

Charge-on-site scheme to estimate the electronic coupling in electron transfer systems

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Abstract

A simple but accurate approach, the charge-on-site scheme, is introduced to calculate coupling matrix elements for electron transfer (ET) in donor–bridge–acceptor (d–b–a) systems. The electronic coupling is explicitly expressed through energies of relevant adiabatic states and charges on the donor and acceptor sites. The method is formulated within two- and multistate models. The proposed scheme can be directly employed in conjunction with any quantum mechanical method providing atomic charges in the ground and excited states. As an illustration, the charge-on-site method is applied to a π stack GAG consisting of three nucleobases.

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1. Introduction

Electron transfer (ET) in donor–bridge–acceptor systems (d–b–a) plays an important role in physics, chemistry and biology [1–4]. Computational modeling of charge transfer reactions provides deep insight into intimate mechanisms of ET making it possible to explore the role of electronic, structural and dynamics factors in bridge-mediated ET processes. Thus, a considerable increase has been observed in the application of modern computational methods to the study of ET in chemical and biological systems [5–7]. Many ET reactions proceed in the nonadiabatic regime. For such processes, the electronic coupling between donor and acceptor, also called electron transfer integral, is of central importance [1,8]. The coupling determines the reaction rate and its dependence on the nature, arrangement and structural fluctuations of the donor, bridge and acceptor sites. The ET properties of organic materials can be well described using the coupling between neighboring units [9–11]. Furthermore, because the electrical conductance of molecular wires is closely related to the ET rate constant [12,13], computa-

tional schemes used for treatment of ET processes may be applied to study the molecular wires.

The electronic coupling is difficult to extract from experimental data, and thus, very often quantum mechanical calculations offer the only way to get this parameter [1–8,10,14,15]. In most cases a two-state model is employed to estimate the matrix element. This model presumes that in the progression to the transition state, only the donor and acceptor states mix with each other and do not interact with the other states of the system. In a d–b–a system, the coupling of the reactant d–b–a⁺ and product d⁺–b–a process is significantly facilitated by the virtual bridge state d–b⁺–a. Because of the significant energy gap between the donor and bridge states, this last state cannot be an intermediate in the ET process.

Because quantum chemical calculations of an entire d–b–a system take into account the contribution of all virtual bridge states, and thus, interference of different ET pathways is appropriately treated, it is thought that accurate estimates for the donor–acceptor coupling, V_{da} , can be derived on bases of the two-state framework. However, a decrease of the donor–bridge energy gap, followed even by a relatively small admixture of bridge states to the adiabatic states of interest, may lead to a situation when the two-state model becomes inappropriate. In this case, to

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obtain correct values of V_{da} several adiabatic states must be considered simultaneously, i.e., a multistate treatment is required. The Generalized Mulliken-Hush approach (GMH) introduced by Cave and Newton [16,17], has become de facto the standard method to evaluate electronic couplings on the bases of quantum chemical calculations of ET. An important advantage of the GMH method is that it is able to deal with systems where more than two adiabatic states enter into the description of relevant diabatic states. Another multistate approach, the fragment charge difference method (FCD) has been recently suggested [18]. While the two-state GMH scheme is widely used to calculate electronic couplings, there have been only several studies dealing with the multistate GMH approach (see, for instance, Refs. [16–20]). Although for some d–b–a systems the two-state scheme provides reasonable estimates, in general, this model fails to reproduce the electronic couplings calculated with the multistate approach [16–19]. Cave and co-workers considered in detail an important case of three-state systems, where two diabatic states (the ground state and a locally excited state) are localized on the donor and a single electron transfer state is localized on the acceptor [21]. The limitation of the two-state model for treatment of d–b–a systems has been analyzed using the perturbation theory [22].

As already noted, in contrast to the two-state GMH model, the multistate GMH scheme still does not enjoy wide application. There is a rather technical reason for that: many of the standard quantum chemical programs do not provide transition dipole moments between excited states, while the corresponding values for the transition between the ground and excited states are usually available. Because of that, the dipole moment matrix required in the GMH scheme cannot be constructed for a system where three- or more states must be considered.

In this Letter, we introduce a simple method which takes into account the effects of bridge states and allows estimating electronic couplings on the bases of adiabatic state energies and charges on the donor and acceptor sites. Hereafter this scheme will be referred to as charge-on-site method (ConS). Like FCD [18], the ConS model employs the charges on the donor and acceptor sites, however, this scheme is much more straightforward than its predecessor.

2. Method

Let us consider a symmetric d–b–a system. φ_d , φ_a and φ_b are diabatic states of the donor, acceptor and bridge, respectively. We assume that these states are orthogonal. In the diabatic Hamiltonian

$$\mathbf{H}_d = \begin{pmatrix} \varepsilon_d & V_{db} & V_{da} \\ V_{db} & \varepsilon_b & V_{ba} \\ V_{da} & V_{ba} & \varepsilon_a \end{pmatrix}, \quad (1)$$

the diagonal matrix elements are diabatic state energies, while the off-diagonal matrix elements correspond to the

electronic coupling between the states. Transformation of the diabatic states to adiabatic representation can be done by multiplication of \mathbf{H}_d by an orthogonal matrix \mathbf{C}

$$\mathbf{H}_d \mathbf{C} = \mathbf{C} \mathbf{E} \text{ or } \mathbf{E} = \mathbf{C}^+ \mathbf{H}_d \mathbf{C}$$

The resulting matrix \mathbf{E} is diagonal (all off-diagonal matrix elements are equal zero).

Conversely, the electronic couplings and diabatic energies may be obtained from the adiabatic energies \mathbf{E} using a reverse transformation $\mathbf{T} = \mathbf{C}^+$ which leads to the diabatic matrix \mathbf{H}_d , $\mathbf{H}_d = \mathbf{T}^+ \mathbf{E} \mathbf{T}$. However, usually the transformation \mathbf{T} is unknown. Different approaches may be used to determine how to transform two or several adiabatic states obtained from quantum mechanical calculations to diabatic states of interest. In the GMH method, for instance, the diabatic states are chosen diagonal with respect to a component of the dipole moment operator [16,17]; in the FCD, the diabatic states are designed in such a way as to maximize the charge transferred from donor to acceptor [18]. Before we proceed further, we consider a numerical example comparing the two- and three-state treatments of a symmetric d–b–a system.

2.1. Numerical example

Because the donor and acceptor are identical, $d = a$, the Hamiltonian \mathbf{H}_d (Eq. (1)) can be defined as follows $\varepsilon_d = \varepsilon_a = 0$, $\varepsilon_b = 1$, $V_{db} = V_{ba} = -0.1$, $V_{da} = -0.01$. Hereafter all values are in eV. The values taken for ε_b , V_{da} and V_{db} are quite typical for thermal charge transfer in π stacks. In the system considered, the bridge state is energetically well separated from the donor and acceptor levels, $|\frac{V_{db}}{\varepsilon_b - \varepsilon_d}| = 0.1$. The adiabatic states obtained by diagonalization of \mathbf{H}_d are

$$\psi_1 = 0.701\varphi_d + 0.136\varphi_b + 0.701\varphi_a, \quad E_1 = -0.029$$

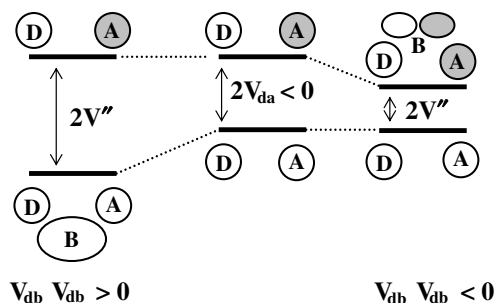
$$\psi_2 = 0.707\varphi_d - 0.707\varphi_a, \quad E_2 = 0.010$$

$$\psi_3 = 0.096\varphi_d - 0.991\varphi_b + 0.096\varphi_a, \quad E_3 = 1.019$$

Two states of the lowest energy, ψ_1 and ψ_2 , correspond to \pm combinations of the donor and acceptor states; ψ_1 contains a small admixture of the bridge state. The adiabatic state ψ_3 is almost completely (98%) localized on the bridge.

Now we employ the two-state model to estimate the donor–acceptor coupling V''_{da} . Because the donor and acceptor are equivalent, the electronic coupling is simply half of the energy gap between the adiabatic states ψ_1 and ψ_2 , $|V''_{da}| = \frac{1}{2}(E_2 - E_1)$.

The resulting $|V''_{da}| \approx 0.020$ is by a factor of 2 larger than accurate value $V_{da} = 0.01$. Moreover, the ratio of $|V''_{da}|/V_{da}$ will deviates from unity much more radically when V_{da} and $V_{db}V_{ba}$ are of the same sign. In particular, for $V_{da} = +0.01$, the calculation gives $|V''_{da}| \approx 0.0001$; thus, in this case the donor–acceptor coupling derived from the two-state model is underestimated by two orders of magnitude. Scheme 1 helps to understand why the two-state model overestimates V_{da} when $V_{db}V_{ba} > 0$, and predicts too small values of V_{da}



Scheme 1.

in the case $V_{db}V_{ba} < 0$. The numerical results appear to be quite unexpected having regard to the fact that the two-state scheme is widely employed to derive the donor-acceptor coupling in symmetric d–b–a systems. This simple example makes it clear that neglecting the bridge state may lead to inaccurate estimates of V_{da} .

However, it should be noted that in some cases, particularly for systems where the donor and acceptor are connected with a σ -bridge, the diabatic state derived with a two-state model (the d–b–a system is considered as a d'–a' complex with $d' = d + b_1$ and $a' = a + b_2$, where b_1 and b_2 are fragments of the bridge, $b_1 + b_2 = b$) may better describe the experimental system under question. In other words, the electronic coupling of the d' and a' diabatic states that have a component of the bridge state in them may be more appropriate than the coupling of the pure state d and a. It is apparent that this problem deserves further investigation.

2.2. Three-state framework

Within the three-state model, the exact V_{da} value can be obtained as

$$V_{da} = E_1 C_{d1} C_{a1} + E_2 C_{d2} C_{a2} + E_3 C_{b3} C_{b3} \quad (2)$$

where E_i is the adiabatic energy and C_{di} is a coefficient at φ_d in the adiabatic state ψ_i , $n = 3$. Taking into account that $\sum_{j=1}^n C_{dj} C_{aj} = 0$, Eq. (2) can be written as

$$V_{da} = -(E_3 - E_1) C_{d1} C_{a1} - (E_3 - E_2) C_{d2} C_{a2} \quad (3)$$

and then

$$V_{da} = -\frac{E_2 - E_1}{2} [C_{d1} C_{a1} - C_{d2} C_{a2}] - \left(E_3 - \frac{E_2 + E_1}{2} \right) [C_{d1} C_{a1} + C_{d2} C_{a2}]. \quad (4)$$

Since ψ_1 and ψ_2 are + and – combinations of donor and acceptor states, the products $C_{d1} C_{a1}$ and $C_{d2} C_{a2}$ are of opposite sign, and the absolute value of the coupling is

$$|V_{da}| = \left| \frac{(E_2 - E_1)}{2} (|C_{d1} C_{a1}| + |C_{d2} C_{a2}|) + \left(E_3 - \frac{E_2 + E_1}{2} \right) (|C_{d1} C_{a1}| - |C_{d2} C_{a2}|) \right| \quad (5)$$

Note that Eq. (5) is accurate within the three-state framework.

By definition, the excess charge is completely localized on the donor, acceptor and bridge in the diabatic states φ_d , φ_a and φ_b , respectively. Therefore, the quantities C_{di}^2 and C_{ai}^2 describe a portion of the excess charge localized on the donor and acceptor sites in the adiabatic state ψ_i . Denoting C_{di}^2 and C_{ai}^2 by q_{di} and q_{ai} we obtain

$$|V_{da}| = \left| \frac{(E_2 - E_1)}{2} (\sqrt{q_{d1} q_{a1}} + \sqrt{q_{d2} q_{a2}}) + \left(E_3 - \frac{E_2 + E_1}{2} \right) (\sqrt{q_{d1} q_{a1}} - \sqrt{q_{d2} q_{a2}}) \right|. \quad (6)$$

Thus, the donor–acceptor coupling is expressed via adiabatic energies and excess charge distributions in the adiabatic states. The first term

$$|V_{da}(2st)| = \frac{(E_2 - E_1)}{2} (\sqrt{q_{d1} q_{a1}} + \sqrt{q_{d2} q_{a2}}) \quad (7)$$

provides the two-state electronic coupling. For d–a systems (without bridge), the expression provides a correct V_{da} value irrespective of whether the donor and acceptor states are in resonance or not. Usually, the charges on donor and acceptor can be easily derived from quantum chemical calculations; for state ψ_i , $q_{di} = \sum_{k \in d} Q_{ki}$ and $q_{ai} = \sum_{k \in a} Q_{ki}$ where the sum is taken over all atomic charges Q_{ki} related to the donor and acceptor, respectively.

The second term in Eq. (6)

$$V_{da}(\text{cor}) = \left(E_3 - \frac{E_2 + E_1}{2} \right) (\sqrt{q_{d2} q_{a2}} - \sqrt{q_{d1} q_{a1}}) \quad (8)$$

describes the correction to the two-state model due to the bridge state. The difference $(E_3 - \frac{E_2 + E_1}{2})$ gives the energy gap between the bridge and d–a adiabatic states. Even for symmetric d–b–a systems the difference $\sqrt{q_{d2} q_{a2}} - \sqrt{q_{d1} q_{a1}}$ is nonzero and the correction is usually of the same magnitude as $V_{da}(2st)$, Eq. (7).

For symmetric systems, $q_{d1} = q_{a1}$ and $q_{d2} = q_{a2}$, and Eq. (6) reduces to

$$|V_{da}| = \left| \frac{(E_2 - E_1)}{2} (q_{d1} + q_{d2}) + \left(E_3 - \frac{E_2 + E_1}{2} \right) (q_{d1} - q_{d2}) \right| \quad (9)$$

When $q_{d1} = q_{d2} = 0.5$, the half splitting expression $|V_{da}| = \frac{(E_2 - E_1)}{2}$ will give accurate coupling values. Obviously, this condition holds for d–a systems (no bridge!), however, in d–b–a complexes $q_{d1} \neq q_{d2}$ and the accuracy of the two-state model strongly depends on the difference $(q_{d1} - q_{d2})$. As noted above, a d–b–a system may be considered as a d'–a' complex with $d' = d + b_1$ and $a' = a + b_2$. In this case, Eq. (7) will give an appropriate value of the donor–acceptor electronic coupling.

Note that in Eq. (3) the sign of V_{da} is still defined. However, Eqs. (5) and (6) are derived at the sacrifice of the sign of the matrix element. Fortunately, in many cases the sign of V_{da} can be neglected because the ET rate constant is

proportional to the coupling squared. If the sign is wanted, it can be obtained from an analysis of adiabatic wave functions [23].

To estimate the donor–bridge or bridge–acceptor coupling, V_{db} or V_{ba} , we employ the two-state model and related charges in the adiabatic states ψ_1 and ψ_3

$$|V_{db}| \approx \frac{(E_3 - E_1)}{2} (\sqrt{q_{d1}q_{b1}} + \sqrt{q_{d3}q_{b3}}) \quad (10)$$

$$|V_{ba}| \approx \frac{(E_3 - E_2)}{2} (\sqrt{q_{a2}q_{b2}} + \sqrt{q_{a3}q_{b3}})$$

Here we assume that the excess charge in the ground state ψ_1 is mostly localized on the donor while in the excited states ψ_2 and ψ_3 , it is localized on the acceptor and bridge sites, respectively. For a symmetric system, we have

$$|V_{db}| = |V_{ba}| = \frac{(E_3 - E_1)}{2} (\sqrt{q_{d1}q_{b1}} + \sqrt{q_{d3}q_{b3}}) \quad (11)$$

Turning back to the numerical example given above, we estimate the couplings using the ConS scheme. In this case, Eq. (4) may be employed instead of Eq. (6). Substituting adiabatic energies $E_1 = -0.029$, $E_2 = 0.010$, $E_3 = 1.019$, and charges on the donor $q_{d1} = 0.491$ and $q_{d2} = 0.500$ in the adiabatic states ψ_1 and ψ_2 , we obtain $|V_{da}| = |V_{da}(2st) + V_{da}(\text{cor})| \approx 0.0193 - 0.0091 = 0.0102$. The resulting coupling is very similar to the reference value of 0.010 (the negligible deviation is due to a rounding off error). This example shows that the correction term (Eq. (6)) can be of the same order of magnitude as a coupling found within the two-state model (Eq. (7)). In a like manner, using Eq. (5) and charges $q_{d1} = 0.491$, $q_{b1} = 0.018$, $q_{d3} = 0.009$ and $q_{b3} = 0.982$, we get $|V_{db}| = |V_{ba}| \approx 0.0985$ in good agreement with the exact value 0.1.

Expressions (6), (7), (9)–(11) can be directly employed in conjunction with any quantum mechanical treatment which provides atomic charges in the ground and excited electronic states. The two-state model, Eq. (7), can be reliably applied when in the ground state, the excess charges on the bridge site is small enough, $|q_{b1}| < 10^{-3}$.

The formula (6) derived for the three-state framework with a single bridge state can be generalized for several bridge states. In this case, instead of Eq. (2) we have

$$V_{da} = E_1 C_{d1} C_{d1} + E_2 C_{d2} C_{d2} + \sum_{j=1}^k C_{dj+2} C_{aj+2} E_{j+2},$$

where the sum over j accounts for k bridge states. Introducing an average energy \bar{E} , $\bar{E} = \frac{\sum_{j=1}^k C_{dj+2} C_{aj+2} E_{j+2}}{\sum_{j=1}^k C_{dj+2} C_{aj+2}}$, we obtain $V_{da} = E_1 C_{d1} C_{d1} + E_2 C_{d2} C_{d2} - \bar{E} (C_{d1} C_{d1} + C_{d2} C_{d2})$. Thus, the problem of k bridge states is reduced to the 3-state framework considered above. Accordingly, the donor–acceptor coupling in the multistate scheme is

$$|V_{da}| = \left| \frac{(E_2 - E_1)}{2} (\sqrt{q_{d1}q_{a1}} + \sqrt{q_{d2}q_{a2}}) + E_{\text{gap}} (\sqrt{q_{d1}q_{a1}} - \sqrt{q_{d2}q_{a2}}) \right| \quad (12)$$

where E_{gap} is an energy gap between the averaged bridge energy \bar{E} and the tunneling energy $(E_2 + E_1)/2$. As a good approximation to \bar{E} , the energy of adiabatic state ψ_i ($i > 2$) with the biggest value of $q_{di}q_{ai}$ can be used.

2.2.1. Limitations

As seen from Eqs. (6), (7), (9)–(11), the coupling depends on the value of $\sqrt{q_{di}q_{ai}}$. When the adiabatic charges are essentially localized on donor and acceptor, the coupling becomes sensitive to how the charges are determined. For instance, if for the ground state ($i = 1$) $q_{di} = 0.990$ and $q_{ai} = 0.010$, $\sqrt{q_{di}q_{ai}} = 0.099$. Using another procedure to derive the donor and acceptor charges one may obtain for the same system $q_{di} = 0.999$, $q_{ai} = 0.001$, and therefore, $\sqrt{q_{di}q_{ai}} = 0.032$. The corresponding couplings will differ by factor of ~ 3 . Our test calculations show that ConS scheme provides accurate results if the excess charge is not very strongly confined to the donor or acceptor site, $0.05 \leq |q_{di}| \leq 0.95$, $0.05 \leq |q_{ai}| \leq 0.95$ in the ground and CT states ($i = 1, 2$). However, the scheme may be of limited use a situation, when for instance in the state $d-b-a^+$ more than 95% of the hole charge is localized on the acceptor, $q_{a1} > 0.95$.

2.2.2. An illustrative application of the ConS scheme

Let us briefly consider application of the charge-on-site scheme to complex of π stacked nucleobases $G_1A_2G_3$. This system has been recently studied at the CASSCF level (see Ref. [24] for details). The adiabatic energies and charges given in Table 1 were taken from that study. As can be seen, the couplings derived within the ConS and GMH schemes are in good agreement both for two-state and three-state models. Thus, the ConS scheme not only provides reliable values for the couplings, but adequately accounts for the multistate effects as well.

It should be emphasized that ConS and GMH use different transformations of adiabatic states to diabatic states; therefore, identical or very similar couplings may be obtained only in some special cases, e.g., for symmetric $d-a$ systems, where both schemes are reduced to the adiabatic energy splitting method. Nevertheless, it seems to be instructive to use different schemes when estimating electronic couplings for large systems. A significant difference (by factor > 1.5) between the calculated values may indicate some important numerical or methodological inconsistencies, which will be difficult to recognize otherwise.

Note that both the GMH and ConS schemes are based on the orthogonal transformation of adiabatic states. Because the adiabatic states form an orthonormal basis set, the resulting diabatic states are orthogonal by construction. It means that no additional assumption about orthogonality of diabatic states is used and/or required. By contrast, within methods operating with nonorthogonal diabatic states of d and a , the calculated matrix element H_{da} should be corrected. Usually the overlap between donor and acceptor is small and Löwdin orthogonalization

Table 1
Electronic couplings of nucleobases in the complex $G_1A_2G_3$

State	Adiabatic properties				Couplings (eV)		
	E_i (eV)	Charges			ConS	GMH	
		G_1	A_2	G_3			
1	0.0	0.951	0.037	0.012	$ V_{da} $, 3st 2st	0.021 0.014	0.021 0.013
2	0.118	0.018	0.042	0.940	$ V_{db} $, 2st	0.063	0.049
3	0.345	0.037	0.907	0.057	$ V_{ba} $, 2st	0.052	0.052

Adiabatic energies and charges on the bases are calculated with CASSCF [24].

of φ_d and φ_a yields $V_{da} \approx H_{da} - \frac{1}{2}(H_{dd} + H_{aa})S_{da}$ (for details see e.g., Refs. [8] and [15]). Because diabatic states derived within ConS are orthogonal, $S_{da} = 0$, no correction of the coupling matrix element is needed.

3. Conclusions

The charge-on-site scheme has been introduced to estimate electronic couplings for thermal charge transfer in donor–bridge acceptor systems. The electronic coupling is explicitly expressed in terms of adiabatic energies and charges on the donor and acceptor sites. The method has been formulated for two- and multistate models. The scheme can be directly employed in conjunction with any quantum mechanical method which provides atomic charges in the ground and excited states.

For a π stacked complex $G_1A_2G_3$, we have compared electronic couplings derived using the ConS and GMH methods and found that the suggested scheme not only provides reliable values for the couplings, but adequately accounts for the multistate effects.

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