uncertainty) while for the 1.0 m solutions the shift varies with the cation, and the $Me_4Gu^+$ and $Na^+$ salt shifts differ by 0.18 to 0.19 ppm with the acid having an intermediate value as would be expected from the activity coefficient data. The shift for the sodium salt with concentration is less than the experimental uncertainty. Thus, although the fluorine chemical shifts are small, as was anticipated, they are, nevertheless, greater than the experimental error and are in the expected order.

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# Intramolecular Electron Delocalization: A Four-Site Model

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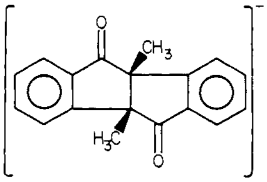
**Abstract:** The question of electron localization in isolated molecules and mixed-valence vs. averaged-valence structure is examined both from purely electronic and from vibronic viewpoints. Generally, a four-site model, in which two sites encompass a localization region in the molecule, is useful; the variation of the distance between the two sites in each region provides the vibronic coupling to localize the electrons. In a simple Hückel picture, we derive a closed-form perturbation-theoretic criterion for the stability of the localized (distorted) geometry; it is favored except for excessively polar structures. Adding the elastic energy of the framework increases the stability of the delocalized (averaged-valence or undistorted) geometry relative to the localized one. We present a diabatic coordinate curve-crossing analysis of the intramolecular electron-transfer problem, which permits straightforward classification of mixed-valent states and transfer processes. The vibronic picture leading to localization is quite similar to that employed in the pseudo-Jahn-Teller effect.

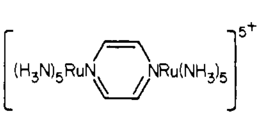
## I. Introduction

The area of mixed-valence chemistry has burgeoned following the early reviews by Robin and Day[1] and Hush.[2] The experimental work of Harriman and Maki,[3] Schroeder and Mazur,[4] and in particular Taube and his students[5-10] has established clearly the existence for isolated molecules of the Robin-Day classifications I (localized valence), III (averaged, delocalized valence), and II (partially delocalized). Although experimental criteria for localization can be defined on any given time scale by the appropriate measurement (electronic spectroscopy for times $\sim 10^{-15}$ s, NMR for $\sim 10^{-5}$ s, etc.),[11] the theoretical situation has been considerably cloudier. A number of conditions for delocalization have been proposed,[12-15] most of which are based on the two-site limit of ordinary narrow-band polaron theory, and involve the competition between kinetic-energy lowering via delocalization and potential-energy lowering via localized bond distortion. While this is certainly entirely satisfactory for the two-site molecular crystal for which it was first developed,[16] its application to molecules seems to rest on dicier foundations.

In intramolecular electron-transfer systems such as the diketone **1** studied by Schroeder and Mazur[4] or the Creutz-Taube[5] ion **2**, there is substantial difficulty in establishing precisely the orbital composition of the electron localization site (the Ru-N bonding region in **2** and the C=O chromophore in **1** seem reasonable choices, but they are not, in any real sense, localized electronic states). While considerable formal work on localized electronic states exists,[17] the problem is certainly not uniquely solved, and



**1**



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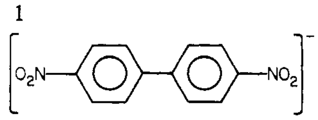

**3**

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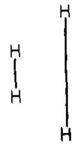

**Figure 1.** $H_2$–$H_2^+$—an example of the molecular crystal model.

therefore the definition of "regions" at "sites" between which intramolecular electron transfer can proceed is not completely clear. Even more important, however, is that these sites will obviously, in the preponderance of cases, have an internal vibrational dynamics and electronic structure of their own. For example, in **1** the C=O stretch vibration will modify the internal electronic structure and provide better or reduced overlap with the ring moiety, while in **2** the displacement along the symmetric Ru–N stretch will effect the overlap with the bridging pyrazine. Thus, for systems whose transfer is dominated by either exchange or chemical mechanisms, the molecular crystal model itself appears inadequate. The transfer occurs between regions which have an internal dynamics of their own, and that internal dynamics is important in determining both electron-transfer rates and extent of localization/delocalization (Robin–Day classification).

The simplest example of the inadequacy of the molecular crystal model is afforded by the very artificial case of two neighboring $H_2$ molecules, one of which has been oxidized to $H_2^+$ (Figure 1). Representing the wave function of each $H_2$ very crudely by the $1s\sigma_g$ or $1s\sigma_u$ combination of H 1s functions, it is clear that the transfer rate will be determined by the overlap between the two $1s\sigma_g$. This will, in turn, depend on the shapes of these $\sigma_g$, which will depend on the two internuclear distances. More formally, we write (in one-electron approximation)

$$\mathcal{H} = \epsilon_l a_l^\dagger a_l + \epsilon_r a_r^\dagger a_r + \hbar(b_r^\dagger + b_r) g_r \omega_r a_r^\dagger a_r + \hbar(b_l^\dagger + b_l) g_l \omega_l b_l^\dagger b_l + (b_r^\dagger b_r + \tfrac{1}{2})\hbar\omega_r + (b_l^\dagger b_l + \tfrac{1}{2})\hbar\omega_l + t_{rl}(R_r,R_l)(a_r^\dagger a_l + a_l^\dagger a_r) \tag{1}$$

Here $a_r^\dagger$ and $a_l^\dagger$ create electrons in the $\sigma_g$ orbitals on the right and the left $H_2$, respectively, with energies $\epsilon_r$ and $\epsilon_l$. The vibron operators $b_r^\dagger$ and $b_l^\dagger$ create a vibrational quantum on the right or left sides so that $(b_r^\dagger + b_r)\hbar/(2m\omega)^{1/2}$ is the displacement coordinate on the right $H_2$; $\omega_r$, $\omega_l$ are just the stretch frequencies. The coupling constants $g_r$ and $g_l$ characterize how much the energies of the electronic stats $\sigma_g$ vary with vibrational displacement. Finally, the transfer integral $t_{lr}$, which depends on the right and left H···H distances $R_r$ and $R_l$, characterizes the transfer rate. In the molecular crystal model, the dependence of $t$ on $R$ is neglected.[16] This is a form of the Condon approximation, but it is more difficult to justify than is the usual Condon approximation for optical transitions, since $t_{lr}$ itself may be so small that its variations become significant.[18] Indeed, if $t_{lr}$ is not small, Robin–Day III behavior and full delocalization are expected. In the $H_2$–$H_2^+$ example, the atomic orbital makeup of the actual $\sigma_g$ orbitals which overlap are fixed by symmetry. This will not generally hold; for the Ru–N chromophore of II, for example, the LCAO coefficients will change with change in the Ru–N distance; this will, in turn, change $t$, $\omega$, and $\epsilon$ in (1); only the last of these occurs in the molecular crystal model. If, however, we were to include the dominant intrasite terms as well as the site-transfer terms of (1), the ensuing model should provide both a reasonable basis for calculation of intramolecular electron transfer and a criterion for delocalization. This paper is devoted to the definition, interpretation, and implementation of such a four-site model.

## II. Four-Site Model: Electronic Considerations and Potential Surface

The intramolecular transfer problem may be idealized as involving two chromophore subunits held semirigidly with respect to one another by a molecular framework; this last qualification differentiates it from the solution electron-transfer problem for which diffusion processes are important, the transfer is generally adiabatic, and the activated complex approach of Marcus[19] (and Hush)[20] provides an elegant and generally satisfactory explanation.[21] Although the chromophoric localization sites will generally be polyatomic, we can, for present arguments, limit them to a pair of basis orbitals on groups which are bonded to one another (the C–O $\pi$ system in **1**, the metal–ligand $\pi$ in **2**, or the NO $\pi$ unit in $((NO)_2C_6H_4)^-$ suggest themselves). These four basic orbitals can then be used to construct the electronic states of the two-site molecule. Then the Hamiltonian of the two-site case generalizes to

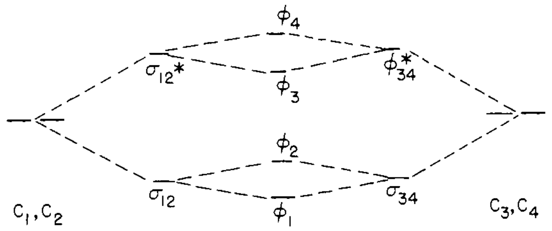

**Figure 2.** Schematic energy-level diagram for a symmetric four-site system.

$$\mathcal{H} = \mathcal{H}_{el} + \mathcal{H}_{vib} + \mathcal{H}_{int} \tag{2}$$

$$\mathcal{H}_{el} = \sum \epsilon_i a_i^\dagger a_i + \beta_1(a_1^\dagger a_2 + cc) + \beta_2(a_3^\dagger a_4 + cc) + \beta'(a_2^\dagger a_3 + cc) \tag{3}$$

$$\mathcal{H}_{vib} = \omega_l(b_l^\dagger b_l + \tfrac{1}{2}) + \omega_r(b_r^\dagger b_r + \tfrac{1}{2}) \tag{4}$$

So long as the parameters $\epsilon_i$, $\beta_1$, $\beta_2$, and $\beta'$ of $\mathcal{H}_{el}$ are allowed to depend on $R_r$ and $R_l$, $\mathcal{H}_{int}$ will be zero. The more usual notation involves a Herzberg–Teller expansion of $\epsilon_i$ and $\beta$ in which case the $\epsilon_i$ of (2) is a fixed value, while

$$\mathcal{H}_{int} = \omega_l \sum_i g_i^l (b_l^\dagger + b_l) a_i^\dagger a_i + \omega_r \sum_i g_i^r (b_r^\dagger + b_r) a_i^\dagger a_i + \omega_l \sum_{ij} \Gamma_{ij}^l (b_l^\dagger + b_l) a_i^\dagger a_j + \omega_r \sum_{ij} \Gamma_{ij}^r (b_r^\dagger + b_r) a_i^\dagger a_j \tag{5}$$

Here the coupling constants $g_i$ describe the change in displacement upon addition or removal of electrons. Formally,

$$\left.\frac{\partial \beta_{ij}}{\partial R_l}\right|_{R_l^0} = (\omega_l/X_l^0)\Gamma_{ij}^l \tag{6a}$$

$$\left.\frac{\partial \epsilon_i}{\partial R_l}\right|_{R_l^0} = (\omega_l/X_l^0) g_i^l \tag{6b}$$

where $X_l^0$ is the zero-point displacement in normal mode l.

We wish to analyze the behavior of the four-site Hamiltonian of (2). First consider only the behavior of $\mathcal{H}_{el}$; for symmetric systems like **1** and **2**, $\beta_1 = \beta_2 = \beta$, and we restrict our attention to this case. Then the energy-level diagram will, in general, resemble that of Figure 2. Localization of the electron on either site will involve roughly equal and opposite changes in $R_l$ and $R_r$ and therefore in $\beta_1$ and $\beta_2$. If the electronic energy lowers upon such a change, the system should, except for possible effects from $\mathcal{H}_{int}$ and/or solvation, favor a charge-localized state. Thus a criterion for charge localization is

$$\left.\frac{\partial \epsilon^l_{total}}{\partial \beta_1}\right|_{\delta\beta_2 = -\delta\beta_1} < 0 \tag{7}$$

Utilizing second-order perturbation theory plus a closed-form

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Table I. HOMO Energies of the Four-Site Model (eq 3) Illustrating the Localization Criterion (eq 8) $\alpha_C \equiv \alpha_2 = \alpha_3 = 0$

| $\alpha_0$ | $-\beta_{CC} = \beta_{23}$ | $-\beta_{12}$ | $-\beta_{34}$ | $-\alpha_0 - (\alpha_0^2 - 4\beta^2)^{1/2}$ | $\epsilon_3$ |
|---|---|---|---|---|---|
| −1.2 | 0.1 | 2.0 | 2.0 | (i) | 1.4242 |
| | | 2.1 | 1.9 | (i) | 1.3734 |
| −3.2 | 0.1 | 2.0 | 2.0 | (i) | 0.8803 |
| | | 2.1 | 1.9 | (i) | 0.8497 |
| −1.2 | 0.01 | 2.0 | 2.0 | (i) | 1.4816 |
| | | 2.1 | 1.9 | (i) | 1.3923 |
| −0 | 1.0 | 2.0 | 2.0 | (i) | 1.951 |
| | | 2.1 | 1.9 | (i) | 1.889 |
| −5 | 0.1 | 2.0 | 2.0 | 2.00 | 0.6127 |
| | | 2.1 | 1.9 | 2.00 | 0.5939 |
| −8 | 1.0 | 2.0 | 2.0 | 1.072 | −0.46887 |
| | | 2.1 | 1.9 | 1.072 | −0.46895 |
| −8 | 1.0 | 2.3 | 2.3 | 1.45 | −0.31192 |
| | | 2.4 | 2.2 | 1.45 | −0.31237 |
| −8 | 1.0 | 1.6 | 1.6 | 0.668 | −0.6516 |
| | | 1.7 | 1.5 | 0.668 | −0.6512 |
| −8 | 1.1 | 2.0 | 2.0 | 1.072 | −0.56221 |
| | | 2.1 | 1.9 | 1.072 | −0.56218 |

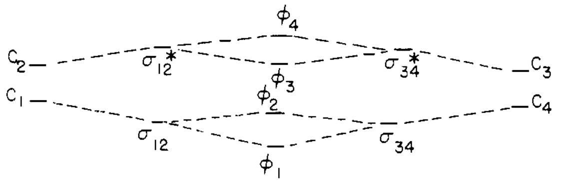

**Figure 3.** Schematic energy-level diagram for a four-site system with $\alpha_1 \neq \alpha_2$.

expression recently derived by one of us[22] for the four-site problem, we can replace (7) by the condition (for delocalization)

$$|\beta'| \geq |\alpha_1 - \alpha_2| \pm [(\alpha_1 - \alpha_2)^2 - 4\beta^2]^{1/2} \tag{8}$$

A numerical test of (8) is given in Table I, where we show that this criterion is very accurate. When the rhs of (8), which appears on column 5 of Table I, is real and greater than $|\beta'| = |\beta_{cc}|$, the value of $\epsilon_3$ is more negative (stabler) for the localized geometry ($\beta_{12} \neq \beta_{34}$) than for the delocalized geometry ($\beta_{12} = \beta_{34}$); the last line indicates how sensitive the criterion 8 is. Qualitatively, (8) is probably best understood as a competition between the strong 1–2 and 3–4 binding and the weaker (delocalizing) 2–3 interaction. For ordinary bonding situations, the 1–2 or 3–4 bonding interaction $\beta$ is substantial; then the excess electron will always localize to minimize the electronic energy. The only exception will occur when the 1–2 bond is very polar so that $\alpha_1 - \alpha_2$ is substantial. Then the lowest four electrons will, to a good first approximation, be clustered about the more electronegative atom. If then an extra electron is added, it will go into the bonding combination of the remaining two atomic orbitals (on the less electronegative atom); this will lead to a favoring of the delocalized state. In general, we suspect that this latter condition should not hold (see Figure 3), and therefore, from a purely electronic point of view, the four-site five-electron ground state will always favor localization. For interacting C–O as in **1**, for example, $\alpha_1 - \alpha_2 \simeq 1.2$ in standard $\beta$ units.[23] Thus unless the 1–2 binding interaction $\beta$ of (3) is very weak, it will always lead to a localized anion.

It is worthwhile to note again that the features of the four-orbital model cannot be fully described by the two-orbital discussion, since the 2–3 effective interaction will depend not only on the magnitude of $\beta'$ but also on the magnitude of the charge on sites 2 and 3, which in turn will be fixed by $\alpha_1 - \alpha_2$ and $\beta$. The actual geometry of the ion and extent of localization, however, will be controlled not only by these purely electronic considerations but also by how much the elastic energy of the bonding framework changes upon localization; this is described by the $\mathcal{H}_{\text{int}} + \mathcal{H}_{\text{vib}}$ of (2) and is responsible for the polaron binding energy usually discussed in the two-site model.

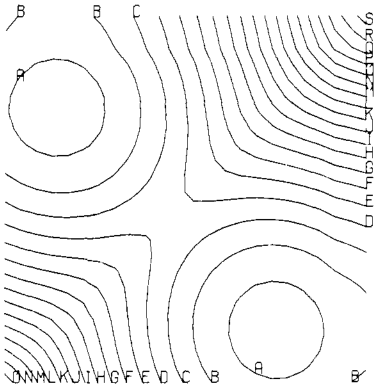

**Figure 4.** Contour levels of ground-state energy surface for the five-electron four-site case. The *x* and *y* values are $\beta_l$ and $\beta_2$. The value of $\beta_l$ is 0.05 eV, while $\beta_1$ and $\beta_2$ run from 1.300 to 1.370 eV.

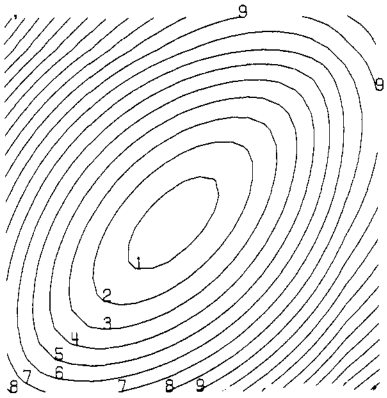

**Figure 5.** The excited-state surface arising from (4) on promotion of the highest lying electron.

When we consider a four-site case, the diagonal coupling constants *g* of (6) are expected to be quite small (the oxygen orbital energy in **1** or Ru orbital energy in **2** does not change with bond stretch), but the Γ of (6) should be substantial, since the overlap is roughly an exponential of the separation. In addition, of course, the harmonic term of (4) will favor an undistorted geometry and therefore a delocalized electron. Thus the criterion for delocalization will be tighter than indicated by (8); for actual localization (distortion) to occur, the energy gained by electronic localization described by (3) must be larger than the harmonic distortion energy characterized by (4). In general, then, we expect the localization criterion to depend on $\omega$ as well as the parameters of (3). As a typical example, we give in Figure 4 the potential-energy surface as a function of the two binding parameters $\beta_1$ and $\beta_2$ for a bridged diketone system like **1**, assuming the standard[23] relationship between $\beta$ and bond length $l$

$$\beta_i = \beta_i^0 f_i \tag{9}$$

where $f_i$ is a tabulated, length-dependent function and assuming a C–O stretch frequency of 1400 cm$^{-1}$. The important feature to notice is the existence of two symmetrically displaced wells corresponding to distorted geometries, which occur only for certain ranges of $\beta_1$ or $\beta_2$. Thus the distorted (localized) state will be favored for certain values of the system parameters ($\omega$, $\beta_1$, $\beta_2$, $\beta'$, $\alpha_i$).

The excited state surface in Figure 5 arises from the ground-state surface of Figure 4 by promoting the odd electron to the fourth MO of (3). There will generally not be degeneracy between these two surfaces, because there are no degenerate representations of the group corresponding to the four-site model problem of (3). These potential surfaces, however, do come close together for $\beta_1 = \beta_2$ and strongly resemble the surfaces for Jahn–Teller doubly degenerate systems (the splitting between the surfaces at $\beta_1 = \beta_2$ will be roughly $2\beta'$, if all $\alpha$ are equal). Indeed, they correspond

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exactly to the second-order Jahn–Teller surfaces which have been invoked to characterize geometries of simple hydride molecules.[24] The close approach of these surfaces at $\beta_1 = \beta_2$ suggests that the problem of interconversion from one geometry of Figure 4 to the other (that is, the rate of intramolecular electron transfer) can be considered as a vibronic coupling problem of pseudo-Jahn–Teller type on the two potential surfaces of Figures 4 and 5.

## III. Intramolecular Electron Transfer Rate Processes

If the species under study shows a distorted ground-state geometry (that is, if the local minima of Figure 4 exist and are separated by a barrier of height greater than the zero-point vibrational energy), the rate of conversion between these minima will be the rate of intramolecular electron transfer; this is the case for molecules such as **3** for which such rates have in fact been measured by EPR.[3] Such rates then correspond to a pseudo-Jahn–Teller transition and can be calculated semiclassically by using the Landau–Zener–Stueckelberg approximation.[25] This is a one-dimensional treatment, and will be valid if the curvature of the reaction coordinate between the local minima of Figure 4 is not large; curved paths will require a more involved vibronic coupling calculation.[26]

To derive the Landau–Zener–Stueckelberg form for the four-site transfer case, we start by assuming an adiabatic wave function with two terms

$$\Psi = \phi_1(\vec{r}\vec{R})\chi_1(\vec{R}) + \phi_2(\vec{r}\vec{R})\chi_2(\vec{R}) \qquad (10)$$

where $\vec{r}$ and $\vec{R}$ are the totality of electronic and nuclear coordinates, respectively, and the electronic functions $\phi_1$ and $\phi_2$ correspond to the lower eigen states in the right and left distorted wells of Figure 4. Then the total energy can be written as

$$E_{\text{tot}} = \int \mathrm{d}\vec{R}\left[E_1(\vec{R})\chi_1^2 + E_2(\vec{R})\chi_2^2 - \sum_\alpha \frac{1}{2m_\alpha}|\vec{\nabla}\Psi|^2\right] \qquad (11)$$

where $E_1$ and $E_2$ are the electronic eigenvalues of $\phi_1$ and $\phi_2$, and the last term is the nonadiabatic coupling ($\alpha$ labels the nuclei). For simplicity, we will restrict the sum in this last term to one nuclear motion (the asymmetric combination of C–O stretches in **1** or of Ru–N breathing in **2**). Then we can replace the mixing term of (11) by its inner projection in the manifold of (10).

$$\int \mathrm{d}R|\nabla\Psi|^2 = 2\int\langle\phi_1\nabla\phi_2\rangle\chi_1\nabla\chi_2\,\mathrm{d}R + 2\int\langle\phi_2\nabla\phi_1\rangle\chi_2\nabla\chi_1\,\mathrm{d}R + \int|\nabla\chi_1|^2\,\mathrm{d}R + \int|\nabla\chi_2|^2\,\mathrm{d}R + \int\langle\phi_1\nabla\phi_2\rangle^2(\chi_1^2 + \chi_2^2)\,\mathrm{d}R \qquad (12)$$

Then defining

$$p = \langle\phi_1\nabla\phi_2\rangle = -\langle\phi_2\nabla\phi_1\rangle \qquad (13)$$

we write (using primes to denote spatial derivatives)

$$E = \int \mathrm{d}RE_1(R)\chi_1^2 + \int \mathrm{d}RE_2(R)\chi_2^2 - \frac{1}{2m}\int \mathrm{d}R[2\chi_1p\chi_1' - 2\chi_2p\chi_1' + \chi_1'\chi_1' + \chi_2'\chi_2'] \qquad (14)$$

This expression is valid in the adiabatic picture, where the coupling elements $p$ are due to the action of the nuclear kinetic-energy operator on the adiabatic electron wave functions $\phi$. By hermiticity, $\langle\phi_1\nabla\phi_1\rangle = 0 = \langle\phi_2\nabla\phi_2\rangle$.

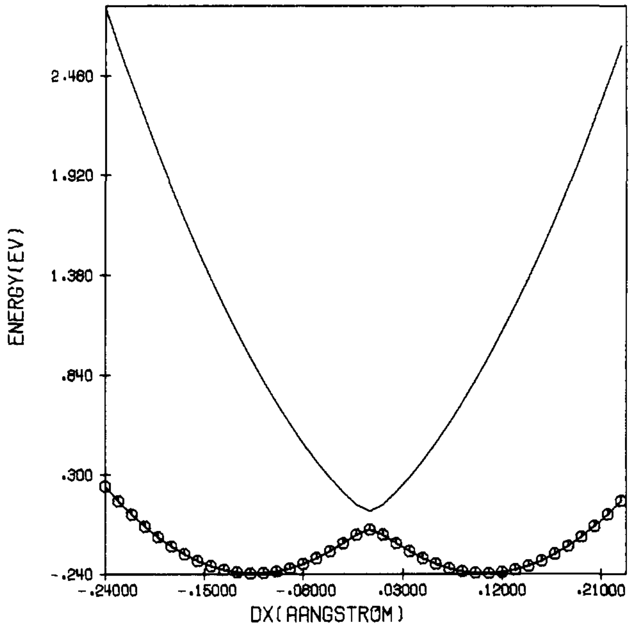

**Figure 6.** A cut of Figure 4 along the line of slope −1 passing through the minima.

It is now convenient to transform to a diabatic representation. We write

$$\begin{aligned} U_1 &= (\cos\theta)\chi_1 + (\sin\theta)\chi_2 \\ U_2 &= -(\sin\theta)\chi_1 + (\cos\theta)\chi_2 \end{aligned} \qquad (15)$$

where the angle $\theta$ is as yet undefined. Then

$$\begin{aligned} \chi_1' &= -\chi_2\theta' + (\cos\theta)U_1' - (\sin\theta)U_2' \\ \chi_2' &= \chi_1\theta' + (\sin\theta)U_1' + (\cos\theta)U_2' \end{aligned} \qquad (16)$$

and the energy expression is

$$E_{\text{tot}} = \int V_1U_1^2\,\mathrm{d}R + \int V_2U_2^2\,\mathrm{d}R + 2\int W_{12}U_1U_2\,\mathrm{d}R - \frac{1}{2m}\int[|\nabla U_1|^2 + |\nabla U_2|^2]\,\mathrm{d}R \qquad (17)$$

where we have defined

$$\theta' = -p \qquad (18)$$

$$V_1 = \tfrac{1}{2}(E_1 + E_2) + \tfrac{1}{2}\cos\theta(E_1 - E_2) \qquad (19)$$

$$V_2 = \tfrac{1}{2}(E_1 + E_2) - \tfrac{1}{2}\cos\theta(E_1 - E_2) \qquad (20)$$

$$W_{12} = W_{21} = \tfrac{1}{2}\sin 2\theta(E_1 - E_2) \qquad (21)$$

It is worthwhile to observe some limiting forms for our diabatic representation. We denote by $X$ the coordinate along which the nuclei move in the transfer process. For large negative $X$, the system is in the right minimum of Figure 4, while for large positive $X$ it is in the left minimum; the energy difference $E_1 - E_2$ is a monotonic function of $|X|$, minimizing at $X = 0$. The function $p(X)$ defined by (18) will maximize for $X = 0$, since the Born–Oppenheimer coupling is largest for smallest energy differences. We expect $p$ and therefore $\theta = \int^X p(X)\mathrm{d}X$ to look as in Figure 6. In the initial state $\theta = 0$, $V_1 \rightarrow E_1$, $V_2 \rightarrow E_2$, $W_{12} \rightarrow 0$, $U_1 \rightarrow X_1$, and $U_2 \rightarrow X_2$. In the final state, $\theta = \pi/2$, $V_1 \rightarrow E_2$, $V_2 \rightarrow E_1$, $W_{12} \rightarrow 0$, $U_1 \rightarrow X_2$, and $U_2 \rightarrow -X_1$. Finally, at the transition state, $\theta = \pi/4$, $E_1 - E_2$ = minimum, $V_1 = V_2 = (E_1 + E_2)/2$, $W_{12}$ = maximum, $U_1 \rightarrow (X_1 + X_2)/\sqrt{2}$, $U_2 \rightarrow (-X_1 + X_2)/\sqrt{2}$. Thus the diabatic picture reduces asymptotically to the adiabatic but is more convenient to use in the actual calculation of rates. Note that (17), like (11), corresponds to a coupled two-state system. The differences lie in the nature of the potentials and the mixing term: in (11), the mixing is of momentum type, whereas in (17) it is the coordinate term $W_{12}U_1U_2$. The angle $\theta$ is fixed by (18); at $\theta = \pi/4$, the two diabatic basis functions are degenerate—this is the set of points along $\beta_1 = \beta_2$ in Figure 4.

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We now wish to calculate the rate of interwell transition in Figure 4, that is, the rate of intramolecular electron transfer. The problem involves motion of the system point along $X$, that is, along the line of slope $-1$ between the two wells.[26a] Along this path the problem is a simple curve-crossing one. The Stueckelberg approach will be valid in the general case, and we can generally neglect tunneling effects, since the masses involved are large. Then the below-the-barrier contribution is unimportant, and the overall rate is well approximated with the usual Landau–Zener formula.[25] For each attempted transit from one local well, we then obtain

$$P_{12} = 1 - e^{-Z} \tag{22}$$

Here the Landau–Zener parameter $Z$ is simply

$$Z = 2\pi W_{12}{}^2/[\hbar v|S_1 - S_2|] \tag{23}$$

where $v$ is the classical nuclear velocity approaching the barrier and $S_1$ and $S_2$ are the slopes of the $V_1$ and $V_2$ curves at the crossing (compare Figure 6). At the closest approach point, $\theta = \pi/4$, so that from eq 19–21

$$2\pi W_{12} \rightarrow 2\pi(E_1 - E_2)^2/4 \tag{24}$$

$$|S_1 - S_2| \rightarrow \frac{d}{dR}(V_1 - V_2) = -2\theta'(E_1 - E_2) \tag{25}$$

$$v \rightarrow [2(E - \tfrac{1}{2}E_1 - \tfrac{1}{2}E_2)/M]^{1/2} \tag{26}$$

Then, remembering (18), we finally obtain

$$Z = \frac{\pi(E_1 - E_2)}{4\hbar[2(E - \tfrac{1}{2}E_1 - \tfrac{1}{2}E_2)/M]^{1/2}p} \tag{27}$$

The forms (27) and (17) are equivalent to (23) and (11) but are expressed in the diabatic, rather than adiabatic, representation. If the intramolecular electron transfer is due to the intrinsic motions of the molecule (and not, for example, an ion pair effect—see section IV), then its rate follows from (22) and (23) or (27), assuming that the reaction coordinate is not bent and that only two symmetry-related states are important.

As very rough numerical values, we can take parameters appropriate to the diketone **1**. Then assuming $\beta = -2.37$ eV, $\alpha_0 = 1.2\,\beta$, $\beta' \simeq -0.06$ eV and taking $M$ as the C–O reduced mass and $p \simeq 1$ bohr$^{-1}$, we obtain

$$Z \simeq 3,\ p_{12} \simeq 1$$

so that the transfer process is adiabatic. Increasing the value of $p$ or reducing $\beta'$ still further can cause nonadiabatic transfer.

## Discussion

The usual treatment of the two-site molecular crystal model yields the criterion[14,15]

$$|\beta_{12}|/g^2\hbar\omega \ll 1 \tag{28}$$

for localization of the valence electron in a species such as **1**, **2**, or **3**; here $\beta_{12}$ is the two-site mixing integral, and the polaron stabilization energy $g^2\hbar\omega$ is the elastic energy gained by electron localization—formally, this $g$ is identical to the $g$ of (5) but is much larger, since in the two-site model, the one-site energy refers to a localized MO, and is sensitive to vibrational displacement. Although (28) is usually derived perturbationally or from time scale arguments,[27] it can also be proved variationally, by looking at the lowest eigen state of the two-site vibronic coupling model. The results obtained for the two-site model are simple and powerful, but may, as has been argued in section I, not be valid for most intramolecular transfer cases. We can draw an analogy between two-site and four-site treatments for a simple species such as **1**, assuming $\beta' \ll (\beta_1,\beta_2)$. In this case, we can, starting with four sites, form LCAO states between sites 1 and 2 and between sites 3 and 4, finally coupling these via the weak residual interaction $\beta'$. This procedure yields local levels on each end of molecule (sites 1, 2, and 3, 4)

$$\alpha^{(2)} = \tfrac{1}{2}[\alpha \pm (\alpha^2 + 4\beta^2)^{1/2}] \tag{29}$$

Mixing these via $\beta'$, we have

$$\epsilon^{(2,2)} = \alpha^{(2)}(\pm)\beta_{cc} = \tfrac{1}{2}\alpha \pm \tfrac{1}{2}(\alpha_2 + 4\beta_2)^{1/2} \pm \beta_{cc} = \pm\beta \pm \beta_{cc} \tag{30}$$

if $\alpha = 0$, where the two ± terms are independent, yielding four eigenvalues. The general four-site solution gives

$$\epsilon^{(4)} = \pm(1/\sqrt{2})[\beta_{cc}{}^2 + 2\beta^2 \pm (\beta_{cc}{}^4 + 4\beta^2\beta_{cc}{}^2)^{1/2}] \tag{31}$$

if $\alpha = 0$. If $\beta_{cc}/\beta$ is small, we expand $\epsilon^{(4)}$ and find

$$\epsilon^{(4)} \rightarrow \pm\beta \pm \beta_{cc}/2 \tag{32}$$

where again the two ±'s are independent. The values of (30) and (32) agree, as they must, when $\beta_{cc} = 0$ (no interaction). For finite $\beta_{cc}$, they will differ, essentially because the strength of the interaction 2···3 will depend on the electronic structure in the 1–2 and the 3–4 linkages; this dependence will be missing in the two-site model.

The result (8) of perturbation theory on the four-site problem is reminiscent of the ordinary Jahn–Teller theorem: it says that under most reasonable conditions the radical ion corresponding to the four-site problem will distort to a nonsymmetric geometry. Indeed, since the coupling of (5), which favors distortion, is linear in the displacements $R_r$ and $R_l$, while the restoring force (4) which favors no distortion is quadratic, some distortion away from perfect symmetry should generally be expected. As (8) indicates, this will fail to be so only if the 1–2 and 3–4 bonds are excessively polar. Just as in ordinary Jahn–Teller cases, however, we expect that the distortion may be slight enough as to be unobservable or that rapid interconversion between the equivalent distorted minima may (as in dynamic Jahn–Teller cases)[28] render the effective averaged geometry undistorted. Finally, the role of electron repulsions has been neglected here (and in nearly all treatments of electron localization).[29] One expects that polarity will be opposed by the Coulomb repulsion and, indeed, the states calculated from simple one-electron models such as those of sections I and II may even become unstable.[30] The importance of this effect should probably be smaller in the four-site than in the two-site case, since the localization site is then more expanded, and should have smaller effective Coulomb repulsion.

The question of adiabatic vs. nonadiabatic transfer has been a hotly debated one in electron-transfer phenomena,[7,34] and recently in intramolecular transfers.[5,9,35,36] It is important[15,27] to distinguish the conditions for electron localization from those for transfer adiabaticity; the former arises from the nature of the potential surface, the latter from dynamical processes. In our present context, the criteria for localization are (8) in the four-site model and (28) for two sites. The adiabaticity is controlled by the transfer probability, and, utilizing our Landau–Zener form, we obtain the criterion for adiabaticity

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$$Z \gg 1 \tag{33}$$

or

$$2\pi W_{12}^2 \gg \hbar v|S_1 - S_2| \tag{34}$$

or

$$(E_1 - E_2) \gg (4\hbar/\pi)(2(E - \tfrac{1}{2}E_1 - \tfrac{1}{2}E_2)/M)^{1/2}p \tag{35}$$

If these are satisfied, the system will effectively cross the barrier in Figure 4 at each collision so that the actual size of the mixing parameter $W_{12}$ (or the splitting $E_1 - E_2$) is unimportant once it is large enough. One then anticipates that the differences in Robin–Day classifications reflect these differing time scale criteria: class III are delocalized in the sense of (8) or (28), while class II are adiabatic in the sense of (33) and class I are nonadiabatic. Even then, of course, the experiment in question is relevant to the question of Robin–Day class, since the transfer rate in the adibatic case will be the rate of collisions with the barrier in Figure 4: if this is very small compared to the experimental time scale, Robin–Day I is observed, if it is of the same order, Robin–Day II is observed, and if the experimental time scale is slow compared to this rate (as is usually true for, say, NMR), Robin–Day III is observed.

Examination of, say, the binuclear metal complexes studied by Taube and others indicates that a number of bridging systems exist for which nonadiabatic transfer, as indicated by dependence of the transfer rate on the bridging,[5] has occurred. These systems are typified by substituted 4,4′-bipyridyl bridged pentammine metal groups (metal = $Co^{III}$, $Ru^{II}$, or $Ru^{III}$), for which the rate depends on the bridging species.

In their pioneering experimental study of intramolecular electron transfer, Harriman and Maki[3] discussed the formation of ion pairs and changes in solvation as the operative driving forces responsible for the intramolecular transfer. Most measurements are made in (solid or liquid) solution so that dynamical effects due to the surroundings can cause transfer to occur. Such effects are, at best, imperfectly described by our models. If the solvent is treated classically as a continuous dielectric medium,[31,34] the solvent interaction can be expanded in a multipolar series, and this dipolar coupling term will then favor charge localization. Then, if $\beta_{23}$ is sufficiently large, one would anticipate the intramolecular transfer rate to depend upon fluctuation times for solvation or of ion pairs. This coupling can be described in the standard way[31,37,38] and will slightly complicate the picture described so far; work on the transfer rates in this limit is continuing.

The situation with respect to the distortion is actually closer to the pseudo-Jahn–Teller or second-order Jahn–Teller effect[24,31] than to the true Jahn–Teller system, since the electronic states involved are neither accidentally degenerate nor degenerate due to symmetry. For a simple two-state case (for instance, the states might be $\phi_1{}^2\phi_2{}^2\phi_3 = \psi_1$ and $\phi_1{}^2\phi_2{}^2\phi_4 = \psi_2$ where the $\phi$ are the four-site Hückel orbitals), the Jahn–Teller secular problem can be obtained by taking a Herzberg–Teller expansion of the potential about the undistorted position and keeping linear and quadratic terms

$$V = V(Q_0) + \left.\frac{\partial V}{\partial Q}\right|_{Q_0}(Q - Q_0) + \tfrac{1}{2}\left.\frac{\partial^2 V}{\partial Q^2}\right|_{Q_0}(Q - Q_0)^2 + \dots \tag{36}$$

Then the secular problem is

$$\det\begin{pmatrix} {}^1/_2kQ^2 - \epsilon & \alpha \mathrm{Q} \\ \alpha Q & {}^1/_2kQ^2 + \delta - \epsilon \end{pmatrix} = 0 \tag{37}$$

where

$$\left\langle \psi_1 \left| \left.\frac{\partial V}{\partial Q}\right|_{Q_0} \right| \psi_2 \right\rangle \equiv \alpha \tag{38}$$

and $\delta$ is the splitting between $\psi_1$ and $\psi_2$ at $Q = 0$. Solving, we obtain

$$\epsilon_\pm = \delta/2 \pm \tfrac{1}{2}(\delta^2 + 4Q^2\alpha^2)^{1/2} + \tfrac{1}{2}kQ^2 \tag{39}$$

This corresponds, in general, both to a distortion and to a softening of the vibrational frequency along $Q$, since

$$\epsilon_- \simeq \tfrac{1}{2}\left(k - \frac{2\alpha^2}{\delta}\right)Q^2 + O(Q^3) \tag{40}$$

In this pseudo-Jahn–Teller model, the criterion for distortion follows from $\partial\epsilon/\partial Q = 0$ and is

$$2\alpha^2/\delta > k \tag{41}$$

In particular, if the harmonic restoring force is ignored, the pseudo-Jahn–Teller treatment always predicts a distorted ground state. The more general criterion is provided by (8), which predicts that for sufficiently polar systems there will be no distortion from a symmetric geometry even if harmonic restoring forces are omitted. The latter prediction is in accord with the numerical data of Table I and is more accurate than (41), because it is based on the response of the exact energy levels[22] of the four-mode problem to the incipient asymmetry rather than on the first-order Herzberg–Teller coupling as in (41).

The pseudo-Jahn–Teller, Herzberg–Teller treatment is useful, since it provides specific analytic forms for the coupled (distorted) problem. The form 41 stresses that distortion will be favored by a small LUMO–SLUMO splitting $\delta$ as well as by a relatively soft chromophore vibration (small $k$). Since the energy level diagram (Figure 2) indicates that $\delta$ will be determined largely by $\beta_{23}$ it is clear that, as expected, increase of $\beta_{23}$ (strong interaction between localization sites) will militate against electron localization (that is, it will favor Robin–Day III behavior). This has indeed been the general conclusion of experiments probing bridged systems[5–12] and follows from straightforward perturbation theoretic arguments.[32–33]

The pseudo-Jahn–Teller discussion also permits some added understanding of the four-site localization criterion 8. For nearly all cases, the radical in (8) is negative, and (for the concept of localization region to be sensible) $\beta_{23}/\beta_{12} < 1$. Then the energy level diagram of Figure 3 will be applicable, and the $\phi_3$ level will be 1–2 and 3–4 antibonding and 2–3 bonding. Since the deformation coordinate $Q$ leading to localization is not totally symmetric, $\langle\phi_3|Q|\psi_3\rangle$ is zero by symmetry (alternatively: the $\phi_3$ level has no ordinary Jahn–Teller distortion). Thus the effect of displacement along $Q$ on the ground state $\phi_1{}^2\phi_2{}^2\phi_3$ arises (as in second-order Jahn–Teller) from its interaction with LUMO $\phi_4$. In this limit, $\phi_4$ is 1–2 antibonding and 2–3 bonding. Thus focusing on the 1–2 overlap region, the $Q$ mode is totally symmetric (a local stretch), while the $\phi_3\phi_4$ product is also totally symmetric; thus $Q$ can mix $\phi_3$ and $\phi_4$, and this mixing leads to distortion in accordance with (37). In the opposite limit of an extremely polar 1–2 link such that (8) implies a delocalized (symmetric, averaged valence) ground state, the level diagram of Figure 3 is inapplicable. Instead, $\phi_3$ will be 1–2 and 3–4 bonding but 2–3 antibonding and $\phi_4$ will be antibonding (with nodes) in 1–2, 2–3, and 3–4 regions. Then in the 1–2 region, $Q$ will be totally symmetric (stretch) as will $\phi_3$, but $\phi_4$ will have a node so that $\langle\phi_3 Q \phi_4\rangle$ will be very small. Thus the pseudo-Jahn–Teller interaction of (38) will in fact be significant only if the criterion (8) implies localization.

The secular problem of (38) for the pseudo-Jahn–Teller activation (without strain or site inequivalence) is again the same as the Holstein molecular crystal model[16] for two equivalent sites or the equivalent site Schatz–Piepho–Krausz[35] model. This holds when the particular choice $\delta = 2\epsilon$ is made. This means, just as it should, that in the symmetric case the splitting at $Q = 0$ is exactly twice the tunnelling matrix element. The form 38 is thus a trivial generalization of the two equivalent site model to the case of two sites which have identical frequencies and vibronic coupling

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but differ in electronic energies; in the Jahn–Teller literature this last difference is usually called a strain term. A molecular realization might involve dimers like **3** in a matrix which slightly shifts the diagonal energies or a species like **1** with a methyl group on one of the benzene rings.

The present theoretical treatment is based on some severe modeling assumptions. First is the neglect of electronic repulsions; these can be included, but we expect, and indeed the work of Cederbaum and co-workers[39] on vibronic problems has demonstrated, that the electron repulsion and the vibronic coupling problems can to a fair degree be separated. The second approximation is the neglect of frequency changes in the elastic energy (eq 4). Much of the study of mixed valence species is in fact based upon[4–6] frequency changes attendant upon electron localization. Inclusion of frequency changes is not a serious complication, and we hope to deal with it in future work. The present four-site model, though expected to be more adequate than the two-site[35,40] or three-site[32] assumptions employed previously, is nevertheless insufficient if the excess electron orbital (HOMO) contains a nonnegligible contribution from atomic orbitals on bridge atoms (as has in fact been calculated[41] for Creutz–Taube ion). Under these conditions a five-site model, with the additional site representing the bridge, seems appropriate. Finally, as has been noted above, we have neglected any role of the solvent in promoting transfer or dissipating energy; work on this problem is also continuing.

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# Electronic Relaxation of Intra- and Intermolecular Exciplexes in the Vapor Phase

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**Abstract:** Intramolecular exciplex formations in the vapor phase of 1-(9,10-dicyano-2-anthryl)-3-(1- and 2-naphthyl)propanes (*βα*- and *ββ*-DCAN) have been studied in the presence and absence of a vibrational relaxer. In the collision-free vapor of DCAN (vapor pressure, approximately $10^{-2}$–$10^{-3}$ torr), excitation wavelength dependences in the spectral region of $S_1 \leftarrow S_0$ on the relative fluorescence quantum yield and lifetimes of the exciplex were observed. A considerable blue shift of the exciplex fluorescence (time-resolved spectra) of the collision-free vapor upon excitation of the upper vibrational states was observed in comparison with excitation of the lower vibrational state. The facts suggest fluorescent relaxation from the upper vibrational state of the exciplex. In the intermolecular system of 9,10-dicyanoanthracene (DCA) and 1,5-dimethylnaphthalene (1,5-DMN), exciplex fluorescence was observed in the vapor phase. However, no significant wavelength dependence of the exciplex fluorescence or the lifetime was observed even in the absence of the buffer gas. The formation and dissociation rate constants of the DCA–1,5-DMN exciplex were determined in the vapor phase. The obtained rates of exciplex formation and of vibrational relaxation suggest that 1,5-DMN seems to behave not only as an electron donor but also as a vibrational relaxer. The electronic relaxation process of the exciplex could be investigated only in the vapor phase of the collision-free condition of the intramolecular electron donor–acceptor system.

In the course of numerous investigations on the exciplex in solution, solvent participation in the formation and stabilization of the exciplex and in the inter- and intramolecular vibrational deactivation of the exciplex has been pointed out.[1,2] Therefore, the observation of exciplex formation in the vapor phase provides us valuable information concerning the electronic interaction between the electron donor and acceptor in the absence of solvent. It also provides information concerning vibrational effects on the radiative and nonradiative deactivation. Previously, exciplex formation in the vapor phase was reported only in 9-cyanoanthracene or substituted 9-cyanoanthracene and alkylamine system.[3,4] Recently, Prochorow et al.[5] and Okajima and Lim[6] reported the exciplex formation in the 1,2,4,5-tetracyanobenzene (TCNB) and *p*-xylene system in the vapor phase. They reported vibrational energy dependence and temperature dependence of the exciplex in the vapor phase, which suggest the importance of intermolecular vibrations in the formation and the radiationless deactivation of the exciplex.

Numerous investigations have been made on the intermolecular exciplex formation in solution of the electron donor–acceptor systems connected by trimethylene chains such as 1-(*N*,*N*-dimethylanilino)-3-(anthryl)propane[7] and 1-(9,10-dicyano-2-anthryl)-3-(1- or 2-naphthyl)propane (*βα*- or *ββ*-DCAN).[8] The association and dissociation processes in these intramolecular

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