DFT estimations of hole transfer parameters in DNA π-stacks

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During the past 15 years, the hole transfer (HT) process in DNA π-stacks has been intensively studied by theoreticians because of its potential applications in nano-electronics [1, 2]. Recently, we showed that unoccupied Kohn-Sham orbitals (UKSO) stemming from DFT calculations of a neutral system can be used to derive accurate estimates of the free energy (ΔG) and electronic couplings (V) for excess electron transfer (EET) in DNA [3]. However, at that moment it was still missing an assessment of DFT functionals for calculating HT parameters in DNA.

We are going to discuss Kohn-Sham DFT (KS-DFT) and Time-dependent DFT (TD-DFT) estimations of the HT parameters in DNA π-stacks. The results are going to be compared with CAS-PT2 data for the same DNA-based systems [4]. The calculations suggest that the KS-DFT in combination with hybrid functionals gives reliable results for the energetics, electronic coupling and hole charge distribution. Also, the GGA BLYP functional provides an accurate description of the electronic coupling. While unreliable data were found for the energetics and electronic coupling values by applying the TD-DFT scheme. The hole charge distribution in the DNA π-stacks is well described by the hybrid functionals in comparison with benchmark results. Also, unrestricted KS-DFT (UKS-DFT) charges are not in agreement with reference data, we found delocalization of the hole in the stacks. More details can be found in Ref. [5].

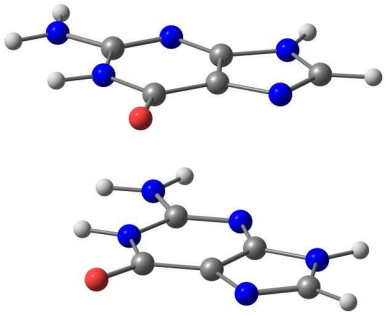

Fig. 1 Arrangement of the 5′-GG-3′ in ideal B-DNA.

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