

Nonadiabatic processes involving quantum-like and classical-like coordinates with applications to nonadiabatic electron transfers

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Nonadiabatic processes may involve both classical-like and quantum-like coordinates. A semiclassical analysis is used to treat the contribution of the former to the Franck–Condon factor in the reaction rate expression, thereby avoiding the usual harmonic oscillator approximation. Microcanonical and canonical rate constants are calculated, yielding an expression which includes contributions from both types of coordinates. The results are applied to nonadiabatic electron transfer reactions in solution, and show how ΔG^0 enters the final rate expression, even though ΔE^0 is present in the initial Golden Rule nonadiabatic formula. This result avoids an approximation which has arisen in the nonadiabatic electron transfer literature.

I. INTRODUCTION

In nonadiabatic processes, some of the degrees of freedom may be treated as largely classical, and for them it is useful to simplify the usual Golden Rule expression for the transition rate of the process. One such example occurs in nonadiabatic electron transfer reactions in solution. In electron transfer reactions the many orientational coordinates of the solvent molecules are typically classical-like and play an important role in electron transfer reactions,^{1–3} considerably influencing their rate.

One purpose of the present paper is to provide insight and justification for a physically reasonable but somewhat *ad hoc* procedure which has sometimes been used for nonadiabatic electron transfers.^{4–6} In that procedure the quantum Franck–Condon overlap factors for some coordinates are combined with a classical treatment^{2,3} for the rearrangement of the remaining coordinates, typically the orientational coordinates of the solvent molecules.

In the final theoretical expression for the reaction rate, sometimes ΔG^0 but more frequently (e.g., Refs. 7–11) ΔE^0 is written, where ΔG^0 is the standard free energy of reaction. ΔE^0 is the standard energy change of reaction, which occurs in the Golden Rule expression for nonadiabatic processes. The appearance of ΔE^0 , instead of ΔG^0 , in the relevant final equations will result from using in such expressions a harmonic oscillator approximation for all the classical-like coordinates. For harmonic oscillators having the same frequencies for reactants as for products, ΔS^0 vanishes and so ΔE^0 and ΔG^0 become equal.¹² For reactions in solution, however, the harmonic oscillator model is inadequate for treating the orientations of the solvent molecules. There can be very large entropic changes accompanying reaction, for example. This approximation is avoided in the present paper by the use of semiclassical theory and generalized (curvilinear) coordinates.

In simplifying the nonadiabatic expression we retain that part of the Franck–Condon factor which relates to any highly quantized degrees of freedom and only use semiclassical theory to convert the remaining part to a classical version. The final result also provides a simple extension of an expression used for “surface hopping”¹³ between two elec-

tronic surfaces via classical trajectories, by allowing some coordinates to be treated purely quantum-like.

II. THEORY

The Golden Rule expression for the unimolecular rate constant $k_{\alpha\beta}$ for a nonadiabatic transition $\alpha i \rightarrow \beta f$ from electronic state α to electronic state β and from a quantum state i of the nuclear motion on surface α to a state f on surface β is

$$k_{\alpha\beta} = \frac{2\pi V^2}{\hbar} |\langle \varphi_f | \varphi_i \rangle|^2 \delta(E_f - E_i + \Delta E^0), \quad (1)$$

where V is the electronic matrix element for the transition (the Condon approximation is made), f denotes the set of quantum numbers ($f_1 \dots f_M$) for the nuclear motion in electronic state β (M coordinates), i denotes those ($i_1 \dots i_M$) for that motion in electronic state α , E_f and E_i are the corresponding energies, in excess of the zero-point energy of the β state and of the α state, respectively, and ΔE^0 is the standard energy of the reaction for process $\alpha \rightarrow \beta$ at 0 K. Equation (1) has been extensively used in the nonadiabatic electron transfer literature, e.g., Refs. 4–10. In that case, α and β denote electronic states of the reactants and of the products, respectively.

We shall suppose that of the M degrees of freedom the first N are classical-like and write

$$\varphi_i = \psi_i \chi_I, \quad \varphi_f = \psi_f \chi_F, \quad (2)$$

where φ_i refers to $i = 1, \dots, N$, χ_I to $I = i = N + 1, \dots, M$, and ψ_f and χ_F to $f = 1, \dots, N$ and $F = f = N + 1, \dots, M$, respectively.

It is convenient to denote that part of the energies E_i and E_f in Eq. (1) associated with the N classical-like coordinates by ϵ_i and ϵ_f and the part associated with the remaining coordinates by E_I and E_F , respectively. We define ΔE_{IF}^0 as the effective ΔE^0 for a transition $\alpha I \rightarrow \beta F$:

$$\Delta E_{IF}^0 = \Delta E^0 + E_F - E_I. \quad (3)$$

Equation (1) now becomes

$$k_{\alpha\beta} = \frac{2\pi V^2}{\hbar} |\langle F | I \rangle|^2 |\langle f | i \rangle|^2 \delta(\epsilon_f - \epsilon_i + \Delta E_{IF}^0). \quad (4)$$

If all the modes of motion were rotational, rather than some being oscillatory, the “primitive” semiclassical wave function ψ_i would be a single term. When some or all of the

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modes of motion are oscillatory the phase of the semiclassical wave function has more than one branch, each branch corresponding to a particular set of signs for the N momenta ($p_1 \dots p_N$). The normalized wave function ψ_i can then be written as the sum in Eq. (5), using a Van Vleck determinant^{14,15} for each term:

$$\psi_i = \sum a^{-1/2} \left| \frac{\partial^2 S_i}{\partial q \partial i} \right|^{1/2} \frac{e^{iS_i/\hbar}}{h^{N/2}}, \quad (5)$$

where the sum is over the various branches of S_i and would contain 2^N terms if all modes of motion were oscillatory, S_i is the phase integral $\sum_k \int p_k dq_k$, taken from some turning point where all the p_k 's vanish, plus various multiples of $\pi/4$, depending on the particular oscillatory branch, e.g., Refs. 14b, 14d, 14f, and a is a determinant of coefficients in the elementary distance expression (Appendix A). $\partial^2 S_i / \partial q \partial i$ denotes an $N \times N$ determinant having elements $\partial^2 S_i / \partial q_j \partial i_k$:

$$|\partial^2 S_i / \partial q \partial i| \equiv \det \partial^2 S_i / \partial q_k \partial i_j. \quad (6)$$

We use this shorthand notation for determinants throughout, as well as an analogous one for differentials and for sets of variables:

$$du \equiv du_1 \dots du_N, \quad u \equiv (u_1 \dots u_N). \quad (7)$$

The normalization factor in Eq. (5) can be verified by first noting that in the product $\psi_i^* \psi_j$ any highly oscillatory terms can be neglected. Only terms in which S_i and S_j are of the same branch then remain. We obtain

$$\begin{aligned} \langle i' | i \rangle &= \int \dots \int \psi_i^* \psi_i \sqrt{adq} \\ &= \sum \int \exp \left[\sum_k (\partial S_i / \partial i_k) (i_k' - i_k) / \hbar \right] d(\partial S_i / \partial i) / h^N, \end{aligned} \quad (8)$$

where the sum Σ is again over the branches of S_i and where we have used the shorthand notation (7). In Eq. (8) S_i in the exponent was expanded about S_i and $|\partial^2 S_i / \partial q \partial i| dq$ was replaced by its equivalent $d(\partial S_i / \partial i)$. Each $\partial S_i / \partial (i_k \hbar)$ is the angle variable conjugate to the classical action $i_k \hbar$ ¹⁶ and its individual domain is the unit interval. However, different branches in the sum correspond, for oscillatory modes of motion, to different parts of this unit domain. (For any rotational motion the single branch covers the whole unit interval.) Upon removing the sum sign in (8) before the integral we recognize the fact that each angle variable ranges, thereby, over its full (0,1) domain. The right-hand side of Eq. (8) then becomes, on integration, a product of Kronecker deltas $\delta_{i_1 i_1'} \dots \delta_{i_N i_N'}$. Thus, the semiclassical ψ_i given by Eq. (5) is properly normalized.

We consider next the Franck-Condon factor¹⁷ $\langle i' | f \rangle$ using Eq. (5) for ψ_i and an analogous expression for ψ_f . The integral over the coordinates q becomes

$$\langle i' | f \rangle = \sum \int \dots \int \left| \frac{\partial^2 S_i}{\partial q \partial i} \right|^{1/2} \left| \frac{\partial^2 S_f}{\partial q \partial f} \right|^{1/2} e^{i(S_f - S_i)/\hbar} \frac{dq}{h^N}, \quad (9)$$

and is evaluated, as is customary for semiclassical Franck-Condon factors, by the stationary phase method. The only terms retained in the sum are those where S_f and S_i belong to the same branch, the remaining terms being highly oscillatory. The stationary phase point is determined by

$$\frac{\partial}{\partial q_k} (S_f - S_i) = 0,$$

i.e.,

$$p_k^f = p_k^i (k = 1, \dots, N) \quad (10)$$

and we have

$$\begin{aligned} S_f - S_i &\cong S_f^0 - S_i^0 + \frac{1}{2} \sum_{k,j} \frac{\partial^2}{\partial q_k \partial q_j} \\ &\quad \times (S_f - S_i)(q_k - q_k^0)(q_j - q_j^0), \end{aligned} \quad (11)$$

where the various quantities on the right are evaluated at the stationary phase point $q = q^0$. Integration in Eq. (9) then yields

$$\begin{aligned} \langle i' | f \rangle &= \sum \left[\left| \frac{\partial^2 S_i}{\partial q \partial i} \right| \left| \frac{\partial^2 S_f}{\partial q \partial f} \right| \left| \frac{\partial^2 (S_f - S_i)}{\partial q^2} \right| \right]^{1/2} \\ &\quad \times e^{i(S_f^0 - S_i^0)/\hbar} / h^{N/2}. \end{aligned} \quad (12)$$

The stationary phase points (10) all occur at the same q , but with different combinations of signs of the p_k 's. If this q^0 is the only stationary phase point, the number of terms in the sum is the same as that in Eq. (5), one per branch of S_i . There may also be stationary phase points at other values of q , and if so they are then included in the sum.

Equation (12) can be simplified in a straightforward way to yield¹⁸

$$\langle i' | f \rangle = \sum \left| \frac{\partial p^i}{\partial i} \right|^{1/2} \left| \frac{\partial q}{\partial f} \right|^{1/2} \frac{e^{iW_f/\hbar}}{h^{N/2}}, \quad (13)$$

where W_f is the value of $S_f - S_i$ at the stationary phase point (10) and the sum is again over the branches of S_i .

From Eqs. (4) and (13) one obtains

$$k_{\alpha\beta} = \frac{2\pi V^2}{\hbar h^N} |\langle F | I \rangle|^2 \sum \left| \frac{\partial p^i}{\partial i} \right| \left| \frac{\partial q}{\partial f} \right| \delta(\epsilon_f - \epsilon_i + \Delta E_{IF}^0). \quad (14)$$

The rate constant for a process $\alpha I \rightarrow \beta F$, when the initial state of motion of the classical-like coordinates is described by $(i_1 \dots i_N)$, is found by integrating Eq. (14) over the f 's. In doing this we first introduce a coordinate system to simplify the resulting expression: The intersection of the two potential energy surfaces $U_\alpha(q)$ and $U_\beta(q)$ occurs where $U_\alpha(q) = U_\beta(q) + \Delta E_{IF}^0$ and defines an $N-1$ dimensional hypersurface in the N -dimensional coordinate space. We define a coordinate q_N which is constant on this hypersurface, and which takes on different values for other values of $U_\beta(q) - U_\alpha(q)$.

Equation (14) is next integrated over the (f_1, \dots, f_N) variables, noting that $|\partial q / \partial f| df$ equals dq . Further, each stationary phase point (10) occurs on the hypersurface just cited, and at that point $\epsilon_f - \epsilon_i$ equals $U_\beta - U_\alpha$, since $p_k^i = p_k^f$ there for all p_k 's. Thus, the $\delta(\epsilon_f - \epsilon_i - \Delta E_{IF}^0)$ in Eq. (14) can be replaced by $\delta(U_\beta - U_\alpha - \Delta E_{IF}^0)$. One can then write dq_N as $d(U_\beta - U_\alpha) / [\partial(U_\beta - U_\alpha) / \partial q_N]$ and define the absolute value S of this difference of slopes:

$$S = |\partial(U_\beta - U_\alpha) / \partial q_N|. \quad (15)$$

In integrating over the f 's in Eq. (14) one notes that $|\partial q / \partial f| df$ equals dq , then uses the $\delta(U_\beta - U_\alpha - \Delta E_{IF}^0)$ in the integration over $d(U_\beta - U_\alpha)$, and so obtains the rate constant for a state $(i_1 \dots i_N)$:^{2,19}

$$k(i_1 \dots i_N) = \frac{2\pi V^2}{\hbar} |\langle F|I \rangle|^2 \times \sum \int \dots \int \frac{\partial p^i}{\partial i} S^{-1} dq_1 \dots dq_{N-1} / h^N. \quad (16)$$

The microcanonical rate constant $k_{IF}(\epsilon)$ for a given transition $\alpha I \rightarrow \beta F$ is obtained by integrating $k(i_1 \dots i_N)$ over all i_k 's such that ϵ_i lies in a narrow interval $(\epsilon, \epsilon + d\epsilon)$ and then dividing by the number $\int \dots \int di_1 \dots di_N$ of states in this interval, i.e., by $\rho_\alpha d\epsilon$, where ρ_α is the density of states of the classical-like degrees of freedom in electronic state α . One next notes that $|\partial p^i / \partial i| di$ equals dp^i , and that when the space of numbers $(i_1 \dots i_N)$ is mapped onto the space of p_k^i 's the various signs of p_k^i 's, which created the various branches in the sum in Eq. (16), serve to map the i_k 's onto all of the relevant p^i space, and so the sum in Eq. (16) disappears. We then have

$$k_{IF}(\epsilon) = \frac{2\pi V^2 |\langle F|I \rangle|^2}{\hbar \rho_\alpha(\epsilon) d\epsilon \hbar^N} \int \dots \int S^{-1} dp_1 \dots dp_N dq_1 \dots dq_{N-1}. \quad (17)$$

The integration in Eq. (17) is restricted to the domain where $(q_1 \dots q_{N-1}, p_1 \dots p_N)$ lies within the energy shell $(\epsilon, \epsilon + d\epsilon)$, and so the integral is proportional to $d\epsilon$.

To obtain the rate constant at a given temperature $k_{IF}(T)$ for the $\alpha I \rightarrow \beta F$ transition, one multiplies Eq. (17) by $\rho_\alpha(\epsilon) \exp(-\epsilon/kT) d\epsilon / Q$, Q being the partition function for the N classical-like coordinates of the reactant, and extends the integration to all values of the $2N - 1$ variables:

$$k_{IF}(T) = \frac{2\pi V^2}{\hbar Q} |\langle F|I \rangle|^2 \int \dots \int \times e^{-\epsilon/kT} S^{-1} dp_1 \dots dp_N dq_1 \dots dq_{N-1}. \quad (18)$$

In passing we note that the stationary phase point for a transition $(i_1 \dots i_N) \rightarrow (f_1 \dots f_N)$ determines a point in the $2N$ -dimensional phase space. When the additional condition on the energy ϵ_f is imposed, via the delta function in Eq. (14), the $i \rightarrow f$ transition corresponds to a point in $2N-1$ dimensional phase space, a point in the domain in Eq. (17) and (18). The integration over this space corresponds to the integration over all i 's and f 's, subject to the one constraint imposed by a delta function.

Equation (18) is first integrated over the momenta. The kinetic energy in ϵ is written as $\frac{1}{2} \sum_{ij} g^{ij} p_i p_j$ and one obtains (Appendix A)

$$k_{IF}(T) = \frac{2\pi V^2}{\hbar} |\langle F|I \rangle|^2 \times \frac{\int \dots \int e^{-U_\alpha/kT} S^{-1} \sqrt{a} dq_1 \dots dq_{N-1}}{\int \dots \int e^{-U_\alpha/kT} \sqrt{a} dq_1 \dots dq_N}. \quad (19)$$

The overall rate constant $k(T)$ is obtained by multiplying Eq. (19) by the probability of finding the system in the state I and summing over all I 's and all F 's:

$$k(T) = \sum_{I,F} k_{IF}(T) e^{-E_I/kT} / Q_I, \quad (20)$$

where Q_I is the partition function $\sum_I \exp(-E_I/kT)$ of the

degrees of freedom associated with the quantum numbers I .

The $k(T)$ for the reverse reaction is obtained by interchanging (I, α) with (F, β) . One can verify that microscopic reversibility is obeyed by these two rate constants, upon noting that U_α equals $U_\beta + \Delta E_{IF}^0$. The ratio of the two rate constants is found to equal, as it should, $\exp(-\Delta E^0/kT)$ times the ratio of the appropriate partition functions.

In the case of an adiabatic reaction one obtains Eq. (19),²⁰ but with several differences [cf. Eqs. (33) and (34) of Ref. 20]: the S^{-1} is absent, the $N - 1$ dimensional surface element differs slightly from that element in Eq. (19), a consequence of the absence of a q_N term in Eq. (17), and a different factor precedes the integral.

To relate Eqs. (19) and (20) to an equation which has been used⁴⁻⁶ for treating nonadiabatic electron transfers when some of the degrees of freedom are treated quantum mechanically and some classically, two further steps will be used. We need to relate the integrals in Eq. (19) to a free energy of formation of a nonequilibrium polarization state^{2,3} appropriate to the transition state of the reaction, and require, thereby, the two integrals to have the same number of coordinates. This nonequilibrium state is one which is "centered"^{3,21} on the intersection hypersurface.

To relate these integrals to this free energy of formation, we first replace the S^{-1} by some average $\langle S^{-1} \rangle$ which we discuss later, and thus obtain an integral involving $\exp(-U_\alpha/kT) \sqrt{a} dq_1 \dots dq_{N-1}$. We next replace this surface distribution by an "equivalent equilibrium distribution",^{3,21} by multiplying by $\exp(-U_N/kT) dq_N$, integrating over q_N , and then dividing by a one-dimensional configuration partition function Q_N for this motion of q_N .²² Here, U_N is an effective potential energy function which vanishes on the intersection surface $U_\alpha = U_\beta + \Delta E_{IF}^0$, and which serves to convert the surface distribution to a volume distribution centered on the intersection surface, the "e.e.d." of Refs. 3 and 21. We now have

$$k_{IF}(T) = \frac{2\pi V^2}{\hbar} |\langle F|I \rangle|^2 \frac{\langle S^{-1} \rangle}{Q_N} \times \frac{\int \dots \int e^{-U_\alpha^*/kT} \sqrt{a} dq_1 \dots dq_N}{\int \dots \int e^{-U_\alpha/kT} \sqrt{a} dq_1 \dots dq_N}, \quad (21)$$

where

$$U_\alpha^* = U_\alpha + U_N. \quad (22)$$

The possibility of having a large entropy of activation for the reaction is allowed in Eqs. (19) or (21): In the transition state region, i.e., at the intersection of the U_α and $U_\beta + \Delta E_{IF}^0$ potential energy surfaces, the behavior of U_α can be very different from its behavior in the region appropriate to the reactants [denominators of Eqs. (19) or (21)]. For example, in an electron transfer reaction the ionic charges of the reactants differ from those of the products, resulting frequently in enormous changes in entropy of solvation. These changes are reflected in a difference in the behavior of U_α in the "reactants' region" of the N -dimensional coordinate space compared with the behavior of U_β in the "products' region". This difference is mirrored in the

behavior of U_α on the intersection hypersurface.

An expression derived for the ratio of integrals in Eq. (21), using a "dielectrically unsaturated" approximation for the response of the solvent outside the coordination shells of the reactants to changes in ionic charges, yielded²³

$$\frac{\int \dots \int e^{-U_\alpha^*/kT} \sqrt{ad} dq_1 \dots dq_N}{\int \dots \int e^{-U_\alpha/kT} \sqrt{ad} dq_1 \dots dq_N} = \exp \left[\frac{-\lambda_0}{4kT} \left(1 + \frac{\Delta G_{IF}^0}{\lambda_0} \right)^2 \right], \quad (23)$$

where λ_0 is a quantity in terms of the molecular properties. For example, if dielectric continuum theory is used it depends on the change in charges of the reactants, the ionic radii of separation distance between reactants, and the dielectric properties of the surrounding medium.²⁴ If any vibrations are included, in addition, in the classical-like coordinates ($q_1 \dots q_N$), λ_0 includes a contribution from them also and then depends also on the changes in the corresponding equilibrium bond lengths and on the vibration frequencies.²⁵ ΔG_{IF}^0 in Eq. (23) is $\Delta G^0 + E_F - E_I$. That is, it is the effective ΔG^0 when the system goes from state I of the quantum degrees of freedom of reactants to state F for those of the products.

We turn next to the remaining factor in Eq. (21) $\langle S^{-1} \rangle / Q_N$. We consider first a simple case, namely where U_α for each value of ($q_1 \dots q_{N-1}$) has a term $\frac{1}{2} k' (q_N - a)^2$ and where U_β behaves as a displaced oscillator at that ($q_1 \dots q_{N-1}$), and so has $\frac{1}{2} k' (q_N - b)^2 - \Delta E_{IF}^0$ there, k' is a force constant assumed independent of ($q_1 \dots q_{N-1}$). Then $|\partial(U_\beta - U_\alpha)/\partial q_N|$ equals $k'\alpha$. Further, $Q_N \int \exp[-k'q_N^2/2kT] dq_N$,²² where $q_N = 0$ is the value of q_N on the intersection hypersurface. Thus, Q_N equals $\sqrt{2\pi kT/k'}$ and so $\langle S^{-1} \rangle / Q_N$ equals $1/\sqrt{2\pi kT k' a^2}$. One can express this quantity in terms of λ_0 , by noting that $\lambda_0/4$ in Eq. (23) is the energy barrier when $\Delta G_{IF}^0 = 0$. For the simple quadratic model for U_α and U_β one finds that $\lambda_0/4$ equals $k'a^2/8$. Thus, we have

$$\frac{\langle S^{-1} \rangle}{Q_N} = \frac{1}{\sqrt{4\pi\lambda_0 kT}}. \quad (24)$$

In the actual many-dimensional case the values of U_α and U_β on any $N - 1$ dimensional hypersurface (fixed q_N) when suitably averaged at that q_N , depend approximately quadratically on a suitably chosen q_N , when one makes a "dielectrically unsaturated" approximation.³ One can show that Eq. (24) is approximately valid for this many-dimensional system also.²⁶

Equations (21)–(24) yield

$$k(T) = \frac{2\pi V^2}{\hbar} \sum_{I,F} \frac{|\langle F|I \rangle|^2 e^{-E_I/kT}}{Q_I (4\pi\lambda_0 kT)^{1/2}} \times \exp \left[-\frac{\lambda_0}{4kT} \left(1 + \frac{\Delta G_{IF}^0}{\lambda_0} \right)^2 \right] \quad (25)$$

an equation used in several recent articles.^{4–6}

We have noted earlier that in the rate expression for nonadiabatic transfers, e.g., Refs. 7 and 10, an exponential containing ΔE^0 instead of the ΔG^0 in Eq. (25) has been sometimes written. In derivations of the latter result it was as-

sumed that all the classical-like coordinates were equivalent to harmonic oscillators, and, as already noted, for such systems, ΔS^0 vanishes and so ΔE^0 and ΔG^0 become equal for the present reaction.¹²

Equation (25) is the rate constant at a fixed separation distance R . If the reaction involves, instead, contributions from a distribution of R 's one can proceed as in Ref. 3. One would obtain Eq. (25), but now instead of ΔG_{IF}^0 one finds ΔG_{IF}^0 , equal to $\Delta G_{IF}^0 + w^p - w^r$, where w^r and w^p denote the work required to bring reactants together and the products together, respectively, to some average distance R in the transition state. One also finds that Eq. (25) is multiplied by a factor $4\pi R^2 \delta R \exp(-w^r/kT)$, where δR is the range of separation distance R contributing significantly to the reaction rate. An elaboration, in which a somewhat slow diffusion may be involved, is described in Ref. 5.

In obtaining Eqs. (14)–(21), all stationary phase points (10) were taken to be real, since the aim in the paper was to treat the q_k 's classically. One quantum correction is that of nuclear tunneling along the q 's. This tunneling occurs when one or more of the p_k 's in Eq. (10) is complex valued. In that case a factor $\exp(-2|\text{Im } W_{fi}|)$ appears in the integrand of Eq. (14) (and in later equations), $\text{Im } W_{fi}$ being the imaginary part of W_{fi} ²⁷ at this complex-valued stationary phase point. Additionally, some subtleties appear in the sum Σ in Eq. (16) and hence in the subsequent equations.²⁸

In concluding this section we comment on the relation between Eq. (18) and an interesting paper of Schmidt.²⁹ He employed Yamamoto's³⁰ expression for the rate constant in terms of the reactive flux correlation function and introduced a classical approximation by a different procedure. To see the connection between that paper and Eq. (18) we begin the present Eq. (4), the $\langle F|I \rangle$ being absent in Ref. 29 since the intent there was to convert all coordinates to classical. After replacing the delta function in (4) by its Fourier integral representation and noting that $\epsilon_i|i\rangle$ and $\epsilon_f|f\rangle$ equal $H_i|i\rangle$ and $H_f|f\rangle$, the H 's being Hamiltonians, one finds

$$k_{\alpha\beta} = \frac{V^2}{\hbar} |\langle F|I \rangle|^2 \langle i|f \rangle \int_{-\infty}^{\infty} \langle f|e^{iH_f t} e^{-iH_i t}|i\rangle e^{i\Delta E_{IF}^0 t} dt. \quad (26)$$

To obtain $k_{IF}(T)$ as in Ref. 29, one sums over all final states f , uses the completeness relation to remove the $\sum_f |f\rangle \langle f|$, multiplies by a Boltzmann factor $\exp(-\beta\epsilon_i)/Q$, and sums over i . A classical-like approximation is then introduced²⁹ by neglecting the commutator of H_f and H_i in Eq. (26). One obtains

$$k_{IF}(T) = \frac{V^2}{\hbar Q} |\langle F|I \rangle|^2 \times \sum_i \left\langle i \left| \int_{-\infty}^{\infty} e^{(H_f - H_i + \Delta E_{IF}^0)t} dt \right| i \right\rangle e^{-\beta\epsilon_i}. \quad (27)$$

$H_f - H_i$ equals $U_\beta - U_\alpha$, and a second use of the integral representation for the delta function then yields an expression frequently used in the physics literature³¹

$$k_{IF}(T) = \frac{2\pi V^2}{\hbar Q} |\langle F|I \rangle|^2 \times \sum_i \langle i|\delta(U_\beta - U_\alpha + \Delta E_{IF}^0)|i\rangle e^{-\beta\epsilon_i}. \quad (28)$$

Because of the neglect of the commutator this type of expres-

sion is sometimes termed "semiclassical"³¹ but it differs from the semiclassical approximation used in the present paper.

Schmidt then replaces the trace in Eq. (28), i.e., the sum over i , by an integral over phase space, and so obtains the desired classical expression. His procedure, beginning with Eq. (4), is clearly very direct. Its one disadvantage is that at an intermediate stage, namely Eq. (28), it can lead to a significant error, seen as follows: Equation (28) has been shown,³² when all coordinates are treated as harmonic oscillators, to lead to another¹¹ expression for the reaction rate. That expression can be inaccurate (calculated³² to be a factor of ~ 20 different from the quantum value for the rate constant of thermoneutral reactions such as the $\text{Fe}^{2+/3+}$ aquoion exchange at room temperature). The physical nature of the approximation has been identified,^{32,33} and one finds that Eq. (28) overestimates the quantum effect.³⁴

III. SUMMARY

Microcanonical and canonical rate constants are derived for a nonadiabatic transition using generalized coordinates for the classical-like degrees of freedom. The results are used to derive Eq. (25), previously used in several studies in the nonadiabatic electron transfer literature.⁴⁻⁶ In Eq. (25) ΔG^0 plays a major role even though it is ΔE^0 which appears in the Golden Rule expression (1).

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APPENDIX A: RELATION BETWEEN COEFFICIENTS a_{ij} AND g_{ij} AND APPLICATION TO EQ. (18)

We consider the coefficients²⁰ a_{ij} and g_{ij} referred to in the text. An infinitesimal element of length ds is given in terms of curvilinear coordinates (q^1, \dots, q^N) by

$$ds^2 = \frac{1}{2} \sum_i \sum_j a_{ij} dq^i dq^j, \quad (\text{A1})$$

where

$$a_{ij} = \sum_k \frac{\partial x^k}{\partial q^i} \frac{\partial x^k}{\partial q^j}, \quad (\text{A2})$$

and the x^k 's are Cartesian coordinates. The usual covariant-contravariant notation²⁰ is used. (We drop this notation in all other sections of the paper.) The kinetic energy is given, on the other hand, by

$$\text{KE} = \frac{1}{2} \sum_{ij} g_{ij} \dot{q}^i \dot{q}^j = \frac{1}{2} \sum g^{ij} p_i p_j, \quad (\text{A3})$$

where

$$g_{ij} = \sum_k m_k \frac{\partial x^k}{\partial q^i} \frac{\partial x^k}{\partial q^j}, \quad (\text{A4})$$

and m_k is the mass associated with Cartesian coordinate x^k .

Equation (A1) leads to the following relation between the determinants:

$$|a_{ij}| = \left| \sum_k \frac{\partial x^k}{\partial q^i} \frac{\partial x^k}{\partial q^j} \right| = \left| \frac{\partial x^k}{\partial q^i} \right|^2, \quad (\text{A5})$$

using the usual product rule. (In the text we have denoted determinants such as $|\partial x^k / \partial q^i|$ by $|\partial x / \partial q|$.) Equation (A4) leads to

$$g_{ij} = \left| m_k \frac{\partial x^k}{\partial q^j} \right| \left| \frac{\partial x^k}{\partial q^i} \right| = |a_{ij}| \prod_k m_k. \quad (\text{A6})$$

$|g_{ij}|$, which equals the reciprocal of $|g^{ij}|$, is denoted conventionally as g . Denoting $|a_{ij}|$ by a , Eqs. (A5) and (A6) yield

$$1/|g^{ij}| = g = a \prod_{k=1}^N m_k, \quad (\text{A7})$$

a result used below and in Appendix B.

We have considered the following momentum integral in treating Eq. (18):

$$I = \int \dots \int \exp\left(-\frac{1}{2} \sum_{ij} g^{ij} p_i p_j / kT\right) dp_1 \dots dp_N. \quad (\text{A8})$$

Integration over the p_j 's and use of Eq. (A7) yields $(2\pi kT)^{N/2} \sqrt{g}$, and hence $\sqrt{a} \prod_k (2\pi m_k kT)^{1/2}$. Introducing this result into the integral in the numerator in Eq. (18) and into the Q there then yields Eq. (19).

APPENDIX B: RELATION OF EQ. (19) TO THE LANDAU-ZENER FORMULA

It is useful to consider the connection between Eq. (19) and that obtained using the one-dimensional Landau-Zener formula for nonadiabatic transitions, since the differences between Eq. (19) and the adiabatic expression are then understood in a simple way. (See Ref. 6 for closely related derivation.)

For weak electronic interactions (small matrix element V) the Landau-Zener probability P of transition from electronic state α to state β is given by³⁵

$$P = 4\pi V^2 / \hbar v_x S_x, \quad (\text{B1})$$

where v_x is the (Cartesian) velocity \dot{x} at the crossing point and S_x is the difference of slopes of the two potential energy curves at that point, the slope being expressed in Cartesian coordinates $S_x = d(U_\beta - U_\alpha)/dx$. The product $v_x S_x$, i.e., $(dx/dt)[d(U_\beta - U_\alpha)/dx]$ can also be written as $d(U_\beta - U_\alpha)/dt$, and hence as $\dot{q}_N \partial(U_\beta - U_\alpha)/\partial q_N$, since $U_\beta - U_\alpha$ depends on only q_N by definition of this coordinate in the text. Systems initially on surface α cross the intersection of the two potential energy curves, and if they do not go to β , reach a classical turning point on α and recross that intersection surface. Equation (B1) includes this probability of a double crossing.

The reaction rate constant $k(T)$ is equal to P_α , the probability of finding the system in a phase space volume element at the crossing point, per unit length along the reaction coordinate, namely by

$$P_\alpha = e^{-\epsilon/kT} dq_1 \dots dq_{N-1} dp_1 \dots dp_N / Q \hbar^N, \quad (\text{B2})$$

multiplied by the velocity \dot{q}_N and by the P given by Eq. (B1), then integrated over all coordinates ($q_1 \dots q_{N-1}$) on the $N-1$ dimensional surface of intersection of U_α and $U_\beta + \Delta E_{IF}^0$, and integrated over all momenta, noting that the ϵ in Eq. (B2) equals $U_\alpha + \frac{1}{2} \sum_{ij} g^{ij} p_i p_j$. (Even p_N is allowed to be positive and negative since the system crosses the intersection hypersurface twice, in the low transition probability limit, for each

crossing in the forward direction.) Using Eq. (A7) of Appendix A one obtains

$$k(T) = \frac{2\pi V^2}{\hbar} \frac{\int \dots \int e^{-U_\alpha/kT} S^{-1} \sqrt{ad} dq_1 \dots dq_{N-1}}{\int \dots \int e^{-U_\alpha/kT} \sqrt{ad} dq_1 \dots dq_N}. \quad (\text{B3})$$

If multiplied by the probability $|\langle F|I \rangle|^2$ Eq. (B3) yields Eq. (19) in the text for $k_{IF}(T)$. Of course, a main purpose of the present paper was to derive Eq. (25) systematically from the Golden Rule expression (1) and not to begin with the classical expression (B2).

¹Recent reviews of the electron transfer literature include those of N. Sutin, *Progr. Inorg. Chem.* **30**, 441 (1983); L. Ebersson, *Adv. Phys. Org. Chem.* **18**, 79 (1982); R. D. Cannon, *Electron Transfer Reactions* (Butterworths, Boston, 1980); D. DeVault, *Quart. Rev. Biophys.* **13**, 387 (1980); J. Ulstrup, *Charge Transfer Processes in Condensed Media, Lecture Notes in Chemistry, No. 10* (Springer, New York, 1979). An early review is given in R. A. Marcus, *Annu. Rev. Phys. Chem.* **15**, 155 (1964).

²R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956).

³R. A. Marcus, *J. Chem. Phys.* **43**, 679 (1965).

⁴S. Efrima and M. Bixon, *Chem. Phys.* **13**, 447 (1976); their results were also utilized by R. P. Van Duyne and S. F. Fischer, *Chem. Phys.* **5**, 183 (1974).

⁵R. A. Marcus and P. Siders, *J. Phys. Chem.* **86**, 622 (1982).

⁶A. Warshel, *J. Phys. Chem.* **86**, 2218 (1982).

⁷V. G. Levich and R. R. Dogonadze, *Collect. Czech. Chem. Commun.* **26**, 193 (1961) (O. Boshko, Translator, Univ. of Ottawa).

⁸V. G. Levich, in *Physical Chemistry, Volume 9B: Electrochemistry*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1970), Chap. 12; R. R. Dogonadze, in *Reactions of Molecules at Electrodes*, edited by N. Hush (Wiley, New York, 1971), pp. 135ff.

⁹N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem.* **78**, 2148 (1974). The authors were aware, of course, of the important role played by ΔG^0 (e.g., in Refs. 2 and 3). I am indebted to Dr. Jortner for first calling the present ΔE^0 problem to my attention.

¹⁰J. Ulstrup, and J. Jortner, *J. Chem. Phys.* **63**, 4358 (1975).

¹¹J. J. Hopfield, *Proc. Natl. Acad. Sci. U.S.A.* **71**, 3640 (1974); M. Redi and J. J. Hopfield, *J. Chem. Phys.* **72**, 6651 (1980).

¹²(a) When $\Delta S^0 = 0$, $\Delta G^0 = \Delta H^0$. ΔH^0 is negligibly different from ΔE^0 for reactions in solution. (b) The entropy of activation (and of reaction) has also been obtained for the particular case that all modes of motion are treated as harmonic oscillators, but of different frequencies for reactants and products, by R. R. Dogonadze, A. M. Kuznetsov, and M. A. Vorontsev, *Phys. Status Solidi B* **54**, 125 (1972). Such an entropy change is expected to be relatively small in comparison with major changes resulting from changes in solvation and associated with restricting or freeing the orientations of solvent molecules.

¹³J. C. Tully, in *Dynamics of Molecular Collisions, Part B*, edited by W. H. Miller (Plenum, New York, 1976), Chap. 5.

¹⁴(a) J. H. Van Vleck, *Proc. Natl. Acad. Sci. U.S.A.* **14**, 178 (1928); (b) J. B. Keller, *Ann. Phys.* **4**, 180 (1958); (c) V. A. Fock, *Vest. Leningrad Univ. Ser. Fiz. Khim.* **16**, 67 (1959); *Technical Translations* **4**, 53 (1960), No. 60-17464; (d) V. P. Maslov, *Zhur. Vychisl. Mat. Mat. Fiz.* **1**, 113, 638 (1961), [English translation: *USSR Comput. Math. Math. Phys.* **1**, 123, 744 (1962)]; (e) R. Schiller, *Phys. Rev.* **125**, 1109 (1962); (f) R. A. Marcus, *J. Chem. Phys.* **59**, 5135 (1973); R. A. Marcus, *Faraday Discuss. Chem. Soc.* **55**, 34 (1973); (g) W. H. Miller, *Adv. Chem. Phys.* **25**, 69, (1974); (h) **30**, 77 (1976). To be sure, all of these articles tacitly or explicitly assume that the phase of the semiclassical wave function S_i/\hbar has a finite number of branches, i.e., it describes a "quasiperiodic" motion, or at least it assumes that the system can be approximated by such a description. Quasiperiodic and chaotic behavior are discussed in D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Annu. Rev. Phys. Chem.* **32**, 267 (1981), and references cited therein.

¹⁵The usual expression has been modified to include in Eq. (5) the curvilinear factor $a^{-1/2}$ and the sum Σ . In our case some motions are oscillatory and some are not. Usually only a single term, or in the one-dimensional oscillatory case, two terms, are written in the literature. The fact that

many branches and hence many terms in Σ may exist is, of course, well known [Ref. 14(b)].

¹⁶If i_k is a quantum number, the relevant classical action is actually $(i_k + \delta)\hbar$, rather than $i_k\hbar$, where $\delta = 0$ for a rotation and $1/2$ for a vibration. However, the value of δ does not affect any of the equations used here, since they involve differentials, such as di_k , or differences, such as $i_k - i'_k$.

¹⁷Examples of "primitive" semiclassical calculations of Franck-Condon factors in the literature include L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, 3rd ed. (Pergamon, New York, 1977), Sec. 51; W. H. Miller, Ref. 14(h); M. S. Child, in *Semiclassical Methods in Molecular Scattering and Spectroscopy*, edited by M. S. Child (Reidel, Boston, 1979), p. 127ff.

¹⁸The argument leading from the various determinants in Eq. (12) to the one in Eq. (13) parallels that in Ref. 14(e) and 14(h): Differentiation of the stationary phase condition (10) with respect to f_i yields

$$\sum_f \frac{\partial^2}{\partial q_k \partial q_j} (S_f - S_i) \frac{\partial q_j}{\partial f_i} + \frac{\partial^2 S_i}{\partial q_k \partial f_i} = 0.$$

[q_j depends on the f 's and the i 's, because of the stationary phase condition (10).] Hence, $|\partial^2(S_f - S_i)/\partial q^2| |\partial q/\partial f|$ equals $|\partial^2 S_f/\partial q \partial f|$, using the product rule for determinants. The ratio of determinants in Eq. (12) then becomes $|\partial^2 S_i/\partial q \partial i| |\partial q/\partial f|$. Since $\partial S_i/\partial q_k$ equals p'_k , Eq. (13) follows. We note, parenthetically, that the determinants in Eq. (13) can be shown to equal $|\partial^2 W_f/\partial i \partial f|$: Using Eq. (10) $\partial W_f/\partial i_k$ equals $-\partial S_i/\partial i_k$, and hence $\partial^2 W_f/\partial f_i \partial i_k$ equals $-\Sigma_k (\partial^2 S_i/\partial q_j \partial i_k) (\partial q_j/\partial f_i)$. Thereby, $|\partial^2 W_f/\partial f \partial i|$ equals $|\partial^2 S_i/\partial q \partial i| |\partial q/\partial f|$, i.e., $|\partial p/\partial i| |\partial q/\partial f|$.

¹⁹In the integration over $d(U_B - U_\alpha)$ the net result is positive, regardless of the sign of the slope, and hence the use of the absolute value sign in Eq. (15).

²⁰R. A. Marcus, *J. Chem. Phys.* **41**, 2624 (1964).

²¹R. A. Marcus, *Discuss Faraday Soc.* **29**, 21 (1960).

²²As in Refs. 3 and 21 we choose the quantity now labeled as U_N in Eq. (22) to be $m(U_\alpha - U_B - \Delta E_{IF}^0)$, [cf. Eq. (13) of Ref. 3, where the potentials were instead defined relative to the same zero], m is a Lagrangian multiplier, which now depends on I and on F ; m is chosen using a procedure analogous to that in the above references, but for the given I and F , i.e., for the given ΔE_{IF}^0 and hence for the given ΔG_{IF}^0 . The Q_N in Eq. (21) is defined in the following way: The surface integral prior to the introduction of U_N in Eqs. (21) and (22) was $\int \dots \int \exp(-U_\alpha/kT) \sqrt{ad} dq_1 \dots dq_{N-1}$ and is written as $\exp[-I(q_N)/kT]$, defining thereby a free energy $I(q_N)$. One multiplies by dq_N , integrates over q_N , and expands $I(q_N)$ as a quadratic function of q_N about its value ($q_N = 0$) on the intersection surface (Ref. 3). Q_N is defined (Ref. 3) as the integral over this exponential and equals $[2\pi I''(0)/kT]^{1/2}$, I'' being the value of $d^2 I/dq_N^2$ at the intersection hypersurface.

²³One can see this comparing Eq. (19) [and Eq. (13)] of Ref. 3 with Eqs. (31) and (81) there. The notation is somewhat different from the present notation.

²⁴In Ref. 3 λ_0 occurs in Eq. (68) and, by comparison with Eq. (89) there, is the coefficient of m^2 in Eq. (89).

²⁵This contribution to λ_0 is labeled λ_1 in Ref. 3 and given by Eq. (84) there.

²⁶We use the e.e.d. to calculate the averages of U_α and U_B and describe these averages using the parameter m . This m entered earlier (Ref. 22) into U_N and like q_N , has played a major role (Ref. 21) in defining the position of the intersection hypersurface: m is varied by varying ΔG_{IF}^0 (Ref. 3 and 21). We write d/dq_N as $(d/dm)(dm/dq_N)$. The difference, $U_B - U_\alpha$, averaged over an e.e.d. at a given q_N (and hence at a given m) can be shown from Eq. (68) of Ref. 3 and from an analogous equation for the free energy of formation of the e.e.d., at this same q_N , on the β surface from the products to be $(m+1)^2 \lambda_0 - m^2 \lambda_0$, plus a term independent of m . That is, $\langle U_B - U_\alpha \rangle$ at this q_N is $(2m+1)^2 \lambda_0 - m^2 \lambda_0$ plus an m -independent term. Hence, $\langle d(U_B - U_\alpha)/dq_N \rangle$ equals $2\lambda_0 dm/dq_N$. Further, the q_N -partition function Q_N is approximately equal to that for the reactants, namely $\int \exp(-\Delta F_\alpha^*/kT) dq_N$, where [Eq. (68)] $\Delta F_\alpha^* = m^2 \lambda_0$. Integration of the latter over q_N yields $\sqrt{\pi kT/\lambda_0} dq_N/dm$. Thus, the approximate value of $\langle S \rangle^{-1}/Q_N$ is $1/\sqrt{4\pi \lambda_0 kT}$. While $\langle S \rangle^{-1}$ is not exactly equal to $\langle S^{-1} \rangle$ except when S is a constant, as it was in the simple harmonic oscillator model, we see that approximately $\langle S^{-1} \rangle/Q_N$ equals $1/\sqrt{4\pi \lambda_0 kT}$, as in Eq. (24).

²⁷For example, in one dimension the exponential factor $\exp(-2|\text{Im } W_f|/\hbar)$ becomes $\exp(-2J/\hbar)$ where, when the slopes $\partial U_\alpha/\partial q_N$ and $\partial U_B/\partial q_N$ are of opposite sign, J is the sum of the absolute values of the phase integrals $\int p_N dq_N$ from the classical turning point on curve α to the crossing

point and from the crossing point to the classical turning point on curve β . When the slopes are of the same sign, J is the difference in absolute values [e.g., Eq. (51.6) of Ref. 17].

²⁸The preexponential factor in the one-dimensional case (or in the case where the q_N coordinate is separable from the others) is a factor of 2 smaller in this case than the factor in Eq. (B1) (also v_x is replaced by $|v_x|$). This result is seen, for example, by comparing Eq. (B1) with the relevant probability factor, the second factor in brackets, in Eq. (14) of T. Holstein, *Philos. Mag.* **B 37**, 49 (1978). The origin of this difference is also evident in the semiclassical wave function in the classically allowed region, there being two exponential terms with imaginary exponents when a turning point occurs, while in the classically forbidden region there is only one term, a decaying exponential [cf. Eq. (51.2) of Ref. 17].

²⁹P. P. Schmidt, *J. Chem. Phys.* **58**, 4384 (1973), Eq. (16).

³⁰T. Yamamoto, *J. Chem. Phys.* **33**, 281 (1960).

³¹M. Lax, *J. Chem. Phys.* **20**, 1752 (1952); D. Curie, *Luminescence in Crystals* (Wiley, New York, 1963), p. 47ff. The following authors obtain the same expression by an expansion in semi-invariants: R. Kubo and Y. Toyozawa, *Prog. Theor. Phys.* **13**, 160 (1955); K. Maeda, *Phys. Chem. Solids* **9**, 335 (1959); T. F. Soules and C. B. Duke, *Phys. Rev. B* **3**, 262 (1971).

³²P. Siders and R. A. Marcus, *J. Am. Chem. Soc.* **103**, 741 (1981).

³³R. A. Marcus, in *Oxidases and Related Redox Systems*, edited by T. E. King, M. Morrison, and H. S. Mason (Pergamon, New York, 1982), p. 3.

³⁴For related comments see J. Jortner, *J. Chem. Phys.* **64**, 4860 (1976).

³⁵L. Landau, *Phys. Z. Sov.* **1**, 88 (1932); **2**, 46 (1932); C. Zener, *Proc. R. Soc. London Ser. A* **137**, 696 (1932).