J. Phys. Chem. **1992,** *96,* 3213-3217

A conical intersection occurs between these states right in the FC region which makes a dynamical treatment extraordinarily elaborate.[79] The initial excitation is to the bound state which couples, however, strongly to the dissociative state. The diffuse structures superimposed to the broad absorption background are, as in the case of water, due to symmetric stretch motion, ***but in the potential well of the bound state rather than on top of the barrier of the dissociative state.***[38,79] The involvement of two electronic states has also consequences for the Raman spectra. In contrast to process 1, the Raman spectrum of H_2S shows activity in the bending coordinate and it exhibits a distinct dependence on the excitation wavelength.[80] Despite some similarities, the dissociations of H_2S and H_2O, both excited in the first absorption band, behave quite differently.

Editor's Note. This Feature Article is longer than normal as it contains additional reviews in a field that the editors felt to be important.

Acknowledgment. R.L.V.M. and F.F.C. gratefully acknowledge the support of the Division of Chemical Sciences, Office of Basic Energy Sciences of the United States Department of Energy. R.J.S. and B.H. acknowledge the assistance of Dr. R. J. Brudzynski in performing the resonance Raman experiments and the support of the US National Science Foundation via grant CHE8816698. V.E., S.H., K.W., and R.S. are grateful to the Deutsche Forschungs Gemeinschaft for continuous financial support.

---

(79) Heumann, B.; Weide, K.; Düren, R.; Schinke, R. To be published.

(80) Brudzynski, R. J.; Sension, R. J.; Hudson, B. *Chem. Phys. Lett.* **1990**, *165*, 487.

ARTICLES

Calculation of Electron-Transfer Matrix Elements of Bridged Systems Using a Molecular Fragment Approach

Prabha Siddarth and R. A. Marcus*

A. A. Noyes Laboratory of Chemical Physics,[†] California Institute of Technology, Pasadena, California 91125
(Received: August 23, 1991; In Final Form: December 20, 1991)

A perturbation method for calculating the electronic coupling for electron-transfer reactions between a donor and an acceptor separated by large or small bridges is developed. In this approach the intervening bridge is subdivided into smaller molecular fragments, thereby enabling calculations on larger systems. This method of molecular fragments is tested for a series of polyproline bridged systems. The results obtained for the electron-transfer matrix element are compared with those obtained from direct diagonalization of the full bridge and with experimental results. Previously, the result for the direct diagonalization of the bridge had been shown to agree with that obtained from diagonalization of the entire donor–bridge–acceptor system. The vertical donor–bridge orbital energy difference is estimated with the aid of a donor–bridge charge-transfer spectrum.

Introduction

The effective electron-transfer matrix element H_{DA} from a donor D to an acceptor A has been expressed in terms of individual atom–atom matrix elements H_{ij}, Coulomb integrals H_{ii}, and overlap integrals S_{ij}, both in perturbative and nonperturbative formalisms. In an early such formulation, McConnell showed that a perturbation approximation to the relevant matrix element is given by[1]

$$H_{\mathrm{DA}} = \frac{-T^2}{W}\left(\frac{t}{W}\right)^{n-1} \tag{1}$$

where T is the matrix element between the donor (acceptor) and the nearest bridge atom in a sequentially connected series of identical bridge atoms, t is the bridge atom–bridge atom matrix element, W is the energy difference between a bridge atom orbital energy and donor or acceptor atom energy, and n is the number of bridge atoms. Extension of this result to a sequence of nonidentical interacting atoms and energy differences yields[2,3]

$$H_{\mathrm{DA}} = H_{\mathrm{D1}}\left(\prod_{i=1}^{n-1} \frac{H_{i,i+1}}{E_{\mathrm{D}} - E_i}\right)\frac{H_{n\mathrm{A}}}{E_{\mathrm{D}} - E_n} \tag{2}$$

where E_i is the Coulombic energy H_{ii} of the ith atom, E_{D} is that of the donor (which equals that of the acceptor E_{A} at a resonant electron transfer), and the H_{ij} are atom–atom matrix elements. It has been pointed out[2-4] that this expression could be further extended by allowing the i to denote the ith collection of atoms, e.g., a molecular fragment, in the bridge.

In the extended Hückel treatment, the atom–atom matrix element in eq 2, H_{ij}, of which H_{D1}, $H_{i,i+1}$, and $H_{n\mathrm{A}}$ are examples, is given by[5]

$$H_{ij} = KS_{ij}\left(\frac{H_{ii} + H_{jj}}{2}\right) \tag{3}$$

where K is taken to be 1.75.

One method of extending the i in eq 2 from atoms to molecular fragments, adopted by Ulstrup and co-workers[6] for proteins, is

---

[†] Contribution No. 8490.

(1) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

(2) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034.

(3) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

(4) Ratner, M. A. *J. Phys. Chem.* **1990**, *94*, 4877.

(5) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397; **1964**, *40*, 2474, 2745.

(6) Christensen, H. E. M.; Conrad, L. S.; Mikkelsen, K. V.; Nielsen, M. K.; Ulstrup, J. *Inorg. Chem.* **1990**, *29*, 2808.

0022-3654/92/2096-3213$03.00/0

to use eq 3 with the H_{ii} now denoting the value for a particular molecular orbital of the ith fragment (e.g., its LUMO for electron transfer or its HOMO for hole transfer), and S_{ij} now given by the overlap integral of the MO on i and that on j. In this modification of the usual extended Hückel approach, K was chosen to be 0.5 (from Ratner and co-workers' calculations[7]) instead of the 1.75 for atom–atom H_{ij}'s.

In the present paper, we describe a related but different method of extending eq 2 to the case where the i's denote molecular fragments. For the procedure adopted here, it is shown for the systems investigated that eq 10 obtained below is an excellent perturbation approximation to the results obtained by a direct diagonalization of the full bridge matrix. Previously,[8] the diagonalization of the full bridge matrix was found to yield results for H_{DA} in good agreement with those obtained from the direct diagonalization of the entire D–bridge–A system.

In a further extension, the requirement that the bridge units be connected sequentially is dropped. Rather, a particular bridge unit may be connected to another some distance away by different paths of other bridge units, the connections being, in the case of proteins, bonds along the sequence of amino acid residues or via hydrogen bond bridges or across small gaps.

Theory

When applied to atoms, the perturbation approximation given by eq 2 poses the problem that $|H_{i,i+1}/(E_D - E_i)|$ and $|H_{nA}/(E_D - E_n)|$ may not be less than unity, as required in a perturbation expansion. For example, in the systems investigated below, the atom–atom coupling elements $H_{i,i+1}$ and H_{nA} are typically about 4–5 eV, and $E_D - E_i$ or $E_D - E_n$ is about the same value. In contrast, when extended to molecular fragments, as in the present paper, the magnitudes of the coupling are typically reduced to 0.2 eV or less, while the magnitudes of $E_D - E_i$ become about 1 eV. In this case, therefore, the extension of eq 2 to fragments makes the new equation an excellent approximation. The coupling between these fragments is smaller because, unlike individual atoms in a bridge, the coefficients of the relevant orbitals at each fragment-to-fragment link are relatively small instead of being unity. (The role of the coefficients is described later in eq 10.)

We introduce a projection operator P_0 which projects onto the space of the molecular orbitals of D and A relevant for the electron transfer, and a projection operator Q_0 projecting onto the space of the relevant molecular orbitals of each of the molecular fragments (the Q_0 space is the union of all these MO's of the molecular fragments). Then, the $(n + 1)$th-order perturbation expression for H_{DA} is given by[9]

$$H_{DA} = \left\langle \phi_D \middle| P_0 \left(\frac{V}{a} Q_0 \right)^n V P_0 \middle| \phi_A \right\rangle \tag{4}$$

when the paths from D to A include no return to D and no successive visitations of A. Such omitted paths correspond to one of many omitted terms in the perturbation series in ref 9, such as $P_0(VQ_0/a)^{n-1}VP_0VP_0$. In eq 4, V is the perturbation, a denotes $E_D - H_0$ in the present resonant case of $E_D = E_A$, these two E's being MO energies. The statement that $E_D = E_A$ in the transition state follows from the theory of electron-transfer reactions.[10] The values of E_D and E_A are influenced by the solvent and the ligands in D and A. H_{DA} is the desired effective matrix element connecting a particular molecular orbital ϕ_D of D to a particular molecular orbital ϕ_A of A. In eq 4, the $P_0|\phi_A\rangle$ and $P_0|\phi_D\rangle$ equal $|\phi_A\rangle$ and $|\phi_D\rangle$, but the P_0's are retained to make the correspondence to the usual perturbation operator clear.

Explicit expressions for P_0 and Q_0 are

$$P_0 = \sum_D |\phi_D\rangle\langle\phi_D| + \sum_A |\phi_A\rangle\langle\phi_A| \tag{5}$$

the sum being over the relevant MO's of D and A, and

$$Q_0 = \sum_i \sum_\alpha |\phi_{\alpha_i}\rangle\langle\phi_{\alpha_i}| \tag{6}$$

where ϕ_{α_i} denotes the αth MO of the ith molecular fragment, and the sum is over all orbitals α of all molecular fragments i. We have

$$\langle\phi_{\alpha_i}|V|\phi_{\beta_j}\rangle = H_{\alpha_i\beta_j} \tag{7}$$

where $H_{\alpha_i\beta_j}$ denotes the matrix element (an extension of the H_{ij} in eq 2) connecting the αth MO of fragment i to the βth MO of fragment j.

The αth molecular orbital of fragment i can be written in terms of the atomic orbitals ψ_{m_i} of that fragment

$$\phi_{\alpha_i} = \sum_{m_i} C_{\alpha_i m_i} \psi_{m_i} \tag{8}$$

where the $C_{\alpha_i m_i}$ are the LCAO-MO coefficients. In this case we have for the donor–fragment, fragment–fragment, or fragment–acceptor $H_{\alpha_i\beta_j}$ of eq 7

$$H_{\alpha_i\beta_j} = \sum_{m_i} \sum_{n_j} C^*{}_{\alpha_i m_i} H_{m_i n_j} C_{n_j \beta_j} \tag{9}$$

With a fairly large fragment of, say, 10 carbon, nitrogen, or oxygen atoms and 4 valence orbitals per atom, each coefficient C in eq 8 is roughly $1/\sqrt{40}$ on the average. (In the case of an atom–atom description, the coefficients would be 1.) With just one or two connecting links between fragments i and j when only a few m_i and n_j contribute significantly, the matrix element $H_{\alpha_i\beta_j}$ is therefore immediately reduced by a factor or at least 20 from the atom–atom value. (E.g., a typical reduction is from ~5 to ~0.2 eV.) As a result, eq 2, generalized to molecular fragments, becomes a useful perturbation expression for electron transfer, even when the ungeneralized eq 2 was not. Its utility is both in terms of physical insight and, in the case of very large systems, making calculations for such systems more practical.

Equations 4, 6, and 8 can be written explicitly as

$$H^{DA}_{\chi\mu} = \sum \frac{(C^*{}_{\chi m_D} H_{m_D m_i} C_{m_i \alpha_i})}{E_\chi - E_{\alpha_i}} \frac{(C^*{}_{\alpha_i n_i} H_{n_i m_j} C_{m_j \alpha_j})}{E_\chi - E_{\alpha_j}} \times \frac{(C^*{}_{\alpha_j n_j} H_{n_j m_k} C_{m_k \alpha_k})}{E_\chi - E_{\alpha_k}} \cdots \frac{(C^*{}_{\alpha_y n_y} H_{n_y m_z} C_{m_z \alpha_z})}{E_\chi - E_{\alpha_z}} \times (C^*{}_{\alpha_z n_z} H_{n_z m_A} C_{m_A \mu}) \tag{10}$$

where m_i and n_i, m_j and n_j, ..., m_z and n_z denote atomic orbitals of the fragment i,j, ..., z; α_i again denotes a molecular orbital of the fragment i; and χ and μ denote the molecular orbitals of the donor D and acceptor A. The summation is over all molecular orbitals of the intervening fragments and over all atomic orbitals in these fragments and in D and in A. In practice, for very large systems, certain fragment to fragment "paths" will predominate. The symmetry of the molecular orbitals of each fragment is fully included in the calculation of H_{DA} since the symmetry is included in the calculation of the molecular orbital coefficients C. For fragment orbitals closest in energy to the donor orbital, typical values of $E_\chi - E_{\alpha_i}$ are about 1.0 eV, while the magnitude of the interaction $H_{\alpha_i\beta_j}$ is about 0.2 eV or less. Thus the ratio $H_{\alpha_i\beta_j}/(E_\chi - E_{\alpha_i})$ is now typically much less than unity.[11]

This approach may be compared with that we used earlier.[8] In the case of bridges which are not too large, it is still possible

---

(7) Pietro, W. J.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 5387.

(8) Siddarth, P.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 2985. Perhaps it should have been explicitly stated in this paper that a Gaussian basis set was used for the calculations. See also ref 21 of the present paper, footnote 33.

(9) Messiah, A. *Quantum Mechanics*; Wiley: New York, 1962; Vol. II.

(10) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; **1965**, *43*, 679.

(11) In eq 10, we have many ratios such as $H_{\alpha_i\beta_j}/(E_\chi - E_{\alpha_i})$. In order for the perturbation approximation to be fully satisfied, these ratios have to be significantly less than 1. However, in the present calculations, we find that even if a few of these ratios for the important orbitals are slightly greater than unity, the perturbation expression still gives reliable results as long as the majority of these ratios for the relevant orbitals are much less than 1. In the present case, for the relevant fragment orbitals given in Table II for $n = 2$, of the 45 such ratios between donor–fragment, fragment–fragment, and fragment–acceptor orbitals, only five ratios are greater than unity. (The ratios are 1.3, 1.5, 1.6, 2.3, and 3.6.)

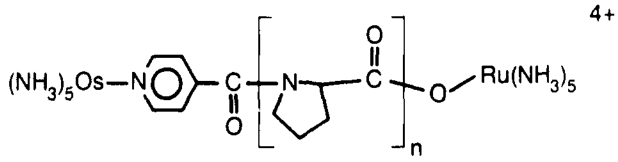

Figure 1. Structure of the polyproline bridged systems, n = 1–4.

to treat all of the bridge as a single unit and to calculate the electron-transfer matrix element using the formalism we have employed previously.[8] In that approach, the electron-transfer matrix element is given by

$$H_{\chi\mu}^{\mathrm{DA}} = \sum_{\alpha} \sum_{m_{\mathrm{D}},m_{\mathrm{B}},n_{\mathrm{B}},n_{\mathrm{A}}} \frac{(C^*{}_{\chi m_{\mathrm{D}}} H_{m_{\mathrm{D}} m_{\mathrm{B}}} C_{m_{\beta}\alpha})(C^*{}_{\alpha n_{\mathrm{B}}} H_{n_{\mathrm{B}} m_{\mathrm{A}}} C_{m_{\mathrm{A}}\mu})}{E_{\chi} - E_{\alpha}} \quad (11)$$

where α's denote the MO's of the full bridge B, and m_{D}, m_{B}, n_{B}, and m_{A} are the atomic orbitals of D, B, B, and A, respectively.

Results

In order to test the validity of the perturbation approximation of eq 10, H_{DA} is calculated for a series of electron-transfer reactions using both this method of molecular fragments and the full diagonalization of the entire bridge. The series chosen is the polyproline bridged systems of Isied et al.,[12] where the donor and the acceptor are kept identical throughout the series and the bridge length is systematically increased (see Figure 1). In contrast to other naturally occurring amino acids, polyprolines are structurally rigid due to the cyclic nature of the proline ring.

In ref 8, H_{DA} was calculated for this series with eq 11 using extended Hückel theory and a Gaussian basis set, but using only the d orbitals for the two metal atoms, and neglecting ligands other than the bridge. Presently, we use a Slater basis set having all the valence orbitals for the metal atoms and including all the ligands on the two metal atoms.[13] In the calculations, $[\mathrm{Os(NH_3)_5}]^{2+}$ is considered as the donor and $[\mathrm{Ru(NH_3)_5}]^{3+}$ as the acceptor. The bridge thus consists of the isonicotinyl group and n prolines. In using eq 10, the isonicotinyl group and each of the n prolines is considered as a fragment. The oxygen atom in Figure 1 adjacent to the Ru is treated as part of the terminal proline fragment. Further, only interactions between nearest-neighbor fragments are included, even though eq 10 allows the consideration of interactions between any pair of molecular fragments. Also, in using the perturbation approximation of eq 10, it is not the core σ orbitals of the fragments which contribute significantly to electron transfer but the "redox" orbitals, namely the orbitals, both occupied and unoccupied, which are close in energy to the energy E_{χ} of the donor (acceptor) orbital.

We consider the electron transfer in a series of reactions

$$\mathrm{Red_1 + Ox_2 \rightarrow Ox_1 + Red_2} \quad (12)$$

and let the generalized reaction coordinates, mentioned below, at the intersection of the reactant–product free energy surfaces (Figure 2) be denoted by (q_1^*, q_2^*). The vertical energy difference Δ_{TS}, from (q_1^*, q_2^*) to the parabolic free energy surface of the products of a donor–bridge charge-transfer excitation process

$$\mathrm{Red_1 + Ox_2 + B \rightarrow Ox_1 + Ox_2 + B^-} \quad (13)$$

where B denotes the bridge, is depicted in Figure 2. This free energy difference is also the energy difference, since the entropies of the two nonequilibrium states are the same. It is this energy difference (no relaxation to the minimum) for any particular molecular orbital of the bridge that appears in the energy denominator for that orbital in the expressions for H_{DA} in eqs 10 and 11, e.g., for the LUMO of the bridge. We consider this difference next, and in particular, when it can be evaluated from the donor to bridge (more precisely adjacent bridge fragment) charge-transfer absorption maximum $h\nu_{\mathrm{CT}}$.

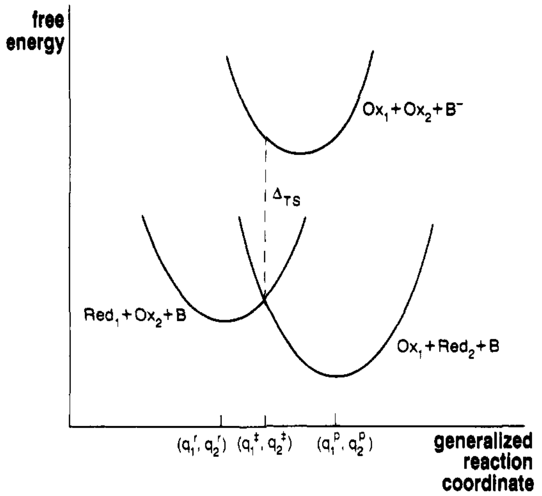

Figure 2. Free energy surface of reactants and surrounding medium (r) and that of products and surrounding medium (p). Δ_{TS} denotes the vertical energy difference from the intersection of these two free energy surfaces to the free energy surface for the situation that the electron resides in the bridge. (No relaxation to the lowest point of the latter surface occurs, since the bridge orbital state serves only as a virtual state.) The plot is schematic: the lowest point of the upper curve does not correspond to the lowest free energy of $\mathrm{Ox_1 + Ox_2 + B^-}$, but rather to the lowest value when the generalized coordinate is constrained to lie on the line joining (q_1^r,q_2^r) to (q_1^p,q_2^p), and with the nuclear configuration around B being the same as in the $\mathrm{Red_1 + Ox_2 + B}$ state [vertical transition at (q_1^*,q_2^*)].

Donor–Bridge Electronic Energy Difference at TS, Δ_{TS}, and Relation to $h\nu_{\mathrm{CT}}$. In the calculation, a quantity of particular interest is $E_{\chi} - E_{\alpha_1}$, where E_{χ} is the donor energy level and E_{α_1} the energy of the (LUMO) unoccupied molecular orbital of the fragment adjacent to the donor. The extended Hückel calculations may be too approximate to obtain this quantity accurately, and so we estimate it using $h\nu_{\mathrm{CT}}$, the absorption maximum associated with charge transfer from the donor to the bridge. In the case of electron transfer via the bridge, the solvent molecules and bridge geometry are those which the neutral bridge has, since the electron does not really reside on the bridge in the present case where the bridge is "off-resonance". For the present purpose we use a simplified treatment to obtain the relation between Δ_{TS} and $h\nu_{\mathrm{CT}}$, since the main purpose is to illustrate the perturbation–fragment method. It can be replaced later by a more elaborate solvational treatment. A generalized coordinate q_i is introduced for each reactant (i = 1, 2), to include both solvent and (low frequency) vibrational contributions to the free energy fluctuations. The free energy G^{r} of the reactants and bridge in reaction 12 is then written as

$$G^{\mathrm{r}} = \left[\frac{k_1}{2}(q_1 - q_1^{\mathrm{r}})^2 + \frac{k_2}{2}(q_2 - q_2^{\mathrm{r}})^2\right] + G_1^{\mathrm{r},0} + G_2^{\mathrm{r},0} + E^{\mathrm{r}} \quad (14)$$

where the first two terms are associated with the fluctuations around reactants 1 and 2, respectively, the next two are the equilibrium solvation free energies, namely the values at $q_i = q_i^{\mathrm{r}}$, and the last term is the electronic energy of the entire system at $q_i = q_i^{\mathrm{r}}$. Correspondingly, for the products, we write

$$G^{\mathrm{p}} = \left[\frac{k_1}{2}(q_1 - q_1^{\mathrm{p}})^2 + \frac{k_2}{2}(q_2 - q_2^{\mathrm{p}})^2\right] + G_1^{\mathrm{p},0} + G_2^{\mathrm{p},0} + E^{\mathrm{p}} \quad (15)$$

where the symbols have the same significance as before. The additivity approximation in eqs 14 and 15 can be replaced by a more elaborate treatment, such as that in refs 10 or 14.

We denote the donor in reaction 12 by 1. For the system where an electron of the donor has been transferred to the adjacent fragment of the bridge, the free energy of the system G^{b} is given by

---

(12) Vassilian, A.; Wishart, J. F.; van Hemelryck, B.; Schwarz, H.; Isied, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 7278.

(13) QCPE Program No. 517, Indiana University, Bloomington IN 47405. The basis set and the valence state ionization energies for the metal atoms were obtained from QCPE Program No. 387.

$$G^{\mathrm{b}} = \left[\frac{k_1}{2}(q_1 - q_1^{\mathrm{p}})^2 + \frac{k_2}{2}(q_2 - q_2^{\mathrm{r}})^2\right] + G_1^{\mathrm{p},0} + G_2^{\mathrm{r},0} + E^{\mathrm{b}} \quad (16)$$

where E^{b} denotes the electronic energy of the entire system when $q_1 = q_1^{\mathrm{p}}$ and $q_2 = q_2^{\mathrm{r}}$. No solvent orientation–vibration polarization of the bridge occurs in this vertical transition. There is some electronic polarization and other terms, to which we briefly return later.

We now note that to obtain $h\nu_{\mathrm{CT}}$, we set $q_1 = q_1^{\mathrm{r}}$ and $q_2 = q_2^{\mathrm{r}}$ in eqs 14 and 16 for G^{r} and G^{b} and obtain

$$\begin{aligned} h\nu_{\mathrm{CT}} &= G^{\mathrm{b}}(q_1^{\mathrm{r}},q_2^{\mathrm{r}}) - G^{\mathrm{r}}(q_1^{\mathrm{r}},q_2^{\mathrm{r}}) \\ &= G_1^{\mathrm{p},0} - G_1^{\mathrm{r},0} + E^{\mathrm{b}} - E^{\mathrm{r}} + \lambda_1 \end{aligned} \quad (17)$$

where $\lambda_1 = k_1(q_1^{\mathrm{p}} - q_1^{\mathrm{r}})^2/2$.

Further, in the transition state TS we have[10,14]

$$q_i^{\ddagger} = q_i^{\mathrm{r}} + m(q_i^{\mathrm{r}} - q_i^{\mathrm{p}}) \quad (18)$$

and $G^{\mathrm{r}}(q_1^{\ddagger},q_2^{\ddagger}) = G^{\mathrm{p}}(q_1^{\ddagger},q_2^{\ddagger})$, leading to

$$-(2m + 1)(\lambda_1 + \lambda_2) = G_1^{\mathrm{p},0} + G_2^{\mathrm{p},0} - G_1^{\mathrm{r},0} - G_2^{\mathrm{r},0} + E^{\mathrm{p}} - E^{\mathrm{r}} \equiv \Delta G^0 \quad (19)$$

the right-hand side being the standard free energy of reaction ΔG^0 and λ_2 being $k_2(q_2^{\mathrm{p}} - q_2^{\mathrm{r}})^2/2$.

The quantity Δ_{TS} is the energy of the lowest unoccupied molecular orbital of the bridge fragment attached to the donor E_{α_1} minus the donor orbital energy in the TS E_{χ}, i.e., when $q_i = q_i^{\ddagger}$ ($i = 1, 2$). It is given by

$$\Delta_{\mathrm{TS}} = G^{\mathrm{b}}(q_1^{\ddagger}, q_2^{\ddagger}) - G^{\mathrm{r}}(q_1^{\ddagger}, q_2^{\ddagger}) \quad (20)$$

Equations 14, 16, and 19 yield

$$\Delta_{\mathrm{TS}} = -\frac{\lambda_1}{\lambda}\Delta G^0 + G_1^{\mathrm{p},0} - G_1^{\mathrm{r},0} + E^{\mathrm{b}} - E^{\mathrm{r}} \quad (21)$$

The first term in eq 21 also appears in ref 15, p 312.

Equations 17 and 21 now yield

$$\Delta_{\mathrm{TS}} = h\nu_{\mathrm{CT}} - \frac{\lambda_1}{\lambda}(\Delta G^0 + \lambda) \quad (22)$$

where λ is $\lambda_1 + \lambda_2$, the reorganization energy for the donor to acceptor electron transfer.

We consider next some omitted bridge effects. In the vertical charge-transfer spectrum from the donor to the adjacent fragment of the bridge, the electron on the bridge polarizes the electrons of the solvent, an effect which lowers the value of $h\nu_{\mathrm{CT}}$. Again, in the case of Δ_{TS}, which is involved in the charge transfer from the donor to acceptor via the superexchange mechanism, the transferring electron in the virtual orbitals of the bridge interacts with solvent polarization, both the electronic and the (static) orientational, an effect which may tend to lower Δ_{TS}. A detailed analysis of these aspects for $h\nu_{\mathrm{CT}}$ and Δ_{TS} requires a more elaborate calculation. For the present paper we shall simply assume that the difference $\Delta_{\mathrm{TS}} - h\nu_{\mathrm{CT}}$ is given by eq 22.

From the charge-transfer spectrum[16] of $[(\mathrm{NH_3})_5\,\mathrm{Os(isonicotinic\ acid)}]^{2+}$, $h\nu_{\mathrm{CT}}$ is known to be 1.75 eV. The standard free energy of the reaction, ΔG^0 of reaction 12, is available from the experimental study[12] (−0.25 eV). The solvent plus vibrational reorganization parameter λ is estimated from the temperature dependence studies of the electron transfer rate[12] to be 1.5 eV. An estimate of λ_1 can be obtained from the literature for related species, $\mathrm{Ru(NH_3)_6}^{3+/2+}$, where λ_1 has been estimated to be 0.6 eV.[17] It is also known that the reorganizational barrier for Os analogs is similar to the corresponding Ru complexes.[18] Accordingly, we take λ_1 for the species $\mathrm{Os(NH_3)_6}^{3+/2+}$ to be 0.6 eV. Equation 22 then yields a value of 1.25 eV for Δ_{TS}. The energy of the LUMO of the isonicotinyl fragment, E_{α_1}, is presently calculated (by extended Hückel theory) to be −10.75 eV. Therefore, the donor orbital energy at the transition state (E_{χ} of eqs 10 and 11) is given by $E_{\alpha_1} - \Delta_{\mathrm{TS}} = -12.0$ eV.[19]

Calculated values of H_{DA} obtained using eqs 10 and 11 are given in Table I and its variation with distance is plotted in Figure 3.

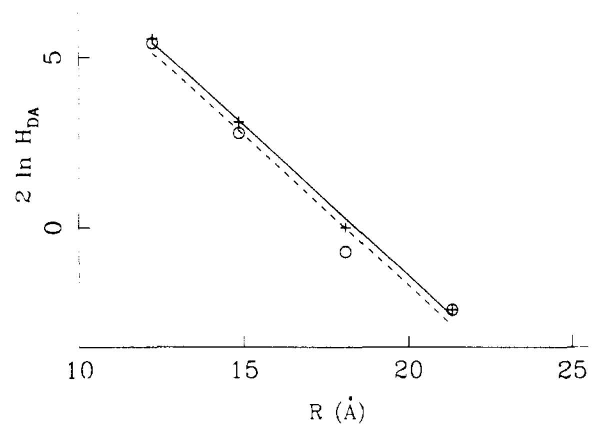

Figure 3. Variation of H_{DA} with distance, calculated using eqs 10 and 11, the circles referring to eq 10 and the pluses to eq 11. The solid line is the least-squares line for the pluses and the broken line is the least-squares line for the circles.

TABLE I: Calculated and Experimental H_{DA} (cm^{-1}) Values for the Series in Figure 1

no. of prolines in bridge, *n*	calc eq 10	 eq 11	expt[a]
1	15.1	16.1	3.9
2	4.0	4.7	1.9
3	0.7	1.0	0.7
4	0.3	0.3	
β, Å^{-1}	0.9	0.9	0.7

[a] Reference 20.

Discussion

From the results in Table I and in Figure 3, it is seen that there is good agreement between the two methods. The results show that the method of subdividing a large bridge into smaller molecular fragments indeed provides a reasonable approach to the calculation of H_{DA} for such systems. Further, in this particular instance of sequential fragments in a bridge, the results also validate the usage of only the interaction terms between nearest-neighbor fragments, even though this approximation need not be invoked. (In the full diagonalization of the entire bridge, interactions between all parts of the bridge are considered.) Indeed, in biological systems such as proteins, where the method of molecular fragments is expected to be most useful, considering only nearest-neighbor interactions may not be sufficient, since two amino acids, even though they may not be directly linked, may still approach each other closely because of the three-dimensional structure of the protein. The method of molecular fragments allows any such interaction to be considered. Further, this method provides a simple way of estimating the effect of any one particular amino acid (or a group of amino acids) on the rate of electron transfer by including the amino acid(s) in the calculation or not.

We next compare these calculated results with experimental estimates[20] of H_{DA}. As noted previously,[8,21] an error in the matrix elements connecting D and A to the bridge will affect the absolute value of H_{DA} but will have less effect in the variation of H_{DA} within

---

(14) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.

(15) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(16) Wishart, J. F., personal communication. See also: Sen, J.; Taube, H. *Acta Chem. Scand.* **1979**, *A33*, 125.

(17) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(18) Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1988**, *27*, 2582.

(19) The extended Hückel value for the energy of the donor orbital, without correcting for solvational and reorganizational effects of the medium, was −13.45 eV. In the calculations, therefore, the energy of the donor orbital was adjusted upward by this difference, 1.45 eV, so that its new value is now −12.0 eV.

(20) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635.

(21) Siddarth, P.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 8430.

TABLE II: Energies and Occupation of the Relevant Fragment Orbitals[a] for $n = 2$

isonicotinyl group	$(\text{proline})_1$	$(\text{proline})_2$
	−9.975, u	
−10.752, u, π^*	−11.284, u	
−12.525, occ, π	−12.499, occ	−12.304, occ
−12.788, occ, π	−13.000, occ	−13.036, occ
−13.444, occ, π	−13.328, occ	−13.495, occ
−13.593, occ, π		

[a] Energies are in eV. The donor (acceptor) level is −12.0 eV (cf. text). For the approximately planar isonicotinyl group, an approximate π,π^* designation is also given. For the prolines, which are nonplanar, an obvious symmetry of that type was not apparent to us. The −9.975 and −11.284 eV orbitals of $(\text{proline})_1$ are mainly carbonyl orbitals, in contrast to all remaining orbitals in the table. $(\text{Proline})_1$ and $(\text{proline})_2$ differ in that the latter includes the oxygen atom attached to Ru (cf. text). u = unoccupied; occ = occupied.

a given series. In that case, the extended Hückel method, which is semiempirical, is more suited to the latter than to the determination of absolute values of H_{DA}. Further, the "experimental" values themselves for H_{DA} are dependent on the various factors which can affect the preexponential factor in the expression for the rate constant, and on the appropriateness of the method used to correct for the distance dependence of the Franck–Condon factor.

The rate constant k_{ET} for electron transfer from a donor to an acceptor can be written using the Golden Rule approximation, as[15]

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2\text{FC} \tag{23}$$

where H_{DA} is the electronic matrix element being calculated presently and FC the Franck–Condon factor. In order to compare the distance dependence of the experimental rate constants[12] with the calculated values of H_{DA} it is necessary to allow for the distance dependence of FC.

One way to correct for the variation of FC with distance is to study the temperature dependence of the rate constant,[15,20] a procedure used by Isied and co-workers. From the experimental heats of activation, the variation of the electronic factor alone in eq 23 and values of H_{DA} are then obtained. In this method, it is tacitly assumed that nuclear tunneling is relatively unimportant. (When it occurs, it could affect the preexponential factor of k_{ET} and thereby affect the value of $|H_{DA}|^2$ inferred from the latter.) The experimental values of H_{DA} for the series are also given in Table I for comparison with the calculated values. As found previously,[8] though the absolute magnitudes are only in approximate agreement, their variation with distance is comparable, and in both cases the calculated dependence is approximately exponential:

$$|H_{DA}|^2 \propto \exp(-\beta R) \tag{24}$$

For the calculated values, β is 0.9 Å^{-1}, while the inferred experimental value is 0.7 Å^{-1}.

The results in Table I have been obtained using all the molecular orbitals of the intervening fragments. However, as noted previously, it is mainly the orbitals close in energy to that of the donor orbital that are primarily responsible for electron mediation between the donor and the acceptor. It is therefore instructive to ask how many such orbitals are required in order to obtain reasonable estimates of both H_{DA} and its variation with distance. For the present series, it is found that approximately five orbitals per fragment gives roughly the same value of H_{DA} (15.3, 3.2, 0.5, and 0.2 cm^{-1} for n = 1, 2, 3, and 4, respectively) and a β of 0.9 Å^{-1}. The energy of these orbitals is given in Table II. It is seen that both occupied and unoccupied orbitals are needed; however, in the present calculation, most (>80%) of the transfer in the present series is actually hole transfer, i.e., makes use of the occupied orbitals of the bridge.

Comparing the results in Table I with our previous calculations of the same series,[8] the β-value is approximately unchanged. (Before, it was 0.8 Å^{-1}.) In those calculations, only the d orbitals for the metal atoms and no groups other than the bridge were considered. The present absolute values of H_{DA} are, on the other hand, significantly smaller. The difference between the results in ref 8 and those in Table I can be attributed to the increased number of orbitals used in Table I for the donor and acceptor principally because of the ligands, thereby diluting the relevant coefficients on the donor and on the acceptor atoms attached to the bridge.

Conclusions

In the present paper, a perturbation appracoh is developed for calculating the electronic matrix element for electron-transfer reactions between a donor and an acceptor linked by large or small bridges. For this purpose, the intervening bridge is subdivided into smaller molecular fragments. The approach is tested for a series of polyproline bridged systems and it is seen that the perturbation approximation for such systems is a useful one which yields results in good agreement with those obtained from the diagonalization of the full bridge.

It is next planned to apply this method to large systems such as proteins, where it may now be possible with this method to treat a larger portion of the protein than was done earlier,[21] by considerably reducing the dimension of the bridge matrices needed to be diagonalized. This method should also permit the determination of important "fragment paths" in proteins, the paths now consisting of amino acid residues, rather than the now customary consideration of paths of individual atoms.[22] The advantages of using paths consisting of amino acid residues is that the effective donor–fragment, fragment–fragment, and fragment–acceptor interaction energies are typically much less than the energy difference between the relevant donor and bridge energy levels, and therefore the perturbation approach remains valid for a quantitative interpretation of the paths.

Acknowledgment. It is a pleasure to acknowledge the support of this research by the Office of Naval Research and the National Science Foundation. We are particularly indebted to Norman Sutin for his very helpful and perceptive comments and to Jim Wishart for providing us with information on the charge-transfer spectra.

---

(22) See, for example: Beratan, D. N.; Onuchic, J. N.; Betts, J. N.; Bowler, B. E.; Gray, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 7915 and references cited therein.