**THEORY AND COMPUTATIONAL MODELING: MEDIUM
REORGANIZATION AND DONOR/ACCEPTOR COUPLING IN ELECTRON
TRANSFER PROCESSES**

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I. INTRODUCTION

Electron transfer (*et*) kinetics plays a central role in a broad array of processes in the physical, chemical, and biological sciences, in both homogeneous and heterogeneous environments [1-4]. The description of these processes involves a number of fundamental issues in chemical energetics, dynamics, and geometric and electronic structure.

Present day mechanistic understanding of *et* is reflected in theoretical models of rapidly increasing sophistication [5-9]. The evolution of these theories has benefited immensely from close interaction with numerous experimental efforts, which have experienced their own spectacular growth in recent times. Of particular interest for the present volume is the recent success in probing interfacial *et* mechanisms by exploiting electrochemical techniques [10-15].

On the theoretical front, the long and successful tradition emanating from the seminal ideas of Marcus [16,17] has recently been enhanced by a number of theoretical and computational advances which permit detailed treatment of the various electronic and heavy-particle modes of complex *et* systems (including both discrete solute species and surrounding medium) at quantum mechanical, semiclassical or classical levels, as dictated by the nature of the relevant competing timescales [5-9,18-24]. Typically, one identifies and treats quantum mechanically, local molecular donor (D) and acceptor (A) sites, and then formulates the manner in which the effective coupling facilitating the *et* process is mediated by the energetic and electronic features of the intervening medium (the "bridge" (B)) as well as the surrounding environment. The energetics and dynamics associated with activation are treated with either classical or quantum mechanical models. A schematic depiction of a generic DBA system is offered in Fig. 1, which applies either to intramolecular *et* (where D and A are covalently linked by a molecular bridge (B)) or intermolecular *et* (where, for example, the

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“bridge” (B) could be solvent). We use the convention whereby the donor (D) donates an electron to the acceptor (A). An example of central importance is the case of interfacial *et* between a redox species (R/O, which may exist in the reduced (R) or oxidized (O) state) in contact with solution and separated from a metal electrode (M) by a film (F). In this example D,B, and A in the DBA entity (Fig. 1) correspond, respectively, to M,F, and O for a reductive (cathodic) process, with the roles of D and A being reversed for the corresponding oxidative (anodic) process (i.e., $D \equiv R$ and $A \equiv M$).

The theoretical models play two important roles (1) leading (in conjunction with modern computing power) to realistic computational implementation, and (2) allowing analysis of the results of such calculations (as well as those from experiment) in terms of compact predictive models grounded in simple concepts of chemical structure and bonding. The power of the current array of theoretical tools for confronting the challenges posed by *et* dynamics is underscored by their typically generic applicability: e.g., to ground-state or photoinitiated processes [18], both homogeneous and interfacial [17, 25] (e.g., at electrodes). The continuing goal, of course, is to convert the rapidly accumulating mechanistic information about *et* kinetics (often representable in terms of simple rate constants) into precise tools for fine-tuned control of the kinetics and for design of molecular-based systems which meet specified *et* characteristics.

The present treatment will be limited to the kinetic framework defined by the assumption of transition state theory (TST). Situations beyond TST, in which medium dynamics (either diffusive or inertial) contribute to or dominate the bottleneck in *et* processes, have been dealt with extensively in the recent literature [5,26,27]. With the above background in mind, the primary objective of this chapter is to report recent advances in the theoretical formulation, calculation, and analysis of energetics and electronic coupling pertinent to *et* in complex

molecular aggregates. The control of *et* kinetics (i.e., enhancing desired processes, while inhibiting others) involves, of course, both system energetics (especially reorganization energies (E_r) and free energy changes (ΔG^0)) and electronic coupling of local D and A sites, which for thermal processes is most directly relevant only after the system has reached the appropriate point (or region) along the "reaction coordinate" (i.e., the transition state) [1,2,8].

In the following sections we first discuss TST rate constant models, emphasizing generic features, but also noting some special features arising when metal electrodes are involved. We then turn to a consideration of detailed aspects of medium reorganization and donor/acceptor coupling. With these theoretical tools in hand, we examine the results of recent applications to complex molecular systems using the techniques of computational quantum chemistry and electrostatics, together with detailed analysis of the numerical results and comparison with recent electrochemical kinetic data [14,15].

II KINETIC FRAMEWORK

A. Two-State Model

When the *et* process of interest is dominated by two states (e.g., the DBA and D^+BA^- states displayed in Fig. 1), whose energy separation is small relative the gaps separating them from all other electronic states, it is often a reasonable approximation to invoke the so-called "two state approximation" (TSA) [1,2,28]. At this level (in which other states play at most a "virtual" role), the golden rule yields the following unimolecular rate constant (in inverse time units):

$$k^{\text{TST}} = (2\pi / \hbar) \sum_{v_i, w_f} P_{v_i} |V_{v_i w_f}|^2 \delta(E_{v_i} - E_{w_f}) \quad (1)$$

where the overall rate constant is displayed as a sum of contributions from all initial (v_i) to all final (w_f) vibronic states, belonging, respectively, to the initial (ψ_i) and final (ψ_f) electronic manifolds. Each initial state (v_i) is weighted according to P_{v_i} (generally taken as a Boltzmann factor), energy conservation is imposed by the delta functions, the $V_{v_i w_f}$ is a *vibronic* matrix element with respect to the full system Hamiltonian (H), and $h = 2\pi\hbar$ is Planck's constant. Invoking the Condon approximation, where we assume that the *electronic* matrix element,

$$H_{if} = \int \psi_i H^{\text{el}} \psi_f d\tau \quad (2)$$

varies slowly with respect to nuclear coordinates (at least in the vicinity of the transition state), we may factor H_{if} out of the summation in Eq. (1), yielding

$$k_{\text{TST}} = (2\pi/\hbar) (|H_{if}|^2) (\text{FCWD}) \quad (3)$$

where "FCWD" is the conventional notation for the so-called thermally weighted Franck-Condon density of states (with respect to energy). In general, FCWD implicitly contains quantal effects associated with nuclear tunnelling. However, in the classical or high-temperature limit (where relevant nuclear vibrational frequencies are small relative to $k_B T/\hbar$, where k_B is the Boltzmann constant), considerable simplification is possible. In order to illustrate this result, it is necessary at this point to define some energy quantities pertinent to the TST model (Fig. 2). The free energy profiles as a function of progress along the reaction coordinate (R), are displayed for the diabatic states ψ_i and ψ_f , corresponding, respectively, to the generic charge-localized valence bond structures DBA and D^+BA^- . These free energy profiles serve as *effective* potential energy curves for nuclear motion and are denoted here as $V^i(R)$ and $V^f(R)$, respectively, for the initial and final states. The crossing point of the energy profiles defines the activation energy (E^a), and the net free energy change is denoted ΔG^0

(equivalently, the driving force is $-\Delta G^0$). For a *given* state, the reorganization energy (E_r^i) or (E_r^f) is given by the energy difference in going from the minimum energy point (i.e., equilibrium) to the non-equilibrium point defined by the minimum energy point for the *other* state. Finally, the magnitudes of the vertical gaps at equilibrium (R_{eq}^i or R_{eq}^f) are given by $E_v^i \equiv E_v(R_{eq}^i)$ and $E_v^f \equiv E_v(R_{eq}^f)$, where the vertical gap at an arbitrary value of R is defined as $E_v(R) \equiv V^f(R) - V^i(R)$.

In the common situation in which the two profiles may (to good approximation) be taken as harmonic (i.e., parabolic), each with the same curvature, we obtain several relationships:

$$E_r = E_r^i = E_r^f = (E_v^i - E_v^f)/2 \quad (4)$$

$$\Delta G^0 = ((E_v^i + E_v^f)/2 \quad (5)$$

$$E^a = (E_r + \Delta G^0)^2/4E_r \quad (6)$$

Furthermore, the vertical gap, E_v , becomes a linear function of R , so that for convenience we may adopt E_v as an alternative definition of the reaction coordinate.

Returning now to Eq. (3), we find that for the harmonic case discussed above,

$$k_{TST} = (2\pi/\hbar) |H_{if}|^2 \rho(0) \quad (7)$$

where $\rho(E_v)$ is the normalized classical density of initial states with respect to the gap E_v (i.e., $\rho(E_v) dE_v$ is the probability of finding the initial state in a configuration corresponding to a vertical gap in the range E_v to $E_v + dE_v$):

$$\rho(E_v) = \exp(-((E_r + \Delta G^0 - E_v)^2/4E_r k_B T))/(4\pi E_r k_B T)^{1/2} \quad (8)$$

Thus in the classical limit, the consequence of the energy-conserving golden rule expression (Eq. (1)) is simply to invoke the classical density of states at the

transition state (i.e., the crossing, where $E_v = 0$), the point to which a radiationless electronic transition is confined due to the constraints of the Franck-Condon principle. Eqs. (6) and (8) allow Eq. (7) to be reexpressed as

$$k^{\text{TST}} = (2\pi/\hbar) |H_{if}|^2 (4\pi E_r k_B T)^{-1/2} \exp(-E^a/k_B T) \quad (9)$$

displaying a weakly temperature-dependent ($T^{-1/2}$) prefactor and a conventional Arrhenius activation factor

B Multi-State Models

While the two-state approximation (TSA) has been shown to give good account of many classes of *et* kinetics, there are, of course, many situations in which a high density of electronic states makes it necessary to generalize the expressions given by Eqs. (1),(2) and (7). A paramount example is given by the case of a metal or semiconductor electrodes, where one must deal essentially with an electronic continuum [10]. In particular, we confine our attention to systems comprised of metal electrodes coupled to redox species in fixed configurations by intervening films (i.e., "rigid" DBA systems), so that the *et* kinetics may be treated in terms of unimolecular rate constants. Adopting a one-particle model characterized by a spectrum of electronic energy levels for the electrode (represented by the continuous variable E) and formal potential E^0 for the redox moiety coupled to the electrode, one may generalize Eqs. (5) and (6) so as to obtain analogs which are functions of E [10,25]:

$$\Delta G_{f,b}^0(E) = \pm e ((-e E^0) - E) \quad (10)$$

$$E_{f,b}^a(E) = (E_r + \Delta G_{f,b}^0(E))^2 / 4E_r \quad (11)$$

where the subscripts f and b are used to distinguish the "forward" and "back" processes, corresponding, respectively to reduction (of the oxidized form) and oxidation (of the reduced form) of the redox species, e is the magnitude of the

electronic charge, and the quantity $-e E^0$ is the free energy charge for the $O + e \rightarrow R$ half reaction; the quantities $-e E^0$ and E are understood to be defined with respect to a common zero of energy, which cancels when the difference is taken in Eq. (10). Defining $k_{f,b}^{TST}(E)$ by replacing E^a in Eq (9) with $E_{f,b}^a(E)$ and, for generality, introducing a state-dependent matrix element ($H_{if}(E)$ [29]) and then integrating over the entire spectrum E , we obtain

$$k_{f,b}^{TST} = \int_{-\infty}^{+\infty} dE \rho_{f,b}^{el}(E) k_{f,b}(E) \quad (12)$$

where the effective electronic density of states, $\rho_{f,b}^{el}$, may be displayed as the product a state density (per unit E), $\rho^{el}(E)$, and the fraction of states at a given E which are filled (for the forward (reduction) reaction) or empty (for the backward (oxidation) reaction), as given by Fermi-Dirac statistics (the second factor in Eq (13)):

$$\rho_{f,b}^{el}(E) = \rho^{el}(E) (1 + \exp(\pm (E - E_F)/k_B T))^{-1} \quad (13)$$

where E_F is the Fermi energy of the electrode, which may be expressed in terms of the electrode potential, E , as $E_F = -e E$.

In implementing Eq. (12) it is customary to neglect the E dependence of $\rho^{el}(E)$ and $|H_{if}(E)|^2$, replacing them by effective or mean values, $\bar{\rho}^{el}$ and $\overline{|H_{if}|^2}$ (e.g., the values at the Fermi level) [10]. Selection of the effective value of $\rho^{el}(E)$ is also guided by the estimated number of atoms of the metal electrode which are in adequate proximity to the relevant portion of the attached film (e.g., see [13b] and Ref 23 of [10]). While the full evaluation of $k_{f,b}^{TST}$ (Eq. (12)) requires a numerical integration, compact closed-form expressions of useful accuracy may be obtained for certain limiting cases. These expressions are analogous to Eq (9), with the counterpart of the driving force ΔG^0 (e.g., as in Eq. (5)) being provided by

$$\Delta G_{f,b}^0 \equiv \Delta G_{f,b}^0(E_F) = \pm ((-eE^\circ) - E_F) \quad (14a)$$

where we employ the functional form introduced in Eq. (10). An equivalent expression in terms of the electrode potential, E , is given by

$$\Delta G_{f,b}^0 = \pm e(E - E^\circ) \quad (14b)$$

Correspondingly, we may define the analog of E^a (Eq. (6))

$$E_{f,b}^a \equiv E_{f,b}^a(E_F) = (E_r + \Delta G_{f,b}^0)^2/4E_r \quad (15)$$

using the notation of Eq. (11). For cases of small driving force ($|\Delta G_{f,b}^0|/E_r \ll 1$), a linear approximation may be employed:

$$E_f^a = E_r/4 + \alpha(\Delta G_{f,b}^0) \quad (16a)$$

$$E_b^a = E_r/4 - (1 - \alpha)(\Delta G_{f,b}^0) \quad (16b)$$

The constant α may be obtained from a linear Taylor expansion of $E_{f,b}^a$ with respect to $\Delta G_{f,b}^0$. Evaluation of the first derivative at $\Delta G_{f,b}^0 = 0$ yields the frequently used value, 0.5.

The Butler-Volmer approximations for $k_{f,b}^{TST}$ may now be expressed as [10]

$$k_f^{TST} = k_0^{TST} \exp(\alpha \Delta G_{f,b}^0/k_B T) \quad (17)$$

$$k_b^{TST} = k_0^{TST} \exp(-(1 - \alpha) \Delta G_{f,b}^0/k_B T) \quad (18)$$

where k_0^{TST} (the "standard" rate constant) is obtained from Eq. (12) for the limiting case of $\Delta G_{f,b}^0 = 0$. Numerical studies [14] of the temperature dependence of k_0^{TST} reveal (aside from a prefactor proportional to $T^{1/2}$) a simple Arrhenius behavior, with activation energy within 1% of $E_r/4$ (as one might expect by analogy

with Eq. (6) for $\Delta G^0 = 0$), provided that $E_r/k_B T \gg 1$ (the $T^{1/2}$ behavior of the prefactor noted above differs from the $T^{-1/2}$ dependence in the two-state case (Eq (9)) as a result of the integration in Eq. (12)).

The preceding models for *et* rate constants, either at the simple two-state level appropriate for homogeneous *et* in solution (Eqs. (3), (7), and (9)) or at the extended level required for heterogeneous *et* when electrodes are involved (Eqs. (12), (17), and (18)), display in concrete fashion the manner in which reorganization (E_r) and D/A coupling (H_{if}) control the kinetics. In the remainder of the chapter, we consider detailed expressions for E_r and H_{if} and then summarize some computational applications which have been especially helpful in guiding and interpreting experimental kinetic studies at film-modified electrodes [14,15], with particular emphasis on the dependence of the kinetic parameters on film thickness. As noted above, the treatment is carried out in a framework appropriate for relatively weak D/A coupling (i.e., non-adiabatic *et*, as governed by the Golden Rule (Eq. (1) and its various elaborations [1,2,28]).

III. SOLVENT REORGANIZATION ENERGY

The reorganization energy (E_r) is a consequence of the Franck-Condon principle, which precludes inertial motion during an electronic transition. In general, E_r has a number of additive (under the usual harmonic assumption) contributions from different inertial modes of the "solute" (DBA in Fig. (1)) and surrounding medium. In the applications dealt with below, the dominant contribution (to which we confine our attention) is from the solvent medium and hence denoted as E_s (the same quantity is often referred to as λ or E_{out} in the literature). Expressions for E_s at the level of dielectric continuum theory may be developed from the Poisson equation for an electrostatic system [30,31] (for an example of a molecular-level treatment see [32]):

$$\nabla^2 \phi_{eq}(\rho) = -4\pi\rho \quad (19)$$

where ρ is a charge density and ϕ_{eq} is the electrostatic potential of a system at equilibrium with ρ (for linear coupling of ρ to the medium, ϕ_{eq} is a linear functional of ρ). The equilibrium free energy of the total system is then given by

$$F_{eq}(\rho) = 1/2 \int_V \phi_{eq}(\rho) \rho \, d\tau \quad (20)$$

where the integration volume is all space. Detailed analysis then shows that E_s may be expressed as [30],

$$E_s = F_{eq}^{op}(\Delta\rho_{if}) - F_{eq}^{st}(\Delta\rho_{if}) \quad (21)$$

where *st* and *op* denote, respectively, a system with full dielectric response (characterized by static dielectric constants ϵ^{st}) and the hypothetical variant in which only the high-frequency (optical) response is operative (characterized by optical dielectric constants $\epsilon^{op} = n^2$, where n is the refractive index), and

$$\Delta\rho_{if} \equiv \rho_f - \rho_i \quad (22)$$

is the change in charge density accompanying the *et* process ($\psi_i \rightarrow \psi_f$). Thus E_s is displayed compactly as a double difference: the *differential* solvation energy (i.e., the difference between total and optical solvation) of the *change* in charge density.

Eq. (19) is typically solved for a piecewise homogeneous model, in which different spatial zones have distinct values of E^{op} and E^{st} . Efficient numerical techniques permit Eq. (19) to be solved accurately for zones of arbitrary shape, thus allowing dielectric continuum models to be realistically adapted to the detailed structure of the *et* system of interest [30,31]. For comparison with the results of exact implementation of Eqs. (19-22), a useful point of reference is provided by the familiar point-charge 2-sphere model of Marcus [17], which in

generic form accomodating examples of both homogeneous and 2-zone heterogeneous systems, may be expressed as,

$$E_s = (\Delta q)^2 (1/\epsilon^{op} - 1/\epsilon^{st}) (\gamma_D/2r_D + \gamma_A/2r_A - \gamma_{DA}/r_{DA}) \quad (23)$$

where local D and A sites are taken as spheres (with radii r_D and r_A , respectively), each with a point charge at its origin (e.g., $\rho_D(\mathbf{r}) = q_D \delta(\mathbf{r} - \mathbf{r}_D)$), which changes by $\pm\Delta q$ in the *et* process ($\Delta q \equiv \Delta q_D = -\Delta q_A$), and where r_{DA} is the inter-site separation (within the spheres, $\epsilon^{op} = \epsilon^{st}$, usually set at the vacuum value (1) or a typical optical value (~ 2)). For the case of two redox species (D and A) in a *homogenous* medium, $\gamma_D = \gamma_A = \gamma_{DA} = 1$. For the 2-zone heterogeneous system, with an infinite planar boundary, corresponding to a *single* redox species in solution (taken here as the acceptor ($A \equiv O$) in a cathodic process (see Section I)) and a metal electrode as the donor, D (taken as an ideal conductor), we adapt Eq. (23) by assigning $\gamma_D = 0$, $\gamma_A = 1$, $\gamma_{DA} = 1$, and " r_{DA} " is now the distance between the actual site (A) and its image in the electrode [33]. This distance is simply twice the distance of A from the planar interface. If on the other hand it is assumed that the metallic screening is quenched, then there is no image term (i.e., $\gamma_{DA} = 0$) [34]. Eq (23) yields the important prediction that E_s is expected to increase linearly with the inverse of r_{DA} , both for homogenous systems and (to the extent that ideal screening pertains) heterogeneous systems with metal electrodes. We note that the same result for E_s (Eq. (23)) is obtained for the reverse (anodic) process in which the roles of D and A are interchanged.

We now consider the more general case of interest, a redox species in solution in proximity to a film-modified metal electrode surface [30]. Eqs (19-22) were solved analytically for the 3-zone dielectric model depicted in Fig 3: a spherical redox species (in a cavity of radius a , with a point charge at its origin undergoing a change Δq in the *et* process) in solution (zone I), separated by

distance d from the edge of a film of thickness L (zone II), in contact with a metal electrode (zone III). Taking zone III as an ideal conductor, we obtain [30]:

$$E_s = \left(\frac{1}{\epsilon_I^{\text{op}}} - \frac{1}{\epsilon_I^{\text{st}}} \right) \frac{(\Delta q)^2}{2a} - \left(\frac{\eta_{\text{II,I}}^{\text{op}}}{\epsilon_I^{\text{op}}} - \frac{\eta_{\text{II,I}}^{\text{st}}}{\epsilon_I^{\text{st}}} \right) \frac{(\Delta q)^2}{4d} + \sum_{\ell=1}^{\infty} (-1)^{\ell} \left\{ \frac{\epsilon_{\text{II}}^{\text{op}} (\eta_{\text{II,I}}^{\text{op}})^{\ell-1}}{(\epsilon_{\text{II}}^{\text{op}} + \epsilon_I^{\text{op}})^2} - \frac{\epsilon_{\text{II}}^{\text{st}} (\eta_{\text{II,I}}^{\text{st}})^{\ell-1}}{(\epsilon_{\text{II}}^{\text{st}} + \epsilon_I^{\text{st}})^2} \right\} \frac{(\Delta q)^2}{d + \ell L} \quad (24)$$

Eq (24) may be viewed as reflecting the contributions from an infinite number of image charges, Δq_n , located at points $2(d + \ell L)$ along the z axis (Fig. 3), for $\ell \geq 1$. In the limit of vanishing film thickness ($L = 0$), Eq. (24) reduces to the single-image 2-zone result (Eq. (23), with $r_D = a$, $r_{DA} = 2d$, $\gamma_D = 0$, $\gamma_A = 1$, $\delta_{DA} = 1$, and ϵ^{st} and ϵ^{op} corresponding to zone I). More discussion in terms of image contributions is given below in conjunction with specific applications. The simple point-charge-in-a-sphere model discussed above is, of course a crude (although often very useful) model. More elaborate implementation of Eq. (21) are possible, using detailed charge densities based on quantum chemical calculations for complex DBA systems in solution [31].

IV Donor/Acceptor Coupling

Since coupling between initial and final diabatic *states*, which are many-electron quantities, can often be adequately represented as one-particle matrix element coupling localized D and A *orbitals* [8], we adopt the notation H_{DA} for the coupling element H_{if} in the following analysis. Within the two-state approximation (see above), it is convenient to distinguish two basic approaches for evaluating D/A coupling, both of which obtain the desired *diabatic* quantities (i.e., H_{DA}) indirectly in terms of adiabatic states (i.e., those which are diagonal with respect to D/A coupling and which we denote as ψ_1 , and ψ_2). These approaches, described below, may be contrasted with an alternative approach in which H_{DA} is

evaluated directly from charge-localized diabatic states [8]. The two approaches differ in that one is defined only at the transition state for *thermal* transfer (i.e., at the diabatic crossing point (Fig. 2), where resonant transfer is possible), while the other is based on the corresponding vertical *optical* process (both process are depicted in Fig. 4).

A Thermal *et*

In thermal *et*, the effective coupling element H_{DA} may be taken as one-half of the vertical adiabatic energy gap at its minimum value with respect to the reaction coordinate (R) [8]. For symmetry-equivalent D and A sites, this result corresponds to

$$H_{DA} = (E_+ - E_-)/2 \quad (25)$$

where E_+ and E_- are the energies of the adiabatic states which are, respectively, symmetric and antisymmetric with respect to the D and A orbitals. For cases in which D and A sites are not symmetry-equivalent, the use of Eq. (25) requires that the D and A orbitals be brought into resonance by some device (e.g., adjustment of the molecular geometry or application of a suitable external electric field [35,36].

B Optical *et*

In optical *et*, H_{DA} may expressed entirely in terms of adiabatic quantities, using the Generalized Mulliken-Hush model [18,34]:

$$H_{DA} = (|\bar{\mu}_{tr}|/|\Delta\bar{\mu}_{DA}|) \Delta E_{12} \quad (26)$$

where $\bar{\mu}_{tr}$ is the transition dipole moment coupling the two adiabatic states, ΔE_{12} is the corresponding adiabatic vertical energy gap (generally quite similar to the diabatic gap, $h\nu$, indicated in Fig 4), and the diabatic dipole moment shift, $\Delta\bar{\mu}_{DA}$,

may in turn be expressed in terms of $\bar{\mu}_{tr}$ and $\Delta \bar{\mu}_{12}$ (the adiabatic dipole moment shift):

$$|\Delta \bar{\mu}_{DA}| = (|\Delta \bar{\mu}_{12}|^2 + 4|\bar{\mu}_{DA}|^2)^{1/2} \quad (27)$$

The use of Eq. (27) obviates the need to approximate $|\Delta \bar{\mu}_{DA}|$ as $e r_{DA}$, where r_{DA} is an assumed D/A separation distance (e.g., based on structural data). In the general case when the various dipole vectors in Eqs (26) and (27) are not collinear, a reference direction must be adopted (e.g., based on $\Delta \bar{\mu}_{12}$), and then the components of the vectors along this direction may be employed in Eqs. (26) and (27).

C "Electron Tunneling"

The D/A coupling embodied in H_{DA} is often described as an effective "electron tunneling" process [28]. To focus the discussion we will consider specifically the dependence of H_{DA} on the D/A separation distance (r_{DA}) and compare the prediction of two quite distinct models, each of which yields exponential decay:

$$H_{DA}(r_{DA}) \propto \exp(-(\beta/2)r_{DA}) \quad (28)$$

(the decay coefficient is defined so that the coupling factor in Eq. (1) decays with coefficient β). While r_{DA} is in general not uniquely defined, a convenient definition may be obtained as $|\Delta \mu_{DA}|/e$, taking $|\Delta \mu_{DA}|$ as defined by Eq. (27).

The phenomenological Gamow (WKB) model [37] is based on tunneling through an electronically homogeneous medium represented by an effective 1-dimensional rectangular barrier of height Δ^G and width r_{DA} :

$$\beta^G = 2(2m_e \Delta^G)^{1/2}/\hbar \quad (29)$$

where m_e is the mass (actual or effective) of the tunneling electron.

Most modern treatments of bridge-mediated electronic coupling do not involve tunneling in the literal sense of the Gamow approach and employ electronically inhomogeneous superexchange (*se*) models [38,39], which take detailed account [8,28] of the electronic structure of the DBA system (Fig. 1). In implementing these models one has the choice of how to subdivide the bridge into subunits. The optimal choice involves various tradeoffs, including chemical transferability (favoring small subunits), compactness of representation when it comes to synthesizing the overall coupling, H_{DA} (favoring larger subunits), and theoretical considerations such as the applicability of perturbation theory (here the tradeoff is complex, but often favors larger subunits [28]). As a simple example for illustration, we adopt the McConnell model [38] based on a bridge consisting of a homologous sequence of units, each of which is represented by a single orbital with energy Δ relative to the common energy of the D and A orbitals, and with nearest-neighbor (NN) bridge orbitals coupled by the "hopping integral" t . From this model, for $|t/\Delta| \ll 1$ we obtain

$$\beta^{se} = -2 (\ln |t/\Delta|) / (\Delta r) \quad (30)$$

where Δr is the width of one subunit.

In comparison with the result from the homogenous model (Eq. (29)), β^{se} reflects the molecular and electronic structure of B, not only through the hopping integral t , but also Δ and Δr , since the values of all the parameters depend on the specific choice of subunit (we also note, in contrast to Eq. (29), that in Eq. (30) the electron mass is implicit in t and Δ). Another important distinction lies in the role of the gap Δ in Eqs. (29) and (30). In the latter case, Δ (for a particular bridge subunit) is in principle (and in some cases in practice) a spectroscopic observable, whereas the phenomenological Δ^G , which represents the full bridge in Eq. (29), is not in general directly accessible as an observable. Effective Δ^G values may, of

course, be inferred from Eq. (29) on the basis of experimental β values, but attempts to use experimentally determined energy gaps (e.g., from polarography) frequently lead to exaggerated β magnitudes [39]. Eq (29) is more usefully applied to the direct or "through-space" (*ts*) D/A coupling when no bridge is present. In this case, Δ^G may be identified with the relevant ionization potential of D [40].

It is important to recognize that E_s frequently provides an additional contribution to the variation of k^{TST} with r_{DA} (see below). Thus caution must be employed in comparing β values inferred from rate constants with values based on H_{DA} [41].

D Superexchange Models

Having introduced the McConnell superexchange model in connection with Eq. (30), we now consider superexchange models in greater detail. The complete McConnell expression [38], which corresponds to the definition of H_{DA} based on thermal *et* (e.g., Eq. (25)), is given as,

$$H_{DA} = (T^2/\Delta)(t/\Delta)^{m-1}, \quad (31)$$

derived in the perturbative limit ($|T/\Delta|$, $|t/\Delta| \ll 1$) for a sequence of m bridge orbitals, whose terminal members are coupled, respectively, to the D and A orbitals via hopping integrals T (the other parameters were introduced above in Eq. (30)). Among the important features revealed by Eq. (31) are the predicted exponential falloff with m (already invoked above in characterizing β^{se} in Eq. (30)) and the possibility of sign alternation with m (the basis of the parity rule [42]), although the detailed sign behavior requires careful analysis, including a clear definition of the phase conventions adopted for the various local orbitals or states of the system (D, A, and B) [8,28]. Eq. (31) also predicts that H_{DA} is sensitive to variations of the gap Δ , e.g., as obtained by chemical modification of the D and A groups [43] or the bridge (B).

Eq. (31) may be generalized in a number of ways including [14]:

1) distinct bridging units:

$$H_{DA} = (T_{D1} T_{mA}/\Delta_1) \prod_{k=1}^{m-1} (t_{kk+1}/\Delta_{k+1}) \quad (32)$$

where the subscripts on T and t denote NN pairs of coupled orbitals, and Δ_ℓ denotes the gap between the D/A level and the energy of bridge unit ℓ .

2) summation over multiple "pathways" of the generic type exemplified by Eq. (32), taking advantage of the additive of the different contributions, and including non-NN as well as NN pathways). In addition, there is, of course, the direct (so-called "through-space") pathway between D and A (T_{DA}), although its quantitative importance is usually small in comparison with that of other pathways in DBA systems.

3) involvement of more than one orbital on each site, including both occupied and unoccupied types, thereby leading to competitive (either constructive or destructive) interference among "hole", "electron", and "hybrid" pathways. In Section VB below, we shall deal specifically with the combined roles of sigma and pi-type molecular orbitals of the bridge units in facilitating overall coupling.

Exponential falloff with m is maintained (although the details change) when the perturbative limits are relaxed, provided that $|T/\Delta|$ remains small and the D/A level avoids resonance with any of the eigenstates of the bridge (i.e., remains outside the bridge "bandwidth" ($4|t|$)) [44].

Indirect D/A coupling of the superexchange type is often referred to as "through-bond" coupling, although in a formal and also quantitative sense, it also applies to DBA systems in which D and A are not linked by a continuous sequence of covalent bonds [28].

V COMPUTATIONAL APPLICATIONS

The computational evaluation of E_s and H_{DA} is reported below for model systems designed to assist in the interpretation of experimental electrochemical

kinetic studies of interfacial *et* between a gold electrode and a ferrocene group linked to the gold surface by intervening self-assembled monolayer (SAM) organic films of variable thickness [10-15]. The films are comprised of homologous chain structures anchored to the gold substrate by terminal sulfur groups. Two basic chain types were employed: alkane chains (oligo-methylene (OM $\equiv$ $(-\text{CH}_2-)_n$) and alternating benzene and acetylene units (oligo-phenylene-ethynylene (OPE) $\equiv$ $(-\text{p-C}_6\text{H}_4) - \text{C} \equiv \text{C}-)_n$). For the OM chains n may be equated to $m + 1$ (e.g., as in Eqs. (31) and (32), where m is the number of C-C sigma bonding orbitals within the chain. The counterpart of Eq. (32) for the case of the OPE chains is presented in Section VB2.

At the outer surface of the film, in contact with aqueous solution, some fraction (typically $\sim 10\%$) of the organic chains are covalently linked to ferrocene (Fc) groups (either directly to one of the cyclopentadienyl (Cp) carbons in the case of OPE, or to a carboxy-substituted Cp ring in the case of OM), while the remainder of the chains (the "diluent") are terminated with $-\text{CH}_3$, $-\text{OH}$, or $-\text{COOH}$, groups (for OM's) or H-atoms (OPE's). Structural studies indicate a close-packed ordered structure for the OM-based SAM's, with the linear axis of the fully-staggered chains tilted $\sim 27^\circ$ from the direction perpendicular to the gold substrate (see citations of structural data in [30]). The studies with redox-active OPE's [15] employed all of the diluents listed above, while those based on redox-active OM's used CH_3 -terminated OM diluents [14].

A Evaluation of E_s

E_s for the OM-based interfacial systems described above was evaluated via Eq. (24) by adapting the 3-zone model of Fig. 3 as follows [30]. An effective radius (a) of $3.8 \text{ \AA}$ was used for the ferrocene (or ferrocenium) moiety, [45,46] which was assumed to be in "contact" with the film (*i.e.*, $d = a$) and Δq was equated to $\pm e$. The equilibrium structures of ferrocene and the ferrocenium cation are quite similar,

and the inner-shell reorganization energy is estimated to be very small (≤ 0.03 eV) [47]. For the aqueous zone (I), $\epsilon_I^{st} = 78$ and $\epsilon_I^{op} = 1.8$ [48], while for an OM film (with an estimated specific gravity of ~ 0.95 g/cc, based on a mean separation of $5\text{\AA}$ between close-packed alkane chains with 27° tilt angles relative to the normal to the metal surface, a value of $\epsilon_{II}^{st} = \epsilon_{II}^{op} = 2.25$ was assigned [30], similar to values inferred for the bulk solid [49] (to good approximation these values may also be applied to OPE films, especially since E_s is quite insensitive to the value of ϵ_{II} in this magnitude range as long as $\epsilon_{II}^{st} \sim \epsilon_{II}^{op}$). For the metal electrode (taken as an ideal conductor), $\epsilon_{III}^{st} = \epsilon_{III}^{op} = \infty$. In all calculations, convergence of the sum in Eq. (24) was very rapid [30].

While the pertinent experimental work has been carried out with a finite ionic strength (I) in the aqueous phase, this effect was ignored in the calculations since E_s is not expected to be strongly affected by ionic strength [17].

Figure 5 presents the calculated E_s values as a function of film thickness L . As expected, the absolute magnitudes of E_s are sensitive to cavity radius (variation of $\pm 0.5\text{\AA}$ relative to the estimate $a = 3.8\text{\AA}$ are displayed). However, the L -dependence is invariant in the sense that plots of $E_s(L)/E_s(L = \infty)$ are nearly independent of the value of a . Variation of E_s magnitude with L is appreciable; e.g., over the range $L = 5 - 15\text{\AA}$, E_s increases from 0.75 eV to 0.86 eV for $a = 3.8\text{\AA}$. For cases near the thermoneutral limit (i.e., where $E \sim E^\circ$, in which case the activation energy is $\sim E_s/4$ (see Eqs. (15) and (16)), this variation corresponds to a mean contribution of $\sim 0.1\text{\AA}^{-1}$ to the overall exponential decay coefficient for the rate constant k_0 (see Eqs. (17) and (18)). For longer range transfer the effect is substantially reduced (e.g., for $L=15-25\text{\AA}$, a change of ~ 0.03 eV in E_s contributes only $\sim 0.03\text{\AA}^{-1}$ to the overall decay coefficient).

Figure 5 reveals that E_s increases by a factor of about two in proceeding between the 2-zone limits of $L = 0$ (no zone II) and $L = \infty$ (where E_s is independent

of zone III). The $L = 0$ (2-zone) limit is accounted for by the Marcus 2-zone expression [17] given in Eq. (21), with $\gamma_D = 0$, $\gamma_A = 1$ and $\gamma_{DA} = 1$ (i.e., full image response in zone III). The $L = \infty$ (2-zone) limit is given by the first two terms of Eq. (24) and corresponds to the general 2-zone expression given previously by Marcus [33] (of which Eq. (21), is a special case).

The form of Eq. (21) makes it of interest to explore the variation of the more general 3-zone E_s expression (Eq. (24)) as a function of $1/(L + a)$. More insight into this and other aspects of E_s in various limiting cases is given by detailed consideration of image charge contributions to Eq. (24). Since $\epsilon_I^{\text{op}} \ll \epsilon_I^{\text{st}}$, E_s is dominated by the optical contribution to Eq. (24). Furthermore, the similarity of the values of ϵ_I^{op} and $\epsilon_{II}^{\text{op}}$ (i.e., $\eta_{II,I}^{\text{op}} \ll 1$) leads to the dominance of a single image charge contribution, corresponding to the $\ell = 1$ term in the summation. In fact, with $\eta_{II,I} = 0$, calculated E_s values are within 1% of the general 2-zone result of ref. 23 (the small departure arises from the higher order image contribution to the static component of Eq. (24)). Neglecting all but the dominant image contribution gives a linear dependence of E_s on $1/(L + a)$ with slope s ,

$$s = - \left\{ \frac{1}{(\epsilon_{II} + \epsilon_I^{\text{op}})^2} - \frac{1}{(\epsilon_{II} + \epsilon_I^{\text{st}})^2} \right\} \epsilon_{II} (\Delta q)^2. \quad (33)$$

where ϵ_{II} is the common value of $\epsilon_{II}^{\text{op}}$ and $\epsilon_{II}^{\text{st}}$ assigned to zone II.

The data in Fig. 5 is plotted in Fig. 6 (solid line) as a function of $1/(L + a)$, and indeed a very nearly linear behavior is observed. The slope (Eq. (33)) based on the dominant image charge, $s = -0.129$ (with $(\Delta q)^2 = 1$ in units of e^2 , is similar to that for the exact results, and the small difference reflects primarily the distinct values of $\epsilon_{II}^{\text{op}}$ and ϵ_I^{op} , which lead to $\eta_{II,I}^{\text{op}} = 0.11$ (see above discussion). The optimal linear fit is excellent, and may be viewed as defining an *effective* single image charge.

To relate the model continuum results specifically to the OM-based systems, one requires an estimate, $L(n)$, of the dependence of film thickness (L) on the number of CH_2 units (n) in the constituent OM moiety. In particular, we focus on the experimentally studied systems based on films with redox-active $(\text{Au})(\text{S})(\text{CH}_2)_n (\text{O}_2\text{C})(\text{Fc})$ components diluted with $(\text{Au})(\text{S})(\text{CH}_2)_{n-1}(\text{CH}_3)$ units. Adopting standard bond lengths and bond angles, including $1.82 \text{ \AA}$ for r_{CS} , $2.80 \text{ \AA}$ for r_{AuS} , 100° for $\angle\text{AuSC}$, and 114° for $\angle\text{SCC}$, and a tilt angle of 27° relative to the direction normal to the surface [50] and assuming a fully staggered conformation for the $(\text{Au})(\text{S})(\text{CH}_2)_n$ backbone, still leaves some variability of $L(n)$ with respect to other conformational degrees of freedom [30]. A detailed consideration of structural models [30] yields the following relationship for the mean height of the Fc iron atom above the gold surface, $h_{\text{Fe-Au}}(n)$:

$$h_{\text{Fe-Au}}(n) = 6.00 + 1.12n (\text{\AA}) \quad (34)$$

The model given in Fig. 3 for the case of "contact" (i.e., $d = a = 3.8$) thus implies the result:

$$L(n) = 2.20 + 1.12n \quad (35)$$

Since most of the film involves the methyl-terminated chains, an independent measure of $L(n)$ is the mean height of these methyl groups. The height of the methyl carbon atom, $h_{\text{Au-C}}(n)$, is estimated as $1.90 + 1.12n$, ($\text{\AA}$), a result quite close to that provided by Eq. (35), and thus supporting the value $\sim 3.8 \text{ \AA}$ for the effective radius for the Fc redox group. The film thickness implied by Eq. (35) is in rough agreement with most previous estimates based on experimental probes or molecular models [50,51]. With Eq. (35) and the linear fit to calculated E_s values (see Fig. 6), we obtain,

$$E_s(n) = 0.95 - 1.72/(6.00 + 1.12n) \quad (36)$$

where $E_s(n)$ is in eV units. Thus $E_s(n)$ is predicted to vary by ~ 0.1 eV over the $n = 5 - 25$ range. Converting these variations to contributions to the variation of $\ln k_0$ with film thickness due to E_s (i.e., positive increments to β values based on H_{DA}), we obtain $0.08 \text{ \AA}^{-1}$ ($n = 5 - 10$), $0.04 \text{ \AA}^{-1}$ ($n = 10 - 15$), and $0.02 \text{ \AA}^{-1}$ ($n = 15 - 25$) [30].

It is clearly of interest to ascertain whether these modest variations of E_s (a consequences of the assumption of ideal metallic screening) are compatible with experimental estimates of E_s . A comparison of calculated [30] and experimental [14] results is displayed in Fig. 7. A slight tendency of the experimental values to increase with n is apparent in this figure, and this behavior is confirmed by additional reorganization energies measured for ferrocene attached to gold by other types of "bridges" (J. F. Smalley, et al., unpublished results). However, uncertainties in both the measurements and the theoretical estimates preclude an unequivocal conclusion regarding the dependence of $E(s)$ on film thickness. The limiting values of E_s for large n based on theory and experiment are seen to be in good agreement.

The counterpart of Eqs. (34-36) for the case of Fc linked to Au by an OPE-thiol is straightforwardly obtained from structural data given in [52], together with the data pertinent to the relevant diluent oligomers [15].

B) Evaluation of H_{DA} and its Dependence on the Nature of the Bridge

1 Results for Model Systems

We have noted in Section IVD the utility of casting the effective D/A coupling in terms of competing superexchange (*se*) pathways involving the various "units" of the intervening bridge. The contributions of these pathways are *implicit* in H_{DA} values inferred from experiment (e.g., via Eqs. (25) or (26)) or from calculation (e.g., via Eqs. (25) or (26), using the results of *ab initio* or semi-

empirical molecular orbital (MO) calculations), but their underlying roles in the overall coupling may be exposed by suitable analysis of detailed electronic structure results [28]. A given *se* model, and any practical procedure for evaluating H_{DA} , entails a decision as to what finite portion of an extended condensed-phase system constitutes the "bridge" (B), and where the "surrounding" medium begins. An example of an approach to this question is provided by model theoretical studies of alkane (OM) chains comparing β values (Eq. (28)) from *in vacuo* results with those in which surrounding solvent is included. The DBA systems are the fully-staggered radical cation or anion species, $1\pi(m)$, as displayed in Fig. 8: $(CH_2)(CH_2)_{m+1}(CH_2)^\pm$, where the $CH_2^\pm$ group serves as the D (-) or A (+) site, and the terminal CH_2 group is the corresponding A(-) or D (+) site. For a given homolog m the OM bridge (B) contains a sequence of m covalent bonds (e.g., as in Eq. (31)). The results in Table 1 allow us to examine the possible role of solvent in modifying the *in vacuo* β values for the radical cation and anion systems [28]. The long-range interaction of a polarized aqueous solvent (as represented by a dielectric continuum model [31]) has no perceptible effect, and even explicit quantum mechanical inclusion of peripheral water molecules causes only a modest reduction of β for the radical cations (presumably due to the role of H_2O lone pairs in accommodating hole transfer), with no effect on the radical anion *et* processes. On the other hand, in other model studies, in which the B portion of the DBA system does not fill the space directly between the D and A groups, the solvent has been shown to play a dramatic role in the D/A coupling [53]. The common picture emerging from model studies of this sort, is that the spatial region most important for H_{DA} (and thus most important for defining the effective bridge) is that more or less directly between D and A, whether occupied by a covalent sequence, solvent, or vacuum. The studies also indicate similar β values for *et* in radical cations and anions.

A systematic study of the influence of conformation on H_{DA} is given in Table 2, for the radical ions of the $1\pi(3)$ system (Fig. 1) [22,28]. Table 2 reveals that H_{DA} is quite sensitive to the conformation of the DBA system, both with regard to sign and magnitude. We emphasize that the "in-plane" and "perpendicular" conformations of D and A orbitals relative to the bridge lead to two different superexchange mechanisms for D/A coupling, involving, respectively, the sigma orbitals of the carbon atom framework and the CH π -type bonds and the bridge (i.e., a hyperconjugative mechanism). The sensitivity to conformation just illustrated for OM-based DBA systems, and found to be equally important (see below) for their OPE-based analogs [15], underscores the crucial importance of detailed structural information in the analysis of *et* kinetics in situations where conformational flexibility exists.

While the results for the model systems discussed above are of interest in themselves, they have been shown to give β estimates in generally good agreement with values inferred experimentally for DBA systems in which the actual D and A groups are complex molecular moieties (e.g., [15] and [23]). In the model studies summarized in Tables 1 and 2, the nominal D and A groups (the sp^2 -hybridized terminal CH_2 - groups) may be viewed as serving as surrogates for the sp^2 carbon atoms by which the actual D/A groups (e.g., aromatic rings or the Cp ring of Fc) are linked to the bridge. The simple form of the NN pathway model of McConnell (Eq. (30)) suggests that the β values for the idealized model system and the actual system of interest will agree to the extent that the effective gap Δ between the D/A energy level and the occupied or unoccupied band edge of B is similar for the two cases. In detailed calculations, the sensitivity of β to Δ may be significantly less than that implied by Eq. (30) as a result of the fact that many different pathways contribute to the overall *se* coupling [20-23]. It may, of course, be possible to induce a sensitivity by forcing the effective gap to be small (e.g., fine-tuning by

chemical substitution [21]), but for sufficiently small gaps the assumptions entailed in the underlying perturbation theory might well be violated, so that the superexchange model would not be applicable.

At any rate, even in situations of complex competition among multiple *se* pathways, the form of the simplistic single pathway McConnell model can be quite valuable for modeling the variation of H_{DA} within a family of DBA systems [28], as illustrated below.

2. Comparison of β values: estimates from model calculations and experiment

Recent experimental studies of interfacial *et* kinetics at film modified gold electrodes have provided a set of data well-suited to comparisons with the results of electronic structure calculations [14,15]. The examples illustrated in Section VB1 were limited to electronically *saturated* bridges. In the case of *unsaturated* bridges, the occupied and unoccupied manifolds of the bridge are expected in general to be energetically more accessible to the D and A groups [20-23] (i.e., the gap Δ in Eqs. (30-32) is expected to be smaller), thus suggesting an appreciable reduction in β relative to the value of $\sim 1\text{\AA}^{-1}$ expected (e.g., see Table 1) for saturated bridges. The electrochemical studies (introduced first Section VA in connection with estimates for E_s) provide important tests of these notions since for a fixed generic assembly type ((Au)(S)(B)(Fc)), they allow a direct comparison of D/A coupling mediated by saturated (OM) and unsaturated (OPE) bridge types [15]. As revealed by Fig. 9, qualitative theoretical expectations about variation of β with bridge type are strongly supported by the results of the electrochemical studies, thus inviting more quantitative contact between theory and experiment, the subject of the following discussion.

While the SAM films are extended close-packed arrays of organic chains, various experimental tests have indicated [10-15] (at least when the redox-active

oligomers are “isolated” by diluents) that the coupling between a given Fc group and the gold surface is strongly dominated by the oligomer to which it is covalently linked (as opposed to more circuitous pathways involving neighboring oligomers; a possible role for inter-chain coupling is discussed in [12b]). This result is consistent with conclusions from model studies [28] (which emphasize the major importance of the region directly between the D and A groups in mediating the coupling, as noted in Section VB1) and indicates that meaningful comparisons may be made between calculations based on isolated DBA systems and experimental results for the extended SAM systems. Furthermore, to the extent that E_s does not vary significantly with r_{DA} (e.g., see [15]), one may compare calculated β values based on H_{DA} with experimental β values based on $\ln k_0$. We note the distinction between r_{DA} (which is independent of the tilt angle of the linear oligomers) and the vertical height of the Fc above the electrode, the quantity which controls the magnitude of E_s and which varies with tilt angle for a given oligomer (as noted in Section VA).

The computational results displayed in Tables 1 and 2 were based on Eq. (25) for symmetry-equivalent D and A groups, using *ab initio* molecular orbital calculations. For the comparison of OM and OPE oligomers the semiempirical INDO/s method [54] was employed for the electronic structure calculations. This semi-empirical method, which has been shown to give results quite similar to those from *ab initio* calculations in a number of comparative tests [55], allows a very efficient scanning of the various conformers of interest in the case of the OPE systems. While coupling through OM oligomers is quite sensitive to conformation (see Table 2), the available evidence indicates that the chains in the OM-based SAM's are in fully staggered conformations [10-14,30]. Thus the comparison with experiment for the OM films employed the model structures $1\pi(m)$ in Fig. 8. In contrast, little is known about the distribution of dihedral

angles of the phenylene groups in the OPE-based films. Since these groups are separated by acetylene units, the intrinsic rotational barriers are expected to be quite small (an upper limit of ~ 0.6 kcal/mole has been estimated for diphenyl acetylene [56]), so that the dihedral angles in the OPE films could be strongly influenced by the environment (i.e., the diluent oligomers). A full resolution of these structural questions would require a very large-scale computer simulation effort and would also entail electronic structure calculations over a broad range of conformations. On the other hand, adequate account of conformational effects is essential for any meaningful treatment of coupling, since the mediation of coupling via OPE bridges will clearly be sensitive to the angular orbital overlap between the different units of the bridge and between the bridge and the D and A groups. A workable compromise for accommodating these issues was achieved [15] by carrying out electronic structure calculations for a limited sample of dihedral angles, and then interpolating the H_{DA} results for any desired set of angles by exploiting the form of the McConnell expression given by Eq. (32), as described below.

Calculations were based on homologs ($3\pi(n)$) of the type shown in Fig. 10, where n is the number of PE units and where as for the saturated analogs, $1\pi(m)$, terminal CH_2 groups serve as D and A sites. In addition to these latter groups and the repeat unit, the $3\pi(m)$ structures contain an additional acetylene unit. This was included for convenience in analyzing the molecular orbitals, since the extra unit yields symmetry-equivalent D and A sites for many of the conformers studied. The coupling was evaluated at the level of the two-state-approximation on the basis of INDO/s CI calculations for the radical ion (cation or anion) states of structures $3\pi(n)$, followed by GMH analysis [15]. The superexchange coupling for the cation and anion systems are expected [20-23] to be dominated, respectively, by the participation of the occupied ("hole" transfer) and unoccupied ("electron"

transfer) electronic manifolds of the bridge, and as for the case of the saturated systems (1π (m)), it is of interest to compare the corresponding β values.

To obtain a compact expression for the coupling, the results of the calculations were fit to the form of the superposition of McConnell type pathways (see Eq. (32)) displayed in Eq. (37). This expression includes pathways involving a hole (for radical cations) or electron-attached (for radical anions) virtual electronic state in either the π or σ manifold of each phenyl group (thus yielding a superposition of 2^n pathways) and also allows the k -th benzene group to be rotated by an arbitrary angle, θ_k , relative to the reference plane of the coplanar D and A CH_2 groups (see Fig. 10):

$$H_{DA} = \sum_{\{x_k\}} (T_{D1}^{x_1}) \prod_{k=1}^{n-1} \left(t_{k,k+1}^{x_k, x_{k+1}} / \Delta_1^{x_k} \right) \left(T_{nA}^{x_n} / \Delta_n^{x_n} \right)$$

where $x_k \equiv \pi_k$ or σ_k and the nearest-neighbor McConnell parameters are expressed as [15]:

$$T_{D1}^{\pi_1} = (T_{D1}^{\pi_1})_0 \cos [\theta_1]$$

$$T_{D1}^{\sigma_1} = (T_{D1}^{\sigma_1})_0 \sin [\theta_1]$$

$$\left(t_{k,k+1}^{\pi_k, \pi_{k+1}} \right)_0$$

$$t_{k,k+1}^{\pi_k, \pi_{k+1}} = \left(t_{k,k+1}^{\pi_k, \pi_{k+1}} \right)_0 (\cos[\theta_k] \cos [\theta_{k+1}] + \sin [\theta_k] \sin [\theta_{k+1}]), \text{ etc.}$$

The parameters denoted by "zero" subscripts were obtained by least-squares fits ($\pm 10\%$) to the GMH results for a sample of 12 different conformers spanning a broad range of dihedral angles in the series $n = 1-4$. The use of the $\cos(\theta)$ and $\sin(\theta)$ factors is an approximation motivated by the fact that, for the purpose of rotation about the OPE axis, the relevant orbitals of benzene have the nodal structure of $2p\pi$ orbitals with respect to the OPE axis, in contrast to the situation

involving porphyrins linked by a biphenyl spacer (analyzed by Helms *et al* [57]). The $2p\pi$ nodal structure pertains not only to the phenylene occupied and unoccupied MO's belonging to the conventional "pi" manifold, but also to the analogous MO's of the same nodal type belonging to the "sigma" manifold (i.e., MO's of $2p\pi$ nodal structure comprised of suitable linear combinations of the phenylene sigma bonds). It is seen that the integer n in Eq. (37), the number of PE units, is the counterpart of m in Eqs. (31) and (32), since the superexchange couplings involve in effect one orbital from the "pi" manifold of each PE unit, and one from the "sigma" manifold.

Results for three limiting conformational cases are displayed in Table 3. The calculated values of $\ln [H_{DA}^2]$ vs m exhibit linear behavior (regression coefficient ≥ 0.99) within a homologous series of a given conformational type; the corresponding β values (Table 3) reveal a strong dependence on spacer conformation, with similar results for the radical anion and cation models. Note that the agreement with experimental values is quite good for both the staggered saturated ($-\text{CH}_2\text{CH}_2-$) and trans unsaturated ($-\text{CH}=\text{CH}-$) bridge units.

The experimental value of β for the OPE spacer is seen to be intermediate between the calculated values for the perpendicular and coplanar ring geometries and in closest agreement with the calculated value for a uniform distribution of dihedral angles. For homogeneous kinetics to be obtained in the case of the uniform distribution, interconversion among the dihedral angles would have to be rapid compared to the rate of electron transfer [58]. Alternatively, the dihedral angles may be narrowly distributed about an intermediate value that gives a H_{DA}^2 value similar to the average value of H_{DA}^2 for the uniform distribution. Neither possibility can be ruled out on the basis of available data, since the barriers to rotation are quite likely to be very small (see above). We note that a distinct set of dihedral angles can be observed in the solid state [52].

VI CONCLUDING REMARKS

The examples of calculated results presented in the last section underscore the important role of computational chemistry in establishing productive contact between theoretical and experimental investigations of electron transfer kinetics in condensed phases. In the context of a broad kinetic framework (albeit one limited to the case of weak D/A coupling) capable of accounting for homogeneous processes and interfacial processes involving metal electrodes, we have placed particular emphasis on two crucial kinetic parameters, the solvent reorganization energy (E_s) and the D/A coupling element (H_{DA}), showing how the behavior of these quantities may be evaluated and analyzed theoretically, and successfully related to results inferred from electrochemical kinetic measurements. The theory underlying the calculations allows the formulation of compact models of predictive utility, suggesting critical new experimental tests of theory and helping to identify principles which will be important in the design of new materials with specified redox characteristics. Results of the type illustrated in Table 3 suggest that the INDO/s quantum chemistry model in conjunction with the Generalized Mulliken Hush model for D/A coupling offers an especially promising approach for efficient treatment of a broad array of *et* systems in a quantitatively reliable manner.

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APPENDIX

A further technical comment is in order with regard to Eq. (37). Clearly, the superexchange model assumed for the purpose of fitting the numerical results (with D and A identified with the terminal CH_2 groups) does not take

explicit account of the "extra" acetylene unit of the $3\pi(n)$ homologs (see Fig. 10). As a result, the T_D and T_A parameters may be interpreted as corresponding to a generalized D and A pair (relative to their nominal definitions as terminal CH_2 groups), which implicitly include the influence of the extra acetylenic group.

REFERENCES

1. M. D. Newton, N. Sutin, *Ann. Rev. Phys. Chem.* **35**, 437 (1984).
2. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta.* **811**, 265 (1985).
3. K. V. Mikkelsen and M. A. Ratner, *Chem. Rev.* **87**, 113 (1987).
4. P. F. Barbara, T. J. Meyer and M. A. Ratner, *J. Phys. Chem.* **100**, 13148 (1996).
5. J. Jortner and M. Bixon, *J. Chem. Phys.* **88**, 167 (1988).
6. M. A. Ratner, *J. Phys. Chem.* **94**, 4877 (1990).
7. J. N. Onuchic and D. N. Beratan, *J. Chem. Phys.* **92**, 722 (1990).
8. M. D. Newton, *Chem. Rev.* **91**, 767 (1991).
9. J. B. Straus, A. Calhoun and G. A. Voth, *J. Chem. Phys.* **102**, 1 (1995).
10. C. E. D. Chidsey, *Science* **251**, 919 (1991).
11. H. O. Finklea and D. D. Hanshew, *J. Am. Chem. Soc.* **114**, 3173 (1992).
12. a) A. M. Becka and C. J. Miller, *J. Phys. Chem.* **96**, 2657 (1992); *J. Phys. Chem.* **96**, 2790 (1992). b) K. Slowinski, R. V. Chamberlain, C. J. Miller and M. Majda, *J. Am. Chem. Soc.* **119**, 11910 (1997).
13. a) M. T. Carter, G. K. Rowe, J. N. Richardson, L. M. Tender, R. H. Terill and R. W. Murray, *J. Am. Chem. Soc.* **117**, 2896 (1995). b) K. Weber, L. Hockett and S. Creager, *J. Phys. Chem.* **101**, 8286 (1997).

14. J. F. Smalley, S. W. Feldberg, C. E. D. Chidsey, M. R. Linford, M. D. Newton and Y.-P. Liu, *J. Phys. Chem.* **99**, 13141 (1995)
15. S. B. Sachs, S. P. Dudek, R. P. Hsung, L. R. Sita, J. F. Smalley, M. D. Newton, S. W. Feldberg, C. E. D. Chidsey. *J. Am. Chem. Soc.* **119**, 10563 (1997).
16. R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956). (b) R. A. Marcus, *J. Chem. Phys.* **24**, 979 (1956).
17. R. A. Marcus, *J. Chem. Phys.* **43**, 679 (1965).
18. R. J. Cave, M. D. Newton, *Chem. Phys. Lett.* **249**, 15 (1996).
9. M. Marchi and D. Chandler, *J. Chem. Phys.* **95**, 889 (1991).
20. L. A. Curtiss, C. A. Naleway and J. R. Miller, *J. Phys. Chem.* **97**, 4050 (1993).
21. K. D Jordan and M. N. Paddon-Row, *Chem. Rev.* **92**, 395 (1992).
22. C. Liang and M. D. Newton, *J. Phys. Chem.* **96**, 2855 (1992).
23. C. Liang and M. D. Newton, *J. Phys. Chem.* **97**, 3199 (1993).
24. A. A. Stuchebrukhov, *Chem. Phys. Lett.* **225**, 55 (1994).
25. (a) R. A. Marcus *J. Chem. Soc., Faraday Trans.*, **92**, 3905 (1996)
(b) W. J. Royea, A. M. Fajardo and N. S. Lewis, *J. Phys. Chem.* **101**, 11152 (1997)
25. (a) H. Sumi and R. A. Marcus, *J. Chem. Phys.* **84**, 4894 (1984).
(b) D. Zusman, *Chem. Phys.* **49**, 295 (1980).

27. J. T. Hynes, *J. Phys. Chem.* **90**, 3701 (1986).
28. M. D. Newton and R. J. Cave, "Molecular Control of Electron and Hole Transfer Processes: Electronic Structure Theory and Application", in *Molecular Electronics* J. Jortner, M. A. Ratner Eds., Blackwell Science Ltd., Oxford, 1997, p73.
29. C.-P. Hsu, R. A. Marcus, *J. Chem. Phys.* **106**, 584 (1997).
30. Y.-P. Liu and M. D. Newton, *J. Phys Chem.* **98**, 7162 (1994).
31. Y.-P. Liu and M. D. Newton, *J. Phys. Chem.* **99**, 12382 (1995).
32. B.-C. Perng, M. D. Newton, F. O. Raineri and H. L. Friedman, *J. Chem. Phys.* **104**, 7177 (1996).
33. R. A. Marcus, *J. Phys. Chem.* **94**, 1050 (1990).
34. N. S. Hush, *Electrochim. Acta* **13**, 1005 (1968).
35. S. Larsson and A. Volosov, *J. Chem. Phys.* **85**, 2548 (1986).
36. L. A. Curtiss, C. A. Naleway and J. R. Miller, *J. Phys. Chem.* **99**, 1182 (1995).
37. G. Gamow, *Z. Phys.* **51**, 204 (1961).
38. H. M. McConnell, *J. Chem. Phys.* **74**, 6746 (1981).
39. J. R. Miller and J. V. Beitz, *J. Chem. Phys.* **74**, 6746 (1981).
40. R. J. Cave, D. V. Baxter, W. A. Goddard, III and J. D. Baldeschwieler, *J. Chem. Phys.* **87**, 926 (1987).

41. S. S. Isied, A. Vassilian, J. F. Wishart, C. Creutz, H. A. Schwarz, N. Sutin, *Chem. Rev.* **91**, 791 (1991).
42. J. W. Verhoeven and P. Pasman, *Tetrahedron* **37**, 943 (1984).
43. M. J. Shepard, M. N. Paddon-Row and K. D. Jordan, *Chem. Phys.* **176**, 289 (1993).
44. J. W. Evenson, M. Karplus, *J. Chem. Phys.* **96**, 5272 (1992).
45. L. I. Krishtalik, N. M. Alpatova, and E. V. Ovsyannikova, *Electrochimica Acta* **36**, 435 (1991).
46. T. Gennett, D. F. Milner, and M. J. Weaver, *J. Phys. Chem.* **89**, 2787 (1985).
47. G. E. McManis, R. M. Nielson, A. Gochev, and M. J. Weaver, *J. Am. Chem. Soc.* **111**, 5533 (1989).
48. N. A. Lange, ed., *Handbook of Chemistry*, 10th ed. (McGraw-Hill Book Company, New York, 1967).
49. J. D. Swalen, R. Santo, M. Take and J. Fischer, *IBM J. Res. Dev.* **21**, 169 (1977).
50. C. E. D. Chidsey, C. R. Bertozzi, T. M. Putvinski, and A. M. Muijsce, *J. Am. Chem. Soc.* **112**, 4301 (1990).
51. R. G. Nuzzo, L. H. Dubois, and D. L. Allara, *J. Am. Chem. Soc.* **112**, 558 (1990).
52. R. P. Hsung, C. E. D. Chidsey and L. R. Sita, *Organometallics* **14**, 4808 (1995).

53. R. J. Cave, M. D. Newton, K. Kumar, M. B. Zimmt, *J. Phys. Chem.* **99**, 17501 (1995).
54. M. C. Zerner, G. H. Loew, R. F. Kirchner and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **102**, 589 (1980).
55. M. D. Newton, "Cluster Models for Condensed-Phase Electron Transfer Processes", in *Cluster Models for Surface and Bulk Phenomena*, G. Pacchioni, P. S. Bagus and F. Parmigiani, Eds., Plenum Press, New York, 1992.
56. K. Okuyama, T. Hasegawa, T., M. Ito and N. Mikami, *J. Phys. Chem.* **88**, 1711 (1984).
57. A. Helms, D. Heiler and G. McLendon, *J. Am. Chem. Soc.* **113**, 4325 (1991).
58. J. Tang, *J. Chem. Phys.* **98**, 6263 (1993).
59. S. Woitellier, J. P. Launay and C. W. Spagler, *Inorg. Chem.* **28**, 273 (1989).

Table 1. Effect of Peripheral Aqueous Solvent on Coupling through Staggered Alkane Bridges ($1\pi(m)$)^a

Nature of Hydration	Decay Coefficient, $\beta(\text{\AA}^{-1})$ ^b	
	Radical Cations	Radical Anions
Absent ^c	0.85	0.95
Dielectric continuum ^d	0.85	0.95
Specific hydration ^e	0.81	0.95
<u>$((\text{CH}_2)_{m+3} (\text{H}_2\text{O})_{m+1})^\pm$</u>		

^aBased on *al initio* SCF energy splittings (Eq. (25)) with the 6-31G** orbital basis [28b] and including *m* in the range 2-6 [Table 6 of [28b], reprinted with permission. Copyright [1997] Elsevier Press].

^bEq. (28), based on a linear least-squares fit of $\ln |H_{\text{DA}}|^2$ as a function of r_{DA} .

^c*In vacuo* results from [31].

^dBased on dielectric cavity model described in [31].

^eAn H₂O interacts with each of $m+1$ CH₂ triads for each (CH₂) _{$m+3$} species, oriented so as to allow the H₂O lone pairs to overlap optimally with the carbon framework (as indicated in structure 2), with van der waals C...O contacts of 3.1Å.

Table 2. Conformational Dependence of $H_{DA}^{\pm}$ for $(CH_2)_6$ Radical Ions ($1\pi(3)$)^a

Conformation of D and A orbitals relative to bridge ^b	Conformation of C ₄ bridge	H_{DA}	
		Radical Cation	Radical Anion
in-plane	trans (C _{2h})	-11.0	-8.4
	gauche (C ₂)	-2.4	-4.5
	cis (C _{2v})	-0.3	-4.3
perpendicular to plane	trans (C _{2h})	-1.1	+0.3
	gauche (C ₂)	+3.6	+2.0
	cis (C _{2v})	+7.9	+9.9

^a H_{DA} given in mhartree (1 mhartree = 0.027 eV $\sim k_B T$ at room temperature), based on energy splitting (Eq. (25) at the Koopmans' Theorem (KT) level, using the 3-21G orbital basis [28]. The sign convention [23] is based on the phases of the D and A orbitals in the two MO's of primarily D/A character and assigns a positive

(negative) sign to the quantity $-H_{DA}$ when the occupation of the "in-phase" ("out-of-phase") MO is energetically favored (the positive sign for $-H_{DA}$ corresponds to the "normal" situation in which in-phase ("bonding") orbital interactions are characterized by a negative transfer integral). For the $(CH_2)_6^\pm$ systems, "in-phase" is taken as transforming according to a_g , a , and a_1 for, respectively, C_{2h} , C_2 , and C_{2v} symmetry in the case of "in plane" D/A conformers, and a_u , a , and b_1 for the corresponding "perpendicular" conformers [Table 2 of [28b], reprinted with permission. Copyright [1997] Elsevier Press].

^bAngle of the D(A) pi orbitals relative to plane formed by the carbon atom of the terminal D(A) methylene group and the closest two carbon atoms of the bridge.

Table 3. Exponential Decay Coefficients^a

Tether Repeat Unit	$\beta(\text{\AA}^{-1})$ Calculated ^b		$\beta(\text{\AA}^{-1})$ Experimental ^c
	Anion	Cation	
A) staggered (-CH ₂ -CH ₂ -) ^d	1.00	0.83	0.9 $\pm$ 0.1 ^e
B) (-C ₆ H ₄ -C $\equiv$ C-) ^f			
Perpendicular ($\theta_k = \pi/2$)	0.99	0.95	
Uniform θ_k Distribution ^g	0.54	0.51	0.57 $\pm$ 0.02 ^h
Planar ($\theta_k = 0$)	0.43	0.39	
C) trans(-CH=CH-)	0.32	0.31	0.2 ⁱ

^a[Table 2 of [15], reprinted with permission. Copyright [1997] American Chemical Society].

^bGMH [18] and INDO/s [54] results based on $\ln |H_{DA}|^2$ vs r_{DA} .

^cResults based on $\ln [k_0]$ vs ℓ (See Fig. 9). The distance ℓ differs by a constant from the distance between the Fc iron atom and the gold surface at the point of attachment to the OPE chain.

^dSee Fig. 8

e)[10-14].

f) See Fig. 10. The θ_k are the set of dihedral angles of the phenylene rings relative to the reference plane of the D and A groups $1 \leq k \leq n$ for 3π (n)).

g) β is based on the rms values of H_{DA} . A small torsional barrier (e.g., a value of $\sim kT$ at room temperature found for the related diphenyl acetylene system [56]) would yield somewhat larger rms values of H_{DA} and smaller values of β .

h)[15].

i)[59].

FIGURE CAPTIONS

Figure 1. Generic electron transfer system, $\text{DBA}/\text{D}^+\text{BA}^-$, comprising local donor (D) and acceptor (A) sites, the intervening bridge (B), and the surrounding medium (or solvent). In the two-state approximation (TSA), the kinetics may be modeled in terms of initial (ψ_i) and final (ψ_f) state wavefunctions, in which the transferring charge is localized primarily on the D and A sites, respectively [Fig. 1 of [28], reprinted with permission. Copyright [1997] Elsevier Press].

Figure 2. Effective energy profiles along the reaction coordinate (R) for the initial ($V^i(R)$) and final ($V^f(R)$) diabatic states, indicating the reorganization energy (E_r), activation energy (E_a), and reaction driving force ($-\Delta G^0$). In a linear system, with parabolic profiles of equal curvature, the free energy change ΔG^0 can be equated (as implied by the figure) to the gap between the minima of the two free energy profiles [35] (a near equality is expected in general [60]), and the vertical energy gap (E_v^i) at the equilibrium configuration for the initial state (DBA) is equal to $E_r^f + \Delta G^0$ [1,2]. Correspondingly, the final state (D^+BA^-) gap ($-E_v^f$) is given by $E_r^i - \Delta G^0$.

Figure 3. A schematic representation of a redox couple in a spherical cavity of radius a , separated from a film of width L by a distance d . The point charge shift at the redox site is Δq , z and ρ are cylindrical coordinates, and ϵ_i ($i = \text{I, II, III}$) are the dielectric constants for the three zones [Fig. 1 of [30], reprinted with permission. Copyright [1994] American Chemical Society].

Figure 4. Schematic representation of optical and thermal *et*, corresponding, respectively, to the vertical transition with excitation energy $h\nu$ and thermally activated passage through the transition-state (or crossing) region. In experimental studies, the thermodynamically stable state, which is the *final* state

in the *thermal et* process, generally serves as the *initial* state in the corresponding *optical* process.

Figure 5. E_s (eV) plotted as a function of the film thickness L (Å), with the cavity in contact with the film ($d = a$ (Fig. 3)) [30]. The solid curve is based on cavity radius $a = 3.8$ Å. The broken curves are based on alternative values of a (3.3 Å and 4.3 Å) [Fig. 2 of [30], reprinted with permission. Copyright [1994] American Chemical Society].

Figure 6. E_s (eV) plotted as a function of $1/(L + a)$ (Å⁻¹): (—), exact results (Eq. (24)); (— — —), linear fit with dominant image charge contribution ($n = 1$ term of Eq. (24)); (----), best linear fit. The slopes s are given in parentheses in units of $(\Delta q)^2$, as in Eq. (33). The value of s for the single-image case is given by Eq. (33). [Fig. 3 of [30], reprinted with permission. Copyright [1994] American Chemical Society]

Figure 7. Plot of E_s vs n : (O), values computed from slopes of Arrhenius plots based on ILIT results (indirect laser induced temperature jump) for $m = 5-9$; (●), values computed from slopes of Arrhenius plots based on chronoamperometric data for $m = 12, 16$, and 18 ; (X) value computed from direct chronamperometric measurement of the potential dependence of k_f and k_b for $n = 16$. The solid line gives the calculated results, as fitted according to Eq. (36). The abscissa may be converted to a distance scale by using (for example), relations of the type given in Eqs. (34) or (35). [Fig. 12 of [14], reprinted with permission. Copyright [1995] American Chemical Society].

Figure 8. *Et* systems $1\pi(m)$, consisting of π -type D/A orbitals (the nonbonding orbitals of the terminal CH_2 groups) linked by a staggered-alkane bridge $((\text{CH}_2)_{m+1})$ possessing m covalent CC bonds (the covalent bonds connecting the D

and A groups to the bridge contribute little to H_{DA} [20-23]). The even and odd- m members correspond, respectively, to C_{2v} and C_{2h} point-group symmetry.

Figure 9. Comparison of $\ln [k_0]$ vs l plots for *et* through OPE and OM-based films: OPE results [15] are displayed for two ($\star$; $n=2$) and three ($\star$; $n=3$) OPE units; the OM results ($\circ$ and $\bullet$) are as given in [14]. Different diluents give very similar results. The error bars are significantly smaller than the size of the symbols. The abscissa l denotes the straight-line distance from the terminal sulfur-bonded oligomer carbon to the attached carbon atom of Fc, based on mean bond distances [52]. A linear oligomer axis was assumed for both OM and OPE systems. [Fig. 1 of [15], reprinted with permission. Copyright [1997] American Chemical Society]

Figure 10. *Et* systems $3\pi(n)$, consisting of the same π -type D/A orbitals as in the case of the $1\pi(m)$ homologs (Fig. 8). The dihedral angle between the common plane of the terminal CH_2 groups and that of the k -th phenylene group is denoted θ_k .

$\psi_i \rightleftharpoons \{ \text{DBA} \}$ (initial state)

$\psi_f \rightleftharpoons \{ \text{D}^+ \text{BA}^- \}$ (final state)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

$$C_{2v} \quad m = 2l, l \geq 1$$

$$C_{2h} \quad m = 2l + 1, l \geq 0$$

$1\pi(m)$

Figure 8

Figure 9

Figure 10

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