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Quantum Effects in Electron-Transfer Reactions

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Abstract: Classical, semiclassical, and quantum theories of outer-sphere electron-transfer reactions in polar media are discussed. For each, the Franck–Condon overlap factors for the hexaamminecobalt, hexaaquoiron and hexaammineruthenium self-exchange rates and for the Fe^{2+}–$Ru(bpy)_3^{3+}$ cross-reaction are evaluated and compared. The quantum effect on the rates is relatively unimportant in the "normal" $\Delta G°$ region. Direct sum and saddle-point evaluations of the quantum Franck–Condon factors are made and compared.

Introduction

An outer-sphere electron-transfer reaction in a polar solvent is characterized by changes in the force constants and bond lengths and bond angles of the reactants and by fluctuations in the surrounding solvent. In many systems the inner-sphere changes are very small, so that the reaction is controlled by fluctuations in

Table I. Structural and Spectroscopic Data[a]

	$Co(NH_3)_6^{2+}$	$Co(NH_3)_6^{3+}$	$Ru(NH_3)_6^{2+}$	$Ru(NH_3)_6^{3+}$
M–N bond length, Å	2.114	1.936	2.144	2.104
$\hbar\omega$ (A_{1g}), cm^{-1}	357	494	350	500
$\hbar\omega$ (E_g)	255	442		
$\hbar\omega$ (F)	325	475		
$\hbar\omega$ (F)	192	331		
$\hbar\omega$ (F)	187	322		
$\hbar\omega$ (F)	143	246		
λ_{outer}, kJ/mol	117		113	

[a] Reference 5. Symmetries are for an effective octahedral geometry.

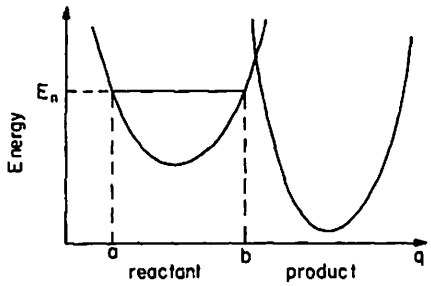

Figure 1. Model harmonic potentials for electron transfer vs. a generalized configuration coordinate q.[9]

the solvent polarization (e.g., $Ru(NH_3)_6^{3+/2+}$[1,2] and $Cr(2,2'\text{-bipyridyl})_3^{3+/2+}$[3]). On the other hand, some redox systems involve substantial internal reorganization (e.g., $Fe(H_2O)_6^{3+/2+}$[2] and $Co(NH_3)_6^{3+/2+}$[4]). In such systems inner-sphere effects are important.

In this paper we briefly describe classical, semiclassical, and quantum theories of electron transfer. It has been suggested that reactions in which inner-sphere reorganization is important are not adequately described by classical theory but require a quantum mechanical treatment.[5,6] A quantum mechanical treatment is available for nonadiabatic electron transfers and was developed at first for the solvent modes[7] and later for the bond vibrations.[6,8,9]

We discuss the nature and magnitude of quantum effects in the particular cases of the very slow hexaamminecobalt self-exchange reaction, the hexaaquoiron self-exchange reaction, the hexaammine ruthenium self-exchange reaction, and the Fe^{2+}–$Ru(bpy)_3^{3+}$ cross-reaction.

It is expected that if nuclear tunneling is to be important, it will be so for systems in which a high-frequency mode undergoes a significant displacement. For example, in the hexaamminecobalt self-exchange reaction the equilibrium position of the symmetric stretching mode, $\hbar\omega \approx 431$ cm^{-1}, is displaced by 0.18 Å (cf. Table I), and in electron-transfer reactions in which an electronically excited bipyridyl complex is quenched, a ring mode, $\hbar\omega \approx 1300$ cm^{-1}, undergoes a substantial equilibrium displacement.

Nuclear tunneling will, other things being equal, be more important for high rather than for low-frequency modes as one can see from the nature of harmonic oscillator eigenstates. We consider for illustration purposes the one-dimensional model surface sketched in Figure 1. Nuclear tunneling depends on the overlap of reactant and product wave functions in the classically nonallowed region, and therefore is directly related to the amplitude of the reactants' wave function in the region $q > b$. This wave function extends further into the classically forbidden region, for any given energy, the higher the vibration frequency. It follows that tunneling from a state of given energy is more probable for a high-frequency mode than for a low-frequency mode, at a given energy.

In the present paper it is found that for the reaction rate constant a reasonable order of magnitude estimate for the contribution of configurational changes of high-frequency quantum modes in the first coordination layer, for typical metal–ligand frequencies, can be provided by a classical expression.[9]

Quantum Treatment

Franck–Condon Factor. An approximate quantum mechanical rate expression based on the golden-rule transition probability has been derived for electron transfer systems in the nonadiabatic limit.[6-8,10] Within the Condon approximation the transition probability in this expression involves the product of the square of an electron-exchange integral and a thermally weighted sum, G, of vibrational Franck–Condon factors (eq 1), where Q is the

$$G = \frac{1}{Q}\sum_n\sum_m e^{-E_n^{vib}/kT}|\langle n|m\rangle|^2\delta(E_n - E_m) \qquad (1)$$

reactants' (vibrational) partition function and n and m designate initial and final vibronic states, respectively. E_n and E_m are initial- and final-state energies. E_n^{vib} is the initial-state *vibrational* energy; $|n\rangle$ and $|m\rangle$ are treated as harmonic oscillator eigenfunctions, equal to a product over the system's degrees of freedom of single-mode harmonic oscillator functions.

The single-mode harmonic oscillator overlap integrals required for evaluating G directly by the sum of eq 1 have been known for many years.[11-15] The expressions used in this work for these integrals are presented in the Appendix (eq A1 and A2) in terms of $f = \omega'/\omega,\omega'$ and ω being the frequencies associated with $|m\rangle$ and $|n\rangle$, respectively, and in terms of the dimensionless change $X^{1/2}$ in equilibrium coordinate value from $|m\rangle$ to $|n\rangle$. For a normal mode $X = F(\Delta Q)^2/2\hbar\omega$, where ΔQ is the change in the normal coordinate, $\omega/2\pi$ is the vibration frequency, and F is the force constant for the mode ($\omega^2 = F$).

In the case of $X \neq 0$ but $\omega' = \omega$, one obtains the well-known limiting form[14] for $n > m$

$$\langle n|m\rangle = X^{(n-m)/2}(m!/n!)^{1/2}e^{-X/2}L_m^{n-m}(X) \qquad (2)$$

where L is an associated Laguerre polynomial. For $n < m$ we have $|\langle n|m\rangle| = |\langle m|n\rangle|$ and then use eq 2 with m and n interchanged.

An approximate simple formula for the multimode case has also been derived elsewhere, together with limitations on its validity.[16] This relation was applied there to the hexaaquoiron

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(8) (a) R. R. Dogonadze and A. M. Kuznetsov, *Elektrokhimiya* 3, 1324 (1967); *Sov. Electrochem. (Engl. Transl.)*, 3, 1189 (1967); (b) R. R. Dogonadze, A. M. Kuznetsov, and M. A. Vorotyntsev, *Phys. Status Solidi B*, 54, 125, 425 (1972); (c) R. Van Duyne and S. Fischer, *Chem. Phys.*, 5, 183 (1974); (d) S. Efrima and M. Bixon, *ibid.*, 13, 447 (1976); (e) J. Jortner, *J. Chem. Phys.*, 64, 4860 (1976).
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self-exchange reaction and to the Fe^{2+}–$Ru(bpy)_3^{3+}$ cross-reaction and shown to give good agreement with the exact quantum values.[26]

Quantum Treatment of the Solvent. The interaction of the solvent with the reactant ions is implicitly included in eq 1 as a set of one or more harmonic modes. Usually only a single frequency, $\hbar\omega_1 = 1$ cm^{-1}, is used in calculations.[6a,8c,17] However, in view of the significant decrease in the real part of the dielectric constant of water at 170 cm^{-1} (and the corresponding peak in the imaginary part)[18,19] we have chosen to use a two-frequency quantum description of the solvent interaction: $\hbar\omega_1 = 1$ cm^{-1} and $\hbar\omega_2 = 170$ cm^{-1}. A dielectric dispersion in the solvent was first treated for electron transfer by Ovchinnikov and Ovchinnikova.[20]

As a first approximation for this two-frequency description we divide the outer-sphere reorganization energy into two parts, writing λ_{out}, which is 4 times the solvent reorganization energy,[21] as

$$\lambda_{out} = \lambda_1 + \lambda_2 \tag{3}$$

where

$$\lambda_1 = \lambda_{out}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_{ir}}\right)\Big/\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_{op}}\right) \tag{4}$$

$$\lambda_2 = \lambda_{out}\left(\frac{1}{\epsilon_{ir}} - \frac{1}{\epsilon_{op}}\right)\Big/\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_{op}}\right)$$

($\epsilon_{ir} = 5.0$[19] = real part of the dielectric constant on the "plateau" between 1 and 170 cm^{-1}; $\epsilon_s = 78.3$[19] = static dielectric constant; $\epsilon_{op} = 1.78^{22} = n_D^2$).

Thus, the quantum treatment of the solvent interaction (the solvent is taken to be aqueous in this paper) involves two harmonic modes included in the degrees of freedom of the system. In performing the quantum mechanical calculation for the solvent eq 2 was again used but X was obtained in the following manner. It is first recalled that for an internal normal mode i of the reactants X_i, which equals $F_i(\Delta Q_i)^2/2\hbar\omega_i$, can be rewritten as $\lambda_i/\hbar\omega_i$, since[9] $\lambda_i = F_i(\Delta Q_i)^2/2$. By analogy, we use for X for the solvent $\lambda_1/\hbar\omega_1$ and $\lambda_2/\hbar\omega_2$ where λ_1 and λ_2 have been defined in eq 3 and 4. The numerical values employed for $\lambda_{1,2}$ are given later in the paper, while $\hbar\omega_{1,2}$ are given above.

Saddle-Point Method. For a system having several vibrational normal modes of different frequencies, the direct evaluation of eq 1 can require considerable computing time. However, G can easily be evaluated approximately by replacing the δ function in eq 1 by its Fourier integral representation and then using the saddle-point method. After some manipulations[23,24] one obtains

$$G = (2\pi Q)^{-1}\int_{-\infty}^{\infty} e^{-i\Delta Et + f(t)}\,dt \tag{5}$$

and, after using the saddle-point method to approximte the integral, one obtains eq 6,

$$G \approx |2\pi f''(t_0)|^{-1/2} Q^{-1} e^{-i\Delta Et_0 + f(t_0)} \tag{6}$$

where ΔE is the energy (endoergicity) of the transition, t_0 is the stationary phase value of t in the integrand in eq 5, and f, f'', and t_0 are given in the Appendix.

In the case of a self-exchange reaction, product modes in the oxidized species are equivalent to reactant modes in the reduced species so that the formulas simplify considerably.[5] In a thermoneutral self-exchange reaction, $t_0 = -i/2kT$. For other cases eq A6 of the Appendix may be solved numerically, e.g., by iterating from the approximate root

$$t_0 \approx -i(\Delta E + \lambda)/2kT\lambda \tag{7}$$

where $\lambda = \sum_{j=1}^{N}\lambda_j$ and each $\lambda_j = {}^1/_2F_j(\Delta Q_j)^2$. Equation 7 gives the exact saddle point in the high-temperature limit, when frequency changes are neglected, and provides a reasonable starting point for iteration in other cases.

Classical Treatment. When all the degrees of freedom of the system are treated in the classical limit, $\hbar\omega/2kT \to 0$, and when frequency changes are neglected, eq 5 reduces to eq 8. This

$$G = (4\pi kT\lambda)^{-1/2}\exp[-(\Delta E + \lambda)^2/4kT\lambda] \tag{8}$$

equation is similar in form to the classical expression for G[2,4] but contains energies rather than free energies. This difference arises because eq 5 tacitly assumes zero entropy of reaction, and indeed the initial equation, (eq 1), with its assumption of harmonic oscillators, does not contain any important $\Delta S°$ term,[25] whereas the actual $\Delta S°$ can be quite large.[25] The classically derived expression is more general in this respect, since it does not assume harmonic oscillations for all motions.[26] As defined earlier, $\lambda_j = {}^1/_2F_j(\Delta Q_j)^2$ and $\lambda = \sum_{j=1}^{N}\lambda_j$. It has been shown[27] that frequency changes may be included in an approximate manner by using an average force constant to calculate λ_j, rather than using the initial force constant. F_j above is an averaged force constant

$$F_{av} = 2FF'/(F + F') \tag{9}$$

where F and F' are the force constants in the reactant and product states, respectively. The classical value of the Franck–Condon sum (eq 8) is computed by using λ's calculated with average force constants given by eq 9.

"Semiclassical" Treatment.[28] Consider first a one-dimensional case with a coordinate Q. The $\delta(E_m - E_n)$ of eq 1 can be introduced into $|\langle n|m\rangle|^2$. When the commutator of the initial and final Hamiltonians, $\mathcal{H}_n$ and $\mathcal{H}_m$ is neglected, $\delta(E_n - E_m)$ in the integral becomes $\delta(\mathcal{H}_n - \mathcal{H}_m)$, which in turn is $\delta(V_n - V_m)$ since the kinetic energy terms in $\mathcal{H}_n$ and $\mathcal{H}_m$ cancel; V_n and V_m are the potential energies of the reactants and products, respectively. By using the identity $\sum_m|m\rangle\langle m| = 1$, we may reduce the thermally weighted double sum of squared overlap integrals in eq 1 to a single sum over n of $\langle n|\delta(V_n - V_m)|n\rangle$ (e.g., see analogous procedure for other problems in ref 29). These integrals are readily evaluated, yielding

(16) Equation 19 of ref 26. The condition for the validity of this eq 19 is given by eq 21 there.

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(24) (a) S. H. Lin, *J. Chem. Phys.*, 44, 3759 (1966); (b) *Theor. Chim. Acta*, 10, 301 (1968).

(25) The only entropy change present in eq 1 (and hence in eq 5) is the minor contribution from inner-sphere frequency changes, whereas the actual $\Delta S°$ can be much larger. For reactions in which the set of reactants' vibration frequencies equals the set of products' vibration frequencies $\Delta S°_{vib} = 0$, where $\Delta S°_{vib}$ is the contribution to $\Delta S°$ from inner-sphere vibration frequency changes. $\Delta S°$ for the Fe^{2+}–$Ru(bpy)_3^{3+}$ cross-reaction (eq 23) is −180 J mol^{-1} K^{-1}.[2] $\Delta S°_{vib}$ for this reaction may be estimated as follows. Symmetric stretching frequencies for $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ are given in the text (389 and 490 cm^{-1}, respectively). For simplicity we will assume that the ratio of a frequency in the reduced state to that in the oxidized state is the same for each of the 15 (octahedral) normal modes. Vibration frequencies in the 2+ and 3+ oxidation states of $Ru(bpy)_3$ are unknown. If by analogy with $Fe(bpy)_3^{2+}$ (for which at least the symmetric stretching frequency is unchanged upon oxidation[32b]) it is assumed that the vibration frequencies in the 2+ and 3+ oxidation states of $Ru(bpy)_3$ are the same, then the $Ru(bpy)_3^{2+/3+}$ couple's vibrations contribute nothing to $\Delta S°_{vib}$. Using standard equations[46] for the quantum mechanical vibrational partition functions and for $\Delta S°$, one obtains $\Delta S°_{vib} = -20$ J mol^{-1} K^{-1} at 300 K, which is only about 10% of the total $\Delta S°$ for the reaction.

(26) R. A. Marcus in "Third International Symposium on Oxidases", T. E. King, H. S. Mason, and M. Morrison, Eds., July 1–4, 1979 (1980 in press).

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

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a sum of factors proportional to $|\chi_n(Q)|^2$, where Q is that value of the coordinate for which the reactant and product potential energies are equal and χ_n is the wave function of the reactants. The remaining sum over n in eq 1 is then readily evaluated to yield[29]

$$G = (2\pi\lambda\hbar\omega \coth \gamma)^{-1/2} \exp[-(\Delta E + \lambda)^2/(2\lambda\hbar\omega \coth \gamma)] \quad (10)$$

where $\gamma = \hbar\omega/2kT$ and ΔE and λ are defined as in eq 7 but λ is for the single mode being considered. Equation 10 is the same as that obtained in ref. 28 by a different procedure. A detailed derivation of eq 10 is given in the appendix.

For systems having two or more frequencies, one obtains a convolution of Gaussians of the form of eq 10. The convolution is itself of the form of eq 10, but $\lambda\hbar\omega \coth \gamma$ must be replaced with $\sum_j \lambda_j \hbar\omega_j \coth \gamma_j$ and λ by $\sum_j \lambda_j$.[26,29]

This method of obtaining G's, which originated in the theory of optical spectra of solids,[29] is sometimes termed "semiclassical" because of neglect of commutators of $\mathcal{H}_n$ and $\mathcal{H}_m$, although the term "semiclassical" has a variety of other meanings (corresponding to other approximations) in the literature.

Calculations and Discussion

We now proceed to consider quantum effects in four particular cases of chemical interest: the hexaamminecobalt and hexaammineruthenium self-exchange reactions, the $Fe^{2+/3+}(aq)$ self-exchange reaction, and the Fe^{2+}–$Ru(bpy)_3^{3+}$ cross-reaction.

Hexaamminecobalt Self-Exchange Reaction. The large difference between the rates of self-exchange reactions 11 and 12 has long been a matter of interest in the theory of electron-transfer rates.

$$Co(NH_3)_6^{2+} + Co(NH_3)_6^{3+} \xrightarrow{k_1} Co(NH_3)_6^{3+} + Co(NH_3)_6^{2+} \quad (11)$$

$$k_1 \leq 10^{-12}\ M^{-1}\ s^{-1} \text{ at } 25\ ^\circ C^{4}$$

$$Ru(NH_3)_6^{2+} + Ru(NH_3)_6^{3+} \xrightarrow{k_2} Ru(NH_3)_6^{3+} + Ru(NH_3)_6^{2+} \quad (12)$$

$$k_2 = 10^3\ M^{-1}\ s^{-1} \text{ at } 25\ ^\circ C^{30,31}$$

In the quantum theory described earlier, the rate constant involves the product of the square of an electronic exchange integral and a sum of Franck–Condon factors. It has been suggested that the electronic factor for reaction 11 may be small because of spin multiplicity restrictions.[1,5] Further, the Franck–Condon term is much smaller for the Co reaction than for the Ru reaction because of the larger change in geometry from $Co(NH_3)_6^{2+}$ to $Co(NH_3)_6^{3+}$ (cf. Table I).

Buhks et al.[5] evaluated the Franck–Condon sums, G, for reactions 11 and 12, by using the saddle-point method described earlier. They found $G(Co) \approx 7 \times 10^{-18}$ cm and $G(Ru) = 1.5 \times 10^{-10}$ cm so that the ratio of Franck–Condon sums contributes a factor of ca. 10^{-8} to the ratio k_1/k_2. But they also found that the *classical* value of $G(Co)/G(Ru)$ was $\sim 10^{-5}$. The gross discrepancy between the classical and quantum values, a factor of 1000, led them to suggest that $G(Co)$ is heavily dependent on quantum effects. There is clearly some error in either the classical or the quantum Franck–Condon factors of ref 5 since tunneling effects should cause $G(Co)/G(Ru)$ to be larger in the quantum case than in the classical one, yet a *smaller* value was found for the quantum case in ref 5.

Actually, we have found that the large classical value of ref 5 for $G(Co)/G(Ru)$ is the result of using the inaccurate estimate (28.5 kJ/mol) of Stynes and Ibers[1] for the hexaamminecobalt internal reorganization energy. The latter seem to have treated the bond length reorganization energy in the hexaamminecobalt ions as containing only diagonal terms $^1/_2 \sum_{i=1}^{6} f_r(\Delta q_i)^2$, where Δq_i is the displacement in the ith Co–N bond length and f_r is the Co–N bond force constant. But the reaction coordinate is actually the symmetric stretching normal mode, and when expressed in terms of bond modes cross-terms are obtained. The totally symmetric F matrix force constant $F_{A_{1g}}$ is given in terms of generalized valence force field (GVFF) constants f by eq 13,[32] where f_r is the

$$F_{A_{1g}} = f_r + 4f_{rr}' + f_{rr} \quad (13)$$

diagonal force constant and f_{rr} and f_{rr}' are off-diagonal force constants. f_{rr}' denotes interaction between displacements perpendicular to each other. f_{rr} denotes interaction between displacements on the same line. The symmetric stretching normal-mode force constant F_1 involves both the F and G matrix elements and equals $F_{A_{1g}}/m_L$,[32] where m_L is the mass of one ligand. The bond length reorganization energy is[33] $^1/_4 F_1(\Delta Q_1)^2$, where ΔQ_1, the normal-mode displacement, is $(6m_L)^{1/2}\Delta q_i$[32] (all six Δq_i's are equal). Thus, this reorganization energy equals $^1/_4(f_r + 4f_{rr}' + f_{rr})6(\Delta q_i)^2$. It thereby involves both diagonal (f_r) and off-diagonal (f_{rr} and f_{rr}') GVFF force constants, and the latter are almost as important as the former.[34] Accordingly, we have made a comparison of the more correct classical value with the quantum sum, as well as with the semiclassical sum for G.

In the high-temperature (classical) limit, the Franck–Condon factors usually depend mainly on modes in which the product potential is displaced in coordinate space relative to the reactant potential (i.e., $\lambda \neq 0$). In the cobalt- and ruthenium–hexaammine self-exchange reactions only the solvent modes and the totally symmetric A_{1g} internal modes have nonzero λ's. Changes of frequency in the other modes would also make some contribution to G, of course, and as an example we include the modes of E_g and F symmetry later in quantum calculations of G. The approximate classical expression for G (eq 8) cannot treat modes for which $\lambda = 0$.

Using the known A_{1g} stretching frequencies (cf. Table I) for cobalt(II/III) hexaammine, we calculated the A_{1g} symmetry force constants F_{III} and F_{II} (i.e., the $F_{A_{1g}}$ for oxidation states III and II) to be 2.45×10^3 and 1.28×10^3 N/m, respectively. Using the average force constant of eq 9 and the Co–N bond lengths in Table I, we found the internal reorganization energy to be about 48 kJ/mol[35] (instead of the 28.5 kJ/mol calculated in ref 1). By analogous calculation, the ruthenium(II/III) hexaammine internal reorganization energy is found to be 2.5 kJ/mol. The total outer-sphere λ's for the cobalt and ruthenium reactions have recently been estimated as 117 and 113 kJ/mol, respectively.[5]

With use of these energy parameters, eq 8 yields as a classical result $G(Co)/G(Ru) \approx 5 \times 10^{-9}$ which is in reasonable agreement with the quantum result, both as given by Buhks *et al.* and as calculated below.

In order to assess the accuracy of the saddle-point method for the hexaamminecobalt system, we compared the value of G obtained by direct sum with that obtained by saddle-point integration. For simplified models consisting of only the A_{1g} internal mode or of both the A_{1g} and one of the two degenerate E_g internal modes, both the direct and saddle-point calculations have been performed. (For the E_g modes ΔQ_i is zero, if in the transition state each reactant has octahedral symmetry, but $\Delta\omega_i$ is nonzero.) The results are given in Table II. At least for the models in this table the saddle-point evaluation is a very good approximation.

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(30) T. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(31) G. Brown and N. Sutin, *J. Am. Chem. Soc.*, **101**, 883 (1979).

(32) (a) C. W. F. T. Pistorius, *J. Chem. Phys.*, **29**, 1328 (1958). (b) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley, New York, 1978.

(33) R. A. Marcus, ref 9a. See eq 4.3.8 (taking $m = ^1/_2$ and $K_s^p = K^e_f$) and the discussion in appendix 2. Note that the internal reorganization energy $\Delta\epsilon^e_f$ involves a sum over both reactants, in the case of the present self-exchange reaction.

(34) K. Schmidt, W. Hauswirth, and A. Müller, *J. Chem. Soc., Dalton Trans.*, 2199 (1975).

(35) The actual value calculated and used was 47.7 kJ/mol.

Table II. Franck-Condon Sums (G)

system[a]	direct sum	saddle-point
$Ru(NH_3)_6^{2+/3+}$ [d]		
quantum solvent, quantum internal	1.04	1.08
classical solvent, quantum internal	0.93	0.97
effective force constant[b]		
classical solvent, quantum internal	1.02	1.02
classical solvent, classical internal[c]	0.82	
$Co(NH_3)_6^{2+/3+}$ [e]		
A_{1g} internal modes		
quantum solvent, quantum internal	20.0	20.0
classical solvent, quantum internal	17.9	17.8
effective force constant[b]		
classical solvent, quantum internal	19.1	19.1
effective force constant[b]		
classical solvent, classical internal[c]	4.4	
A_{1g} and E_g internal modes		
classical solvent, quantum internal	15.6	15.6
all internal modes		
classical solvent, quantum internal		3.3

[a] "internal" refers to intramolecular degrees of freedom of reactants. Frequencies and displacements from Table I. [b] Effective internal frequency used (see eq 9). The saddle-point approximation is exact in this case. [c] Equation 8. [d] All values for G have been mutiplied by 10^9 cm^{-1}. [e] All values for G have been multiplied by 10^{18} cm^{-1}.

Table III. Franck–Condon Sums for Hexaaquoiron and Tris(bipyridyl)ruthenium Self-Exchange and Cross-Reactions

reaction	quantum	classical	semiclassical
Fe^{2+}–Fe^{3+}	8.5[a]	2.4[a]	145[a]
$Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$	1.4[b]	1.4[b]	1.6[b]
Fe^{2+}–$Ru(bpy)_3^{3+}$	2.5[c]	1.5[c]	3.8[c]
$k_{12}/(k_{11}k_{22}K_{12}f_{12})^{1/2}$ [d]	0.94	1.00	0.40

[a] Multiplied by 10^{15} cm^{-1}. [b] Multiplied by 10^6 cm^{-1}. [c] Multiplied by 10^7 cm^{-1}. [d] Cf. eq 17. Rate constants are from Table IV. k_{11}, k_{22}, and k_{12} are the rate constants for the preceding three reactions, in the order listed.

For the complete hexaamminecobalt system consisting of all the frequencies listed in Table I ($\Delta Q_i = 0$ for the E_g and F modes), the direct sum was found to require excessive computation time, so only the saddle-point value of the Franck–Condon sum was calculated. Assuming that it is reliable, we find (cf. Table II) $G(Co)/G(Ru) \approx 10^{-8}$, in agreement with the saddle-point method value in ref 5.

Also listed in Table II are values of G calculated by using the two-frequency quantum solvent model described earlier and analogous values calculated by assuming wholly classical solvent interaction. As expected, the classical solvent model yields a slightly smaller value of G (less nuclear tunneling). The effect is small, about 10% in the systems considered.

Hexaaquoiron(II/III) Self-Exchange Reaction. Like the hexaamminecobalt self-exchange reaction, the hexaaquoiron self-exchange reaction proceeds with a large internal reorganization energy involving the metal–ligand internal modes. Using metal–oxygen symmetric stretching frequencies in the ferric and ferrous ions of roughly 490 and 389 cm^{-1}, respectively,[2] and a change in equilibrium bond length of 0.14 Å,[36] we calculated the internal reorganization energy to be 35 kJ/mol, when an effective single frequency of 431 cm^{-1}, based on eq 9, is used. The outer-sphere reorganization energy has been estimated as 27 kJ/mol.[2]

It has been suggested that in a system like this one, in which a high-frequency mode undergoes a significant bond length change, quantum effects should be large. But calculation of the sum over Franck–Condon factors yields a quantum value of about 3.5 times the classical value (cf. Table III). Thus, as in the hexaamminecobalt self-exchange reaction, no very large quantum effect on the Franck–Condon sum is observed. Indeed, the discrepancy

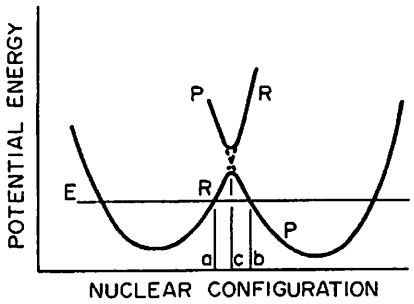

Figure 2. Curve similar to Figure 1, but for a nearly thermoneutral reaction ($\Delta E \simeq 0$). Points a and b here are classical "turning points" of motion on the reactants' and products' potential energy curves, for the given energy E. Point c is at the intersection of the two potential energy surfaces. The actual nuclear tunneling distance is ab (Cf. ref 26).

Table IV. Rate Constants For Hexaaquoiron and Tris(bipyridyl)ruthenium Self-Exchange and Cross-Reactions[a]

reaction	k_{calcd} (quantum)	k_{calcd} (classical)	k_{obsd}
Fe^{2+}–Fe^{3+}	6.3	1.7	4.2[41]
$Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$	4.9×10^8	4.6×10^8	1.2×10^9 [42]
Fe^{2+}–$Ru(bpy)_3^{3+}$	1.4×10^8	8.4×10^7	7×10^5 [43,44]

[a] Units are M^{-1} s^{-1}.

is smaller than the other uncertainties in the overall calculation of the reaction rates, and the quantum expression is more complex (cf. the cancellation of terms in the classical expression, leading to the simple cross-relation expression[21] given below).

The "semiclassical" result in Table III is seen to be in large error. It was shown in ref 26 that the semiclassical method corresponds, tacitly, to assuming that the nuclear tunneling distance along the abscissa is ac in Figure 2, whereas it is actually ab. This assumption is valid only when the products' curve at the intersection is very steep, for then point $b \simeq$ point c, and so is valid when ΔE is quite negative. Identical remarks apply to the reverse reaction when $-\Delta E$ is quite negative and hence, by microscopic reversibility, to the forward reaction when ΔE for the forward reaction is quite positive. For $\Delta E \simeq 0$ one concludes, since $ac \ll ab$, that the "semiclassical" tunneling rate will exceed the quantum one,[26] a result confirmed in Table III (Fe^{2+}–Fe^{3+}). Related remarks apply to use of the semiclassical result in the so-called inverted region ($|\Delta E| \gg \lambda$), only now the semiclassical answer is too low, for now it was shown[26] the actual nuclear tunneling distance is less than the tacitly assumed one.[26]

Cross-Reactions. Quantum effects on the classical cross-relation[37] are found below to be relatively small, in the "normal" $\Delta G°$ regime. In this relation, the rate constant k_{12} of

$$A_1(ox) + A_2(red) \rightarrow A_1(red) + A_2(ox) \qquad (14)$$

is related to those (k_{11}, k_{22}) of the self-exchange reactions (15) and (16) when the work terms are either small or nearly cancel,

$$A_1(ox) + A_1(red) \rightarrow A_1(red) + A_1(ox) \qquad (15)$$

$$A_2(ox) + A_2(red) \rightarrow A_2(red) + A_2(ox) \qquad (16)$$

via eq 17,[21] where K_{12} is the equilibrium constant of reaction 14

$$k_{12} \simeq (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (17)$$

and f_{12} is given by eq 18, where Z is the collision frequency in

$$\ln f_{12} = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)] \qquad (18)$$

solution. Expressed in terms of the classical G's, this expression can be rewritten as eq 19, where

$$\bar{G}_{12} = (\bar{G}_{11}\bar{G}_{22}K_{12}\bar{f}_{12})^{1/2} \qquad (19)$$

(36) N. Hair and J. Beattie, *Inorg. Chem.*, 16, 245 (1977).

(37) R. A. Marcus, *J. Phys. Chem.*, 67, 853, 2889 (1963).

$$\ln \bar{f}_{12} = (\ln K_{12})^2/[4 \ln (\bar{G}_{11}\bar{G}_{22})] \quad (20)$$

$$\bar{G}_{ij} = (4\pi\lambda_{ij}kT)^{1/2}G_{ij} \quad (21)$$

The classical results in Tables III and IV are those for a classical adiabatic result

$$k_{ij} = Z\bar{G}_{ij} \quad (22)$$

where Z is defined above (and is taken to be 10^{11} M^{-1} s^{-1} [21,27]). Equation 22 is valid when work terms for formation of the precursor and successor complexes are neglected and when nonadiabaticity is negligible. To assess a quantum correction, we obtained the "quantum results" in Tables III and IV by using eq 21 and 22 but with the G_{ij} in eq 21 replaced by its quantum value. The "semiclassical" values in Table III were calculated by introducing the semiclassical value of G_{ij} into eq 21 and 22. From the results of Table III for the cross-reaction

$$Fe^{2+} + Ru(bpy)_3^{3+} \rightarrow Fe^{3+} + Ru(bpy)_3^{2+} \quad (23)$$

one can see that the quantum effect on the calculated cross-reaction rate (eq 17) is only a factor of 2 for reaction 23. The quantum effect on the cross-relation, i.e., on the ratio of the left- to the right-hand side in eq 17, is calculated to be a factor of 0.94.

In obtaining these results, the inner- and outer-sphere reorganization energies for the $Ru(bpy)_3^{2+/3+}$ self-exchange reaction were taken from ref 2: $\lambda_{inner} \simeq 0$ and $^1/_4\,\lambda_{out} \simeq 13.4$ kJ/mol. The reorganization energies for the $Fe^{2+/3+}$ self-exchange are given above. The inner- and outer-sphere reorganization energies for reaction 23 were then estimated from the additivity rule[27] to be 17.6 and 20.1 kJ/mol, respectively. To allow direct comparison between the quantum and classical results, we employed the effective frequency 431 cm^{-1} for the $Fe^{2+/3+}$ symmetric stretch, according to the rule for effective force constants given by eq 9. The free energy of reaction for reaction 23 is readily calculated to be −47.3 kJ/mol from the reduction potentials of $Ru(bpy)_3^{3+}$ (1.26 eV[38-40]) and Fe^{3+}(aq) (0.770 eV[22]).

The calculated self-exchange rate constants in Table IV agree reasonably well with the measured rate constants. However, the calculated values of the rate constant for the cross-reaction differ from the experimental value by 2–3 orders of magnitude. Several explanations for the apparent failure of the theory to predict this particular cross-reaction rate, when it predicts many others so well, have been offered:[2,44,45] (1) large differences in the stability of the precursor and successor complexes, (2) nonadiabaticity, and (3) nuclear tunneling. Since the quantum and classical calculated rate constants are in good agreement, the third suggestion, nuclear tunneling, can now be eliminated, so that the discrepancy is probably due to 1 or 2.

Conclusion

We have shown that the Franck–Condon contributions to the rates of the hexaamminecobalt, hexaammineruthenium, and hexaaquoiron self-exchange reactions at 300 K can be reasonably well approximated by the classical expression (factors of 4.3, 1.2, and 3.5, respectively). These corrections are relatively minor, in view of the uncertainties in the various quantities involved in the rate expression. A nonadiabatic model was assumed, but analogous results would be expected for an adiabatic model.

Also for these systems, we have seen by direct comparison with the exactly evaluated quantum sum of Franck–Condon terms that the saddle-point approximation is a very good approximation to the exact sum. The "semiclassical" approximation (eq 10) is a poor one for self-exchange reactions such as Fe^{2+}–Fe^{3+}.

The quantum effect on the cross-reaction relation (eq 17) for hexaaquoiron(II) with tribipyridylruthenium(III) is negligible (a factor of 0.94), since some cancellation of quantum effects occurs in the calculation of cross-reaction rates.

We conclude that a reasonable order of magnitude estimate for the contribution of configurational changes of high-frequency quantum modes in the first coordination layer, for typical metal–ligand frequencies, to the rate constant can be provided by a classical expression. Preexponential factors and activation energies are expected to be more sensitive to use of the classical approximation (they are to other approximations also) and will be discussed in a subsequent paper.

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Appendix

Harmonic Oscillator Overlap Integrals. The overlap integral $\langle n|m\rangle$ is given by eq A1, where f and X are described in the text,

$$\langle n|m\rangle = (-1)^{m+n}\left[2\sqrt{f}/(1+f)\right]^{1/2}(2^{m+n}m!n!)^{-1/2}e^{-Xf/(1+f)} \times [(1-f)/(1+f)]^{(m+n)/2}\sum_{l=0}^{\infty}\frac{m!n!}{l!(m-l)!(n-l)!} \times \left[4\sqrt{f}/(1-f)\right]^{l}F_{n-l}\left(f\sqrt{\frac{2X}{1-f^2}}\right)\mathcal{H}_{m-l}\left(\sqrt{\frac{2Xf}{1-f^2}}\right) \quad (A1)$$

for $f < 1$. $\mathcal{H}_n$ is the Hermite polynomial of order n, and $F_n(x) = i^nH_n(ix)$. (Eq A1 is given, for example, in ref 14 and 15 although with a few misprints.) For $f > 1$ one obtains for $\langle n|m\rangle$ an expression whose absolute value is the same as that of the right-hand side of eq A1.

For the case $X = 0$ and $f \neq 1$, eq A1 reduces to eq A2.[13]

$$\langle 2n|2m\rangle = \left[\frac{4f}{(1+f)^2}\right]^{1/4}\left(\frac{2n!2m!}{2^{2n+2m}}\right)^{1/2}(-1)^n\left(\frac{f-1}{f+1}\right)^{n+m} \times \sum_{l=0}^{\infty}\frac{(-1)^l}{2l!(n-l)!(m-l)!}\left[\frac{16f}{(f-1)^2}\right]^{l} \quad (A2)$$

$$\langle 2n+1|2m+1\rangle = \left[\frac{4f}{(1+f)^2}\right]^{3/4}\left[\frac{(2n+1)!(2m+1)!}{2^{2n+2m}}\right]^{1/2}(-1)^n\left(\frac{f-1}{f+1}\right)^{n+m} \times \sum_{l=0}^{\infty}\frac{(-1)^l}{(2l+1)!(n-l)!(m-l)!}\left[\frac{16f}{(f-1)^2}\right]^{l}$$

$$\langle 2n|2m+1\rangle = \langle 2n+1|2m\rangle = 0$$

The sums in eq A1 and A2 are only formally infinite; they are actually terminated by the factorials in the denominators of the terms of the sums when l exceeds either m or n.

Generating Function for the Saddle-Point Approximation. $f(t)$ (eq 5 and 6) is found (using methods in ref 23 and 24) to be given by

$$f(t) = -\sum_{j=1}^{N}\tfrac{1}{2}\ln\left[\sinh 2\beta_j \sinh 2\alpha_j(\omega_j \tanh\beta_j + \omega_j' \tanh\alpha_j) \times (\omega_j \coth\beta_j + \omega_j' \coth\alpha_j)/(\omega_j\omega_j')\right] + 2\lambda_j\omega_j'/(\hbar\omega_j)/(\omega_j \coth\alpha_j + \omega_j' \coth\beta_j)] \quad (A3)$$

The second derivative of $f(t)$ is

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(46) E. A. Moelwyn-Hughes, "Physical Chemistry", 2nd ed., Pergamon Press, New York, 1961, pp 347, 352.

$$f''(t) = -\tfrac{1}{2}\hbar^2\sum_{j=1}^{N}\{\omega_j^2\,\mathrm{csch}^2\,2\beta_j + \omega_j'^2\,\mathrm{csch}^2\,2\alpha_j + \frac{\omega_j'^3\,\mathrm{sech}^3\,\alpha_j\sinh\alpha_j + \omega_j^3\,\mathrm{sech}^3\,\beta_j\sinh\beta_j}{2(\omega_j\tanh\beta_j + \omega_j'\tanh\alpha_j)} + \frac{(\omega_j^2\,\mathrm{sech}^2\,\beta_j - \omega_j'^2\,\mathrm{sech}^2\,\alpha_j)^2}{4(\omega_j\tanh\beta_j + \omega_j'\tanh\alpha_j)^2} + \frac{(\omega_j'^2\,\mathrm{csch}^2\,\alpha_j - \omega_j^2\,\mathrm{csch}^2\,\beta_j)^2}{4(\omega_j\coth\beta_j + \omega_j'\coth\alpha_j)^2} - \frac{\omega_j'^3\,\mathrm{csch}^3\,\alpha_j\cosh\alpha_j + \omega_j^3\,\mathrm{csch}^3\,\beta_j\cosh\beta_j}{2(\omega_j\coth\beta_j + \omega_j'\coth\alpha_j)} + \frac{2\lambda_j\omega_j'^2(\omega_j'\,\mathrm{csch}^3\,\alpha_j\cosh\alpha_j + \omega_j\,\mathrm{csch}^3\,\beta_j\cosh\beta_j)}{\hbar(\omega_j\coth\alpha_j + \omega_j'\coth\beta_j)^2} - \frac{2\lambda_j\omega_j'^3\omega_j\,(\mathrm{csch}^2\,\alpha_j - \mathrm{csch}^2\,\beta_j)^2}{\hbar(\omega_j\coth\alpha_j + \omega_j'\coth\beta_j)^3}\} \quad \text{(A4)}$$

where N is the number of harmonic modes in the system

$$\beta_j = \tfrac{1}{2}\hbar\omega_j\left(\frac{1}{kt} - it\right) \qquad \text{(A5)}$$
$$\alpha_j = \tfrac{1}{2}\,i\hbar\omega_j't, \quad \lambda_j = \tfrac{1}{2}\omega_j^2(\Delta Q_j)^2$$

and ω_j, ω_j', and ΔQ_j are defined in the text. t_0 is the saddle-point value of t, i.e., t such that

$$0 = f'(t) = \tfrac{1}{2}\,i\hbar\sum_{j=1}^{N}\left\{\omega_j\coth 2\beta_j - \omega_j'\coth 2\alpha_j + \frac{\omega_j^2\,\mathrm{sech}^2\,\beta_j - \omega_j'^2\mathrm{sech}^2\,\alpha_j}{2(\omega_j\tanh\beta_j + \omega_j'\tanh\alpha_j)} + \frac{\omega_j'^2\,\mathrm{csch}^2\,\alpha_j - \omega_j^2\,\mathrm{csch}^2\,\beta_j}{2(\omega_j\coth\beta_j + \omega_j'\coth\alpha_j)} - \frac{2\lambda_j\omega_j'^2(\mathrm{csch}^2\,\alpha_j - \mathrm{csch}^2\,\beta_j)}{\hbar(\omega_j\coth\alpha_j + \omega_j'\coth\beta_j)^2}\right\} \quad \text{(A6)}$$

"Semiclassical" Franck–Condon sum. The "semiclassical" Franck–Condon sum (eq 10) may be derived from eq 1, the golden-rule expression for the Franck–Condon sum, using techniques originally applied to other problems.[29] Consider first the case in which a single normal vibrational mode, of frequency ω, normal-mode force constant $k = \omega^2$, and normal coordinate q, characterizes both the reactants and the products. The reactant Hamiltonian is

$$\mathcal{H}_r = p^2/2 + kq^2/2 \qquad \text{(A7)}$$

The products' Hamiltonian, in which the equilibrium value of q is displaced by an amount a, is

$$\mathcal{H}_p = p^2/2 + \tfrac{1}{2}\,k(q-a)^2 + \Delta E \qquad \text{(A8)}$$

where ΔE is the reaction endoergicity. Equation 1 gives

$$G = (hQ)^{-1}\sum_n e^{-(n+1/2)\hbar\omega/kT}\int_{-\infty}^{\infty}\sum_m \langle n|m\rangle\langle m|n\rangle\; e^{i(E_m-E_n)t/\hbar}\,dt \qquad \text{(A9)}$$

where the Fourier integral representation of the δ function has been introduced. Inserting the exponential in the coordinate integral and noting that the wave functions corresponding to $|n\rangle$ and $|m\rangle$, χ_n and χ_m are eigenfunctions of $\mathcal{H}_r$ and $\mathcal{H}_p$, respectively, one obtains

$$G = (hQ)^{-1}\sum_n e^{-(n+1/2)\hbar\omega/kT}\int_{-\infty}^{\infty}\sum_m \langle n|m\rangle\langle m|e^{i\mathcal{H}_p t/\hbar}e^{-i\mathcal{H}_r t/\hbar}|n\rangle\,dt \qquad \text{(A10)}$$

If all commutators of $\mathcal{H}_r$ and $\mathcal{H}_p$ are neglected, which is the semiclassical approximation in this approach, then[29a]

$$e^{i\mathcal{H}_p t/\hbar}e^{-i\mathcal{H}_r t/\hbar} = e^{i(\mathcal{H}_p-\mathcal{H}_r)t/\hbar} \qquad \text{(A11)}$$

From eq A7 and A8 it is found that $\mathcal{H}_p - \mathcal{H}_r = -ka(q - \tfrac{1}{2}a - \Delta E/ka)$, so eq A10 becomes

$$G = (hQ)^{-1}\sum_n e^{-(n+1/2)\hbar\omega/kT}\int_{-\infty}^{\infty}\langle n|e^{-itka(q-1/2a-\Delta E/ka)}|n\rangle\,dt \qquad \text{(A12)}$$

where use has been made of the identity $\sum_m|m\rangle\langle m| = 1$. Equation A12 may be rewritten as

$$G = (ka\hbar Q)^{-1}\sum_n e^{-(n+1/2)\hbar\omega/kT}\langle n|\delta(q - \tfrac{1}{2}a - \Delta E/ka)|n\rangle \qquad \text{(A13)}$$

or simply

$$G = (ka\hbar Q)^{-1}\sum_n e^{-(n+1/2)\hbar\omega/kT}|\chi_n(q^*)|^2 \qquad \text{(A14)}$$

where $q^* = \tfrac{1}{2}a + \Delta E/ka$ is the value of q for which the reactant and product potential energies are equal. According to Mehler's formula,[23] the sum in eq A14 may be reduced to the single term

$$G = (2\pi\lambda\hbar\omega\coth\gamma)^{-1/2}\exp[-(\Delta E + \lambda)^2/2\lambda\hbar\omega\coth\gamma] \qquad \text{(A15)}$$

where $\gamma \equiv \hbar\omega/2kT$ and $\lambda \equiv \tfrac{1}{2}ka^2$, and we have used $Q = [2\sinh(\hbar\omega(2kT)]^{-1}$.[46]

Consider now a system having N normal vibrational modes, each characterized by a frequency ω_j and normal-mode force constant $k_j = \omega_j^2$. Let a_j be the difference between the equilibrium values of the jth normal coordinate in the product and reactant. Define $\lambda_j = \tfrac{1}{2}k_j a_j^2$ and $\gamma_j = \hbar\omega_j/2kT$. $G_j(\Delta E)$ is given by eq A15 for each mode individually. $G(\Delta E)$ for the N-mode system, where ΔE is again the reaction endoergicity, is a convolution of the G_j's ($j = 1, 2, \ldots, N$). That is

$$G(\Delta E) = \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}G_1(y_1)\ldots G_{N-1}(y_{N-1})G_N(\Delta E - \sum_{j=1}^{N-1}y_j)\,dy_1\ldots dy_{N-1} \qquad \text{(A16)}$$

Note that each $G_j(y)$ is a Gaussian distribution in y. G(ΔE) is a convolution of the gaussians G_j. Therefore $G(\Delta E)$ is itself a Gaussian distribution and has a mean equal to the sum of the means of the G_j and variance equal to the sum of the variances of the G_j.[47] Thus $G(\Delta E)$ for an N-mode system is given by eq A15, but with $\lambda = \sum_{j=1}^{N}\lambda_j$ and $\lambda\hbar\omega\coth\gamma = \sum_{j=1}^{N}\lambda_j\hbar\omega_j\coth\gamma_j$. Explicitly

$$G = (2\pi\sum_{j=1}^{N}\lambda_j\hbar\omega_j\coth\gamma_j)^{-1/2}\exp[-(\Delta E + \sum_{j=1}^{N}\lambda_j)^2/(2\sum_{j=1}^{N}\lambda_j\hbar\omega_j\coth\gamma_j)] \qquad \text{(A17)}$$

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