# Molecular Orbital Analysis in Evaluation of Electron-Transfer Matrix Element by Koopmans' Theory

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There are several approaches to evaluation of an electron-transfer (ET) matrix element. Among them, Koopmans' theory is a relatively simple one and can be used for large molecules. However, a limitation of this method is the application to some cases of a small donor−acceptor distance. In such cases, Koopmans' theory has been found to behave badly. The reasons of the failure are discussed in the present work. Investigation shows that the two orbitals included must be properly selected in evaluating the ET matrix element. It has been concluded that the sum of two relevant orbitals should be localized on the donor (acceptor), but the difference between them should be localized on the acceptor (donor). Different types of ET systems have been selected to show how to correctly employ Koopmans' theory to small donor−acceptor distance cases. According to our work, one can find what is the reason leading to the failure of Koopmans' theory, and it is suggested that such failures can be avoided by tracing the energy change of the frontier molecular orbitals against the donor−acceptor distance.

## Introduction

The electron-transfer (ET) matrix element $V_{DA}$, which represents the strength of interaction between charge-localized states $\eta_D$ and $\eta_A$, is a very important factor in ET.[1−4] A correct calculation of the value of $V_{DA}$ is crucial in evaluating the coupling strength between $\eta_D$ and $\eta_A$ and testing the validity of the theoretical model applied. A greatly underestimated value of $V_{DA}$ possibly leads to a misunderstanding of the energy splitting and of the reaction type, e.g., adiabatic or nonadiabatic processes. There are several theoretical methods for the calculation of $V_{DA}$, such as the variational treatment on the basis of the two-state model[5] (TM), the energy difference method based on Koopmans' theorem[6,7] (KT), and the energy difference method considering the nonadiabatic and adiabatic activated states.[8] In applying TM, two charge-localized states need to be calculated at the nuclear configuration of the transition state at first, so this method is difficult to apply to large molecules. In the KT approach, the value of $V_{DA}$ for the cation system is simply approximated as one-half of the splitting energy between the highest occupied molecular orbital (HOMO) and the next HOMO (abbreviated as HOMO-1) of the neutral molecule. On the other hand, $V_{DA}$ for the anion system is approximated as one-half of the energy difference between the lowest unoccupied molecular orbital (LUMO) and the next LUMO (hereafter abbreviated as LUMO+1) of the same neutral molecule. Because of the simplicity and cheapness in computation, KT has been widely applied to estimate $V_{DA}$ in organic molecular systems.[6,7,9−23] In the past, one of the authors studied self-exchange ET reaction between parallel neutral benzene and its cation radical.[22] The center-to-center distance dependency of $V_{DA}$ was calculated by both KT and TM as shown in Figure 1. It can be seen from Figure 1 that $V_{DA}$ values obtained by KT deviate from those obtained from the direct calculation by TM when the distance is less than about 0.4 nm. The deviation
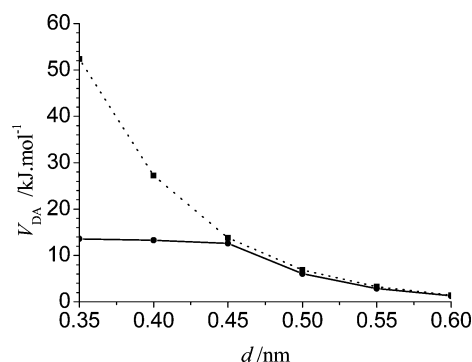


**Figure 1.** $V_{DA}$ vs distance between benzene and its cation. Dashed line, TM; solid line, KT.

increases with the decrease of the donor−acceptor distance. This behavior has not been paid much attention to, and what causes the failure of the KT method in the small-distance cases is unclear so far. It is the usual case that a realistic van der Waals system possesses a intermolecular distance of about ∼0.3−0.4 nm. So the bad behavior of Koopmans' theory in such a case will cause troubles.

In the present work, we focus on the orbital reordering and the molecular orbital (MO) analysis. In particular, we pay attention to the orbital pair that can be used to perform a $V_{DA}$ estimation according to KT. Through the deduction of the relationship between the KT and TM methods, an explanation on the failure of KT for $V_{DA}$ in some cases has been given. The new approach of KT for small donor−acceptor distance cases has been successfully applied to several types of ET reactions.

## Methodology

A well-known profile for the variation of the potential energy against the reaction coordinate is sketched in Figure 2 when the one-dimension approximation is adopted.[24] We use $\eta_D$ and $\eta_A$ to represent the two diabatic states, which refer to the

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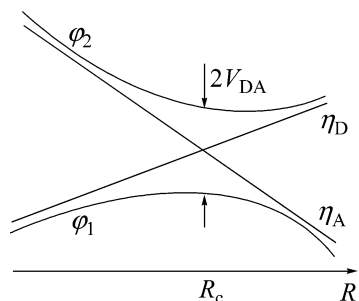
**Figure 2.** Two-state profile.

different charge-localized states in ET reactions. An important quantity in any ET theory is the "interaction energy", $H_{DA} = \langle \eta_D | \mathbf{H} | \eta_A \rangle$, where $\mathbf{H}$ is the electronic Hamiltonian (total Hamiltonian excluding the nuclear repulsion terms) of the system. ET involves an electronic transition from the diabatic state $\eta_D$ to the diabatic state $\eta_A$ at the crossing $R_c$ and is governed by the Franck–Condon principle.[25,26] Since the description of ET in double-well potentials requires the charge localizations of $\eta_D$ and $\eta_A$, a practical way to prepare these two states is to perform the induced self-consistent field (SCF) calculation by two charge-localized sets of MOs. $\eta_D$ and $\eta_A$ obtained in this way are sometimes called the quasidiabatic states.[5] If $H_{DA} \neq 0$, i.e., the diabatic states $\eta_D$ and $\eta_A$ do not diagonalize the electronic Hamiltonian $\mathbf{H}$, the degeneracy at the crossing of the diabatic energy surfaces (in one-dimension-case energy curves) will be effectively removed, and two adiabatic states $\varphi_1$ and $\varphi_2$ are formed. According to the variational principle, the secular equation can be written as

$$\begin{vmatrix} H_{DD} - E & H_{DA} - ES_{DA} \\ H_{AD} - ES_{AD} & H_{AA} - E \end{vmatrix} = 0 \quad (1)$$

where $S_{DA} = S_{AD} = \langle \eta_D | \eta_A \rangle$ and $E$ is the energy eigenvalue. Because $\mathbf{H}$ is hermitian, $H_{DA} = H_{AD}$. At the transition state of ET, we have $H_{DD} = H_{AA}$. Here $H_{DD}$ and $H_{AA}$ denote the expectation values of $\mathbf{H}$, i.e., $H_{DD} = \langle \eta_D | \mathbf{H} | \eta_D \rangle$ and $H_{AA} = \langle \eta_A | \mathbf{H} | \eta_A \rangle$. After solving eq 1, the eigenvalues and eigenvectors of $\mathbf{H}$ can be obtained as

$$E_1 = \frac{H_{DD} + H_{DA}}{1 + S_{DA}} \qquad E_2 = \frac{H_{DD} - H_{DA}}{1 - S_{DA}} \quad (2)$$

$$\varphi_1 = \frac{1}{(2 + 2S_{DA})^{1/2}} (\eta_D + \eta_A)$$

$$\varphi_2 = \frac{1}{(2 - 2S_{DA})^{1/2}} (\eta_D - \eta_A) \quad (3)$$

Hence, $V_{DA}$ is given by[5]

$$V_{DA} = (E_2 - E_1)/2 = \frac{H_{DA} - S_{DA}H_{DD}}{1 - S_{DA}^2} \quad (4)$$

As mentioned above, we call this the TM method. If $S_{DA}$ is negligibly small, we have

$$\varphi_1 = (\eta_D + \eta_A)/(2)^{1/2} \qquad \varphi_2 = (\eta_D - \eta_A)/(2)^{1/2} \quad (5)$$

and

$$\eta_D = (\varphi_1 + \varphi_2)/(2)^{1/2} \qquad \eta_A = (\varphi_1 - \varphi_2)/(2)^{1/2} \quad (6)$$

Equation 6 indicates that the sum of $\varphi_1$ and $\varphi_2$ and the difference

between them are both charge localized, and the localized electron or hole is just what will be transferred.

Let us make a simple analysis at the MO level and consider a simple case so as to find the relationship between the calculation methods of $V_{DA}$ mentioned above. For a neutral system with $2N$ electrons, the spin-restricted Hartree–Fock (RHF) calculation will give a set of canonical MOs, $\{\phi_i\}$. The Slater determinant wave function for the $2N$-electron system, which is the zero-order wave function, is as follows

$$\varphi(2N) = \frac{1}{((2N)!)^{1/2}} |\phi_1 \bar{\phi}_1 \cdots \phi_N \bar{\phi}_N| \quad (7)$$

where $\phi_i$ and $\bar{\phi}_i$, respectively, refer to the $\alpha$ and $\beta$ spin orbitals. We denote HOMO as $\phi_N$ and LUMO as $\phi_{N+1}$. Expanding $\phi_N$ and $\phi_{N+1}$ to the basis sets of atomic orbitals (AO), we have

$$\phi_N = \sum_{i \in D} c_{N,i} \chi_i^D + \sum_{j \in A} c_{N,j} \chi_j^A \quad (8)$$

$$\phi_{N+1} = \sum_{i \in D} c_{N+1,i} \chi_i^D + \sum_{j \in A} c_{N+1,j} \chi_j^A \quad (9)$$

Here we consider a donor–acceptor system and decompose the basis set of AO into two subsets, $\{\chi_i^D\}$ and $\{\chi_i^A\}$. The former is contributed from the atoms in the donor moiety and the latter from the acceptor moiety.

We at first discuss the hole transfer in a donor–acceptor system. Among the occupied MOs, we can usually find a MO, $\phi_X$, which is generally HOMO-1, as

$$\phi_X = \sum_{i \in D} c_{X,i} \chi_i^D + \sum_{j \in A} c_{X,j} \chi_j^A \quad (10)$$

This $\phi_X$ needs to satisfy the condition that the combination of $\phi_X$ and $\phi_N$ (or HOMO) can produce the charge-localized MO, i.e.

$$\Phi_D = \frac{1}{(2)^{1/2}} (\phi_X + \phi_N) = \frac{2}{(2)^{1/2}} \sum_{i \in D} c_{N,i} \chi_i^D \quad (11)$$

$$\Phi_A = \frac{1}{(2)^{1/2}} (\phi_X - \phi_N) = \frac{2}{(2)^{1/2}} \sum_{j \in A} c_{N,j} \chi_j^A \quad (12)$$

Like $\phi_N$ and $\phi_X$, $\Phi_D$ and $\Phi_A$ remain orthonormalized. Moreover, we consider a system with $2N - 1$ electrons and let MOs remain fixed when one electron is removed; the determinants with the electron being removed from $\phi_N$ and $\phi_X$ can be respectively expressed as

$$\varphi_1(2N - 1) = \frac{1}{((2N-1)!)^{1/2}} |\phi_1 \bar{\phi}_1 \cdots \phi_X \bar{\phi}_X \cdots \phi_N| \quad (13)$$

$$\varphi_2(2N - 1) = \frac{1}{((2N-1)!)^{1/2}} |\phi_1 \bar{\phi}_1 \cdots \phi_X \cdots \phi_N \bar{\phi}_N| \quad (14)$$

Using $\Phi_D$ and $\Phi_A$ instead of $\phi_N$ and $\phi_X$ in eqs 13 and 14 will produce the charge-localized Slater determinant wave functions as

$$\eta_D(2N - 1) = \frac{1}{((2N-1)!)^{1/2}} |\phi_1 \bar{\phi}_1 \cdots \Phi_D \cdots \Phi_A \bar{\Phi}_A| \quad (15)$$

$$\eta_A(2N - 1) = \frac{1}{((2N-1)!)^{1/2}} |\phi_1 \bar{\phi}_1 \cdots \Phi_D \bar{\Phi}_D \cdots \Phi_A| \quad (16)$$

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It can be tested that all the determinants, $\varphi_1(2N-1)$, $\varphi_2(2N-1)$, $\eta_D(2N-1)$, and $\eta_A(2N-1)$, given above satisfy the mutual transformations as given in eqs 5 and 6.

Up to this stage, we can see that $V_{DA}$ for a hole transfer may find its values through different ways as follows:

(i) By construction of the charge-localized Slater determinants $\eta_D(2N-1)$ and $\eta_A(2N-1)$, the solution of the secular equation as shown in eq 1 can give the value of $V_{DA}$ according to eq 4. Two charge-localized sets of MOs should be adopted to induce the calculation at the SCF stage. To guarantee the equality of $H_{DD}$ and $H_{AA}$, the nuclear configuration of the transition state of ET needs to be determined in advance, and then the induced SCF calculation follows. In our present work, we perform such a calculation by means of the subroutines coded in HONDO99.[27] The calculation details are given in the following sections.

(ii) By tracing the two delocalized MOs, $\phi_N$ and $\phi_X$, $V_{DA}$ can be estimated according to Koopmans' theory instead, i.e.

$$V_{DA} = (I_X - I_N)/2 = (\epsilon_N - \epsilon_X)/2 \tag{17}$$

where $I_i$ and $\epsilon_i$ ($i = X$ and $N$) are the ionization potential and the eigenvalue of the canonical MO $\phi_i$, respectively. When $\phi_X$ is HOMO-1, $V_{DA}$ in such cases is given by

$$V_{DA} = (\epsilon_{HOMO} - \epsilon_{HOMO-1})/2 \tag{18}$$

Equation 18 is just the case in other literature. However, when HOMO-1 does not satisfy the request as shown in eqs 10−12, eq 18 will lead to an incorrect estimation of $V_{DA}$, just like what we have mentioned in the section of introduction.

When we apply KT for the estimation of $V_{DA}$, the orbitals of the cation system are assumed to be the same as those of the neutral system; in other words, we take them "frozen". This treatment neglects the fact that the orbitals in the cation case will be different from those of the neutral system, so the energy of the cation will tend to be higher than it "should" be, giving a too-large ionization potential.[28]

(iii) On the other hand, if we can obtain the expected values of the Hamiltonian for $\varphi_1(2N-1)$ and $\varphi_2(2N-1)$, $V_{DA}$ can also be evaluated by using the energy difference, i.e.

$$V_{DA} = (\langle \varphi_2 | \mathbf{H} | \varphi_2 \rangle - \langle \varphi_1 | \mathbf{H} | \varphi_1 \rangle)/2 \tag{19}$$

but the key step for this method is to induce the HF calculation of the open-shell system ($2N-1$ electrons) properly by using the MO set $\{\phi_i\}$ of the closed-shell system ($2N$ electrons). We call this approach the $\Delta$HF method. This method will improve the result when compared with the KT approach, because this method includes electronic relaxation effects but ignores in part the electron correlations. In our present work, we use the original MO order of the neutral system as an initial guess to calculate the energy of $\varphi_1(2N-1)$. Moreover, in calculating the energy of state $\varphi_2(2N-1)$, the initial guess is obtained by exchanging the order of $\phi_N$ and $\phi_X$. UHF calculations have been employed in this work.

Parallel discussions can be made for the transfer of an extra electron in an anion system. In this case, we will find an MO, $\phi_V$, among the virtual orbitals of the neutral system with $2N$ electrons. Similar to $\phi_X$, the selected $\phi_V$ should be such that the combination of $\phi_{N+1}$(or LUMO) and $\phi_V$ yields the charge-localized MOs. Koopmans theory approach in this case is as follows

$$V_{DA} = (EA_{N+1} - EA_V)/2 = (\epsilon_V - \epsilon_{N+1})/2 \tag{20}$$

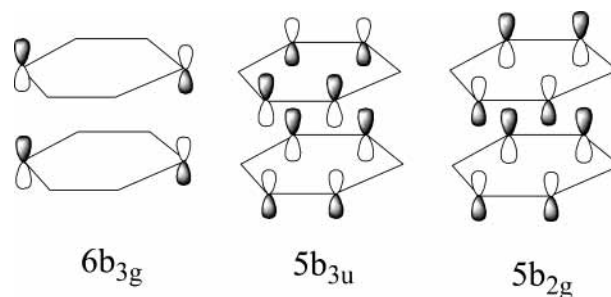where $EA_i$ ($i = V$ and $N+1$) is the electron affinity of the



**Figure 3.** Three HOMOs of $(C_6H_6)_2$ with $D_{2h}$ symmetry. The principal axis links the centers of the two benzene rings.

virtual orbital $\phi_i$. When $\phi_V$ is LUMO+1, as is the usual case, $V_{DA}$ is given by

$$V_{DA} = (\epsilon_{LUMO+1} - \epsilon_{LUMO})/2 \tag{21}$$

$\Delta$HF method for the extra ET in an anion system takes the analogous technique like the hole-transfer case but exchanges the order for $\phi_{N+1}$ and $\phi_V$ to induce the UHF calculation of the excited state $\varphi_2(N+1)$. One can see from the following section that such a method works well for the estimation of $V_{DA}$.

As mentioned above, all the calculations of $V_{DA}$ by different methods should be carried out at the nuclear configuration of the transition state of ET. For a polyatomic system, important information may be obtained from the double-well potential within the frame of the transition-state theory, but the determination of the accurate reaction pathway is a rather difficult task.[29] Therefore the concerted linear reaction coordinate $R$ is usually adopted,[5] and the nuclear rearrangement along the $R$ can be expressed as

$$Q_i = (1 - R)Q_i^D + RQ_i^A \tag{22}$$

where $Q_i$ refers to the $i$th internal coordinate (bond length, bond angle, or dihedral angle) and D and A refer to the reactant state in which the hole or the extra electron is localized on the donor moiety and the product in which the charge is localized on the acceptor, respectively. For a self-exchange reaction, the transition state is at the configuration corresponding with $R$ equal to 0.5. Although there is a problem of how to select the $3N-6$ independent internal coordinate from the $3N$ coordinates, our experiences showed that the selection only applies a trivial influence.

## Results and Discussions

**1. Application of KT to the Cation Case.** In the case of the cation system, $V_{DA}$ is usually estimated by the energy difference between HOMO and HOMO-1. In the previous work by one of the authors,[22] the influence of distance ($d$) between benzene and the benzene cation radical on this quantity was studied. It has been found that the values of $V_{DA}$ calculated by TM and by KT match very well when $d \geq 0.45$ nm. When $d \leq 0.40$ nm, however, the KT approach works badly. No answer has been found for this inconsistency. In this work, we use the same geometric parameters and basis set, DZP (Dunning's (9s,5p)/ (3s,2p) basis set with polarization functions on all atoms), to repeat the calculation for that ET system. After calculation for the neutral system $(C_6H_6)_2$ at the RHF/DZP level with the nuclear configuration of transition state ($D_{2h}$ symmetry, $R = 0.5$ in eq 22), the MO coefficients are obtained and the three HOMOs are schematically shown in Figure 3. The energy changes for these MOs against the donor−acceptor distance are shown in Figure 4. From the MOs shown in Figure 3, we can
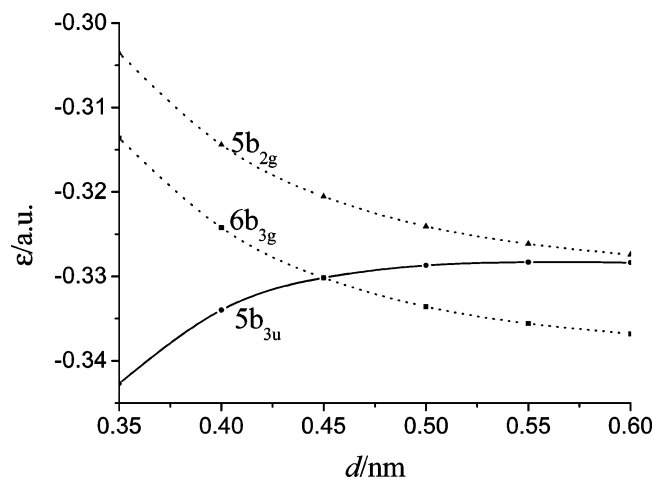
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**Figure 4.** Energy change vs the donor−acceptor distance.

**TABLE 1: $V_{DA}$ at Different Distances between Benzene and Its Cation Radical**

| $d$/ nm | $V_{DA}$ (TM)/ kJ·mol$^{-1}$ [a] | $V_{DA}$ (KT)/ kJ·mol$^{-1}$ [b] | $V_{DA}$ ($\Delta$HF)/ kJ·mol$^{-1}$· |
|------|------|------|------|
| 0.35 | 52.38 | 13.61 (49.96) | 55.56 |
| 0.40 | 27.22 | 13.27 (25.64) | 29.08 |
| 0.45 | 13.38 | 12.59 | 14.94 |
| 0.50 | 6.86 | 6.08 | 7.50 |
| 0.55 | 3.28 | 2.86 | 3.60 |
| 0.60 | 1.46 | 1.27 | 1.61 |

[a] From ref 22. [b] By eq 18. Data in parentheses are obtained by using $V_{DA} = (\epsilon_{HOMO} - \epsilon_{HOMO-2})/2$.

see that the sum of $5b_{3u}$ and $5b_{2g}$ localizes on the bottom benzene ring but the difference between them localizes on the upper one. The eigenvalues of these MOs (see Figure 4) change with the donor−acceptor distance dramatically. In the range of $d \geq 0.45$ nm, $5b_{2g}$ is HOMO and $5b_{3u}$ is HOMO-1. Within this range, eq 18 gives a correct estimation for $V_{DA}$ and the value of $V_{DA}$ (KT) agrees well with $V_{DA}$ (TM) obtained by eq 4. However, when $d < 0.45$ nm, $5b_{3u}$ and $6b_{3g}$ change the order and $5b_{3u}$ becomes HOMO-2. In this case, we need to trace $5b_{3u}$ to perform the estimation of $V_{DA}$, in other words, $V_{DA}(KT) = (\epsilon_{HOMO} - \epsilon_{HOMO-2})/2$. If we ignore the order change and still use HOMO and HOMO-1 to perform the estimation, an unreasonable value would be obtained since the combination of $5b_{2g}$ and $6b_{3g}$ does not yield the charge-localized orbitals. This is the exact reason $V_{DA}(KT)$ behaves badly. When we use HOMO-2 instead of HOMO-1, the values of $V_{DA}$ obtained by TM (eq 4) and by KT (eq 17) coincide very well (see Table 1). Hence we should first find the two MOs and then use the correct formula to calculate $V_{DA}$ in the framework of KT.

As mentioned above, KT ignores in part the electronic relaxation effects. So we calculate directly the energies of states $\varphi_1(2N - 1)$ and $\varphi_2(2N - 1)$ with the UHF method, using the different initial guesses. We at first calculate the neutral complex $(C_6H_6)_2$ with the RHF method, and then the cation system $(C_6H_6)_2^+$ state is calculated with UHF by using the MOs of the neutral $(C_6H_6)_2$ as initial guesses, with an electron being removed from $5b_{2g}$. Finally the cation system $(C_6H_6)_2^+$ state is calculated with UHF by changing the order of $5b_{2g}$ and $5b_{3u}$. In the range of $d \geq 0.45$ nm, the initial guess is given by exchanging HOMO and HOMO-1. When $d < 0.45$ nm, the initial guess is given by exchanging HOMO and HOMO-2. The value of $V_{DA}$ is obtained from the total energy difference of these two states (see eq 19 and Table 1). If the values of $V_{DA}$ obtained by TM are taken as accurate, the error percentage of

**TABLE 2: Energies of Different States of $(C_6H_6)_2^+$ at Different Levels**

|  | UHF | CIS(16,17)[a] | CAS(8,7)[b] |
|------|------|------|------|
| $E_0(D_0)$ /au | −461.18444 | −461.15759 | −461.23629 |
| $E_1$ (D$_1$)/au | −461.17417 | −461.14756[c] | −461.22879[c] |
| $E_2$ (D$_2$)/au | −461.16229 | −461.13808[d] | −461.21722[d] |
| $E_1-E_0$/kJ·mol$^{-1}$ | 26.96 | 26.33 | 19.69 |
| $E_2-E_0$/kJ·mol$^{-1}$ | 58.15 | 51.22 | 50.06 |

[a] Sixteen active orbitals and 17 active electrons are used for CIS. [b] Eight active orbitals and 7 active electrons are used in CASSCF. [c] The reference configuration is that HOMO-1 is singly occupied. [d] The reference configuration is that HOMO-2 is singly occupied.
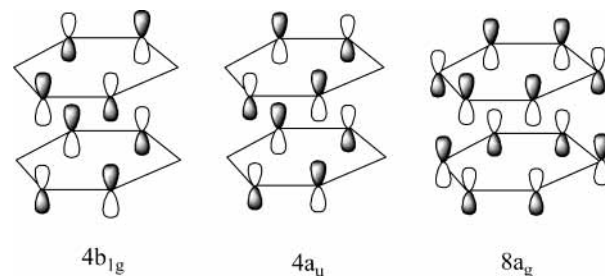


**Figure 5.** Three LUMOs of $(C_6H_6)_2$.

$V_{DA}$ by KT is less than 14%, and the error percentage of $V_{DA}$ by $\Delta$HF is less than 12%.

To make comparison with higher levels of calculation, the energies of ground state, the first excited state, and the second excited state of the cation system $(C_6H_6)_2^+$, in which the distance between donor and acceptor is set 0.40 nm, are calculated by using the CIS/DZP method and CASSCF/DZP at the transition state ($R = 0.5$). Sixteen active orbitals and 17 active electrons are used for CIS calculations, while 8 active orbitals and 7 active electrons are used in CASSCF calculations. Constraint of $D_{2h}$ symmetry is applied. The results are listed in Table 2. From the calculated results, it can be easily seen that if we still use half of the energy gap between the first excited state and the ground state to evaluate $V_{DA}$,[23] the values of $V_{DA}$, 13.48 kJ·mol$^{-1}$ by UHF, 13.16 kJ·mol$^{-1}$ by CIS, and 9.85 kJ·mol$^{-1}$ by CASSCF, will be much less than those obtained by TM, 27.22 kJ·mol$^{-1}$. However, if we use that of the second excited state and the ground state, which corresponds to the one-electron transition from HOMO-2 to HOMO (see the footnotes of Table 2), the value of $V_{DA}$ will be found consistent with that obtained by TM.

**2. Application of KT to the Anion Case.** In the case of the anion radical, $V_{DA}$ is estimated in general to be one-half of the energy difference between LUMO and LUMO+1. We take the benzene and its anion radical as the second example. This system was studied early.[20] When the distance between two benzene rings is less than 0.49 nm, KT does not work well. In this paper, the symmetry constraints of $D_{6h}$ and $D_{2h}$ are used in optimizing the geometries of neutral $C_6H_6$ and anion radical $(C_6H_6)^-$, respectively, at the HF/DZP level. At the nuclear configuration of the transition state ($D_{2h}$, $R = 0.5$ in eq 22), calculation for the neutral system $(C_6H_6)_2$ at the RHF/DZP level gives the frontier virtual orbitals as shown in Figure 5. One can see that the sum of $4b_{1g}$ and $4a_u$ localizes on the bottom benzene ring, but the difference between them localizes on the upper one. The eigenvalues of these MOs (see Figure 6) change with the donor−acceptor distances. In the range of $d \geq 0.49$ nm, $4b_{1g}$ is the LUMO and $4a_u$ is LUMO+1. Within this range, eq 21 gives a correct estimation for $V_{DA}$. However, when $d < 0.49$ nm, $4a_u$ and $8a_g$ change the order and $4a_u$ becomes LUMO+2. In this case, we need to trace $4a_u$ to perform the estimation of $V_{DA}$,
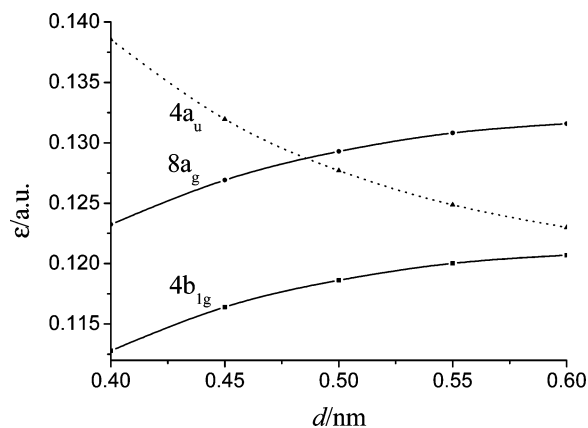
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**Figure 6.** Orbital energies of the three LUMOs vs the donor–acceptor distance.

**TABLE 3: $V_{DA}$ at Different Distances between Benzene and Its Anion Radical**

| $d$/ nm | $V_{DA}$ (TM)/ kJ·mol$^{-1}$ | $V_{DA}$ (KT)/ kJ·mol$^{-1a}$ | $V_{DA}$ ($\Delta$HF)/ kJ·mol$^{-1}$ |
|---|---|---|---|
| 0.40 | 29.76 | 13.73 (33.82) | 32.51 |
| 0.45 | 17.15 | 13.80 (20.41) | 19.17 |
| 0.50 | 9.66 | 11.91 | 10.98 |
| 0.55 | 5.06 | 6.35 | 5.81 |
| 0.60 | 2.52 | 3.02 | 2.75 |

$^a$ By eq 21. Data in parentheses are obtained by $V_{DA} = (\epsilon_{\text{LUMO}+2} - \epsilon_{\text{LUMO}})/2$.

i.e., $V_{DA}(\text{KT}) = (\epsilon_{\text{LUMO}+2} - \epsilon_{\text{LUMO}})/2$. If we ignore the order change and still use LUMO and LUMO+1 to perform the estimation, an unreasonable value would be obtained because the combination of $4b_{1g}$ and $8a_g$ does not yield the charge-localized orbitals. When we use LUMO+2 instead of LU-MO+1, the values of $V_{DA}$ obtained by TM (eq 4) and by KT (eq 20) coincide very well (see Table 3). So we should also first find the two MOs and then use the correct formula to calculate $V_{DA}$ in the framework of KT. The $\Delta$HF method is also applied to this ET system. We first calculate the neutral complex $(C_6H_6)_2$ with the RHF method, and then the anion system $(C_6H_6)_2^-$ state is calculated with UHF by using the MOs obtained from the RHF calculation of the neutral system as initial guess, with the extra electron filling in $4b_{1g}$. Finally the anion system $(C_6H_6)_2^-$ state is calculated with UHF by using the initial-guess MOs with changing the order for $4b_{1g}$ and $4a_u$, with the extra electron filling in $4a_u$. This means that $d > 0.49$ nm, the initial guess is given by exchanging LUMO and LUMO+1. When $d < 0.49$ nm, the initial guess is given by exchanging LUMO and LUMO+2. The value of $V_{DA}$ is obtained from the total energy difference of these two states (see eq 19 and Table 3).

**3. ET between the Neutral Radical and Its Anion.** Phenol is the side chain of tyrosine. Considering the protonation and the deprotonation of the peptides in the solvent environment and the redox processes, phenol species can present in different forms: the neutral molecule, the radical, and the ion. Before ET, the proton attached to the O atom may be removed.[30] We do not intend to give detailed discussion on the mechanisms of the deprotonation but only take the dimer system as a model molecule to verify the validity of our approach to evaluation of $V_{DA}$. We at first optimize the geometries of isolated donor and acceptor at UHF/6-31G level. Both of them have plane configuration. Then we put the donor and acceptor parallel at a different distance and optimize the structure of the electron-localized state at the same level. To use KT to evaluate the
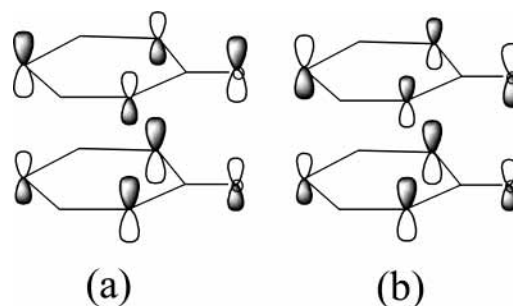


**Figure 7.** The LUMOs of $(C_6H_5O\cdot)_2$. (a) LUMO; (b) LUMO+1.

**TABLE 4: $V_{DA}$ at Different Distances between the Dehydro-Phenol Radical and Its Anion**

| $d$/ nm | $V_{DA}$ (TM)/ kJ·mol$^{-1}$ | $V_{DA}$ (KT)/ kJ·mol$^{-1a}$ | $V_{DA}$ ($\Delta$HF)/ kJ·mol$^{-1}$ |
|---|---|---|---|
| 0.35 | 37.50 | 38.51 | 34.68 |
| 0.40 | 18.02 | 19.36 | 17.05 |
| 0.45 | 8.97 | 9.82 | 8.60 |
| 0.50 | 3.50 | 3.86 | 3.40 |
| 0.55 | 1.14 | 1.25 | 1.12 |
| 0.60 | 0.31 | 0.34 | 0.24 |

$V_{DA}$ of this ET system, the neutral dimer system should be calculated by using the UHF method with different spin multiplicities based on the configuration of transition state. When the distance between the donor and the acceptor is 0.40 nm, the energies of triplet and singlet states are $-609.7253$ and $-609.5426$ au, respectively. Obviously, the total energy of the triplet state is much lower than that of the singlet state, so the triplet state is applied to KT. To make the triplet state of the neutral system become the doublet state of the anion system, a $\beta$ electron must be added. So the energies of $\beta$ MOs should be used to evaluate $V_{DA}$. The beta MOs are schematically shown in Figure 7. From the UHF calculations, we have found that the sum of the two orbitals is localized on one phenol ring and the difference between them is localized on the other one. From the analysis of the MOs, we have concluded that $V_{DA}$ in this case should be estimated by the energy difference between the two LUMOs with $\beta$ spin. The calculations show that the order of the three LUMOs does not change with the distances changing from 0.60 to 0.35 nm. The values of $V_{DA}$ in this anion system are also calculated by using the TM, KT, and $\Delta$HF methods, and the results are collected in Table 4.

**4. Application of KT to the Cross Reaction.** All of the above examples are self-exchange ET. Now we consider a cross reaction and take the cation system of benzene–chlorobenzene as a example, i.e.

$$C_6H_5Cl^+ + C_6H_6 \rightarrow C_6H_5Cl + C_6H_6^+$$
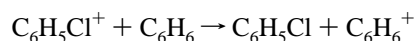
We at first optimize the geometries of isolated donors and acceptors at the HF/6-31G level. All of the species have planar configurations. Then we put the donor and the acceptor parallel at different distances and optimize the structure of the charge-localized state at the same level. After geometry optimization, the donor and acceptor are almost but not exactly parallel to each other. Unlike the self-exchange ET, the position of the transition state is no longer located at $R_c = 0.5$. Therefore, we need at first to determine the transition-state configuration. We construct the double-well potential and find the crossing point for this purpose. The double-well potential and crossing point (transition state) have been obtained by using the linear reaction coordinates approach (eq 22). The calculations show that $R_c$ is about 0.24. At the nuclear configuration of transition state,
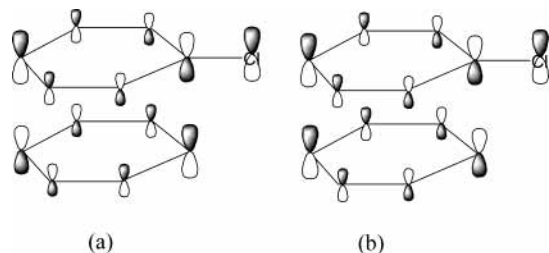
**Figure 8.** Two relevant occupied MOs of the $C_6H_6 \cdots C_6H_5Cl$ system. (a) HOMO-1 ($d \geq 0.45$ nm) and HOMO-2 ($d < 0.45$ nm); (b) HOMO.

**TABLE 5. $V_{DA}$ at Different Distances between Chlorobenzene and Benzene[a]**

| $d$/ nm | $V_{DA}$ (KT)/ kJ·mol$^{-1}$ [b] | $V_{DA}$ (TM)/ kJ·mol$^{-1}$ |
|---|---|---|
| 0.40 | 15.61 (19.94) | 21.00 |
| 0.45 | 9.33 | 9.45 |
| 0.50 | 3.79 | 3.43 |
| 0.55 | 2.23 | 1.08 |

[a] Calculations of $V_{DA}$ are performed at $R_c = 0.24$ (see eq 22). [b] By eq 18. Data in parentheses are obtained by using $V_{DA} = (\epsilon_{HOMO} - \epsilon_{HOMO-2})/2$.

calculation for the neutral system at the RHF/6-31G level gives the frontier orbitals as shown in Figure 8. It can be easily seen that the sum of parts a and b of Figure 8 localizes on chlorobenzene but the difference of them localizes on benzene. So we should use these two MOs to estimate the ET matrix element. The calculations show that the orbital shown in Figure 8b is always a HOMO. The one shown in Figure 8a is a HOMO-1 in the case of large donor—acceptor separation, but it becomes HOMO-2 when the distance is smaller than 0.45 nm. We have failed in the calculation of $V_{DA}$ with $\Delta$HF method to this system because the convergence problem fails when we change the order of MOs as the initial guess. The values of $V_{DA}$ in this system are calculated by using TM and KT methods, and the results are collected in Table 5.
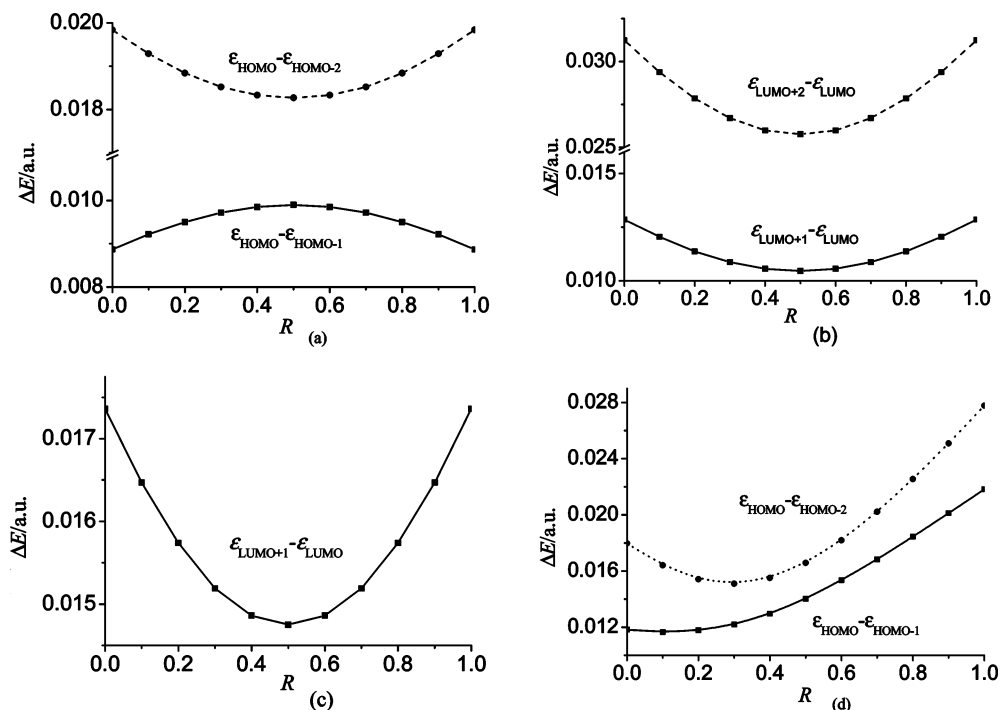
In addition, we test some other systems, for example, benzene—pyrazine and benzene—pyridine. However, we have failed in the application of KT to these systems. MO analysis shows that both HOMOs and LUMOs for those systems are localized. It seems that there are some limitations for the application of KT. We feel that we can safely apply KT to those systems for which the corresponding MOs satisfy eqs 12 and 13.

**5. Location of the ET Transition State by KT.** The geometry of the transition state of ET can be found along the linear reaction coordinates $R$ by searching for the minimal energy gap between HOMO and HOMO-1 for the cation system or that between LUMO+1 and LUMO for the anion system.[21,22] From our present work, we have pointed out that the energy gap should be calculated by using proper MOs. Let us take the distance of all the examples of the ET systems being 0.40 nm. As mentioned above, the energy difference between LUMO+1 and LUMO for anions and that between HOMO and HOMO-1 for cations is no longer valid for the evaluation of $V_{DA}$. In such a case, does the method of minimal energy gap keep useful in searching for the nuclear configuration of transition state along the one-dimensional reaction coordinate $R$? To answer this question, we have calculated the energy differences between relevant MO pairs at the same level mentioned above for all four examples. The energy differences are shown in Figure 9. It can be seen from Figure 9a that the energy gap (solid line), which represents the energy difference between HOMO and HOMO-1, is maximal at the geometry of the transition state, $R = 0.5$. If the solid line is still used to search for the transition state by finding the minimal energy gap, we will fail. However, if the dashed line, which represents the energy gap between HOMO and HOMO-2, is used, the transition state will be found at $R = 0.5$. As for benzene and its anion, it can be seen from Figure 9b that both approaches give proper transition states. However, the value of $V_{DA}$ obtained by the energy gap between the LUMO and LUMO+1 way is false. In the case of the dehydro-phenol radical and its anion system, both approaches



**Figure 9.** The energy difference between the two MOs along the reaction coordinate $R$ for (a) benzene and its cation radical, (b) benzene and its anion radical, (c) dehydro-phenol radical and its anion, and (d) chlorobenzene and benzene.

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give the same results for the systems as shown in Figure 9c. The calculations for this system show that the energy sequence keeps unchanged when the distance between donor and acceptor change. In the case of chlorobenzene and benzene, it can be seen from Figure 9d that both curves have a minimal energy gap. The dashed line which represents the energy gap between HOMO and HOMO-2 reaches the minimum at $R = \sim0.28$. This value does not deviate from that by double-well potential ($R_c = \sim0.24$) severely. However, the solid line which represents the energy gap between HOMO and HOMO-1 reaches the minimum at $R = \sim0.10$. This value severely deviates from that by double-well potential construction. These reflect the failure of KT in the small donor−acceptor distance. The above results prove further the validity of the energy gap method for the transition-state location of ET along $R$, but the included MOs should be carefully selected. From the above discussion, we need to take cautions in applying KT to the evaluation of $V_{DA}$. An elementary criterion is that the two MOs obtained in the neutral system are in the range of frontier orbitals. The sum of them localizes on the donor (or acceptor), and the difference between them localizes on the acceptor (or donor), and one of them is the HOMO for the cation or the LUMO for the anion. In this way, we can find the transition state by searching for the minimal energy gap. Moreover, we can evaluate $V_{DA}$ of the system, which is just one-half of the minimal energy gap.

## Conclusions

In the present article, the method of evaluating $V_{DA}$ through KT has been expanded. According to KT, the energies of the occupied orbitals of an $N$-electron system provide the ionization potentials in the frozen orbital limit (i.e., not allowing final-state relaxation of the ions). This approach is also applicable to cases of electron affinity, in which the orbital energies of the unoccupied orbitals give the values of electron affinity in the same frozen orbital limit. It is known that KT ignores the electronic relaxation effects and part of electron correlation effects. Fortunately, the two effects often oppose to each other.[28] However, when KT is applied to evaluate the $V_{DA}$, the orbitals $\phi_X$ for the cation system and $\phi_V$ for the anion system should be properly chosen. The relationship between TM and KT has been deduced in the present work. According to this relationship, the two MOs must be selected carefully in evaluating $V_{DA}$ within the KT framework. It has been concluded that if the sum of the two frontier orbitals localizes on one part (donor/acceptor) and the difference of them localizes on the other part (acceptor/donor) of the system, one-half of the energy difference of the two orbitals can thus been used to evaluate the $V_{DA}$ of the system. Four different types of ET have been chosen and investigated to prove this conclusion. From the MO analysis for different cases, we find KT can be employed without difficulty but the choice of the two involved MOs needs to be paid particular attention to, depending on the case and the donor−acceptor distance. A feasible criterion is that we find a MO below the HOMO for the cation system so that the sum of this orbital and the HOMO is localized on the donor (or acceptor) but the difference of them is localized on the acceptor (or donor). On the other hand, in the anion case, we need to find such a MO near but higher than the LUMO in energy. The choice should meet the need of the localization feature, like the cation case. Calculation and MO analysis show that the present treatment can be generalized to some simple unsymmetrical ET systems. However, for the more complicated

unsymmetrical system, it is obviously difficult to give a judgment on whether the two concerned MOs can give the desired localization or not. On the other hand, our experience tells us that KT works well as usual in the case of long-distance ET. Therefore, we can trace the orbital energy change against the donor−acceptor distance and then obtain the estimation of $V_{DA}$ for the case of short donor−acceptor separation of the large ET system, if needed.

In addition, we have used the $\Delta$HF method to calculate directly the energies of two delocalized states by using different initial guesses. The value of $V_{DA}$ is one-half of the energy difference between the two delocalized states. In the past, the value of $V_{DA}$ was approximated as one-half of the energy difference between the ground and the first excited state of the ionic system.[23] However, the calculations in the present work show that this is not always the case. For example, the value of $V_{DA}$ for the system consisting of benzene and its cation system should be calculated using the splitting energy between the ground state and the second excited state when $d < 0.40$ nm.

All the calculations were carried out by using the HONDO99 package.[27]

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