Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Efficient algorithms for the simulation of non-adiabatic electron transfer in complex molecular systems: application to DNA

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Electronic supplementary information

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I. METHODOLOGY

It will be shown here that the derivatives of basis functions do not appear in the equations of motion of the quantum system, i.e. that the second term on the right-hand side of Eq. 6 in the article

$$\dot{a}_m = -\frac{i}{\hbar}\sum_n H_{mn}a_n - \sum_n a_n \cdot \langle\varphi_m|\dot{\varphi}_n\rangle \tag{1}$$

vanishes because for every pair of molecular fragments m and n:

$$\langle\varphi_m|\dot{\varphi}_n\rangle = 0 \tag{2}$$

It will be sufficient to show that

$$\left\langle \varphi_m \middle| \frac{\partial\varphi_n}{\partial r_a} \right\rangle = 0 \tag{3}$$

(where r_a is any of the x, y and z coordinates of all of the atoms in the system) for every pair of molecular fragments m and n because

$$\langle\varphi_m|\dot{\varphi}_n\rangle = \langle\varphi_m|\nabla\varphi_n\rangle \cdot \dot{\vec{r}} = \sum_a \left\langle \varphi_m \middle| \frac{\partial\varphi_n}{\partial r_a} \right\rangle \cdot \dot{r}_a \tag{4}$$

In our work, the basis is orthonormal, i.e. the overlap of basis functions is

$$S_{mn} = \delta_{mn} \tag{5}$$

identically. Therefore, the derivative of every overlap matrix element with respect to the displacement of any atom vanishes,

$$\frac{\partial S_{mn}}{\partial r_a} = \frac{\partial}{\partial r_a}\langle\varphi_m|\varphi_n\rangle = \left\langle \frac{\partial\varphi_m}{\partial r_a} \middle| \varphi_n \right\rangle + \left\langle \varphi_m \middle| \frac{\partial\varphi_n}{\partial r_a} \right\rangle = 0 \tag{6}$$

Now we may distinguish several cases:

- r_a corresponds to the displacement of an atom that does not belong to the molecular fragment n. Then, the examined term vanishes trivially because

$$\left|\frac{\partial\varphi_n}{\partial r_a}\right\rangle = 0 \tag{7}$$

- r_a corresponds to the displacement of an atom that belongs to fragment n, and $m = n$. Then

$$\frac{\partial S_{nn}}{\partial r_a} = \left\langle\frac{\partial\varphi_n}{\partial r_a}\middle|\varphi_n\right\rangle + \left\langle\varphi_n\middle|\frac{\partial\varphi_n}{\partial r_a}\right\rangle = 0 \tag{8}$$

  and the fact that we deal with real-valued functions φ_n leads to

$$2\left\langle\varphi_n\middle|\frac{\partial\varphi_n}{\partial r_a}\right\rangle = 0 \tag{9}$$

- r_a corresponds to the displacement of an atom that belongs to fragment n, and $m \neq n$. Then, the derivative of φ_m with respect to r_a vanishes, and only the second term remains:

$$\left\langle\varphi_m\middle|\frac{\partial\varphi_n}{\partial r_a}\right\rangle = 0 \tag{10}$$

With this, all of the terms containing the derivatives of fragment orbitals in the equations of motion are bound to vanish.

We are grateful to Thomas Niehaus for pointing out this line of thoughts.

II. MOBILITY OF HOLE AND RATE OF TRANSFER

TABLE I: The parameter L (see text for definition) evaluated along simulations of 1 ns. MF – mean-field simulation; SH – surface-hopping scheme.

with interval = 0.1 ps				
	AAAA		GGGG	
ESP scaling	MF	SH	MF	SH
no	1997	180	986	59
1/1.4	3246	921	2004	298
1/1.5	3738	1179	2389	331
with interval = 0.4 ps				
	AAAA		GGGG	
ESP scaling	MF	SH	MF	SH
no	734	68	428	32
1/1.4	1090	339	792	141
1/1.5	1218	415	907	139

TABLE II: Rate of next-neighbor transfer (ns^{-1}) along the homogeneous sequences studied, obtained from surface-hopping (SH) and Born–Oppenheimer (BO) simulations.

with the criterion corresponding to 5/8 of reorganization energy = 0.75 V divided by the ESP scaling factor

	AAAA		GGGG	
ESP scaling	SH	BO	SH	BO
no	26	47	23	16
1/1.4	140	87	85	45
1/1.5	175	166	86	84

with the criterion corresponding to 7/8 of reorganization energy = 1.05 V divided by the ESP scaling factor

	AAAA		GGGG	
ESP scaling	SH	BO	SH	BO
no	14	31	21	12
1/1.4	90	31	65	29
1/1.5	75	78	50	58