Charge transfer in dynamic DNA

Yuri A. Berlin

Department of Chemistry
Center for Nanofabrication and Molecular Self-Assembly
and Material Research Center
Northwestern University
2145 Sheridan Road
Evanston, IL 60208-3113
USA

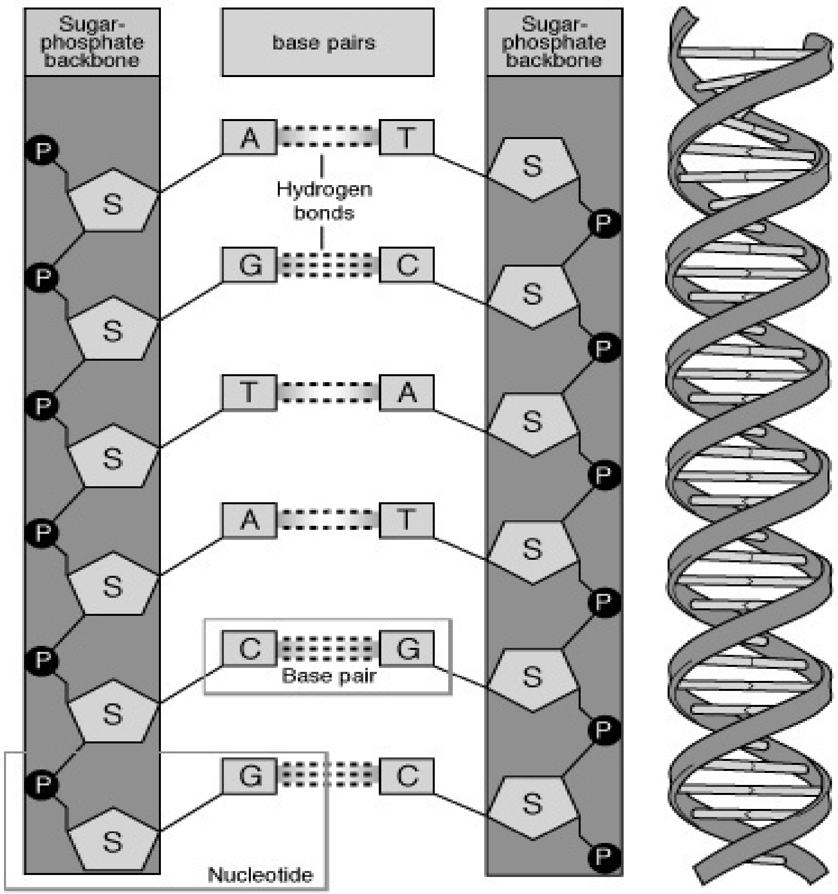
NORTHWESTERN UNIVERSITY

Outline

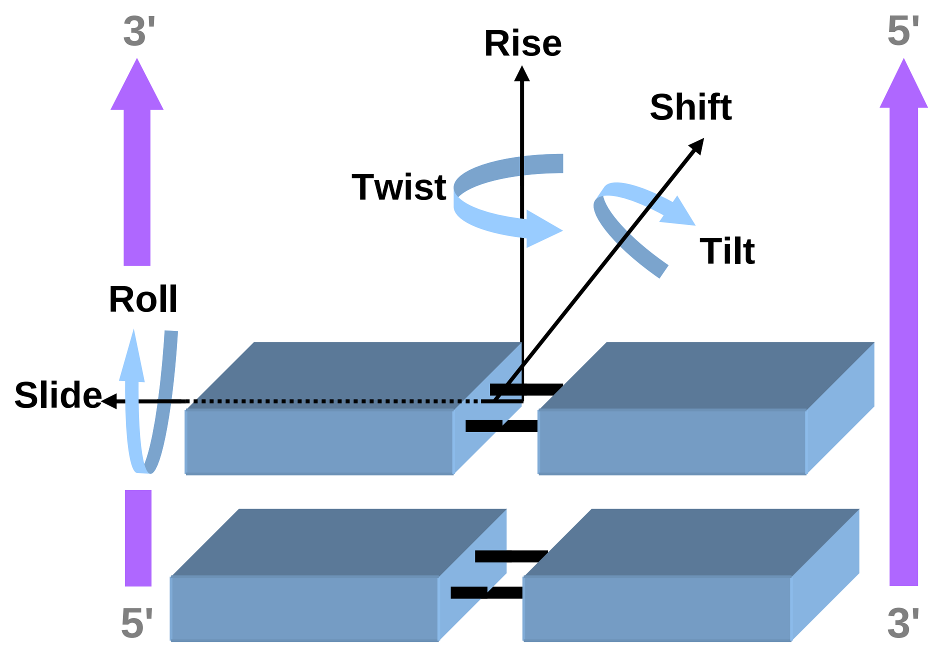
- What is the meaning of the notion "dynamic DNA“?
- Qualitative analysis of the effect of DNA dynamics on charge transfer.
- Tight-binding models and the possibility to study charge transfer beyond the Condon approximation.
- Effects that exist in dynamic DNA

NORTHWESTERN UNIVERSITY

Static and Dynamic DNA Structures



Ideal structure: **Rise=3.38 Å, twist=36º,other parameters are assumed to be zero**

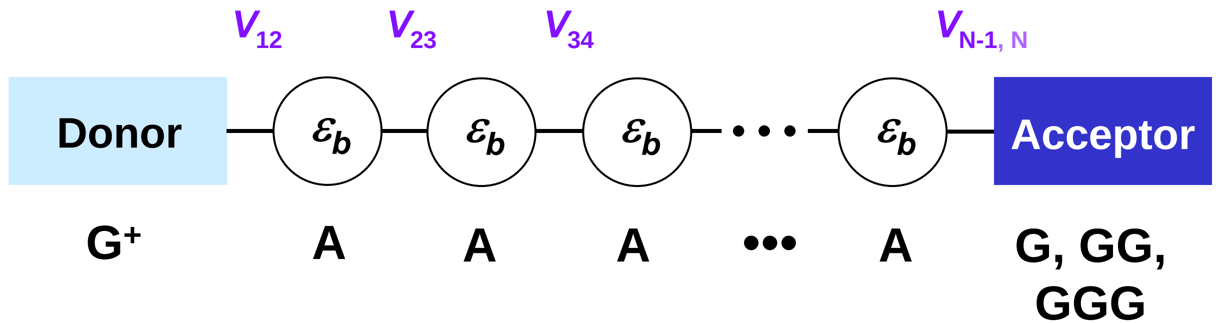


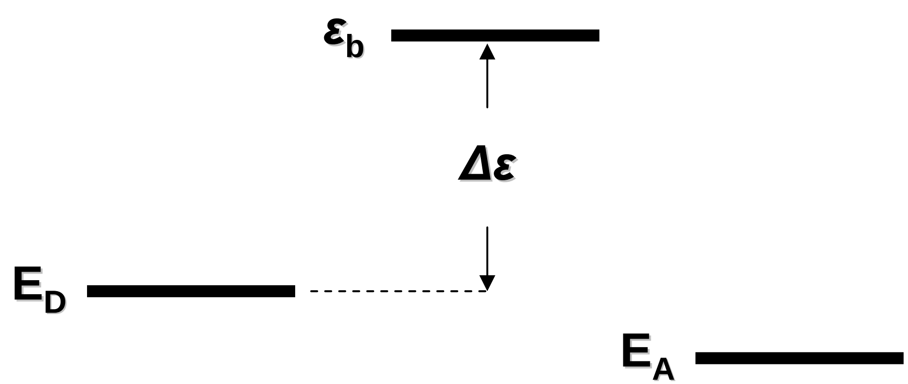
Real structure (X-ray data for 400 base pairs): **Rise=3.2÷3.6 Å, Shift=-1.0÷1.6 Å , Slide=-2.4÷2.8 Å Twist=20÷41 º, Tilt=-7.8÷6.6 º, Roll=-8.6÷25 º**

Is Dynamics Important indeed?

NORTHWESTERN UNIVERSITY

Incoherent (hopping) transport





Will dynamics affect the rate of elementary hopping steps?

NORTHWESTERN UNIVERSITY

Common Description of Elementary Hopping Step

Electronic coupling, *V*, between D and A is depends on nuclear coordinates *Q* parametrically

↓

Squared transition matrix element can be factored into an electronic part and a nuclear part (Frank-Condon factor)

↓

$$w_a = \frac{2\pi}{\hbar}\left|V_{eff}\right|^2 \rho_{FC}$$

Qualitative Analysis of non-Condon Torsional Effects

$$k_{CT} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \exp(i\omega_{DA} t) C_V(t) C_{FC}(t)$$

$\tau_{rot} << \tau_{CT}$

$C_V(t)$ is the electronic coupling correlation function and $C_{FC}(t)$ is the time-dependent Franck-Condon factor with the decay time τ_{FC}

$$C_V(t) = \sigma_V \exp\left(-\frac{t}{\tau_{rot}}\right) + \langle V(t)\rangle^2$$

$$\sigma_V = \langle V(0)^2\rangle - \langle V(t)\rangle^2 = \langle V^2\rangle - V_0^2$$

with the finite time-averaged value $\langle V(t)\rangle = V_0$ and the mean-square deviation of electronic coupling σ_V

$$k_{CT} \propto \int_{-\infty}^{+\infty} dt \exp(i\omega_{DA} t) C_V(t) C_{FC}(t) \approx C_V(0) \int_{-\infty}^{+\infty} dt \exp(i\omega_{DA} t) C_{FC}(t) \cong C_V(0)\rho_{FC}.$$

$\tau_{CT} >> \tau_{rot} >> \tau_{FC}$

$$k_{CT}(t) = \int_{\theta} P(\theta, t) k(\theta) d\theta$$

$\tau_{CT} \tilde{<} \tau_{rot}$

$P(\theta,t)$ is the probability density *to find the two adjacent molecular subunits in the conformation with the torsion angle between* θ and $\theta + d\theta$ at time t

Important Limits

- Fast torsional motion $\tau_{CT} >> \tau_{rot} >> \tau_{FC}$ and small structural fluctuation $\sigma_V << \langle V(t) \rangle^2 = V_0$

$$k_{CT} = \frac{2\pi}{\hbar} |V_0|^2 \rho_{FC}$$

Marcus-Hush-Jortner equation

- Fast torsional motion $\tau_{CT} >> \tau_{rot} >> \tau_{FC}$ and large structural fluctuation $\sigma_V >> \langle V(t) \rangle^2 = V_0$

$$k_{CT} = \frac{2\pi}{\hbar} \langle V^2 \rangle \rho_{FC}$$

Static non-Condon effect

- Slow torsional motion $\tau_{CT} \tilde{<} \tau_{rot}$

$$k_{CT}(t) = \int_\theta P(\theta, t) k(\theta) d\theta$$

Dynamic non-Condon effect

Computational Approach

NORTHWESTERN UNIVERSITY

The wave function of the charge, Ψ, is written as a linear combination of orbitals localized on each site

$$\Psi(t) = \sum_{i=1}^{N} c_i(t)\varphi_i \quad \text{with} \quad c_i(t{=}0) = \delta_{1,i}$$

Charge motion is treated quantum mechanically

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H\Psi(t)$$

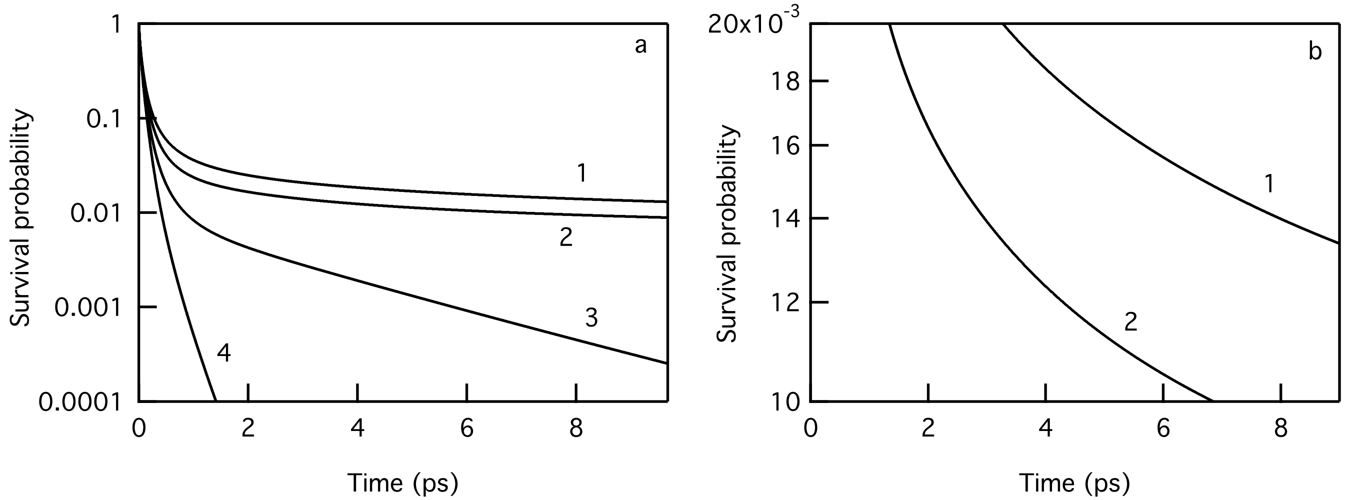
$$H = \begin{pmatrix} \varepsilon_{11} & V_{12} & 0 & \cdots & 0 \\ V_{21} & \varepsilon_b & & & \\ 0 & & \ddots & & \\ \vdots & & & \ddots & \\ 0 & & & & \varepsilon_{NN} - \frac{i\hbar}{\tau} \end{pmatrix}$$

Bridge dynamics is treated classically

$$\Delta\theta_i = -\frac{D_{rot}}{k_B T} \frac{\partial U_{tor}(\theta_i)}{\partial \theta_i} \Delta t + \Delta\theta_{dif}$$

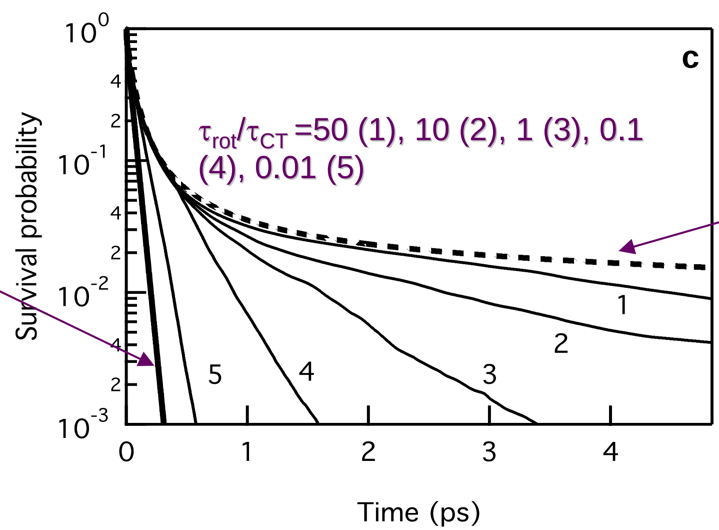
where $D_{rot} = 1/(2\tau_{rot})$ and $\Delta\theta_{dif} = (24 D_{rot} \Delta t)^{1/2} \chi$, $\chi \in [-1/2, 1/2)$

Computational Verification for Static (a and b) and Dynamic (c) Torsional Disorder



σ_V of the charge transfer integral with the average value of 0.3 eV is $3.61 \cdot 10^{-2}$ eV^2 (1), $3.28 \cdot 10^{-2}$ eV^2 (2), $2.89 \cdot 10^{-2}$ eV^2 (3), $2.44 \cdot 10^{-2}$ eV^2 (4); $\Delta\varepsilon$=0.6 eV

Fast fluctuation limit $\tau_{rot}/\tau_{CT} << 1$

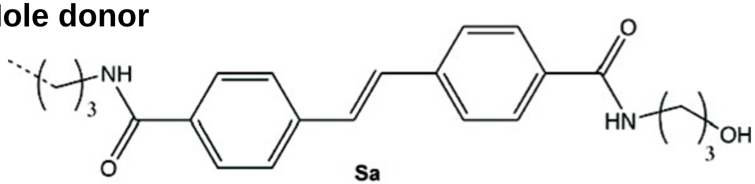


Static disorder limit $\tau_{rot}/\tau_{CT} >> 1$

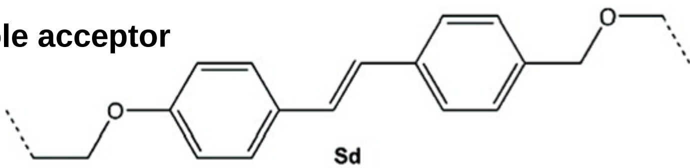
Y. A. Berlin et al. J. Phys. Chem. C **112**, 10988 (2008)

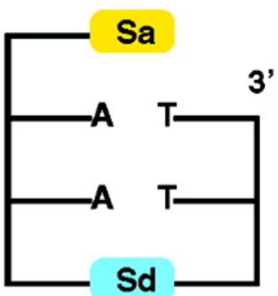
Examples DNA Hairpins

Hole donor

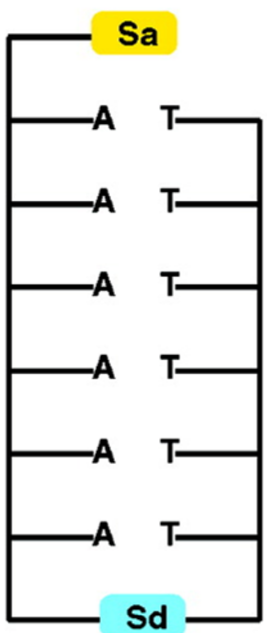


Hole acceptor

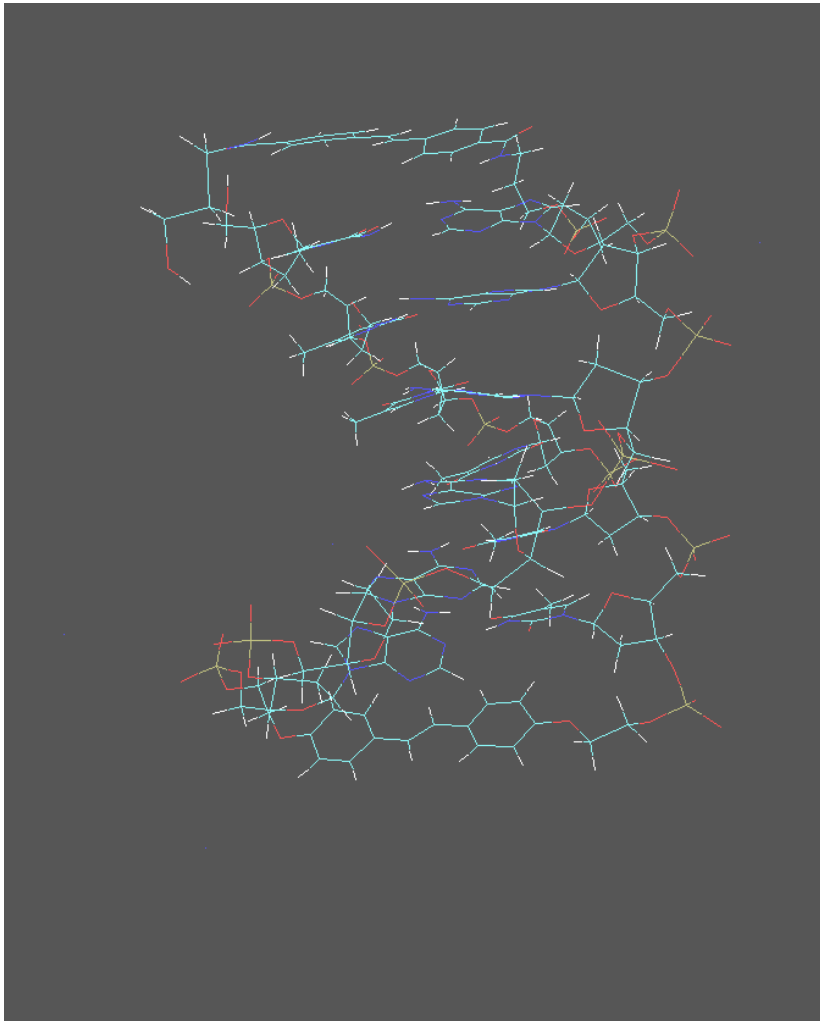




2

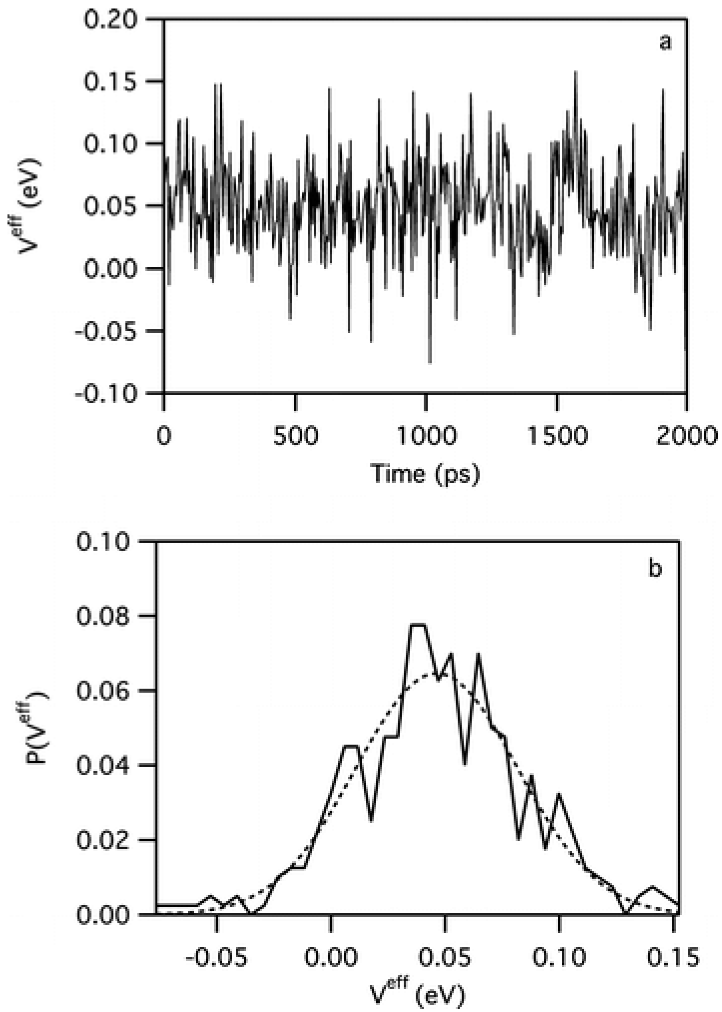


6



NORTHWESTERN UNIVERSITY

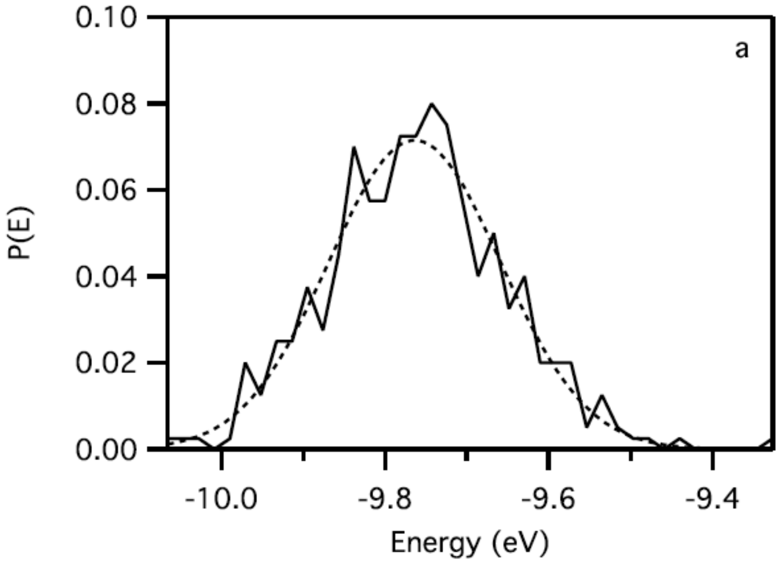
Electronic Coupling in Dynamic DNA Hairpins

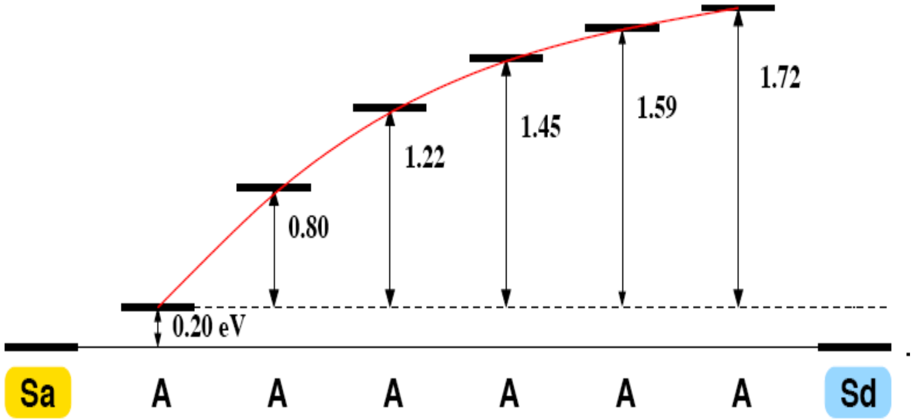


- Coupling fluctuates on sub-ps timescale
- A-A coupling peaks at 0.05 eV and is larger than similar coupling in static B-DNA structure
- Number of AT base pairs, N_{AT}, does not significantly influence the distribution of the values of V_{eff} between neighboring adenines if $N_{AT} \leq 6$
- Couplings between Sa and A and between Sd and A are small (0.005 eV and 0.02 eV, respectively) while the mean-square deviation is about 0.06 eV. These findings suggest the importance of deviations from the average V^{eff} values for charge injection process.

F. C. Grozema et al. J. Am. Chem. Soc.**130**, 5157 (2008)

Site Energies in Dynamic DNA



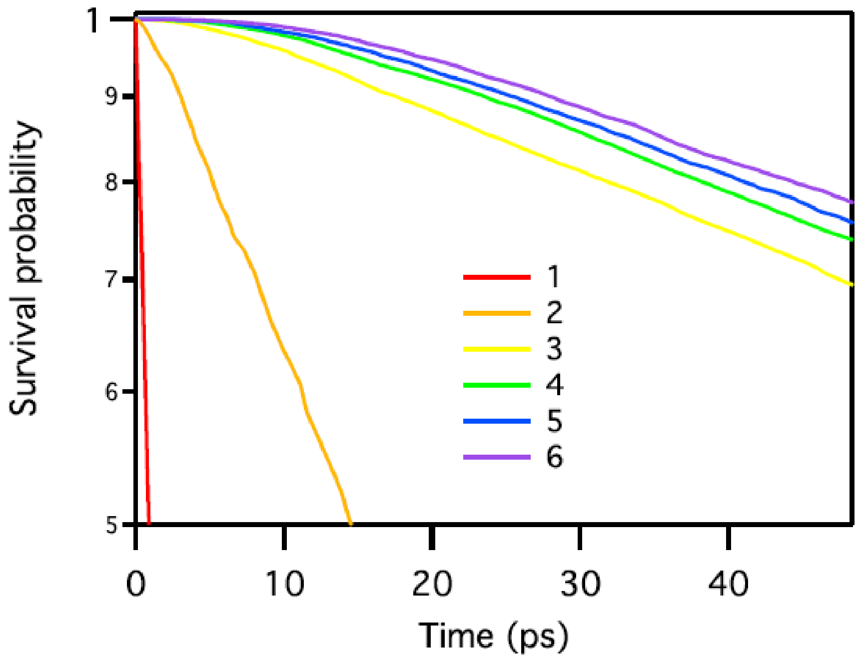


- Mean-square deviation in the fluctuating value of the adenine site energy is 0.15 eV
- Site energies gradually increase with distance (number of AT base pairs)
- The energy barrier for hole injection from Sa* into the first adenine was found to be ≤0.4 eV

F. C. Grozema et al. J. Am. Chem. Soc.**130**, 5157 (2008)

NORTHWESTERN UNIVERSITY

Charge Transfer Simulations



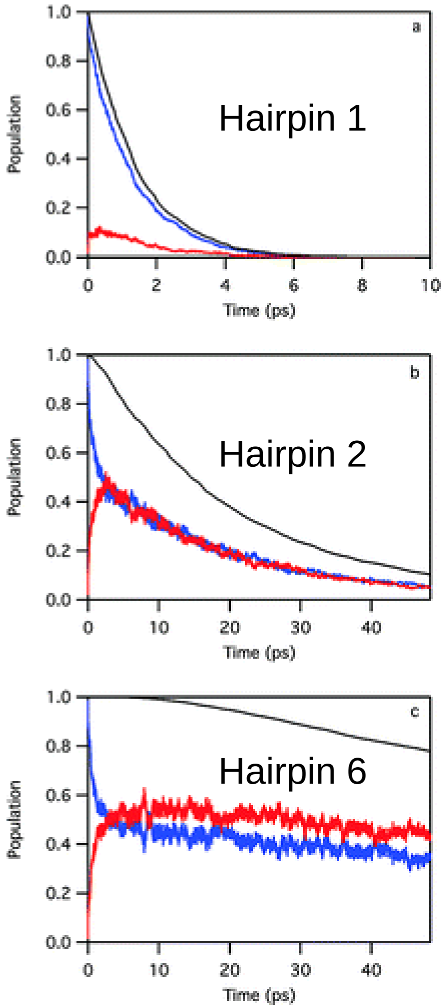
Survival probability:

$$P(t) = \sum_{n}^{N} \left| c_n(t) \right|^2$$

- Charge spreads from first site over the bridge
- Charge decays irreversibly at acceptor
- Total population decays in time

NORTHWESTERN UNIVERSITY

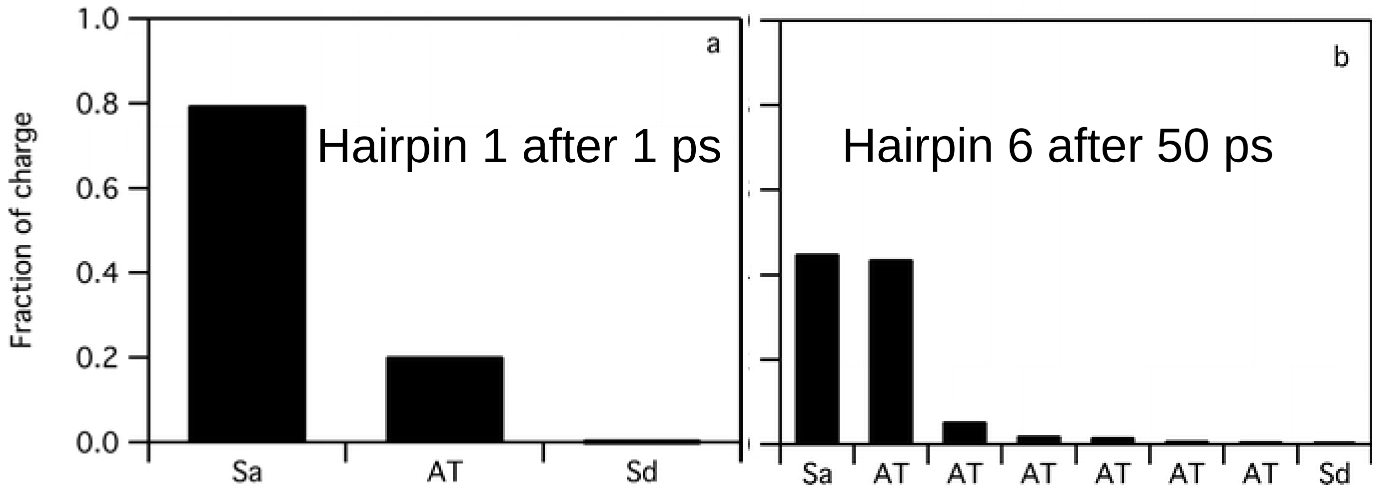
Hole Population as a Function of Time and Charge Distribution in Dynamic DNA Hairpins



Population on donor, $c_1^2(t)$

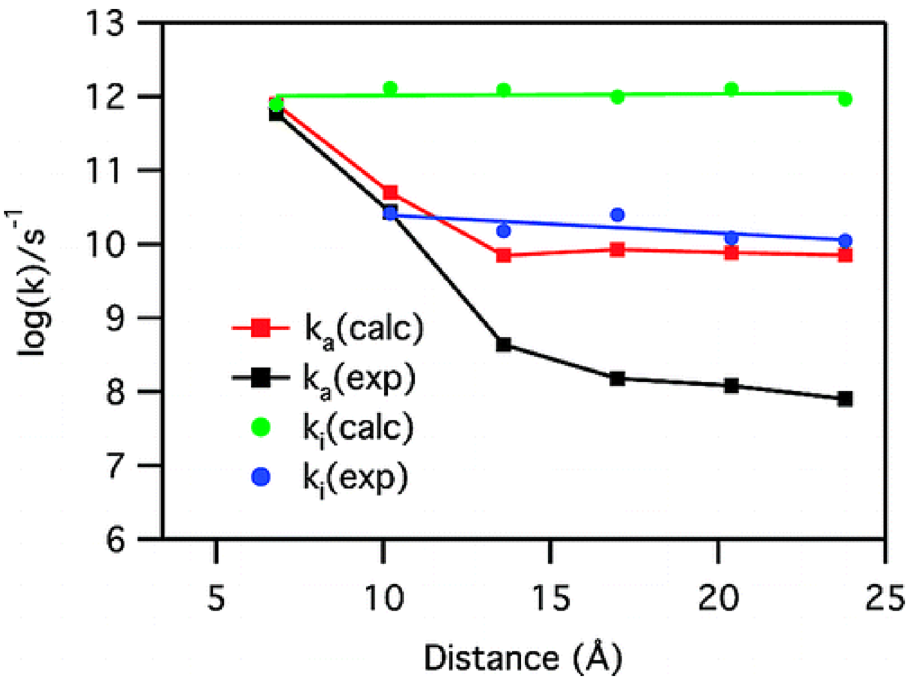
Population on all bridge sites, $\sum_{n=2}^{N-1} c_n^2(t)$

Total population = Survival probability



Kinetics of hole transfer. Effects of Electrostatic Interaction and Structural Fluctuations

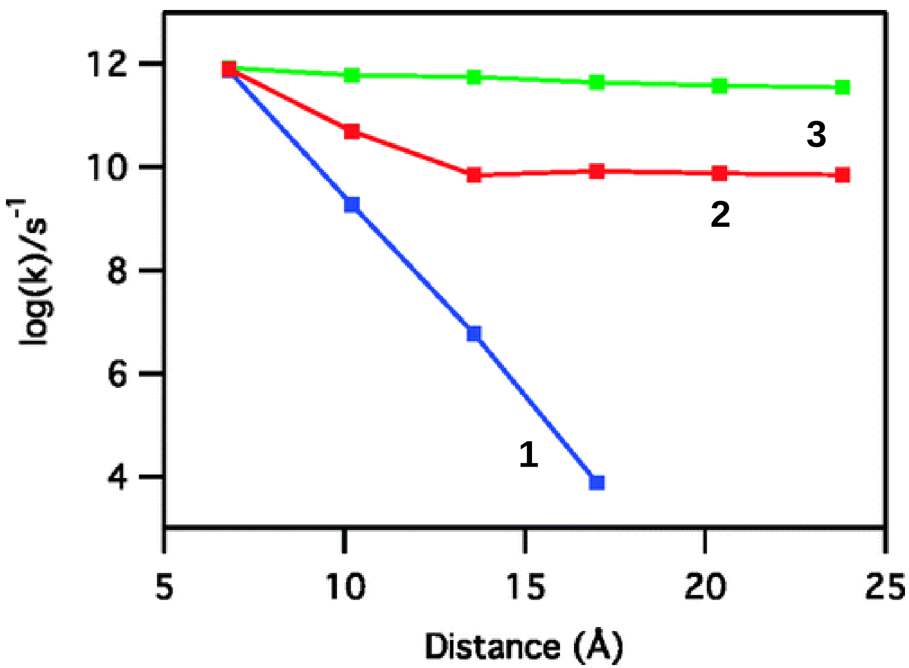
NORTHWESTERN UNIVERSITY



Calculations: F. C. Grozema et al. J. Am. Chem. Soc. **130**, 5157 (2008)

Experiment: F. D. Lewis et al. J. Am. Chem. Soc. **128**, 791 (2006)

F. C. Grozema et al. Angew. Chem., Int. Ed. **45**, 7982 (2006)



Curve 1: No fluctuations, electrostatic interaction is included

Curve 2: Both fluctuations and electrostatic interactions are included

Curve 3: No electrostatic interaction, fluctuations are included

Conclusions

- The extensive study of hole transfer in dynamic DNA hairpins reveals two important factors that affect charge motion, but so far did not receive the attention they deserve in theoretical investigations of hole transport through DNA with static structure. One factor is structural fluctuations which change the values of electronic coupling and site energies. Another is the electrostatic interaction between a hole and donor anion giving rise to the barrier for charge propagation through DNA.
- Our analysis shows that the inclusion of these factors in the formalism of electron transfer requires to consider the process of charge transition from donor to acceptor beyond the Condon approximation. It was demonstrated that this can be done analytically in two important limits of slow and fast fluctuations.
- Based on the computational results obtained, we propose a simple tight-binding model that allows the qualitative description of recent kinetics data on hole transfer in DNA hairpins without fitting parameters.
- We also show that in short AT tracks with less than 4 base pairs, charge transfer from the hole donor to the capped stilbene acceptor occurs via tunneling through the electrostatic barrier between donor and acceptor subunits, while for longer AT tracks the process can be viewed as fluctuation-assisted incoherent hopping.

NORTHWESTERN UNIVERSITY

Acknowledgments

Delft University of Technology,
The Netherlands:

Prof. Ferdinand C. Grozema

Prof. Laurens D.A. Siebbeles

Northwestern University,
Evanston, IL, USA:

Prof. Mark Ratner

Dr. Stefano Tonzani

Prof. George Schatz

Acknowledgments

This work supported by the Dutch Foundation of Scientific Research (NWO) through an NWO-VENI grant to Ferdinand Grozema. The National Science Foundation (NSF) is acknowledged for financial support through the grant CHE-0628130 to George Schatz. Mark Ratner and Yuri Berlin thanks the Chemistry Divisions of the NSF and ONR for financial support.