Tight Binding Parameters for Charge Transport in DNA

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

[1] *Materials Science Department, University of Patras, GR-26504 Rio, Greece*
[2] *Institute of Materials Science,NCSR Demokritos, GR-15310 Athens, Greece*

**georgek@upatras.gr*

We examine the tight-binding parameters pertinent to charge transfer along DNA. The π molecular structure of the four DNA bases, adenine (A), thymine (T), cytosine (C), and guanine (G), is investigated within the linear combination of atomic orbitals approach, using a recently introduced parametrization [1,2]. The HOMO and LUMO wavefunctions and energies of DNA bases are then used for calculating the corresponding wavefunctions of the two B-DNA base-pairs, adenine-thymine (A-T) and guanine-cytosine (G-C). These results are used for estimating charge transfer parameters between neighboring bases and also between successive base-pairs, considering all possible combinations between them [3]. The calculated microscopic quantities can be used in mesoscopic theoretical models of electron or hole transfer along the DNA double helix, as they provide the parameters for a tight-binding phenomenological description based on the π molecular overlap [3,4]. The obtained results for the HOMO and LUMO base energies are in good agreement with experimental values.

A tight-binding description of a single carrier (electron or hole) is obtained assuming that a hole travels through HOMOs and an electron through LUMOs. Such a description may be either at the base-pair level or at a single-base level. In the former case charge transfer is considered to occur between successive base-pairs of the DNA. The HOMO/LUMO (H/L) base-pair wavefunctions are given through

$$\Psi_{H/L}^{bp}(r)=\sum_{i=1}^{N} C_i^{H/L}\, p_z^i(r) \quad , \tag{1}$$

where the sum is extended over the N atoms (contributing p_z electrons) of the whole base-pair (N =18 for A-T base-pairs and N =19 for G-C). The time-dependent wavefunction of the whole DNA molecule is written as

$$\Psi_{H/L}^{DNA}(r,t)=\sum_{\lambda} \mathrm{A}_\lambda(t)\,\Psi_{H/L}^{bp(\lambda)}(r) \quad , \tag{2}$$

with the sum extended over all base-pairs of the DNA segment under consideration. The time evolution of the coefficients $A_\lambda(t)$ is obtained through time-dependent Schrödinger equation $i\hbar \dfrac{d\Psi_{H/L}^{DNA}}{dt} = H^{DNA}\Psi_{H/L}^{DNA}$. Following standard assumptions one obtains the following system of equations [3]:

$$i\hbar\frac{d\mathrm{A}_\lambda}{dt} = E_{H/L}^{bp(\lambda)}\mathrm{A}_\lambda + t_{H/L}^{bp(\lambda;\lambda-1)}\mathrm{A}_{\lambda-1} + t_{H/L}^{bp(\lambda;\lambda+1)}\mathrm{A}_{\lambda+1} \, , \tag{3}$$

where $E_{H/L}^{bp(\lambda)}$ is the HOMO/LUMO energy of the corresponding base-pair, while the hopping parameters $t_{H/L}^{bp}$ are obtained through

$$t_{H/L}^{bp(\lambda;\lambda')} = \sum_{i=1}^{N_\lambda}\sum_{j=1}^{N_{\lambda'}} C_{i(\lambda)}^{H/L\,*}\; C_{j(\lambda')}^{H/L}\; V_{ij} \; . \tag{4}$$

The matrix elements V_{ij} are given by the Slater-Koster expression [5]

$$V_{ij} = V_{pp\sigma}\sin^2\phi + V_{pp\pi}\cos^2\phi \, , \tag{5}$$

where ϕ is the angle formed by the line connecting atoms i and j and the base-pair plane. The intermolecular matrix elements $V_{pp\sigma}$ and $V_{pp\pi}$ are provided by approximate exponentially decaying expressions [6,7].

The tight-binding description at the single-base level considers charge transfer between neighboring bases. Here the starting point is the molecular single-electron HOMO or LUMO wavefunction for the bases

$$\Psi_{H/L}^{b}(r)=\sum_{i=1}^{N} c_i\, p_z^i(r) \, , \tag{6}$$

where the sum is now extended over the N atoms of the base, that contribute p_z electrons (N =11 for G, N =10 for A, and N =8 for C and T). In this case the time-dependent wavefunction of DNA is

$$\Psi_{H/L}^{DNA}(r,t) = \sum_{\lambda} \left[\mathrm{A}_{\lambda}(t)\, \Psi_{H/L}^{b(\lambda,1)}(r) + B_{\lambda}(t)\, \Psi_{H/L}^{b(\lambda,2)}(r) \right], \tag{7}$$

where λ denotes base-pairs and the sum is again over all successive base-pairs of DNA. $\Psi_{H/L}^{b(\lambda,1)}$, $\Psi_{H/L}^{b(\lambda,2)}$ are HOMO/LUMO wavefunctions of bases located at the one and the other DNA strands, respectively. The corresponding tight-binding equations for the time dependent coefficients in Eq. (7) read

$$\begin{aligned} i\hbar \frac{dA_{\lambda}}{dt} &= E_{H/L}^{b(\lambda,1)} \mathrm{A}_{\lambda} + t_{H/L}^{b(\lambda,1;\lambda,2)} B_{\lambda} + t_{H/L}^{b(\lambda,1;\lambda-1,1)} \mathrm{A}_{\lambda-1} + t_{H/L}^{b(\lambda,1;\lambda+1,1)} \mathrm{A}_{\lambda+1} + t_{H/L}^{b(\lambda,1;\lambda-1,2)} B_{\lambda-1} + t_{H/L}^{b(\lambda,1;\lambda+1,2)} B_{\lambda+1} \\ i\hbar \frac{dB_{\lambda}}{dt} &= E_{H/L}^{b(\lambda,2)} B_{\lambda} + t_{H/L}^{b(\lambda,2;\lambda,1)} A_{\lambda} + t_{H/L}^{b(\lambda,2;\lambda-1,2)} B_{\lambda-1} + t_{H/L}^{b(\lambda,2;\lambda+1,2)} B_{\lambda+1} + t_{H/L}^{b(\lambda,2;\lambda-1,1)} \mathrm{A}_{\lambda-1} + t_{H/L}^{b(\lambda,2;\lambda+1,1)} \mathrm{A}_{\lambda+1} \end{aligned} \tag{8}$$

Here $E_{H/L}^{b}$ are base HOMO/LUMO energies and the hopping parameters t_H^b or t_H^b are inter-base transfer integrals of the following form

$$t_{H/L} = \sum_{i=1}^{N_1} \sum_{\mathrm{j}=1}^{N_2} c_{i(1)}^{H/L\,*}\, c_{j(2)}^{H/L} V_{ij} \ , \tag{9}$$

with V_{ij} given from Eq. (5).

We have calculated all the tight-binding parameters appearing in Eqs. (3) or (8), for both electrons and holes, and for all possible combinations of neighboring base-pairs or bases, respectively [3]. As an example, Table 1 below shows the hopping parameters $t_{H/L}^{bp}$ of Eq. (3), for all combinations between successive base-pairs.

Base-pair sequence	t_H^{bp} (meV)	t_L^{bp} (meV)
AA, TT	-8	-29
AT	20	0.5
AG, CT	-5	3
AC, GT	2	32
TA	47	2
TG, CA	-4	17
TC, GA	-79	-1
GG, CC	-62	20
GC	1	-10
CG	-44	-8

Table 1. Transfer parameters between successive base-pairs XY (first column) given in the direction 5'-3'. The notation XY denotes successive base-pairs X-$\mathrm{X}_{\mathrm{complementary}}$ and Y-$\mathrm{Y}_{\mathrm{complementary}}$, where the one DNA strand contains the XY bases in the direction 5'-XY-3', while the complementary strand is 3'-$\mathrm{X}_{\mathrm{complementary}}\mathrm{Y}_{\mathrm{complementary}}$-5'. Hole hopping parameters t_H^{bp} are shown in second column and electron hopping parameters t_L^{bp} in third column.

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