focused attention on the different roles of quickly responding solvent electronic polarization and slowly responding orientational polarization. For this class of models, our exact results agree with the traditional estimates concerning these different roles. The quantum transition-state theory procedure of computing rate constants through the control of the electron path centroid was also examined and shown to be in accord with the traditional estimates.

On the other hand, for the case of solvent electronic polarization fast compared to the time scale of the transferring electron, our exact results are in discord with those derived by Kim and Hynes through their application of a self-consistent mean field approximation.[3-6] We have shown that this approximate procedure applied to the spin–boson model reproduces the principal results of refs 4 and 5 for the free energy of activation. The differences between those results and the traditional estimates are thereby shown to be artifacts of the self-consistent mean field approximation.

In this paper we have considered primarily the case in which the high-frequency polarizations are effectively infinitely fast compared to all other dynamics. In general, through active vibrations as well as electronic modes, there is a continuum of time scales. If we consider k_{ct} as a function of $\hbar\omega_e/K$, where ω_e represents an effective frequency for the spectrum of high-frequency polarization modes, we have from section III,

$$\ln k_{ct} \sim -\beta s_o + \ln [\beta K I_1(\beta K)/\bar{q}(\beta K,\beta s_o)], \quad \hbar\omega_e/K \to \infty$$
$$\sim -\beta(s_o + s_e) + \ln [\beta K I_1(\beta K)/\bar{q}(\beta K,\beta s_o+\beta s_e)], \ \hbar\omega_e/K \to 0 \tag{5.1}$$

A correct general theory must successfully interpolate between these limits. Whether the more general case can be usefully analyzed with the centroid principle or some other approach remains for future study.

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Schrödinger Equation for Strongly Interacting Electron-Transfer Systems

R. A. Marcus

Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91125
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The Schrödinger equation for strongly interacting electron-transfer systems is described, the eigenvalues depending on a dielectric polarization function $\mathbf{P}(\mathbf{r})$ for the medium, on the internal coordinates $\mathbf{q}$, and, when the electron transfer is coupled to a dissociation, on a generalized coordinate Q. A choice of the reaction coordinate for the variation of $\mathbf{P}(\mathbf{r})$, $\mathbf{q}$, and Q, so as to reach the saddle-point, and the calculation of the free energy of activation are described. The question of suitable data on the solvent dependence of strong-overlap systems is also considered.

Introduction

Electron-transfer reactions between weakly interacting reactants are the customary ones treated theoretically. For such systems, the free energy of reorganization of the solvation has been calculated and used to obtain the reaction rate.[1] Electron transfers are also expected to occur where there is a strong electronic orbital overlap of the reactants. A Schrödinger equation for the latter has been considered[2,3] but corresponded to a case where the transferring electron was treated as "fast" relative to the electronic motion of the solvent.[4] Of much more relevance to strong overlap electron transfers is, instead, the case where the transferring electron is treated as "slow". An illuminating analysis of the problem is given by Chandler and co-workers, using a model Hamiltonian of the spin–boson type.[5]

In the present paper, dielectric-continuum-based equations are given for the case of strong electronic interaction between the solvent and the reactants when the transferring electron is "slow". This derivation is in agreement both with the analysis of Chandler and co-workers and with the analysis in ref 6, and corrects the development in ref 2. The dependence on any internal coordinates q, such as ligand bond lengths, and on any generalized dissociation coordinate Q is also included. The many-electron Schrödinger equation is first given and then specialized to the one-electron approximation, eq 15 below. A choice of a reaction coordinate for the calculation of the activation free energy is then described. The final eqs 14 and 15 are, apart from the fact that bond coordinates are also considered, equivalent to those used earlier[6] in a related but simpler problem (eqs 10–12 of ref 6). In that system, an electron interacted strongly with a dielectric continuum and weakly with a second reactant.

† Contribution No. 8476.

In a concluding section, the question of comparing theory and experiment for the solvent effects on strong-overlap electron-transfer systems is considered, with a view to examining which data might be suitable for comparison with treatments of solvent effects for such reactions.

Theory

We first consider a system where a "slow" electron is moving in an electrostatic potential due to two nuclei, and this system interacts with an atom some distance away via the electronic polarizability α of the atom. The two nuclei have charges Z_1e and Z_2e. The electric field, due to a charge Z_1e situated at $\mathbf{R}_1$, Z_2e situated at $\mathbf{R}_2$, and to the electron of charge $-e$ situated at $\mathbf{r}_1$, varies with the field point $\mathbf{r}$ and is denoted by $\mathbf{D}(\mathbf{r})$:

$$\mathbf{D}(\mathbf{r}) = -\nabla_r\left(-\frac{e}{|\mathbf{r}-\mathbf{r}_1|} + \frac{Z_1e}{|\mathbf{r}-\mathbf{R}_1|} + \frac{Z_2e}{|\mathbf{r}-\mathbf{R}_2|}\right) \tag{1}$$

The leading term in the quantum mechanical energy of interaction of the three charges with the distant atom is $-\alpha D(\mathbf{r}_a)^2/2$, where $\mathbf{r}_a$ denotes the position of the atom. Thus, the Schrödinger equation for this electron in such a system, is, in units of $\hbar = m = 1$

$$[-\tfrac{1}{2}\nabla_1^2 + V(\mathbf{r}_1) - \tfrac{1}{2}\alpha\mathbf{D}^2(\mathbf{r}_a)]\Psi(r_1) = E\Psi(\mathbf{r}_1) \tag{2}$$

(1) For example: Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
(2) Marcus, R. A. *Faraday Symp. Chem. Soc.* **1975**, *10*, 60.
(3) Kim, H. J.; Hynes, J. T. *J. Phys. Chem.* **1990**, *94*, 2736; *J. Chem. Phys.* **1990**, *93*, 5194, 5211. "Fast" and "slow" treatments are described by Jortner, J. *Mol. Phys.* **1962**, *5*, 257. Various aspects of the electronic motion are discussed in ref 31.
(4) Chandler, D. Private communication.
(5) Gehlen, J. N.; Chandler, D.; Kim, H. J.; Hynes, J. T. *J. Phys. Chem.*, preceding paper in this issue.
(6) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 3477.

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where $V(\mathbf{r}_1)$ denotes the last two Coulombic terms in parentheses in eq 1, with $\mathbf{r}$ replaced by $\mathbf{r}_1$.

With this result in mind, we consider next the case where the electrons of two reactants (or of one reactant in the case of an intramolecular electron transfer) interact with each other, with the nuclei of the reactant or reactants, and with the orientational, vibrational, and electronic dielectric polarization of the surrounding medium. The set of coordinates $\mathbf{r}_1, ..., \mathbf{r}_N$ of the N electrons of the reactant(s) is denoted collectively by $\mathbf{r}_e$. The free energy of formation of nonequilibrium polarization state of the medium with an arbitrary orientational–vibrational polarization is then given by $W_{rev}(\mathbf{r}_e)$ when the nuclear motion is treated as "slow" and the electronic motion of the solvent as "fast",[7] a point to which we return later.

$$W_{rev}(\mathbf{r}_e) = -[(1 - 1/D_{op})/8\pi]\int \mathbf{D}^2(\mathbf{r})\, d\mathbf{r} - \int \mathbf{P}\cdot\mathbf{D}(\mathbf{r})\, d\mathbf{r} + 2\pi c \int \mathbf{P}^2\, d\mathbf{r} \quad (3)$$

upon neglecting dielectric image effects. Here, $\mathbf{D}(\mathbf{r})$ is given by

$$\mathbf{D}(\mathbf{r}) = -\nabla_r\left(\sum_j \frac{Z_j e}{|\mathbf{r} - \mathbf{R}_j|} - \sum_{i=1}^{N} \frac{e}{|\mathbf{r} - \mathbf{r}_j|}\right) \quad (4)$$

the first sum being over the nuclei j of the reactants; $1/c$ is $1/D_{op} - 1/D_s$, $\mathbf{r}$ is any point in the solvent, $\mathbf{P}(\mathbf{r})$ is a *function*[7] of the arbitrary orientational–vibrational dielectric polarization (and not this polarization itself), and D_{op} and D_s are the optical and static dielectric constants of the solvent, respectively. The integration over $d\mathbf{r}$ in eq 3 is only over the volume occupied by the solvent.

The Schrödinger equation based on eqs 3 and 4 is given by

$$[-\tfrac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + V_{tot}(\mathbf{r}_e) + W_{rev}(\mathbf{r}_e)]\Psi(\mathbf{r}_e) = E\Psi(\mathbf{r}_e) \quad (5)$$

where $V_{tot}(\mathbf{r}_e)$ denotes the Coulombic interaction of all the electrons in the reactants with each other and with the nuclei of the reactants, and of the nuclei with each other. For a given $P(\mathbf{r})$, eq 5 is solved for the many-electron wave function $\Psi(\mathbf{r}_e)$ and for the eigenvalue E. Typically, in real systems, $V_{tot}(\mathbf{r}_e)$ can be expected to depend on internal coordinates q_i and, in the dissociative case, on Q. So, therefore, will $\Psi(\mathbf{r}_e)$ and E. For brevity, however, the q_i's and Q are suppressed in the notation.

For the weak-overlap case, the present results are readily shown to reduce to those obtained earlier in ref 1: When the overlap is weak, we have

$$\Psi(\mathbf{r}_e) \simeq c_r^{1/2}\Psi_r(\mathbf{r}_e) + c_p^{1/2}\Psi_p(\mathbf{r}_e) \quad (6)$$

where $\Psi_i(\mathbf{r}_e)$ is a many-electron wave function having the electronic distribution of the reactants (i = r or p denoting that the extra electron is on the donor or acceptor, respectively) and $c_r + c_p = 1$. The overlap of Ψ_r and Ψ_p is neglected in this normalization for the weak-overlap problem.

Introduction of eq 6 into 5, multiplication by Ψ_j^* (j = r or p), and integration over $\mathbf{r}_e$ yields

$$E = G_i \qquad (i = r, p) \quad (7)$$

where

$$G_i = \int \Psi_i^*\left[-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + V(\mathbf{r}_e) + W_{rev}(\mathbf{r}_e)\right]\Psi_i\, d\mathbf{r}_e \quad (8)$$

G_i is the energy (really free energy of solvation plus q_i- and Q-dependent electronic energy of the solute) when the extra electron is on the original donor (i = r), or on the acceptor (i = p). Thus, eqs 7 and 8 yield

$$G_r(\mathbf{P}) = G_p(\mathbf{P}) \quad (9)$$

a result deduced earlier in ref 1 by a related argument. As in ref 1, $\mathbf{P}$ is then obtained by minimizing $G_r(\mathbf{P})$, subject to the constraint on $\mathbf{P}$ imposed by eq 9. The resulting $\mathbf{P}(\mathbf{r})$ is given later in eq 16. As noted earlier, these G_i's are also, in general, a function of the q_i's and of any Q.

(7) Reference 6, Appendix 1.

The interactions of a solute molecule (here, the donor–acceptor pair) with the solvent molecules may be conveniently classified as noncorrelative ("electrostatic") and correlative (electron–electron correlations). The former involve the charge, dipole (permanent and induced), and multipole interactions. The correlative interactions are, instead, those of the London dispersion type, typically attractive, and the exchange repulsion Pauli-exclusion type. Solute–solvent electron correlations of the dispersion type have been treated in ref 31 below, assuming a dielectric continuum for the solvent electrons.

In the present paper, we focus our attention on the effect of the "electrostatic" solute–solvent interactions on the solute electronic wave function. It will then be supposed that once these electronic wave functions of the different electronic states of the solute molecule (the donor–acceptor pair) have been determined, the correlative contribution to the solute–solvent interaction energy could be estimated, e.g., in the case of the London-dispersion forces, using second-order perturbation theory. For a noninteracting donor and acceptor pair, such correlative interactions reduce to those for the reactants or products interacting with the solvent molecules in a way often modeled with Lennard-Jones 6–12 or exp-6 atom–atom potentials.

There are several frequencies describing the electronic motion of the solute. Within a donor or acceptor molecule, the transferring electron is of a fairly high frequency, of the order of several electronvolts. When there is also a weak donor–acceptor electronic interaction, there is also a low-frequency component to the motion, a measure of lowness being the ratio of the spectral frequency corresponding to the difference between the energies of lowest and first excited electronic state of the solute in the transition state, as compared with the lowest excitation frequency of the electrons of the solvent. The first difference is perhaps of the order of 0.03 eV for weak-overlap electron transfers, and of the order of ~0.5 eV for strong-overlap ones. In contrast, the lowest excitation frequency for the electrons of solvents is usually in the 5–10-eV range. The core electrons of the solute will have excitation energies comparable to those of the electrons of the solvent.

The electronic wave function may be represented approximately as an antisymmetrized combination of terms

$$\Psi = A\Psi_{te}(\mathbf{r}_1)\,\Psi_{core}(\mathbf{r}_2 \cdots \mathbf{r}_n) \quad (10)$$

where A is the antisymmetrizer operator and Ψ_{te} denotes the wave function of the transferring electron. For a given Ψ_{core}, we note from eq 3 that two limiting situations, one preaveraged and the other not preaveraged over the core electrons, would have from a single term in eq 10 an energy difference proportional to

$$\Delta E = \int \langle\Psi_{core}|(\mathbf{D}_{core}^2 - \langle\Psi_{core}|\mathbf{D}_{core}|\Psi_{core}\rangle^2)|\Psi_{core}\rangle\, d\mathbf{r} = \int \langle\Psi_{core}|(\mathbf{D}_{core} - \langle\Psi_{core}|\mathbf{D}_{core}|\Psi_{core}\rangle)^2|\Psi_{core}\rangle\, d\mathbf{r} \quad (11)$$

with

$$\mathbf{D}_{core}(\mathbf{r}) = -\nabla_r\sum_{i=2}^{N}\frac{-e}{|\mathbf{r} - \mathbf{r}_i|} \quad (12)$$

The term in eq 3 linear in $\mathbf{D}_{core}(\mathbf{r})$ cancels in eq 11 and so does not contribute to this ΔE. The integration over the field point $\mathbf{r}$ in eq 11 is only over the volume occupied by the solvent (cf. similar remark earlier for eq 3).

Because there is little fluctuation in the charge distribution arising from the core electrons, even in the transition-state region, one can expect terms such as the ΔE given by eq 11 to be small. In contrast, the analogous term for the transferring electron can be quite large, particularly in weak-overlap electron transfers. In the latter, when the electron is transferred a significant distance in the transition state, there is a large fluctuation inside the wave function Ψ_{te} of that electron in the transition-state region: there are two contributions to it arising from electronic configurations having two very different charge distributions. Thus, for this electron, it is important to use the $\mathbf{D}(\mathbf{r})$ for electron 1 which is not preaveraged, as in eq 4 and in eq 14 below.

We consider next a common approximation in which the transferring electron 1, situated at $\mathbf{r}_1$, moves in an averaged po-

tential $V(\mathbf{r}_1)$, the sum of the Hartree potential (due to the nuclei and the other electrons of the reactants) and the exchange-correlation potential. The problem then reduces to a one-electron one, with the $W_{rev}(\mathbf{r}_1)$ given by eq 3, but with $\mathbf{r}_e$ replaced by $\mathbf{r}_1$ and with $\mathbf{D}$ now given by eq 14 instead of by eq 4

$$W_{rev}(\mathbf{r}_1) = -[(1 - 1/D_{op})/8\pi]\int \mathbf{D}^2(\mathbf{r})\,d\mathbf{r} - \int \mathbf{P}\cdot\mathbf{D}(\mathbf{r})\,d\mathbf{r} + 2\pi c\int \mathbf{P}^2\,d\mathbf{r} \quad (13)$$

$$\mathbf{D}(\mathbf{r}) = -\nabla_1\left(-\frac{e}{|\mathbf{r}-\mathbf{r}_1|} + \sum_j \frac{-Z_j e}{|\mathbf{r}_1 - \mathbf{R}_j|} + \int \frac{\rho_{core}(\mathbf{r}')\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right) \quad (14)$$

where $\rho_{core}(\mathbf{r}')$ denotes the electron charge density at $\mathbf{r}'$ due to the $N-1$ core electrons. In eq 14 the major difference in the contribution of electron 1 and the core to $\mathbf{D}(\mathbf{r})$ in this approximation is that $\mathbf{D}(\mathbf{r})$ contains an average over the positions of the core electrons but not over that of electron 1.

The one-electron Schrödinger equation thus is

$$[-\tfrac{1}{2}\nabla_1^2 + V(\mathbf{r}_1) + W_{rev}(\mathbf{r}_1)]\Psi(\mathbf{r}_1) = E\Psi(\mathbf{r}_1) \quad (15)$$

where $V(\mathbf{r}_1)$ may depend on the q_i's and Q, and, hence, so may E and $\Psi(\mathbf{r}_1)$. Equation 15, without the q_i's and Q, replaces eq 5.4 of ref 2, and eq 14 replaces eq 5.2 there. These alterations correspond to the replacement referred to by Gehlen et al.[5] following their eq 4.9.

In solving eq 15, one procedure is to first omit the electronic–orientational–vibrational polarization of the solvent and use a quantum chemical calculation for the N-electron problem to determine properties such $\rho_{core}(\mathbf{r})$, the charge density of the core, and $V(\mathbf{r}_1)$, the effective potential (Hartree plus exchange correlation). Equation 15 is then solved for some parametrized form of $\mathbf{P}(\mathbf{r})$, the parameters chosen so that $\mathbf{P}(\mathbf{r})$ can be varied smoothly from the function appropriate to the reactants to that appropriate to the products, and for some parametrized form of the q_i and Q discussed later. In an initial parametrization for $\mathbf{P}(\mathbf{r})$, the function associated with weak-overlap electron transfers given by[1] eq 16 can be used

$$4\pi c\mathbf{P}(\mathbf{r}) = \mathbf{D}_r(\mathbf{r}) + m[\mathbf{D}_r(\mathbf{r}) - \mathbf{D}_p(\mathbf{r})] \quad (16)$$

and eq 15 then solved. In eq 16, $\mathbf{D}_r(\mathbf{r})$ and $\mathbf{D}_p(\mathbf{r})$ denote the $\mathbf{D}(\mathbf{r})$ when the reacting species are the reactants and the products, respectively. (Equation 16 is obtained by minimizing $W_{rev}(\mathbf{r}_1)$ in eq 13, with $\mathbf{D}$ replaced by $\mathbf{D}_r$, subject to the weak-overlap constraint imposed by eq 9 that $W_{rev}(\mathbf{r}_1)$ remains unchanged when $\mathbf{D}_r$ is replaced by $\mathbf{D}_p$.)[1] m is a Lagrangian parameter[1] which equals 0 initially and −1 at the end of the reaction. Depending on the model chosen (e.g., two spheres, ellipsoid, or other), $\mathbf{D}_r(\mathbf{r})$ and $\mathbf{D}_p(\mathbf{r})$ will take on different but readily expressed forms.

When $\mathbf{P}(\mathbf{r})$ is in the form given by eq 16, it is derivable from a potential and the dot products of the vectors in eq 13 can then be rewritten more simply in terms of purely scalar quantities (products of charges and potentials): We let $\mathbf{D}_i(\mathbf{r})$ denote a field derivable from a potential $\Phi_i(\mathbf{r})$

$$\mathbf{D}_i(\mathbf{r}) = -\nabla_r\Phi_i(\mathbf{r}) \quad (17)$$

$$\Phi_i(\mathbf{r}) = \int \rho_i(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}' \quad (18)$$

where $\rho_i(\mathbf{r}')$ is a charge density, which may be a sum of terms with or without one or more delta functions, and with or without an additional continuum charge distribution. We then have

$$\frac{1}{4\pi}\int \mathbf{D}_i(\mathbf{r})\cdot\mathbf{D}_j(\mathbf{r})\,d\mathbf{r} = \int \rho_i(\mathbf{r})\,\Phi_j(\mathbf{r})\,d\mathbf{r} = \int \rho_j(\mathbf{r})\,\Phi_i(\mathbf{r})\,d\mathbf{r} \quad (19)$$

and a standard expression for $\Phi(\mathbf{r})$ for the r and ρ configurations (e.g., ellipsoid) can now be introduced appropriately for each of the terms in eq 3 for $W_{rev}(\mathbf{r}_1)$.

When the eigenvalue E also depends on internal coordinates q_i with equilibrium values q_i^r and q_i^p in the "diabatic" r and p states, and when the dependence of the energy E of each of these two diabatic states on q_i is quadratic, the q_i which minimizes G_r, subject to the constraint given by eq 9, satisfies[8]

$$q_i = q_i^r + m(q_i^r - q_i^p) \quad (20)$$

In a particular case[9] of electron transfer accompanied by dissociation along some displacement coordinate q, when the potential energy U has a Morse-curve dependence on q in the diabatic state r, and an exponential repulsive-like potential energy dependence on q[9,10] in the diabatic state p, we have

$$U_r(q) = D(1 - e^{-\alpha q})^2, \quad U_p(q) = Ae^{-2\beta q} \quad (21)$$

it is convenient to introduce a coordinate:

$$Q = \exp(-\alpha q) \quad (22)$$

When $\beta = \alpha$ and $A = D$, as in refs 9 and 10, it is seen from eq 21 that the energy of each diabatic state r and p is a quadratic function of Q. In parallel with eq 20, one again finds, from the variation of G_r subject to the constraint imposed by eq 9,

$$Q = Q^r + m(Q^r - Q^p) \quad (23)$$

with m being the same as in eqs 16 and 20. The values of Q^r and Q^p are seen from eq 21 to be 1 and 0, respectively. Equation 21 still applies even when U_p has some shallow minimum due to an attractive term represented approximately[10] by $-B\exp(-\alpha q)$, but now Q^p is no longer zero.

The eigenvalue E in eq 15 is varied by varying the parameter m in $\mathbf{P}(\mathbf{r})$, q_i, and, in the dissociation case, Q, so as to obtain the saddle-point value of E along the reaction coordinate. An improvement in this E can be made by then expressing $\mathbf{P}(\mathbf{r})$ in terms of its Fourier components c_k and truncating the set of components. The eigenvalue E in eq 15 is now a function of these c_k's, q_i's, and Q, and techniques analogous to those[11] employed in current calculations of potential energy surfaces for reactions can be used to reach the saddle-point region, the $\mathbf{P}(\mathbf{r})$, q_i, and Q in the "transition state" previously obtained by varying m now serving as a starting point. The resulting E, minus the E when $m = 0$, is the solvational and electronic contribution to the free energy of formation of the transition state.

Using the functional two-state form for E obtained in ref 5 or often used before, we would have

$$E(P,q,Q) = \tfrac{1}{2}[G_r(\mathbf{P},\mathbf{q},Q) + G_p(\mathbf{P},\mathbf{q},Q)] - [\tfrac{1}{4}(G_r - G_p)^2 + H_{rp}^2]^{1/2} \quad (24)$$

where now the dependence of the diabatic eigenvalues G_r and G_p of the r and p states, respectively, on $\mathbf{P}$, $\mathbf{q}$, and Q is exhibited explicitly, and where the coupling term H_{rp} may be chosen to best fit the results of the initial quantum chemistry calculation. While there is no need to impose the functional form given by eq 23, it may serve as an approximate estimate of E for comparison with the actual solution of eq 15 which minimizes E in the saddle-point region.

Discussion

Various extensions of the present eq 5 are possible: (1) use of a statistical mechanical treatment, e.g., a Monte Carlo calculation or a mean spherical approximation, instead of dielectric continuum one for the solvent; (2) inclusion of dynamics of the bath, in which the different time scales of the vibrational and orientational polarization of the solvent are incorporated in the calculation (large quantum effects due to the high-frequency vibrations of water in weak-overlap electron transfers have been found, for example);[12,13] (3) adding the effect of the correlative solute–solvent

(8) For example, for weak-overlap electron transfers: Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21; *J. Chem. Phys.* **1965**, *43*, 679.
(9) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.
(10) Wentworth, W. E.; George, R.; Keith, H. *J. Chem. Phys.* **1969**, *51*, 1791.
(11) For example: Schlegl, H. B. *Adv. Chem. Phys.* **1987**, *67*, Part 1, 249.
(12) Bader, J. S.; Kuharski, R. A.; Chandler, D. *J. Chem. Phys.* **1990**, *93*, 230.

interaction mentioned earlier. Extensions 1[14-17] and 2[12,13] have been implemented previously for weak-overlap electron transfers. In this way, important issues have been discussed, such as the quadratic nature of the free energy curves for fluctuations of the solvent polarization, quantum effects for the solvent medium, more rigorous formulations of chemical dynamics and of transition-state theory, and relation of simulations to more analytical treatments, such as the mean spherical or dielectric continuum approximations. Indeed, use of the mean spherical approximation (MSA), which allows for the finite size of the solvent molecules and which has shown a fair agreement with computer simulations, shows that corrections to dielectric continuum theory (enlarging the ion size) provides a correction in the desired direction.[18] Dielectric continuum theory is expected to be increasingly valid the smaller the size of the solvent molecules relative to that of the reactants.[19]

At present, computer simulations of electron-transfer reactions do not usually include the electronic polarizability of the solvent, but it can be argued[20] that the model used in ref 12 does match the orientational response of the solvent to an electric field. It will be interesting to make comparisons with a solvent model which does contain the electronic polarizability explicitly.[21]

Of particular interest is, of course, the comparison of theory and experiment for the case of strong-overlap electron-transfer (ET) processes. For weak-overlap ET's, it may be recalled, the comparison often involves the testing of theoretically based relationships, such as that between rate constants k of cross reactions and of self-exchange reactions, the effect of ΔG° on k's, the "inverted effect", the effect of the activation overpotential on electrochemical k's, the relation between homogeneous and electrochemical k's and between ET k's and the spectral maxima of charge-transfer spectra, among others. An advantage of testing relationships between k's is that the sometimes unknown detailed molecular-based properties approximately cancel in the ratios being examined. There have also been comparisons of theoretical and experimental absolute values of k's, and comparisons of the experimental and theoretically based (usually dielectric continuum-based) dependence of k's on the solvent, as well as correlations between solvent effects on one electron-transfer reaction or charge-transfer spectral series with those in another system (e.g., with the Kosower Z-function or with Gutmann's donor or acceptor number, among others).[22]

The theoretical relationships described earlier depend on the existence of a simple functional form in the theory. In particular, for the dielectric continuum model[1] and for a more general statistical mechanical one,[8] a quadratic dependence of the free energy of fluctuations along the reaction coordinate has played a major role. For strong-overlap ET's, either some simple functional behavior should be formulated, or, in its absence, the tests of theory with experiments will be largely limited to the comparison of individual k's rather than of relationships. Such individual comparisons are subject to the well-known uncertainties which accompany the calculation of potential energy surfaces for these many-coordinate systems, and indeed of few-coordinate systems.

The simplest functional behavior for a strong-overlap system would be a two-state one, an approximation to eq 24: Some generalized reaction coordinate q could be introduced[23] and the results of the original quantum plus statistical mechanical calculations fitted by an equation of a functional form

$$G(q) = \tfrac{1}{2}(G_r + G_p) - [\tfrac{1}{4}(G_r - G_p)^2 + H_{rp}^2]^{1/2} \quad (25)$$

where now there is only a dependence on the generalized coordinate.

$$G_r(q) = \frac{k}{2}(q - q^r)^2, \quad G_p(q) = \frac{k}{2}(q - q^p)^2 + \Delta G^\circ \quad (26)$$

k is the curvature of the "assumed quadratic" G_r and G_p curves, and the fitted H_{rp} is assumed independent of q.

The free energy barrier to reaction is obtained by minimizing G with respect to q, so defining $q = q^\ddagger$, and then subtracting the value of G at $q = q^r$, the equilibrium value of q for the reactants

$$\Delta G^\ddagger = G(q^\ddagger) - G(q^r) \quad (27)$$

It is also useful to consider the charge-transfer spectrum, since it may be the most relevant for investigating the solvent dependence of strong-overlap electron transfers. The spectral absorption maximum of the relevant charge-transfer spectral transition is the value of G for the upper state at $q = q^r$ minus that for the lower state, and so equals

$$h\nu_a^{max} = [\{G_p(q^r) - G_r(q^r)\}^2 + 4H_{rp}^2]^{1/2} \quad (28)$$

From eqs 26 and 28, we have

$$h\nu_a^{max} = [(\lambda + \Delta G^\circ)^2 + 4H_{rp}^2]^{1/2} \quad (29)$$

where

$$\lambda = \frac{k}{2}(q^r - q^p)^2 \quad (30)$$

As noted earlier, the G_r, G_p, and H_{rp} appearing in eqs 25 to 28 are evaluated by fitting $G(q)$ to the results of the quantum plus statistical mechanical calculations.

Equation 27 for $\Delta G^\ddagger$ can be further approximated when the value of $q^\ddagger$ obtained from the minimization of G_r is approximately equal to the q where the curves $G_r(q)$ and $G_p(q)$ intersect. We then have $G_r(q^\ddagger) = G_p(q^\ddagger)$. In that case, one finds

$$\Delta G^\ddagger = \frac{\lambda}{4}\left(1 + \frac{\Delta G^\circ}{\lambda}\right)^2 - H_{rp} \quad (31)$$

Equation 31 contains for strong-overlap ET's the quadratic dependence of the free energy of reaction customary for weak-overlap ET's, but under the additional assumptions just cited.

If the λ appearing in these equations proves to have the same additive property that it has for weak-overlap ET's, i.e., if the λ for a cross reaction, λ_{12}, is given by

$$\lambda_{12} \simeq \tfrac{1}{2}(\lambda_{11} + \lambda_{22}) \quad (32)$$

where λ_{11} and λ_{22} are the λ's for the self-exchange reactions, and if the H_{rp} for the cross reaction is approximately the average of that for the self-exchange reactions, then when $|\Delta G^\circ|$ is not too

(13) Warshel, A.; Chu, Z. T. *J. Chem. Phys.* **1990**, *93*, 4003.
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(18) Cf. Jayaram, B.; Fine, R.; Sharp, K.; Honig, B. *J. Phys. Chem.* **1989**, *93*, 4320. Further results on comparison of continuum and molecular (statistical mechanical) calculations of solvation energies are given in: Jean-Charles, A.; Nocholls, A.; Sharp, K.; Honig, B.; Tempezyk, A.; Hendrickson, T. F.; Still, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 1454.
(19) In this context, an interesting description of some experiments is given by: Krishtalik, L. I.; Alpatova, N. M.; Ovsyannikova, E. V. *Electrochim. Acta* **1991**, *36*, 435.
(20) Chandler, D. Private communication.
(21) A discussion of the effect of approximatelty including the electronic polarizability (via mean field or via a classical oscillator) on dynamical and static properties is given in: Sprik, M., Klein, M. L., Watanabe, K. *J. Phys. Chem.* **1990**, *94*, 6483, and in references cited therein. Electronic polarizability has been included in molecular dynamics free energy simulations by: Straatsma, T. P.; McCammon, J. A. *Chem. Phys. Lett.* **1991**, *177*, 433.
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(23) For example, for weak ET's such a coordinate was introduced in: Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21, and an analogous coordinate was introduced in ref 13.

large, we would have for the rate constants k

$$k_{12} \simeq (k_{11}k_{22}K_{12})^{1/2} \tag{33}$$

upon neglecting the term quadratic in ΔG° in eq 31.

For weak-overlap electron transfers ($H_{rp} \simeq 0$), there is the well-known result that $h\nu_a^{max} \approx 4\Delta G^\ddagger$ when $\Delta G^\circ = 0$. For strong-overlap processes, eqs 29 and 31 lead instead to eq 34 when $\Delta G^\circ = 0$:

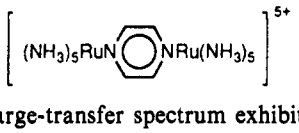
$$\frac{h\nu_a^{max}}{\Delta G^\ddagger} = 4\left[1 + \left(\frac{2H_{rp}}{\lambda}\right)^2\right] \Big/ \left(1 - \frac{4H_{rp}}{\lambda}\right) \tag{34}$$

Given suitable examples for the testing of such relationships and, thereby, the assumptions on which they are based, a principal role for theory then becomes one of calculating the reorganization parameter λ appearing in eqs 29 and 31, for example, by calculating $G(q)$ with the continuum model for the solvent as discussed earlier in this article, or, better still, by using a molecular model such as one which is computer-simulation based or employs a statistical mechanical approximation such as the mean spherical one. Until now, one method which has been used[24-26] to approximate λ for strong-overlap ET's is to assume that it equals the value for the corresponding weak-overlap ET, multiplied by a factor α^2

$$\alpha = H_{rp}/h\nu_a^{max} \tag{35}$$

α^2 representing in first-order perturbation theory the factor describing the reduction of charge on the donor center due to the strong electronic interaction of the charged centers. α has been estimated from the intensity of the charge-transfer spectrum, when the extra electron is not too delocalized.

The focus of the present paper has been on a formulation for treating solvent effects. A principal question is whether there is a body of experimental data on strong-overlap ET's with which such calculations can be compared. The most well-known strong-overlap ET system is the Creutz–Taube ion.[24,27]



However, its charge-transfer spectrum exhibits no solvent dependence. This ion is now accepted as having a highly delocalized electronic charge distribution.[28] Its H_{rp} is estimated to be very large (about 3300 cm^{-1}). It is perhaps also worth recalling here that a three-site model has been used recently for this very strong-overlap ET system, as being more appropriate than a two-site one, the third site being the pyrazine bridge.[29,30] Other examples with these very large H_{rp}'s are also available (~3500 cm^{-1}),[24,25] as are many with much smaller H_{rp}'s (e.g., 100–400 cm^{-1} usually),[24] the value of H_{rp} depending upon the metal atoms, the bridge, and the other ligands. The replacement of the $(NH_3)_5$ in the Creutz–Taube ion with the large $(bpy)_2Cl^-$, for example, serves to reduce H_{rp} to 400 cm^{-1},[24] by diluting the molecular orbital coefficient on the Ru and so reducing H_{rp}. An example of a system with an H_{rp} of 900 cm^{-1} is the Creutz–Taube ion with the $Ru(NH_3)_5$ replaced by $Fe(CN)_5$.

The study of the solvent dependence of the CT spectrum for systems of H_{rp} in an intermediate range would be of interest. Because of the bridges involved, a three-state or multistate model may be more appropriate than the two-state one just discussed. Nevertheless, it is possible that the results of the quantum and statistical mechanical calculations may still be fitted to equations such as 25 and 26.

Another class of systems involving a strong-overlap ET would be inner-sphere ET's where the bridging group is very small. However, the small distance between the redox centers in this case can imply that only a relatively small change occurs in the geometry of the charge distribution interacting with the solvent. The resultant relatively small solvent dependence of these electronic effects could be dominated by other solvent effects. Other strong-overlap ET's, such as those accompanied by bond dissociation and separation of the fragments, would have additional specific solvent effects which would tend to obscure the solvation effects considered in eq 5. Perhaps the most suitable systems for investigating solvent effects of the type discussed in ref 3 and here are charge-transfer spectra and intramolecular ET's, with a charge-separation distance which is not too small and where the value of H_{rp} is intermediate in value. Such systems are expected to be better regarded as three-site ones than as two-site, or, depending on the ligands, a four-or-more-site system.

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(27) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *94*, 1086.

(28) For example: Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Joss, S. *J. Am. Chem. Soc.* **1989**, *111*, 548.

(29) Ondrechen, M. J.; Ko, J.; Zhang, L.-T. *J. Phys. Chem.* **1989**, *93*, 3030, and references cited therein.

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