

Electronic Couplings in DNA π -Stacks: Multistate Effects

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In this study, we employ a *multistate* generalized Mulliken–Hush approach for calculating electronic couplings V_{da} for charge transfer (CT) in DNA π -stacks consisting of three, four, and five base pairs. In these systems the guanine donor and acceptor sites are separated by several (AT) pairs. The Hartree–Fock calculations of the stacks are carried out with the standard 6-31G* basis sets. All possible superexchange pathways are accounted for. We examine electronic couplings estimated using the two-state and multistate models. Although for some systems the two-state scheme provides reasonable estimates of V_{da} , in general this simple model fails to reproduce the electronic couplings calculated with the multistate approach. The two-state treatment of π -stacks with a tunneling gap less than 0.3 eV, for instance, GAAG and GAAAG, may lead to invalid estimates of V_{da} . We consider the dependence of V_{da} on the length and composition of the bridge. The calculations show that V_{da} is less sensitive to the arrangement of nucleobases in the bridge, as can be predicted on the basis of electronic couplings between adjacent base pairs.

Introduction

The control of charge transfer through DNA π -stacks has received a considerable attention over the past 15 years. A number of experimental and theoretical studies have been performed in order to understand mechanisms of charge migration in the double helix.¹ In model systems, one can estimate the probability of charge transfer between several guanines connected by (AT)_{*n*} bridges.^{1–4} Although the electronic couplings between neighboring base pairs is found to be ~ 0.1 eV,^{5,6} the interactions between second-nearest neighbors are several times weaker, and therefore DNA π -stacks, where donor and acceptor are separated by one or more intervening base pairs, are expected to fall well within the nonadiabatic regime. In this case, the rate of electron hole transfer is predicted to be proportional to the square of the electronic coupling V_{da} between the donor and acceptor sites.⁷ The quantum mechanical treatment of the donor–acceptor coupling has been considered in detail by Newton.⁸ Theoretical aspects of charge transfer in DNA have recently been considered by Berlin et al.⁹ Beratan and co-workers have performed a comprehensive computational study of the hole transfer rates in DNA including estimation of electronic couplings and reorganization energies.¹⁰ The application of different models to estimate V_{da} in DNA stacks has been discussed recently.¹¹

Because guanine (G) is the most easily oxidized nucleobase, the cation radical G^+ is a key intermediate in the hole transfer process mediated by DNA.^{1–4} Each elementary hopping step $G_i^+ \rightarrow G_j$ when donor and acceptor (GC) pairs are separated by a short (AT)_{*n*} bridge ($n \leq 3$) can be represented as superexchange tunneling.^{9–17}

Several years ago, Cave and Newton introduced the generalized Mulliken–Hush (GMH) method.^{18,19} This scheme employs a transformation of adiabatic states to diabatic states that diagonalizes the adiabatic dipole moment matrix. Once the unitary transformation T is defined, the electronic couplings (off-diagonal matrix elements of the diabatic Hamiltonian) can be calculated as

$$V_{da} = \sum T_{id} E_i T_{ia}$$

where \mathbf{E} is the diagonal matrix of the adiabatic energies. Within the two-state model, the electronic coupling can be expressed via the vertical excitation energy $E_2 - E_1$, the difference $\mu_1 - \mu_2$ of the adiabatic dipole moments, and the transition dipole moment μ_{12}

$$V_{da} = \frac{(E_2 - E_1)|\mu_{12}|}{\sqrt{(\mu_1 - \mu_2)^2 + 4\mu_{12}^2}} \quad (1)$$

The GMH method allows calculation of V_{da} in various systems, independent of symmetry and geometric constraints.^{18,19} An important advantage of the GMH method is that it is able to deal with multistate situations where more than two adiabatic states enter into the description of the diabatic states of interest. When electronic levels of the bridge or neighboring sites are energetically close to those of the donor and acceptor, the diabatic states may represent a combination of more than two adiabatic states. In this case the multistate model should be employed. Very recently, a diagnostic has been developed for determining when a third state has to be considered within GMH calculations.²⁰ Furthermore, all of the coupling elements of interest can be derived from a single calculation. However, it should be noted that the number of states considered simultaneously within a GMH procedure should be kept as small as possible.¹⁹

Comparison of GMH with an alternative approach, fragment charge method, has been done recently for calculating V_{da} in systems consisting of several nucleobases.²¹ Excellent agreement between both methods has been found. The GMH model was recently applied to study photoinduced hole transfer in DNA hairpins from the excited state of a chromophore (electron hole donor) to guanine (hole acceptor) separated by several (AT) pairs.²² The initial d^*a and final d^+a^- states in the charge separation process were described with a multiconfigurational

approach based on the semiempirical INDO/S Hamiltonian. It has been shown that the nature of the donor has a significant influence on the distance dependence of the photoinduced hole transfer.²²

On the basis of a theoretical model for hole transfer through DNA, Berlin, Burine, and Ratner predicted that switching from the superexchange to an alternative hole transfer mechanism in DNA takes place when three or more bridging AT base pairs separate the d–a sites.²³ A similar conclusion was derived by Beratan and co-workers from comparison of the calculated and observed hole transfer rates in several π -stacks.¹⁰ Therefore, estimation of V_{da} for bridges containing more than three base pairs appears to be unnecessary.

In this study, we consider the multistate effects by calculating electronic couplings for hole transfer in DNA π -stacks in which the guanine donor and acceptor sites are connected by one, two, and three (AT) pairs.

Computational Details

The coupling V_{da} depends on the details of the electronic structure of the stack. Adiabatic state properties can be found within different quantum chemical approaches. In many cases one can reliably estimate electron-transfer matrix elements on the basis of a one-electron approximation.⁸ Recently it has been demonstrated that even for photoinduced charge transfer (where many-electron effects are expected to be much more important than for electron hole shifting in π -stack) the GMH scheme based on the one-electron model provides reasonable estimates of electronic couplings.²⁴

The energy of adiabatic state I ($I = 1, 2, \dots, N$) of a radical cation system may be estimated as the one-electron energy of the molecular orbital (MO) with the number $K + 1 - I$, where K is the number of HOMO (highest occupied MO) in the corresponding closed-shell neutral system. The difference $\mu_I - \mu_J$ of the adiabatic dipole moments and the transition moment μ_{IJ} is calculated as

$$\mu_I - \mu_J = \sum_{\lambda, \nu=1}^M (C_{\lambda, K+1-I} C_{\nu, K+1-I} - C_{\lambda, K+1-J} C_{\nu, K+1-J}) d_{\lambda \nu}$$

$$\mu_{IJ} = \sum_{\lambda, \nu=1}^M C_{\lambda, K+1-I} C_{\nu, K+1-J} d_{\lambda \nu}$$

Here, $d_{\lambda \nu}$ is the matrix element of the dipole operator defined for atomic orbitals λ and ν . M is the number of basis functions.

We estimated the electronic couplings at the Hartree–Fock level. All quantum chemical calculations were carried out with the program Gaussian 98.²⁵ Structures of π -stacks were generated as described previously.⁶

Results and Discussion

GAG and GTG. First, we applied the GMH procedure to two systems consisting of three base pairs. In GAG, adenine (A) is on the same strand as the guanine donor and acceptor sites, while in GTG the base is on the opposite strand.

Each system has three centers, two G's and one A, which can trap an electron hole. According to our calculation, the diabatic energy of the hole state localized on the bridge in GAG and CAC (the duplex notation CAC is equivalent to GTG; see Scheme 1) is higher than the average energy of G^+ states by 0.24 and 0.76 eV, respectively. This difference is due to the effects of neighboring pairs. The stabilizing effect of X on a hole states B^+ in XBX decreases in the order $G > A > T \sim$

SCHEME 1

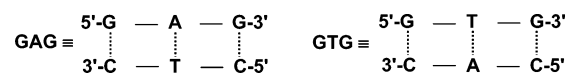


TABLE 1: Electronic Coupling of G_2 and G_4 in $X\text{-}G_2AG_4\text{-}X$ and $X\text{-}G_2TG_4\text{-}X$ Stacks ($X = G, A, T, *$) Calculated Using Both Multistate and Two-State Models, in meV

system	X	2-state model	multistate model ^a
X- G_2AG_4 -X	* ^b	19.1	4.16
	G	8.72	5.46
	A	14.2	4.27
	T	19.5	4.24
X- G_2TG_4 -X	* ^b	1.72	2.46
	G	0.30	2.09
	A	1.68	2.19
	T	1.48	2.30

^a Five-state and three-state models are applied to stacks consisting of three and five base pairs, respectively. ^b No flanking base pairs; the GAG and GTG stacks are considered.

C.²⁶ In GAG, the adjacent guanine bases stabilize A^+ better than the cytosine bases in GTG. The three lowest energy states of an electron hole are mainly localized on the purine bases of the stacks. Table 1 lists the electronic couplings of G's calculated within two- and three-state models. A substantial difference in V_{da} is found for the GAG stack. The two-state model overestimates the coupling by a factor of 5. Inspecting the lowest energy hole states in the system reveals that the adiabatic states represent an admixture of three diabatic states. For instance, the ground state of the radical cation contains a remarkable contribution, 12%, of the diabatic state A^+ with a hole localized on the bridging adenine base. As a result, the GAG stack cannot be properly described with the two-state model. By contrast, the electronic coupling in GTG may be well estimated within the two-state scheme. In this case, the donor–acceptor states are well separated energetically (by ~ 0.76 eV) from the bridge state and only insignificantly, less than 1%, contaminated by the A^+ state. Thus, using the two-state model for π -stacks with a tunneling gap less than 0.3 eV may lead to poor estimates of V_{da} .

The differences between the V_{da} values obtained for GAG and GTG within the multistate and two-state schemes can be also explored in terms of the GMH scheme. The transition dipole moment between two adiabatic states reflects the mixing of the corresponding diabatic states. In turn, the mixing is determined by the electronic coupling and the energy gap between the diabatic states. That is why the analysis of dipole moments can be used for estimation of V_{da} . In terms of GMH, the interaction between two states 1 and 2 is related to the ratio of the corresponding transition dipole moment to the difference in the diabatic state dipole moments, $|\mu_{12}/\Delta\mu_{12}|$ (see eq 1). Let “d”, “a”, and “i” be the diabatic states where an electron hole is localized on the donor, acceptor, and bridge sites, respectively. Because in DNA stacks DB_iA , where donor and acceptor are separated by a single base pair, $\Delta\mu_{di}$ and $\Delta\mu_{ia}$ are about 15 D and $\Delta\mu_{da} = \Delta\mu_{di} + \Delta\mu_{ia}$ is about 30 D (subsequently, the ratios $\Delta\mu_{di}/\Delta\mu_{da}$ and $\Delta\mu_{ai}/\Delta\mu_{da}$ are approximately 0.5), one can consider only transition dipole moments. The absolute values of μ_{di} and μ_{ai} , 4.72 and 3.01 D, are similar to $\mu_{da} = 4.58$ D. These data point to a strong mixing of the three states in GAG. As a result, a three-state treatment is required. However, in GTG the calculated values of μ_{di} and μ_{ai} , about 0.5 D, are considerably smaller than $\mu_{da} = 2.68$ D, and therefore, the multistate effects in this stack should be less significant than in GAG. As already mentioned, V_{da} values in GTG estimated using the two-state

TABLE 2: Electronic Couplings V_{ij} of Adjacent Pairs^a i and j and V_{da} of (GC) Pairs in GB₁B₂G Stacks (X, Y = A, T)^b

system	V_{12}		V_{23}		V_{34}		V_{da} , in meV		
							5-state	2-state ^c	SE ^c
GAAG	G–A	119	A–A	35.6	A–G	35.3	0.237	0.028	1.98
GATG	G–A	119	A\A	46.7	A/G	23.5	0.344	0.503	0.429
GTAG	G\A	22.1	A/A	49.2	A–G	36.1	0.189	0.429	0.294
GTTG	G\A	22.7	A–A	35.5	A/G	23.2	0.773	1.251	0.067

^a The positions of two purine bases P_i and P_j ($P = G, A$) in the stack are denoted as P_i – P_j for intrastrand arrangement, and P_i/P_j and $P_i\backslash P_j$ for the two different interstrand arrangements. ^b The V_{da} values are estimated using the five- and two-state GMH scheme as well as the superexchange (SE) model. ^c The values are given only for comparison and are not recommended for estimating CT efficiency in DNA stacks.

and three-state models are similar while the matrix elements calculated for GAG are quite different.

Note that the electronic couplings of guanines in the GAG stack have already been estimated using different computational schemes.^{6,10,21,27,28} Its value ranges from 1.6 to 19.1 meV. These estimates have been computed at different geometries of the stack. Because the electronic coupling of nucleobases is very sensitive to structural fluctuations of π -stacks,^{29,30} thorough analysis of the differences in the V_{da} values appears to be hardly possible.

Effects of Flanking Base Pairs. Let us consider the influence of the flanking base pairs X in X-GAG-X and X-GTG-X on the electronic coupling between G's. One may expect the effect of the external base pairs to be rather small. X can affect the coupling only by modulating the tunneling gap. No new superexchange pathways from donor to acceptor are coming into play by extension of GBG to XGBGX. Table 1 compares electronic couplings calculated for complexes X-GAG-X using two and five states. The five-state treatment predicts a moderate change in V_{da} by variation of X in X-GAG-X: the coupling ranges from 4.24 to 5.46 meV for X = T and X = G, respectively. The two-state model provides a physically unreasonable result: the coupling decreases by a factor of 2 when one goes from X = G to X = A and T, and consequently, the two-state model cannot be employed to treat electronic couplings in systems such as GGBGG, where donor and/or acceptor consist of two (or more) guanines. It should be noted that GG and GGG stacks have been extensively employed as hole acceptors in experimental studies on charge transfer in DNA.^{1–4} In X-GTG-X (Table 1) (X = *, A, and T), the matrix element V_{da} calculated within two-state and multistate models are in good agreement; however, the electronic coupling of G's in GGTGG cannot be estimated properly using the two-state approach. Because the effect of flanking base pairs is rather small, quite reliable estimates of V_{da} may be obtained for a donor–bridge–acceptor system without accounting for external base pairs X. Neglecting the flanking pairs leads to substantial decrease of computational time and makes it possible to consider more extended models.

GB₁B₂G. Now we consider stacks where the donor and acceptor sites are separated by two (AT) pairs. Using the multistate method, one can obtain all the coupling elements and energetics of the diabatic states from a single calculation. This means in particular that the calculation of V_{da} in a DNA stack GB₁B₂G gives also the couplings between neighboring sites (G–B₁, B₁–B₂, and B₂–G) and energies of states, where a hole is localized on the donor and acceptor (the guanine bases) as well as on the bridging (AT) pairs (on the B₁ and B₂ sites). Table 2 lists electronic couplings calculated within the four-state GMH model. Besides V_{da} , the couplings between neighboring pairs in GB₁B₂G are also presented. As expected, the coupling matrix elements between neighboring pairs depend on the nature and arrangement of nucleobases but remain almost unchanged in

different systems. For instance, the intrastrand A–A coupling is calculated to be 35.5 and 35.6 meV in GAAG and GTTG, respectively. Comparison of V_{da} in X-GAG-X and X-GTG-X (Table 1) suggests that the coupling of G's separated by A is double as strong as in the GTG stack. This means that the intrastrand interaction G–A–G is stronger than the interstrand coupling G\A/G (see Scheme 1). However, an opposite result can be derived from data calculated for GXYG stacks (Table 2). The coupling in GAAG with intrastrand purines is smaller than in GTTG. Directional asymmetry of the coupling between neighboring nucleobases may be seen from G–A and A–G couplings in GAAG, which are 119 and 35.3 meV, respectively. Comparison of the V_{da} values in GATG and GTAG clearly demonstrates the directional dependence of the donor–acceptor coupling in extended DNA stacks. The coupling in the first system is calculated to be twice as strong as V_{da} in the second stack. The effect of directional asymmetry for hole transfer has been predicted on the basis of calculated V_{da} between neighboring nucleobases⁵ and base pairs⁶ and was subsequently detected by O'Neill and Barton.³¹

Interestingly, V_{da} in GTAG calculated using the four-state approach (0.19 meV) is essentially smaller than that in GTTG (0.77 meV), while all the couplings between neighboring base pairs in GTAG are stronger than (or almost equal to) the corresponding values in GTTG. The energies and electronic couplings of diabatic states can be used to estimate V_{da} within a superexchange (SE) model⁸ in which only one state per bridge is accounted for. For a system DB₁B₂A

$$V_{da}(\text{SE}) = \frac{V_{d1}V_{12}V_{2a}}{(E_t - E_1)(E_t - E_2)} \quad (2)$$

where the tunneling energy E_t is set to the average of the donor and acceptor energies, E_1 and E_2 are diabatic energies of the bridge states. The superexchange approach predicts the V_{da} in GTAG (0.29 meV) to be essentially stronger than in GTTG (0.067 meV). Considerable deviations of SE couplings from the reference values estimated within the multistate GMH method (Table 2) demonstrate a limitation of the perturbation approach based on a single superexchange pathway. As discussed in detail previously, several electronic states of bridging (AT) pairs are responsible for mediating the superexchange interaction between donor and acceptor in DNA stacks, and the interference of these pathways plays an important role.³² Thus, even qualitative predictions on relative strengths of the donor–acceptor interaction may be misleading when based on a single-pathway scheme. It should be noted that all possible superexchange pathways are taken into account when V_{da} is derived from quantum mechanical calculations of whole donor–bridge–acceptor systems.^{8,10,22}

As seen from Table 2, the calculations of V_{da} using the two-state model lead to reasonable values for GATG and GTTG;

TABLE 3: Donor–Acceptor Electronic Coupling in GB₁B₂B₃G Double-Strand Stacks Calculated Using the Five- and Two-State GMH Scheme and the Superexchange (SE) Model, in meV

B ₁ B ₂ B ₃	AAA	AAT	ATA	TAA	TTA	TAT	ATT	TTT
5-state	0.054	0.032	0.028	0.019	0.026	0.033	0.023	0.045
2-state ^a	0.104	0.113	0.169	0.091	0.312	0.043	0.012	0.005
SE ^a	0.192	0.047	0.121	0.027	0.029	0.008	0.039	0.009

^a The values are given only for the purpose of comparison and are not recommended for estimating CT efficiency in DNA stacks.

however, this scheme remarkably underestimates the coupling in GAAG ($V_{da} = 0.028$ meV instead of 0.237 meV).

GB₁B₂B₃G Stacks. Finally, we consider systems where the donor and acceptor sites are linked with a bridge consisting of three (AT) pairs. Table 3 lists V_{da} values for all possible bridges estimated using five-state and two-state GMH models as well as the superexchange approach. Note that couplings calculated within the multistate approach are used as reference values while the data obtained within the two-state scheme and the superexchange model are provided only for comparison. Taking into account that the V_{da} values derived using the two-state model differ considerably from the corresponding reference data (Table 3), one can conclude that the two-state approach gives rather unreliable estimates for the donor–acceptor coupling mediated by three base pairs.

Interestingly, the donor–acceptor electronic coupling is found to be not very sensitive to switching between (AT) and (TA) pairs in the bridge (see five-state GMH results in Table 3). The largest coupling is found for the AAA bridge, 0.054 meV. A somewhat smaller value is calculated for the TTT bridge, 0.046 meV. In both linkers adenine bases are on the same strand, and therefore, intrastrand A–A electronic couplings mediate the superexchange interaction of the donor and acceptor. The V_{da} magnitude in six other complexes ranges from 0.02 to 0.03 meV. This result is a little surprising when one recalls considerable differences in V_{da} values between adjacent base pairs⁶ (see also V_{ij} in Table 2).

Comparing electronic couplings estimated within the SE model with the reference data derived from the multistate GMH calculation for GB₁B₂G (Table 2) and GB₁B₂B₃G (Table 3), one can see that the SE values are remarkably more responsive to the bridge structure as compared with reference matrix elements. The results suggest that interference of many superexchange pathways decreases the sensitivity of V_{da} mediated by bridges, as can be predicted using the single-pathway model.

Using electronic coupling in GBG, GB₁B₂G, and GB₁B₂B₃G (Tables 1–3), one can estimate the falloff parameter β_{el} for the decay of the hole transfer rate due to the V_{da} variation. On average, the calculated matrix element decreases by an order of magnitude for each additional base pair inserted between donor and acceptor. The average donor–acceptor coupling of G's linked by one, two, and three (AT) pairs is about 3.3, 0.35, and 0.032 meV, respectively. Because the rate is proportional to the matrix element squared⁷ and the distance between base pairs in DNA is about 3.4 Å, we obtain $\beta_{el} \approx 2$ Å⁻¹. The experimental decay parameter for photoinduced hole transfer ranges from 0.6 to 1.5 Å⁻¹.^{2–4} Thus, the discrepancy is quite large. Recently it has been demonstrated that the nature of the chromophore has a significant influence on the distance dependence of the hole transfer. For instance, in hairpins bearing two different stilbene derivatives as hole donors, the β values are computed to be ~0.4 and 0.7 Å⁻¹.²² Thus, the efficiency of hole transfer considerably depends on the injection energy,²² and the experimental β values should be compared with the parameters calculated for models containing the hole injector.

Conclusion

In this study, we report donor–acceptor electronic couplings in several DNA π -stacks based on Hartree–Fock calculations. These calculations take into account all possible superexchange pathways mediated by AT pairs between the guanine donor and acceptor sites. We employ the *multistate* GMH approach to estimate V_{da} in the π -stacks and compare the results with the matrix elements derived by using the *two-state* method and the superexchange model.

This work shows that significant multistate effects can arise even in rather short systems consisting of three base pairs, making the two-state model inapplicable. For example, the V_{da} value in GAG predicted by the two-state is 5 times larger than the coupling calculated with the multistate method. The two-state scheme cannot be applied to systems with the GG or GGG acceptor site. Although for some stacks the two-state method provides accurate estimates of V_{da} , in general this model fails to reproduce the electronic couplings calculated with the multistate approach. Using the two-state model for systems with a tunneling gap less than 0.3 eV, e.g., for stacks with intrastrand purine bases, may lead to invalid estimates of V_{da} .

It has been shown that the nature of adjacent base pairs external to the donor–bridge–acceptor unit has only a small effect on the coupling. Despite the electronic couplings of neighboring base pairs being strongly dependent on the nature and arrangement of nucleobases, in systems with a bridge consisting of two and three base pairs, the V_{da} matrix elements are found to be less sensitive to the bridge structure as can be predicted using the single-pathway superexchange approach.

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