, J. Leszczynski, J. Comput. Chem. **25**, 768 (2004).
95. D. Varsano, R. Di Felice, M.A.L. Marques, A. Rubio, J. Phys. Chem. B **110**, 7129 (2006).
96. T. Fleig, S. Knecht, C. Hättig, J. Phys. Chem. A **111**, 5482 (2007).
97. H. Zhang, X.Q. Li, P. Ham, X.Y. Yu, Y.J. Yan, J. Chem. Phys. **117**, 4578 (2002).
98. M.K. Shukla, J. Leszczynski, J. Phys. Chem. A **106**, 4709 (2002).
99. `http://www.jmol.org/`.
100. T. Cramer, S. Krapf, T. Koslowski, J. Phys. Chem. B **108**, 11812 (2004).
101. R. Di Felice, A. Calzolari, E. Molinari, Phys. Rev. B **65**, 045104 (2001).
102. A.A. Voityuk, J. Jortner, M. Bixon, N. Rösch, J. Chem. Phys. **114**, 5614 (2001).
103. R.G. Endres, D.L. Cox, R.R.P. Singh, arXiv:cond-mat/0201404v2 (2002).
104. L. Blancafort, A.A. Voityuk, J. Phys. Chem. A **110**, 6426 (2006).
105. A. Migliore, S. Corni, D. Varsano, M.L. Klein, R. Di Felice, J. Phys. Chem. B **113**, 9402 (2009).
106. H. Mehrez, M.P. Anantram, Phys. Rev. B **71**, 115405 (2005).
107. A.A. Voityuk, N. Rösch, M. Bixon, J. Jortner, J. Phys. Chem. B **104**, 9740 (2000).
108. K. Senthilkumar, F.C. Grozema, C.F. Guerra, F.M. Bickelhaupt, F.D. Lewis, Y.A. Berlin, M.A. Ratner, L.D.A. Siebbeles, J. Am. Chem. Soc. **127**, 14894 (2005).
109. T. Kubar, P.B. Woiczikowski, G. Cuniberti, M. Elstner, J. Phys. Chem. B **112**, 7937 (2008).