## On the Modeling of the Charge Transfer along 1-D Molecular Chain at T=300K

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## Holstein Hamiltonian averaged by state $|\Psi\rangle$

$$\hat{H} = \sum_{n,k} \nu_{nk} |n\rangle \langle k| \qquad |\Psi\rangle = \sum_{n} b_{n}(\tilde{t})|n\rangle \qquad n = 1, \dots, N$$

$$H = T + U + \left\langle \Psi \right| \hat{H} \left| \Psi \right\rangle =$$

$$= \frac{1}{2} \sum_{n=1}^{N} M \dot{u}_{n}^{2} + \frac{1}{2} \sum_{n=1}^{N} K u_{i}^{2} + \sum_{m \neq n} \nu_{mn} b_{m} b_{n}^{*} + \sum_{n} \nu_{nn} b_{n} b_{n}^{*} + \sum_{n} \alpha' u_{n} b_{n} b_{n}^{*}.$$

 $b_n(t)$  is the probability amplitude describing the charge evolution on the site *n*.  $u_n(t)$  is intrasite oscillations near the mass center

Probability distribution of the charge affects the movement of classical sites, and site displacement changes the probability of charge localization on it

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### **DNA model**







Nucleotide pair as a site

Sites move in a plane perpendicular to the DNA helix direction Excess electron or hole (quantum particle) migrates along chain of classical sites.

## **Equations of motion**

$$i\hbar \frac{db_n}{d\tilde{t}} = (\alpha_n^{\ 0} + \alpha'_n \tilde{u}_n)b_n + \nu_{n,n+1}b_{n+1} + \nu_{n,n-1}b_{n-1},$$
$$M_n \frac{d^2 \tilde{u}_n}{d\tilde{t}^2} = -K_n \tilde{u}_n - \gamma_n \frac{\tilde{u}_n}{d\tilde{t}} - \alpha'_n |b_n|^2 + \tilde{\mathcal{A}}_n(t),$$

$$\langle \tilde{\mathcal{A}}_k(t) \rangle = 0, \quad \langle \tilde{\mathcal{A}}_k(t) \tilde{\mathcal{A}}_n(s) \rangle = \delta_{kn} \delta(t-s) 2k_B \mathrm{T} \gamma_k,$$

variables:  $b_n$  – probability amplitude of finding the charge on the *n*-th site ,

> $u_n$  – displacement of *n*-th site from its equilibrium, n = 1, ..., N,

T –temperature of thermostat

## **Computer simulations**

One sample is trajectory of the system with its own random time-series  $\{A_n(t)\}$  and from its initial data

E.g., displacements and velocities of sites correspond to temperature prescribed

$$egin{aligned} &\langle ilde{u}
angle &= 0, &\langle ilde{v}
angle &= 0, &\langle ilde{u} ilde{v}
angle &= 0, && \ &\langle ilde{u}^2
angle &= k_B \mathrm{T}/m\omega^2, &\langle ilde{v}^2
angle &= k_B \mathrm{T}/m && \end{aligned}$$

and the charge is localized at n-th site – donor:

 $|b_n(t=0)| = 1$ , other  $|b_k| = 0$ 

## Set of samples

There exists natural parallelism when solving these equations. We calculate each sample (the dynamics of the charge distribution from the different initial conditions and with different values of the random force) on a single node, using MPI to collect data at the master node, and averaging by ensemble the time-dependences:

Probability of charge  $\langle I \rangle$  localization at *n*-th site

$$\left\langle P_n(t) \right\rangle = \left\langle |b_n(t)|^2 \right\rangle$$

Total energy of the system

$$\left\langle E_{tot}(t) \right\rangle = \left\langle \eta \sum b_n b_{n\pm 1}^* + \frac{1}{2} \sum v_n^2 + \frac{\omega^2}{2} \sum u_n^2 + \chi \sum u_n b_n b_n^* \right\rangle$$
  
Parameter of delocalization  $\left\langle R(t) \right\rangle = \left\langle \frac{1}{\sum_n |b_n(t)|^4} \right\rangle$ 

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## **Evolution to the thermodynamic equilibrium state**



Dynamics of  $\langle \boldsymbol{R}(t) \rangle$ , calculated from different initial distribution of the charge. The bottom (black) curve represents calculation from the initial 'polaron distribution'. The upper (red) curve – from uniform initial distribution of the charge over all the sites.

Each curve is the average on 50 samples

## **Computations on distributed resources**

For adaptation to distributed computing, original program was divided into 2 parts.

The first program calculates one sample.

Using special script many copies of the program run with the same parameters and random initial data. Finally the files of results are compressed and transmitted to a predefined SE.

Fialka@lcgui:~/hipcos/499_2							
[fialka@lcgui 499_2]\$ 1							
lvar_1.jdl lvar.jdl 1 [fialka@lcgui 499 215 .	[fialka@lcgui 499tst]\$ ./status.sh						
task 1 submitted	https://egee-rb-01.cnaf.infn.it:9000/qT-HjnXW6xA7VAkkyKffsA	Done					
task 2 submitted task 3 submitted	ce01.grid.acad.bg:2119/jobmanager-lcgpbs-biomed						
task 4 submitted	retrieving						
task 6 submitted	btps://ogoo_rb_01 cnof infn it.0000/cm_HinYW6y07V0kbyKffc0	Carod					
task 7 submitted	https://egee-ib-bi.chat.ihth.it.sooo/qi-hjhkwoxk/vkkyktisk	saveu					
task 9 submitted	https://egee-rb-U1.cnat.infn.it:9000/JNvaKEDaVQb8ccM97bo59w	Running					
task 10 submitted	gridba2.ba.infn.it:2119/jobmanager-lcgpbs-infinite						
task 12 submitted	https://egee-rb-01.cnaf.infn.it:9000/sgRD1iULRA3L0gFFNuodMO	Running					
task 13 submitted task 14 submitted	lcace nen ru:2119/jobmanager-lcaphe-bjomed	1990-1990 - 1990 - 199 <b>-</b> 19					
task 15 submitted	http://www.com/common and include the second and a second se	÷					
	https://egee-rb-01.cnaf.infn.it:9000/MhJuDon0xackk2EmgL6z]g	Running					
	ce.epcc.ed.ac.uk:2119/jobmanager-lcgpbs-biomed						
	https://eqee-rb-01.cnaf.infn.it:9000/nzlv4IwZN0r0Tz7Qdqu-nQ	Running					
	ceOl.isabella.grnet.gr:2119/jobmanager-pbs-biomed						
	https://egee_rh_01_cnef_infn_it:9000/lniz-pyDctGrspOpOrhPio	Waiting					
	actor article way of an 2110/interproperty Lagran biomed	warerna					
	Celul.grid.ucy.ac.cy:2119/ Jobmanager-Icgpbs-blomed						
	https://egee-rb-01.cnaf.infn.it:9000/GcuikUtnMIJf1qUkxQR_7w	Scheduled					
	ce.epcc.ed.ac.uk:2119/jobmanager-lcgpbs-biomed						
	https://egee-rb-01.cnaf.infn.it:9000/ndIbAbysbNP3aIUfcD3nLA	Scheduled					
	lcace01 aridon rl ac uk:2119/jobmanager-lcanbs-bioL						

## **Averaging of calculations**

After calculating enough number of samples, the second program runs. It must calculate average values.

A special script is sent to be calculated on WN. This WN takes from SE files with results of samples in series of 10 items, for every series the averaging program runs. At the same time if for some reason output file of one realization is absent or defective, it is ignored, and the next output file is taken. To files obtained the same program of averaging applies again.

./mean_grid.c	retrieving lfn.fjelke 44
<pre>param.res retrieving lfn:fialka_1 retrieving lfn:fialka_2 retrieving lfn:fialka_3 retrieving lfn:fialka_4 retrieving lfn:fialka_4 retrieving lfn:fialka_5 var = 5 new_zero = 2499 retrieving lfn:fialka_6 retrieving lfn:fialka_7 retrieving lfn:fialka_7 retrieving lfn:fialka_8</pre>	retrieving lfn:fialka_45 retrieving lfn:fialka_45 var = 5 new_zero = 2499 retrieving lfn:fialka_47 retrieving lfn:fialka_47 retrieving lfn:fialka_49 retrieving lfn:fialka_50 var = 9 new_zero = 2499 pr.res dsp.res l.res tpr.res b_sum.res b2n.res b2n.res

# Experiments on the charge transfer along DNA fragments

Hole transfer from guanine G (donor) to guanine triplet GGG (acceptor), separated by adenine-thymine (A-T) bridges of various lengths



Fig. from: B. Giese et al, *Nature*, 412, 318 (2001)

The rate of charge transfer between donor and acceptor decreases with increasing bridge – for short fragments

For long bridge – the transfer rates exhibit only a weak distance dependence

## **Parameter values**

#### are taken from literature data

oxidation potential			Electronic coupling matrix elements						
				$v_{nn+1}$ , eV	$\eta_{n n+1}$		$v_{n n+1}$ , eV	$\eta_{n n+1}$	
	α°, ev	$\eta_{nn}$		GG	0.084	1.276	GT	0.137	2.081
G	1.24	0	]	ТТ	0 158	24	TG	0.085	1 291
Α	1.69	6.84			0.100			0.000	1.201
Т	1.9	10.		AG	0.049	0.744	GA	0.089	1.352
C	10	10		AA	0.030	0.456	CA	0.029	0.441
С	1.9	10.		AA	0.030	0.456	CA	0.029	0.44

 $\tau = 10^{-14} \sec,$   $m \approx 10^{12}$  Hz ( $\omega = 0.01$ )  $0 \le \alpha' \le 0.3$  eV /Å  $M_n = 10^{-21}$  g

J. Jortner, M. Bixon, A.A. Voityuk, N. Rosch (2002) J. Phys. Chem. A 106, 7599-7606.

G.B. Schuster (2000) Acc. Chem. Res. 33, 253-260.

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## **Simulation experiments**



 $\langle R(t) \rangle$  (top) and average probability on donor  $\langle P_G(t) \rangle$  and on acceptor  $\langle P_{GGG}(t) \rangle$  (bottom) for GAAGGG. T=300K

Time interval  $t_{\text{TDE}}$  from the initial state "the charge is localized at the donor G" to the attainment of the thermodynamic equilibrium state  $t_{\text{TDE}} \sim 60000$ 

## Modeling of charge transfer in GA...AGGG chains at T=300K

The length of the chain *N* varies from 5 (i.e. GAGGG – the bridge of one A) to 100 (i.e. GA. . .AGGG with 96 adenines).

For each N we have calculated the average for 100 samples on time interval of reaching the TDE state.



## **Experiments and Simulation Results**



Fig. from: B. Giese et al, Nature, 412, 318 (2001)

Dependencies of the transfer rate  $1/t_{\text{TDE}}$  on the chain length *N* for different friction coefficient

## Conclusion

In biophysical experiments, it was found that for short chains (N < 9), lengthening the bridge on one site reduces the relative charge transfer rate by an order of magnitude. For chains with  $N \ge 9$ , the relative transfer rates are approximately constant.

Based on the Holstein model with Langevin term, computational modeling demonstrates that the time intervals of charge transfer from initial localization on donor to thermodynamic equilibrium state have a qualitative similar dependence on N.

It can be assumed that (similarly to the case of homogeneous chains) in short chains the charge is in the polaron state, and in long chains the charge is delocalized, and the charge transfer from the donor to the acceptor occurs by different mechanisms.

## Thank you for attention!

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#### Термодинамические параметры

Полная энергия системы

$$\left\langle E_{tot}(t)\right\rangle = \left\langle \eta \sum b_n b_{n\pm 1}^* + \frac{1}{2} \sum v_n^2 + \frac{\omega^2}{2} \sum u_n^2 + \chi \sum u_n b_n b_n^* \right\rangle$$



 $\langle R(t) \rangle$ , выход на состояние термодинамического равновесия

## Stationary solution, T=0

$$i\dot{b}_{n} = \eta(b_{n-1} + b_{n+1}) + \chi u_{n}b_{n},$$
  

$$0 = -\omega^{2}u_{n} - \chi |b_{n}|^{2} \implies u_{n} = -\frac{\chi}{\omega^{2}} |b_{n}|^{2}$$
  

$$b_{n} = r_{n} \exp(iWt)$$
  

$$-W r_{n} = \eta(r_{n-1} + r_{n+1}) - (\chi/\omega)^{2} r_{n}^{3} \qquad n = 1, \dots, N$$
  

$$\sum r_{n}^{2} = 1$$

Systems with parameters  $(\eta, \chi, \omega)$ {I} and  $(\eta, C\chi, C\omega)$ {II} have the same steady-state solutions { $r_1, ..., r_N, W$ } (but  $u_{n\{I\}} \neq u_{n\{II\}}$ ) and the same energy values

## $T \neq 0$ . Partition function

$$Z = C_1 \cdot \int_{\Omega} \exp\left(-\frac{1}{C_2 T} E(b_n, b_n^*, u_n, v_n)\right) db_1 \cdots du_n \cdots dv_N$$
$$E = \eta \sum b_n b_{n\pm 1}^* + \frac{1}{2} \sum v_n^2 + \frac{\omega^2}{2} \sum u_n^2 + \chi \sum u_n b_n b_n^*$$

$$\Omega = \mathbb{R}^{2\mathbb{N}} \times \mathbb{S}_{2\mathbb{N}} : u_n \in (-\infty; +\infty), v_n \in (-\infty; +\infty), \Sigma_n(b_n b_n^*) = 1$$

$$\left\langle E\right\rangle = \frac{\int_{\Omega} E \cdot \exp(-E(b, b^*, u, v) / C_2 T) dw}{\int_{\Omega} \exp(-E(b, b^*, u, v) / C_2 T) dw}$$

## **Total energy**

Substitution 
$$u_n \mapsto U_n = \omega u_n + \frac{\chi}{\omega} |b_n|^2$$

$$\left\langle E_{tot} \right\rangle = NC_2 T + \left[ \int_{S} \exp\left(-\frac{F}{C_2 T}\right) ds \right]^{-1} \cdot \int_{S} F \exp\left(-\frac{F}{C_2 T}\right) ds$$
  
where  $S = \left\{ \sum_{n=1}^{N} |b_n|^2 = 1 \right\}$  and  
 $F = \eta \sum (b_n b_{n+1}^* + b_{n+1} b_n^*) - \frac{1}{2} \frac{\chi^2}{\omega^2} \sum |b_n|^4$ 

For systems{I} ( $\eta, \chi, \omega$ ) и {II} ( $\eta, C\chi, C\omega$ )

$$Z_{\{\mathrm{I}\}} = \left(\frac{1}{C}\right)^{N} Z_{\{\mathrm{II}\}} \text{ and } \left\langle E_{\{\mathrm{I}\}} \right\rangle = \left\langle E_{\{\mathrm{II}\}} \right\rangle, \left\langle R_{\{\mathrm{I}\}} \right\rangle = \left\langle R_{\{\mathrm{II}\}} \right\rangle, \dots$$



averaging over 50 samples



#### $\chi/\omega$ =const.

Time intervals of evolution to thermodynamic equilibrium are different,

calculated values are close to each other.

## Homogeneous chains. Dependence of electronic part of energy on the thermal energy.



Charge distribution (polaron or delocalized state) in thermodynamic equilibrium state depends not only on the temperature, but also on the length of the chain

## Homogeneous chains in TDE

