

SELF-TRAPPING, BRIDGE ASSISTANCE, SUPEREXCHANGE AND INTRAMOLECULAR ELECTRON TRANSFER: SOME OBSERVATIONS

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ABSTRACT. — Controlled intramolecular nonadiabatic electron transfer is one of the earliest proposed schemes for molecular electronics. We discuss the general pictures and computational schemes appropriate for such systems, focusing on bridged binuclear ruthenium complexes as a specific example. The existence of distinct self trapped minima on the potential surface is shown to be necessary for the existence of an intramolecular electron transfer rate constant. While the Cordon approximation (independence of the electronic mixing matrix element on nuclear geometry) will not generally be valid, its use facilitates discussion of the transfer process in terms of simple electronic structure concepts such as superexchange. Some examples of self-trapped energy minima, and the corresponding physical and electronic structures, are calculated at the extended Hückel level; the wave functions are quite strongly localized on half of the molecule, although the energy depth of the self-trapped (mixed valency) structure is small. Pyrazine and bis (pyridyl) Be bridges show no self-trapped minima (Robin/Day III) while a 4,4'-bipyridyl bridge does show such asymmetric structures (Robin/Day II).

I. Introduction

One of the most widely discussed processes in molecular electronics is controlled intramolecular electron transfer. This process is critical to a number of biological mechanisms, and its discussion in terms of molecular rectification was an early, and still important, concept in the molecular electronics field.¹⁻⁴ The control of the rate and directionality of electron transfer can be afforded by appropriate chemical design of the molecular electronic matrix element.

Theoretical calculation, and prediction, of controlled intramolecular electron transfer rates thus relate both to synthetic molecular electronic materials and to such biological systems as the photosynthetic reaction center, cytochrome *c*/cytochrome oxidase complexes, modified hemoglobin and cytochrome moieties, and a number of important synthetic systems, including binuclear metal complexes. The subject has been extensively investigated,¹⁻⁵ and we should like here to concentrate on the relative roles of self-trapping, bridge assistance, and superexchange in determining the rates of intramolecular electron transfer.

A well-defined rate for intramolecular electron transfer requires the existence of well-defined precursor and successor, or initial and final, states.⁶ The definition of such states, the definition of a rate constant, and the relationship to the polaron self-trapping process is discussed in section II. Section III focuses on the nature of these extended, many-electron states. It discusses the roles of orthogonality in determining the effective electronic mixing, and the nature of non-adiabatic electron transfer. Section IV discusses how

one-electron matrix elements and the attractive superexchange formalism relate to the correct nonadiabatic electron transfer rate expression in terms of an interaction matrix element between many-electron states. Particular examples, involving extended Hückel level calculations on mixed valency species of ruthenium with different bridges, are found in section V. Finally, section VI contains some general remarks.

II. Electron transfer rates, precursor and successor states and polaron self-trapping

The process of intramolecular electron transfer is nearly universally discussed⁶ in terms of the configuration coordinate diagram, such as that in Figure 1. The two local minima corresponding to precursor and successor geometries are denoted Q_i and Q_r , respectively. The total reorganization energy is indicated as λ . The overall exoergicity, ΔG^0 , is basically identical to ΔE^0 , and the splitting of the electronic levels at the crossing point is $2H_{if}$.^{6a} Here the subscripts *i* and *r* denote left and right, and *i* and *f* correspond to initial and final states (or precursor and successor states). The potential is, of course, many-dimensional and these higher dimensionality effects have profound consequences, particularly when subsidiary minima occur on the potential surface. For our discussion, however, the situation as outlined in Figure 1 is sufficient.

The double minimum geometry of Figure 1 corresponds to the so called normal electron transfer regime, in which λ

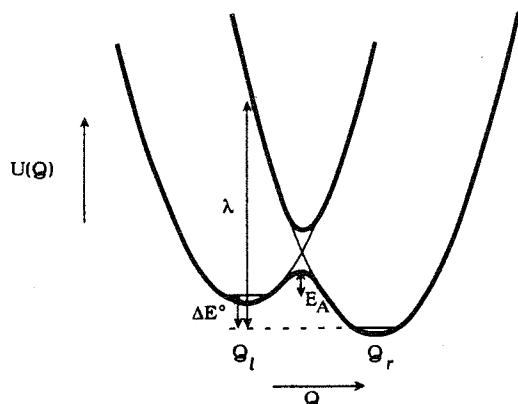


Figure 1. — Schematic configuration coordinate diagram showing adiabatic (heavy) and diabatic (light) potential surfaces for an intramolecular electron transfer event. The various free energy changes and quantities are referred to in the text. ΔG° and ΔE° differ by small entropic terms, but are considered to be identical for use in this text. $2H_{if}$ is the distance between the ground and excited state surfaces at the crossing point.

exceeds $|\Delta G^\circ|$. When $|\Delta G^\circ|$ equals λ , no maximum on the curve occurs, and for $|\Delta G^\circ|$ greater than λ , one enters the inverted regime—these are shown in Figure 2. Energetic control of reaction rates can be obtained by going from the situation with a large barrier in figure 1, to the zero barrier situation of Figure 2a (where the transfer is essentially instantaneous, limited by viscosity and other dynamical effects rather than by activation processes) to the inverted regime of Figure 2b.⁷ Again, as our topic here involves bridge control of reactions, rather than energetic control, we will not discuss the situation of Figure 2.

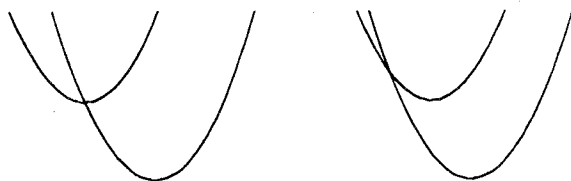


Figure 2. — Figure 2a shows the schematic configuration coordinate diagram for a situation in which the activation energy for electron transfer vanishes, and Figure 2b shows the situation of the so-called inverted regime, in which ΔG° exceeds the reorganization energy.

If the electronic mixing is strong enough, as indicated in equation 1a,

$$H_{if} \gtrsim \lambda/4 \quad (1a)$$

$$H_{if} \ll \lambda/4 \quad (1b)$$

then the curve of Figure 1 becomes that of Figure 3, with no stable minima corresponding to precursor and successor.^{7a} Under these conditions, one cannot, experimentally, expect to find a rate constant: rates refer to passage from one well-defined structure to another, and such structures are not found in situation such as that of Figure 3, in which the zero point energy is sufficient to assure delocalization. This is the situation to be found, for example, in a cofacial pair of benzenes, with one electron removed: while for very extended

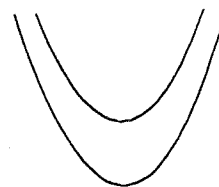


Figure 3. — Various schematic potential curves for a situation of very strong mixing, in which separated precursor and successor states do not exist and therefore, no intramolecular electron transfer rate can be defined or measured.

geometries (say a 5 Å separation between the rings) one can certainly define and observe electron motion from one ring to the other, for smaller separations the electron is delocalized, and one can neither define initial and final states or observe a transfer rate.⁸ In the chemistry of mixed valence species, the situation such as that of Figure 3 defines so-called Robin/Day class III substances,⁹ such as $[(\text{NH}_3)_5\text{Ru}(\text{N}_2)]^{5+}$ (dinitrogen bridged ruthenium pentamines, in the total valency state plus 5). In this situation, as Hush has stressed,¹⁰ the wavefunction is delocalized, and discussion of rates of electron transfer is experimentally illegitimate.

In molecular electronics applications,¹⁻⁴ one is generally interested in situations in which initial and final states are defined, and electron transfer between them can be controlled. We thus return to the situation of Figure 1. One then distinguishes between adiabatic and nonadiabatic electron transfer. This is most simply understood in terms of the semiclassical Landau-Zener construction,⁶ in which one considers passing along the diabatic (dotted) curves in Figure 1, and whether or not the system passes from the precursor parabola to the successor parabola on crossing. Using¹¹ a semiclassical picture in which the nuclei move classically, one can calculate electron transfer in terms of a probability P_0 , describing the probability of crossing from one surface to the other on a single transit of the transition region. Extension to a many-crossing situation then yields

$$\kappa_{et} = \frac{2P_0}{1 + P_0} \quad (2)$$

$$P_0 = 1 - e^{-2\pi\gamma} \quad (3)$$

$$2\pi\gamma = |H_{if}|^2 \left(\frac{\pi^{3/2}}{h\nu_n} \right) (kTE^*)^{-1/2} \quad (4)$$

Here ν_n is the characteristic nuclear frequency at the bottom of the precursor well, E^* is the activation barrier, and H_{if} is the matrix element mixing precursor and successor geometries, and causing the splitting of the adiabatic (solid) curves in Figure 1. While corrections to the Landau-Zener formula are available,¹² it is commonly used in discussions of nonadiabatic electron transfer, at least in the situation where viscosity effects, or diffusional transfer, or relaxation dynamics, are unimportant. (Relaxation dynamics are in fact critical in many electron transfer situations, and have been extensively discussed elsewhere.⁷)

When the nonadiabatic electronic factor of equation (2) is substituted into the transition state theory expression in equation (5), one obtains the common form,^{6,13} of equation (6)

$$k_{ET} = e^{-\Delta E^\circ/RT} \nu_n \kappa_{et} \quad (5)$$

$$k_{ET} = \frac{2\pi}{h} \left(\frac{1}{4\pi kTE^*} \right)^{1/2} |H_{if}|^2 e^{-\Delta E^\circ/RT} \quad (6)$$

The activation energy term, which is simply the barrier height, is given by

$$\Delta E^* = (\Delta G^0 + \lambda)^2 / 4\lambda. \quad (7)$$

Notice that equation (6) holds in the limit of nonadiabatic electron transfer: that is, in a limit where the exponent in equation (3) is small. Thus the condition for nonadiabatic electron transfer, in the absence of frictional effects, is given by

$$2\pi\gamma \ll 1. \quad (8)$$

The opposite limit, of adiabatic transfer, with rate independent of electronic mixing between precursor and successor, is simply given by equation (5) with $\kappa_{el} = 1$. In this adiabatic case one cannot control electron transfer by modification of the bridge or the electronic structure, but only by changing the relative energetics. Such cases are probably less relevant for molecular electronics, therefore we do not discuss them further.

The formulation that we have taken ignores the process of nuclear tunnelling, and assumes that the rate occurs by passage over the barrier top, yielding the activated complex form of equation (5). Generalizations to permit nuclear tunnelling are quite simply given in terms of a polaron theory of electron transfer, and are discussed fully elsewhere.⁶ For our purposes here, this distinction is not crucial since our focus will lie on the electronic structure term given by H_{if} ; in the vibronic theory, the generalization of equation (6) still has the H_{if}^2 prefactor, but the activation term and the square root prefactor are replaced by density of states weighted Franck-Condon factors.^{5,6}

The two conditions of equations (8) and (1b) assure nonadiabatic electron transfer, with a well-defined rate constant between two well-defined states. It is in the electronic structure analysis of such situations that we are primarily interested. Formally, the initial states and final states can be defined as polaron-type self-trapped minima on the potential surface: they arise because the nuclear geometry changes as the electronic wavefunction does, and the potential energy minimizes when the nuclear geometry is that of the (differing) precursor and successor states. Specific examples will be given in section V.

Given the polaron self-trapped states defining initial and final, or precursor and successor, states, and the existence of a rate constant between them given in the transition state limit by equation (6), we now wish to specify precisely how to calculate and understand the electronic mixing matrix element H_{if} .

III. Initial and final extended states, nonorthogonality, and nonadiabaticity

In the limit of nonadiabatic transfer, equation (6) shows that a combination of vibronic and energetic factors with electronic structure determines the transfer rate. Thus far, we have not specified the actual value of H_{if} , except to indicate in Figure 1 that the splitting between the adiabatic states is roughly twice this value. We can formulate the rate process in terms, say, of a generalized scattering theory approach; in this case, the term denoted H_{if} in equation (6) is a generalized T -matrix element,¹⁴ which, to lowest order, is simply the electronic matrix element between the electronic state locali-

zed at Q_i and that localized at Q_f . To this lowest order, H_{if} is well-defined as

$$H_{if} = \langle \Psi_i(Q) | H | \Psi_f(Q) \rangle. \quad (9)$$

The notation and the understanding of equation (9) are, however, not simple. The physical statement of equation (9) is that one evaluates the electronic mixing matrix element between the initial many-electron state Ψ_i and the final many-electron state, Ψ_f . These states are themselves defined as eigenstates of the so-called crude Born-Oppenheimer, or Herzberg-Teller, hamiltonian. The electronic eigenstates themselves are defined by equations (10)-(13).

$$H_{el}(Q) = H(Q_L) + (Q - Q_L) \partial H / \partial Q|_{Q_L} + \dots \quad (10)$$

$$H_{el}(Q) = H(Q_R) + (Q - Q_R) \partial H / \partial Q|_{Q_R} + \dots \quad (11)$$

$$H_{el}(Q_L) \Phi_s(Q_L) = \varepsilon_s(Q_L) \Phi_s(Q_L) \quad (12)$$

$$H_{el}(Q_R) \Phi_T(Q_R) = \varepsilon_T(Q_R) \Phi_T(Q_R) \quad (13)$$

The expansions in equations (10) and (11) are about the minimum geometries on the left and right (precursor and successor, or initial and final) minima of figure 1. The many-electron eigenstates of equations (12) and (13) are defined at these minima, and Ψ_i and Ψ_f are respectively the lowest energy Φ states of equations (12) and (13). In equations (10) and (11), we have truncated the Taylor expansion of the Born-Oppenheimer electronic hamiltonian after the first term.

The matrix element H_{if} of equation (9) is calculated at any arbitrary value of the nuclear coordinate Q . In a Condon approximation, (9) would be evaluated at the crossing point, whereas the eigenstates of equations (12) and (13) are defined at the self-trapped minimum geometries. The fact that (9) is to be calculated at the point at which initial and final vibrational polaronic energies are identical, or the so-called coincidence event geometry,¹⁵ is a consequence of the polaron model, or the linear coupling between electronic and vibrational motion. Note that the use of equations (9) and (6) implies a Condon-type simplification: electronic mixing is calculated only at one geometry, and its variation with geometry is not included. This Condon restriction is in general not adequate,¹⁶ in particular for situations in which orientational or twisting degrees of freedom strongly modulate the electron transfer mixing.^{17,18} Under these conditions, one must generalize equation (6) by defining the mixing matrix element H_{if} as a function of these non-vibrational degrees of freedom, and then averaging over the appropriate wavefunction distribution (or thermal distribution if kT is much greater than $\hbar\omega$). Again, we will not consider these geometrically constrained situations, except to point out that by control of such geometries one might well be able to change very substantially the rate of electron transfer, and thus provide some measure of control. In phthalocyanine molecular metals, precisely such a difference appears to hold in Ni(pc)x, where with different counterions x one changes the orientational angle between nickel phthalocyanines, and proceeds from metallic to semiconductive transport.^{18,19}

The electronic states of equations (9), (12), and (13) are many-electron states.⁸ They can, through reasonable approximation, often be defined as single determinant self-consistent field type states, consisting of occupied molecular orbitals.^{11,20} Such orbitals are in general delocalized; moreover, the wavefunctions of equations (12) and (13) are defined in terms of different electronic hamiltonians (since the hamiltonians are defined at different nuclear geometries) and there-

fore are not orthogonal to one another. One can correct H_{if} for the nonorthogonality effect by direct solution of the time dependent two site problem, resulting in the form

$$H_{if} = \frac{1}{1 - S_{if}^2} (H'_{if} - S_{if} H'_{ii}). \quad (14)$$

Here S_{if} is $\langle \Psi_i | \Psi_f \rangle$ while the matrix elements H' are those between the nonorthogonal states—that is, H' of equation (14) is in fact evaluated in equation (9).^{20, 21} The prime notation denotes calculation in terms of nonorthogonal wavefunctions, and the H_{if} of equation (14) is the correct one to use in the overall transfer and expression of equation (6).

Thus, within the generalized approximations that we have used (Condon approximation, Born-Oppenheimer separation, Herzberg-Teller expansion, polaron model, negligible friction effects, nonadiabatic limit, and neglect of barrier tunneling), equations (6-14) permit calculation of the electron transfer rate. We now focus on the calculation, and interpretation, of the mixing element H_{if} .

IV. Superexchange and effective matrix elements

Molecular electronics applications of controlled electron transfer involve nonadiabatic transitions modulated by bridging structures. For example, either the candidate molecular rectifier species of Figure 4c, or the bridged binuclear complex of Figure 4b entail electron transfer between reasonably

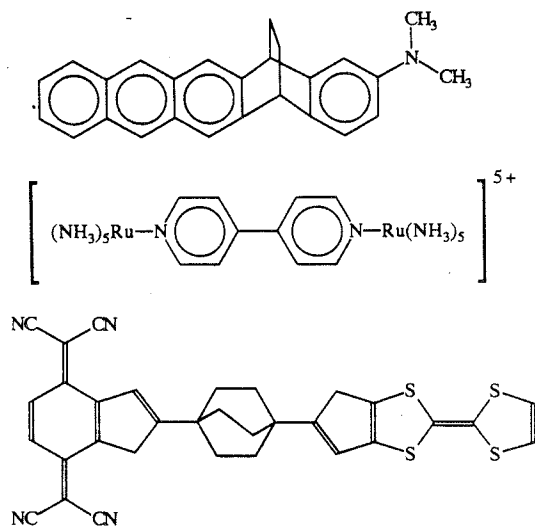


Figure 4. — Three structures in which intramolecular electron transfer between well-defined precursor and successor states should be observed. Figures 4a and 4b have been prepared and extensively studied, while Figure 4c is a proposed molecular rectifier molecule.

well-localized sites, occurring through a bridge (respectively bicyclo octane, or bipyridyl). For such situations, the direct transfer element overlap between donor and acceptor is relatively small. In a large number of the synthetic molecules recently prepared to examine intramolecular transfer, including bridged porphyrin quinone complexes, and organic bridges containing decalins or extensive fused norbornyl networks, and in modified protein systems containing two metal centers separated by large distances²² (greater than 12 Å),

direct interaction between donor and acceptor regions can generally be neglected. One then deals with a phenomenon of bridge assisted transfer, and specification of how bridge structures can promote or modulate electron transfer in such systems lies at the heart of controlled nonadiabatic transfer.

Generally, one understands the electronic structure of such molecular species in terms of an orbital basis. The nonrelativistic electronic hamiltonian, at a given geometry Q , can then be written as

$$H_{el}(Q) = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} \left\langle ij \left| \frac{1}{r} \right| kl \right\rangle a_i^\dagger a_j^\dagger a_k a_l. \quad (15)$$

Here the operator a_j^\dagger creates an electron in the j -th basis function, h_{ij} is the matrix element of the one-electron operator between basis functions i and j , and the matrix element in the second term is a Coulomb interaction, resulting in exchange or Coulomb integrals. If one chooses atomic basis functions, then the overlap matrix elements between basis functions i and j in equation (15) are non-vanishing, and the anti-commutation relations are no longer simply delta functions. Alternatively, one can expand in the molecular orbitals that are orthogonal (for any given Q) and then the operator algebra is simply that of independent fermions. The electronic hamiltonians of equations (10-13) are precisely that of equation (15), with the nuclear geometry chosen to be that of the right or left stable minimum in Figure 1. The *correct* evaluation of the H_{ij} element entering into equation (6) then follows from equations (14) and (9), with Ψ_i and Ψ_f the many-electron wavefunctions.⁸

Newton, in extensive and very important studies of transition metal complex systems,^{11, 20} has pioneered the use of a corresponding orbital scheme,²³ both to calculate and to discuss the mixing matrix elements. In this description, single determinant approximations to Ψ_i and Ψ_f are written in molecular orbital representation, with the highest, singly occupied molecular orbitals of Ψ_i and Ψ_f being substantially different. If, then, the overlaps of the doubly occupied molecular orbitals in Ψ_i and Ψ_f are very close to unity, the entire interaction matrix element is effectively reduced to a one electron matrix element, between the two singly occupied molecular orbitals. In this picture, one then simply evaluates the matrix elements in equation (14) between the singly occupied orbitals. Indeed, half the splitting at the barrier top, indicated as $2H_{if}$ in Figure 1 (see caption), is often^{11, 20} an excellent approximation to the true effective interaction. This corresponding orbital scheme not only permits the approximate description of the many electron mixing in terms of single electron functions, but it also indicates when such mixing is inappropriate: if the doubly occupied molecular orbitals are substantially different, one needs to consider the full multi-electron interaction rather than its one-electron limit.

There is, nevertheless, substantial difference between single one-electron matrix elements such as h_{ij} of equation (15) and the effective H_{if} to be used in equation (6). This has to do with the nature of the eigenstates Ψ_i and Ψ_f that enter into equation (9). These are polaron trapped states, and they will generally be substantially delocalized over the entire supermolecule geometry. In particular, the molecular orbitals will not, in general, be localized either on any one given atom or even in any one substructure, but will extend from the donor region towards the acceptor and (although very slightly) onto the bridge. Such delocalization has been discussed extensively by a number of workers; Fischer²⁴ refers to these states as soliton type states, but they are most simply

understood as the correct electronic eigenstates corresponding to the energy minima in Figure 1.

Much of the work in understanding electron delocalization and transfer in long-range intramolecular systems has been based on the superexchange model first discussed by McConnell.^{14, 25} This is most easily understood by ignoring the two-electron terms in equation (15), and rewriting the one-electron part in the form of equations (16) and (17).

$$H = H_0 + V \quad (16)$$

$$H_0 = \sum_{\lambda} \epsilon_{\lambda} a_{\lambda}^{\dagger} a_{\lambda} \quad (17a)$$

$$V = \sum' V_{\lambda\mu} a_{\lambda}^{\dagger} a_{\mu} \quad (17b)$$

Here the orbitals indexed by λ can be chosen fairly arbitrarily; ordinarily, one would understand them as those in which, on the basis of chemical intuition, one might expect electron localization. For example, in mixed valence ruthenium species they might be chosen as the singly occupied d -function on the ruthenium center, while in the bridged species of Figure 4c, they might correspond to the frontier orbitals on the TCNQ or TTF ends. For proteins, several groups have now developed models based on such a description, with the orbitals being frontier orbitals on particular amino acids.^{26, 27}

If the description of equation (17) is chosen, the effective matrix element to be used in equation (6) can be found easily using perturbation theory (other approaches, including partitioning^{27a} or effective-hamiltonian schemes,² can be used as well). This is most simply done on the basis of Brillouin-Wigner perturbation theory, or Green's function analysis,¹⁴ although equivalent formulations in terms of perturbed wavefunctions are also available.^{27, 28, 29} The Green's function analysis starts with

$$T_{\lambda\mu} = V_{\lambda\mu} + \sum_{\sigma\tau} V_{\lambda\sigma} G_{\sigma\tau} T_{\tau\mu} \quad (18)$$

where $V_{\lambda\mu}$ is the matrix element of equation (17b), $G_{\sigma\tau}$ is the electronic Greens function, and $T_{\lambda\mu}$ is the scattering operator matrix element between local functions λ and μ . $T_{\lambda\mu}$ depends upon the energy of the donor and acceptor states, which is assumed to be the same. Iteration of equation (18), using the one-electron form of equation (17), yields

$$T_{\lambda\mu}(E) = V_{\lambda\mu} + \sum_{\sigma} \frac{V_{\lambda\sigma} V_{\sigma\mu}}{E_{\sigma} - E} + \sum_{\sigma\tau} \frac{V_{\lambda\sigma} V_{\sigma\tau} V_{\tau\mu}}{(E_{\sigma} - E)(E_{\tau} - E)} \quad (19)$$

Further iteration yields higher-order terms, and the form of these terms is precisely that of the superexchange theory of McConnell. The sums as written directly in equation (19) are unqualified; alternatively, one can define particular pathway expansions, such that only irreducible parts of the sums are kept. The important point is in the interpretation: equation (19) indicates, for example, that transfer from a ruthenium d to another ruthenium d can occur through excited orbitals of energy E_{σ} , and that the contribution of that particular pathway would be given by the appropriate term in the sums of equation (19). One can then distinguish hole type transfer from electron type transfer, depending on whether the intervening orbitals [labelled σ , τ ... in equation (19)] are of electronic type or hole type, respectively.³⁰

There then appears to be a difference in level of description between the simple statement of equation (6) or equation (9), which suggests a single electronic integral

between initial and final many-electron states, and the superexchange formulation of equation (19) which builds in many higher excited states. It is legitimate to ask whether in fact the physical information involved in both is the same, or if there is something extra in the superexchange formulation absent in the simpler form. The answer to this latter question is no: in fact, the formulation of equation (6) is more general than that of (19), since (6) does not ignore two-electron contributions to the hamiltonian. [Extension of (19) to include two-electron terms, at least at the Hartree-Fock level, can be done but generally is not.]

While the many-electron, polaron model, corresponding orbital scheme includes the superexchange-type formulation of equation (19), it is in fact both more general and more useful. The superexchange approach is heuristically valuable, since it permits interpretation of the effectiveness of given bridging structures in terms of their molecular orbital energies. The difficulty is that one has no general procedure for selecting the orbitals labelled by the Greek indices in the one-electron hamiltonian. If one chooses them as localized atomic functions, then the mixing matrix elements $V_{\lambda\sigma}$ are substantially larger than typical energy denominators, and the superexchange perturbation series does not converge. It is thus more appropriate, and more chemically reasonable, to choose them as localized structures such as the frontier orbitals on amino acid bridging groups in proteins.²⁷ Again, though, electronic basis states are not uniquely defined, and different choices may give different rates of convergence, and even different answers.

Even more serious, one generally does not know what the initial and final choices for donor and acceptor one-electron functions are. For mixed valency situations in bimetallic complexes, one might approximate these localization sites as singly occupied d -functions, but such a picture may fail with organometallic ligands, and in general is quite arbitrary. When the localization sites are extended, as they are in porphyrin quinone complexes or the structure of Figure 4c, it is again arbitrary precisely how one chooses donor and acceptor. In the correct formulation, there is no ambiguity: the wavefunctions Ψ_i and Ψ_f are the polaron-trapped, ground-state wavefunctions corresponding to the energy minima in Figure 1. It is possible that at high temperatures one needs also to consider thermal contributions from higher excited states, but generally such complications are not considered important.

For polaron-trapped, many electron states, Ψ_i and Ψ_f will in general be extended species, and their molecular orbital representation can lead to calculation, through the corresponding orbitals method, of H_{if} of equation (6). This scheme is general and appropriate, and deals with such complications as definition of the initial state, arbitrariness in the electronic structure description of the bridges, and the role of electron repulsion. It can experience difficulties with large coupling elements, in which case other approaches may be preferable. Applications to a number of systems^{30a} have been given by Newton,¹¹ by the IBM group,³¹ and by Ohta and collaborators.³² We will give a few examples of how the delocalization occurs in the case of one-electron models of extended Hückel type, and in mixed valency species.

V. Examples: mixed valency and bridge assistance

For illustrative purposes, we will consider calculations for cases of mixed valency in binuclear bridged ruthenium complexes. Such species have been an important test area for

concepts of intramolecular electron transfer since they were first introduced by Taube's group more than twenty years ago.³³ In these molecules, the differentiation between fully delocalized (e.g., Robin/Day III) and weakly localized (Robin/Day II) systems is determined by the intramolecular competition between electronic delocalization, which lowers the kinetic energy of the electron, and valency trapping, which can result from both selective solvation and ion pairing.

Ruthenium binuclear species have been extensively studied both theoretically and experimentally; vibronic coupling models have been applied, the importance of the bridge sites and of bridge vibronic coupling has been stressed, and the nature of the frontier orbitals appropriate for discussion of the electrical transfer process has been pointed out.^{2, 5, 6, 11, 20, 30, 33, 34, 35} Our focus here is on the nature of the electronic states, and their variation with the strength of the bridging interaction.

We have calculated the total energies of the mixed valent binuclear species using the extended Hückel model, with standard parameterization. All environmental effects are ignored.

Figure 5a shows the calculated potential curve for the Creutz-Taube ion $(\text{NH}_3)_5\text{Ru-pyz-Ru}(\text{NH}_3)_5^{+5}$. This is expected, on purely experimental grounds,³⁶ to be a fully delocalized Robin/Day III system. Figure 5a indeed shows a single minimum potential; the total electronic energy is plotted as a function of a distortion parameter Q , that indexes departure from symmetry around the midpoint. In the case of Figure 5a, Q indexes a symmetric stretch of all metal to ligand distances about one ruthenium and a symmetric compression of all distances about the other. Specifically, for $Q = \pm 10$, all metal to ligand distances about one Ru have been stretched by 0.2 Å (relative to the bond distances at the minimum energy geometry), while all those distances about the opposite Ru have been compressed by 0.2 Å. Under the conditions outlined above, we expect no localization, no stable precursor or successor states, and no intramolecular electron transfer. Rather, one should observe transitions such as an optical excitation from the second highest orbital to the half filled, highest occupied orbital (see Fig. 3; this would be represented by a transition from the ground state to the first excited state). This transition is the limiting case of the intervalence transfer band^{33, 37} observed in localized mixed valency species.

Figure 5b schematically shows the density in the singly occupied frontier orbital. Notice that it is indeed delocalized, with large amplitude on the Ru centers, plus substantial amplitude on the bridging pyrazine.³⁸ The simple picture of bonding in terms only of ruthenium d -orbitals is inadequate, as has already been stressed by Ondrechen³⁴ and by Launay and Joachim.² When the bridging ligand is changed from pyrazine to 4,4'-bipyridyl, interesting changes can occur in the potential functions. If the twist angle around the single bond linking the two rings in the bipyridyl is 90° (perpendicular rings), the potential curve shown in Figure 6a is obtained. Though the calculated energy barrier is clearly small, this shows localization into precursor and successor states, between which transitions, corresponding to intramolecular electron transfer, will occur. The schematic configuration coordinate Q is in fact a complex linear combination of the motions in the molecule, and is determined locally using a simplex algorithm. The localization of the electronic wave function in the precursor geometry corresponding to the left minimum of figure 6a is indicated in Figure 6b, showing the singly occupied MO electron density. While very

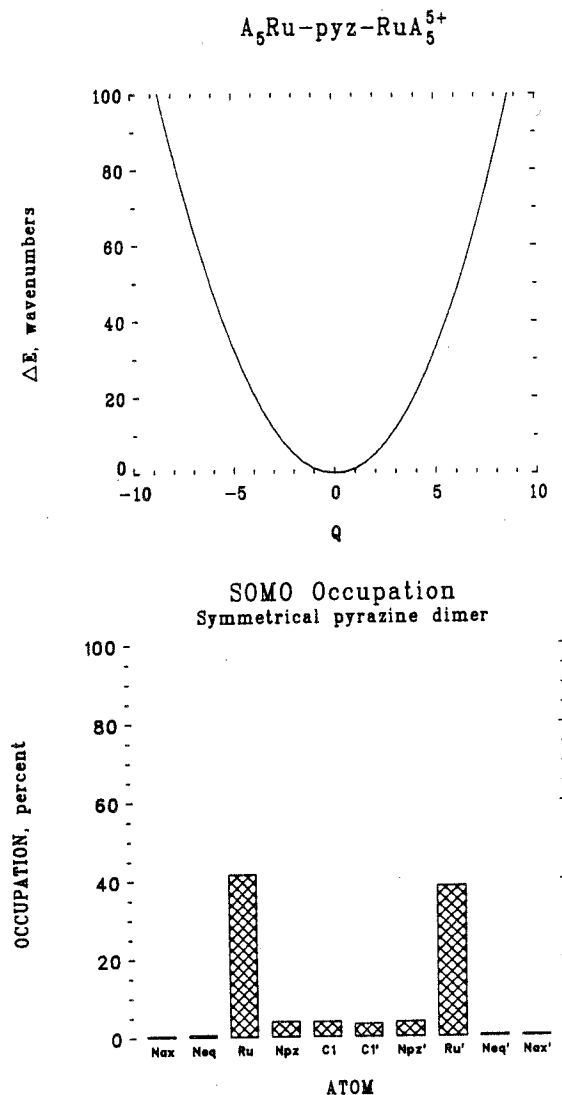


Figure 5. — Potential curves and singly occupied molecular orbital (frontier orbital) densities of the Creutz-Taube ion, $[(\text{NH}_3)_5\text{Ru-pyz-Ru}(\text{NH}_3)_5]^{+5}$. Note that in Figure 5a, there is only a single minimum of total energy as a function of asymmetric displacement generalized coordinate Q . Figure 5b then shows that the frontier orbital is completely delocalized over the two rutheniums, with considerable contributions from the ligands.

strongly dominated by the ruthenium on the right, the density nevertheless delocalizes fairly substantially about the right-hand side of the molecule. Its extension on to the ruthenium on the left is very small, an important manifestation of the localization phenomenon. If the geometry along the distortion coordinate Q is made symmetric (i.e., at $Q=0$), one obtains the wavefunction at the barrier top Q_T . In moving from the minimum to the barrier top, the wave function itself changes substantially; Figure 6c shows the single occupied MO calculated at Q_T . Here we observe a delocalized wave function quite comparable to that of the Creutz-Taube ion. At this symmetric geometry, once again the intervalence transfer band becomes a transition between delocalized bonding and anti-bonding MO's. Calculations of the effective coupling in bipyridyl-bridged binuclear complexes have been

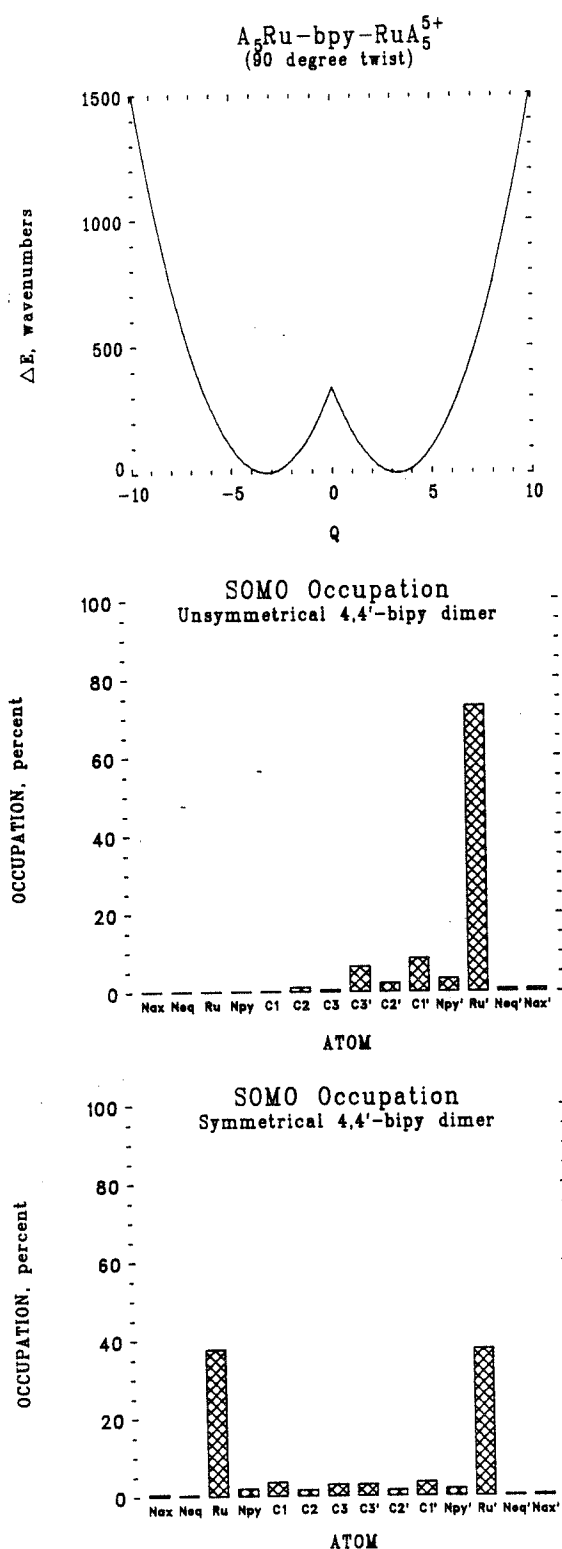


Figure 6. — As in Figure 5, but this time for the 4,4'-bipyridyl bridge, with a 90° twist around the internal single bond. Notice in Figure 6a that separable minima corresponding to precursor and successor exist, and in Figure 6b that the frontier MO is largely localized on one side. Figure 6c shows the frontier orbital density calculated at the symmetric geometry, corresponding to the top of the cusp in 6a (*i. e.*, at $Q = 0$).

previously presented by Woitellier *et al.*,² who consider the different contributions to the overall coupling.

The orbital wave functions calculated at the precursor and successor minima of Figure 6a are substantially localized, and very non-orthogonal. The nonorthogonality is important and can be rigorously dealt with (at least at the single configuration level) using the corresponding orbital transformation method.^{20, 23}

Figure 7 shows the potential curve calculated for planar bridging 4,4'-bipyridyl; in Figure 8, a beryllium atom has been inserted along the single bond bridging the two (assumed perpendicular) pyridines. In both of these cases, one observes essentially Robin/Day III behavior, as the increased bridge electronic mixing bridge dominates the vibrational trapping.

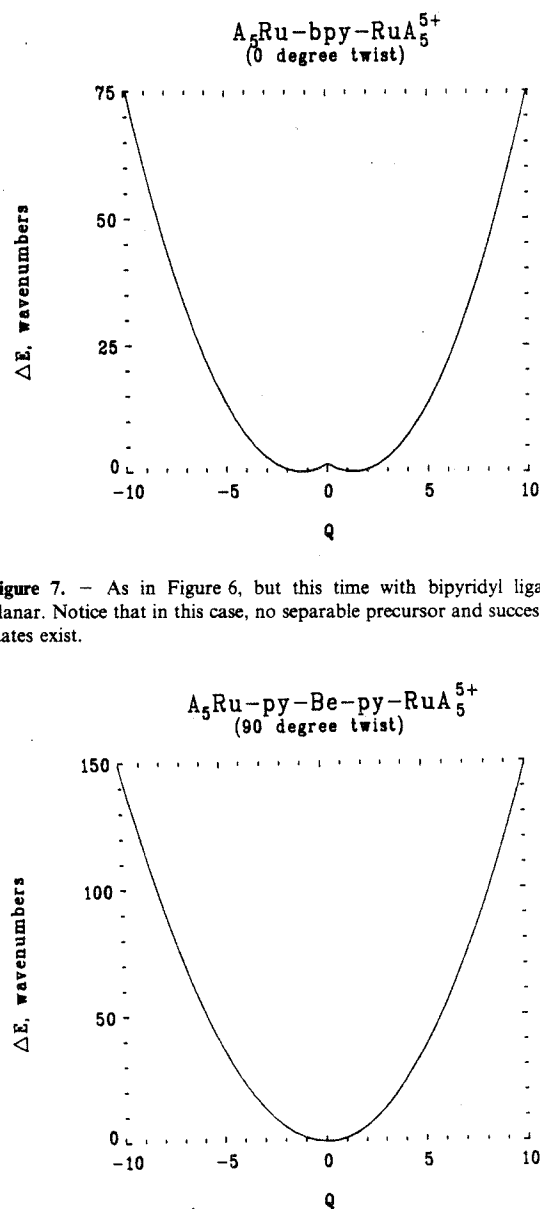


Figure 7. — As in Figure 6, but this time with bipyridyl ligand planar. Notice that in this case, no separable precursor and successor states exist.

Figure 8. — As in Figure 6, with a beryllium inserted in the single bond between the two bipyridyl rings. In this case, despite the 90° twist, the beryllium atom results in strong enough mixing that no distinguishable minima exist on the potential energy curve.

These calculations suggest that, in the absence of effects due to environmental trapping, among the four species considered only the one with weakened conjugation across the bridge permits distinguishable precursor and successor geometries and therefore will show measurable rates of intramolecular electron transfer.

VI. Remarks

Despite the fact that the notion of molecular rectifiers was put forward almost two decades ago, a complete theory for field control of intramolecular electron transfer is not yet in place, despite interest and extensive work on the subject. Control of electron transfer rates in *dc* fields is really fixed by control of the overall exoergicity ΔG° , and, in the absence of relaxation effects, the role of ΔG° in controlling electron transfer should be straightforward. The focus of the present paper is really on assuring controllability of an electron transfer reaction, by assuring separation of precursor and successor states.³⁹ Such separation mirrors the idea of Aviram of a tunnelling bridge, needed to separate the precursor and successor geometries, to provide two minima on a potential curve, and to permit actual switching from one to another. Recent suggestive experiments⁴ make it even more imperative to understand, in a proper formal way, precisely how control of intramolecular electron transfer can be achieved. The notions of relaxation and state accessibility are of major importance in this area, as is the dissipation of energy into the environment.

The principal focus in this manuscript has been examination of the existence of precursor or successor complexes in a simple set of well studied examples based on binuclear metal complexes. Important findings include: (1) Very slight changes in the structure of the bridge between the metals results in major differences in the behavior, including a transition from Robin/Day II to Robin/Day III classification. This has been noted previously^{2, 28} using different approaches. (2) Extensive delocalization over one side of the molecule is found even in the Robin/Day II case; such delocalization, referred to as a soliton state by Fischer and collaborators,²⁴ is important in calculation of the electronic matrix elements and coupling energies. (3) Even very small energy barriers separating precursor and successor states imply very substantial localizations of the wave function on one geometry or the other, and the concomitant non-orthogonality of precursor and successor states must be dealt with directly. Such non-orthogonality refers not only to the highest occupied molecular orbital, but to all of the molecular orbitals calculated in the two different geometries. (4) Breakdown of the Condon approximation should be of substantial importance in these systems, since the mixing depends so strongly on the nuclear coordinate. (5) The corresponding orbitals method, which permits inclusion of non-orthogonality effects, is probably needed to compute directly the tunneling matrix elements. (6) At the crossing point, the behavior of the lower potential curve is cuspy: such cuspidity is real, and does not disappear when many points are calculated.

Because of their extensive experimental importance, and their easy preparation, binuclear metal complexes will continue for the foreseeable future to be testing grounds for controlled intramolecular electron transfer, and other concepts of molecular electronics.

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REFERENCES

- Aviram A., Ratner M. A., *Chem. Phys. Lett.*, 1974, **29**, 277.
- Joachim C., *J. Phys.*, 1988, **A19**, 2549; Joachim C., Launay J. P., in Carter F. L. *et al.*, "Molecular Electronic Devices" Elsevier, 1988, p. 149; Kahn O., Launay J. P., *Chemtronics*, 1988, **3**, 140; Woitellier A., Launay J. P., Joachim C., *Chem. Phys.*, 1989, **131**, 481.
- Aviram A., Ed. "Molecular Electronics" The Engineering Society, New York (1990); Aviram A., *J. Am. Chem. Soc.*, 1988, **110**, 5687.
- Metzger R. M., Panetta C. A., Miura Y., Torres E., *Synth. Metals*, 1987, **18**, 787; Metzger R. M., Panetta C. A., in Aviram A., Ed. *Molecular Electronics*, The Engineering Society, New York (1990) p. 293; Geddes N. J., Sambles J. A., Couch N. R., Sandman D. J., to be published.
- Ratner M. A., in ref. 3, p. 1; Ratner M. A., in "Perspectives in Photosynthesis", Jortner J., Pullman B., Eds., Kluwer, 1990, p. 185.
- Newton M. D., Sutin N., *Ann. Revs. Phys. Chem.*, 1984, **35**, 437; Sutin N., *Prog. Inorg. Chem.*, 1983, **30**, 441. (6a) The true splitting is $2H_{12}$ if overlap considerations are unimportant, if the corrections to the Condon approximation are ignored, if all many-electron effects are omitted and if a simple two-state model is used. All of these issues are discussed briefly in the rest of the paper.
- Cannon R. D., "Electron Transfer Reactions", Butterworths, London (1980); Marcus R. A., Sutin N., *Biochem. Biophys. Acta*, 1985, **811**, 265; Ulstrup J., "Charge Transfer Processes in Condensed Media", Springer, Berlin, 1979; Mikkelsen K. V., Ratner M. A., *Chem. Revs.*, 1987, **87**, 113; Fleming G. R., "Chemical Applications of Ultrafast Spectroscopy", Oxford, New York (1986); Kosower E. M., Huppert D., *Ann. Revs. Phys. Chem.*, 1988, **37**, 127; Kahlow, M. A., Kang T. J., Barbara P. F., *J. Phys. Chem.*, 1987, **91**, 6452; Grote A. F., Hynes J. T., *Chem. Phys.*, 1982, **77**, 1295; Simon J. D., *Acc. Chem. Res.*, 1988, **21**, 128; Simon J. D., Su S. G., *J. Phys. Chem.*, 1988, **92**, 2395; *J. Chem. Phys.*, 1988, **89**, 908; Nadler W., Marcus R. A., *J. Chem. Phys.*, 1987, **86**, 3906; Sumi H., Marcus R. A., *J. Chem. Phys.*, 1986, **84**, 4272; Zusman L. D., *Chem. Phys.*, 1980, **49**, 295; Calef C. F., Wolynes P. G., *J. Phys. Chem.*, 1983, **87**, 3387; Hynes J. T., *J. Phys. Chem.*, 1986, **90**, 3701; Murillo M., Cukier R. I., *J. Chem. Phys.*, 1985, **89**, 6736; Zusman L. D., *Chem. Phys.*, 1988, **51**, 119. (a) The referee has pointed out Hush's comment¹⁰ that the $\lambda/4$ value, that arises from the shape of the crossed parabolas, should be replaced by $\lambda/2$, since the electronic tunnelling stabilizes the energy levels at the bottom, as well as the top, of the potential curve.
- Mikkelsen K. V., Ratner M. A., *J. Phys. Chem.*, 1989, **93**, 1759; *J. Chem. Phys.*, 1989, **90**, 4237. Note that in this work the full many electron matrix elements are calculated.
- Robin M. B., Day P., *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
- Hush N. S., *Chem. Phys.*, 1975, **10**, 361.
- Newton M. D., in "Perspectives in Photosynthesis", Jortner J., Pullman B., Eds., Kluwer, 1990, p. 157.
- Nikitin E. E., "Theory of Elementary Atomic and Molecular Processes in Gases", Clarendon, Oxford, 1974, p. 99.
- Marcus R. A., *J. Phys. Chem.*, 1963, **67**, 853, 2889; *J. Chem. Phys.*, 1956, **24**, 966, 979; *Ann. Revs. Phys. Chem.*, 1965, **16**, 155; Hush N. S., *Trans. Far. Soc.*, 1961, **57**, 557; *Electrochem. Acta*, 1968, **13**, 1005.

- ¹⁴ Ratner M. A., *J. Phys. Chem.*, 1990, **94**, 4877; Goldman C., preprint.
- ¹⁵ Emin D., *Phys. Rev.*, 1971, **B4**, 3639.
- ¹⁶ Beratan D. N., Hopfield J. J., *J. Chem. Phys.*, 1984, **81**, 5753.
- ¹⁷ Ratner M. A., Madhukar A., *Chem. Phys.*, 1978, **30**, 201.
- ¹⁸ Hale P. D., Ratner M. A., *J. Chem. Phys.*, 1985, **83**, 5277.
- ¹⁹ Pietro W., Marks T. J., Ratner M. A., *J. Am. Chem. Soc.*, 1985, **107**, 5387.
- ²⁰ Newton M. D., *J. Phys. Chem.*, 1986, **90**, 3437; *ibid.*, 1988, **92**, 3049; *A.C.S. Symp. Ser.*, 1982, **198**, 255.
- ²¹ Todd M. D., Ratner M. A., Mikkelsen K. V., unpublished.
- ²² Pennington D. E., in "Coordination Chemistry", Martell A. E., Ed., 1978, vol. 2: 476. American Chemical Society. Taube H., *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 329; Balzani V. F., Bolletta M. T., Gandolfi M., Maestri, *Topics in Current Chemistry*, 1968, **75**, 1; Gust D. et al., *J. Am. Chem. Soc.*, 1987, **109**, 604; Leland B. A., Joran A. D., Felker P. M., Hopfield J. J., Zewail A. H., Dervan P. B., *J. Phys. Chem.*, 1985, **89**, 5571; Calcaterra G. I., Green J. N., Penfield K. W., Miller J. R., *J. Phys. Chem.*, 1986, **90**, 3673; Wasielewski M. R., Niemczyk P. M., *J. Am. Chem. Soc.*, 1984, **106**, 5043; Wasielewski M. R. et al., *J. Am. Chem. Soc.*, 1990, **112**, 2823; Sykes A. G., *Chem. Soc. Rev.*, 1985, **14**, 283; Isied S. S., Worosila G., Atherton S. J., *J. Am. Chem. Soc.*, 1982, **104**, 7659; Isied S. S., Kuehn C., Worosila G., *J. Am. Chem. Soc.*, 1984, **106**, 1722; Bechtold R., Kuehn C., Depre C., Isied S. S., *Nature*, 1986, **322**, 286; McGourty J. L., Blough N. V., Hoffman B. M., *J. Am. Chem. Soc.*, 1983, **105**, 4470; Ho P. S., Sutoris C., Liang N., Margolias E., Hoffman B. M., *J. Am. Chem. Soc.*, 1985, **107**, 1070; Peterson-Kennedy S. E., McGourty J. L., Kalweit J. A., Hoffman B. M., *J. Am. Chem. Soc.*, 1986, **108**, 1739; McLendon J. R., Miller G., *J. Am. Chem. Soc.*, 1985, **107**, 7811; McLendon G., Guarr G. T., McGuire M., Simoto K., Strauch S., Taylor K., *Coord. Chem. Rev.*, 1985, **64**, 113; Chung E., Taylor K., Kornblatt J. A., English A. M., McLendon G. L., Miller J. R., *Proc. Natl. Acad. Sci. U.S.A.*, 1986, **83**, 1330; Conklin K. T., McLendon G., *Inorg. Chem.*, 1986, **25**, 4804; Brunshwig B. S., Delaive P. J., English A. M., Goldberg M., Gray H. B., Mayo B., Sutin N., *Inorg. Chem.*, 1985, **24**, 3743; Gray H. B., *Chem. Soc. Rev.*, 1986, **15**, 17; Mayo S. I., Ellis W. R. Jr., Crutchley R. J., Gray H. B., *Science*, 1986, **233**, 948; Yokom K. M., Winkler J. R., Nocera D. G., Bordignon E., Gray H. B., *Chem. Scr.*, 1983, **21**, 29; Kostic N. M., Margalit R., Che C. M., Gray H. B., *J. Am. Chem. Soc.*, 1983, **105**, 7765; Margalit R., Kostic N. M., Che C. M., Blair D. F., Chiang H. J., Pecht I., Shelton J. B., Schroeder W. A., Gray H. B., *Proc. Natl. Acad. Sci. U.S.A.*, 1984, **81**, 6554; Nocera D. G., Winkler J. R., Yocom K. M., Bordignon E., Gray H. B., *J. Am. Chem. Soc.*, 1984, **106**, 5145; Scott R. A., Mauk A. G., Gray B., *J. Chem. Educ.*, 1985, **62**, 932; McLendon G., Winkler J. R., Nocera D. J., Mauk M. R., Mauk A. G., Gray H. B., Gray J., *Am. Chem. Soc.*, 1985, **107**, 739; Liang N., Pielak G. J., Mauk A. G., Smith M., Hoffman B. M., *Proc. Natl. Acad. Sci. U.S.A.*, 1987, **84**, 1249; Liang N., Mauk A. G., Pielak G. J., Johnson J. A., Smith M., Hoffman B. M., *Science*, 1988, **240**, 311; Axup A. W., Albin M. A., Mayo S. L., Crutchley R. J., Gray H. B., *J. Am. Chem. Soc.*, 1988, **110**, 435; Cowan J. A., Upmacis R. K., Beratan D. M., Onuchic J. M., Gray H. B., *Ann. N.Y. Acad. Sci.*, 1988, **550**, 68; Wasielewski M., Niemczyk M. A., Johnson G., Svec W. A., Minsk D. W., in "Perspectives in Photosynthesis", Jortner J., Pullman B., Eds., Kluwer, (1990), p. 347; Closs G., Miller J. R., *Science*, 1988, **240**, 440.
- ²³ King H. F., Stanton R. E., Kim H., Wyatt R. E., Parr R. G., *J. Chem. Phys.*, 1967, **47**, 1936.
- ²⁴ Knapp E. W., Fischer S. F., *J. Chem. Phys.*, 1989, **90**, 354; Nussbaum I., Fischer S. F., *Phys. Lett.*, 1986, **115**, 268.
- ²⁵ McConnell H. M., *J. Chem. Phys.*, 1961, **35**, 508.
- ²⁶ Onuchic J. N., Beratan D. N., *J. Chem. Phys.* (in press).
- ²⁷ Christensen H. E. M., Conrad L. S., Mikkelsen K. V., Nielsen M. K., Ulstrup J., *Inorg. Chem.*, 1990, **29**, 2808. (a) Larsson S., *J. Am. Chem. Soc.*, 1981, **103**, 4034.
- ²⁸ Onuchic J. N., Beratan D. N., *J. Am. Chem. Soc.*, 1987, **109**, 6771; Beratan D. N., Onuchic J. N., Hopfield J. J., *J. Chem. Phys.*, 1987, **86**, 448.
- ²⁹ Ratner M. A., Kosloff R., *Isr. J. Chem.*, 1989, **30**, 45.
- ³⁰ Hupp J. T., *J. Am. Chem. Soc.*, 1990, **112**, 1563. (a) Mikkelsen K. V., Dalggaard E., Swanström P., *J. Phys. Chem.*, 1987, **91**, 3081.
- ³¹ Farazdel A., Dupuis M., Clementi E., Aviram A., *J. Am. Chem. Soc.*, 1990, **112**, 4206.
- ³² Ohta K., Okada T., Yoshida T., *J. Phys. Chem.*, 1989, **93**, 932.
- ³³ Creutz C., Taube H., *J. Am. Chem. Soc.*, 1973, **91**, 3988; Richardson D. E., Taube H., *J. Am. Chem. Soc.*, 1983, **105**, 40; *Prog. Inorg. Chem.*, 1983, **30**.
- ³⁴ Ko J.-J., Ondrechen M., *Chem. Phys. Lett.*, 1985, **112**, 507.
- ³⁵ Piepho S. B., Krausz E. R., Schatz P. N., *J. Am. Chem. Soc.*, 1979, **101**, 2793.
- ³⁶ Furholz U., Burgi H. B., Wasner F. E., Stabler A., Ammeter J. H., Krausz E., Clark R. J. H., Stead M. J., Ludi A., *J. Am. Chem. Soc.*, 1984, **106**, 121.
- ³⁷ Hush N. S., *Prog. Inorg. Chem.*, 1967, **8**, 391.
- ³⁸ Slight asymmetry in the orbital occupations is the result of numerical roundoff errors in the calculation.
- ³⁹ The actual molecular electronics application, involving a molecular circuit element in applied fields, is beyond the scope of the discussion here, which is devoted to the nature of intramolecular ET in isolated species.