Chem. Rev. 1991, 91, 767–792

Quantum Chemical Probes of Electron-Transfer Kinetics: The Nature of Donor–Acceptor Interactions

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Received November 19, 1990 (Revised Manuscript Received April 10, 1991)

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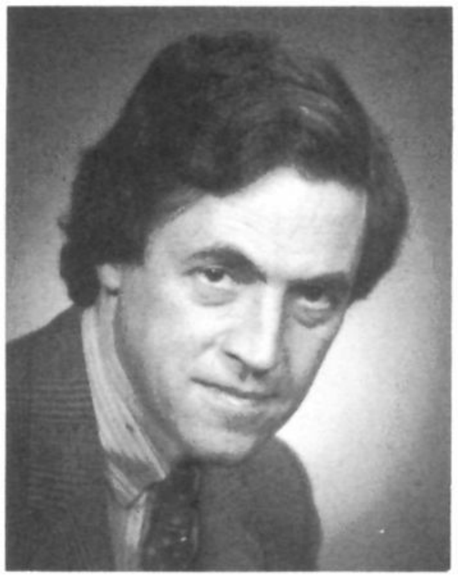
I. Introduction

Recent years have witnessed explosive and mutually stimulating advances in experimental and theoretical techniques for probing the mechanisms of electron-transfer kinetics and related chemical processes.[1-6] Against the background of the widespread success of the traditional adiabatic Marcus–Hush[7,8] theory, attention is being increasingly directed toward problems of long-range electron transfer in which indirect coupling of local donor and acceptor sites is mediated by the electronic properties of the intervening material.[3b,6,9-39] Thus, while the overall kinetic mechanism may involve a number of dynamical factors (both nuclear and electronic),[40,41] and while the electronic and nuclear manifolds may be strongly coupled,[42] there is an increasing interest in the details of the donor/acceptor coupling per se. This interest cuts across all branches of chemistry and includes inorganic, organic, and biochemical systems. Electronic coupling is clearly a crucial factor in intramolecular electron transfer over 10's of angstroms, such as occurs in protein- and porphyrin-based systems,[15-18,25,33-36] but its dynamical influence is also significant for redox partners in much closer contact, as exemplified by the bimolecular reactions of small transition-metal complexes[2,3,43-46] and other molecular species.[41,47]

The intellectual excitement generated by the above considerations has been enhanced by the recognition that the donor/acceptor interactions crucial to electron-transfer kinetics are also of central importance in a larger context which includes photoelectron (PES) and electron transmission (ETS) spectroscopy,[31,32] triplet energy transfer,[12c] and long-range coupling of electron spins.[36,48] A broad array of modern electronic structural techniques has allowed important progress toward the goal of a unified theoretical approach encompassing a broad range of situations including intra- and intermolecular coupling, electronically saturated and unsaturated bridging groups, and ground and electronically excited states.[22-45,47-51] Electronic modulation due to the long-range influence of the surrounding medium may also be included.[41,49-51] As the impact of electronic factors on the elucidation of electron-transfer mechanisms continues to expand, one increasingly encounters reference to the terminology of electronic mechanisms and pathways (e.g., "through-space" (TS) and "through-bond" (TB) coupling,[13,23] and "superexchange" of the "hole" and "electron" type[11,12]), and to the possibility of interference among them (both constructive and destructive).[5,6c,6d,11,12,26,27,31,32,44d]

The specific focus of this review is to survey recent progress in the application of theoretical and computational techniques of quantum chemistry to the elucidation of electronic factors controlling donor/acceptor interactions in electron-transfer reactions. The experimental data which provides the impetus for most of the theoretical work addressed here pertains pre-



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0009-2665/91/0791-0767$09.50/0

dominantly to condensed-phase systems involving disordered (i.e., nonperiodic) media. For the most part we shall be able to deal with models based on discrete molecular clusters (either large molecules or supermolecules) consisting of localized donor, acceptor, and intervening bridging sites. We shall confine our attention to cases of relatively weakly interacting donor/acceptor systems where, indeed, the occurrence of localized states may be safely assumed. The recent review of solid-state electron-transfer processes by Mikkelsen and Ratner[5] dealt also with situations of more extended electronic states which may be important in periodic environments. As much as possible, the present review will deal with purely electronic aspects of electron transfer, although attention will be drawn to vibronic factors[42] as deemed necessary.

The overall goal of the review is to provide a unified picture of the combined capabilities of modern quantum chemistry in yielding accurate quantitative measures of the strength of electronic coupling and at the same time providing compact models for understanding the coupling in terms of the concepts of molecular bonding and electronic structure. The review should thus serve to complement other recent reviews which have dealt with electron-transfer kinetics on a broader basis.[2,3,4a,5]

The remainder of the paper is organized as follows. A brief sketch of the kinetic and spectroscopic background is given in section II so as to provide a focused context for the electronic structural considerations. In section III a number of theories for donor/acceptor coupling are presented in terms of suitably defined electronic states and their constituent orbitals. The various direct and indirect coupling pathways are discussed in terms of many-electron or effective one-particles ("electron" or "hole") models. Specific aspects of computational implementation are dealt with in section IV. Results for a set of illustrative applications are given in section V, and conclusions are summarized in section VI.

II. Kinetic and Spectroscopic Context

Electron-transfer processes are conveniently discussed in terms of suitable electronic wave functions, $\psi_k(\{X_q\})$, within the Born–Oppenheimer framework, in which the wave functions and corresponding electronic Hamiltonian, $H_{el}(\{X_q\})$, depend parametrically on the nuclear coordinates, $\{X_q\}$.[2,3,5,42] We consider the transition between an initial electronic state of a system, ψ_i, in which an electron can be said to be localized in a donor region (D), and a final state, ψ_f, in which an electron has in effect been transferred from the donor region to a spatially distinct "acceptor" region (A). We defer until the next section the question as to how literally such a process can be taken as an actual "one-electron process" (i.e., one in which all but one of the electrons in the whole system are passive in the course of the process). The various contributions to the transfer dynamics from the nuclear and electronic degrees of freedom may be described by suitable classical, semiclassical, or quantum mechanical theories.[2,3,5,52,53] For electron-transfer processes occurring in dissipative condensed-phase media, the dynamics can often be cast as a chemical kinetic process characterized by a rate constant, k_{et},[26,29] as in eq 1

$$\mathrm{D^-{-}B{-}A} \xrightarrow{k_{et}^{intra}} \mathrm{D{-}B{-}A^-} \tag{1a}$$

$$\mathrm{D^-{-}L + L'{-}A \rightarrow D^-{-}L \cdots L'{-}A} \xrightarrow{k_{et}^{inter}} \mathrm{D{-}L \cdots L'{-}A^- \rightarrow D{-}L + L'{-}A^-} \tag{1b}$$

Equation 1 distinguishes schematically two types of electron-transfer process: an intramolecular (or unimolecular) process in which the reacting sites are considered to be chemically bound (generally through covalent links to an intervening bridge, B), and an intermolecular (or bimolecular) process in which separate reactants come into contact, forming a bimolecular encounter complex, which then reacts, eventually yielding separate product species. In order to facilitate comparison of the two types of process, we represent each reactant in the bimolecular case as having a localized D or A site and a complementary moiety, L or L′ (the notation L and L′ is employed in a very general and schematic sense, although in the case of transition-metal complexes, one may make the obvious identification with "ligand").

In spite of the superficially sharp distinction between the processes of eqs 1a and 1b, the differences in practice may tend to be blurred. Effective electronic overlap between D and A does not necessarily require covalent bonding between reactants,[43–45] and superexchange models of the TB type may be applied to more general situations provided that the space between donor and acceptor sites is spanned by sequences of overlapping orbitals. Furthermore, the multiplicity of approach geometries expected in a bimolecular process can have its counterpart in the intramolecular process, if the molecule has accessible low-frequency conformational degrees of freedom.[29c,54,55] A unified view of eqs 1a and 1b is possible if the encounter complex is taken as a "supermolecule", in which case the L···L′ aggregate corresponds formally to the bridge B.

The kinetic bottleneck in eq 1 may or may not involve the electron hop from D to A, depending on the competition between the dynamics of the electronic manifold and that of the nuclear modes (e.g., translational or orientational diffusion involving the solute or solvent molecules).[40] Thus a comprehensive treatment of the kinetics must involve the dynamics of all the manifolds. Nevertheless, for the purpose of illustrating the role of the electronic coupling of donor and acceptor we first consider thermally activated electron transfer and adopt a conventional transition-state model[2,3,5,7,8]

$$k_{et} = \nu_{eff}\kappa_{el}\Gamma_n \exp(-E^*/k_BT) \tag{2}$$

where the three prefactors denote, respectively, the effective frequency for motion along the reaction coordinate (Q), the electronic transmission factor, and the nuclear tunneling factor, and where E^* is the activation energy. In the case of an intermolecular process (eq 1b), it is generally assumed (in the absence of diffusional bottlenecks) that the concentration of the encounter complex, D⁻–L···L′–A, is related to that of the separate reactants by a preequilibrium constant.[3a]

The quantities appearing in eq 2 may be understood in terms of the energy profiles presented in Figure 1. We adopt a standard diabatic representation in which the initial and final electronic states are by construction taken as the valence bond structures corresponding, respectively, to the reactants and products of the re-

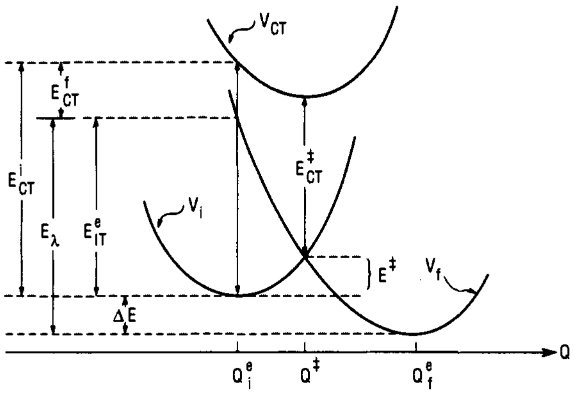


Figure 1. Diabatic energy profiles for ψ_i (V_i), ψ_f (V_f), and an intermediate charge-transfer state (V_{CT}), as a function of the electron-transfer reaction coordinate Q. The equilibrium values of Q for ψ_i and ψf, and the transition state for thermal electron transfer are given, respectively, by Q^e_i, Q^e_f, and $Q^{\ddagger}$. The reorganization energy, E_λ, is the sum of the reaction energy ΔE (taken as positive for an exothermic process), and the optical (IT) excitation energy, E^e_{IT}. The diabatic activation energy for thermal electron transfer is $E^{\ddagger}$, and the vertical separation between $V_i = V_f$ and V_{CT} at $Q^{\ddagger}$ is $E^{\ddagger}_{CT}$. The corresponding vertical charge-transfer energies at Q^e_i are E^i_{CT} (from V_i) and E^f_{CT} (from V_f).

action.[2,43,44] The diabatic representation is not diagonal with respect to the electronic Hamiltonian; i.e., in general

$$H_{if} \equiv \langle \psi_i | H_{el} | \psi_f \rangle \equiv \int \psi_i^* H_{el} \psi_f \, d\tau \neq 0 \qquad (3)$$

(where we introduce standard bra and ket notation), in contrast to the adiabatic representation, where by definition, H_{el} is diagonal (in the remainder of this review, the subscript el is suppressed). For orthogonal ψ_i and ψ_f, where

$$S_{if} \equiv \langle \psi_i | \psi_f \rangle = 0 \qquad (4)$$

H_{if} is the so-called electron-transfer integral (the more general case,[2,5,30,38,43,56] where $S_{if} \neq 0$ is dealt with in section III).

Each diabatic state has an associated potential energy function for nuclear motion:

$$V_s(\{X_q\}) \equiv \langle \psi_s(\{X_q\}) | H | \psi_s(\{X_q\}) \rangle \qquad s = \mathrm{i, f} \qquad (5)$$

In the simplest diabatic model the $\{X_q\}$ dependence of ψ_s is suppressed and ψ_s (s = i or f) is evaluated for some convenient set of $\{X_q\}$, (e.g., the equilibrium values). A coordinate of particular significance in the present discussion is the reaction coordinate Q which connects the minima of the reactant (V_i) and product (V_f) wells. In the case illustrated in Figure 1,[2,3,7,8] the intersection of V_i and V_f at $Q^{\ddagger}$ defines the diabatic activation energy $E^{\ddagger}$ for thermal electron transfer. More complex situations may arise, of course, in the case of multidimensional configuration spaces (e.g., gated control of the kinetics).[54,55]

The occurrence of thermal electron transfer at the diabatic crossing is a manifestation of Franck–Condon control of electronic processes (the nuclear kinetic energy is the same before and after the transition).[7,8] For optical electron transfer, generally referred to as intervalence transfer (IT), the same Franck–Condon control causes the most probable process to be the vertical one corresponding to E^e_{IT} and occurring at the equilibrium geometry (Q^e_i) of ψ_i (see Figure 1).[8b,57] In general, the reaction coordinate Q has contributions

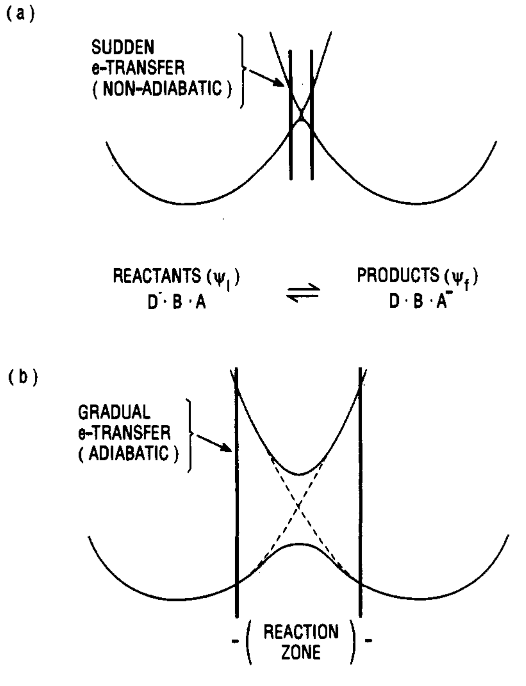


Figure 2. Schematic depiction of the limits of (a) weak (nonadiabatic) and (b) strong (adiabatic) coupling, illustrated for the case of intramolecular electron transfer (eq 1a). The assignment of nonadiabatic and adiabatic limits is based on the assumption of no dynamical involvement of solvent in the rate-determining step (cf. ref 40).

from vibrational modes of the reactants and also from the polarization models of the surrounding medium.[7,8,50]

The transfer integral (H_{if}) is of central importance in the present review, providing a compact link between the electronic structural details of the donor/acceptor interactions and the overall rate (for thermal) or intensity (for optical) of the electron-transfer process.[2,3,5,8b] In the diabatic representation adopted here, we assume that the magnitude of H_{if} dominates that of the electronic matrix elements associated with the nuclear momentum and kinetic energy operators (the nonadiabatic coupling terms).[2] This situation usually pertains, if as described above, ψ_i and ψ_f are chosen to correspond to single valence bond structures which by their nature are little affected by changes in nuclear coordinates (the nuclear operators of course, yield zero matrix elements in the limit where the ψ_k are defined to be totally independent of $\{X_q\}$). In cases where H_{if} in the diabatic representation does turn out to be very small or zero (e.g., because of symmetry), then one must include the nonadiabatic coupling terms.[58]

In cases of weakly interacting systems, the diabatic representation provides a very convenient zeroth-order basis set. However, in general it is also useful to examine the energies in the adiabatic representation, in which H is diagonal.[2,5,43,44] The avoided crossing relative to the diabatic crossing (at $Q^{\ddagger}$) becomes increasingly pronounced as the magnitude of H_{if} increases. As depicted in Figure 2, we find a transition from "sudden" electron transfer in the nonadiabatic Franck–Condon regime (where the coupling is weak) to the adiabatic regime in which the electron transfer occurs more "gradually" with progress along the reaction coordinate. The "cuspy" nature of the energy curves tends to convey a distinctive character to electron-transfer reactions in weakly interacting systems, whereas for stronger coupling, the smooth profile of the adiabatic energy curve for electron transfer resembles that for other classes of thermal reactions.[43d]

The avoided crossing leads to a correction to the diabatic estimate for the activation energy. In a simple harmonic model, the correction is simply $-|H_{if}|$.[3,5] However, when the solvent dominates the reaction coordinate, the correction is expected to have a more complex form and to be smaller in magnitude if the influence of the electronic polarization response of the solvent and the transfer integral H_{if} are included in a fully self-consistent manner. In this approach, introduced recently by Kim and Hynes,[50] the wave functions are allowed to vary with Q in contrast to the traditional approximate model based on fixed diabatic wave functions. A related approach has been advocated by Knapp and Fischer.[59]

Useful insight into the role of the transfer integral in thermal electron transfer in cases where nuclear tunneling may be neglected is provided by the semiclassical Landau–Zener model,[60] in which the electronic transmission coefficient κ_{el} is given as[2,3,53]

$$\kappa_{el} = 2P_0/(1 + P_0) \qquad (6)$$

where the probability P_0 for a transition from the initial state (V_i) to the final state (V_f) diabatic energy surface on a single passage of the system through the crossing region is given by

$$P_0 = 1 - \exp(-2\pi\gamma) \qquad (7)$$

and where in the harmonic limit where $V_i(Q)$ and $V_f(Q)$ have the same curvature

$$2\pi\gamma = |H_{if}|^2\pi^{3/2}/h\nu_{eff}[k_BTE_\lambda]^{1/2} \qquad (8)$$

The quantity E_λ in eq 8 is the reorganization energy,[3,7,8] which is equal to the sum of E^{e}_{IT} and the exothermicity ΔE (see Figure 1). For a thermoneutral exchange process ($\Delta E = 0$), we have[2,3,5,53]

$$E_\lambda \cong 4E^* \qquad (9)$$

The treatment of Kim and Hynes[50] leads to more complex relationships between E_λ and E^* and also has implications for the formulation of the surface hopping probability, P_0.

When H_{if} is sufficiently small in magnitude, the exponential of eq 5 can be expanded and truncated after the linear term, yielding the nonadiabatic limit in which κ_{el} is proportional to

$$\kappa_{el} = 2|H_{if}|^2\pi^{3/2}/h\nu_{eff}[k_BTE_\lambda]^{1/2} \qquad (10)$$

In the other limit, in which $2\pi\gamma \gg 1$, then $\kappa_{el} \approx 1$, and the reaction becomes adiabatic. In this limit, in cases where solvent polarization dominates the reaction coordinate, the dynamical bottleneck controlling the rate constant may switch from the inertial crossing of the barrier (as in the transition-state model) to the diffusional dynamics of the solvent motion.[40] The transfer integral also plays a key role in more complicated situations in which electron-transfer dynamics cannot necessarily be characterized by a conventional rate constant, as discussed, for example, by Joachim,[28] Reimers and Hush,[29] and Kosloff and Ratner.[26] These analyses have yielded a number of interesting predictions which await experimental confirmation in suitably designed materials.

We have discussed the manner in which the transfer integral H_{if} helps to control the thermal electron-transfer rate constant, k_{et}. In favorable situations, values of H_{if} may accordingly be inferred from experimental values for k_{et}.[2,3,5] In a similar vein, the intensity of the optical electron transfer process (the vertical excitation characterized as E^{e}_{IT} in Figure 1) can be related to the magnitude of H_{if} in terms of the transition moment, $\vec{\mu}^{op} \equiv \langle\psi^a_1|\vec{\mu}|\psi^a_2\rangle$, where $\vec{\mu}$ is the electronic dipole operator.[8b,57] An approximate expression for $\vec{\mu}^{op}$, based on first-order perturbation theory (and thus restricted to small ratios, H_{if}/E^{e}_{IT}), is given by[8b]

$$|\vec{\mu}_{op}| = e\bar{r}|H_{if}|/E^{e}_{IT} \qquad (11)$$

where $\bar{r}$ is the effective donor/acceptor separation distance, assumed to be related to dipole moment expectation values by

$$\bar{r} = |\vec{\mu}_{ii} - \vec{\mu}_{ff}|/en \qquad (12)$$

and where e is the electronic charge and n is the number of electrons in the system. Hush has derived the following expression, consistent with eq 11, which allows H_{if} to be estimated directly from optical data:[3b]

$$|H_{if}|\ (\mathrm{cm}^{-1}) = [(2.06 \times 10^{-2})/\bar{r}]\{\epsilon_{max}\bar{\nu}_{max}\Delta\bar{\nu}_{1/2}\}^{1/2} \qquad (13)$$

where $\bar{r}$ is in angstroms, where ϵ_{max} is the molar extinction coefficient, and $\bar{\nu}_{max}$ and $\Delta\bar{\nu}_{1/2}$ (in cm^{-1}) are the maximum frequency and half-width of the optical absorption spectrum.

As noted above, a number of additional spectroscopic probes of the transfer integral H_{if} are available, and we shall make specific reference to these in the remainder of the review.

III. Theoretical Models for the Transfer Integral

A. Characterization of States

In section II, adopting a conventional two-state Landau–Zener model,[60] we have seen the central kinetic role played by the electron-transfer integral, H_{if}, which couples initial (ψ_i) and final (ψ_f) diabatic states. Here we pursue the detailed formulation of models for H_{if}. After first reviewing expressions defined in terms of generic states, we shall then turn to the specific characterization of the states so as to understand the manner in which H_{if} captures the electronic details of donor and acceptor interactions, as mediated by the presence of molecular "bridges" (see eq 1). In the two-state model, it is assumed that all the dynamics may be satisfactorily treated by a single pair of electronic states over the relevant range of coordinate values (of course, for an adiabatic process a single (adiabatic) state suffices by definition). Of particular importance is the range of the reaction coordinates Q between Q^e_i and Q^e_f (Figure 1). However, variations with respect to other nuclear coordinates (orthogonal to Q) must frequently be considered as discussed below. Within the two-state framework one may, of course, employ as large an auxiliary basis set as necessary to yield appropriate representation of the two-state space of interest. This space may be expressed either in terms of a stationary (adiabatic) or nonstationary (diabatic) pair of states. While the Landau–Zener model in eqs 7 and 8 is displayed in a diabatic two-state basis, one should note that it can equally well be represented in the corresponding adiabatic basis.[2]

We adopt the following notation for the two-state model. The diabatic states (the valence bond structures corresponding to reactants and products) are denoted $\psi_1^{\rm d} \equiv \psi_{\rm i}$ and $\psi_2^{\rm d} \equiv \psi_{\rm f}$, while the adiabatic states are labeled $\psi_1^{\rm a}$ and $\psi_2^{\rm a}$. The two bases are related by the transformation ρ

$$\psi_u^{\rm a} = \sum_s \psi_s^{\rm d} \rho_{su} \qquad u = 1 \text{ or } 2 \tag{14}$$

$\psi_1^{\rm a}$ and $\psi_2^{\rm a}$ are orthonormal, whereas $\psi_1^{\rm d}$ and $\psi_2^{\rm d}$ are not orthogonal in general. The basis for expanding diabatic functions is denoted $\{\chi\}$

$$\psi_s^{\rm d} = \sum_j \chi_j C_{js}^{\rm d} \qquad s = 1 \text{ or } 2 \tag{15}$$

Correspondingly, the adiabatic functions are given in this basis by the transformation

$$\mathbf{C}^{\rm a} = \mathbf{C}^{\rm d}\rho \tag{16}$$

The set $\{\chi\}$ is taken as orthonormal and its members are assumed to correspond to fixed charge distributions (i.e., independent of nuclear coordinates, $\{\chi_q\}$). However, it is important to note that $\psi_1^{\rm d}$ and $\psi_2^{\rm d}$ (and hence also $H_{\rm if}$) may depend on $\{X_q\}$ through the $\{X_q\}$ dependence of the mixing coefficients $C_{js}^{\rm d}$. We also note that $\psi_1^{\rm a}$ and $\psi_2^{\rm a}$ depend on $\{X_q\}$ through the $\{X_q\}$ dependence of both the $C_{js}^{\rm d}$ and the ρ_{su}.

For clarity below, we reserve the fixed subscripts i and f for the diabatic states, whereas j,s and u are variable subscripts. Furthermore, we note that the Schrödinger Hamiltonian and the associated wave functions (ψ's and χ's) involve in general the full number of electrons (n) in the reactive system. As a first approximation, the χ_j's defined above may be taken as a set related by various one-particle excitations (electron or hole, as discussed below). In more general situations one might allow many-electron relaxation to accompany the primitive one-particle transfers, e.g., by including virtual many-particle excitations or by adopting distinct basis sets (say, $\{\chi_j^{\rm i}\}$ and $\{\chi_j^{\rm f}\}$) to reflect state-specific relaxation effects associated with the initial ($\psi_{\rm i}$) and final ($\psi_{\rm f}$) diabatic states. Distinct bases might also be adopted if one employed different zeroth-order Hamiltonians (channel Hamiltonians, $H^{\rm i}$ and $H^{\rm f}$)[59,61] to define $\psi_{\rm i}$ and $\psi_{\rm f}$. The use of "one-particle" language introduced above suggests that effective one-particle models may be projected out of the full n-electron model, a subject dealt with in section III.D.

In employing the two-state model, one assumes that the diabatic and adiabatic states essentially coincide in the vicinity of the initial ($Q_{\rm i}^{\rm e}$) and final ($Q_{\rm f}^{\rm e}$) equilibrium configurations:

$$\psi_1^{\rm a} \approx \psi_1^{\rm d} \equiv \psi_{\rm i} \qquad Q \approx Q_{\rm i}^{\rm e} \tag{17a}$$

$$\psi_2^{\rm a} \approx \psi_2^{\rm d} \equiv \psi_{\rm f} \qquad Q \approx Q_{\rm f}^{\rm e} \tag{17b}$$

While this is generally a reasonable assumption for ground-state thermal processes,[2] it may not be for photoinitiated processes in which one may prepare initial states which are superpositions of two or more adiabatic states, over and above whatever adiabatic state (or states) may be necessary to characterize the final state of the process.[33-35] In this situation, or in the general case where a high density of molecular electronic states renders a two-state model inadequate, one must have recourse to more general dynamical models than the Landau–Zener model. The reader is referred to a number of discussions of such models in the literature.[24f,26,28,29,42,62] An obvious example of a multistate effect is provided by the situation in which some intermediate diabatic state is sufficiently low in energy that the kinetic process involves a residence of finite duration in this state in the course of the overall electron transfer.[26,29,36b,c,42] When energy separations are large relative to off-diagonal coupling elements and reorganization energies, then intermediate states enter only as virtual states (χ_j) which contribute to the overall electron transfer integral, $H_{\rm if}$. Vibronic effects associated with such states may be eliminated by the use of the Condon approximation and the closure relation for vibrational wave functions[42] (see also ref 27d).

The formulation of a discrete electronic model requires the definition of a "system" in terms of a molecular or supermolecular species (as depicted in eq 1) whose electrons are treated explicitly. For condensed-phase processes, the energetic and dynamical influence of the longer range environment may be simulated by a variety of devices,[24,25,33c,41,49-51] some of which are discussed below. It is noteworthy that statistical mechanical treatments employing path integral techniques are now capable of treating the long-range influence of a thermally disordered medium on electronic structure in a self-consistent manner, although so far the applications are limited to a single electronic degree of freedom.[51]

One has great flexibility in defining the components of the molecule or supermolecule representing the reactive system. The intervening material between the donor (D) and acceptor (A) sites may be characterized by a single aggregate bridge (B) or may be subdivided into a number of subunits, B_m. This decomposition is especially useful when the "bridge" is actually composed of nonbonded units in contact (e.g., the L and L′ units in eq 1b)[44d] or when it consists of a number of chemically meaningful moieties linked by covalent bonds (e.g., methylene groups in an alkyl chain).[22-27,31,32] It is often convenient to identify the index of a basis function, χ_j, with a particular site in situations where the overall electron transfer from donor to acceptor sites is analyzed in terms of a sequence of virtual intermediate states. In this approach (the essence of superexchange coupling), basis states χ_1, χ_{j+1} (j = 1 to m), and χ_{m+2} may, for example, represent zeroth-order (virtual) states in which an electron is located, respectively on the donor site (χ_1), the $j^{\rm th}$ of m bridge sites (χ_{j+1}), and the acceptor site (χ_{m+2}), with the remaining electrons confined to an ($n-1$)-electron core. An analogous notation may be employed for the complementary superexchange process in which a hole passes from the acceptor site to the donor site. These ideas will be elaborated below, after establishing the correspondence between many-electron states and one-electron orbitals.

B. Two-State Models

We review a number of relationships within the two-state framework, which will be employed in subsequent sections. The correspondence between diabatic and adiabatic two-state models arises from the secular determinant (with the assumption that $S_{\rm if}$ = 0):

$$|\mathbf{H} - E^{a}\mathbf{1}| = 0 \qquad (18)$$

where

$$\mathbf{H} = \begin{pmatrix} H_{ii} & H_{if} \\ H_{fi} & H_{ff} \end{pmatrix} \qquad (19)$$

and where E^a is the energy eigenvalue and 1 is the unit matrix. Except as noted, all quantities are assumed to refer to an arbitrary value of Q. We also assume real quantities. If the transformation ρ (eq 16) is expressed as

$$\rho = \begin{pmatrix} \cos\eta & -\sin\eta \\ \sin\eta & \cos\eta \end{pmatrix} \qquad (20)$$

then the adiabatic eigenvalues are given by[24f]

$$E_1^a = H_{ii} + H_{if}\tan\eta \qquad (21a)$$

$$E_2^a = H_{ff} - H_{if}\tan\eta \qquad (21b)$$

and

$$\tan 2\eta = 2H_{if}/(H_{ii} - H_{ff}) \qquad (22)$$

(note that eq 2 of ref 24f should involve tan η instead of cot η).

These equations allow the parameters of the adiabatic representation (ρ, E_1, and E_2) to be specified in terms of the elements of the diabatic Hamiltonian.[5,24g] Conversely, the elements of **H** (eq 19) may be obtained from the adiabatic quantities; e.g., we find that

$$H_{if} = (1/2)(E_2^a - E_1^a)\sin 2\eta \qquad (23)$$

where sin 2η is given by $-2(\rho_{11})(\rho_{12})$.[25a,b] (We denote the adiabatic splitting by $\Delta_E{}^a = E_1^a - E_2^a$). This equation, which is exact for a two-state problem, also offers a useful device for approximating an effective transfer integral in situations where two adiabatic states are dominated by two basis functions and are well separated from other adiabatic states.[25,28] In this case, the coefficients of the dominant functions may be used to approximate the value of η according to eq 20 after any necessary orthogonalization and renormalization have been carried out.

If $S_{if} \neq 0$ (cf. eq 4) then the effective Hamiltonian matrix, **H′**, for the two-state dynamical process is replaced by

$$\mathbf{H}' = \left(1/(1-S_{if}^2)\right)\begin{pmatrix} H_{ii} - S_{if}H_{fi} & H_{if} - S_{if}H_{ff} \\ H_{fi} - S_{fi}H_{ii} & H_{ff} - S_{fi}H_{if} \end{pmatrix} \qquad (24)$$

This matrix may be derived as a generalization of the orthogonal two-state model employed by Zener.[60a] It may also be derived in a dynamic context, where the time-dependent Schroedinger equation is represented by a nonorthogonal two-state basis.[61] If in addition, ψ_i and ψ_f are defined as eigenfunctions of zeroth-order channel Hamiltonians H^i and H^f, respectively, then the elements of **H′** may be written in terms of the operators V^i and V^f, which are defined by

$$H = H^i + V^f = H^f + V^i \qquad (25)$$

The off-diagonal elements of the overlap-adapted **H** matrix (i.e., **H′**) have the proper invariance with respect to the zero of energy.[43a] However, **H′** is seen to be non-Hermitian for $H_{ii} \neq H_{ff}$. In a more general vibronic framework, any discrepancy in electronic energy for a radiationless process would be compensated by energy flow between electronic and vibrational manifolds. Within a purely electronic framework, the desired Hermitian behavior (necessary to satisfy the requirements of detailed balance) may be achieved by various devices, including orthogonalization of ψ_i and ψ_f, or simply replacing H_{ii} and H_{ff} in H_{fi} and H_{if}, respectively, by an average value[38,56] (e.g., the arithmetic or geometric mean or the value at the crossing). In the limit of small S_{if}, symmetric (Lowdin)[63] orthogonalization yields (via Taylor expansion)

$$H'_{if} = H'_{fi} \cong H_{if} - \mathrm{S}_{if}(H_{ii} + H_{ff})/2 \qquad (26)$$

accurate through second order in off-diagonal elements (S_{if} and H_{if}). H'_{if} is the generalized transfer integral for the case of nonorthogonal diabatic states. In the remainder of the paper the "prime" on **H′** will be included only when the distinction between **H** and **H′** is of specific interest.

Equations 18–23 give the exact (variational) two-state results. When $|H_{ii} - H_{ff}| \gg |H_{if}|$ (or equivalently, sin $\eta \approx \eta$ and tan $2\eta \approx 2\eta$) then the adiabatic energies and coefficients are well approximated, respectively, by second- and first-order Rayleigh-Schrödinger perturbation theory (RSPT):

$$\psi_1^a \cong \psi_i + (H_{if}/(H_{ii} - H_{ff}))\,\psi_f \qquad (27)$$

$$\psi_2^a \cong \psi_f + (H_{if}/(H_{ff} - H_{ii}))\,\psi_i \qquad (28)$$

The optical transition moment between these two states

$$\vec{\mu}_{12}^{\,op} \equiv \langle\psi_1^a|\vec{\mu}|\psi_2^a\rangle \qquad (29)$$

is then equivalent to eq 11, under the assumption that $\vec{\mu}_{if} \equiv \langle\psi_i|\vec{\mu}|\psi_f\rangle$ may be neglected (the form of eq 11 is, of course, applicable to any value of Q such that the requirements of perturbation theory are satisfied). The effective donor/acceptor separation $\bar{r}$ (eq 11) may be evaluated by a suitable interatomic distance, based on the atomic coordinates of the reactive system.

With the *exact* two-state model fully specified, we now turn to the more challenging task of defining an *effective* two-state model and a corresponding two-state **H** matrix, projected on a space of $m + 2$ zeroth order basis functions, χ_j. If good zeroth order candidates for ψ_i and ψ_f are identified (say $\chi_1 \approx \psi_i$ and $\chi_{m+2} \approx \psi_f$), then a number of methods based either on time-independent or time-dependent perturbation theory may be employed to calculate effective values of H_{if}.[26,29] These results are generally valid when the energies of the "intermediate states", χ_{j+1} ($j = 1-m$), are well separated from those of states χ_1 and χ_{m+2} (i.e., by gaps large relative to the coupling elements H_{jk}, $j \neq k$).

Joachim has attempted to define an effective two-state Hamiltonian using a nonperturbative time-dependent procedure applicable in cases where the adiabatic states are dominated by two basis functions (say χ_1 and χ_{m+2}, as discussed above):[28]

$$\psi_1^a = C_{11}\chi_1 + C_{m+2,1}\chi_{m+2} + \ldots \qquad (30a)$$

$$\psi_2^a = C_{12}\chi_1 + C_{m+2,2}\chi_{m+2} + \ldots \qquad (30b)$$

When these coefficients form a nearly orthonormal pair of vectors; i.e.

$$\sum_{j=1\text{ and }m+2} C_{ju}C_{jv} \cong \delta_{uv} \qquad u,v = 1 \text{ or } 2 \qquad (31)$$

Joachim's effective (2 × 2)-Hamiltonian matrix approaches that defined by Larsson (e.g., see the expression for H_{if} in eq 23) for use in situations where the two-state approximation is valid. However, when intermediate states begin to come into near resonance with χ_1 or χ_{m+2}, then discontinuities may arise in Joachim's procedure.[28] Reimers and Hush have argued that no effective two-state model is valid in this case and have offered an alternative definition of the effective transfer integral.[29] (One should carefully distinguish two different senses in which the term "resonance" is employed here: resonance between donor and acceptor levels (at the crossing, $H_{\mathrm{ii}} = H_{\mathrm{ff}}$) and resonance between donor (or acceptor) levels and intermediate ("bridge") levels. This usage differs somewhat from the dynamically based definition of resonance adopted by Joachim). Further perspective on the two-state model has been obtained by Kosloff and Ratner through a comparison of results based on time-independent and time-dependent perturbation theory, and also nonperturbative time-dependent dynamics involving a four-state model with provision for damping.[26]

C. Perturbative Approaches

We now consider specific results for effective two-state transfer integrals based on perturbation theory (RSPT) and related techniques. A superscript "(n)" denotes n-th order quantities (i.e., those including terms through n-th order in the coupling elements $H_{jk} \equiv \langle \chi_j | \mathrm{H} | \chi_k \rangle$, $j \neq k$, where H is the full system Hamiltonian). For simplicity we assume initially that the coupling among $m + 2$ zeroth-order functions, χ_j, is governed by a tight-binding approximation; i.e., only nearest neighbor coupling elements have non-zero values, where $j = k \pm 1$ (see comments about the definition of basis states at the end of section III.A). The tight-binding assumption, of course, includes neglect of "direct" coupling, i.e., $H_{1,m+2} = 0$ for $m \geq 1$). The assumption that bridge-mediated superexchange coupling will always dominate direct coupling is not always justified, and in general it is of interest to ascertain how the two types of coupling interfere with each other[30,32] (i.e., constructively or destructively). These matters are considered below. Finally, we define $E_j^{(0)} \equiv \langle \chi_j | H | \chi_j \rangle$ (i.e., if the χ_j are taken as eigenfunctions of some effective $H^{(0)}$, then the first-order energies $H_{jj}^{(1)}$ are zero, where $H = H^{(0)} + H^{(1)}$).

1. A Single Bridge State (m = 1)

a. Resonant Case. We first consider resonant electron transfer ($E_1^{(0)} = E_3^{(0)}$, with $|H_{j2}/(E_j^{(0)} - E_2^{(0)})| \ll 1$, $j = 1$ and 3), and employ RSPT, obtaining the following first-order approximations for ψ_{i} and ψ_{f}:

$$\psi_{\mathrm{i}}^{(1)} = \chi_1 + (H_{12}/\Delta E^{(0)})\chi_2 \tag{32a}$$

$$\psi_{\mathrm{f}}^{(1)} = \chi_3 + (\mathrm{H}_{32}/\Delta \mathrm{E}^{(0)})\chi_2 \tag{32b}$$

where $\Delta E^{(0)} = E_1^{(0)} - E_2^{(0)} = E_3^{(0)} - E_2^{(0)} = -E_{\mathrm{CT}}^{*}$ (Figure 1). Accordingly, we find

$$H_{\mathrm{if}}^{(2)} = (2H_{12}H_{32}/\Delta E^{(0)})(1 + E_2^{(0)}/2\Delta E^{(0)}) \tag{33}$$

$$H_{\mathrm{ii}}^{(0)} = H_{\mathrm{ff}}^{(0)} = E_1^{(0)} \tag{34}$$

and

$$S_{\mathrm{if}}^{(2)} = H_{12}H_{32}/(\Delta E^{(0)})^2 \tag{35}$$

Hence from eq 24 we obtain

$$(H'_{\mathrm{if}})^2 = H_{12}H_{32}/\Delta E^{(0)} \tag{36}$$

Note that this derivation for the resonant case does not require $H_{12} = H_{32}$. Note also that the leading (i.e., second-order) term in H'_{if} involves only the zeroth-order diagonal elements of H_{el} ($H_{\mathrm{ii}}^{(0)}$ and $H_{\mathrm{ff}}^{(0)}$).

An alternate route to the result in eq 36 is to obtain the adiabatic states ψ_1^{a} and ψ_2^{a} by using degenerate second-order perturbation theory. For a symmetric situation, where $H_{11} = H_{33}$ and $H_{12} = H_{32}$, we may write

$$(\psi_{12}^{\mathrm{a}})^{(0)} = (\chi_1 \pm \chi_3)/\sqrt{2} \tag{37}$$

Adding the first-order correction due to χ_2 yields a splitting of the second-order adiabatic energies:

$$(\Delta E^{\mathrm{a}})^{(2)} = 2(H_{12}H_{32}/\Delta E^{(0)}) \tag{38}$$

and

$$H_{\mathrm{if}}^{(2)} = (\Delta E^{\mathrm{a}})^{(2)}/2 = H_{12}H_{32}/\Delta E^{(0)} \tag{39}$$

In the case where $H_{12} \neq H_{32}$, eqs 37–39 still describe the effective two-state model at the point of minimum energy separation, but this point does not coincide with the crossing point of the diabatic surfaces, H_{ii} and H_{ff}. This distinction also arises in the context of the partitioning method,[64] which is closely related to the present RSPT approach, as seen below in section III.C.2.

b. Nonresonant Case. We now consider the nonresonant situation, where all three zeroth-order energies are well separated relative to the magnitudes of H_{13} and H_{23}. Second-order RSPT yields approximate adiabatic states:

$$(\psi_1^{\mathrm{a}})^{(2)} = \chi_1 + (H_{12}/\Delta E_{12}^{(0)})\chi_2 + (H_{12}H_{23}/\Delta E_{12}^{(0)}\Delta E_{13}^{(0)})\chi_3 \tag{40a}$$

$$(\psi_2^{\mathrm{a}})^{(2)} = \chi_3 + (H_{32}/\Delta E_{32}^{(0)})\chi_2 - (H_{32}H_{21})/(\Delta E_{32}^{(0)}\Delta E_{13}^{(0)})\chi_1 \tag{40b}$$

where

$$\Delta E_{jk}^{(0)} = E_j^{(0)} - E_k^{(0)}$$

In terms of Figure 1, $\Delta E_{12}^{(0)}$, $\Delta E_{13}^{(0)}$, and $\Delta E_{32}^{(0)}$ correspond, respectively, to $-E_{\mathrm{CT}}^{\mathrm{i}}$, ΔE, and $-E_{\mathrm{CT}}^{\mathrm{f}}$. It is straightforwardly demonstrated that, as required for adiabatic states, $H_{12}^{\mathrm{a}} = \langle (\psi_1^{\mathrm{a}})^{(2)} | H | (\psi_2^{\mathrm{a}})^{(2)} \rangle$ and the corresponding S_{12}^{a} are exactly zero, based on the present model. We obtain the effective value of H_{if} by evaluating the optical transition moment

$$\vec{\mu}_{12}^{\mathrm{op}} = \langle (\psi_1^{\mathrm{a}})^{(2)} | \vec{\mu} | (\psi_2^{\mathrm{a}})^{(2)} \rangle \tag{41}$$

and equating it to the two-state result in eq 11, replacing $E_{\mathrm{IT}}^{\mathrm{e}} = -(H_{\mathrm{ii}} - H_{\mathrm{ff}})$ there by $-\Delta E_{13}^{(0)}$. Equations 40 and 41 yield (through second order), aside from a phase factor of ±1,

$$|(\vec{\mu}_{12}^{\mathrm{op}})^{(2)}| = e\bar{r}H_{12}H_{32}\left[\frac{\Delta E_{12}^{(0)} + \Delta E_{32}^{(0)}}{2(\Delta E_{13}^{(0)})(\Delta E_{12}^{(0)})(\Delta E_{32}^{(0)})}\right] \tag{42}$$

where $\bar{r} = |\vec{\mu}_{33} - \vec{\mu}_{11}|/ne$ (we take $\vec{\mu}_{jk} = 0$ for $j \neq k$, where $\vec{\mu}_{jk} \equiv \langle \chi_j | \vec{\mu} | \chi_k \rangle$). In obtaining eq 42 we also assume for simplicity (see below) that $\vec{\mu}_{22} = (1/2)(\vec{\mu}_{11} + \vec{\mu}_{33})$.

Equating the right hand sides of eqs 11 and 42, and also equating the $\bar{r}$ in each equation, we obtain

$$H_{\mathrm{if}}^{\mathrm{eff}} \equiv H_{\mathrm{if}}^{(2)} = H_{12}H_{23}[(1/2)(1/\Delta E_{12}^{(0)} + 1/\Delta E_{32}^{(0)})] = H_{12}H_{32}/\Delta E_{\mathrm{eff}}^{(0)} \quad (43)$$

where

$$\Delta E_{\mathrm{eff}}^{(0)} = 2(\Delta E_{12}^{(0)}\Delta E_{32}^{(0)})/(\Delta E_{12}^{(0)} + \Delta E_{32}^{(0)}) \quad (43a)$$

Thus $\Delta E_{\mathrm{eff}}^{(0)}$ has the standard form of a reduced energy difference. Although the present derivation is not valid for the resonant or near-resonant case, we note, nevertheless, that $\Delta E_{\mathrm{eff}}^{(0)}$ becomes equal to $\Delta E^{(0)}$ for the resonant case (see eq 32) when $E_1^{(0)}$ and $E_3^{(0)}$ are equated. If the constraint of $(\vec{\mu}_{11} + \vec{\mu}_{33})/2 = \vec{\mu}_{22}$ is relaxed, but with the assumption that the three centroids, $\vec{\mu}_{jj}/ne$, $j = 1$ to 3, are collinear (with $\vec{\mu}_{22}/ne$ lying between the other two), then $1/\Delta E_{\mathrm{eff}}^{(0)}$ may be generalized as

$$1/\Delta E_{\mathrm{eff}}^{(0)} = \frac{\Delta E_{12}^{(0)}f_{12} + \Delta E_{32}^{(0)}f_{32}}{\Delta E_{12}^{(0)}\Delta E_{32}^{(0)}} \quad (44)$$

where the weighting factors are given by $f_{12} = |\vec{\mu}_{22} - \vec{\mu}_{11}|/ne\bar{r}$ and $f_{32} = |\vec{\mu}_{33} - \vec{\mu}_{22}|/ne\bar{r}$ (note that $f_{12} + f_{32} = 1$). The result given in eq 43a for $m = 1$ may be straightforwardly generalized to higher m; e.g., for $m = 2$, assuming that the $\vec{\mu}_{kk}$ form a colinear grid of uniformly spaced points, we find

$$(\Delta E_{\mathrm{eff}}^{(0)})^2 = \frac{3\Delta E_{12}\Delta E_{13}\Delta E_{42}\Delta E_{43}}{\Delta E_{12}\Delta E_{13} + \Delta E_{13}\Delta E_{42} + \Delta E_{42}\Delta E_{43}} \quad (43b)$$

If the nonorthogonal first-order expressions for ψ_{i} and ψ_{f} (obtained by truncating the second-order terms in eq 37) are applied to the present nonresonant case, then the result given by eq 43 is obtained provided that the $S_{\mathrm{if}}H_{\mathrm{ff}}$ and $S_{\mathrm{fi}}H_{\mathrm{ii}}$ terms in eq 24 are replaced by the mean value $S_{\mathrm{if}}(H_{\mathrm{ii}} + H_{\mathrm{ff}})/2$, which in the present context is given by $S_{\mathrm{if}}(E_1^{(0)} + E_3^{(0)})/2$.

As a final observation, we note that the second-order adiabatic wave functions given in eq 42 yield the correct effective H_{if} according to the prescription of Joachim and Larsson (see eq 23 and the discussion in connection with eqs 30 and 31) provided that $\sin 2\eta \approx 2\eta$ is taken as the arithmetic mean of the χ_3 coefficient in eq 40a and the negative of the χ_1 coefficient in eq 42b.

The results obtained in eqs 36, 39, and 43 are in general agreement with those presented elsewhere.[2,22,24-29] Some differences of a factor of 2 may be attributed to the fact that the nonorthogonality effects ($S_{\mathrm{if}} \neq 0$), included in the present derivation, were not included in the earlier analyses. The device of employing the adiabatic transition dipole to define $H_{\mathrm{if}}^{\mathrm{eff}}$ was also employed in ref 27a, but nonorthogonality effects were apparently neglected.

Note that the result for resonant transfer (eqs 36 and 39) refers to thermal transfer at $Q^*(H_{\mathrm{if}}^{\mathrm{th}})$, whereas the nonresonant result eq (43) would refer, for example, to optical transfer occurring at $Q_{\mathrm{i}}^{\mathrm{e}}$ or $Q_{\mathrm{f}}^{\mathrm{e}}(H_{\mathrm{if}}^{\mathrm{op}})$. For a harmonic thermoneutral system ($\Delta E = 0$) where the CT state has the same curvature as the diabatic curves and is centered at Q^* (see Figure 1), we find[6d]

$$H_{\mathrm{if}}^{\mathrm{th}}/H_{\mathrm{if}}^{\mathrm{op}} = 1 - \left(\frac{E_{\lambda}/2}{E_{\mathrm{CT}} - E_{\lambda}/2}\right)^2 \leq 1 \quad (45)$$

This offers an interesting example of how H_{if} may vary with Q, although for typical energy parameters, the effect is modest (i.e., the ratio is >0.9 for $E_{\mathrm{CT}} > 2E_{\lambda}$; for simplicity here and in the following, we suppress the double dagger in $E_{\mathrm{CT}}^{\ddagger}$ (Figure 1)).

2. Lowdin Partitioning Method

Larsson[24,25] has employed the Lowdin partitioning method[64] to rearrange the secular determinant for a Hamiltonian matrix of dimension m+2

$$|\mathbf{H} - E\mathbf{1}| = 0 \quad (46)$$

(where E is the energy eigenvalue and 1 is the unit matrix) to an equivalent form

$$\begin{vmatrix} \bar{H}_{\mathrm{ii}}(E) - E & \bar{H}_{\mathrm{if}}(E) \\ \bar{H}_{\mathrm{fi}}(E) & \bar{H}_{\mathrm{ff}}(E) - E \end{vmatrix} = 0 \quad (47)$$

where $\bar{\mathbf{H}}$ is an effective energy-dependent two-state Hamiltonian matrix with respect to the two basis functions of primary interest (here, χ_1 and χ_{m+2}). Larsson has used this technique to define an effective two-state Hamiltonian for a number of resonant electron-transfer processes. For example, taking the case of a single bridge ($m = 1$), assigned the zeroth-order state function χ_2, we have at resonance[24a,36b-c]

$$\bar{H}_{\mathrm{ii}}(E) = \bar{H}_{\mathrm{ff}}(E) = H_{\mathrm{ii}} - (H_{\mathrm{i2}})^2/(H_{22} - E) = H_{\mathrm{ff}} - (H_{\mathrm{2f}})^2/(H_{22} - E) \quad (48)$$

$$\bar{H}_{\mathrm{if}}(E) = -H_{\mathrm{i2}}H_{\mathrm{2f}}/(H_{22} - E) \quad (49)$$

It is apparent that the crossing of the effective surfaces, $\bar{H}_{\mathrm{ii}}$ and $\bar{H}_{\mathrm{ff}}$, as in eq 48, does not coincide with the crossing of the original diabatic surfaces, H_{ii} and H_{ff}, unless $H_{\mathrm{i2}} = H_{\mathrm{f2}}$, as noted in ref 36b.

If $\psi_{\mathrm{i}}^{(0)}$ and $\psi_{\mathrm{f}}^{(0)}$ (i.e., χ_1 and χ_3) interact only weakly (the direct interaction, H_{13}, is assumed negligible) and are well separated from χ_2 in energy (i.e., $|H_{\mathrm{ii}} - H_{22}| = |H_{\mathrm{ff}} - H_{22}|$ are large in comparison with H_{i2} and H_{f2}), then we may to good approximation replace E in $\bar{H}_{\mathrm{ii}}(E)$ and $\bar{H}_{\mathrm{ff}}(E)$ by its zeroth-order value $H_{\mathrm{ii}} = H_{\mathrm{ff}}$ or by a mean value if $H_{\mathrm{ii}} \neq H_{\mathrm{ff}}$ (see above). The E appearing in $\bar{H}_{\mathrm{if}}(E)$ may then be replaced either by H_{ii} or $\bar{H}_{\mathrm{ii}}$ (for cases of weak coupling, the two choices are expected to yield very similar values). The former choice yields an expression equivalent to eqs 36 and 29 (recall that $H_{\mathrm{ii}} - H_{22}$ is equated to ΔE_{12}^{0}). Adopting the latter choice, where the energy argument of $\bar{H}_{\mathrm{ii}}$ has in turn been assigned a zeroth-order value, we obtain the following effective transfer integral:

$$H_{\mathrm{if}}^{\mathrm{eff}} \equiv \bar{H}_{\mathrm{if}}(\bar{H}_{\mathrm{ii}}) = -H_{\mathrm{i2}}H_{\mathrm{2f}}/(H_{22} - \bar{H}_{\mathrm{ii}}) \quad (50)$$

Note that the sign as well as the magnitude of $H_{\mathrm{f}}^{\mathrm{eff}}$ is significant since the sign controls the nature of the interference when multiple coupling pathways are involved. The sign of H_{if} in the partitioning approach is incorrect in some of the previous literature although no conclusions are affected since interference effects were not dealt with.

For the general resonant case involving m bridge states (with the usual nearest neighbor tight-binding approximation), Larsson obtains[24a] (with sign corrected)

$$H_{\mathrm{if}}^{\mathrm{eff}} = (H_{12}/\Delta E_{12}^{(0)})\left(\prod_{j=1}^{m-1} (H_{j+1,j+2}/\Delta E_{1,j+2}^{(0)})\right)(\mathrm{H}_{m+1,m+2}) \quad (51)$$

where $m \geq 2$ and where a factor occurs for each of the $(m + 1)$ nearest neighbor interactions in the assumed linear sequence and where it is assumed that each such factor is small relative to unity. The same perturbation result has been obtained by Beratan et al.[27] and by Ratner,[26b] using, respectively, time-independent and time-dependent (propagator) techniques. These techniques are all straightforwardly extended to cases in which each bridging unit has several electronic states, thereby generalizing each factor in eq 51 into a superposition of competing pathways (e.g., "electron" vs "hole" transfer,[26b,27e] if a particular bridge has accessible both occupied and unoccupied orbitals, as discussed below). For simplicity, the energy denominators in eq 51 are based on zeroth-order energies. However, they could also incorporate second-order energy corrections by replacing $E_1^{(0)}$ with the analogue of $\bar{H}_{ii}$ (see eqs 48 and 50).

In nonresonant cases (i.e., $H_{ii} \neq H_{ff}$), the specification of E in eq 47 involves additional ambiguities.[29b] We have already seen (section III.C.1) how the transition dipole may be employed in defining effective energy denominators in such situations.

3. The McConnell Model and Its Generalization[22b]

An alternative to the above treatment of resonant transfer in the m-bridge case was offered by McConnell. In this approach, one considers the m-bridge unit to be a single bridge possessing m locally excited states χ_{j+1}, $j = 1$ through m, reserving as usual, χ_1 and χ_{m+2} for the donor and acceptor states. Diagonalization of the mxm bridge block of the Hamiltonian matrix $\mathbf{H}$, yields eigenfunctions (ψ_s^{B}) and eigenvalues (E_s^{B})

$$\langle \psi_s^{\mathrm{B}} | H | \psi_t^{\mathrm{B}} \rangle = \delta_{st} E_s^{\mathrm{B}} \tag{52}$$

$$\psi_s^{\mathrm{B}} = \sum_{j=1}^{m} \chi_{j+1} C_{js}^{\mathrm{B}} \qquad s = 1\text{–}m \tag{53}$$

(Larsson's partitioning approach also employs the eigenfunctions of the bridge units.) Using standard RSPT, we then obtain[22b] the following expression for the splitting of the adiabatic states ($\Delta E^{\mathrm{a}} = 2H_{\mathrm{if}}^{\mathrm{eff}}$), obtained from the mixing of the bridge eigenfunctions with the zeroth-order adiabatic states $\chi_\pm = (1/\sqrt{2})(\chi_1 \pm \chi_{m+2})$:

$$\Delta E^{\mathrm{a}} = E_+^{\mathrm{a}} - E_-^{\mathrm{a}} = 2\sum_{s=1}^{m} \frac{\langle \chi_1 | H | \psi_s^{\mathrm{B}} \rangle \langle \psi_s^{\mathrm{B}} | H | \chi_{m+2} \rangle}{E_1^{(0)} - E_s^{\mathrm{B}}} \tag{54a}$$

From the expansion in eq 53 we obtain the equivalent expression

$$\Delta E^{\mathrm{a}} = 2(H_{12}H_{m+1,m+2}) \sum_{s=1}^{m} (C_{2s}^{\mathrm{B}})'(C_{m+1,s}^{\mathrm{B}})'/(E_1^{(0)} - E_s^{\mathrm{B}}) \tag{54b}$$

where E_1^0 is the energy of both χ_+ and χ_- since direct coupling ($H_{1,m+2}$) is assumed negligible. For uniformity of notation in eq 54b we employ $(C_{js}^{\mathrm{B}})' \equiv C_{j-1,s}^{\mathrm{B}}$, since the C^{B} matrix defined in eq 53 only involves the set χ_2 to χ_{m+1}.

McConnell originally derived this expression for the special case in which all bridge basis functions were equivalent (differing only in spatial origin), with $T \equiv H_{12} = H_{m+1,m+2}$, with $t \equiv H_{j+1,j+2}$, $j = 1$ to $m - 1$, and with the constant (positive) excitation energy, $D \equiv -\Delta E_{1,j+1}^{(0)}$ for $j = 1$–m. For consistency with the notation defined in Figure 1, we denote McConnell's energy D by E_{CT}. In the limit $|t/E_{\mathrm{CT}}| \ll 1$, the result

$$\Delta E^{\mathrm{a}} = 2\left(\frac{T^2}{-E_{\mathrm{CT}}}\right)\left(\frac{t}{-E_{\mathrm{CT}}}\right)^{m-1} \tag{55}$$

is obtained by expanding $1/(E_1^0 - E_s^{\mathrm{B}})$ in a Taylor series and collecting the leading terms arising under the tight-binding approximation

$$\frac{1}{(E_1^{(0)} - E_s^{\mathrm{B}})} = \frac{1}{(-E_{\mathrm{CT}} - E_s^{\mathrm{B}})} = \left(\frac{1}{-E_{\mathrm{CT}}}\right) \sum_{p=0}^{\infty} (\hat{E}_s^{\mathrm{B}}/E_{\mathrm{CT}})^{\mathrm{p}}(-1)^{\mathrm{p}} \tag{56}$$

where the eigenvalues $\hat{E}_s^{\mathrm{B}}$, $s = 1$ to m, are related to the E_s^{B} by a constant energy shift which references them to the degenerate zeroth-order energy level of the bridge, $(E^{\mathrm{B}})^0 \equiv E_{j+1}^{(0)}$, $j = 1$ to m:

$$\hat{E}_{\mathrm{s}}^{\mathrm{B}} = E_{\mathrm{s}}^{\mathrm{B}} - (E^{\mathrm{B}})^{(0)} \tag{56a}$$

In terms of E_{CT}, $(E^{\mathrm{B}})^{(0)}$ may be reexpressed as

$$(E^{\mathrm{B}})^{(0)} = E_1^{(0)} + E_{\mathrm{CT}} \tag{56b}$$

The simple form of eq 55, equivalent to the more general expression eq 51 in the present limit of m equivalent bridge orbitals, has a number of interesting implications which we examine below. Here we point out a generalization of eq 55 which immediately suggests itself if one focuses on its derivation via eq 56. Relaxing the requirement of tight binding among equivalent bridge orbitals, we define a *mean* energy denominator, $\bar{E}_{\mathrm{CT}}$, on the basis of the (positive) quantities $-\Delta E_{1,j+1}^{(0)}$, $j = 1$ to m. From the properties of the Schrodinger matrix equation (eq 57), where $H_{\mathrm{jk}}^{\mathrm{B}} \equiv$

$$\mathbf{H}^{\mathrm{B}}\mathbf{C}^{\mathrm{B}} = \mathbf{C}^{\mathrm{B}}\hat{\boldsymbol{E}}^{\mathrm{B}} \tag{57}$$

$H_{j+1,k+1} - \delta_{jk}\bar{E}_{\mathrm{CT}}$ (j, $k = 1$ to m), and where the eigenvalues $\hat{E}^{\mathrm{B}}$ are defined analogously to eq 56a, with E_{CT} replaced by $\bar{E}_{\mathrm{CT}}$, we find

$$\sum_{s=1} C_{js}^{\mathrm{B}}(\hat{E}_s^{\mathrm{B}})^p C_{ks}^{\mathrm{B}} = \{(\mathbf{H}^{\mathrm{B}})^p\}_{jk} \tag{58}$$

with j, $k = 1$ to m. While for the tight-binding case the first non-zero term corresponds to $p = m - 1$, in the more general case of coupling within the bridge, but with the bridge still coupled to the donor and acceptor groups only via the "terminal" states, χ_2 and χ_{m+1}, respectively, we have

$$\Delta E^{\mathrm{a}} = 2\left(\frac{H_{12}H_{m+1,m+2}}{-\bar{E}_{\mathrm{CT}}}\right) \sum_{p=0}^{\infty} (-1)^p \frac{H_{2,m+1}^{(p)}}{(\bar{E}_{\mathrm{CT}})^p} \tag{59}$$

where the coupling element, $H_{2,m+1}^{(p)}$ is given by

$$H_{2,m+1}^{(p)} \equiv \{(\mathbf{H}^{\mathrm{B}})^p\}_{1m} \tag{59a}$$

Equation 59 may be useful if the concept of a mean energy denominator seems suitable (i.e., a relatively tight cluster of excited states well separated from $E_1^{(0)} = E_{m+2}^{(0)}$) and if convergence of the infinite series is rapid. The form of eq 59 readily lends itself to an interpretation in terms of a superposition of paths which may be displayed as the various terms arising from the expansion of $(\mathbf{H}^{\mathrm{B}})^p$ over the range of p, thus yielding a

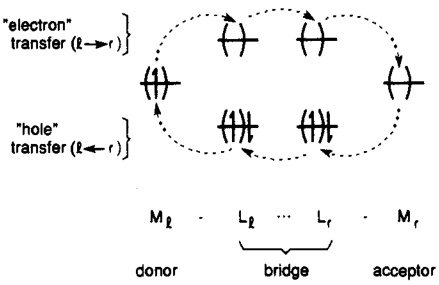


Figure 3. Schematic orbital representation of bridge-mediated superexchange of the "electron" (top, left to right) and "hole" (bottom, right to left) type, illustrated for the case of intermolecular electron transfer between two metal/ligand (M/L) complexes (see eq 1b).

picture analogous to that developed by Ratner.[26b] Equation 59 may be further generalized if the donor/acceptor coupling to the bridge is not limited to the terminal states χ_2 and χ_{m+1}.

Alternative schemes for analyzing the contributions to H_{if} (represented as the adiabatic energy splitting, ΔE^a, in a one-electron model applied to photoelectron spectra) have been implemented by Heilbronner and Schmelzer[65] (an additive perturbative model) and Paddon-Row, Wong, and Jordan (a nonperturbative, procedure involving sequential "turning-on" of individual coupling terms).[66] Other nonperturbative approaches are dealt with in refs 28 and 29.

D. Derivation of One-Electron Models

1. Orbital Wave Functions

The expressions for H_{if} developed in the previous section (III.C) are defined in terms of a generic set of basis functions, χ_j, which in general may be taken as many-electron states associated with the chosen encounter complex for the process of interest. Since we are interested in "one electron (or hole) transfer processes", we anticipate that ultimately one can treat the processes in terms of an effective one-particle model, either an independent-particle model or a mean-field model such as given by Hartree–Fock theory. Here we establish some connections between the many-electron and one-electron pictures, adopting for ease of discussion, an independent-particle model. We define the many-electron basis functions as antisymmetrized n-electron configurations $\chi_j = a(\Pi_k^n \phi_k^j)$; i.e., Slater determinants generated by the operation of the antisymmetrizer, a, on orbital configurations, $(\Pi_k^n \phi_k^j)$, where the occupied orbital sets ϕ_k^j are based on the following orbital space, assumed for simplicity to be orthonormal: ϕ_D, donor; ϕ_A, acceptor; $\{\phi_l\}$, occupied bridge orbitals, $l = 1, n - 1$; $\{\phi_l^*\}$, unoccupied bridge orbitals, $l = 1, p$. Superexchange is commonly subdivided into processes corresponding to "electron" transfer, in which an *electron* transfers from ϕ_D to ϕ_A by making use of available *unoccupied* orbitals (ϕ_l^*), and "hole" transfer, in which a *hole* moves from ϕ_A to ϕ_D by passing through the manifold of *filled* orbitals ($\{\phi_l\}$, as illustrated in Figure 3). Even though both mechanisms can be cast as one-particle processes, it is convenient to treat them separately.

a. "Electron" Transfer. Using the above orbitals we specify orthogonal basis states, χ_k as follows:

$$\chi_1 = \psi_i^{(0)} = a(\phi_D \prod_{k=1}^{n-1} \phi_l) \tag{60a}$$

$$\chi_{p+2} = \psi_f^{(0)} = a(\phi_A \prod_{k=1}^{n-1} \phi_l) \tag{60b}$$

$$\chi_{j+1} = a(\phi_j^* \prod_{l}^{n-1} \phi_l) \qquad j = 1 \text{ to } p \tag{60c}$$

We then construct ψ_i and ψ_f as

$$\psi_i^e = \sum_{j=1}^{p+2} C_{ji}^e \chi_j \tag{61a}$$

$$\psi_f^e = \sum_{j=1}^{p+2} C_{jf}^e \chi_j \tag{61b}$$

where the column vectors $\mathbf{C}_i^e$ and $\mathbf{C}_f^e$ are assumed to be orthogonal. Since all the χ's in eq 60 have a common $(n - 1)$-electron core

$$\psi_{\text{core}}^e = a(\prod^{n-1} \phi_l) \tag{62}$$

we may reexpress ψ_i^e and ψ_f^e as single determinants in which the occupied orbital outside the core is written, respectively, as

$$\phi_D^e = C_{1i}^e \phi_D + \sum_{j=1}^{p} C_{j+1,i}^e \phi_j{}^* + C_{p+2,i} \phi_A \tag{63a}$$

and

$$\phi_A^e = C_{1f}^e \phi_D + \sum_{j=1}^{p} C_{j+1,f}^e \phi_j{}^* + C_{p+2,f} \phi_A \tag{63b}$$

(note that $\langle \phi_D^e | \phi_A^e \rangle = 0$). In the weakly interacting systems of interest here, the effective donor (ϕ_D^e) and acceptor (ϕ_A^e) orbitals are expected to be somewhat delocalized versions of the zeroth-order orbitals (ϕ_D and ϕ_A). Since ψ_i^e and ψ_f^e are thus single determinants differing only in the occupation of a single orbital we may write

$$\langle \psi_i^e | H | \psi_f^e \rangle = \langle \phi_D^e | h | \phi_A^e \rangle \tag{64}$$

if H can be approximated as an independent-particle operator, $H_1 = \sum_{q=1}^{n} h(r_q)$, where h is an effective one-electron Hamiltonian.

b. Hole Transfer. The hole analysis is quite analogous to that for electron transfer, with the same two primary basis functions

$$\chi_1 = \psi_i^{(0)} = a(\phi_D \prod_{k=1}^{n-1} \phi_l) \tag{65a}$$

$$\chi_{n+1} = \psi_f^{(0)} = a(\phi_A \prod_{k=1}^{n-1} \phi_l) \tag{65b}$$

and with $n - 1$ "hole" basis functions

$$\chi_{j+1} = a \phi_D \phi_A \prod_{l \neq j}^{n-1} \phi_l \qquad j = 1 \text{ to } n - 1 \tag{65c}$$

For convenience below we convert the basis functions χ_j to "canonical form" by suitable orbital permutations. This form is obtained by the following procedure. Define a reference $(n + 1)$-electron state

$$\chi^{(n+1)} = a(\phi_D \phi_A \prod_{l=1}^{n-1} \phi_l) \tag{66}$$

and obtain the $(n + 1)$ functions χ_j' (differing by at most a phase factor of −1 from the original χ_j's) by cyclic permutations of the orbitals in $\chi^{(n+1)}$ until the orbital in which the hole is to be created becomes the first member of the antisymmetrized orbital product corresponding to $\chi^{(n+1)}$. In the χ' basis we then write

$$\psi_{\mathrm{i}}^{\mathrm{h}} = \sum_{j=1}^{n+1} C_{j\mathrm{i}}^{\mathrm{h}} \chi_j' \tag{67a}$$

$$\psi_{\mathrm{f}}^{\mathrm{h}} = \sum_{j=1}^{n+1} C_{j\mathrm{f}}^{\mathrm{h}} \chi_j' \tag{67b}$$

and once again, these multideterminantal expressions may be recast as single-determinant states defined in terms of sets (respectively, ϕ_k^{i} and ϕ_k^{f}, $k = 1$ to $n + 1$) obtained as transformations of the original set of $(n + 1)$ orbitals consisting of ϕ_{D}, ϕ_{A}, and $\{\phi_l\}$:

$$\psi_{\mathrm{i}}^{\mathrm{h}} = a\left(\prod_{k=1}^{n} \phi_k^{\mathrm{i}}\right) \tag{68a}$$

$$\psi_{\mathrm{f}}^{\mathrm{h}} = a\left(\prod_{k=1}^{n} \phi_k^{\mathrm{f}}\right) \tag{68b}$$

Relative to $\chi^{(n+1)}$, each of these states is characterized by a "hole" orbital defined as follows:

$$\phi^{\mathrm{h(i)}} \equiv \phi_{n+1}^{\mathrm{i}} = C_{1\mathrm{i}}^{\mathrm{h}} \phi_{\mathrm{A}} + \sum_{j=1}^{n-1} \mathrm{C}_{j+1,\mathrm{i}}^{\mathrm{h}} \phi_{\mathrm{j}} + C_{n+1,\mathrm{i}}^{\mathrm{h}} \phi_{\mathrm{D}} \tag{69a}$$

and

$$\phi^{\mathrm{h(f)}} \equiv \phi_{n+1}^{\mathrm{f}} = C_{1\mathrm{f}}^{\mathrm{h}} \phi_{\mathrm{A}} + \sum_{j=1}^{n-1} \mathrm{C}_{j+1,\mathrm{f}}^{\mathrm{h}} \phi_j + C_{n+1,\mathrm{f}}^{\mathrm{h}} \phi_{\mathrm{D}} \tag{69b}$$

(note that the orbitals ϕ_j on the right hand sides of eq 69 are the hole orbitals by which the corresponding χ_{j+1}''s on the right hand sides of eq 67 differ from $\chi^{(n+1)}$). If the column vectors $\mathbf{C}_{\mathrm{i}}^{\mathrm{h}}$ and $\mathbf{C}_{\mathrm{f}}^{\mathrm{h}}$ defined in eq 67 are taken as orthonormal, then the hole orbitals $\phi^{\mathrm{h(i)}}$ and $\phi^{\mathrm{h(f)}}$ are also orthonormal. Since the ϕ_j's are spin-orbitals, many of the $C_{j+1,\mathrm{i}}^{\mathrm{h}}$ and $C_{j+1,f}^{\mathrm{h}}$ will be zero by spin orthogonality; e.g., if the bridge contains m doubly filled bridge orbitals (i.e., $n - 1 = 2m$) then only the m ϕ_j's of the same spin as ϕ_{D} and ϕ_{A} will yield non-zero coefficients. In analogy with comments made regarding the effective donor ($\phi_{\mathrm{D}}^{\mathrm{e}}$) and acceptor ($\phi_{\mathrm{A}}^{\mathrm{e}}$) orbitals for electron transfer (eq 63), we observe that the effective hole orbitals $\phi^{\mathrm{h(i)}}$ and $\phi^{\mathrm{h(f)}}$ are, respectively, the somewhat delocalized versions of the zeroth-order hole orbitals of χ_1 (i.e., ϕ_{A}) and χ_{n+1} (i.e., ϕ_{D}).

As in the case of $\psi_{\mathrm{i}}^{\mathrm{e}}$ and $\psi_{\mathrm{f}}^{\mathrm{e}}$, we see that since $\psi_{\mathrm{i}}^{\mathrm{h}}$ and $\psi_{\mathrm{f}}^{\mathrm{h}}$ differ only by the location of a single hole orbital (defined relative to $\chi^{(n+1)}$), we have the hole counterpart of eq 64

$$\langle \psi_{\mathrm{i}}^{\mathrm{h}} | H | \psi_{\mathrm{f}}^{\mathrm{h}} \rangle = \langle \phi^{\mathrm{h(i)}} | h | \phi^{\mathrm{h(f)}} \rangle \tag{70}$$

The fact that (according to the present model) $\phi^{\mathrm{h(i)}}$ and $\phi^{\mathrm{h(f)}}$ are mutually orthogonal holes relative to the function χ^{n+1} implies that there must be an $(n - 1)$-electron core, $\phi_{\mathrm{core}}^{(n-1)}$ common to both $\psi_{\mathrm{i}}^{\mathrm{h}}$ and $\psi_{\mathrm{f}}^{\mathrm{h}}$. Thus we may write

$$\psi_{\mathrm{i}}^{\mathrm{h}} = a(\phi^{\mathrm{h(f)}} \psi_{\mathrm{core}}^{(n-1)}) \tag{71a}$$

and

$$\psi_{\mathrm{f}}^{\mathrm{h}} = a(\phi^{\mathrm{h(i)}} \psi_{\mathrm{core}}^{(n-1)}) \tag{71b}$$

revealing the important result that in hole transfer, the *hole* orbital (relative to $\chi^{(n+1)}$) in one state ($\psi_{\mathrm{i}}^{\mathrm{h}}$ or $\psi_{\mathrm{f}}^{\mathrm{h}}$) is the *occupied* orbital (over and above $\psi_{\mathrm{core}}^{(n-1)}$) in the other state. Thus for both the electron- and the hole-transfer processes one may defined a one-electron model in which a passive $(n - 1)$-electron core is common to both states.

The preceding analysis is, of course, dependent on the assumption of a compact orthonormal basis of states and orbitals common to both initial and final states, and on the assumed orthogonality of the vectors $\mathbf{C}_{\mathrm{i}}^{\mathrm{e}}$ and $\mathbf{C}_{\mathrm{f}}^{\mathrm{e}}$ and the vectors $\mathbf{C}_{\mathrm{i}}^{\mathrm{h}}$ and $\mathbf{C}_{\mathrm{f}}^{\mathrm{h}}$. The resulting single-determinant form for ψ_{i} and ψ_{f} arises from the restriction of χ bases to sets whose members are related by one-particle excitations. The question remains as to how realistic these conditions are in practice. It may be noted that they are obeyed exactly at the level of Koopmans' theorem[67] (KT), when the n-electron system is described in terms of the orbitals of the SCF functions for the corresponding $(n + 1)$- or $(n - 1)$-electron problem.[32] We defer this topic until section IV.

Detailed studies of metallocene/metallocenium electron-exchange systems[44d] in which the expansion coefficients **C** in eqs 63, 68, and 69 are obtained by a corresponding orbital analysis[68] of SCF calculations at the INDO level,[69] give excellent quantitative support for the validity the one-particle models inferred on the basis of the above arguments. The effective electron (eq 63) and hole (eq 69) orbitals were found to correspond, respectively, to the canonical highest occupied orbital (HOMO) of the reductant species and the canonical lowest unoccupied orbital (LUMO) of the oxidant species in the reaction, as expected from the above analysis. The corresponding orbital analysis also demonstrated the near invariance (departures of less than 10%, based on overlap integrals as discussed in section III.E.1) of the $(n - 1)$-electron cores ($\psi_{\mathrm{core}}^{(n-1)}$) associated with ψ_{i} and ψ_{f}. The ferrocene and cobaltocene systems were found to correspond to essentially pure limiting cases of electron and hole transfer, respectively. On the other hand, in cases where both mechanisms are simultaneously operative, thereby involving electron/hole pairs within the bridge manifold, then rigorous condensation of multideterminantal states to single-determinant ones (the crux of the above analysis) cannot in general be carried out, and the validity of an effective one-particle model is less clear. Nevertheless, in the limit of weak coupling of ϕ_{D} and ϕ_{A} with bridge orbitals, one may still to good approximation define single-determinant initial and final states which can be partitioned into an $(n - 1)$-electron core and an effective donor/acceptor orbital pair, thus justifying the use of a one-particle model. In this case, the effective donor and acceptor orbitals involve mixing of ϕ_{D} and ϕ_{A} with both occupied and unoccupied bridge orbitals. In terms of the schematic pathways depicted in Figure 3, this more general situation would entail hybrid virtual transfers between the filled orbital of one ligand (L) and the empty orbital of the other (i.e., the creation or destruction of electron/hole pairs).

2. McConnell's Superexchange Model

In McConnell's model for electronic coupling,[22b] the adiabatic energy splitting was given by second-order RSPT (eq 54a), assuming at the outset a one-electron model. We may arrive at his result, in somewhat more general form, by first taking eq 54a as referring to a many-electron representation involving the independent-particle Hamiltonian H_1 defined following eq 64. If the χ_j are taken as the single-determinant basis functions defined in eq 60 or 65, we note that the bridge eigenfunctions ψ_s^{B} (eq 53) are also single determinants. (The reasoning is the same as that employed in section III.D.1.) We then obtain straightforwardly the following orbital counterparts of eq 54a for the case of electron and hole transfer

$$\Delta E_{\mathrm{e}}^{\mathrm{a}} = 2\sum_{j=1}^{p}\left(\frac{\langle\phi_{\mathrm{D}}|h|\phi_j^*\rangle\langle\phi_j^*|h|\phi_{\mathrm{A}}\rangle}{\epsilon_{\mathrm{D}} - \epsilon_j^*}\right) \tag{72}$$

$$\Delta E_{\mathrm{h}}^{\mathrm{a}} = 2\sum_{j=1}^{n-1}\left(\frac{-\langle\phi_{\mathrm{D}}|h|\phi_j\rangle\langle\phi_j|h|\phi_{\mathrm{A}}\rangle}{-(\epsilon_{\mathrm{D}} - \epsilon_j)}\right) \tag{73}$$

where the ϵ_j^* and ϵ_j are the eigenvalues (with respect to the operator h) of the bridge orbitals, ϕ_j^* and ϕ_j, respectively, and where $\epsilon_{\mathrm{D}} = \langle\phi_{\mathrm{D}}|h|\phi_{\mathrm{D}}\rangle = \epsilon_{\mathrm{A}}$ and $\epsilon_j^* > \epsilon_{\mathrm{D}} > \epsilon_j$. To emphasize the importance of signs we include separately, the two compensating minus signs which appear, respectively, in the numerator and denominator, when eq 73 is derived from eq 54a. The minus sign in the numerator arises from the permutational symmetry of the single-determinant wave functions, as noted by Richardson and Taube.[10] Given the definition of H_1, the orbital energy denominators in eqs 72 and 73 are equivalent to the many-electron quantities $E_1^{(0)} - E_j^{\mathrm{B}}$ in eq 54. Note that $E_j^{\mathrm{B}} - E_1^{(0)}$ is a positive excitation energy, for both the "hole" and "electron" cases, and the minus sign in the denominator of eq 73 arises since $\epsilon_{\mathrm{D}} > \epsilon_j$.

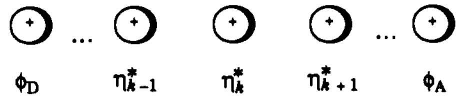
The relative signs of $\Delta E_{\mathrm{e}}^{\mathrm{a}}$ and $\Delta E_{\mathrm{h}}^{\mathrm{a}}$ depend on the details of the orbitals. Let us consider, for example, a bridge consisting of a sequence of m equivalent bridging units, B_k, $k = 1$ to m, each possessing a bonding (η_k) and an antibonding (η_k^*) orbital. Models based on such local bonding and/or antibonding orbitals have been employed in a number of previous studies of bridge-mediated coupling.[13,27a,32a] The orbital eigenfunctions of the bridge, $\{\phi_j\}$ and $\{\phi_j^*\}$, are expanded, respectively, in the η and η^* bases. We consider initially the case where either the electron or hole pathway is dominant, and neglect mixing between $\{\eta\}$ and $\{\eta^*\}$ sets. Adopting the usual tight-binding approximation, and proceeding analogously to McConnell,[22b] we obtain

$$\Delta E_{\mathrm{e}}^{\mathrm{a}} = 2\left(\frac{\langle\phi_{\mathrm{D}}|h|\eta_1^*\rangle\langle\eta_m^*|h|\phi_{\mathrm{A}}\rangle}{-\epsilon_{\mathrm{CT}}^*}\right)\left(\frac{t^*}{-\epsilon_{\mathrm{CT}}^*}\right)^{m-1} \tag{74a}$$

$$\Delta E_{\mathrm{h}}^{\mathrm{a}} = 2\left(\frac{\langle\phi_{\mathrm{D}}|h|\eta_1\rangle\langle\eta_m|h|\phi_{\mathrm{A}}\rangle}{\epsilon_{\mathrm{CT}}}\right)\left(\frac{t}{\epsilon_{\mathrm{CT}}}\right)^{m-1} \tag{74b}$$

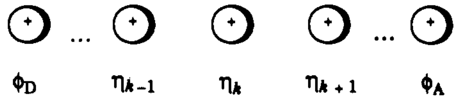
where $t^* \equiv \langle\eta_k^*|h|\eta_{k+1}^*\rangle$ and $t \equiv \langle\eta_k|h|\eta_{k+1}\rangle$, $k = 1$ to $m - 1$, and where the *positive* orbital excitation energies are given by $\epsilon_{\mathrm{CT}}^* = \langle\eta_k^*|h|\eta_k^*\rangle - \epsilon_{\mathrm{D}}$ and $\epsilon_{\mathrm{CT}} = \epsilon_{\mathrm{D}} - \langle\eta_k|h|\eta_k\rangle$, $k = 1$ to m. Because of the assumed equivalence of the bridge sites, the parameters t, t^*, ϵ_{CT}^*, and ϵ_{CT} are independent of k.

SCHEME I



SCHEME II

SCHEME III



In order to understand the expected sign behavior of ΔE^{a} as m is varied we must now consider the nodal structure of the orbitals (ϕ_{D}, ϕ_{A}, $\{\eta\}$. and $\{\eta^*\}$) and adopt a phase convention. In McConnell's original application,[22b] the coupling corresponded to superexchange of the "electron" type ($\Delta E_{\mathrm{e}}^{\mathrm{a}}$), and each virtual orbital η_k^* was taken as a 3dδ orbital (i.e., one symmetric with respect to reflection in the xy plane through its origin, where the z axis coincides with the D/A vector). Thus for the purpose of displaying local orbital symmetry with respect to the z axis, the orbitals may be represented schematically as in Scheme I. Note that Scheme I and also Schemes II and III employ a common phase convention for the local orbitals: The nodeless orbitals are all assigned positive phase, while for the anti-symmetric η^* functions in Scheme II, the right-most lobes are taken as positive. These phases, which are of course arbitrary, do *not* imply particular linear combinations of the local orbitals. They are chosen solely to facilitate the following discussion. Since all orbitals in Scheme I have the same phase, it is reasonable to assume that all the finite coupling elements (i.e., off-diagonal matrix elements of h) are *negative*. However, in the present case, in contrast to McConnell's example, the chosen *antibonding* nature of the η^* functions is consistent with to the nodal structure in Scheme II. For the situation represented by Scheme II, eq 74a may be rewritten as

$$\Delta E_{\mathrm{e}}^{\mathrm{a}} = 2\frac{(T^*)^2}{\epsilon_{\mathrm{CT}}^*}\left(\frac{t^*}{\epsilon_{\mathrm{CT}}^*}\right)^{m-1}(-1)^{m-1} \tag{75}$$

where t^* is assumed to be *positive*, since the overlapping lobes of adjacent orbitals have opposite phases, and $T^* = \langle\eta_m^*|h|\phi_{\mathrm{A}}\rangle = -\langle\phi_{\mathrm{D}}|h|\eta_1^*\rangle$.

Turning now to the case of "hole"-type superexchange, involving localized bridge orbitals which are *bonding* in character, in Scheme III, we adopt the same modal structure and orbital phases as in Scheme I. All coupling elements consistent with Scheme III are expected to be *negative*, since they involve overlap of lobes with the same phase, and accordingly we obtain from eq 74b:

$$\Delta E_{\mathrm{h}}^{\mathrm{a}} = 2\frac{T^2}{\epsilon_{\mathrm{CT}}}\left(\frac{|t|}{\epsilon_{\mathrm{CT}}}\right)^{m-1}(-1)^{m-1} \tag{76}$$

The salient result of the foregoing analysis is that both $\Delta E_{\mathrm{e}}^{\mathrm{a}}$ and $\Delta E_{\mathrm{h}}^{\mathrm{a}}$ have the *same* sign (all the sign information is contained in the common factor, $(-1)^{m-1}$).

We emphasize once again that the orbital phases in Schemes I–III were assigned arbitrarily. However, our conclusions are of course independent of convention adopted.

a. Interference between Electron and Hole Pathways. We now consider the simultaneous presence of electron and hole coupling (see also the earlier discussion in section III.D.1).[26,27e] For the case of a single bridge unit ($m = 1$), we have

$$\Delta E^{a} = \Delta E^{a}_{e} + \Delta E^{a}_{h} = 2\left(\frac{(T^{*})^{2}}{\overset{*}{\epsilon}_{CT}} + \frac{T^{2}}{\epsilon_{CT}}\right) \qquad (77)$$

Thus the two pathways are seen to interfere *constructively*. For a consistent treatment when $m > 1$, one must take account of η–η^{*} mixing (i.e., $\langle \eta_k | h | \overset{*}{\eta}_{k\pm1} \rangle$ as well as mixing within the η and η^{*} manifolds). A detailed analysis has been carried out by Onuchic and Beratan,[27e] demonstrating that the splitting (ΔE_{a}) may still be represented as an overall product of factors arising from each "in series" link in the sequence, but now each of the ($m - 1$) factors (c.f., eqs 75 and 76) has the "parallel" structure of eq 77.

b. Dependence on m. When the bridge units are defined as above in terms of local bonding or antibonding units, we find that both the electron (eq 75) and the hole (eq 76) pathways predict an alternation of sign with m, consistent with the trends predicted earlier by Paddon-Row[13] and Verhoeven and Pasman[70] on the basis of HOMO and LUMO arguments, which are generally found to track the trends given by the full bonding or antibonding manifolds provided that perturbation theory is applicable. Note that these sign effects are observables and not a manifestation of arbitrary phase factors (i.e., the energy of the symmetric state (E^{a}_{+}, eq 54a lies, respectively, below or above that of the antisymmetric state E^{a}_{-}, for m even or odd).

A notable feature of eqs 75 and 76 is the exponential decay of the magnitude, irrespective of whether or not sign alternation occurs.[22b] Pronounced departures from this behavior (e.g., fall-off as an inverse power of m)[4a,27c,29,71] are expected as bridge states begin to approach the donor/acceptor levels (in contrast to the assumptions, $|T^{*}|, |t^{*}| \ll \overset{*}{\epsilon}_{CT}$, $|T|, |t| \ll \epsilon_{CT}$, which underlie the derivation of eqs 75 and 76 and their various generalizations). Departures from simple exponential behavior may also occur in cases where the tight-binding approximation must be relaxed.

When a single pathway is dominant (i.e., either electron or hole), the decay of ΔE^{a} magnitude per bridging unit, denoted ϵ (employing the notation of ref 27, not to be confused with the subscripted ϵ's demoting eigenvalues in the preceding discussion), may be written according to eqs 76 and 77 as

$$\epsilon^{e} = |t^{*}/\overset{*}{\epsilon}_{CT}| \qquad (78a)$$

or

$$\epsilon^{h} = |t/\epsilon_{CT}| \qquad (78b)$$

(in the more general case, a decay parameter of the type $\epsilon = \epsilon^{e} + \epsilon^{h}$ may be defined[27e]). These may be converted into measures of distance dependence of $H_{if} = \Delta E^{a}/2$ provided one can define an effective donor/acceptor separation r (e.g., as in eqs 11–13) as a function of bridge size. For example, we may define $r = r_0 + m\Delta r$, where r_0 is a nearest neighbor contact distance of donor and acceptor in the absence of the bridge, and Δr is the effective size of each bridge unit. While Δr may be equated with the projection of the "length" of the bridge unit onto the straight-line vector between donor and acceptor, it may sometimes be more meaningful (considering the "through-bond" (TB) nature of superexchange coupling) to define Δr in terms of the actual bond lengths for the TB sequence pertinent to the pathway being modeled. At any rate we may write

$$H_{if}(r) = H_{if}(r_0)\exp[-(\beta/2)\,(r - r_0)] \qquad (79)$$

where

$$\beta/2 = -(ln\epsilon)/\Delta r \qquad (80)$$

and where ϵ denotes either ϵ^{e} or ϵ^{h} (eq 78). The notation $\beta/2$ reflects the fact that distance dependence is frequently defined in terms of H_{if}^{2}, which is proportional to the nonadiabatic rate constant[3] (see section II).

Beratan and Hopfield[72] have suggested that the use of purely electronic expressions like eqs 75 and 76 may be problematical for very long distance transfer since the validity of the separation of nuclear and electronic degrees of freedom which underlies the Born–Oppenheimer[1a,2] approximation may be questionable in this limit. However, Freed[73] has noted difficulties with their analysis (see related dynamical studies of Kotler et al.).[74]

3. Direct vs Superexchange Pathways

It is generally assumed that bridge electronic manifolds are sufficiently accessible to render nearest neighbor (tight-binding) superexchange pathways competitive with more direct pathways. On the other hand, in the most general situation (e.g., as represented by eq 59), one may consider a superposition of all possible m-th order pathways, summed over all values of m, where m is the number of virtual transfers involving bridge states. For this purpose one may generalize the transfer integrals, T and t, from fixed, nearest neighbor quantities (as in eq 55), to the variable quantities $t(r)$ and $T(r)$. Assuming for simplicity that $t(r)$ and $T(r)$ are identical, and that $r_0 = \Delta r$ (cf., eqs 79 and 80), and writing

$$t(r) = t(\Delta r)\exp(-(\beta^{d}/2)(r - \Delta r)) \qquad (81)$$

where $\beta^{d}/2$ refers to direct, through-space (TS) overlap, we find that superexchange (as given by eq 55) dominates direct exchange provided[2,45a]

$$t(\Delta r)/E_{CT} > \exp(-(\beta^{d}/2)(\Delta r)) \qquad (82)$$

The original quantities t and T (e.g., as in eq 55) are given by $t \equiv t(\Delta r)$ and $T \equiv T(\Delta r)$ in this simplified illustrative model. In a similar fashion, the TS coupling of ϕ_D and ϕ_A may be represented by an equation analogous to eq 81.

4. Use of Koopmans' Theorem

Going beyond the naive independent particle model, a more sophisticated approach for defining a one-particle model is provided by Koopman's Theorem (KT),[67] which involves self-consistent field (SCF) approximations to the many-electron problem. According to KT, the one-electron energies of the occupied orbitals of an n-electron system provide the ionization energies in the frozen orbital limit (i.e., not allowing final state relaxation of the ions). This approach is also applicable to cases of electron attachment, in which case the orbital energies of the unoccupied orbitals give the electron affinities in the same frozen orbital limit. Accordingly, in the case of symmetric systems (at Q^{*}), the splittings (ΔE^{a}) of the adiabatic energies, E^{a}_{+} and E^{a}_{-} (see eq 54a) for the corresponding ($n-1$)- and ($n+1$)-electron systems may be approximated by the splittings of the appropriate one-electron energies obtained from the n-electron SCF calculations. Paddon-Row and Jordan have exploited this device in ab initio studies of a wide variety of spacer groups.[32] In applications to PES and ETS analysis, calculations are generally based on the equilibrium structure of the neutral system. However, when the focus is on electron-transfer processes, the calculations could just as well be executed at the transition state structure ($Q^{\ddagger}$). At any rate, H_{if}, is not expected in general to depend strongly on Q, (examples are noted in section IV.B).

E. Many-Electron Effects

So far we have considered direct and superexchange coupling primarily in a one-electron framework; i.e., we have defined the many-electron matrix elements, H_{if} in terms of orbital matrix elements with respect to an independent-particle Hamiltonian or the frozen-orbital equivalent implicit in the use of Koopmans' theorem.[67] We note here some specific consequences of full many-electron behavior.

1. Electronic Relaxation Effects

Fully flexible models for ψ_i and ψ_f would include charge–state-specific relaxation effects which would take one beyond the limited framework (section III.D.1) in which a single compact set of occupied and unoccupied orbitals was used to describe both initial and final states. An example of this is provided by the Hartree–Fock model. Because of the nonlinear structure of the Hartree–Fock effective Schrödinger equation, distinct, symmetry-broken solutions are obtained for ψ_i and ψ_f in weakly coupled systems, even when the nuclear framework for the transition state reflects symmetry equivalent of the donor and acceptor moieties.[30,38,43,44,56] In such a situation, one may attempt to "soak up" the many-electron effects in an electronic Franck–Condon factor, $S_{if}^{(n-1)}$, which reflects the departure of the ($n-1$)-electron cores of ψ_i and ψ_f from rigorous invariance under the $\psi_i \rightarrow \psi_f$ process.[43d,44,75] Thus one may generalize the form of eqs 64 and 70 to read

$$H_{if} = h_{DA} S_{if}^{(n-1)} \qquad (83)$$

Studies by Newton et al.[43d,44] have shown that $S_{if}^{(n-1)}$ is typically close to unity (generally >0.9), as noted in section III.D.1.

The electronic relaxation inherent in the symmetry-broken solutions (relative to the symmetry-constrained SCF level) may be considered to be a physically meaningful electron correlation effect, which is typical of many weakly interacting systems. We emphasize that H_{if} as obtained from symmetry-broken wave functions corresponds to an energy splitting ΔE^{a} based on 2-configuration (adiabatic) wave functions. While such 2-configuration wave functions may be obtained directly in a fully self-consistent manner,[84b] taking due account of nonorthogonality,[84a] applications to date for electron-transfer processes have obtained ψ_i and ψ_f from independent SCF calculations.

As a final cautionary comment, we note that symmetry breaking may be viewed as an artifact of the SCF model, and one must recognize that for some molecular situations (including cases of relatively strong coupling), it may not provide a physically useful representation.[76]

It would of course, be desirable, to incorporate more electron correlation into ψ_i and ψ_f, especially when the calculations involve very weak coupling of donor and acceptor. However, recognition of the fact that H_{if} may be expressed as the energy splitting (ΔE^{a}) of two states which to a reasonable approximation differ by a one-electron excitation may help to explain why SCF calculations have been so useful in evaluating H_{if}. Attempts to incorporate electron correlation into symmetry-broken SCF wave functions using a multiconfiguration SCF approach have recently been reported by Braga, Broo, and Larsson.[24e]

2. Direct vs Double Exchange

Even in the absence of the type of state-specific relaxation noted above, it is still of interest to examine the consequences of the two-electron part of the Hamiltonian. Thus if we write

$$H = \sum_{q}^{n} h(r_q) + \sum_{q<q'}^{n} e^2/|\vec{r}_q - \vec{r}_{q'}| \qquad (84)$$

the "direct" matrix element is given by

$$H_{if}^{dir} = \langle \psi_i^0 | H | \psi_f^0 \rangle = \langle \phi_D | h | \phi_A \rangle + \sum_{l}^{n-1} \{ (DA)|ll) - (Dl|lA) \} \qquad (85)$$

where $\psi_i^{(0)}$ and $\psi_f^{(0)}$ are the single determinant states introduced in eqs 60a and 60b based on orthonormal orbitals ϕ_D, ϕ_A, and occupied bridge orbitals ϕ_l, $l = 1$ to $n-1$, and where in standard notation

$$(ab|cd) = \int \phi_a^*(1)\phi_b(1)(1/r_{12})\phi_c^*(2)\phi_d(2) \qquad (86)$$

Thus in addition to the one-electron TS term we also find a two-electron contribution. The first two-electron term can be neglected if direct ϕ_D/ϕ_A overlap is negligible. However, the second term, $\sum_l^{n-1}(Dl|lA)$, is essentially the same as the "double exchange" term, H_{if}^{double}, discussed by Halpern and Orgel[22a] and others.[10] Like the direct term, it involves no virtual intermediate states. It can be described[10,22a] as a mechanism involving a superposition of concerted processes associated with each occupied orbital of the bridge. The lth such process involves an electron being passed from ϕ_D to ϕ_l in concert with another electron being passed from ϕ_l to ϕ_A. A more transparent expression for H_{if}^{double} is obtained by expanding the ϕ_l in a localized basis of p atomic orbitals, η_k (analogous to what was done in connection with eq 74),

$$\phi_l = \sum_{k}^{p} \gamma_{kl} \eta_k \qquad (87a)$$

$$H_{if}^{double} \simeq \sum_{k,k'}^{p} (Dk|k'A)\, \rho_{kk'} \qquad (87b)$$

$$\simeq (D1|pA)\rho_{1p} \qquad (87c)$$

and

$$\rho_{kk'} = \sum_{l}^{n-1} \gamma_{kl} \gamma_{k'l} \qquad (87d)$$

where it is assumed that (D1|pA) is the dominant two-electron integral, involving the terminal atomic orbitals of the bridge, η_1 and η_p.

Thus the double exchange is approximately given by a Coulombic integral whose fall-off with distance r is expected to go as $1/r^x$, where x depends on the multipolar nature of the nearest neighbor charge distributions, $(\phi_D)(\eta_l)$ and $(\eta_p)(\phi_A)$, and the bond order between the bridge termini (expected to fall off as $1/r$). While for some electronic structure models, the neglect of H_{if}^{double} may be justified (e.g., in the context of the semiempirical INDO method),[44d] it is not at all clear in general under what circumstances the magnitude of the double exchange term will be negligible compared to that of the superexchange terms. Even if H_{if}^{double} is not negligible, it may still be possible to cast H_{if} as an *effective* one-electron matrix element. At any rate, one should note the qualitative distinction between $\langle \phi_D | h | \phi_A \rangle$ and H_{if}^{double}: the former involves long-range TS *overlap*, while the long-range TS coupling in the latter involves *Coulombic interaction* between local charge distributions.

In an interesting analysis of long-range coupling, Bertrand has shown[77] that additional exchange contributions (denoted as "multiple exchange" terms) arise from the one-electron part of H (eq 84) if the orbitals ϕ_l are not mutually orthonormal.

3. *Relationship of One- and Two-Electron Exchange*

The general formulation of superexchange coupling of donor and acceptor sites provides a number of compact relationships between the one-electron coupling of interest in electron transfer kinetics and the two-electron coupling of localized unpaired spins (i.e., the Heisenberg exchange coupling, generally denoted by the coefficient J_{ab}, where a and b are the orbitals containing the coupled electrons).[23c,78] These relationships provide important self-consistency tests which are of considerable importance, since experimental one- and two-electron exchange data is available for several systems of interest; e.g., comparisons of electron transfer and triplet energy transfer;[12c] and comparisons of photoinitiated electron transfer in bacterial photosynthetic systems, and related splitting of final singlet and triplet states.[36,48] For example, consider the following scheme involving orbitals ϕ_a, ϕ_b, and ϕ_c:

$$\underset{(\psi_i)}{\phi_a^2\phi_b^0\phi_c^0} \xrightarrow{h\nu} \underset{(\psi_i{}^*)}{\phi_a^1\phi_b^1\phi_c^0} \xrightarrow{\text{et}} \underset{(\psi_f)}{\phi_a^1\phi_b^0\phi_c^1} \tag{88}$$

We find (when RSPT is valid) that

$$J_{ac} = \frac{t_{bc}^2}{(\Delta E_{bc})^2} J_{ab} \tag{89}$$

where $2J_{ab}$ and $2J_{ac}$ give the singlet/triplet splittings for the ab and ac orbital pairs in ψ_i^* and ψ_f, respectively, where t_{bc} governs the one-electron superexchange coupling of orbitals b and c, ΔE_{bc} is the mean energy change for the electron transfer occurring in the singlet and triplet manifolds. Using the partitioning method,[64] Marcus has obtained[36b,c] the following refinement of eq 89:

$$J_{ac} = \frac{t_{bc}^2 \, J_{ab}}{({}^1\Delta E_{bc})({}^3\Delta E_{bc})} \tag{90}$$

where distinct singlet and triplet ΔE_{bc} values are now incorporated. We note that the mechanisms implicit in eqs 89 and 90 ignore the possibility of "hole" pathways involving occupied orbitals of the acceptor species in the electron-transfer process. Redi and Hopfield have suggested[79] that the two-electron superexchange might be dominated by t_{ac} (i.e., direct coupling of ϕ_a and ϕ_c) instead of the indirect coupling of ϕ_a and ϕ_c via ϕ_b which is involved in eqs 89 and 90. However, this latter coupling seems more likely to predominate.

IV. Computational Aspects

We summarize the various computational electronic structure approaches employed in evaluating the electron-transfer integral, H_{if}, and in analyzing the calculated results.

A. One-Electron Models

There are several one-electron models for evaluating H_{if}, each of which is capable of including the long-range influence of the medium.

1. *Orbital Approaches*

Studies along the lines initiated by Kuznetsov et al.[49] and based on 1s-type donor and acceptor orbitals interacting with a point charge in a dielectric continuum, have suggested the possibility of an appreciable Q-dependent modulation of donor and acceptor wave functions arising from the orientational polarization of the solvent, an effect which becomes increasingly significant as the donor/acceptor separation is extended. This effect is likely to be quite modest if the relevant charged species in the model are surrounded by finite cavities of low dielectric constant. The recent model of Kim and Hynes,[50] which includes the influence of electronic as well as orientational polarization, suggests rather small ($\lesssim 20\%$) modulation of H_{if} by the medium for short-range electron transfer when realistic cavities are employed.

2. *Path Integral Approaches*

Generalized free-energy computer simulations based on discretized Feynman path integral techniques have been used to evaluate H_{if} (from energy splittings, ΔE^a) for a ruthenium-modified myoglobin system, assuming a frozen geometry for the environment[51a] and for the thermally equilibrated aqueous Fe^{2+}/Fe^{3+} exchange reaction (in the latter work, similar results were also obtained by using a discrete basis set).[51b–d]

3. *Phenomenological Tunneling Models*

Finally, we note a number of phenomenological one-electron tunneling models,[5,11a,39,80] including a recent approach by Brooks et al.,[39] in which calculated (KT) electron affinities of amino acid units are employed in modeling the effective potential for electron tunneling in protein systems.

B. Many-Electron Models

1. *Independent-Particle Models*

Tight-binding models have been employed in studying the electron transmission capabilities of various hydrocarbon spacer groups.[13,27,70] Beratan and coworkers have combined this approach with the imposition of periodic potentials and the specification of donor and acceptor sites by suitable boundary conditions to investigate the dependence of transfer integral on the number of bridging units in the limit when donor and acceptor coupling with the bridge is weak.[27] They have obtained a number of closed form expressions comparing different types of bridging unit (including multiple-path interference effects)[27c] and find interesting qualitative trends which invite more qualitative follow-up studies. The approach generally yields H_{if} directly in terms of diabatic states (characterized as one-electron orbital states), although the energy splitting of adiabatic states may also be obtained.[27a] The direct evaluation of H_{if} may be implemented either for thermal (resonant) or optical electron transfer.[27a]

Extended Huckel theory (EHT)[81] has been employed by Larsson,[24a,b,25a,e;45] Joachim,[28b,28c] and Siddarth and Marcus[37a] in evaluating H_{if} from energy splittings for a number of organic, inorganic, and bioinorganic systems. The use of EHT with the partitioning approach[64] in many of these applications is advantageous for very large systems since the effective transfer integrals of small magnitude may be obtained with greater precision in comparison with results obtained from the solution of the full secular equation. However, there may be loss of accuracy due to the perturbative nature of the approach.

In solving the EHT secular equation (whether exactly or via the partitioning method[64]), the full overlap matrix is generally retained.[28b,c,37,81] In Larsson's applications, the overlap integrals are employed as usual in evaluating the off-diagonal Hamiltonian matrix elements;[81] however, the overlap matrix appearing in the secular equation has generally been replaced by the unit matrix.[24a,b,25a,e,45a]

It is important to recognize that the independent-particle models discussed here are generic ones which do not offer a unique prescription for the specification of parameters. Hence when assessing the various applications it is difficult to ascertain what controls the location of donor and acceptor levels relative to bridge levels. The necessary parameters are not in general fitted to data directly related to the electron-transfer systems of interest, and are based primarily on empirical values for atomic or molecular transition energies. These comments apply also to the CNDO/S[82] and INDO[33b,33c,34,69] methods discussed later.

2. *Self-Consistent Field Methods*

a. Semiempirical Methods. The semiempirical CNDO/S[82] and INDO,[33b,c,34,69] and related[25d,33a,35] methods have been exploited by several groups in estimating H_{if}, either from evaluating adiabatic energy splittings,[24c,25b–e,29c,44b–d] or from direct calculations based on symmetry-broken SCF calculations for ψ_i and ψ_f.[44b–d] Comparisons between H_{if} values based on INDO and ab initio results for a set of model redox systems indicate agreement to within ~20%.[44e] The INDO approach[69] has also been employed by Richardson and Taube[10] in evaluating H_{if} for optical (IT) processes in mixed-valence inorganic binuclear complexes.

b. Ab Initio Models. Ab initio SCF techniques have been used to evaluate H_{if} for electron transfer in a number of ionic species, including metal diatomics,[56] organic systems,[24d,30,38a] and transition-metal complexes[38b,43] and other inorganic systems.[47] These studies all exploited the properties of symmetry-broken SCF solutions for weakly coupled systems although comparisons were also made with results based on delocalized representations and on isolated fragment wave functions. The computational consequences of nonorthogonality associated with symmetry-broken SCF models for ψ_i and ψ_f were dealt with through the use of biorthogonal transformations of the occupied orbitals in ψ_i and ψ_f.[68,83]

For positively charged systems, the basis-set dependence of the calculated H_{if} values is found to be modest if reasonably flexible molecular valence basis sets are employed (i.e., of at least split valence quality). For the case of radical anions,[30,47] sensitivity of H_{if} magnitude to basis set can be appreciable,[30] both for through-space (TS) and through-bond (TB) components, and it is generally desirable to include spatially diffuse functions in the basis (such functions may also be significant for TS coupling in positively charged systems).

Caution is necessary in dealing with model anion species within the Hartree–Fock framework, since their energies may lie above those of the corresponding neutral systems (in contrast to the situation for the actual condensed-phase anionic systems which are being modeled). In such cases, unlimited expansion of the basis set would cause the excess electron to leak away if an unrestricted Hartree–Fock (UHF) wave function is employed. Similar problems have been dealt with in molecular orbital treatments of resonances in electron transmission spectroscopy (ETS).[84]

Paddon-Row and Jordan have evaluated energy splittings for n-electron hydrocarbon radical ions using Koopmans' theorem, based on the corresponding ($n \pm 1$)-electron closed-shell neutral systems (see section III.D.4).[32] The comments above regarding basis set sensitivity also apply to the KT results, especially in cases of unbound anions (i.e., negative electron affinity).[84]

Mikkelsen and co-workers[41] have developed an ab initio approach which includes the influence of a self-consistently polarized dielectric continuum on H_{if}. Solvent modulation effects are modest when realistic cavities are employed for the discrete supermolecular species. These results, which are based on equilibrium solvent polarization, also suggest that H_{if} will not vary strongly with the solvent component of the reaction coordinate, Q, at least for the types of supermolecule clusters dealt with in reported applications. H_{if} has also been found rather insensitive to variations in intramolecular components of Q.[38a,43b] Pronounced sensitivity *is* observed with respect to certain other coordinates (those "perpendicular" to Q), as discussed in section V.

Aside from problems of *accuracy* associated with basis set or electron correlation effects in the applications of many-electron SCF methods, there are problems of precision due to numerical differencing, which become increasingly significant with increasing size of the system and weakness of the coupling. (This applies both to energy splittings (ΔE^a) and to direct evaluation of H_{if} from symmetry-broken ψ_i and ψ_f wave functions.) Thus numerically reliable evaluation of couplings strength for systems with, say, 50–100 electrons becomes extremely demanding computationally when H_{if} magnitudes are $\lesssim 10$ cm^{-1}.

Finally, we note successful applications of discrete variable local exchange techniques (DV-Xα) in calculating π–π energy splittings in "molecular metals".[85]

3. *Excited-State Electron Transfer*

The definition of excited diabatic initial (ψ_i) and final (ψ_f) states involves a judicious mixture of physical criteria and intuitive input.[39] For ground-state processes the SCF model generally yields satisfactory results, either directly through charge-localized solutions or indirectly through calculated energy splittings based on delocalized solutions. For excited-state processes, the SCF approach is not generally applicable unless the state of interest happens to be the orthogonal by virtue of symmetry or otherwise weakly coupled to lower-lying states. An alternative is to obtain H_{if} from energy splittings based on configuration interaction (CI) estimates for adiabatic states[25b] or to obtain ψ_i and ψ_f by suitable constrained CI calculations.[33b–c,35] For example, in the case of porphyrin systems, this might involve CI calculations of excited diabatic states based on the 4-orbital frontier model[86] in which excitations are limited to specified local or charge-transfer contributions.[39]

Another consideration in the formulation of initial and final excited states relates to the dynamics of the medium surrounding the molecular aggregate. Whereas in the isolated aggregate, a charge-transfer component, for example, might be coherently coupled to some other component of an initial state, if the charge-transfer component were sufficiently strongly coupled to the medium, this would render the coupling incoherent, thus effectively eliminating it as a component of the initial state.[33c]

A number of model studies of photoinitiated electron transfer among the chromophores in the bacteria photosynthetic (BPS) system have been carried out on the basis of orbital wave functions obtained at the π-only (PPP) or all-valence (CNDO or INDO) levels.[25b,33–35] Estimates of H_{if} between pairs of chromophores have been obtained from one-electron matrix elements based on localized highest occupied and lowest unoccupied molecular orbitals of the respective chromophores.[33a,34] Plato et al. exploited the assumed proportionality between overlap (S_{if}) and coupling element (H_{if}).[34] Scherer and Fisher employed configuration interaction calculations for the excited states of the photosynthetic hexamer (i.e., the six primary porphyrin-based chromophores) in inferring H_{if} values.[33c] In this study, effective localized orbitals and states were inferred from the delocalized orbitals and states obtained in the full hexamer calculations.

Larsson has attempted to estimate H_{if} for the BPS system as an energy splitting based directly on calculated CNDO/S CI energies.[25b] He has also employed similar CNDO/S-based CI techniques to characterize the coupling for photoinitiated electron transfer involving π-electron donor and acceptor interactions mediated by norbornyl bridging units.[24c] As discussed by Larsson[24c] and also Reimers et al.,[58] there is some uncertainty as to the roles of electronic as opposed to nuclear momentum coupling in these electron-transfer processes.

C. Calculation of Energy Splittings

The evaluation of H_{if} as one-half the adiabatic energy splitting (ΔE^a) presupposes that one is located at the transition state (where $Q = Q^{\ddagger}$); i.e., on the surface of intersection of the diabatic energy surfaces in the effective two-state model (see comment following eqs 39 and 49), or alternatively, at the region of closest approach of the corresponding adiabatic energy surfaces. A symmetry relation between donor and acceptor will define the transition surface, but one generally desires the minimum energy point on this "seam". Koga and Morokuma have developed a gradient-based scheme for locating such a point.[87] Alternatively, one may obtain an approximate result by interpolating between initial (Q_i^e) and final (Q_f^e) equilibrium structures.[38a]

In the absence of symmetry one may still be able to approach the minimum energy point on the $Q^{\ddagger}$ surface if enough information about the potential energy surfaces is available, (e.g., by using a full gradient method).[87] If the energy as a function of location on the transition surface ($Q^{\ddagger}$) is quite flat, then configurational averaging of H_{if} over this surface may be necessary.[29c]

If one happens not to be located on the transition surface ($Q = Q^{\ddagger}$), for some assumed structure of the supermolecule employed in the calculation, then one may attempt to move to $Q^{\ddagger}$, by varying judiciously chosen coordinates of the supermolecule.[24b,25a] A related approach is to add external perturbations, e.g., an electric field simulated by point charges, thereby incorporating in effect the contributions of the surrounding medium to the reaction coordinate, Q, and to the relative energies of the states with respect to Q.[24c,25d] These external degrees of freedom can be "tuned" until the vertical energy separation of the two adiabatic states ψ_1^a and Ψ_2^a is minimized. In this sense the desired avoided crossing is attained. While an ad hoc procedure of this type is often a useful computational device, it may be expected to be susceptible to artifacts in cases where H_{if} is quite sensitive to electric field effects (e.g., by modulation of the contributions of "hole" and "electron" superexchange). Available tests suggest that such sensitivity may frequently be minor.[38a,41] A final device, easily implemented when using independent-particle models, is to artificially alter the values of the diagonal matrix elements $\langle\phi_D|h|\phi_D\rangle$ and $\langle\phi_A|h|\phi_A\rangle$ until the desired avoided crossing of orbital energy is achieved.[24a,28b,37]

If $Q \neq Q^{\ddagger}$, but close enough so that the two-state model is valid, then $\Delta E^a(Q)$, and hence $H_{if}(Q)$, may be evaluated by exploiting the approach discussed in section III.B, in connection with eqs 23 and 30.[25b,28] One may also calculate H_{if} directly from ψ_i and ψ_f, for $Q \neq Q^{\ddagger}$,[38] but then one must deal with ambiguities in the definition of H_{if}, as discussed following eq 24.

D. Degenerate or Nearly Degenerate States

While most kinetic models for electron transfer are based on the assumption of a two-*state* model, in practice one is frequently dealing with a two-*level* system involving degenerate or nearly degenerate states. The degeneracy may arise from spatial or spin coordinates.[43d,43e] While such situations potentially raise questions about quantum interference effects, in practice the kinetics is often treated as the superposition of all the various state-to-state processes arising from the two levels.[43d,44,88] Alternatively, for weak-coupling situations, one may define an effective two-state model, employing, for example, an rms value of H_{if} based on all the possible processes.[44,45a] Kestner, Logan, and Jortner[52] have discussed the requirements on state widths and separations for maintaining the validity of the "golden rule" rate constant.

E. Analysis of Calculated Transfer Integrals

Evaluationm of H_{if} from orbital wave functions generally obscures the role of individual direct, double, and superexchange contributions.[2,5,43,44] This information is implicitly contained in the degree of delocalization of the calculated ψ_i and ϕ_f, and the MO's which comprise them. A number of ab hoc techniques have been introduced in attempts to decompose the calculated overall transfer integrals. For energy splitting approaches which by construction employ one-electron models (e.g., an independent-particle model or the Koopmans' theorem[67] approach), one procedure has been to transform the effective one-electron Hamiltonian to a symmetrized basis of local bonding, antibonding, and lone pair orbitals. If donor and acceptor levels are well separated from bridge levels, then second-order RSPT allows an additive partitioning of bridge orbital contributions to ΔE^a, and hence, to H_{if}.[65] In an alternative, nonperturbative approach, the coupling elements between local bridge and donor/acceptor levels may be "turned on" in a sequential manner, revealing the evolution of the value of the splitting at each stage of the sequence.[66] This approach may yield useful insight, although it does not provide a unique additive decomposition since the results can depend appreciably on the order in which contributions are "turned on".

In more general situations, in which a one-electron model is not strictly imposed, an effective one-electron model may nevertheless be obtained[44d] by subjecting ψ_i and ψ_f to corresponding orbital transformations.[68] This simultaneously leads to the definition of effective donor and acceptor orbitals, ϕ_D and ϕ_A, and a maximally invariant core (see eq 83), as discussed specifically in connecting with metallocene systems in section III.D.1. This analysis is free of any preconceived notions about the nature of ϕ_D, ϕ_A, and the core, yielding an essentially variational result[44d] from an unbiased application of the corresponding orbital method[88] to the entire occupied n-electron manifold of ψ_i and ψ_f. The corresponding orbital method thus plays a crucial role both in the evaluation and in the interpretive analysis of H_{if}.

V. Computational Results

The preceding sections have dealt with a number of theoretical models for donor/acceptor coupling and with various computational approaches for implementing these models so as to provide numerical results which may be used either to test the simple theories or to make direct comparison with experimentally determined transfer integrals. We illustrate some of these results, focusing on studies which help to characterize the dependence of transfer integral magnitude on geometrical and electronic structural factors.

A. Variation of H_{if} with D/A Separation

Among the geometrical factors which control the magnitude of the transfer integral, the most critical are expected to be those which affect the distance separating donor and acceptor groups, either the direct through-space (TS) distance, or the effective distance involving indirect through-bond (TB) coupling, and the dependence of the transfer integral on such distances provides a particularly interesting point of contact between theory and experiment. We emphasize that there are in general a number of sources of distance dependence in the electron-transfer process.[6b,18] Thus the distance dependence of H_{if}, dealt with here, is distinct from that of the overall rate constant k_{et} (e.g., eq 2) or oscillator strengths (for optical transfer), or even from that κ_{el} (eq 10), as a result of the distance dependence of the reorganization energy, E_λ (see Figure 1).

1. Intramolecular Transfer

In considering the donor–bridge–acceptor complex, DB_mA, where the bridge is taken as a sequence of m subunits, we note that when simple superexchange models (e.g., eq 55) are valid, the overall coupling is conveniently factored into contributions involving the coupling of the bridge with D and A (T^2/D) and other contributions involving coupling within the bridge (t/E_{CT}). Of course, these latter contributions also reflect the influence of D and A through the energy gap, E_{CT}. Furthermore, the donor and acceptor orbitals on D and A, respectively, determine which portion of the bridge electronic manifold is involved in the transfer. Nevertheless, we may expect that the variation of transfer integral with bridge length will not depend strongly on many of the details of the D and A groups, with the most important factors being the properties local to the points of attachment to the bridge. This situation is particularly useful in theoretical studies, since it allows complicated D and A groups of interest to be meaningfully replaced by smaller model groups, provided that these groups do not appreciably alter the energetics or other aspects of the electronic manifolds primarily responsible for coupling with the bridge.

We consider the distance dependence associated with five different homologous bridge types, as displayed in Table I. Even though the coupling in all five cases is dominated by TB interactions, it is still convenient to characterize the variation with number of bridge units in terms of the direct, center-to-center D/A separation distance (r_c) since in all cases, the DB_mA sequences are roughly linear in shape. In Table I the dependence of H_{if} on r_c is expressed in terms of mean exponential decay parameters $\bar{\beta}$, where $\bar{\beta}$ is defined by the best fit to the form given by eq 79. To within estimated uncertainty, the experimentally based H_{if} values exhibit pure exponential decay. While the calculated H_{if} values conform reasonably well to the exponential form, we note that they exhibit modest systematic departures from this limiting behavior. Defining a local decay parameter, $\beta(r_c)$, which by construction yields the exact H_{if} results according to eq 79, we find $\beta(r_c)$ for the EHT data of ref 37a generally to *increase* with r_c (variations of up to ~30% relative to the mean) over the range of r_c values dealt with, while the ab initio data for the norbornyl spacers (see also Table II) yields a small *decrease* in $\beta(r_c)$ (within 10% of the mean).

One could undertake an alternative analysis in terms of the number of bonds (n_b) linking D and A in the shortest TB path.[11b,32b,32c] The decay parameter defined

TABLE I. Distance Dependence of H_{if}

bridging groups	$\bar{\beta}$, Å$^{-1\,a}$ observed	$\bar{\beta}$, Å$^{-1\,a}$ calculated	$\overline{dr_c/dn_b}$, Å^{b}
	Saturated Bridge		
edge-fused cyclohexyl rings^{c}	1.0 (th)^{d}	0.9 (th,EHT)^{e}	1.2
spiro-linked cyclobutyl rings (1(l))^{f}	0.8 (op)^{g}	0.9 (th,EHT)^{e} 1.3 (op,tb)^{h}	1.1
peptide-linked proline groups^{i}	0.6 (th)^{j}	0.7 (th,EHT)^{e,k}	1.0
edge-fused norbornyl groups (2(l))^{l}	0.6 (op)^{m}	0.5 (th,EHT)^{e} 1.0 (th,SCF/KT)^{n} 1.0 (th,CNDO/SCI)^{o}	1.3
	Unsaturated Bridge		
trans-linked olefin groups (polyene)^{p}	0.2 (op)^{q}	0.2 (th,EHT)^{r} 0.3 (op,CNDO)^{s} 0.3–0.4 (th,CNDO)^{s}	1.2

[a] The distance dependence of H_{if} is characterized by the mean decay coefficient $\bar{\beta}$, defined in terms of the effective center-to-center separation, r_c, of the D and A groups, and evaluated by fitting H_{if} values to the exponential form given by eq 79. The listed $\bar{\beta}$ values are based on the indicated $\overline{dr_c/dn_b}$ values together with the appropriate experimental or calculated H_{if} values. Due to some uncertainty in the determination of r_c (and hence also, $\overline{dr_c/dn_b}$), some of the $\bar{\beta}$ values given here differ slightly from the original literature values (the uncertainty is especially pronounced in the case of norbornyl spacers, as indicated by a consideration of refs 14, 24c, and 32a); th and op denote, respectively, thermal and optical electron transfer. The calculated th and op results are based, respectively, on energy splittings (ΔE^a) and transition moments. [b] The quantity $\overline{dr_c/dn_b}$ is the mean change in r_c per change in number (n_b) of framework bonds, where n_b is counted along the most direct covalent sequence connecting donor and acceptor. [c] D = 4-biphenylyl anion radical, A = 2-naphthyl. [d] Reference 11b. [e] Extended Hückel theory (EHT)[81] results from ref 37a. The partitioning technique[64] yielded the same $\bar{\beta}$ values as the results from full diagonalization, except for the cyclohexyl case, where the respective results are 1.0 and 0.9. [f] D = $Ru(NH_3)_5^{2+}$, A = $Ru(NH_3)_5^{3+}$. Here $n_b = 2 + 2l$. [g] Reference 9a. [h] "tb" here stands for the tight-binding method of ref 27a, which employed a periodic bridge potential. [i] D = $Os(NH_3)_5^{2+}$–isonicotinyl, A = $Ru(NH_3)_5^{3+}$. [j] Reference 18. [k] A value of 1.1 Å^{-1} based on EHT calculations for a peptide-linked bridge was reported in refs 25a and 25c for the thermal electron-transfer process, but apparently[25c] for the case of a σ-electron donor, in contrast to the π-type donors (see footnote i) dealt with in refs 18 and 37a. According to ref 25a, transfer is much more facile for π-type donors, but no $\bar{\beta}$ value was presented for the π case. [l] D = edge-fused dimethoxynapththyl anion radical; A = dicyanovinyl. Here $n_b = 2 + 2l$. [m] Reference 14. [n] Ab initio KT results[32b,32c] based on a neutral closed shell with the same type of norbornyl bridge as employed in the experimental study, but with edge-fused ethylenic D and A groups. The KT splittings are based on the ethylenic π^* orbitals and employed an STO-3G basis (see Table II).[89] [o] Based on thermal electron-transfer process occurring between excited states of the neutral system.[25d] [p] D = $Ru(NH_3)_5^{2+}$–pyridyl; A = $Ru(NH_3)_5^{3+}$–pyridyl. [q] Reference 21. [r] Reference 28c. [s] Reference 29c.

in this manner, $\bar{\beta}_{n_b}$, would be related to $\bar{\beta}$ through the expression

$$\bar{\beta}_{n_b} = (\bar{\beta})(\overline{dr_c/dn_b})$$

when the quantities given in the last column of Table I are used.

The overall agreement between observed and calculated results in Table I is reasonably good (of course, the analysis of the experimental data also involves theory, since it requires a detailed model for the rate constant). While the decay parameter for the unsaturated bridge is significantly smaller than those for the saturated bridges, we also find considerable variation in $\bar{\beta}$ among the four different examples of the latter type. Similar trends are found in terms of $\bar{\beta}_{n_b}$ (see above) since the various $\overline{dr_c/dn_b}$ values cover a rather small range (~1.0 to 1.3 Å per bond).

The variation in $\bar{\beta}$ values among the saturated bridges in part reflects corresponding variations in the effective energy denominators (see eq 55); e.g., with the exception of the cyclohexyl bridge case, the EHT $\bar{\beta}$ values decrease monotonically with the mean energy denominators given in ref 37a. Variations among the saturated bridges are hardly surprising, since they represent considerable diversity in bonding, including angle strain, topology, and even degree of σ bond character, if the partial double bond character associated with the amide linkages in the polyproline bridges is taken into account (furthermore, the peptide carbonyl groups provide relatively low-lying excited bridge states).

The finite, albeit small, value of $\bar{\beta}$ found for the polyene bridge reflects the influence of bond length alternation and can be contrasted with the asymptotic value of zero inferred in ref 28c when the bond alternation is suppressed.[24f]

All the data in Table I pertains to transfer of π-type electrons; i.e., the donor and acceptor orbitals have π symmetry, defined with respect to the bond vectors associated with the bonds linking the D and A groups to the bridge. For two cases closely related to those of Table I, Larsson has compared TB transfer integrals for σ- and π-type electron transfer. For NH_2 groups linked by trans-staggered alkane chains, he obtains at the EHT level $\bar{\beta}$ = 1.2 Å^{-1} for π transfer (cf., $\bar{\beta}$ = 0.9 Å^{-1} for the cyclohexyl systems in Table I), while a much weaker decay is found for σ transfer ($\bar{\beta}$ = 0.4 Å^{-1}).[24d] Similar trends were found at the CNDO/S and ab initio levels. Treating the polyglycine spacer at the EHT level, Larsson found facile π-electron transfer (no $\bar{\beta}$ value was presented), compared with less efficient σ transfer, which was characterized by $\bar{\beta} \approx 1.1$ Å^{-1}.[25a,25c]

According to the McConnell model (see discussion in section III.D.2), where m may be identified with n_b in the present discussion, one expects an alternation in the sign or H_{if} (or equivalently, ΔE^a) as the number of bonds (n_b) changes from odd to even. This effect has been referred to as the "parity rule".[13] Sign alternation consistent with the parity rule has been observed by Larsson for the alkane chains referred to above. However, in ref 37a, no occurrence of such alternation is evident in the cases where both even and odd numbers of bonds are involved (i.e., the cyclohexyl and the polyproline spacers).

Except for the cyclohexyl- and proline-based bridges, the experimental decay parameters are based on optical (IT) transfer integrals, whereas most of the calculated results are for thermal transfer integrals, being based on energy splittings (ΔE^{a}). The results for the unsaturated bridge, obtained from a CNDO-based electronic structure model, indicate similar decay parameters for the thermal and optical processes.[29c] This similarity reflects the fact that, barring specific instances of near-resonance between D/A and B levels, transfer integrals are not expected to vary appreciably with progress along the reaction coordinate Q. This result may be understood in terms of eq 45. Other examples of minor Q dependence of H_{if} have been noted, both for short-range molecular[38,43b] and longer range solvent components of Q.[50]

The extended Hückel theory (EHT)[81] calculations[37a] reported in Table I yield very similar results, whether from the solution of the full secular equation or from the perturbative partitioning method,[64] indicating that the D and A levels are reasonably well separated from bridge levels relative to the magnitudes of local coupling elements. The EHT transfer integrals are dominated by the unoccupied bridge orbitals (mean gaps with respect to its D and A levels being ~2 eV), thus implying a predominant superexchange mechanism of the "electron" type.[37] For the case of the dithia spiro-linked cyclobutyl ring bridges (**1**(l)), this result is opposite to the conclusion of a study based on the assumption of tight binding and a periodic bridge potential, which yielded coupling dominated by "hole" transfer.[27a]

1(l)

These divergent results from rather similar independent particle models underscore the importance of striving for systematic and objective criteria for selecting critical parameters in generic semiempirical orbital methods, especially for cases of transition-metal ions where parameters controlling D/A–bridge gaps may be quite sensitive to oxidation state.

Another critical feature of the spiro bridge system is the stereoelectronic aspect of the D/A–bridge linkage, as discussed below.

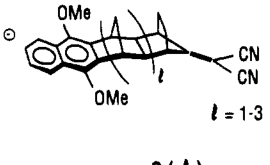
While simple theories seem capable of accounting for the decay of transfer integrals with distance in a reasonably quantitative manner, it should be noted that the absolute magnitudes of the calculated transfer integrals (reflecting the influence of D- and A-bridge coupling as well as intrabridge coupling), are in rather erratic agreement with observed values, varying from the latter by factors ranging from ~0.2 to ~50.

TABLE II. Comparison of Koopmans' Theorem (KT) Energy Splittings and Observed Transfer Integrals for Norbornyl Spacers[a]

		$\Delta E^{\mathrm{a}}/2$, eV[d]			
		electron attachment		ionization	
number of σ bonds in TB path (n_{b})[b]	H_{if}, eV[c]	KT[e]	obs[f]	KT[e]	obs[g]
4	(0.30 ± 0.04)	0.42	0.40	0.49	0.44
6	(0.11 ± 0.02)	0.11	0.13	0.17	0.16
8	(0.06 ± 0.02)	0.033		0.065	
10		0.0095		0.032	
12		0.0029		0.015	
$\bar{\beta}$, Å^{-1} [h]	0.6 ± 0.2	1.0	0.9	0.7	0.8
$\beta(10, 12)/\beta(4, 6)$[i]		0.9		0.8	

[a] See footnote n of Table I. [b] Refers to the number of σ bonds in the shortest through-bond (TB) path connecting D and A groups. For compound **2**(l), this number is given by $2 + 2l$. [c] Inferred from optical data for **2**(l).[14] For purposes of comparison with calculated results for related norbornyl systems,[a] we have arbitrarily scaled the original data[14] to give an exact match for $n_{\mathrm{b}} = 6$. The unscaled values are 0.16 ± 0.02, 0.06 ± 0.01, and 0.03 ± 0.01 eV, respectively. [d] ΔE^{a} is the energy splitting of the symmetric and antisymmetric ion states obtained from the neutral diene by electron attachment or ionization. [e] KT splittings[32c] based on orbitals of predominantly π^* (electron attachment) and π (ionization) character. [f] Reference 97. [g] Reference 98. [h] $\bar{\beta}$ is a mean value over the whole range of n_{b} values. Note that $\bar{\beta}$ as defined here is distinct from, but essentially proportional to, the β's defined in ref 32. [i] This ratio gives a measure of the gradual decrease of local β values ($\beta(r_{\mathrm{c}})$) over the range $n_{\mathrm{b}} = 4$ to $n_{\mathrm{b}} = 12$ ($\beta(i, j)$ is based on the splittings from $n_{\mathrm{b}} = i$ and $n_{\mathrm{b}} = j$); $\beta(i, i + 2)$ appears to have converged at $n_{\mathrm{b}} \approx 10$.[32c] Because of experimental uncertainty, no meaningful β variation can be inferred from the optical H_{if} data.

For the case of the norbornyl spacer, we provide more detailed information in Table II, comparing H_{if} estimates inferred from the experimental optical data[14] for the radical anion system **2**(l) with experimental and theoretical $\Delta E^{\mathrm{a}}/2$ values for the radical anion states of the related norbornyl-bridged diene systems.[32b,32c] Comparison with the corresponding radical cation states is provided as well. The theoretical results are KT estimates based on ab initio (STO-3G[89]) SCF results for the associated neutral closed-shell systems. The observed and calculated $\Delta E^{\mathrm{a}}/2$ values are in good agreement for both the radical anions and cations. The $\bar{\beta}$ values based on observed and calculated ΔE^{a} values are in good agreement, with values for the radical anions somewhat larger than those for the radical cations. Recent experimental data for the cyclohexyl bridge system (Table I) has yielded $\bar{\beta}$'s for the radical cation and radical anion processes that are nearly identical. The $\bar{\beta}$ value based on the diene radical anion energy splittings (ΔE^{a}) is appreciably greater than the $\bar{\beta}$ value inferred from the optical data for the **2**(l) systems. The local $\beta(r_{\mathrm{c}})$ values based on KT energies exhibit a modest decrease with increasing bridge length over the range $n_{\mathrm{b}} = 4$ to $n_{\mathrm{b}} = 12$ (~10% and 20%, for the electron attachment and ionization processes, respectively), and appear to converge at ~$n_{\mathrm{b}} = 10$.[32c] Recent basis set comparisons reveal that $\beta(r_{\mathrm{c}})$ variations for the electron-attachment process are more pronounced with more flexible basis sets (a decrease of ~30% for the 3-21G[91] basis, compared with the 10% decrease noted above for the STO-3G[89] basis).[32c]



2(l)

2. *Calculated Through-Space Coupling*

So as to provide a point of reference, we list in Table III some calculated decay parameters ($\bar{\beta}^{\mathrm{d}}$, eq 81) for D/A through-space (TS) coupling. As noted by Cave et al.,[56] the TS decay can be reliably estimated from a knowledge of the asymptotic form of the donor orbital involved in the process of interest:

$$\phi_{\mathrm{D}}(r) \approx \exp[-(2mE_{\mathrm{IP}}/\hbar^2)^{1/2}r] \qquad (91)$$

where m is the electron mass and E_{IP} is the ionization

TABLE III. Calculated Through-Space (TS) Distance Dependence of the Transfer Integral

donor/acceptor	$\bar{\beta}^d$, Å^{-1}[a]
Fe^{2+}/Fe^{3+}	5.0,[b] 5.3[c]
$H_2O/(H_2O)^{1+}$	4.6,[d], 4.8[e]
group II M/M^{1+}	2.5–3.2[f]

[a] $\bar{\beta}^d$ is the mean value of β^d obtained by fitting the calculated data to the form given by eq 81. [b] Reference 51b (one-electron effective potential model). [c] Newton, M. D. Unpublished material (ab initio SCF). The corresponding TS value when ligands were simulated by a point-charge crystal field is 4.2 Å^{-1}.[43a,b] [d] Reference 45a (ab initio SCF). The corresponding through-bond (TB) estimate for $\bar{\beta}$ (where H_2O and H_2O^{1+} interact through a chain of H_2O molecules) is 2.4 Å^{-1} (ref 45a). [e] Reference 43b (ab initio SCF). Here, the TS interacting H_2O's are complexed to Fe ions ($Fe^{2+}(H_2O)\cdots(H_2O)Fe^{3+}$). [f] Reference 56 (ab initio SCF).

energy associated with removal of an electron from ϕ_D. Thus β^d is obtained as twice the coefficient of r in eq 91. The $\bar{\beta}$'s dominated by TB coupling (Tables I and II) are appreciably smaller than the sample presented in Table III, demonstrating how electronic screening due to bridge orbitals serves to reduce the effective ionization energies associated with D and A orbitals. For the case of the norbornyl spacer, even for the shortest bridge studied ($n_b = 4$), the TS contribution to the transfer integral is estimated to be ≤2%.[38c] For H_2O/H_2O^+ coupling, the TS $\bar{\beta}^d$ value is seen to be ~2 times the "TB" value (the notation "TB" is used here since significant overlap occurs between nearest neighbor water molecules, even though no covalent links are present).

B. Stereoelectronic Effects

Aside from the basic topology of the DBA system and the effective D/A separation distance, there are a number of structural degrees of freedom involving the bridge, the D/A groups, or their linkage with the bridge, whose variation can have an appreciable effect on orbital overlap, thereby leading to stereoelectronic modulation of H_{if}.

1. Trans vs Cis Bridge Configurations

In the case of saturated hydrocarbon spacers it has been noted that trans configurations of D and A groups with respect to the spacer yield larger coupling than for isomeric situations involving cis configurations, as inferred from the corresponding electron-transfer rate constants.[90] The trends observed for the rate constants are reproduced by corresponding KT energy splittings;[32b] e.g., for the 6-σ-bond norbornyl-bridging system (2(2)), the ratio of $(\Delta E^*)^2$ for the all-trans case compared with the case involving one cis linkage, is ~12, whereas for the 8-σ-bond case, comparing the all-trans structure and one with two cis linkages, the ratio is ~18. These trends have been rationalized by Paddon-Row in terms of the orbital coefficients of the terminal atomic orbitals of the molecular orbitals of the bridge nearest to the band gap.[13]

2. The Torsional Mode of the 4,4-Bipyridine Bridge

The electronic coupling of Ru^{2+} and Ru^{3+} ions mediated by a 4,4-linked bipyridine (bpy) bridge is, not surprisingly, quite sensitive to the torsion angle about the C–C bond joining the two pyridyl groups. Some results for planar and perpendicular conformations are given in Table IV. For the planar conformation (0°), the π-type overlap is considerably more effective than for the symmetries spanned by the other 4d t_{2g} orbitals (here π corresponds to $4d_{yz}$, if bpy lies in the xz plane, with the Ru atoms aligned along the z axis). The calculated optical H_{if} value[29c] is in good agreement with the observed value[21] (corrected[29c] for effects of nonplanarity). For the 90° twisted conformation, where the two pyridyl rings lie, respectively, in the xz (donor end) and yz (acceptor end) planes, the local π-type 4d orbitals (respectively $4d_{yz}$ and $4d_{xz}$) are orthogonal, and the dominant pathway (which departs slightly from being thermoneutral) involves coupling of two $4d_{yz}$ Ru orbitals, which are, respectively, of the π type (with respect to the pyridine at the donor end) and π′ type (at the acceptor end). The notation π′ denotes an in-plane π-type interaction with the pyridine σ orbitals. In view of this involvement of bridging σ orbitals, it is perhaps not surprising (cf. Table I), that the twisted conformation yields much weaker superexchange coupling than that found for the planar structure. However, there are other cases of 90° twisted bridges which exhibit efficient superexchange coupling. We now cite two examples involving rigid spiro-linked spacers.

TABLE IV. Calculated Torsion-Angle Dependence of H_{if} for the 4,4-Bipyridine (bpy) Bridge[a]

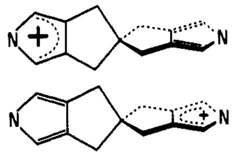
torsion angle, deg	symmetry of ϕ_D and ϕ_A	H_{if}, cm^{-1}	
		thermal[b]	optical[c]
0	π–π	420[d] 480[f]	476[e] 460 (obs)[g]
	π′–π′	10[d]	
	δ–δ	10[f]	
90	π–π′	8[f] 20[d]	

[a] The D/A groups, $Ru(NH_3)_5^{2+/3+}$, are complexed to the pyridyl nitrogen atoms, and these latter atoms and the Ru atoms are taken as lying along the z axis. For the planar (D_{2h}) case (0°), bpy lies in the xz plane, whereas for the twisted (D_{2d}) case, the pyridyl rings lie respectively, in the xz and yz planes. The π-type Ru 4d orbitals (xz and yz) are either parallel (π′) or perpendicular (π) to their pyridyl ligands, while δ corresponds to $4d_{xy}$. These symmetry designations are employed in classifying the orbital interaction types for the planar and twisted conformations. [b] Based on two-state energy splitting (ΔE^*). [c] Based on transition moment. [d] Reference 28b (EHT). [e] Reference 29c (CNDO). Reference 29c also reports estimated thermal H_{if} values in the range 214–443 cm^{-1}, based on various effective two-state and more general models for H_{if}. [f] Reference 25d (CNDO). [g] References 21 and 29c.

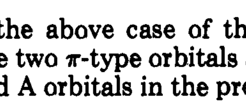
3. Bridge Based on Spirononane

Farazdel et al.[38a] considered symmetrical electron exchange for a radical cation (3) formed by fusing two pyrrole rings to the respective outer edges of spiro nonane (two spiro-linked cyclopentyl rings), and then removing one electron from the resulting $C_{13}N_2H_{14}$ species, yielding charge-localized C_{2v} equilibrium structures (**3a** and **3b**) which are related by a mirror plane, and a D_{2d} transition-state structure.

3a



3b



In contrast to the above case of the twisted Ru–bpy–Ru, where the two π-type orbitals are orthogonal, the effective D and A orbitals in the present case both transform as b_1 in D_{2d} symmetry (i.e., antisymmetric in *both* planes containing the 2-fold axis), and a substantial transfer integral is obtained from diabatic SCF wave functions obtained with either a minimal (STO-3G)[89] basis (280 cm^{-1}) or an extended (3-21G)[91] basis (360 cm^{-1}). The large coupling is noteworthy since the central atom has no basis functions tranforming as b_1. Hence, the superexchange pathways must involve direct coupling between nonbonded methylene groups.

4. Spiro-Linked Cyclobutyl Bridges

In the spiro-linked cyclobutyl bridge systems ($1(m)$), facile coupling is provided by the totally symmetric manifold of the saturated bridge, both for odd and even numbers of spacers. Previous models have assumed[9b,27a] that the Ru atoms lie on the 2-fold axis of the bridge, thereby leaving no mechanism for coupling of the active Ru orbitals (π-type t_{2g} 4d orbitals) and the totally symmetric bridge orbitals. Recently, Hush et al.[92] have pointed out that sulfur bonded to two alkyl groups and a Ru ion has a strong preference for a local *pyramidal* geometry,[93] and thus the two Ru atoms are expected to lie well off the 2-fold axis in the complexes under present discussion. This structural situation has the important stereoelectronic consequence of facilitating effective coupling between the local π orbitals of Ru (defined relative to the Ru–S axis) and the totally symmetric orbitals of the bridge.

5. Linkage of D and A to Cyclohexane-Based Bridges

The first entry in Table I deals wtih aromatic D and A groups bonded to cyclohexane-based bridging groups by single equatorial C–C bonds. From examination of the experimental rate constants for thermal electron transfer in the radical axion systems,[11b,30] it is clear that the strength of TB coupling depends on the configuration of the D–B and D–A attachment (equatorial (eq) vs axial (ax)) and on the conformation of the D and A aromatic groups about the single-bond linkages to the bridge. Model calculations[30] for the following process:

$$H_2C^{-}\text{–}C_6H_{10}\text{ – }\dot{C}H_2 \rightarrow H_2\dot{C}\text{–}C_6H_{10}\text{–}CH_2^{-} \quad (92)$$

where C_6H_{10} is a 1,4-substituted cyclohexane in the chair conformation, have yielded the results summarized in Figure 4 (see also the discussions in refs 12a and 12b). Figure 4 parts a and b refer, respectively, to cases of diequatorial (eq,eq) and diaxial (ax,ax) CH_2 substituents, and display the total conformational energy and the transfer integral for a range of torsional angles associated with the transition-state "seam" (i.e., where $Q = Q^*$). The stereoelectronic effects are striking. For the eq,eq configuration, the maximum in H_{if} (denoted $H_{if}^{eq,eq}$) coincides with the conformational *minimum* in the total energy, whereas for the ax,ax case, the maximum in the asymmetric $H_{if}^{ax,ax}$ curve coincides with the conformational *maximum* energy. To obtain more realistic conformational energetics, molecular mechanics (MM) calculations were carried out[30] for cyclohexanes 1,4-substituted (eq,eq and ax,ax) with the actual aromatic D and A groups employed in the experiments (respectively, 4-biphenylyl and 2-naphthyl groups). The eq,eq minimum remained at 0,0 while the ax,ax minimum was found at ~55°,±55°. These results are thus in qualitative accord (on a relative basis) with the experimentally inferred H_{if} magnitudes, which are found

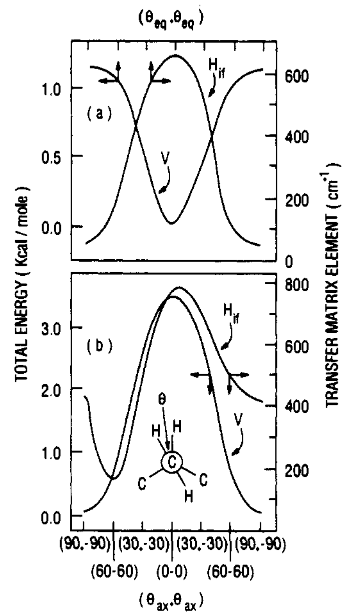


Figure 4. Calculated diabatic energy V ($V \equiv V_i = V_f$) and transfer integral H_{if} for 1,4-dimethylene cyclohexane radical anion at Q^*, as a function of the torsional angles (θ) of the terminal methylene groups (the cyclohexane ring has a chair conformation): (a) diequatorial and (b) diaxial configuration. As indicated in the conformational projection, $\theta = 0$ corresponds to coplanarity of the terminal CH_2 group and the CH bond belonging to the adjacent carbon atom (adapted from Figure 1 of ref 30; copyright 1986 American Chemical Society).

to yield ratios of ~1.2–1.7 for $(H_{if}^{eq,eq}/H_{if}^{ax,ax})^2$. Theory and experiment are also in accord in predicting less effective coupling for the hybrid (ax,eq) isomeric systems.[30]

C. Control of Transfer Integral Magnitude by Ligand/Field Mixing

Electron exchange between transition-metal complexes in contact may be analyzed in terms of a DBA model in which the metal ions take the role of the D and A groups, and the set of ligands (L), or the subset of them which occupy the region between the metal ions, collectively constitute the bridge (B). In terms

$$ML_n^{z+} + ML_n^{(z+1)+} \rightarrow ML_n^{(z+1)+} + ML_n^{z+} \quad (93)$$

of the superexchange model represented by eq 55, we expect the overall transfer integral to depend on both the ligand/field mixing within each reactant (D/B and A/B coupling) and on the coupling between contact ligand/ligand pairs created when the two reactants come together.

1. $ML_6^{2+/3+}$ Systems

Stereoelectronic effects may lead to interesting coupling between the D/B and A/B interactions and the intrabridge interactions. For example, comparing the two octahedral complexes, $Fe(H_2O)_6^{2+/3+}$ and $Co(NH_3)_6^{2+/3+}$, we find[44b] on the basis of INDO SCF calculations (employing the spectroscopic version developed by Zerner et al.[69b–d]), that for π-type transfer (i.e., involving the t_{2g} Fe 3d orbitals), the transfer integral magnitude is greatest for an interpenetrating (face-to-face) approach of the reactants along a common 3-fold axis, whereas for σ-type transfer (involving e_g Co orbitals), H_{if} is maximized for an apex-to-apex approach along a common 4-fold axis. These results are illus-

TABLE V. Calculated Dependence of H_{if} on Encounter Geometry in Bimolecular Electron Exchange[a]

orientation[b]	H_{if}, cm^{-1} [c]	r_{MM}, Å[d]
π-Electron Exchange:[e] $Fe(H_2O)_6^{2+/3+}$		
face-to-face	40	5.3
edge-to-edge	21	6.4
apex-to-apex	17	7.4
σ-Electron Exchange:[f] $Co(NH_3)_6^{2+/3+}$		
face-to-face	74	5.8
edge-to-edge	120	6.9
apex-to-apex	580	7.0

[a] Reference 95. These RHF values (see footnote *c*), differ somewhat from earlier values[44b] based on the unrestricted Hartree Fock (UHF) method. [b] The three indicated orientations correspond to approach geometries in which the two octahedral reactants, have, respectively, a common 3-, 2-, and 4-fold axis. [c] The H_{if} are obtained from calculated splittings (ΔE^*) on the basis of restricted Hartree Fock (RHF) INDO[69b–d] SCF wave functions for the $[(ML_6)^{2+}(ML_6)^{3+}]$ supermolecule complex. In general, a number of low-lying supermolecule electronic configurations are possible due to the spatial and spin degeneracy of the separate reactants. The listed H_{if} values correspond to those supermolecule states which yield H_{if} values of greatest magnitude. [d] Metal/metal separations for reactants at van der Waals contact for each orientation. [e] Exchange of a t_{2g}-type electron. [f] Exchange of an e_g-type electron, based on low-spin states of $Co^{2+}(^2E_g)$ and $Co^{3+}(^1A_{1g})$.

trated in Table V, which underscores the fact that the donor/acceptor separation distance, is not a generally reliable index of H_{if} magnitude.

a. Spin–Orbit Coupling Effects. There is another twist to the story for the $Co(NH_3)_6^{2+/3+}$ exchange. The data in Table V refer to low-spin states of the two oxidation states, whereas the ground state of $Co(NH_3)_6^{2+}$ is high-spin. A recent study[44c] based on ab initio estimates of high-spin/low-spin energy separations led to the conclusion that the observed kinetics involves spin/orbit mixing in the ground electronic state. Attenuation due to this spin/orbit coupling reduces the effective H_{if} values by a factor of $\sim 10^{-2}$ (relative to the low-spin values in Table V) and yields an estimate of $\sim 10^{-4}$ for κ_{el} (see eq 2). This latter estimate is within 2 orders of magnitude of estimates[94] based on experimental data ($\kappa_{el} \gtrsim 10^{-2}$). The spin/orbit mixing just discussed may be viewed as a key ingredient of a generalized superexchange mechanism in which initial and final states with high-spin reductants (i.e., $Co(NH_3)_6{}^{2+}$) are coupled through a series of virtual excitations involving not only local charge-transfer steps but also high-spin/low-spin interconversions. The Q dependence of the multiplet splitting energies, and hence of the spin/orbit coupling strength, provides a modest but interesting contribution to non-Condon behavior of H_{if}.[44c]

b. Charge-Transfer Pathways. It is found that the charge-transfer superexchange mechanism for both $Co(NH_3)_6^{2+/3+}$ and $Fe(H_2O)_6^{2+/3+}$ complexes is predominantly of the "hole" type (Figure 3), since the H_2O and NH_3 ligands provide high-lying *occupied* orbitals, but no accessible *unoccupied* orbitals. Ab initio studies for a series of model $ML^{2+}\cdots LM^{3+}$ systems (M = Fe,Co,Ru; L = H_2O,NH_3) in the "apex-to-apex" configuration have demonstrated quantitatively the dominance of a hole mechanism in terms of the covalency parameter λ which defines the antibonding ligand/field mixing between M and L orbitals.[43d] By using H_{if} and λ values based on the ab initio SCF results (λ was inferred from the coefficients of the donor (ϕ_D) and acceptor (ϕ_A) orbitals), the following expression was found to give an excellent fit to the calculated results:

$$H_{if} = \lambda^2 \bar{h}_{LL} \tag{94}$$

where $\bar{h}_{LL}$ is a mean effective intrabridge transfer integral coupling the ligands in contact, common to all the systems studied and determined by least-squares fitting to have a magnitude of 5000 cm^{-1}. Equation 94 is equivalent to the standard perturbation theory result, e.g., eq 55, where λ represents T/E_{CT} and h_{LL} corresponds to t.

For an apex-to-apex approach of the model ML reactants, the primary contact involves H···H interactions, and the success of eq 93 in fitting the calculated data suggests that the primary role of λ is to specify the degree of delocalization of ϕ_D and ϕ_A from the metal center onto the ligand hydrogen atoms. In the case of the face-to-face approach, however, where mode ab initio studies employed an $Fe(H_2O)_3^{2+}/Fe(H_2O)_3^{3+}$ supermolecule cluster,[43b] the complexes are in much more intimate contact (r_{MM} = 5.3 Å), and the above λ correlation (eq 94) only accounts for about half the total H_{if} magnitude, thus implicating other superexchange pathways, including O···H and O···O coupling, and perhaps even some Fe···O or Fe···Fe contributions.[43d] Unfortunately, there is no unique straightforward way to decompose calculated transfer integrals based on variational (SCF) many-electron wave functions into individual direct and superexchange pathways. It is true that comparable estimates of H_{if} were obtained from calculations based on point-charge crystal-field models[43a] (or in the limit when the ligands are totally absent) and from calculations for the $Fe(H_2O)_3^{2+}/Fe(H_2O)_3^{3+}$ supermolecules including all the ligand electrons explicitly, thus indicating that in the absence of the full influence of the ligand field, effective direct (TS) coupling is possible. However, the available evidence indicates that the Fe 3d orbitals (including radial as well as angular extent) and the transfer integral which depends on them, are strongly affected by ligand/field mixing (e.g., the magnitude of H_{if} is reduced by a factor of $\sim$3 when the model $Fe(H_2O)_3$ reactants are replaced by $Fe(H_3O)_6$ complexes),[95] and thus there is no compelling evidence that direct Fe–Fe coupling is a dominant factor when the full ligand manifold is included.

The one-electron model of Chandler et al.,[51b–d] employing a radial effective potential for the redox electron, and either a discrete basis or a thermally averaged path-integral approach, has yielded a sizable transfer integral for the aqueous Fe^{2+}/Fe^{3+} system ($\sim$120 cm^{-1} for a 5.5 Å Fe–Fe separation), which is found to be rather insensitive to the presence of solvent. This result appears to imply an essentially direct coupling mechanism, in contrast to the results based on conventional orbitals models (as discussed above). While the one-electron model is in principle capable of including an "electron" superexchange contribution (through delocalization of the redox orbitals), by its nature it precludes the possibility of the "hole" transfer found so important in the orbital models.

2. $Cp_2M^{0/1+}$ Systems

Electron exchange involving metallocene/metallocenium redox pairs ($Cp_2M/(Cp_2M)^{1+}$, where Cp ≡ cyclo-

TABLE VI. Calculated and Experimental H_{if} Values for $Cp_2M^{0/1+}$ Electron Exchange

	H_{if}, cm^{-1}					
	M = Fe(δ)[b]		M = Co(π)[b]			
orientation[a]	calcd[e]	exp	calcd[e]	exp	$E_{intermol}$, Kcal/mol[c]	r_{MM}, Å[d]
	Intermolecular					
D_{5h}	135	35[f]	920	175[f]	−5.8	6.75
C_s	99		70		−5.7	6.50
C_{2h}	27		222		−3.8	5.29
D_{2h}	11		27		−1.7	5.92
	Intramolecular					
C_{2h}	1050	≳600[g]	2100	≳1100[g]		5.14[h]

[a] The four orientations listed for intermolecular exchange correspond, respectively, to axial, perpendicular, size-by-side (displaced), and side-by-side approach geometries (ref 44d). The one intramolecular case corresponds to a trans conformation of the two Cp_2M moieties with respect to the covalent bond which links them. [b] δ and π refer to the symmetry (in pseudodiatomic notation) of the redox active orbital. [c] Calculated intermolecular energy, including electrostatic, induction, and dispersion terms (ref 44d). [d] M/M separation for reactants in contact. [e] Reference 44d. The comparison with the observed values is based on orientations with lowest intermolecular energies. [f] Reference 46 (based on thermal kinetic data). [g] Reference 96 (based on optical (IT) data). [h] Based on the *trans*-bimetallocenium structure.[44d]

pentadienyl) offers interesting contrasts in superexchange coupling, as a result of the following "selection rules". Adopting a pseudodiatomic model for Cp_2M, where the 5-fold axis coincides with the z axis, and a zeroth-order bonding model based on the M^{2+} and $(Cp)_2^{2-}$ species, we may classify the metal d orbitals as $\sigma_g(d_{z^2})$, $\pi_g(d_{xz},d_{yz})$, and $\delta_g(d_{x^2-y^2},d_{xy})$, while the 2p$\pi$ manifold of the Cp rings yields a π_g and a δ_g pair (respectively filled and empty for $(Cp)_2^{2-}$). Accordingly, the ligand/field mixing for M = Fe, where the redox active orbital is of δ_g symmetry can only yield "electron"-type superexchange (involving the *empty* zeroth-order δ_g ligand orbitals), whereas for M = Co, the redox active π_g orbital lead to a "hole"-type mechanism. The results for H_{if} obtained[44d] at the spectroscopic INDO level,[69b–d] using charge-localized SCF diabatic states (see section IV.B.2), are summarized in Table VI. Important points to note are the following: (1) The H_{if} magnitudes vary widely with approach geometry, spanning the nonadiabatic and adiabatic regimes, and in a manner not correlated with the M–M separation. (2) The magnitudes of H_{if} for M = Co, are uniformly greater than for M = Fe, reflecting the difference in coupling mechanism noted above and the more efficient M–L overlap in the π_g manifold compared with the δ_g manifold. (3) The H_{if} values associated with the lowest intermolecular energies bracket the values inferred from experimental data.[46] In addition, the calculated values for the covalently linked bimetallocene systems are consistent with lower limits obtained from experimental optical (IT) data.[96]

VI. Concluding Remarks

We have reviewed recent theoretical efforts to characterize the nature of donor/acceptor interactions in electron-transfer processes. When the energy levels of the system make appropriate the identification of an effective two-state model, the D/A coupling is compactly represented by the transfer integral, H_{if}, which couples the two states (initial and final) and which may be related directly to the electronic transmission factor governing the electron-transfer rate constant. In addition to its direct relationship to kinetics, H_{if} may also be placed in a larger context of D/A interactions, which includes the splitting of photoelectron and electron-transmission spectroscopy, and the two-electron coupling associated with localized spins and triplet energy transfer. This broader context provides greater insights into the nature of H_{if}, and also offers important cross-relations and self-consistency checks which help in the evaluation and interpretation of H_{if} magnitudes.

Several routes are available for formulating the transfer integral. Perturbative techniques, when applicable (both stationary and dynamical), lead to a number of compact analytical forms displaying the breakdown of H_{if} into various direct and indirect (i.e., superexchange) pathways. The overall pattern includes linear superpositions of "parallel" pathways, which may interfere with each other destructively or constructively, together with sequential pathways involving primitive hops "in series". In spite of their great potential for yielding interpretive insight, the perturbative approaches so far have been implemented with rather primitive electronic structural models. In contrast, sophisticated many-electron variational techniques (SCF and CI) have been applied in calculating H_{if} magnitudes for a number of complex molecular systems. While such calculations seem capable of yielding results with useful accuracy, a continuing disadvantage is that the ease of interpreting the results decreases with increasing sophistication of the electronic structure model. Furthermore, due to the differencing inherent in most of these approaches, numerical accuracy rapidly becomes a significant problem in cases of very weak coupling.

We have noted various situations in which an effective one-electron model for H_{if} emerges from a general many-electron framework, so that the many-electron transfer integral may be represented as the matrix element of an effective one-electron Hamiltonian which couples a well-defined donor and acceptor orbital. In a few cases, it has been possible to extract such a one-electron model from many-electron SCF results, demonstrating that all but one of the system electrons reside in a nearly invariant core which serves both initial and final states.

While large-scale SCF techniques are routinely being used to define ground-state diabatic or adiabatic states, the general situation from formulating initial and final states governing excited-state electron-transfer reactions (e.g., those initiated by photoexcitation) is much less well under control, although a number of interesting (but ad hoc) approaches based on configuration interaction have been employed.

Among areas deserving of concerted attention in the future, we emphasize the need for a more systematic formulation of the electronic states involved in ground- and excited-state electron transfer (including an assessment of the importance of electron correlation), and for a more comprehensive perspective on the validity of the Condon approximation. The two goals are, of course, interrelated. In establishing a computational procedure for defining electronic states (e.g., in terms of some discrete molecular cluster), it is essential to know which degrees of freedom of the system (both electronic and nuclear) are sufficiently important that they must be explicitly included in the initial Hamiltonian defining the system wave function, and which may be safely ignored or included more indirectly (e.g., via reaction field terms arising from a polarizable dielectric medium). In addition to understanding how wave functions, and hence, H_{if}, vary with the reaction coordinate Q (necessary for meaningful comparison of thermal and optical data), it is important to explore the sensitivity of results for a given value of Q (i.e., a hypersurface) to values of the various coordinates "perpendicular" to Q, especially those associated with large-amplitude notion, which may therefore require averaging of Q over these coordinates. With regard to the electron correlation problem, the appropriateness of using symmetry-broken SCF solutions to define variationally the diabatic charge-localized states (ψ_i and ψ_f), required further investigation. The symmetry breaking may be thought of as an aspect of electron correlation (relative to the symmetric solutions) which arises from legitimate physical sources (the predominance of local self-trapping ("solvation") over delocalization energy in situations of weak coupling. However, SCF symmetry breaking in other contexts has undesirable artifactual aspects.

Clearly an important goal is to combine the complementary advantages of several promising avenues into a unified approach for studying the energetics and dynamics of electron transfer in a complex polar medium. These avenues include the many-electron electronic structure techniques for molecular clusters, techniques such as the path-integral method, which allow the detailed modulation of the wave function by a disordered electronic medium (but so far limited to one-electron models), and a variety of dynamical models and simulation techniques which can treat nonadiabatic as well as adiabatic electronic processes and which give important perspective on the validity of simple kinetic models based on effective two-state models.

Acknowledgments. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We gratefully acknowledge a number of colleagues for thoughtful, detailed comments on the manuscript (Drs. C. Liang, J. R. Miller, and N. Sutin, and Profs. K. D. Jordan, N. R. Kestner, and M. A. Ratner) and for supplying preprints prior to publication (Drs. M. V. Basilevsky, D. N. Beratan, M. Dupuis, H. J. Kim, and N. Sutin, and Prof. K. D. Jordan).

References

(1) (a) Ulstrup, J. *Lecture Notes in Chemistry*; Springer-Verlag: Berlin, 1979; p 419. (b) *Faraday Discuss. Chem. Soc.* **1982**, *74*, 413.

(2) Newton, M. D.; Sutin, N. *Ann. Rev. Phys. Chem.* **1984**, *35*, 437.

(3) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(4) (a) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. (b) *J. Phys. Chem.* **1986**, *90*, 3657–3862.

(5) Mikkelsen, K. V.; Ratner, M. A. *Chem. Rev.* **1987**, *87*, 113.

(6) (a) *Electron Transfer in Biology and the Solid State: Inorganic Compounds with Unusual Properties*; Johnson, M. K., King, R. B., Kurtz, D. M., Kutal, C. Norton, M. L., Scott, R. A., Eds.; Advances in Chemistry Series 226, American Chemical Society: Washington, DC, 1990. (b) *Electron Transfer in Inorganic, Organic and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chyemistry Series 228, American Chemical Society: Washington, DC, 1991 (in press). (c) Sutin, N.; Brunwchwig, B. S. Reference 6a, p 65. (d) Sutin, N. Reference 6b.

(7) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 979. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(8) (a) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 155. (b) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(9) (a) Stein, C. A.; Lewis, N. A.; Seitz, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 2596. (b) Stein, C. A.; Lewis, N. A.; Seitz, G.; Baker, D. *Inorg. Chem.* **1983**, 22, 1124.

(10) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(11) (a) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (b) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

(12) (a) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173. (c) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.

(13) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

(14) 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.

(15) Bowler, B. E.; Meade, T. J.; Mayo, S. L.; Richards, J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 8757.

(16) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 260, 160.

(17) Petterson-Kennedy, S. E.; McGourty, J. L.; Kalweit, J. A.; Hoffman, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 1739.

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

(19) Wasielewiski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562.

(20) (a) Heitele, H.; Michel-Beyerle, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 8286. (b) Heitele, H.; Michel-Beyerle, M. E. *Chem. Phys. Lett.* **1987**, *134*, 273.

(21) Woitellier, S.; Launay, J. P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758.

(22) (a) Halpern, J.; Orgel, L. E. *Discuss. Faraday Soc.* **1960**, *29*, 32. (b) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

(23) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1976**, *98*, 4392. (c) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884. (d) Gleiter, R.; Schafer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

(24) (a) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034. (b) Larsson, S.; Matos, J. M. O. *J. Mol. Struct. THEOCHEM* **1985**, *120*, 35. (c) Larsson, S.; Volosov, A. *J. Chem. Phys.* **1986**, *85*, 2548. Larson, S.; Volosov, A. *J. Chem. Phys.* **1987**, *86*, 5223. Larsson, S.; Volosov, A. *J. Chem. Phys.* **1987**, *87*, 6623. (d) Broo, A.; Larsson, S. *Chem. Phys.* **1990**, *148*, 103. (e) Braga, M.; Broo, A.; Larsson, S. *Chem. Phys.*, submitted for publication. (f) Larsson, S. *Chem. Phys. Lett.* **1982**, *90*, 136. (g) Larsson, S. *Theor. Chim. Acta* **1981**, *60*, 111.

(25) (a) Larsson, S. *J. Chem. Soc. Faraday Trans.* 2 **1983**, *79*, 1375. (b) Källebring, B.; Larsson, S. *Chem. Phys. Lett.* **1987**, *138*, 76. (c) Larsson, S. *Chem. Scripta* **1988**, *28A*, 15. (d) Larsson, S.; Broo, A.; Källebring, B.; Volosov, A. *Int. J. Quantum Chem., Quantum Biol. Symp.* **1988**, *15*, 1. (e) Broo, A.; Larsson, S. *Int. J. Quantum Chem., Quantum Biol. Symp.* **1989**, *16*, 185.

(26) Kosloff, R.; Ratner, M. A. *Israel J. Chem.* **1990**, *30*, 45. (b) Ratner, M. A. *J. Phys. Chem.* **1990**, *94*, 4877.

(27) (a) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584. (b) Beratan, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 4321. (c) Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771. (d) Beratan, D. N.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1987**, *86*, 4488. (e) Onuchic, J. N.; Beratan, D. N. *J. Chem. Phys.* **1990**, *92*, 722. (f) Beratan, D. N.; Onuchic, J. N.; Betts, J. N.; Bowler, B. E.; Gray, H. G. *J. Am. Chem. Soc.* **1990**, *112*, 7915. (g) Beratan, D. N.; Onuchic, J. N. Reference 6b.

(28) (a) Joachim, C. *Chem. Phys.* **1987**, *116*, 339. (b) Woitellier, S.; Launay, J. P.; Joachim, C. *Chem. Phys.* **1989**, *131*, 481. (c) Joachim, C.; Launay, J. P.; Woitellier, S. *Chem. Phys.* **1990**, *147*, 131.

(29) (a) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1989**, *131*, 323. (b) Reimers, J. R.; Hush, N. S. Reference 6a, p 27. (c) Reimers, J. R.; Hush, N. S. *Inorg. Chem.* **1990**, *29*, 3686. (d) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1990**, *146*, 89.

(30) Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. *J. Am. Chem. Soc.* **1986**, *108*, 1319.

(31) (a) Balaji, V.; Jordan, K. D. *Chem. Phys. Lett.* **1985**, *119*, 294. (b) Balaji, V.; Jordan, K. D.; Fleiter, R.; Jähne, G.; Müller, G. *J. Am. Chem. Soc.* **1985**, *107*, 7321.

(32) (a) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1989; p 115. (b) Paddon-Row, M. N.; Wong, S. S. *Chem. Phys. Lett.* **1990**, *167*, 432. (c) Jordan, K. D.; Paddon-Row, M. N. Singlet and Triplet Splittings in a Series of Non-Conjugated Dienes. To be published.

(33) (a) Fischer, S. F.; Scherer, P. O. J. *Chem. Phys.* **1987**, *115*, 151. (b) Scherer, P. O. J.; Fischer, S. F. *Chem. Phys.* **1989**, *131*, 115.

(c) Scherer, P. O. J.; Fischer, S. F. *J. Phys. Chem.* **1989**, *93*, 1633.

(34) Plato, M.; Möbius, K.; Michel-Beyerle, M. E.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1988**, *110*, 7279.

(35) (a) Warshel, A.; Creighton, S.; Parson, W. W. *J. Phys. Chem.* **1988**, *92*, 2696. (b) Parson, W. W.; Creighton, S.; Warshel, A. In *Primary Processes in Photobiology*; Kobayoshi, T., Ed.; Springer-Verlag: Berlin, 1987; p 113.

(36) (a) Haberkorn, R.; Michel-Beyerle, M. E.; Marcus, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4185. (b) Marcus, R. A. *Chem. Phys. Lett.* **1987**, *133*, 471. (c) Marcus, R. A. *Chem. Phys. Lett.* **1988**, *146*, 13.

(37) (a) Siddarth, P.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 2985. (b) Siddarth, P.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 8430. (c) Cave, R. J.; Siders, P.; Marcus, R. A. *J. Phys. Chem.* **1986**, *90*, 1436.

(38) (a) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A. *J. Am. Chem. Soc.* **1990**, *112*, 4206. (b) Farazdel, A.; Dupuis, M. *Phys. Rev. B* Submitted for publication.

(39) (a) Sneddon, S. F.; Morgan, R. S.; Brooks, C. L., III *Biophys. J.* **1988**, *53*, 83. (b) Sneddon, S. F.; Brooks, C. L., III *Int. J. Quantum Chem., Quantum Biol. Symp.* **1988**, *15*, 23.

(40) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701.

(41) (a) Mikkelsen, K. V. Ph.D. Thesis, Aarhus University, 1985. Mikkelsen, K. V.; Dalgaard, E.; Swanstrom, P. *J. Phys. Chem.* **1987**, *91*, 3081. (b) Mikkelsen, K. V.; Ratner, M. A. *J. Phys. Chem.* **1989**, *93*, 1759. (c) Mikkelsen, K. V.; Ratner, M. A. *J. Chem. Phys.* **1989**, *90*, 4237.

(42) Kuznetsov, A. M.; Ulstrup, J. *J. Chem. Phys.* **1981**, *75*, 2047.

(43) (a) Newton, M. D. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 363. (b) Logan, J.; Newton, M. D. *J. Chem. Phys.* **1983**, *78*, 4086. (c) Newton, M. D. *J. Phys. Chem.* **1986**, *90*, 3734. (d) Newton, M. D. *J. Phys. Chem.* **1988**, *92*, 3049. (e) Logan, J.; Newton, M. D.; Noell, J. O. *J. Quantum Chem.* **1984**, *18*, 213. (f) Cox, P. A. *Chem. Phys. Lett.* **1980**, *69*, 340; Girerd, J.-J. *J. Chem. Phys.* **1983**, *79*, 1766.

(44) (a) Newton, M. D. *ACS Symp. Ser.* **1989**, *394*, 3783. (b) Newton, M. D. In *Perspectives in Photosynthesis*; Jortner, J., Pullman, B., Eds., Kluwer Academic Publishers: Boston, 1990; p 157. (c) Newton, M. D. *J. Phys. Chem.* **1991**, *95*, 30. (d) Newton, M. D.; Ohta, K.; Zhong, E. *J. Phys. Chem.* **1991**, *95*, 2317. (e) Newton, M. D. In *Cluster Models for Surface and Bulk Phenomena*; Pacchioni, G., Bagus, P. S., Eds.; NATO ASI Series; Plenum Press: New York, in press.

(45) (a) Larsson, S. *J. Phys. Chem.* **1984**, *88*, 1321. (b) Larsson, S.; Stahl, K.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 3033.

(46) McManis, G. E.; Nielson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

(47) (a) Ohta, K.; Morokuma, K. *J. Phys. Chem.* **1987**, *91*, 401. (b) Ohta, K.; Okada, O.; Yoshida, T. *J. Phys. Chem.* **1989**, *93*, 932.

(48) Michel-Beyerle, M. E.; Bixon, M.; Jortner, J. *Chem. Phys. Lett.* **1988**, *151*, 188.

(49) (a) Kuznetsov A. M.; Ulstrup, J. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 31. (b) Kuznetsov, A. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 49. (c) Kuznetsov, A. M. *Chem. Phys. Lett.* **1982**, *91*, 34.

(50) (a) Kim, H. J.; Hynes, J. T. *J. Phys. Chem.* **1990**, *94*, 2736. (b) Kim, H. J.; Hynes, J. T. *J. Chem. Phys.* **1990**, *93*, 5194. (c) Kim, H. J.; Hynes, J. T. *J. Chem. Phys.* **1990**, *93*, 5211.

(51) (a) Kuki, A.; Wolynes, P. G. *Science* **1987**, *236*, 1647. (b) Kuharski, R. A.; Bader, J. S.; Chandler, D.; Sprik, M.; Klein, M. D.; Impey, R. W. *J. Chem. Phys.* **1988**, *89*, 3248. (c) Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501. (d) Marchi, M.; Chandler, D. To be published. (e) Wheeler, R. A.; McCammon, J. A. *Chem. Phys. Lett.* **1990**, *174*, 369.

(52) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148.

(53) Brunschwig, B.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

(54) (a) Hoffman, B. M.; Ratner, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 6237. (b) Hoffman, B.; Ratner, M. A. Reference 6a, p 125.

(55) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454.

(56) Cave, R. J.; Baxter, D. V.; Goddard, W. A., III; Baldeschwieler, J. D. *J. Chem. Phys.* **1987**, *87*, 926.

(57) Kuznetsov, A. M.; Ulstrup, J. *Commun. Inorg. Chem.* **1990**, *10*, 197.

(58) (a) Reimers, J. R.; Hush, N. S.; Sammeth, D. M.; Callis, P. R. *Chem. Phys. Lett.* **1990**, *196*, 622. (b) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1990**, *146*, 105.

(59) Knapp, E. W.; Fischer, S. F. *J. Chem. Phys.* **1989**, *90*, 354.

(60) (a) Zener, C. *Proc. R. Soc. London, A* **1932**, *137*, 696. (b) Zener, C. *Proc. R. Soc. London A* **1933**, *140*, 660. (c) Landau, L. *Phys. Z. Sowjetunion* **1932**, *1*, 88. (d) Landau, L. *Phys. Z. Sowjetunion* **1932**, 2, 46.

(61) Efrima, S.; Bixon, M. *J. Chem. Phys.* **1976**, *64*, 3639.

(62) (a) Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061. (b) Webster, F.; Rossky, P. J.; Friesner, R. A. *Comp. Phys. Commun.* **1991**, *63*, 494. (c) Hu, Y.; Mukamel, S. *Chem. Phys. Lett.* **1989**, *160*, 410. (d) Hu, Y.; Mukamel, S. *J. Chem. Phys.* **1989**, *91*, 6973. (e) Basilevsky, M. V.; Chudinov, G. E. Multiconfiguration Theory of Adiabatic Electron Transfer in Polar Solvents. To be published.

(63) Löwdin, P. O. *J. Chem. Phys.* **1950**, *18*, 365–375.

(64) (a) Löwdin, P. O. *J. Mol. Spectrosc.* **1963**, *10*, 12. (b) The analysis of ref 64a, as implemented by Larsson for effective two-state models, is essentially equivalent to degenerate second-order perturbation theory; e.g.; see Schiff, L. I. *Quantum Mechanics*, 2nd ed.; McGraw Hill: New York, 1955; p 156.

(65) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.

(66) (a) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710. (b) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans.* 2 **1990**, 417.

(67) Koopmans, T. *Physica* (Utrecht), **1933**, *1*, 104.

(68) (a) King, H. F.; Stanton, R. E.; Kim, H.; Wyatt, R. E.; Parr, R. G. *J. Chem. Phys.* **1967**, *47*, 1936. (b) Amos, A. T.; Hall, C. G. *Proc. R. Soc. London, Ser. A* **1961**, *A263*, 483.

(69) (a) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026. (b) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21. (c) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728. (d) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.

(70) Verhoeven, J. W.; Pasman, P. *Tetrahedron* **1981**, *37*, 943.

(71) Schipper, P. S. *Int. Rev. Phys. Chem.* **1986**, *5*, 283.

(72) Beratan, D. N.; Hopfield, J. J. *J. Chem. Phys.* **1984**, *81*, 5753.

(73) Freed, K. F. *J. Chem. Phys.* **1986**, *84*, 2108.

(74) Kotler, Z.; Nitzan, A. *Chem. Phys. Lett.* **1988**, *153*, 483.

(75) Harris, R. A.; Falicov, L. M. *J. Chem. Phys.* **1971**, *55*, 21.

(76) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4383.

(77) Bertrand, P. *Chem. Phys. Lett.* **1987**, *140*, 57.

(78) (a) Kramers, H. A. *Physica* **1934**, *1*, 182. (b) Anderson, P. W. *Phys. Rev.* **1950**, *79*, 350. (c) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2. (d) Bertrand, P. *Chem. Phys. Lett.* **1985**, *113*, 104.

(79) Redi, M.; Hopfield, J. *J. Chem. Phys.* **1980**, *82*, 6651.

(80) Beratan, D. N.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1985**, *83*, 5325.

(81) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 295. (c) Wolfsberg, M.; Helmholz, L. *J. Chem. Phys.* **1952**, *20*, 837.

(82) (a) del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807. (b) Ellis, R. L.; Kuehnlenz, G.; Jaffé, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

(83) (a) Voter, A. F.; Goddard, W. A., III *Chem. Phys.* **1981**, *57*, 253. (b) Voter, A. F.; Goddard, W. A., III *J. Chem. Phys.* **1981**, *75*, 3638.

(84) (a) Falcetta, M. F.; Jordan, K. D. *J. Phys. Chem.* **1990**, *94*, 5666; *J. Am. Chem. Soc.* **1991**, *113*, 2903. (b) Chen, D.; Gallup, G. A. *J. Chem. Phys.* **1990**, *93*, 8893. (c) Heinrich, N.; Koch, W.; Frenking, G. *Chem. Phys. Lett.* **1986**, *124*, 20.

(85) (a) Doris, K. A.; Ellis, D. E.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2491. (b) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragala, I.; Herbstein, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748.

(86) (a) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138. (b) Gouterman, M. *J. Mol. Spectrosc.* **1963**, *11*, 108.

(87) Koga, N.; Morokuma, K. *Chem. Phys. Lett.* **1985**, *5*, 371.

(88) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014.

(89) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(90) (a) Kroon, J.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *Recl. Trav. Chim.* **1988**, *107*, 509. (b) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366.

(91) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(92) Rendell, A. P. L.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1988**, *110*, 8343.

(93) Coll, R. K.; Fergusson, J. E.; McKee, V.; Page, C. T.; Robinson, W. T.; Keong, T. S. *Inorg. Chem.* **1987**, *26*, 106.

(94) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(95) Newton, M. D. Unpublished work.

(96) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988**, 27, 1827.

(97) Balaji, V.; Ng, L.; Jordan, K. D.; Paddon-Row, M. N.; Patney, H. K. *J. Am. Chem. Soc.* **1987**, *109*, 6957.

(98) (a) Grimme, W.; Schumachers, L.; Gleiter, R.; Gubernator, K. *Angew. Chem. Int., Ed. Engl.* **1981**, *20*, 113. (b) Paddon-Row, M. N.; Patney, H. K.; Brown, R. A.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575. (c) Jørgensen, F. S.; Paddon-Row, M. N.; Patney, H. K. *J. Chem. Soc., Chem. Commun.* **1983**, 573. (d) Paddon-Row, M. N.; Patney, H. K.; Peel, J. B.; Willett, G. W. *J. Chem. Soc., Chem. Commun.* **1984**, 564.