differ by a factor of $(\hbar\omega)^{1/2}$, depending on whether a wave function $\Phi_{m'}$ was normalized to a delta function of the energy or whether as in a bound state, to a delta function of the quantum numbers.[10] In the present case, however, where we have employed dimensionless energies, the two normalizations are identical.[12]

In eq B5 k_m is $[2(E - H_{11}(z))]^{1/2}$ and $k_{m'}$ is $[2(E - H_{22}(z))]^{1/2}$ or $[2(E - E_-)]^{1/2}$, according as $H_{22}(z)$ or E_- is the potential used. z_c is the crossing point between the curves $H_{11}(z)$ and $H_{22}(z)$ [or $E_-(z)$] and z_1, $z_{m'}$ are the left-hand classical turning points for nuclear motion in the potential energy curves $H_{11}(z)$ and $H_{22}(z)$ [or $E_-(z)$], respectively.

When the system was in the $m = 0$ state, the energy of that initial vibrational state was typically somewhat close to the potential energy at the crossing point x_c. For each such calculation in the semiclassical case, a uniform approximation version of eq B4 was used, namely[13]

$$\langle \Phi_m | \Phi_j \rangle = (|F(z_c)|\pi)^{1/2}\zeta^{1/4}Ai(-\zeta) \quad \text{(B7)}$$

where $F(z_c)$ is given by (B6) and where ζ is positive and equals $(^3/_2|\Theta(z_c)|^{2/3})$.

(12) E.g., for a bound state one uses a normalization to $\delta_{m,m'}$ or, when the levels are so closely spaced that sums can be replaced by integrals, to $\delta(m - m')$. But $\delta(m - m') = \hbar\omega\delta(E_m - E_{m'})$, leading to a normalization of the $\Psi_{m'}$ for an unbound state which differs from that of the bound state $\Psi_{m'}$ by a factor of $(\hbar\omega)^{1/2}$ or, in the present case of dimensionless units, which is identical, $\delta(m - m') = \delta(E_m - E_{m'})$ when the E's are in units of $\hbar\omega$.

(13) Reference 10; cf. eqs 20 and 27a with the present (B4) and (B7).

Comparison of Experimental and Theoretical Electronic Matrix Elements for Long-Range Electron Transfer

Prabha Siddarth and R. A. Marcus*

Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91125
(Received: August 15, 1989; In Final Form: October 20, 1989)

The dependence of electron-transfer rates on the number of intervening groups is treated by using a single calculational method for four separate series of compounds: a biphenylyl donor and a 2-naphthyl acceptor, separated by various rigid saturated hydrocarbon bridges, a dimethoxynaphthyl donor and a dicyanovinyl acceptor, separated by norbornyl groups, a $Ru(NH_3)_5^{II}$ donor and a $Ru(NH_3)_5^{III}$ acceptor, separated by different numbers of dithiaspiro rings, and an $Os(NH_3)_5^{II}$ donor and an $Ru(NH_3)_5^{III}$ acceptor separated by an isonicotinyl plus a variable number of proline groups, which again provide a rigid spacer. The results for the electron-transfer matrix element obtained both with direct diagonalization and with the partitioning method are compared with each other, with the experimental results and, where available, with previously calculated results.

Introduction

There is a considerable interest in the dependence of electron-transfer rates on separation distance, as well as on the driving force, $-\Delta G°$, and on reorganizational and other molecular parameters. A number of experimental and theoretical studies have been reported on the separation distance dependence, e.g., refs 1–20. One would, as a result of such studies, also like to answer questions such as which are the most probable paths for long-range electron transfers, in various proteins, for example. A second important question is the relative importance of through-bond and through-space interactions in long-range electron transfer.[18] For the problems involving proteins some quantum mechanical method of calculating electronic matrix elements for very large systems is desirable.

In the present paper we consider the distance dependence of the electron-transfer rate from a donor D to an acceptor A, the distance being varied by varying the number of intervening groups in a molecular bridge B. Several such series have been studied experimentally. The theoretical method employed in the present article is one of the simplest available, the extended Hückel method (cf. refs 9, 10, 14, and 20). This method is a semiempirical one-electron method.[21] In the present calculations no new parameters have been introduced and the needed parameters, including calculated overlap integrals, for the systems considered here were obtained from standard sources.

Four series of compounds are considered, in each system there being a covalent link between the donor and the acceptor. The four series considered are given in Figures 1–4, two of them being purely organic and two of them involving metal ions connected by an organic bridge. Three of these four series have been previously studied theoretically, to some degree at least, in each case using a different method of calculation and in some cases with

† Contribution No. 8020.

(1) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.
(2) Oevering, J.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258.
(3) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693.
(4) Stein, C. A.; Lewis, N. A.; Seitz, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 2596.
(5) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584.
(6) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635.
(7) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173.
(8) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061.
(9) Larsson, S.; Volosov, A. *J. Chem. Phys.* **1986**, *85*, 2548. Larsson, S.; Volosov, A. *J. Chem. Phys.* **1987**, *87*, 6623.
(10) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034.
(11) Larsson, S.; Matos, J. M. O. *J. Mol. Struct.* **1985**, *120*, 35.
(12) Larsson, S. *Chem. Scr.* **1988**, *28A*, 15. Larsson, S.; Broo, A.; Kallebring, B.; Volosov, A. *Int. J. Quantum Chem.: Quantum Biol. Symp.* **1988**, *15*, 1.
(13) Beratan, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4321. Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771.
(14) Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. *J. Am. Chem. Soc.* **1986**, *108*, 1319.
(15) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1726, 1732. Isied, S. S.; Vassilian, A.; Magnuson, R. H.; Schwarz, H. A. *J. Am. Chem. Soc.* **1985**, *107*, 7432.
(16) Axup, A. W.; Albin, M. A.; Mayo, S. L.; Crutchley, R. J.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 435. Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. (USA)* **1987**, *84*, 1249. Jackman, M. P.; McGinnis, J.; Powls, R.; Salman, G. A.; Sykes, A. G. *J. Am. Chem. Soc.* **1988**, *10*, 5880.
(17) Sneddon, S. F.; Morgan, R. S.; Brooks III, C. L. *Biophys. J.* **1988**, *53*, 83. Sneddon, S. F.; Morgan, R. S.; Brooks III, C. L. *J. Phys. Chem.* **1989**, *93*, 8115.

0022-3654/90/2094-2985$02.50/0

less detailed geometry. The present study provides a common basis for comparison of experimental with theoretical trends for all four series.

Theory

The rate constant for electron transfer k_{ET} for a donor–acceptor pair separated by a rigid molecular bridge can be written, using the Golden-Rule approximation, as[19,22,23]

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 FC \tag{1}$$

where H_{DA} is the electronic matrix element for the electron transfer and FC the Franck–Condon factor. A purely classical form of FC is[19,22]

$$FC = \frac{1}{(4\pi\lambda k_B T)^{1/2}} e^{-(\Delta G^\circ + \lambda)^2/4\lambda k_B T} \tag{2}$$

where ΔG° is the standard free energy of reaction for the donor–acceptor pair DA for an electron transfer at a fixed DA separation distance R, and λ is a reorganizational term which contains solvent and vibrational contributions. A version in which the intramolecular contributions are treated quantum mechanically is often used instead, while the solvent is still treated classically.

When the DA pair is treated as a pair of spheres embedded in a dielectric medium of static dielectric constant D_S, the solvent contribution to λ, denoted by λ_0, is given by[19]

$$\lambda_0 = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_S} \right) \tag{3}$$

where Δe is the charge transferred from D to A (typically a unit charge), a_1 and a_2 are the radii of the two spherical reactants D and A, R is their center-to-center separation distance, and D_{op} is the optical dielectric constant (the square of the refractive index) of the solvent. An expression is also available for a model where the two charges, D and A, are placed at the foci of an enveloping ellipsoid.[24,25]

The quantities in eqs 1 and 2 dependent on R are ΔG°, λ, and H_{DA}, and some resolution of the dependence of H_{DA} from the other factors is needed.[26] As already noted, an extended Hückel calculation of H_{DA} is used in the present paper.

An electron transfer is normally preceded by thermal fluctuations of the various coordinates (e.g., orientations of solvent molecules, lengths of various bonds) in or near the DA pair. They permit the system to cross a suitable potential energy hypersurface in many-dimensional coordinate space, on which the zeroth-order many-electron energy of the DA pair is equal to that of a second electronic configuration, the reaction product D^+A^-.[19] Electron transfer can then occur during this crossing and satisfy the Franck–Condon principle. To calculate the electron-transfer electronic matrix element H_{DA} one procedure is to seek the two lowest energy many-electron wave functions of the DA pair where, as a result of a suitable fluctuation in the coordinates, the extra electronic charge is equally divided between D and A. By varying the orbital energies of either the D or the A uniformly upward or downward, to simulate the effect of thermal energy fluctuations of the environment or on the intramolecular energy in each reactant, two adjacent delocalized states of the DA pair can be made to have a 50%–50% distribution of the extra charge. Then, the energy difference of these two delocalized many-electron states of the system equals $2H_{DA}$, the desired matrix element. Various one-electron descriptions may be used instead, in which delocalized orbitals are formed from individual orbitals localized on D and on A and the same procedure is then employed. In the one-electron approximation this $2H_{DA}$ is the energy difference $\Delta\epsilon$ of the two delocalized orbitals which are distributed over D and A. One such orbital is, in effect, symmetric and the other antisymmetric with respect to the two centers D and A.

Using perturbation theory, it is possible to estimate H_{DA} by considering the interaction matrix elements of the donor and acceptor with the bridge and their relative energy levels.[27] In one approximation, employed by Larsson,[10,11] a partitioning technique[28] is used in which a localized molecular orbital of D is made resonant with one of A (i.e., made to have the same energy). In the transition state for electron transfer, the energies of the initial and final states are equal. To achieve this equality in a one-electron description, the change in energy when the electron is transferred from the molecular orbital of D to that of A is made to vanish. The bridge orbitals themselves are usually off-resonance from the relevant D and A orbitals.

When the donor and the acceptor are each linked to one atomic orbital of the bridge, H_{DA} is given by[10]

$$H_{DA} = \eta_D \eta_A \sum_v \frac{c_{Dv} c_{Av}}{b_v - a} \tag{4}$$

where η_D is the matrix element for the interaction between D and the adjacent atomic orbital of the bridge, η_A is that for A and its adjacent bridge atomic orbital, a is the localized molecular orbital (MO) energy for D (the same as that for A, at resonance), b_v is the energy of the vth molecular orbital of the bridge B, c_{Dv} is the coefficient of that bridge orbital v at the point of contact of B with D, and c_{Av} is the corresponding quantity at the point of contact of B with A.[29a] η_D and η_A can be calculated by using the Wolfsberg–Helmholtz approximation[29b]

$$\eta_i = 1.75 S_{ij}(a_i + e_j)/2 \qquad (i = D, A) \tag{5}$$

where j is the adjacent atom of the bridge orbital. Here, a_i is the energy of the D(i=D) or A(i=A) orbital (they are made equal) and e_j is the energy of the adjacent atomic orbital of B.

When D and A are each linked to more than one atomic orbital of the bridge, eq 4 is replaced by[11]

$$H_{DA} = \sum_v \frac{\gamma_v \delta_v}{b_v - a} \tag{6}$$

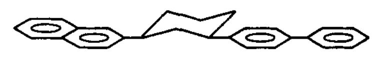
where

$$\gamma_v = \sum_j \lambda_j c_{jv}, \quad \delta_v = \sum_k \mu_k c_{kv} \tag{7}$$

and where the λ_j are the matrix elements for interaction of the D orbital and the jth adjacent atomic orbital of B, and μ_k is the corresponding quantity for A. Equation 7 is obtained as a special case (only one orbital on D, one on A, and more than one on B) of eq 8.

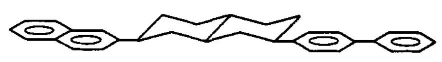
It is also possible to extend the above formalism to treat the case of electron transfer in compounds where the donor and acceptor are large groups rather than metal ions.[11] For these systems

(18) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1989.
(19) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
(20) Newton, M. D. *J. Phys. Chem.* **1988**, *92*, 3049. Newton, M. D. *J. Phys. Chem.* **1986**, *90*, 3734. Logan, J.; Newton, M. D. *J. Chem. Phys.* **1983**, *78*, 4086. Newton, M. D. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, No. 14, 363.
(21) Hoffmann, R. J. *J. Chem. Phys.* **1963**, *39*, 1397; **1964**, *40*, 2474; **1964**, *40*, 2745.
(22) Levich, V. G. *Adv. Electrochem. Electrochem. Eng.* **1966**, *4*, 249.
(23) Kestner, N. R.; Jortner, J.; Logan, J. *J. Phys. Chem.* **1974**, *78*, 2148. Ulstrup, J. *Charge Transfer Processes in Condensed Media*; Springer: Berlin, 1979.
(24) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 1261.
(25) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.
(26) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731.
(27) Halpern, J.; Orgel, L. E. *Discuss. Faraday Soc.* **1960**, *29*, 32. McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.
(28) Löwden, P. O. *J. Mol. Spectrosc.* **1963**, *10*, 12; *J. Math. Phys.* **1962**, *3*, 969.
(29) (a) The molecular orbital energies (a, b_v) and coefficients (c_{D_v}, c_{A_v}) are obtained by diagonalizing the extended Hückel Hamiltonian matrix (separately) for the donor, the acceptor, and the bridge. The matrix elements used in the latter are obtained from refs 29b and 34–36, as described there. (b) Wolfsberg, M.; Helmholtz, L. *J. Chem. Phys.* **1952**, *20*, 837.

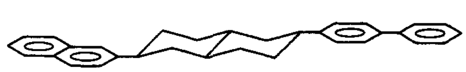


I

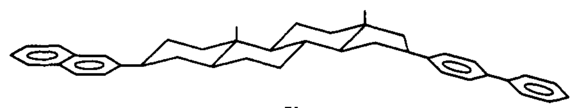
II



III



IV



V

Figure 1. Structures of the biphenylyl–naphthyl systems attached with various saturated bridges, series (i).

such as the ones studied by Closs et al.,[1] and Oevering et al.,[2] it is necessary to take into account the electronic structure of the donor and acceptor groups also. In this case, the matrix element H_{DA} is again given by eq 6 but with

$$\gamma_v = \sum_j \sum_l c^D{}_{l\chi} \lambda_{jl} c_{jv}$$

$$\delta_v = \sum_k \sum_m c^A{}_{m\rho} \mu_{mk} c_{kv} \qquad (8)$$

Here, χ and ρ denote the molecular orbitals on D and A whose splitting we wish to calculate; l and m denote the atomic orbitals of D and A while j and k denote the atomic orbitals on B connected to D and A, respectively. The c^D and c^A are the MO coefficients of D and A. The λ_{jl} are the interaction matrix elements of the donor and bridge orbitals and μ_{mk} are the corresponding quantities for the bridge and acceptor orbitals. These are obtained from the Wolfsberg–Helmholtz approximation given by eq 5. The size of the partitioned matrix used to determine the coefficients γ_v and δ_v in eq 8 equals the sum of the number of donor orbitals and acceptor orbitals. It is reduced in size from the original Hamiltonian matrix by the number of bridge orbitals. This partitioning formalism becomes increasingly valuable as the size of the bridge is increased (e.g., a protein).

The following systems are treated in the present study.

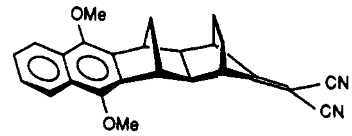
(i) D–B–A (Figure 1), where D is 4-biphenylyl, A is 2-naphthyl, and B is one of the following spacers:[7] (a) a cyclohexyl group attached to D and to A at the 1- and 3-positions, (b) a cyclohexyl group attached to D and to A at the 1- and 4-positions, (c) a decalyl group attached at the 2- and 6-positions (d) a decalyl group attached at the 2- and 7-positions, and (e) an androstanyl group attached at the 3- and 16-positions. Only the equatorial–equatorial isomers were considered, so as to keep the stereoelectronic effects constant throughout the series. Closs and co-workers[14] have performed extremely interesting ab initio calculations on a simpler molecule, 1,4-dimethylenecyclohexane, and have shown that the attachment of the spacer to donor–acceptor pair, equatorial versus axial, can have a significant effect on the coupling.

(ii) D–B–A (Figure 2), where D is a dimethoxynaphthyl group, A is a dicyanovinyl group, and B is a series of norbornyl type rings.[2] This system has been investigated previously by using a CI CNDO/S calculation.[9]

(iii) $[(NH_3)_5Ru^{II}–B–Ru(NH_3)_5{}^{III}]^{5+}$, where B is a 2-, 3-, or 4-dithiaspiro ring compound (Figure 3).[4] An earlier study of this system was made using a modified tight binding calculation.[5] It is related to the extended Hückel approximation used here, but differs from the present calculation in that it neglects non-nearest-neighbor interactions and makes use of a periodic approximation to treat the bridge.

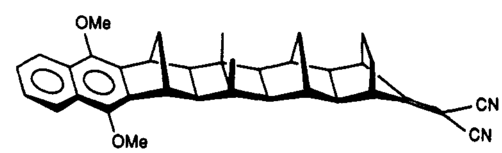
(iv) $[(NH_3)_5Os^{II}–iso–(pro)_n–Ru(NH_3)_5{}^{III}]^{4+}$, where iso is isonicotinyl, pro is proline, and n = 1–4 (Figure 4).[6] These oligoprolines provide a rigid spacer, in contrast to the use[11] of flexible peptides such as gly-gly and phe-phe. The trans isomers were used in the experimental study, and we have confined our attention to these.

The molecular geometries needed for the calculations were obtained from crystallographic data[30] in the case of (ii), and from



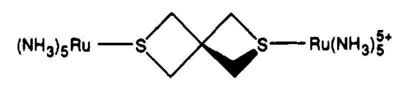
I

II

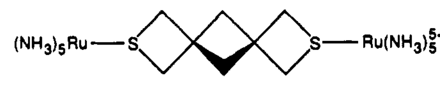


III

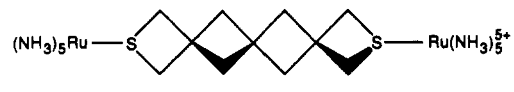
Figure 2. Structures of the dimethoxynaphthyl–dicyanovinyl systems attached with norbornyl bridges, series (ii).



I



II



III

Figure 3. Structures of the $Ru(NH_3)_5{}^{II}–Ru(NH_3)_5{}^{III}$ systems attached with dithiaspiro ring bridges, series (iii).

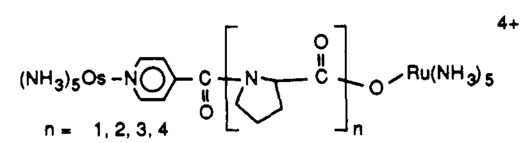


Figure 4. Structures of the $Os(NH_3)_5{}^{II}–Ru(NH_3)_5{}^{III}$ systems attached with isonicotinyl–(proline)$_n$ bridges, series (iv).

(30) Craig, D. C.; Paddon-Row, M. N. *Aust. J. Chem.* **1987**, *40*, 1951.

TABLE I: Dependence of H_{DA} on Number of Bridge Groups in the Biphenylyl–Bridge–Naphthyl Systems

compd[a]	H_{DA}, cm^{-1}: calc, present, using $\Delta\epsilon$	H_{DA}, cm^{-1}: calc, present, using eq 6	H_{DA}, cm^{-1}: expt[1]
I	237	228	184
II	180	167	140
III	77	55	64
IV	46	37	33
V	10	8	6
β, $Å^{-1}$	0.9	1.0	1.0
α, $Å^{-1}$		0.05	
$\langle b_v - a\rangle$, eV		1.9	

[a] Compound numbers refer to Figure 1. α denotes the decrease of $c_{jv}c_{kv}$ for a typical important LUMO v on going from the first to the last compound, calculated per Å, as discussed in text. $\langle b_v - a\rangle$ is an average of the energy of the LUMO bridge orbitals v, relative to the (matched) energy of the D (and hence A) orbital.

molecular mechanics calculations[31] for the remaining three series. H_{DA} was calculated both from the energy difference of the two delocalized orbitals and by making use of the partitioning technique.[32] In the calculations,[33] for the first-row atoms, a minimal atomic orbital basis set of Huzinaga[34] was used. For the metal ions, only d orbitals were used and the energy levels were taken from ref 35 and the overlap integrals needed to calculate the interaction matrix elements (λ and μ) in eq 7 were obtained from master tables.[36] Since the calculational method we have employed, namely the extended Hückel method, is relatively simple, we have chosen only the above minimal basis set.

Results and Discussion

The results obtained for the four series are given in Tables I–IV, and they are compared there with experimental and previously calculated results.

In order to compare the R dependence from experiment with theoretical calculations of the R dependence of H_{DA}, it is necessary to allow for any R dependence of FC. One possibility is for the value of R to be so large that the R dependence of FC becomes minor in relation to that of $|H_{DA}|^2$. Another is to make the studies under conditions where a plot of k_{ET} versus $\Delta G°$ (in a series of DA pairs in which $\Delta G°$ is varied at fixed R) is at a maximum ($\Delta G° = -\lambda$). Then, FC should have little R dependence. Still another possibility is to study the temperature dependence of the rate constant. This alternative has been followed, for example, for the series (iv) and it was found that the distance dependence of the nuclear factor is larger than that of the electronic factor. In the case of series (i), the distance dependence of λ_0 was taken into account in the framework of the dielectric continuum model while for series (ii) and (iii), the experimental estimate of H_{DA} was obtained from fitting different values of λ_0 for each of the molecules in the series to the charge-transfer spectra, thereby tacitly including the R dependence of FC. Hence, it is to be remembered that the "experimental" values themselves are dependent on the model chosen to correct for the R dependence of FC. In the following comparison, therefore, it is preferable to compare the distance dependence of the experimental and the presently calculated electronic matrix elements rather than the actual elements themselves.

(31) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
(32) Equation 6 was used, and the energies of the D orbitals alone were changed in order to match the D and A energies. This involved uniform changes in all of the D orbitals and so the change in any particular D orbital turned out to be very small, e.g., 0.03–0.01 eV. Had the correction been larger, it would have been necessary to have been more precise, namely to have changed both D and A energies, by noting the solvation of each and the fluctuations in solvation and in vibrational energy needed to reach the transition state. We hope to explore this question in a subsequent publication.
(33) The present program was taken from the Caltech MQM files. Overlap elements were included both in solving the secular equation and, of course, in eq 5. For series (iii) and (iv), ligands other than the bridge were left out, as was done in refs 5 and 10.
(34) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(35) Bearden, J. A.; Burr, A. F. "Atomic Energy Levels"; U. S. Atomic Energy Commision Report, 1965.
(36) Boudreaux, E. A.; Cusachs, L. C.; Dureaux, L. *Numerical Tables of Two-center Overlap Integrals*; Benjamin: New York, 1970.

TABLE II: Dependence of H_{DA} on Number of Bridge Groups in Dimethoxynaphthyl–Bridge–Dicyanovinyl System

compd[a]	H_{DA}, cm^{-1}: calc, present, using $\Delta\epsilon$	H_{DA}, cm^{-1}: calc, present, using eq 6	H_{DA}, cm^{-1}: expt[8]	H_{DA}, cm^{-1}: calc[9]
I	241	219	1317	507
II	138	129	483	112
III	64	59	241	35
β, $Å^{-1}$	0.6	0.6	0.7	1.1
α, $Å^{-1}$		0.03		
$\langle b_v - a\rangle$, eV		1.7		

[a] Compound numbers refer to Figure 2. α and $\langle b_v - a\rangle$ are as described in footnote *a* of Table I.

TABLE III: Dependence of H_{DA} on Number of Bridge Groups in the $(NH_3)_5Ru^{II}$–Bridge–$Ru(NH_3)_5^{III}$ Systems

compd[a]	H_{DA}, cm^{-1}: calc, present, using $\Delta\epsilon$	H_{DA}, cm^{-1}: calc, present, using eq 6	H_{DA}, cm^{-1}: expt[4]	H_{DA}, cm^{-1}: calc[5]
I	160	171	138	59
II	64	57	55	11
III	22	20	24	3
β, $Å^{-1}$	0.9	0.9	0.8	1.3
α, $Å^{-1}$		0.05		
$\langle b_v - a\rangle$, eV		2.4		

[a] Compound numbers refer to Figure 3. α and $\langle b_v - a\rangle$ are as described in footnote *a* of Table I.

TABLE IV: Dependence of H_{DA} on Number of Bridge Groups in the $(NH_3)_5Os^{II}$–Bridge–$Ru(NH_3)_5^{III}$ Systems

no. of proline units in bridge, n[a]	H_{DA}, cm^{-1}: calc, present, using $\Delta\epsilon$	H_{DA}, cm^{-1}: calc, present, using eq 6	H_{DA}, cm^{-1}: expt[b]
1	241	307	3.9
2	108	118	1.9
3	22	30	0.7
4	8.5	11	
β, $Å^{-1}$	0.8	0.75	0.7
α, $Å^{-1}$		0.034	
$\langle b_v - a\rangle$, eV		2.1	

[a] Structures given in Figure 4. α and $\langle b_v - a\rangle$ are as described in footnote *a* of Table I. [b] Reference 6. When the dependence of the $\lambda^{1/2}$ on r in eq 2 is corrected for, the experimental β becomes 0.6 (Sutin, N., private communication).

The individual results are described below.

(i) The present results for H_{DA} for series (i) are compared in Table I with the experimental values.[1] The latter were obtained in ref 1 from the measured rate constants by approximately correcting for the distance dependence of λ using the dielectric continuum model. $\Delta G°$ was measured to be independent of distance.[7] For the present system we find an exponential decrease, $|H_{DA}|^2 \propto \exp(-\beta R)$, where R is now the edge-to-edge separation distance between donor and acceptor, and where $\beta \simeq 0.9$–1.0 $Å^{-1}$. The experimental value is also 1.0 $Å^{-1}$.

(ii) The results for this system (Figure 1b) are given in Table II, where they are compared with experimental values[8] obtained from absorption coefficients of charge-transfer bands and with CI CNDO/S results.[9] The value of β calculated in the present case is 0.6 $Å^{-1}$, which is comparable with the experimental value of 0.7 $Å^{-1}$.

(iii) The calculated results for H_{DA} for this series are given in Table III, where they are compared with values[4] obtained from the experimentally observed intervalence transition bands and with previous calculations[5] based on a modified tight-binding approximation. The presently calculated value of β is 0.9 Å^{-1}, while the experimental value is 0.8 Å^{-1}.

(iv) The results for this series are given in Table IV. A plot of 2 ln H_{DA} versus R yields a slope β of 0.75 Å^{-1}. The value obtained in ref 6 from the analysis of the temperature effect on the rate constant, and from it from the preexponential factor, is 0.68 Å^{-1}, obtained as follows: The effect of the Franck–Condon factor (via the λ_0 and $\Delta G°$ terms in eqs 2 and 3) was estimated to contribute 0.91 Å^{-1} to β, while the overall experimental β was 1.59 Å^{-1}, leaving 0.68 for this electronic contribution to β. In a study[12] of an analogous system connected via a flexible oligoglycin bridge containing two to ten peptide bonds (i.e., $(gly)_n$, n = 3–11), a value of β = 1.1 Å^{-1} was obtained.

The results for the relative values of H_{DA} within a series (as measured by the values of β in the tables) are in better agreement with the results inferred from experiment than are the absolute values of H_{DA}. The absolute agreement is best for the series in Table I and poorest for that in Table IV. It is seen from eq 4 that errors in the calculated η_D and η_A will affect the absolute rather than the relative values of H_{DA} within a series and so it is perhaps not surprising that the latter are in better agreement with the experimental data. Investigation of other systems, both experimentally and theoretically, would, of course, be desirable.

The expression for the electronic coupling matrix element given by eq 6 involves, in effect, certain interaction matrix elements between the donor and acceptor states with the electronic states of the bridge, divided by the difference in the energy of the transferring electron and that of the bridge states. Hence, a bridge orbital which contributes significantly to electron transfer will tend to have relatively large coefficients on the atoms connected to the donor and acceptor and will also have an energy not too far removed from the energy of the orbital on D (A) containing the transferring electron. An inspection of the energies and coefficients of the bridge orbitals reveals that, for all the series presently studied, it is principally only the few lowest unoccupied energy states (virtual states) of the bridge that are responsible for the electron transfer. This situation is primarily due to the energetic proximity of these states with those of the donor and acceptor. These energy difference values, $b_v - a$ in eq 6, for the series (i)–(iv) are, on the average, about 1.9, 1.7, 2.4, and 2.1 eV, respectively. Thus, even though most of the bridges involve saturated organic groups, the energy levels of the bridges are nevertheless fairly close to that of the transferring electron, and so it is not surprising in retrospect that long-range electron transfer occurs at an appreciable rate in each of these systems.

The difference in the attenuation of the electronic matrix element H_{DA} among the four series is associated primarily with the difference in the coefficients of the bridge atoms at the point of contact with the donor and acceptor (c_{jv} and c_{kv} in eqs 7 and 8). In order to be able to make a comparison between different series, we give below and in the tables the value of α, the decrease of a typical product of these coefficients per angstrom; i.e., we divide the actual decrease in these coefficients along the series by the difference in R, the edge-to-edge separation distance of the donor and acceptor, for the first and last molecule of the series. The value of α is expected to provide a rough measure of the attenuation of the electronic overlap between the donor and acceptor with the bridge. Three or four bridge orbitals v (LUMO's) contribute significantly to H_{DA} in each system. For the series (i), the product of the coefficients $c_{jv}c_{kv}$ for a typical v decreases from 0.4 to 0.06, on going from compound I to V in Table I.[37] This decrease corresponds to a decrease of 0.05 per Å. For series (ii), the decrease is only from 0.4 to 0.25, which is equivalent to an α of 0.03 Å^{-1}. For series (iii), a decrease of 0.4 to 0.13 is found, giving an α of 0.05 Å^{-1}, while for series (iv), the coefficients decrease from 0.4 to 0.1, giving an α of 0.034 Å^{-1}. The ratio α/β is fairly constant, in the vicinity of 0.05 in the four series, and so β and α change in a more or less parallel manner on going from series to series. This parallelism reflects the approximate constancy of the average energy denominator, $\langle b_v - a\rangle$, on going from series to series (the averages cited earlier and in the tables).

This analysis suggests why the value of β is rather high in series (i) and (iii) (high α) while it is relatively low in (ii) and (iv) (low α). Further, in the case of series (ii) there are two points of contact for the bridge with the donor. Hence, the magnitude of the interaction of the bridge with the donor is greater than in, for example, series (i) with only one point of contact. It is clear from Tables I–IV that β is not an universal parameter and depends on the electronic structure of the bridge.

It is also seen from Tables I–IV that the partitioning results and the exact diagonalization results are generally very close. It is nevertheless useful to review why the difference is somewhat larger in certain cases (III and V in Table I) than in others: The partitioning equation is exact, but to obtain the splitting, the energy in the denominators is approximated by some average of the zeroth-order energies of the two principal orbitals in the partitioned matrix. If, instead of using the average, an exact energy had been used in the denominators, one of the solutions of the quadratic equation resulting from the partitioning method would have been precisely this exact eigenvalue. The other solution would have been an approximation to the second eigenvalue. The difference between it and the actual second eigenvalue of the exact secular equation reflects the error in using a mean value in the energy denominators. In each case, this error was examined and found to be indeed comparable to the difference in the two columns of the tables for H_{DA}. Some secular equations simply entailed a larger error when an average value of the energy was used in the denominators in the partitioned secular equation.

We plan next to explore the extension of these types of calculations to electron transfers in proteins.

Acknowledgment. We are pleased to acknowledge the support of this research by a grant from the National Science Foundation.

Supplementary Material Available: Structures and tables of coordinates of the systems presently studied (27 pages). Ordering information is given on any current masthead page.

(37) In this comparison, we ordered the important LUMO's (three in the case of Table I) by energy and compared for compounds I and V the product $c_{jv}c_{kv}$ for corresponding LUMO's. For Tables II–IV, there were four important LUMO's.