

Non-orthogonality problem and effective electronic coupling calculation: Application to charge transfer in π -stacks relevant to biochemistry and molecular electronics.

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This file includes the values of the effective electronic couplings (or charge-transfer integrals) and the diabatic energy differences for the different conformations of the perylenediimide (PDI) π -stack (Table S1) and the quinol-semiquinone redox couple at different donor-acceptor distances R_{DA} (Table S2). The overlap integrals are also reported for the latter system.

Table S1. Charge-transfer integrals for hole ($V_{\text{IF}}^{(h)}$) and electron transfer ($V_{\text{IF}}^{(e)}$) in a PDI stack (x shift = 1.60 Å, y shift = 0.94 Å, z shift = 3.40 Å), and pertinent diabatic energy differences ($\Delta E_{\text{IF}}^{(h)}$ and $\Delta E_{\text{IF}}^{(e)}$, respectively), at the nuclear coordinate sets $Q_j = Q_t + j\delta Q/10$ ($j = 1, \dots, 10$), where Q_t is the transition state coordinate and $Q_t + \delta Q$ is the coordinate after geometry optimization on the H atoms of one PDI molecule at the BHH/6-31g* computational level. The geometry optimization was not performed with a basis set of high accuracy, because the only purpose of this optimization was to move the system away from Q_t . These results were obtained by using the M06-2X hybrid function and the 6-311g** basis set. All the energy quantities are given in meV.

j	$\Delta E_{\text{IF}}^{(h)}$	$V_{\text{IF}}^{(h)}$	$\Delta E_{\text{IF}}^{(e)}$	$V_{\text{IF}}^{(e)}$
1	0.04	35.9	0.10	129.7
2	0.08	35.7		
3	0.12	35.6		
4	0.16	35.4		
5	0.20	35.6	0.48	128.8
6	0.24	35.4		
7	0.28	35.4		
8	0.32	35.4		
9	0.36	35.4		
10	0.40	35.2	0.95	127.6

Table S2. Effective electronic couplings (V_{IF}), diabatic energy differences ($|\Delta E_{\text{IF}}| \equiv |E_{\text{I}} - E_{\text{F}}| = -\Delta E_{\text{IF}}$), and overlap integrals ($S_{\text{IF}} \equiv \langle \psi_{\text{I}} | \psi_{\text{F}} \rangle$) for electron transfer in the quinol-semiquinol redox couple at the indicated donor-acceptor distances (R_{DA}). The pertinent calculations were performed using the M06-HF XC hybrid functional, with the aug-cc-pVTZ basis set for the O atoms and the cc-pVTZ basis set for the other atoms. All the energy quantities are reported in eV.

$R_{\text{DA}} (\text{\AA})$	V_{IF}	$-\Delta E_{\text{IF}}$	S_{IF}
1.54	17.2	0.005	0.949
2.0	7.9	0.113	0.915
2.5	1.5	0.298	0.628
3.0	3.9×10^{-1}	0.371	0.356
3.5	1.3×10^{-1}	0.401	0.173
4.0	5.9×10^{-2}	0.412	8.39×10^{-2}
4.5	2.9×10^{-2}	0.417	3.81×10^{-2}
5.0	1.4×10^{-2}	0.419	1.68×10^{-2}
5.5	6.1×10^{-3}	0.422	7.04×10^{-3}
6.0	2.3×10^{-3}	0.424	2.79×10^{-3}
6.5	6.2×10^{-4}	0.427	8.56×10^{-4}
7.0	7.7×10^{-5}	0.427	1.13×10^{-4}