

Article

# Supplementary Information: Modeling charge transfer reactions by hopping between electronic ground state minima: application to hole transfer between DNA bases

Alessandro Nicola Nardi <sup>1</sup> , Marco D'Abramo <sup>1\*</sup>  and Andrea Amadei <sup>2\*</sup> <sup>1</sup> Department of Chemistry, Sapienza University, 00185 Rome, Italy<sup>2</sup> Department of Chemical and Technological Sciences, Tor Vergata University, 00133 Rome, Italy

\* Correspondence: marco.dabramo@uniroma1.it (M.D.); andrea.amadei@uniroma2.it (A.A.)

## 1. The electronic transition energy when DNA or solvent perturbation alone is considered: mean, standard deviation, distributions and correlations

Table S1. Helix

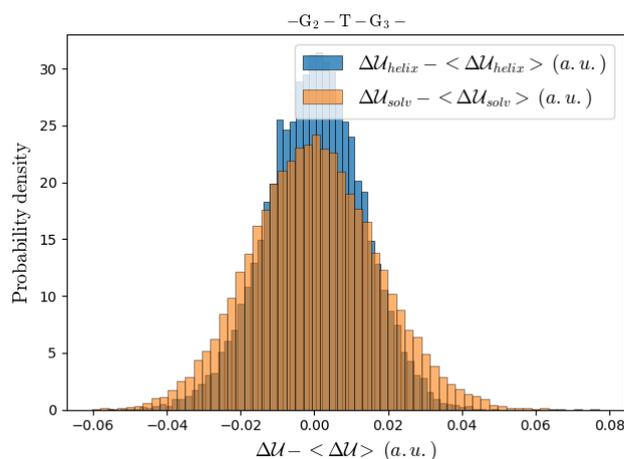
n	$\langle \Delta U_{e,helix} \rangle (a.u.)$	$\sigma_{helix} (a.u.)$
[A] <sub>n</sub>		
1	0.071366	0.013125
2	0.091630	0.016957
3	0.093723	0.018504
1 <sup>a</sup>	0.074134	0.016200
[T] <sub>n</sub>		
1	0.078946	0.013047
2	0.100051	0.016660
3	0.109994	0.017487
1 <sup>a</sup>	0.062964	0.018546

<sup>a</sup> Interstrand.

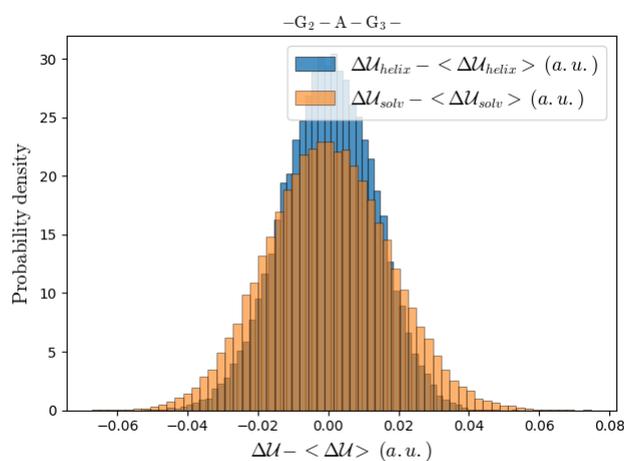
Table S2. Solvent

n	$\langle \Delta U_{e,solvent} \rangle (a.u.)$	$\sigma_{solvent} (a.u.)$
[A] <sub>n</sub>		
1	0.013220	0.017224
2	0.010379	0.021241
3	0.015150	0.023238
1 <sup>a</sup>	0.013412	0.020066
[T] <sub>n</sub>		
1	0.001969	0.016973
2	-0.003840	0.020914
3	-0.006024	0.022348
1 <sup>a</sup>	0.016899	0.023098

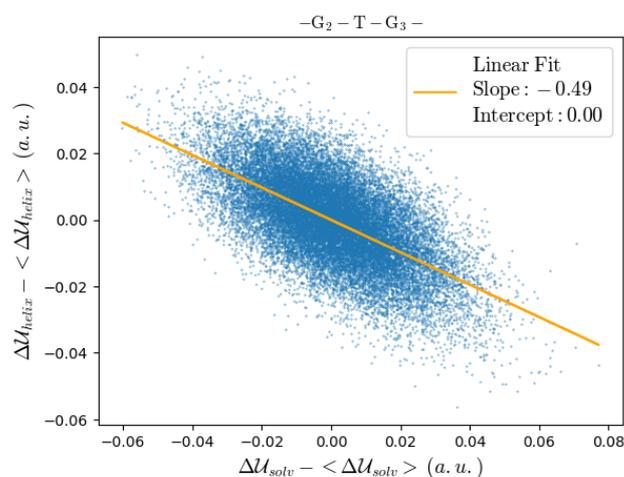
<sup>a</sup> Interstrand.



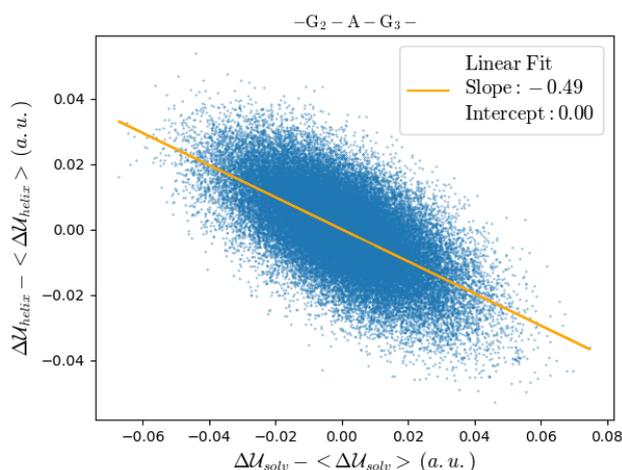
**Figure S1.** Electronic transition energies (scaled by their respective mean value) distributions obtained when the solvent or helix perturbing electric field alone is considered.



**Figure S2.** Electronic transition energies (scaled by their respective mean value) distributions obtained when the solvent or helix perturbing electric field alone is considered.



**Figure S3.** Correlation between the electronic transition energy trajectories (scaled by their respective mean value) obtained when the solvent or helix perturbing electric field alone is considered.



**Figure S4.** Correlation between the electronic transition energy trajectories (scaled by their respective mean value) obtained when the solvent or helix perturbing electric field alone is considered.

## 2. Electronic transition energies of step 1 and 2

**Table S3.** Step 1 and 2.

n	$\langle \Delta \mathcal{U}_{e,1} \rangle (a.u.)$	$\langle \Delta \mathcal{U}_{e,2} \rangle (a.u.)$	$\sigma_1 (a.u.)$	$\sigma_2 (a.u.)$
$[A]_n$				
1	-0.102081	0.186643	0.012189	0.013883
2	-0.103511	0.205520	0.012268	0.014044
3	-0.105349	0.214212	0.011874	0.014008
1 <sup>a</sup>	-0.101209	0.188735	0.012218	0.013657
$[T]_n$				
1	-0.102804	0.183731	0.012258	0.013791
2	-0.108871	0.205134	0.011957	0.013901
3	-0.109923	0.214028	0.011655	0.014074
1 <sup>a</sup>	-0.103670	0.183528	0.012328	0.013685

<sup>a</sup> Interstrand.

**Table S4.** Step 1 and 2, helix contribution.

n	$\langle \Delta \mathcal{U}_{e,helix,1} \rangle (a.u.)$	$\langle \Delta \mathcal{U}_{e,helix,2} \rangle (a.u.)$	$\sigma_{helix,1} (a.u.)$	$\sigma_{helix,2} (a.u.)$
$[A]_n$				
1	0.753346	-0.681980	0.018213	0.015579
2	0.819494	-0.727863	0.019186	0.015687
3	0.844254	-0.750530	0.018203	0.016310
1 <sup>a</sup>	0.760421	-0.686287	0.017604	0.020094
$[T]_n$				
1	0.764474	-0.685527	0.016540	0.013764
2	0.815915	-0.715863	0.019697	0.014639
3	0.854893	-0.744898	0.017001	0.013963
1 <sup>a</sup>	0.765608	-0.702644	0.018357	0.017191

<sup>a</sup> Interstrand.

**Table S5.** Step 1 and 2, solvent contribution.

n	$\langle \Delta U_{e,solv,1} \rangle (a.u.)$	$\langle \Delta U_{e,solv,2} \rangle (a.u.)$	$\sigma_{solv,1} (a.u.)$	$\sigma_{solv,2} (a.u.)$
<b>[A]<sub>n</sub></b>				
1	-1.135103	1.148323	0.020190	0.019512
2	-1.202729	1.213108	0.021119	0.019323
3	-1.244585	1.238182	0.019110	0.019278
1 <sup>a</sup>	-1.141347	1.154760	0.019901	0.021715
<b>[T]<sub>n</sub></b>				
1	-1.147036	1.149006	0.019270	0.018237
2	-1.208250	1.204409	0.021294	0.019079
3	-1.244585	1.238182	0.019110	0.019278
1 <sup>a</sup>	-1.149028	1.165927	0.021101	0.020008

<sup>a</sup> Interstrand.**3. ESP charges of (GAG)<sup>+</sup> and (GTG)<sup>+</sup> triplets including water solvent and dispersion**

**Table S6.** ESP charges of (GAG)<sup>+</sup> and (GTG)<sup>+</sup> stacks in water solvent (SMD [1] model was used). The GD3 empirical dispersion [2] was included. Two sets of ESP charges for each triplet are reported: one where the 5' Guanine is in its neutral relaxed geometry and the 3' Guanine in its cationic relaxed geometry and one where the Guanine geometries were swapped.

Base	q
CAM-B3LYP/SMD + GD3	
5' G <sup>+</sup>	0.96
A	0.04
3' G	0.00
5' G <sup>+</sup>	0.99
T	-0.01
3' G	0.02
5' G	0.00
A	0.03
3' G <sup>+</sup>	0.97
5' G	0.03
T	-0.03
3' G <sup>+</sup>	1.00

**4. Calculated kinetic constants for G<sub>2</sub><sup>+</sup>-A-G<sub>3</sub> sequence containing substrates with different force fields and water models**

Additional MD simulations were performed to test other force fields and solvent model, i.e. the BSC1 [3] force field and the TIP3P [4] water model. In Table S7 is reported the comparison between calculated rate constants with the same theoretical-computational method we presented, using BSC1 force field and the TIP3P water model.

**Table S7.** Comparison between the calculated kinetic constants  $\mathcal{K}_{R_A}$  for the intrastrand charge transfer of the G<sub>2</sub><sup>+</sup>-A-G<sub>3</sub> sequence containing substrates. A comparison between AMBER99 and BSC1 force fields and between SPC and TIP3P water models are given.

	$\mathcal{K}_{R_A} (s^{-1})$
ff	PMM
AMBER99 <sup>a</sup>	$2.8 \cdot 10^4$
BSC1 <sup>a</sup>	$1.9 \cdot 10^4$
solv. model	PMM
SPC <sup>b</sup>	$2.8 \cdot 10^4$
TIP3P <sup>b</sup>	$5.2 \cdot 10^4$

<sup>a</sup> The SPC water model was used. <sup>b</sup> The AMBER99 force field was used.

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## References

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