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On Quantum, Classical and Semiclassical Calculations of Electron Transfer Rates

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ABSTRACT

Similarities and differences between quantum, semiclassical and classical treatments of electron transfer reactions are described. All of these methods can be described as "vibrationally assisted electron-tunneling." A simple approximate expression is given for an infinite sum of Bessel functions which appears in the nonadiabatic quantum description. The condition of its validity is also obtained. The expression has been tested for some systems when the frequencies contain those in the range of the usual metal - ligand frequencies ($\sim$450 cm^{-1}) and of the low frequencies of the environment.

The nonadiabatic classical expression provides a useful lower bound, because it has no nuclear tunneling, to the nonadiabatic quantum result. The quantum correction is calculated for some actual systems. The "semiclassical" approximation is sometimes larger and sometimes smaller (in the "normal" and "inverted" regions, respectively) than the quantum result. This behavior is readily understood in terms of WKB theory.

The quantum correction to the classical cross-relation of rate constants was calculated for a case of interest and found to be minor. A symmetric form of ($\ln k_r$, ΔG^0) plots is described, even for the usually skewed quantum plots.

INTRODUCTION

During an electron transfer reaction there can be a readjustment of bond lengths and angles of the reactants and of reorientational and other structural changes in the surrounding polar environment, both before and after the electron transfer act. In many compounds, such as $Ru(NH_3)_6^{+2,+3}$, $Ru(bpy)_3^{+2,+3}$ (bpy = bipyridyl), and $MnO_4^{-1,-2}$, the change in bond lengths appears to be very small, the change then being largely in the orientations of molecules in the surrounding environment.[1] Typically, one expects a similar situation for other metal-ligand complexes, having phenanthrolinone and bipyridyl ligands. In contrast, in ions such as $Fe(H_2O)_6^{+2,+3}$, as well as other aquo ions, appreciable changes in bond lengths can occur ($\sim$0.14 Å in the case cited), and so both the types of contributions (intramolecular vibrational and environmental) then contribute.

CLASSICAL EXPRESSION FOR RATE CONSTANT[2]

One commonly used theory of electron transfer treats the motion of the nuclei in a classical manner.[2] The reaction may be "adiabatic" or "nonadiabatic" and this aspect was treated via the Landau-Zener theory of curve crossing.[2d,2e,3] For a qualitative description of the phenomenon, use can be made of the profiles of potential energy plots in many-dimensional space, for the reactants plus environment (R) and for the products plus environment (P), such as those in Fig. 1 and, in the case of sufficiently highly exothermic reactions, those in Fig. 2.[2b] In Fig. 1 reaction occurs when the system initially on the lower R curve ends up on the lower P curve, either by surmounting the energy barrier in Fig. 1 or by a nuclear tunneling through it.

In Fig. 1 when the splitting of the R and P surfaces is large enough at the intersection of these surfaces, a system initially on the R surface tends to end up, in a motion from left to right, on the P surface, and the reaction is adiabatic. [The κ in Eq. (24) of ref. 2d is then unity.] In reactions where the splitting is small, a reacting system passing through the intersection region of Fig. 1 has little probability of ending up as products, κ is thereby small and the reaction is nonadiabatic (cf Eq. 25, ref. 2d; footnote 3, ref. 3).

In highly exothermic reactions such as those in Fig. 2, an increase in exothermicity, i.e., a vertical lowering of the P curve relative to the R one results in an

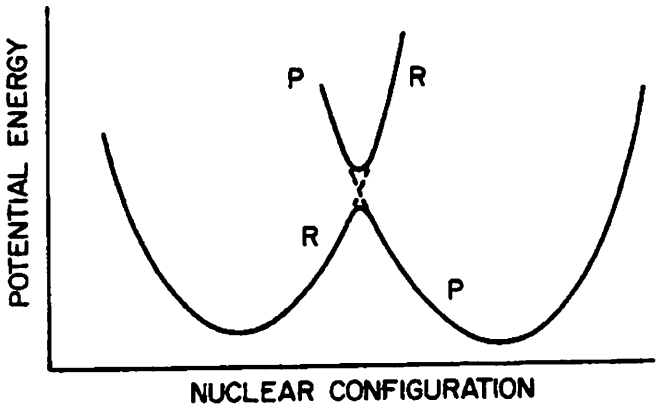

Fig. 1. Plot of profiles of potential energy surface of reactants (R) and products (P) in many-dimensional coordinate space.[2b,c]

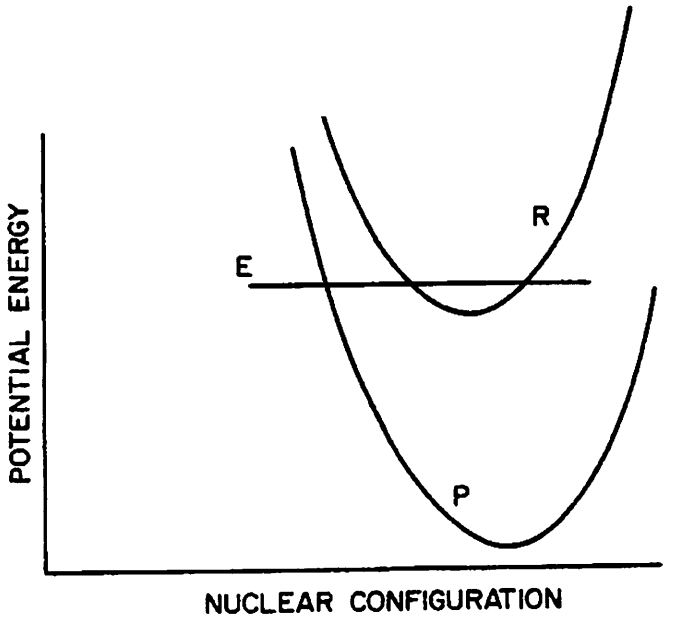

Fig. 2. Legend in Fig. 1 but for the "inverted" region.

intersection which occurs at a higher potential energy than before, and the reaction is then expected to be slower. This region was termed the "inverted" region[2b] and this phenomenon of decreased rate with increased exothermicity, at sufficiently high exothermicities, has its analog in radiationless transitions, in the form of the energy gap law.[4] It may have application to the back reaction in bacterial photosynthesis.[5b]

The form found for a first order rate constant k_r (reactants in fixed sites) at temperature T, is[2]

$$k_r = \kappa \nu \exp[-(\Delta G^0 + \lambda)^2/4\lambda\ kT], \tag{1}$$

where ΔG^0 is the standard free energy of reaction of that step, λ is a nuclear reorganization parameter and ν is a typical frequency for motion in this reaction across the transition state (i.e., across the intersection in Figs. 1 or 2) ($\sim 10^{13} s^{-1}$). For a bimolecular reaction between two species free to move in a solvent, the rate constant is given instead by[2]

$$k_r = \kappa Z \exp(-w^r/kT) \exp[-(\Delta G^0_R + \lambda)^2/4\lambda\ kT] \tag{2}$$

where Z is the collision frequency in solution ($\sim 10^{11}$ ℓ mole^{-1}s^{-1}). w^r is the work (both coulombic and noncoulombic) to bring the reactants from ∞ to a separation distance r, ΔG^0_R is $\Delta G^0 + w^p - w^r$, w^p being the work required to bring the products

from ∞ to r. λ is the sum of two terms, one due to the intramolecular changes (λ_i) and the other to changes in environment (λ_0):

$$\lambda = \lambda_i + \lambda_0 \tag{3}$$

Contributions to λ_i arise from changes in geometry and force constants. When λ_i is mainly due to changes in bond lengths Δq in the reacting species with a force constant k, λ_i is essentially[2]

$$\lambda_i = \frac{1}{2} \sum_j k_j \, (\Delta q_j)^2 \tag{4}$$

where the sum is over the vibrations of the reactants and where k_j is related to the k_j^r (reactants) and k_j^p (products) by being equal to $2\, k_j^r k_j^p / k_j^r + k_j^p)$.[2e] Using a general expression for Δ_0,[2e] one finds Eq. (5) for the case[2a] where the reactants are, in their polar interactions with the environment, treated as two spheres (radii a_1, a_2) separated by a distance r in a medium of static dielectric constant ε_s and optical dielectric constant ε_{op}. The reorganization described by λ_0 is that in the dielectric polarization of the environment.

$$\lambda_0 = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \tag{5}$$

where Δe is the charge transferred from one reactant to the other. Various tests of Eq. (5) have been described.[2,3,5] A significant contrast between (4) and (5) may be noted. Eq. (4) has a sum of terms, one set from one reactant and one set from the other. The 1/r term prevents such characterization in Eq. (5). Instead of the reorganization being the sum of that of the reactants it is the reorganization of the entire environment.

In the limit of a nonadiabatic reaction, use of the Landau-Zener formula for κ converts (1) to[3]

$$k_r = \frac{2\pi}{\hbar} \, \varepsilon^2 \, \frac{1}{(4\pi\lambda \, kT)^{1/2}} \exp[(\Delta G^0 + \lambda)^2 / 4\lambda \, kT] \tag{6}$$

where ε is the electron transfer integral. Similarly the κ in (2) is found to be replaced by $(2\pi\varepsilon^2/\hbar\nu)/(4\pi\lambda \, kT)^{1/2}$.

The dependence of rate on separation distance r occurs via the 1/r term in (5), the w^r and w^p terms in (2) and, in the nonadiabatic case, the ε term in (6). The decay of ε with r in (6) is exponential-like.

In the case of reactions at a metal-solution interface Eq. (2) is again obtained for the case where the reactant is not specifically bound to the interface, with Z now being the collision frequency of the reactant with unit area of the electrode, the $1/2a_2$ terms now being absent from (5), r being the distance of the reactant from its dielectric image (i.e., twice the reactant-interface separation

distance), and ΔG^0 now being replaced by $ne(E - E_0)$. E is the electrode-solution potential difference and E_0 is the "standard" potential for this half-cell (in the prevailing environment).[2]

Applications of these equations to various types of experimental data are described elsewhere.[2,3,5,6]

QUANTUM ASPECTS OF THE NUCLEAR MOTION

(a) Multiphonon Expression[6-8]

The quantum theory for the nuclear rearrangement in electron transfer reactions was introduced by Levich and Dogonadze,[6] who assumed the reaction to be a non-adiabatic one. Such an assumption permitted them to use Fermi's Golden Rule for a first-order rate constant for reactants in fixed sites:

$$k_r = \frac{2\pi\varepsilon^2}{\hbar} \sum_{i,f} |\langle\psi_f|\psi_i\rangle|^2 \delta(E_f - E_i)\rho_i, \tag{7}$$

where ρ_i is the Boltzmann population of systems in an initial vibrational state i. The ψ_i and ψ_f are the vibrational wave functions of the entire system in its reactants' and its products' form, respectively. δ is the Dirac delta function, which ensures energy conservation in the electron transfer reaction. E_i and E_f are initial and final energies.

Levich and Dogonadze treated the vibrations of the polar solvent as harmonic of a given frequency, omitting any damping and the intramolecular vibrations, and then evaluated the double sum. A similar sum occurs in optical transitions in solids,[9] and it was possible for these authors to make extensive use, they noted, of the techniques and results which had been obtained in these earlier solved spectral problems. The result for the first order rate constant was

$$k_r = \frac{2\pi\varepsilon^2}{\hbar} F(-\Delta G^0), \tag{8}$$

where $F(-\Delta G^0)$ is the Franck-Condon factor; it depends on $-\Delta G^0$, on the vibration frequency ν and on the temperature T:

$$F(-\Delta G^0) = \frac{1}{h\nu} I_p(x) \exp[-x \cosh\gamma - (\Delta G^0/2kT)] \tag{9}$$

$$x = (\lambda/h\nu)/\sinh\gamma,\ \gamma = h\nu/2kT,\ p = -\Delta G^0/h\nu \tag{10}$$

$I_p(x)$ is the modified Bessel function of order p and argument x. λ is given by (5). When the asymptotic expression for $I_p(x)$, $(1/2\,\pi x)^{1/2}\exp[x - (p^2/2x)]$,[6b] is introduced and when one lets $h\nu/2kT \to 0$, Eq. (8) reduces to its classical limit given by Eq. (6). To obtain Eq. (8) from Eq. (7), E_i was written as a vibrational energy $(n + \frac{1}{2})h\nu$, and E_f was written as a vibrational energy $(m + \frac{1}{2})h\nu$ plus ΔU^0, the potential energy difference between the minima of the R and P curves in Figs. 1 or 2. The resulting expression would violate microscopic reversibility when ΔU^0 is different from ΔG^0, and so we replaced the potential energy change of ref. 6 by ΔG^0. In this way, the correct classical limit, given by (6), is obtained.

This defect of multiphonon theory occurs when $\Delta U^0 \neq \Delta G^0$. It arises since the initial and final states of the environment were treated quantum mechanically in a simplified way which ignores any ΔS^0 of reorientational effects of the solvent molecules. ΔS^0 is large, for example, in the second reaction in Table I.

Table I. Comparison of Results for $Fe^{+2,+3}$ and $Fe^{+2} - Ru(bpy)_3^{+3}$

Reaction	F(Exact)	F(Eq. 19)	F(Class.)	F(Semiclass.)
Fe^{+2}-Fe^{+3}	3.14[a]	3.14	0.94	47.8
Fe^{+2}-$Ru(bpy)_3^{+3}$	1.85[b]	1.84	1.16	2.61

[a] All results in this row were multiplied by 10^{12}.

[b] All results in this row were multiplied by 10^4.

Eqs. (8)-(10) assume there is only one frequency, and so apply either when there is a Δq or a change in dielectric polarization (subject to the caveat noted earlier) but not both. The treatment leading to (8)-(10) was extended by several groups to include both intramolecular vibrations and environmental changes.[7,8] In some treatments the infinite sums (or the integrals) were evaluated by a saddle point (Gaussian) method,[7] while in other cases the sum was evaluated numerically.[8] We describe this case where there are two or more frequencies next.

When there are two vibration frequencies the initial wave function ψ_i can be written as a product, $\psi^i_{n_1}\psi^i_{n_2}$, for states n_1 and n_2 of the two vibrations. Similarly, ψ_f can be written as $\psi^f_{m_1}\psi^f_{m_2}$. The ρ_i becomes $\rho^i_{n_1}\rho^i_{n_2}$, and so Eq. (7) becomes

$$k_i = \frac{2\pi\varepsilon^2}{\hbar} \sum_{m_1} \sum_{n_1} \sum_{m_2} \sum_{n_2} |\langle\psi^f_{m_1}|\psi^i_{n_1}\rangle|^2 |\langle\psi^f_{m_2}|\psi^i_{n_2}\rangle|^2 \tag{10'}$$

$$\delta\,(E^f_{m_1} - E^i_{n_1} + E^f_{m_2} - E^i_{n_2} + \Delta G^0)\rho_{n_1}\rho_{n_2} \ ,$$

where the E^f_m's and E^i_n's now denote vibrational and/or solvent polarization energy. The distribution of final states in (7) and (10) is continuous. Introducing a δ-function $\delta(E^f_{m_1} - E^i_{n_1} - y)$,

$$1 = \int_{-\infty}^{\infty} \delta\,(E^f_{m_1} - E^i_{n_1} - y)dy$$

and correspondingly replacing the $E^f_{m_1} - E^i_{n_1}$ in (10) by y leads to a convolution expression:

$$k_r = \frac{2\pi\varepsilon^2}{h} \int_{-\infty}^{\infty} F_1(-\Delta G^0 - y)F_2(y)dy \tag{11}$$

When changes in frequency and anharmonicities are minor, $F_1(-\Delta G^0 - y)$ and $F_2(y)$ are given by (9), with $-\Delta G^0$, λ and ν replaced by $-\Delta G^0-y$, λ_1 and ν_1 and by y, λ_2 and ν_2, respectively. Here, λ_k (k = 1,2) is the λ given by (4) for intramolecular vibrations or by (5) (or some analogous expression for different geometries) for environmental dielectric polarization changes. Remembering that in Eq. (10') the distribution of final states is assumed to form a continuum, the integral over y will be replaced by a sum over p (p = y/hν), where ν is some appropriate frequency, e.g., ν_1 or ν_2.

$$k_r = \frac{2\pi\varepsilon^2}{\hbar} \frac{1}{h\nu} \sum_{-\infty}^{\infty} F_1(-\Delta G^0 - ph\nu)F_2(ph\nu) \tag{12}$$

Similarly, for three different frequencies, one would obtain a convolution with the third Franck-Condon factor:

$$k_r = \frac{2\pi\varepsilon^2}{\hbar} \frac{1}{h\nu} \sum_{p=-\infty}^{\infty} \sum_{s=-\infty}^{\infty} F_1(-\Delta G^0 - ph\nu)F_2(ph\nu - sh\nu)F_3(sh\nu) \tag{13}$$

and so on, for higher numbers of different frequencies. These sums are readily calculated on the computer, including those where frequency shifts and anharmonicities may also occur.

Once again when the asymptotic expressions are introduced for F_1 and F_2, and γ_1 and γ_2 are made small, one again obtains a classical expression.

(b) Semiclassical Expression[10]

We consider first a one-dimensional case with a coordinate q. The $\delta(E_f - E_i)$ in (7) can be introduced into the integral $\langle\psi_f|\psi_i\rangle$, i.e., into $\int\psi_f^*\psi_i dq$. When the commutator of the initial and final Hamiltonians H_f and H_i is neglected this $\delta(E_f - E_i)$ becomes $\delta(H_f - H_i)$, which in turn is $\delta(V_f - V_i)$ since the kinetic energy terms in $H_f - H_i$ cancel. V_f and V_i are the potential energies of the products P and reactants R, respectively, in Figs. 1 and 2. One can now write $\Sigma_f|f\rangle\langle f|$ as unity and note that in the integral which remains,[11,12]

$$\int \psi_i^*(q)\delta(V_f - V_i)\psi_i(q)dq,$$

the presence of the delta function requires that $\psi_i(q)$ be replaced by its value at the intersection point of the two curves in Fig. 1 (or in Fig. 2). One can then readily evaluate the sum in Eq. (7) and find (and again replacing ΔU^0 by ΔG^0 to avoid breakdown of microscopic reversibility when $\Delta S^0 \neq 0$),

$$k_r = \frac{2\pi\varepsilon^2}{\hbar} F_{sc}(-\Delta G^0) \tag{14}$$

where the semiclassical Franck-Condon term $F_{sc}(-\Delta G^0)$ is

$$F_{sc}(-\Delta G^0) = \frac{1}{(2\pi\lambda h\nu \coth\gamma)^{1/2}} \exp\left[-\frac{(\Delta G^0+\lambda)^2}{2\lambda h\nu \coth\gamma}\right] \tag{15}$$

Here, λ is given by (4) for intramolecular changes or by (5) for changes in dielectric polarization. Eq. (15) was obtained by Hopfield for intramolecular changes (with ΔG^0 replaced by ΔU^0).[10] When there are two frequencies one may again use (10') and hence (12) and (13). The convolution of two Gaussians is a Gaussian, and one again obtains (15) but with (in the case of two or more frequencies) $\lambda h\nu \coth\gamma$ and λ replaced by $\Sigma_i \lambda_i h\nu_i \coth\gamma_i$, and $\Sigma_i \lambda_i$, respectively.[10] When compared with the exact result, we found the semiclassical results to be sometimes too high (low exothermicities) and sometimes too low (quite high exothermicities). The results and the origin of these discrepancies are described later.

(c) A Simplified Multiphonon Expression

We have already noted that when ΔS^0 is quite different from zero, it is incorrect to use the multiphonon (or the semiclassical) theory to treat the relevant reorganizational changes. When the ΔS^0 arises largely from the environmental changes, as it frequently does, one can use, instead, the classical expression derived earlier for those changes and use a quantum treatment for the intramolecular vib-

rations. For example, the classical value of $F_2(ph\nu)$ is the coefficient of $2\pi\varepsilon^2/\hbar$ in (6), with $\Delta G^0 + \lambda$ replaced by $-ph\nu + \lambda_0$. Eq. (12) then yields (16), on choosing ν to be ν_1 and denoting it by ν_i, the intramolecular vibration frequency,

$$k_r = \frac{2\pi\varepsilon^2}{\hbar} \sum_{p=-\infty}^{\infty} F_1(-\Delta G^0 - ph\nu_i) \frac{1}{(4\pi\lambda_0 kT)^{1/2}}$$

$$\chi \exp[-(ph\nu_i - \lambda_0)^2/4\lambda_0 kT] \tag{16}$$

where

$$F_1(-\Delta G^0 - ph\nu_i) = I_{p-p}(\lambda_i/h\nu_i \sinh \gamma_i)$$

$$\chi \exp[(\{-\Delta G^0 - ph\nu_i\}/2kT) - (\lambda_i/h\nu_i)\coth \gamma_i] \tag{17}$$

and

$$p = (-\Delta G^0/h\nu_i) \tag{18}$$

where λ_i is given by (4).

Typically, an intramolecular vibration whose equilibrium position changes only relatively slightly (rather than becoming, say, a free rotation) contributes negligibly to ΔS^0, and in fact makes a zero contribution when ν_i for reactants and that for products are the same.

The sum in (16) can readily be calculated on a computer. An approximate value for it can be obtained[13] by rewriting the Gaussian function in the form of the asymptotic expansion of a Bessel function of order p and then using the addition theorem[14] for modified Bessel functions. One finds

$$k_r = \frac{2\pi\varepsilon^2}{\hbar h\nu_i} I_p\left(\frac{\lambda_i}{h\nu_i \sinh\gamma_i} + \frac{\lambda_0}{h\nu_i\gamma_i}\right) \exp\left[(-\Delta G^0/2kT) - \right.$$

$$\left. (\lambda_i/h\nu_i)\coth\gamma_i - \frac{\lambda_0}{h\nu_i\gamma_i}\left(1 + \frac{\gamma_i^2}{2}\right)\right] \tag{19}$$

When λ_i is small, Eq. (19) reduces to (6).

The approximation in (19) was in replacing an "asymptotic expansion" by $I_p(x)$ for the case that $x = \lambda_0/h\nu_i\gamma_i$. (No asymptotic expansion was made for the I_{p-p} in Eq. (17)). When the most important p's in the sum are around p = 0, this asymptotic expansion is good even at $x \sim 1$. However, larger x's are needed for larger $|p|$'s. For example, for a p = 6 and x = 4 the error of the asymptotic expansion is 20%. The value of p for the maximum term in (16) is roughly estimated (using an asymptotic expansion for I_{p-p}) to be

$$p_{max} \tilde{=} P/[1 + (\lambda_i/\lambda_0)\ (\sinh\gamma_i/\gamma_i)] \qquad (20)$$

(The equation is only as accurate as the asymptotic expansion of I_{p-p}.) Thus, when $\lambda_0 \sim \gamma_i$ and $\sinh \gamma_i \sim \gamma_i$, $p^{max} \tilde{=} P/2$, i.e., half of the exothermicity then goes into excitation of the intramolecular vibrations and half into environmental dielectric polarization changes, as expected.

The condition for validity of (19) is that p_{max} be less than, or at least not much greater than, the argument of $I_p(\lambda_0/h\nu_i\gamma_i)$, i.e.

$$p_{max} \lesssim \lambda_0/h\nu_i\gamma_i \qquad (21)$$

where p_{max} is given by (20).

An analogous equation can be derived for the case where both coordinates are treated in a quantum manner, but the results are omitted here for brevity.[13]

SUMMARY OF NUMERICAL RESULTS

A comparison of the various approximations with the exact result for the values of the parameters below is given in Table I for two actual systems. The λ's were taken from Ref. 1. The $\lambda_i/4$ and $\lambda_0/4$ in Ref. 1 for $Fe^{+2,+3}$ were 8.4 and 6.4 kcal mol^{-1}, respectively, and for $Ru(bpy)_3^{+2,+3}$ ca 0 and 3.2. The $\lambda_i/4$ and $\lambda_0/4$ for the Fe^{+2} - $Ru(bpy)_3^{+3}$ were then estimated from the additivity rule[2] to be 4.2 and 4.8, respectively. The frequency ν_i was estimated to be 435 cm^{-1} from the ν_i's for reactants and products used in ref. 1, on employing the rule[2] for effective force constant $k_i \tilde{=} 2k_i^r k_i^p/(k_i^r + k_i^p)$.

Results are given for various other values of the parameters in Table II. The γ_i of 1.044 was chosen to correspond to the intramolecular frequency of 435 cm^{-1} and a temperature of 300° K. From the perspective of electron transfer rates in solution where one is trying to understand reaction rates which can differ by twelve orders of magnitude at room temperature, the quantum corrections factors of 3 and 1.5 in Table I are minor.[15] More importantly, the effect on the classical cross-relation[2] is also small. In this relation, the rate constant k_{12} of

$$A_1(ox) + A_2(red) \longrightarrow A_1(red) + A_2(ox) \qquad (22)$$

is related to those (k_{11},k_{22}) of the self-exchange reactions

$$A_1(ox) + A_1(red) \longrightarrow A_1(red) + A_1(ox) \qquad (23)$$

Table II. Results for Various λ's and ΔG^0's ($\gamma_i = 1.044$)[a]

$\frac{-\Delta G^0}{h\nu_0}$	$\frac{\lambda_i}{h\nu_i}$	$\frac{\lambda_0}{h\nu_i}$	Exact	Eq. (19)	Class.	Semiclass.
0	13.5	15.4	3.95	3.96	2.13	15.6
0	23.8	5.1	6.35	6.36	2.13	50.8
0	27.0	20.6	3.14	3.14	0.94	47.8
10	13.5	15.4	1.85	1.84	1.16	2.61
10	13.5	5.1	1.57	1.57	1.19	1.60
10	3	3	4.51	7.30	4.14	4.68
15	3	3	8.06	40.0	1.45	3.72
20	3	3	1.90	46.3	$6.5\ 10^{-3}$	$7.2\ 10^{-2}$

[a]In the third and fourth rows, the λ's used are actually 27.0337 and 20.5971 (row 3) and 13.5168 and 15.4478 (row 4). The results for rows 1 to 8 should be multiplied by 10^{-8}, 10^{-8}, 10^{-12}, 10^{-4}, 10^{-2}, 10^{-2}, 10^{-4}, and 10^{-6}, respectively.

$$A_2(ox) + A_2(red) \longrightarrow A_2(red) + A_2(ox) \tag{24}$$

via[2]

$$k_{12} \cong (k_{11}k_{22}K_{12}f_{12})^{1/2}, \tag{25}$$

where K_{12} is the equilibrium constant of reaction (22) and f_{12} is a known function of k_{11}, k_{22}, and K_{12}. From the results of Table I, one can see that the quantum effect is found to be only a factor of $1.5/\sqrt{3}$, i.e., about unity.

Eq. (19) is seen in Table II to be very accurate in the region for which Eq. (21) is fulfilled. The beginnings of breakdown when Eq. (21) is no longer fulfilled are seen in row 6 of Table II, and the breakdown continues with increasing P in rows 7 and 8, as anticipated.

The breakdown of the semiclassical approximation, Eq. (15), has been pointed out previously[8d] for P = 0, i.e., for $-\Delta G^0 = 0$, a breakdown also seen in Tables I and II. The discrepancy is less at small enough $\lambda_i/h\nu_i$ (in results not shown here). The semiclassical approximation (15) first improves with increasing P, i.e., with increasingly negative $-\Delta G^0$, as seen in a comparison of the first and fourth rows in Table II. However, when P becomes quite large the semiclassical approximation again breaks down, as in the last row of Table II and in other results.

The reasons for this behavior are considered next. In the "normal case," represented by Fig. 1, the square of the overlap of the vibrational wave functions ψ_i and ψ_f for an energy below that of the intersection of the R and P curves, is represented in WKB theory[16] for the wave functions approximately by a nuclear tunneling factor

$$T_{i\to f} \tilde{=} e^{-2\int_a^c \frac{|p_i|dq}{\hbar}} e^{-2\int_c^b \frac{|p_f|dq}{\hbar}} \qquad (22)$$

Here, a and b are two classical turning points of the motions on the R and P curves at this energy (Fig. 3) and the intersection occurs at q = c; p_i and p_f are the (imaginary) momenta, calculated as a function of the coordinate q for the given total energy and for vibrational potential energies V_i and V_f. Instead of (22), one calculates in the semiclassical method $|\psi_i|^2$ at q = c, and so instead of (22) one has

$$T_{i\to f}^{SC} \tilde{=} e^{-2\int_a^c |p_i|\frac{dq}{\hbar}} . \qquad (23)$$

Clearly (23) can be much larger than (22), because the second factor in (22) is now missing, and so result in a considerable error when c and b are far apart. I.e., here the "semiclassical" approximation given by (23) and hence by (15) yields too high a result - too much nuclear tunneling. This effect is the greater the greater the relevant barrier for tunneling, $\lambda_i/4$ for P = 0, in Fig. 3.

In the case of Fig. 4, replacing the vibrational wave functions by their WKB counterparts and evaluating the overlap integral by contour integration yields[17]

$$T_{i\to f} \tilde{=} e^{\frac{-2}{\hbar}\left(\int_c^a |p_i|dq - \int_c^b |p_f|dq\right)} \qquad (24)$$

Instead, in the "semiclassical" approach in (15) one evaluates $|\psi_i|^2$ at the intersection q = c. Thereby, the semiclassical value of $T_{i\to f}$ is, instead of (24),

$$T_{i\to f}^{SC} \tilde{=} e^{\frac{-2}{\hbar}\int_c^a |p_i|dq} \qquad (25)$$

This resulting tunneling rate predicted by (25) and hence by (15) is now too small because of the absence of the second term in the exponent of (24). The ensuing breakdown is seen in the last row of Table II. If the P curve were almost vertical near the intersection, the integral over $|p_f|$ in (22) and (24) from c to b would be negligible and so the two results would then again agree.

In summary, when nuclear tunneling occurs in the exact results the semiclassical equation (15) can only be relied upon when the P curve in Figs. 3 and 4 intersects the R curve sufficiently steeply. Otherwise, it predicts too much tunneling at low $|\Delta G^0|$'s and too little tunneling at moderate to high $|\Delta G^0|$'s. When nuclear tunneling is unimportant, the classical expression can be used instead.

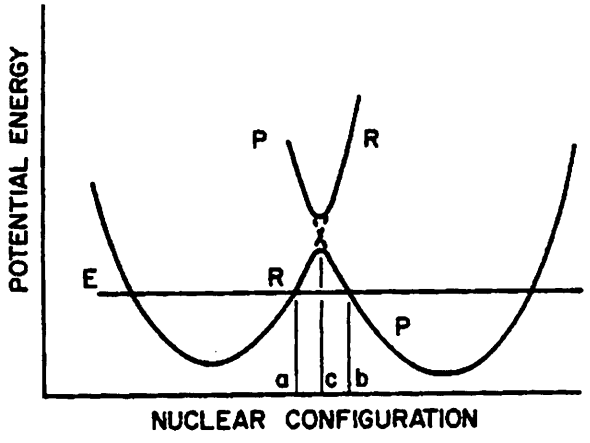

Fig. 3. Projection of Fig. 1 onto the V versus vibrational coordinate plane. Two of the classical turning-points of motion at a given vibrational energy E are labeled a and b.

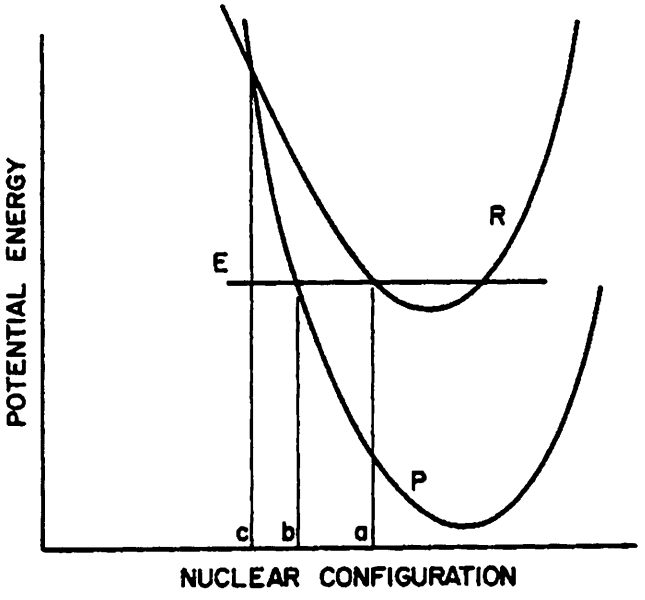

Fig. 4. Legend as in Fig. 3, but for the "inverted region."

Under the condition given by (21), Eq. (19) is a useful approximation when a simple expression is desired.

In the present paper attention has been focussed on quantum effects, using a nonadiabatic formulation. A discussion of other data is given elsewhere[2,3,5,6] (cf Ref. 18 for a recent reevaluation of some biological data). By evaluating the κ in Ref. 2 in a way which includes nuclear tunneling, one can treat both the

nonadiabatic and adiabatic limits. (Use is made of the present equations (22) and (24).) The treatment of the intermediate ("partially nonadiabatic") case is readily given for the "normal region" (Fig. 3), but in the inverted region only numerical results are presently available.[19]

One final topic which will be considered here is the question of ln k_r versus ΔG^0 plots. These plots are highly symmetrical (parabolic) in the classical or semiclassical approximation but are highly skewed[6-8] when quantum effects become important. However, the result can be replotted in a different way which once again restores their symmetry. In the quantum approximation the rate constant is given by Eq. (26) which we shall write as

$$k_r(\Delta G^0) = \frac{2\pi\varepsilon^2}{\hbar} F(-\Delta G^0) \tag{26}$$

We now consider a reaction which, instead of being thermoneutral or downhill, is uphill, with a free energy of reaction ΔG_2^0. For the rate constant k_r' for the reverse of this new reaction we have

$$k_r'(\Delta G_2^0) = \frac{2\pi\varepsilon^2}{\hbar} F(-\Delta G_2^0) \tag{27}$$

when $\Delta G_2^0 = -\Delta G^0$ the Franck-Condon factor $F(-\Delta G_2^0)$ equals that in $F(-\Delta G^0)$, as one can see by a term-by-term comparison. The forward rate constant k_r is obtained from k_r' by the equilibrium constant, whence

$$k_r(\Delta G_2^0) = \frac{2\pi\varepsilon^2}{\hbar} F(-\Delta G_2^0) e^{-\Delta G_2^0/kT} \tag{28}$$

Thus, for this case of $\Delta G_2^0 = -\Delta G^0$ we have, since $F(-\Delta G_2^0) = F(-\Delta G^0)$,

$$k_r(-\Delta G^0) = \frac{2\pi\varepsilon^2}{\hbar} F(-\Delta G) e^{\Delta G^0/kT} \quad . \tag{29}$$

Comparing (26) and (29) we see that

$$k_r(-\Delta G^0) e^{-\Delta G^0/2kT} = k_r(\Delta G^0) e^{\Delta G^0/2kT} \tag{30}$$

Thus a plot of $\ln(k_r \exp \Delta G^0/2kT)$ is a symmetric function of ΔG^0.

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DISCUSSION

SOLOMON: What are the important normal modes which must be considered for the biological electron transfer proteins in the configurational coordination diagram you present. As the different possibilities might have very different vibrational frequencies, could a reasonable assignment be reached through an experiment sensitive to tw, for example, a temperature dependence?

MARCUS: The most important modes depend upon the specific electron transfer reaction. In some reactions, such as those between metal-phenanthrolines involving metal bipyridyl complexes, the important modes appear to be those of the dielectric polarization in the environment outside the complex ions. In other reactions such as those involving iron acquo ions, both metal ligand modes and environmental modes contribute roughly equal amounts. In the case of the cytochrome c - cytochrome a reaction, the answer is not yet known but may involve environmental modes and, perhaps, a metal-axial ligand stretching mode (depending upon how much the metal-axial ligand bond length changes upon change of redox state. When one can measure the rate constant k_r at sufficiently low temperatures T so that the $\ln k_r$ vs 1/T plot becomes curved (and eventually flat at low enough T), the temperature where the curvature sets in is related to the characteristic frequency of the predominant vibrational reaction mode. At least it does when the curvature is not due to some new mechanism occurring, of course.

JORTNER: You have discussed the electronic coupling responsible for electron transfer in terms of a tunneling formula which contains the electron mass in the exponential. The low temperature tunneling in the electron transfer processes involves tunneling between nuclear potential surfaces. This can be nicely demonstrated by showing that for exothermic processes, the nuclear Franck-Condon vibrational overlap, which determines the rate, can be recast in the form of the Gamov tunnelling formula. The concept of nuclear tunnelling prevails not only for electron transfer but also for group transfer, such as the low temperature recombination of CO with hemoglobin. Thus a variety of processes can be described from a unified point of view. I would recommend to retain the notion of "tunnelling" for the nuclear part as here it is an experimentally meaningful concept.

MARCUS: On the nonadiabatic theory for electron transfer rates, an overlap integral for the vibrational wave function occurs (the Franck-Condon factor), as does an electronic matrix element ε. When WKB theory is used for the vibrational wave functions, the nuclear overlap integral becomes equivalent to a nuclear-

tunnelling formula, as in my paper, when the vibrational energy is below the energy of the intersection (Figures 3, 4). While it is best to evaluate the electronic matrix element ε with the full electronic wave functions and Hamiltonian as I argued much as you do many years ago, one can obtain a rough estimate for it by approximating the Hamiltonian, yielding an overlap integral of electronic wave functions. Use of WKB theory for the latter then yields an electron-tunnelling expression analogous to Hopfield's and serves to relate ε to the earlier calculation by Chance and DeVault.

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