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Parameters For Excess Electron Transfer in DNA. Estimation Using Unoccupied Kohn−Sham Orbitals and TD DFT

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We show that the energetics and electronic couplings for excess electron transfer (EET) can be accurately estimated by using unoccupied Kohn−Sham orbitals (UKSO) calculated for neutral π stacks. To assess the performance of different DFT functionals, we use MS-PT2 results for seven π stacks of nucleobases as reference data. The DFT calculations are carried out by using the local spin density approximation SVWN, two generalized gradient approximation functionals BP86 and BLYP, and two hybrid functionals B3LYP and BH&HLYP. Best estimations within the UKSO approach are obtained by the B3LYP and SVWN methods. TD DFT calculations provide less accurate values of the EET parameters as compared with the UKSO data. Also, the excess charge distribution in the radical anions is well described by the LUMOs of neutral systems. In contrast, spin-unrestricted DFT calculations of radical anions considerably overestimate delocalization of the excess electron. The excellent results obtained for the ground and excited states of the radical anions (excitation energy, transition dipole moment, electronic coupling, and excess electron distribution) by using UKSO of neutral dimers suggest an efficient strategy to calculate the EET parameters for DNA π stacks.

Introduction

Radical anions of organic and biological molecules have been intensively studied both experimentally and computationally.[1] The radical-anion states of nucleobases are involved in such processes as excess electron transfer (EET) through DNA π stacks;[2] strand breaks via dissociative electron attachment[3] and splitting of pyrimidine photodimers.[4,5] Because of biological significance of the EET in DNA, theoretical and computational insights into the mechanistic issues of this process have been of special interest.[6−8] The ability of DNA to mediate an excess electron is associated with the formation of radical-anion states of nucleobases. Two types of states are found for radical anions of nucleobases: the dipole-bound state in which the excess electron is located far outside the molecule, and the valence (or covalently bound) state with the negative charge delocalized over the molecule.[9,10] In the gas phase, the radical anions can be described as electron-dipole bound states, whereas the formation of hydrogen bonds between the nucleobase and water molecules stabilizes the valence state.[10] The radical anions of the basepairs AT and GC form covalently bound states in which the excess charge is localized on pyrimidine bases.[10−12] Accounting for the polar environment of DNA should further stabilize the valence anion state and suppress the formation of the diffuse dipole-bound state.

The difference of the electron affinities (EAs) of nucleobases in a π stack determines the free energy of electron transfer between these sites. Much effort has been made to determine the EAs of isolated nucleobases and their complexes.[2,9−16] The EA of the pyrimidine bases thymine (T) and cytosine (C) is significantly larger than that of adenine (A) and guanine (G). The order of the adiabatic valence EAs derived from different computational studies is T > C > A > G with EA(G) nearly 1 eV less than EA(T).[2,13] Because of that, the excess electron transport occurs via intermediate formation of T and C radical anions, whereas the corresponding states of A and G, which are remarkably higher in energy, serve as superexchange bridges connecting the pyrimidine bases. Note that the energy of a radical anion state B^- in the stack 5′-XBY-3′ is strongly influenced by the neighboring bases X and Y, [17] and therefore, the EA values of individual nucleobases or basepairs provide only a rough measure of the free energy for EET.

Another key parameter of EET is the electronic coupling of diabatic states of the donor and acceptor sites. The coupling can be derived by using either electronic properties of adiabatic states of the system or approximate diabatic states.[18] The first approach appears more consequent. Within this approach, the generalized Mulliken−Hush method introduced by Cave and Newton can be employed.[19,20] For π stacks consisting of two nucleobases, a two-state model is a good approximation, whereas for more extended systems, the multistate effects can be significant.[21] By using the two-state model, the electronic coupling can be expressed via the vertical excitation energy $E_{12} = E_2 - E_1$, the transition dipole moment μ_{12}, and the difference of the diabatic dipole moments $|\mu_d - \mu_a|$:

$$V_{da} = \frac{\Delta E_{12}|\mu_{12}|}{|\mu_d - \mu_a|} \tag{1}$$

Quantum chemical treatment of donor−acceptor couplings for electron transfer in DNA has been recently considered in detail.[22,23] Note that conformational dynamics of DNA considerably influences the coupling between nucleobases in π stacks,[24,25] and therefore, reliable values of this parameter should be obtained by averaging the coupling values over many hundred conformations.[25−27] This is possible only if efficient quantum chemical methods are employed. Because reliable values of electronic coupling cannot be deduced from experiment even for simplest models of EET in DNA, there are no experimental

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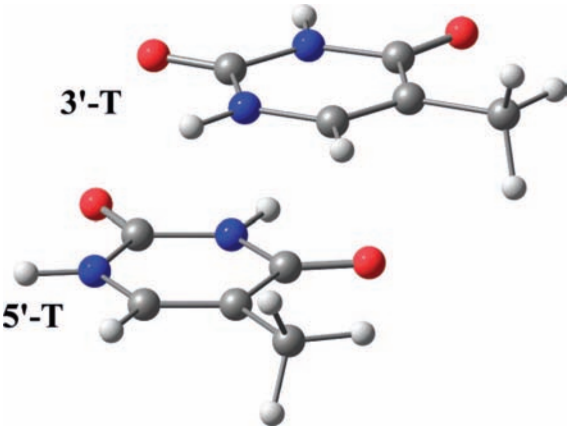

Figure 1. Arrangement of adjacent thymine nucleobases in the TT π stack.

data to take up for the assessment of computational methods. Thus, the following question arises: how accurate are the calculated couplings? To answer this question, the results of high-level calculations should be invoked.

Recently, the MS-PT2 method (multistate formulation of CASPT2 which accounts for the nonorthogonality of the CASPT2 wave function[28]) has been employed to calculate the adiabatic excitation energies, electronic couplings, and excess charge distribution in radical anions consisting of π-stacked nucleobases.[29] Seven π stacks TT (Figure 1), CT, TC, AT, TA, GT, and TG have been considered (hereafter, the base sequence XY is written in the 5′ → 3′ direction). Although these systems represent a very simple model for EET in DNA, the computed parameters are ideally suited to evaluate the performance of more efficient (but less sophisticated) techniques. DFT calculations permit the treatment of extended models (up to 5 basepairs), and thus, they are promising to study EET in DNA.

Two DFT-based approaches can be employed to derive the EET parameters. First, by analogy with Koopmans' theorem for Hartree−Fock (HF) theory, one may try using unoccupied Kohn−Sham orbitals (UKSO) calculated for the neutral system to describe electronic properties of the corresponding radical anion. Alternatively, the excitation energy and transition dipole moment required to derive the coupling matrix element (eq 1) can be directly calculated for the radical anion by TD-DFT. Because each of these approaches has its limitation, it is very difficult to predict a priori which computational strategy would provide better results.

The occupied Kohn−Sham (KS) orbitals and their eigenvalues have been proven to be quite useful,[30,31] and they are widely employed for analysis and description of electronic structure of radical cations. In particular, the hole transfer properties of organic materials and biological molecules have been intensively studied by using KS orbitals and their eigenvalues stemming from DFT calculations of neutral systems.[32,33] A good linear correlation of experimental ionization energies with the KS eigenvalues has been found for different density functionals (see ref 34 and references therein). Note that the eigenvalues of occupied KS orbitals describe the electronically relaxed ionization energies.[35] Thus, the occupied KS orbitals appear quite helpful to study hole transfer in different materials. By contrast, there is a broad consensus that UKSO and their energies calculated for neutral systems cannot be used to describe the energetics of radical anions.[30] A systematic comparison provided for different functionals has not revealed any significant correlation between the UKSO eigenvalues and the experimental EAs.[34] On the other hand, the HOMO−LUMO gap calculated by DFT can be used for estimation of the transition energy.[34,36] More reliable and accurate description of excited-state properties is provided by the TD-DFT.[37] However, it is known that standard TD-DFT calculations show poor performances for charge-transfer electronic transitions.[38,39] The excitation energies for such states are usually drastically underestimated. Dreuw and Head-Gordon have analyzed the TD-DFT equations and provided a clear explanation for this limitation (the Coulomb interaction between separated charges is ill-described because of the self-interaction error).[40] They have also shown that the use of a hybrid functional should give more reasonable estimates for the excitation energy and potential energy surfaces of CT states relative to valence-excited states.[40] The use of asymptotically corrected potentials may considerably improve the performance of DFT by calculating excitation energies.[41] The application of various exchange−correlation functionals in TD-DFT calculations has been reviewed.[36,42] Very recently, Kumar and Sevilla employed TD-DFT with the hybrid functionals B3LYP and BH&HLYP to study the role of $\pi\sigma^*$ excited states in electron-induced breaks of the DNA strand.[43,44] Both functionals are found to provide good estimates of the transition energy for radical anion states of the DNA bases. However, it is still not clear whether these functionals will provide good results for CT excitations in the systems with an excess electron.

The aim of this paper is to demonstrate that a simple UKSO approach, which makes use of UKSO of neutral π stacks, provides quite accurate estimates of the energy and electronic coupling for EET between nucleobases and therefore may be very useful for exploring EET dynamics in DNA and related systems. Also, we assess the performance of the TD-DFT with two hybrid functionals.

Computational Details

Electronic Couplings. The electronic couplings were derived by using the generalized Mulliken−Hush (eq 1).[19,20] The difference $|\mu_d - \mu_a|$ can be estimated as eR_{da} or found as $[(\mu_1 - \mu_2)^2 + 4\mu_{12}^2]^{1/2}$.[19,20] Note that in eq 1, one should use projections of the transition and dipole moments onto a predetermined axis rather than the length of these vectors. For the π stacks under study, we computed the component of these vectors along the axis perpendicular to the base planes. Because in all dimers, the distance R_{da} between these planes is taken 3.38 Å, $|\mu_d - \mu_a| = eR_{da} = 16.2$ D. The values obtained from MS-PT2 calculations for the complexes are in the range of 15.8 (GT)−16.1 (TG).

Charge Distribution. Within the UKSO approach, the excess charge distribution in the ground state and excited states of the radical anion is derived from LUMO and LUMO+1 of the neutral system. The charge on fragment F in the ground state was estimated as

$$q(\mathrm{F}) = \sum_{i\in \mathrm{F}} C_{i,\mathrm{LUMO}} \sum_{j=1}^{N} C_{j,\mathrm{LUMO}} S_{ij} \qquad (2)$$

Here, S_{ij} is the overlap of atomic orbitals i and j; i runs over AOs associated with fragment F, whereas j runs over all AOs. In a similar manner, by using LUMO+1 in eq 2, one obtains the fragment charge in the excited state of the radical anion.

Quantum Mechanical Calculations. The HF and DFT calculations of neutral stacks are carried out for seven π stacks consisting of two nucleobases. The mutual position of the nucleobases in the dimers corresponds to the regular B-DNA structure. The Cartesian coordinates of the systems are given

TABLE 1: Excitation energy ΔE_{12}, Transition Dipole Moment μ_{12}, Electronic Coupling V, and Excess Charge Distribution in the Ground and Excited States Calculated for the TT Dimer[a]

				ground state		excited state	
method	ΔE_{12}, eV	μ_{12}, D	V, eV	$Q(T_1)$	$Q(T_2)$	$Q(T_1)$	$Q(T_2)$
MS-PT2	**0.155**	**0.686**	**0.0067**	**−0.980**	**−0.020**	−0.**046**	**−0.954**
HF/6-31G*	0.193	1.141	0.0141	−0.971	−0.029	−0.023	−0.977
SVWN/6-31G*	0.125	0.354	0.0028	−0.986	−0.014	−0.013	−0.987
BP86/6-31G*	0.127	0.441	0.0035	−0.987	−0.013	−0.013	−0.987
BLYP/6-31G*	0.127	0.514	0.0041	−0.985	−0.015	−0.013	−0.987
B3LYP/6-31G*	0.134	0.761	0.0066	−0.983	−0.017	−0.015	−0.985
BH&HLYP/6-31G*	0.151	1.026	0.0099	−0.978	−0.022	−0.018	−0.982

[a] MS-PT2 data[29] were obtained for the radical anion, whereas the HF and DFT results are derived by using LUMO and LUMO+1 of the neutral stack.

in the Supporting Information of ref 29. In this paper, we examine the LSDA functional SVWN,[45] two GGA functionals BLYP and BP86,[46−48] and two hybrid functionals B3LYP and BH&HLYP.[49−51] Also, TD-DFT calculations of the radical anions were carried out with the hybrid exchange−correlation functionals B3LYP and BH&HLYP. All the calculations were performed by using the program Gaussian03.[52]

Basis Sets. It is well-known that extended basis sets supplemented with diffuse functions are required to describe molecular anions. However, in some cases, computational results for radical-anion states of nucleobases and their complexes are negatively affected by including the diffuse functions in the basis set.[13,23] For instance, Li and Sevilla have shown that DFT calculations without diffuse functions produce reasonable estimates of the relative valence EAs, whereas the results become worse by including diffuse functions due to contamination of the valence state with dipole-bound states.[13] Also, it has been shown that the diabatic states for electron transfer may be represented by LUMOs stemming from the HF calculation of the neutral DNA π stack only if the diffuse functions are explicitly excluded from the basis set.[23] Thus, within the UKSO model, we use the standard 6-31G* basis set. The TD-DFT calculations were carried out with the standard and extended 6-31+G* basis sets (the last basis set includes diffuse functions on heavy atoms).

Results and Discussion

In EET, one is primarily interested in the energy difference between the states involved in the process rather than in the absolute energy of the electron attachment. When an excess electron moves in DNA from one nucleobase to another, the relevant states are physically very similar, and therefore, the reorganization and correlation terms and the self-interaction errors should cancel each other in large part in the energy difference of these states, $\Delta E_{12} = E_2 - E_1$. Thus, we expect that the UKSO approach may provide reasonable estimates for EET energetics in spite of its failure to predict the EA.

Let us consider in detail the electron transfer process in the radical anion 5′-TT-3′ consisting of two thymine nucleobases. Within MS-PT2 and TD-DFT, the adiabatic splitting of the electronic states ΔE_{12} is calculated as the first excitation energy of the radical anion. Alternatively, by using KS orbitals of the neutral stack TT, we can estimate ΔE_{12} as the difference of the eigenvalues of LUMO+1 and LUMO. The computed data are compared in Table 1. According to the MS-PT2 calculation,[29] in the ground state of the radical anion, the excess electron is almost completely localized on 5′-T, whereas in the excited state, it is localized on T-3′. Independently of the employed functional, the UKSO scheme gives very similar charge distribution (Table 1). Thus, the states T^-T and TT^- with an excess electron on the first and second nucleobase represent the initial and final states of the EET reaction, respectively.

Within the two-state model, the difference of diabatic energies of donor and acceptor Δ_{da} can be directly expressed via adiabatic splitting ΔE_{12} and electronic coupling V, $\Delta_{da} = (\Delta E_{12}^2 - 4V^2)^{1/2}$. In most cases under study, $\Delta_{da} \approx \Delta E_{12}$, because V is essentially less than ΔE_{12}. As seen from Table 1, the UKSO model with the LSDA and GGA functionals slightly underestimates the reference adiabatic splitting, whereas the HF calculation provides a larger value of ΔE_{12}. As expected, the results obtained with the hybrid B3LYP and BH&HLYP are between the HF and BLYP data and very close to the benchmark values.

According to eq 1, the electronic coupling is determined by the adiabatic splitting ΔE_{12} and the transition dipole moment μ_{12} (the difference of the diabatic dipole moments depends only on the donor−acceptor distance and therefore is quite robust to the method of calculation). It is well-known that μ_{12} is very sensitive to the shape of the corresponding wave functions in the region between the donor and acceptor. For instance, the CASSCF and MS-PT2 values of μ_{12} in TT, 0.370 and 0.686,[29] differ by a factor of 2. The BLYP and B3LYP functionals provide very good estimates of μ_{12}, whereas HF overestimates and SVWN and BLYP underestimate the transition moment. The comparison of electronic couplings shows that B3LYP accurately reproduces the MS-PT2 results, whereas pure functionals predict smaller values. BH&HLYP and HF overestimate this charge transfer integral. Overall, the obtained data suggest that the UKSO model may give good estimates for the EET parameters in the stack. Below, we compare the performance of the functionals by using the MS-PT2 results for all stacks considered in ref 29. The Supporting Information provides detailed data for each stack (Tables S1−S7).

Adiabatic Splitting. As seen from Table 2, the MS-PT2 values of adiabatic splitting are in the range from 0.1 eV for CT to 1.0 eV for GT, covering the whole range of the EET energy. Rough estimates of this energy may be derived from EAs calculated for isolated nucleobases. For instance, the adiabatic EA values for T and G in the gas phase are calculated to be 0.22 and −0.75 eV, respectively,[13] giving the energy of 0.99 eV for electron transfer from T^- to G in both GT and TG radical. However, the splitting energies in TG and GT derived from MS-PT2 are quite different; the corresponding values are 0.590 and 1.054 eV (Table 2). As noted above, the EET energetics is strongly influenced by the electrostatic interaction of the donor and acceptor sites with adjacent nucleobases.[17] Because the dipole moment of nucleobases X and Y in XY and YX stacks have different directions, the energy of the ion-

TABLE 2: Comparison of EET Energy (in eV) Calculated by Using UKSO Model[a] with the MS-PT2 Results for π-Stacked Nucleobases

	HF	SVWN	BP86	BLYP	B3LYP	BH&HLYP	**MS-PT2**
TT	0.193	0.125	0.127	0.127	0.134	0.151	**0.155**
TC	0.409	0.393	0.394	0.397	0.407	0.410	**0.401**
CT	0.119	0.053	0.052	0.054	0.067	0.089	**0.098**
TG	0.798	0.665	0.678	0.686	0.699	0.728	**0.590**
GT	1.277	1.068	1.077	1.079	1.112	1.164	**1.054**
AT	0.660	0.507	0.524	0.539	0.554	0.588	**0.504**
TA	0.668	0.563	0.579	0.593	0.603	0.626	**0.435**
MD[b]	0.132	0.025	0.033	0.040	0.054	0.080	
MAD[b]	0.132	0.040	0.049	0.053	0.063	0.082	
SD[b]	0.160	0.059	0.067	0.074	0.082	0.104	

[a] Excitation energy ΔE_{12} is estimated as a difference of the eigenvalues of LUMO+1 and LUMO calculated for neutral systems within HF/6-31G* and DFT/6−31G*. [b] Statistical evaluation: mean deviation, MD; mean absolute deviation, MAD; and standard deviation, SD.

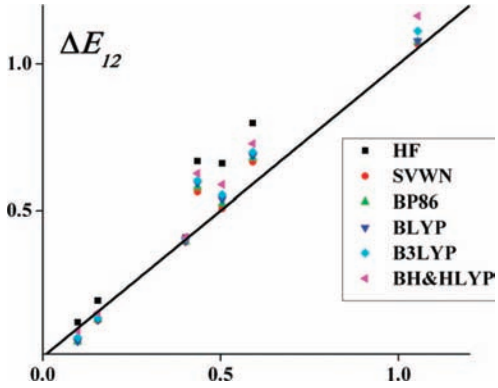

Figure 2. Excitation energy ΔE_{12} of the π stacks calculated by using the UKSO model with different functionals versus MS-PT2 results. The solid line indicates an ideal correlation. All data are in eV.

dipole interaction in these radical anions changes when passing from XY to YX.

The ΔE_{12} value of the TT anion is higher than in CT (Table 2), although the opposite is expected when neglecting the interaction between adjacent nucleobases. This is another example of the essential effects of neighboring nucleobases on the EET energetics. Figure 2 compares UKSO values of ΔE_{12} with the MS-PT2 data. All functionals give reasonable estimates of the charge-transfer excitation energies in the radical anions. On average, the best performance is obtained with the LDA functional (SVWN). Small deviations are also found for the data calculated by using GGA functionals. Because the HF method overestimates the energies by 0.13 eV, including a portion of exact HF exchange in hybrid functionals leads to less satisfactory agreement with the reference data; the deviations in ΔE_{12} found with B3LYP and BH&HLYP are larger than those derived by using the nonhybrid functionals. The largest error is found for TA. In this case, relative deviations range from 30% (SVWN) to 44% (BH&HLYP). For other system, the errors are considerably smaller. On average, the UKSO model overestimates the excitation energy (see mean deviations in Table 2). The adiabatic splitting values predicted by nonhybrid functionals are relatively accurate with standard deviations varying from 0.059 eV (SVWN) to 0.074 eV (BLYP).

Overall, the simple UKSO model gives accurate estimates for the charge-transfer excitation energy. The very good performance of the SVWN functional appears to be quite unexpected.

TABLE 3: Comparison of Electronic Couplings (in eV) Estimated by Means of the UKSO Model[a] with the MS-PT2 Results

	HF	SVWN	BP86	BLYP	B3LYP	BH&HLYP	**MS-PT2**
TT	0.014	0.003	0.004	0.004	0.007	0.010	**0.007**
TC	0.097	0.054	0.052	0.052	0.060	0.074	**0.059**
CT	0.058	0.025	0.026	0.026	0.033	0.044	**0.046**
TG	0.048	0.035	0.033	0.031	0.036	0.042	**0.023**
GT	0.148	0.074	0.074	0.072	0.087	0.110	**0.082**
AT	0.044	0.011	0.011	0.010	0.017	0.026	**0.015**
TA	0.022	0.009	0.008	0.008	0.011	0.015	**0.021**
MD[b]	0.025	−0.006	−0.006	−0.007	0.000	0.010	
MAD[b]	0.025	0.009	0.009	0.009	0.006	0.012	
SD[b]	0.033	0.011	0.011	0.011	0.008	0.015	

[a] HF and DFT calculations of the neutral systems were carried out by using the 6-31G* basis set. [b] Statistical evaluation: mean deviation, MD; mean absolute deviation, MAD; and standard deviation, SD.

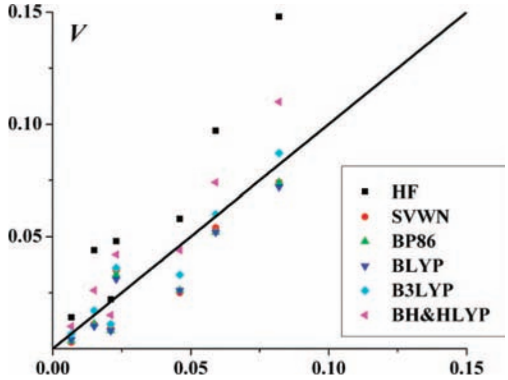

Figure 3. Electronic coupling V calculated by using the UKSO model with different functionals versus MS-PT2 results. The solid line indicates an ideal correlation. All data are in eV.

Electronic Couplings. The calculated data are listed in Table 3. The electronic coupling is known to be quite sensitive to the shape of the electronic density in the ground and excited states.[23] However, the UKSO model provides good estimates for the matrix element. The couplings calculated by using DFT/6-31G* with different functionals are in acceptable agreement with the reference data (Figure 3). It means that the LUMO and LUMO+1 of the neutral stacks describe satisfactorily the ground and excited states of the anion radicals. Figure 3 shows that the HF method overestimates the coupling values; both the MD and MAD amount to 0.025 eV. The DFT calculations reproduce the benchmark values more accurately (Table 3). The B3LYP method provides the best estimation with SD of 0.008 eV. The functionals SVWN, BP86, and BLYP show similar performance with SD of 0.011 eV, which is smaller than that of HF by a factor of 3. On average, these functionals underestimate the couplings values (MD is −0.006 eV). Although BH&HLYP overestimates the reference values, it describes accurately the changes in the coupling when going from one π stack to another; the MD and MAD amount to 0.010 and 0.012 eV, respectively.

These results suggest that the UKSO approach allows accurate estimation of the donor−acceptor coupling for EET between stacked nucleobases. B3LYP shows the best performance.

As already noted, the valence states can be contaminated by dipole bound states if the calculation is carried out by using basis sets augmented by the diffuse functions.[13,23] Because only the valence states are relevant for EET in DNA, basis sets without diffuse functions should be employed. Our test computations showed that the EET parameters are significantly affected by the diffuse functions. The use of the 6-31+G* basis

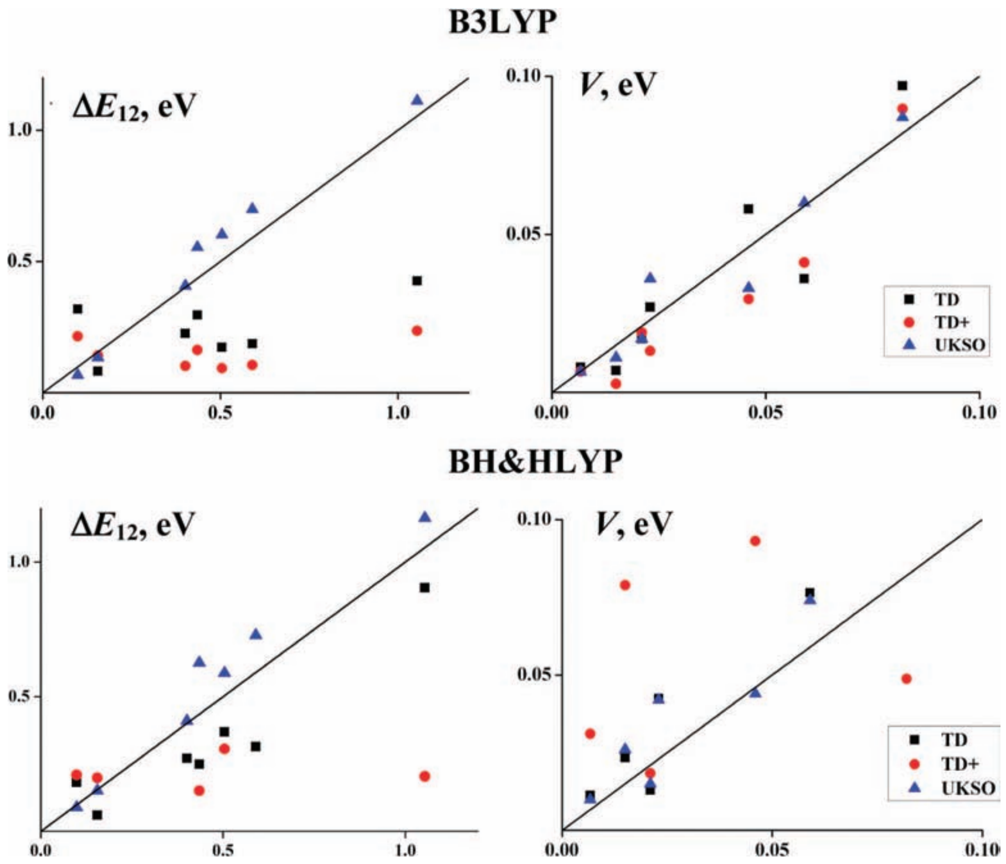

Figure 4. Excitation energy ΔE_{12} and electronic coupling V calculated by using the time-dependent method and UKSO model with the B3LYP and BH&HLYP functionals versus MS-PT2 results. TD-DFT results obtained with the 6-31G* and 6-31+G* basis sets are denoted with TD and TD+. The solid line indicates an ideal correlation with MS-PT2.

set instead of 6-31G* not only decreases the computational efficiency of the UKSO approach but also leads to less accurate results.

TD-DFT Calculations. The excitation energy and transition dipole moment of the radical-anion dimers were also estimated by using TD B3LYP and TD BH&HLYP. These calculations were carried out with and without diffuse functions (6-31+G* and 6-31G* basis sets, respectively). The results are listed in Tables S8 and S9 (see the Supporting Information) and shown in Figure 4. Unfortunately, the TD-DFT calculations of the radical anions are not very robust. For instance, TD-BH&HLYP/6-31+G* does not converge for the TG dimer and gives a negative excitation energy for the TC stack. These problems appear to be traced back to very small adiabatic energy gaps in the radical-anion stacks. Estimates of the EET parameters obtained with the standard and extended basis sets are similar for some dimers but quite different for others. As seen from Figure 4, the adiabatic splitting calculated with TD-DFT is remarkably smaller than the MS-PT2 values. BH&HLYP/6-31G* gives acceptable estimated of ΔE_{12} and V. Including diffuse functions in the basis set leads to less reliable results. The TD B3LYP method cannot well reproduce the excitation energy, whereas the electronic couplings are in satisfactory agreement with the MS-PT2 data.

Thus, the TD-DFT calculations being computationally more expensive by an order of magnitude provide less accurate estimates for the EET parameters in the π stacks than the UKSO approach.

Excess Charge Distribution. As already briefly discussed, an excess electron in the TT stack is confined to a single base both in the ground and excited states (Table 1). As a consequence, by excitation of the radical anion, the charge is almost completely transferred from 5′-T to T-3′. The calculations of other stacks (except CT) give similar charge distributions (Table 4). MS-PT2 predicts that the excess charge in the ground state of TC is confined to T. Similar conclusion may be derived from the UKSO model: analysis of LUMO in the neutral stack suggests that the negative charge should be localized on the thymine. The best agreement between the UKSO and MS-PT2 charges is found for the B3LYP functional.

However, spin-unrestricted (SU) DFT calculations of the radical anions considerably overestimate the delocalization of the excess electron (Table 4). For example, according to SU B3LYP, the negative charge in TC is almost equally distributed over the nucleobases, and the partial charges on T and C are −0.45 and −0.55, respectively. As already discussed in the literature,[53] this deficiency of the functionals may be reduced by using long-range corrections.

5′-CT-3′ is the only dimer where, according to MS-PT2, the excess electron is delocalized. This calculation predicts that in the ground state of CT, $Q(\text{C}) = -0.65$ and $Q(\text{T}) = -0.35$. All DFT calculations also predict the excess electron to be delocalized (Table 4). Note that the excess charge distribution is very sensitive to the parameters ΔE_{12} and V. The difference of charges Δq on the nucleobases X and Y in the stack XY can be estimated as $|\Delta q| = (1 - 4V^2/\Delta E_{12}^2)^{1/2}$. This equation can be directly derived from eq 1 of ref 54, by taking into account that $\Delta E_{12}^2 = \Delta_{\text{da}}^2 + 4V^2$. If $\Delta E_{12} \gg 2V$, $\Delta q = 1$, and therefore, the excess electron is confined to a single base; in contrast, the charge is delocalized over X and Y, $\Delta q = 0$, when $\Delta E_{12} = 2V$. The small adiabatic splitting found in the 5′-CT-3′ π stack, ΔE_{12}

TABLE 4: Excess Charge Distribution in the π Stacks Derived from the LUMO of Neutral Systems and Calculated for the Radical Anions by Using MS-PT2, UHF, and Spin-Unrestricted (SU) DFT Calculations[a]

π stack	TC		CT		AT		GT	
	Q(T)	Q(C)	Q(C)	Q(T)	Q(A)	Q(T)	Q(G)	Q(T)
MS-PT2	**−0.966**	**−0.334**	**−0.643**	**−0.357**	**−0.014**	**−0.986**	**0.013**	**−1.013**
HF								
LUMO	−0.936	−0.064	−0.620	−0.380	−0.028	−0.972	−0.030	−0.970
UHF	−0.419	−0.581	0.176	−1.176	−0.020	−0.980	−0.021	−0.979
BP86								
LUMO	−0.979	−0.021	−0.415	−0.585	−0.012	−0.988	−0.013	−0.987
SU	−0.378	−0.622	−0.378	−0.622	−0.456	−0.544	−0.320	−0.680
SVWN								
LUMO	−0.978	−0.022	−0.346	−0.654	−0.013	−0.987	−0.015	−0.985
SU	−0.431	−0.569	−0.431	−0.569	−0.135	−0.865	−0.322	−0.678
BLYP								
LUMO	−0.980	−0.020	−0.376	−0.624	−0.013	−0.987	−0.014	−0.986
SU	−0.366	−0.634	−0.366	−0.634	−1.067	−0.067	−0.318	−0.682
B3LYP								
LUMO	−0.974	−0.026	−0.492	−0.508	−0.015	−0.985	−0.017	−0.983
SU	−0.454	−0.546	−0.454	−0.546	−0.454	−0.546	−0.221	−0.779
BH&HLYP								
LUMO	−0.963	−0.037	−0.580	−0.420	−0.019	−0.981	−0.021	−0.979
SU	−0.375	−0.625	−0.375	−0.625	−0.205	−0.795	−0.046	−0.954

[a] All calculations have been done by using the 6-31G* basis set.

$\approx 2V$ (see Tables 2 and 3) leads to delocalization of the excess electron within the dimer.

Relatively large values of ΔE_{12} in AT and GT, $\Delta E_{12} \gg 2V$ (see Tables 2 and 3), cause the excess charge to localize on thymine. Again, independently of the functional in use, the UKSO data are in good agreement with MS-PT2 results. On the contrary, the SU-DFT calculations overestimate the charge delocalization significantly (Table 4). Similar results are obtained for TA and TG (see the Supporting Information).

The excess charge distribution found for the ground and excited states of the radical anions XY within MS-PT2 is well reproduced by LUMO and LUMO+1 stemming from the DFT calculations of the corresponding neutral stacks. Both methods suggest that by excitation of the dimers, the excess electron is almost completely transferred from thymine to an adjacent nucleobase. By contrast, the SU-DFT calculations overestimate the charge delocalization considerably (see Tables S1−S7 in the Supporting Information).

Conclusions

In the present study, we have evaluated the performance of various density functionals for describing the EET parameters in DNA. We have shown that the energetics, electronic couplings, and excess charge distribution are accurately estimated by using UKSO of neutral π stacks. In general, good results are obtained by using the local spin-density approximation (SVWN), generalized gradient approximation functionals (BP86 and BPLYP), and hybrid functionals (B3LYP and BH&HLYP). The best estimation for the EET parameters is provided by the B3LYP method. The SVWN calculations give most accurate values of the EET energy. Thus, the UKSO model based on the DFT/6-31G* calculation can be used as an efficient and reliable computational tool to model EET in DNA. However, physically unreasonable results can be obtained when employing a basis set augmented by diffuse functions because of contamination of valence states by dipole-bound states.

In comparison with the UKSO approach, the TD-DFT calculations, which are computationally more expensive by an order of magnitude, provide less accurate estimates for the EET energy and electronic coupling in the π stacks. BH&HLYP/6-31G* gives acceptable estimates of ΔE_{12} and V. Including diffuse functions in the basis set leads to less reliable data. The TD B3LYP method cannot well reproduce the excitation energy, whereas the electronic couplings are in satisfactory agreement with the MS-PT2 values.

We have also found that the excess charge distribution in the ground and excited states of the radical anions is well described by the LUMO and LUMO+1 of neutral dimers. In all π stacks, the excess electron is predicted to localize on a single nucleobases, in agreement with MS-PT2 result. In contrast to this, the SU-DFT calculations of radical anions considerably overestimate the delocalization of the excess electron.

The computational efficiency of the UKSO approach (especially in combination with the SVWN functional) makes it affordable to carry out computations of many conformations of the π stack to take into account the effects of structural fluctuations on the EET parameters. Therefore, the suggested strategy should provide reliable description of the EET in DNA.

Although the excellent performance of the UKSO model has been demonstrated only for π stacks of nucleobases, we believe that this approach can also be applied to study EET in different organic materials where charge transfer properties are controlled by π stacking of the subunits.

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Supporting Information Available: Tables S1−S7 list calculated parameters including dipole matrix elements for each system. The TD-DFT results are given in Tables S8 and S9. This material is available free of charge via the Internet at http://pubs.acs.org.

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