PHYSICOCHEMICAL HYDRODYNAMICS

V. G. Levich Festschrift

VOLUME I

EDITED BY

D. BRIAN SPALDING

Imperial College of Science and Technology, London

ADVANCE PUBLICATIONS LIMITED

THEORIES OF ELECTRODE KINETICS

R. A. Marcus

Department of Chemistry
University of Illinois
Urbana, Illinois

ABSTRACT

The present lecture consists of two parts. In the first, a comparison is made of theory and experiment for simple electron transfer reactions in solution and at electrodes, reactions for which no bonds are broken or formed. The data are numerous and were recently reviewed in part elsewhere.

The main part of the lecture is concerned with electrode reactions involving the breaking and forming of chemical bonds and principally with the hydronium ion discharge reaction, $H_3O^+ + M(e) \rightarrow H_2O + H\text{-}M(ads.)$. The treatment of this reaction has been the subject of some controversy (cf. 1965 Faraday Discussions on Proton Transfer and more recent literature). To provide further insight, a more dynamical theory of this elementary step for general potential energy surfaces is described. It is then shown how, depending on the nature of the potential energy surface, the theory leads to various approaches in the literature. For example, depending on the surface, the system may or may not for dynamical reasons be able to reach sufficiently easily the saddle-point region or, again, Franck-Condon solvation effects may or may not contribute to the rate. There is a clear need for the application of recent theoretical methods of electronic structure to determine the essential features of the potential energy surface.

The abstract on p. 443 refers to this paper.

ELECTRON TRANSFER REACTIONS

Having recently reviewed the principal features of the theory of simple electron transfer reactions (those without bond rupture or bond formation) [1], I shall, in the interests of brevity, call attention to that article and to several other reviews [2,3]. The notable contributions of Levich and coworkers [3], particularly on the quantum aspects of these electron transfers are well known. Recently, his ideas have appeared in related approaches for understanding the temperature dependence of electron transfers at very low temperatures [4] and the behavior of highly exothermic reactions, where the process may occur in the so-called inverted region [5].

Theory and experiment in electron transfer reactions have had a very fortunate marriage during the past two decades [1]. Numerous comparisons, correlations, and predictions have been possible. A major role in the theory has been played by the Franck-Condon principle [6]: The electron transfers so rapidly that the other coordinates do not have time to change their values during this instantaneous act. Thereby, it was shown [7], their distribution must be reorganized before the electronic transition, if the latter is to occur, as well as after. The relation between this concept and the role of two intersecting potential energy surfaces in facilitating the electron transfer has been described [8].

These simple electron transfer reactions involve no breaking or forming of chemical bonds. Among other things we consider in this paper the question of when do analogous Franck-Condon considerations apply to proton transfers.

HYDROGEN ION DISCHARGE REACTION

We consider a particular electrode reaction in which a bond is ruptured and one is formed and which has been the subject of considerable attention, the hydrogen ion discharge reaction at the interface between a solution and a metal electrode M. Related remarks apply to proton transfer reactions in solution. A mechanism for the reaction is given by Eqs. (1)-(3), and we shall focus attention on the first step (1):

$$H_3O^+ + M(e) \rightarrow H_2O + H\text{-}M \qquad (1)$$

$$H_3O^+ + H\text{-}M(e) \rightarrow H_2O + H_2 + M \qquad (2)$$

$$2H\text{-}M \rightarrow H_2 + M \qquad (3)$$

The reaction, step (1) for example, has been treated from two very different points of view [9-14]. One view, used nowadays particularly by Bockris, by Conway, and their coworkers [10-14], is an application of transition state theory [14], wherein one calculates or assumes some potential energy surface, decides on the transition state and calculates the rate. The transition state is typically assumed to be a hypersurface passing through a saddle-point in the potential energy surface or to lie at the intersection of a potential energy surface for reactants with one for products. A second view, due to Levich and coworkers [9,10], is to assume that the individual or collective motions of the reactants and those of the products and the solvent medium can be treated as harmonic oscillators, and then use first-order perturbation theory (Fermi's Golden Rule) or other methods to calculate the reaction rate.

The relation between these two approaches can be seen with the aid of a suitable potential energy diagram, which will also serve to formulate an approach, described later, which in a sense encompasses both. Initially, we focus attention on two coordinates, the O-H distance and the O-Metal distance, and plot the potential energy of the system versus these two coordinates. Treating for the moment the H_2O-H-M as a linear three-center complex, one can introduce the usual skewed axes diagram [15] for three-center reactions, here H_2O, H and M, with a scaled O-M distance between the nearest metal atom and the center of mass of H_3O as abscissa and a scaled distance between H and the center of mass of H_2O as ordinate. The scaling parameters and skewing angle are the usual functions of the three masses (i.e., of H_2O, H, and M), and the kinetic energy then has the same effective mass for both scaled coordinates [15]. Such a plot is given in Fig. 1 for the case where the reaction is nearly thermoneutral.

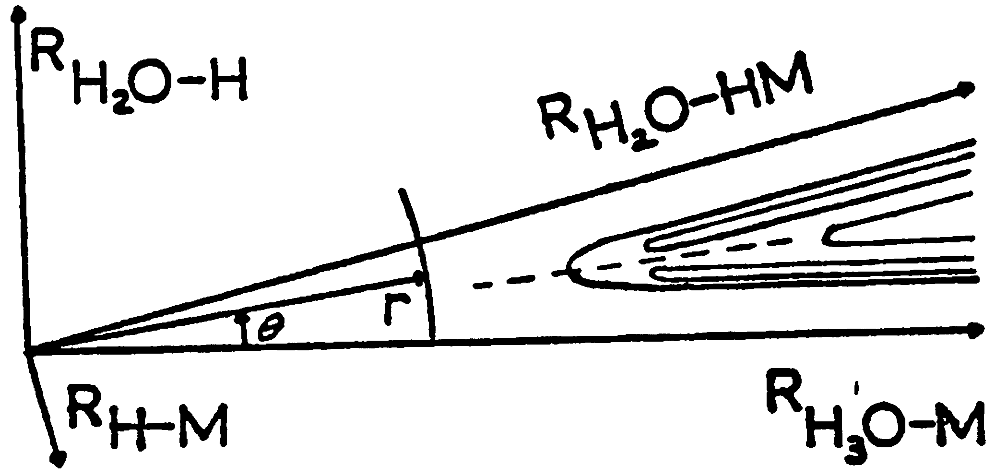

Fig. 1 Potential energy contour plot (schematic) for the three center reaction H_2O-H-M at a fixed value of the other coordinates q and at a given metal-solution potential difference. The mass of H_2O is taken as concentrated on the O, and the mass of M as infinite. The rotated axes are scaled H_2O-HM and H-M distances, again with the H_2O mass centered on the O. Polar coordinates r and θ are also indicated. The configurations along the dashed line form the conventional transition state.

Introducing polar coordinates (r,θ) with the apex of the triangle as origin, the r-motion corresponds to an O-M motion and the θ-motion to the transfer of the proton between O and M. A profile of the potential energy versus $r\theta$ at fixed r is given in Fig. 2 (solid curve). In addition, the potential energy is a function of all other coordinates q, including the various orientations of the solvent molecules that solvate the three-center system. Fig. 2 is for a given q. As r decreases, the barrier height separating the two wells usually decreases, and at small enough r the double well merges into a single well.

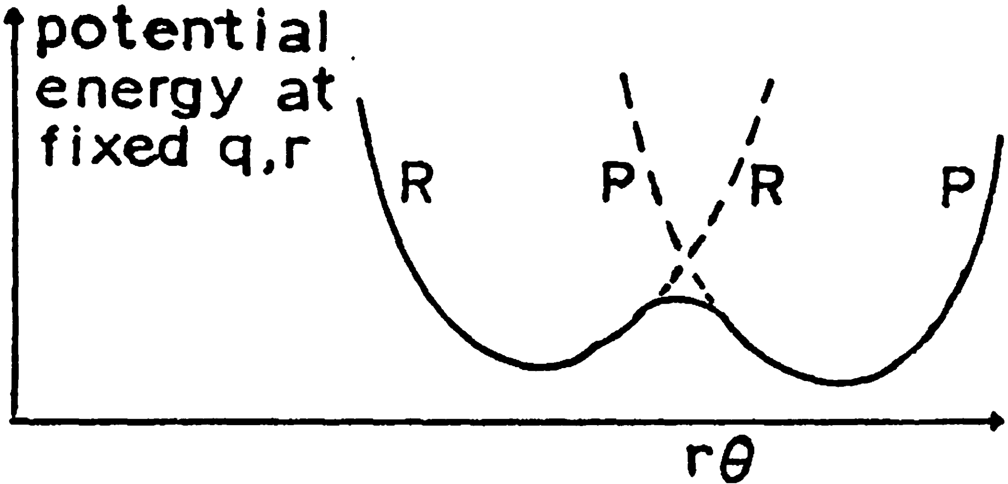

Fig. 2 Solid line: Profile of the potential energy V, in Fig. 1, at fixed r and q, versus the protonic distance coordinate rq. Dashed lines: a two electronic state ("weak overlap") model of this profile with one curve for reactants R and the other for products P.

The difference in potential energy of the minima of two wells in Fig. 2 depends on the electrode-solution potential difference, and, so, thereby, do the barrier in Fig. 2 and the reaction rate.

Fig. 1 depicts a potential energy surface for a roughly thermoneutral reaction. For a highly exothermic reaction the surface resembles instead that in Fig. 3.

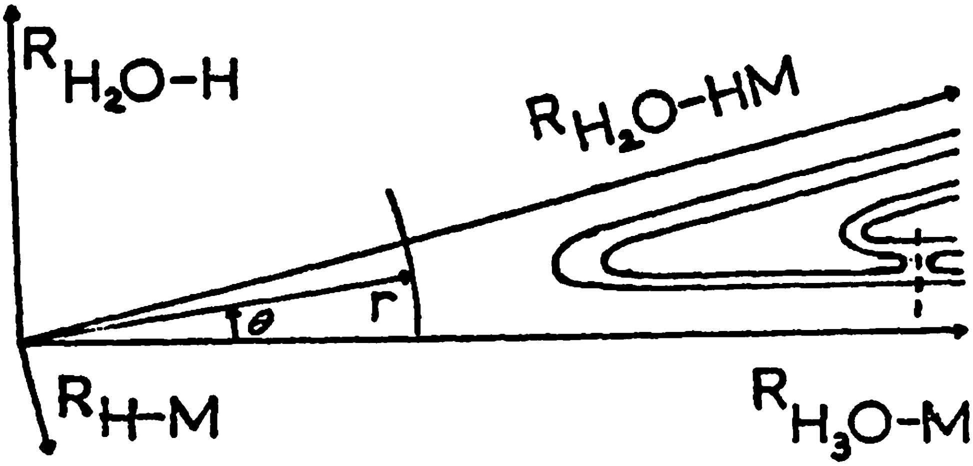

Fig. 3 Legend as in Fig. 1, but the reaction is now highly exothermic. The dashed line again denotes the transition state.

We can now summarize the two approaches:

(1) Transition State Theory

. Here, one typically expands the potential energy quadratically in the vicinity of the saddle-point of the potential energy surface and uses the local frequencies to calculate the partition function and (tunneling) transmission coefficient, for use in the transition state expression for the rate [15].

In the case of a highly exothermic reaction the transition state is in the reactants' channel, as in Fig. 3. In the case of a highly endothermic reaction the transition state is, correspondingly, in the exit channel. In both cases the reaction coordinate in the vicinity of the transition state is seen to be the O-M distance r whereas in the more nearly thermoneutral case in Fig. I the reaction coordinate in the vicinity of the transition state was a proton vibrational coordinate θ.

Franck-Condon effects on solvation, if any, are omitted in the usual [15] transition state approach. The free energy difference between the transition state and the reactants $\Delta G^{\ddagger}$ is computed and from it the reaction rate: Examples of the application are given in [10-14].

(2) Radiationless Transition Theory (Levich and coworkers)

The second theory [9,10] parallels that used for radiationless transitions between two electronic states. The surface in Figs. I and 3 for reaction (I) is an electronically-adiabatic one. One can imagine instead surfaces, corresponding to two electronic states as in Fig. 2 (dashed lines), in one of which the proton is localized in the reactants' channel, i.e., is close to the O, and in the other of which it is localized in the products' channel, and so is close to the M. Each localized state has a series of protonic vibrational energy levels. (The presence of a perturbation forms from the two localized electronic states two other electronic states, of which the lower energy one has a double well solid curve profile of Fig. 2.)

Initially, the system (at $r = \infty$) is in one of these localized electronic-protonic quantum states. The reaction probability is calculated at any given r using Fermi's Golden Rule and the above perturbation [9,10]. One takes into account the vibrational overlap integrals of the two localized protonic states just described and also of the solvation states associated with each of those two protonic states. The appropriate r for this calculation would be determined by some optimizing procedure.

We also consider a third approach, one proposed here.

(3) A Unified Approach

(a) General considerations

A detailed theory for reaction (I) should take into account (i) the shape of the actual potential energy surface, (ii) an appropriate method, dynamical where necessary, for defining a "transition state," and (iii) a method for handling the Franck-Condon effect, if any, on the coordinates q.

A suitable ab initio potential energy surface or, in the absence of that, a semiempirical surface such as BEBO, serves to capture at least the qualitative features of (i). In the case of (ii) the analysis should include the effect of any large zero-point or higher O-H vibrational energy $E_n(r)$ in the reactants' channel. If $E_n(r)$ exceeds the barrier in Fig. 2 at some $r > r_{\text{saddle-point}}$, the H will transfer before the saddle-point region is reached. We sketch in the next section a method for determining a typical r at which the proton transfer occurs and for determining dynamically a "transition state".

Item (iii) is considered next, namely, any Franck-Condon effect for the solvation coordinates q. When the proton moves from the reactants' to the products' channel, either near the saddle-point or at a larger r (for the vibrational energy reason just cited), it moves so rapidly because of its small mass that neither r nor q nor their conjugate momenta change appreciably during that protonic motion. For this reason a Franck-Condon principle applies to a proton jump, just as it did in electron transfer reactions, though less rigorously now.

The charge distributions of the two channels are quite different but tend to approach each other when the two channels merge, e.g., in Fig. 1 at the r corresponding to the saddle-point region. One can make an estimate of the difference of the charge distributions in two channels and, thereby, at the most probable value of r for proton transfer. A Franck-Condon reorganization is needed when the proton jumps between well-separated channels. One can then apply solvent reorganization considerations analogous to those used earlier for electron transfer calculations [1-10]. No solvent reorganization of this type is needed for transfer at r's where the channels merge, for the channels' charge distributions are then similar.

The effect of a "jump" in Fig. 1 at small r is, incidentally, expected to be smaller for proton than for electron transfers, since in the former case the jump is probably usually a very short one (e.g., ~0.5Å) while in the electron transfer case the electron "jump" between charge centers which are of the order of 5 to 10 Å apart (typical ionic diameters of complex ions).

In the case of a highly exothermic reaction (Fig. 3) depending on whether the system passes through the saddle-point region or whether the proton jumps at a larger r (because of a large $E_n(r)$, say) theory (1) or theory (2) is the more applicable. Analogous remarks apply, by microscopic reversibility, for the highly endothermic reaction. If the system does pass through the saddle-point region in the case of Fig. 3, any details of a subsequent (exothermic) or prior (endothermic) proton jump are no longer relevant to the calculation of the reaction rate, and conventional transition state theory should again suffice.

(b) Dynamical Considerations

To treat the dynamical question of finding the r where most of the proton transfer occurs the present unified theory would make use of dynamics' formalism [16-18] of semiclassical theory, and can use physically-based approximations to simplify the dynamics. The system is originally in a quantum state of reactants whose totality of quantum numbers is denoted by n and proceeds to a products' quantum state m. The transition probability is the square of an S-matrix element S_{mn}. It is computed [16-18] using classical trajectories leading to products, beginning in state n and with all possible initial vibrational phases of the motion. Whenever tunneling occurs, the trajectories become complex-valued rather than remaining real-valued [16-18], and make $|S_{mn}|^2$ exponentially small.

A dynamical approximation which could be adopted (to replace detailed trajectory calculations) is that (a) the protonic oscillation remains vibrationally-adiabatic [19] as long as the trajectory remains in the entrance channel (i.e., the O-H vibration remains in state n), (b) when each trajectory (tunneling when necessary) crosses from the entrance channel to the exit one it does so essentially at a fixed r because of the rapidity of the protonic motion, and (c) thereafter the protonic oscillation again remains vibrationally-adiabatic but now in the exit channel (i.e., the H-M vibration is present in some final state $\bar{n}$). The classical mechanical analog of a quantum number n, it will be recalled, is the action variable J [19], related to it by the Bohr-Sommerfeld quantization rule, e.g., $J = (n + 1/2)h$ for a vibration. Constancy of n means, classically, constancy of J. Classical adiabaticity is discussed in [19].

Each initial phase w_0 of the proton motion will determine the value of r where the H will strike the barrier in Fig. 2. Typically, the system will penetrate the entrance channel as far as it can or until the localized protonic vibrational energy $E_n(r)$ exceeds the barrier at some r in Fig. 2. In the former instance it may reach the products' channel without tunneling or by tunneling at its last contact with the θ-barrier, for the θ-barrier is thinner and smaller there.

DISCUSSION

The preceding discussion can be used to compare approaches (1) and (2) with each other and with (3). Some differences in (1) and (2) are:

(i) The transfer in theory (1), in the case of Fig. 1, occurs in a saddle-point region, usually, at small r. The transfer in theory (2), based a zeroth order pair of harmonic oscillators treatment plus a first-order perturbation formalism, is appropriate instead at sufficiently large r. (Cf dashed lines in Fig. 2.)

(ii) Since the transfer in theory (1), in the case of Fig. 1, occurs at an r where the wells and hence the charge distributions of the localized states have merged, no solvent reorganization of the Franck-Condon type is needed. In Fig. 3, since the reaction coordinate in theory (1) is the O-H distance any Franck-Condon reorganization is irrelevant. In constrast, in theory (2) the proton jump is always rate-determining and occurs at large r where there is a substantial separation of the wells and, thereby, a substantial difference of the charge distributions. The resulting Franck-Condon solvent reorganization in theory (2) can be treated either in a classical mechanical description [1] or, via Franck-Condon overlap integrals of the collective solvent vibrational wave functions, quantum mechanically [3].

(iii) The dynamics of the actual proton transfer is treated differently in theories (1) and (2), usually being that of a classical or a tunneling motion in the vicinity of the saddle-point in theory (1) and involving overlap integrals and first-order perturbation theory in theory (2).

Both approaches represent, in a sense, two limiting forms of the unified theory.

Involved in the existing controversy was another approach [11] in which free energy for the reactants at a fixed OH distance was plotted versus a proton coordinate [11]. The free energy of the products was also plotted. The transition state was assumed to lie at the intersection of the two free energy curves. However, the q-distribution tacitly assumed for the reactants' plot was the equilibrium one appropriate to the reactants' charges, while that for the products' plot was a different equilibrium one appropriate to the products charges. Potential energy plots should be made instead, and at the same q-distribution for both curves, as discussed elsewhere for homogenous electron transfers [20]; any intersection of free energy plots and the resulting discussion is thereby misleading. The Franck-Condon q-reorganization at large r described in the preceding section was thereby omitted. Also not included was the energy needed for penetrating an intervening water molecule by transferring H^+ at large r's (~3.5 Å) or, if a cavity was present, the energy of first creating a cavity.

CONCLUDING REMARKS

During the course of the above discussion we have attempted to answer a question which has frequently been raised. Does the Franck-Condon principle play the same role in proton transfers that it does in electron transfers? When there is a jump between two distinct wells, the jump is so quick that the solvation appropriate to the first well in Fig. 2 does not have time to adjust to the proton jump into the second well. In that case, there is a Franck-Condon reorganization of the solvation (the q-coordinates). A method was described for determining the r where the proton "jump" occurs. If it occurs at an r where the wells have merged the Franck-Condon effect vanishes. The Franck-Condon is also irrelevant in another case, which was described.

Several theories were compared, the source of their differences analyzed, and a "unified" theory outlined.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the support of this research by the Office of Naval Research.

REFERENCES

[1] Marcus, R. A. 1975. Electron Transfer in Homogeneous and Heterogeneous Systems, E. D. Goldberg, ed., Dahlem Konferenz on the Nature of Sea Water. Phys. Chem. Sci. Rept. 1, Abakon Verlag, Berlin. pp. 477-504; Marcus, R. A. Theory and Applications of Electron Transfers at Electrodes and in Solution, in "Special Topics in Electrochemistry", P. A. Rock, ed. (Elsevier, Amsterdam, 1977), p. 161.

[2] Schmidt, P. P. 1975. The Theory of Electron Transfer Reactions in Polar Media. Electrochemistry Spec. Period, Rep. 5:21-131.

[3] Levich, V. G. 1966. Present State of the Theory of Oxidation-Reduction in Solution (Bulk and Electrode Reactions). Adv. Electrochem. Electrochem. Eng. 4:249-371; Dogonadze, R. R. 1971. Theory of Molecular Electrode Kinetics. In Reactions of Molecules at Electrodes, ed. N. S. Hush, pp. 136-227. Wiley and Sons, New York.

[4] Hopfield, J. J. 1974. Electron Transfer Between Biological Molecules by Thermally Activated Tunneling. Proc. Nat. Acad. Sci. 71: 3630-3644; Jortner, J. 1976. Temperature Dependent Activation Energy for Electron Transfer Between Biological Molecules. J. Chem. Phys. 64: 4860-4867.

[5] Efrima, S., and Bixon, M. 1974. On the Role of Vibrational Excitation in Electron Transfer Reactions with Large Negative Free Energies. Chem. Phys. Lett. 25:34-37; Van Dyne, R. P., and Fischer, S. F. 1974. Nonadiabatic Description of Electron Transfer Reactions Involving Large Free Energy Changes. Chem. Phys. 5:183-197.

[6] W. F. Libby. 1952. Theory of Electron Exchange Reactions in Aqueous Solution. J. Phys. Chem. 56:863-868.

[7] Marcus, R. A. 1956. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. J. Chem. Phys. 24:966-978.

[8] Marcus, R. A. 1960. Theory of Oxidation-Reduction Reactions Involving Electron Transfer. Part IV. A Statistical-Mechanical Basis for Treating Contributions from Solvent, Ligands, and Inert Salt. Discussions Faraday Soc. 29:21-31; Marcus, R. A. 1965. On the Theory of Electron-Transfer Reactions. VI. Unified Treatment for Homogeneous and Electrode Reactions. J. Chem. Phys. 43:679-701.

[10] A recent review is given in Sen, R. K., Yeager, E. and O'Grady, W. E. 1975. Theory of Charge Transfer at Electrochemical Interfaces, Annu. Rev. Phys. Chem. 26:287-314.

[11] Matthews, D. B. and Bockris, J. O'M. The Mechanism of Charge Transfer from Metal Electrodes to Ions in Solution. Mod. Aspects Electrochem. 6 242-326; Bockris, J. O'M., Srinivasan, S. and Matthews, D. B. 1965. Proton Transfer Across Double Layers. Discuss. Faraday Soc. 39:239-252.

[12] Conway, B. E., and Solomon, M 1964. Isotope Effects in Electrochemical Proton Discharge, Bes. Bunsenges. Phys. Chem. 68:331-340; Solomon, M., Enke, C. and Conway, B. E. 1965. Some Aspects of the Energetics and Kinetics of Electrochemical Proton Transfer. J. Chem. Phys. 43:3989-3998; Solomon, M, and Conway, B. E. 1965. Classical and Quantum Mechanical Effects in Electrochemical Proton Discharge and the Kinetics at Low Temperatures. Discuss. Faraday Soc. 39:223-238.

[13] Christov, S. G. 1968. Some Aspects of the Theory of Proton Transfer Processes. J. Res. Inst. Catal. Hokkaido Univ. 16: 169-194.

[14] For recent reviews see Appleby, A. J. 1974. Electrocatalysis. Mod. Aspects Electrochem. 9: 369-478; Appleby, A. J., Bockris, J. O'M., Sen, R. V., and Conway, B. E. 1973. The Quantum Mechanical Model for Electronic Charge Transfer at Interfaces. MTP Internat. Rev. Sci., Phys. Chem. Series. Chap. 1, Butterworths, London. 6:1-40.

[15] Glasstone, S., Laidler, K. J., and Eyring, H. 1941. The Theory of Rate Process. McGraw-Hill, New York.

[16] Marcus, R. A. 1973. Semiclassical S-Matrix Theory. VI. Integral Expression and Transformation of Conventional Coordinates. J. Chem. Phys. 59:5135-5144, and references cited therein. cf. Marcus, R. A. 1970. Extension of the WKB Method to Wave Functions and Transition Probability Amplitudes (S-Matrix) for Inelastic or Reactive Collisions. Chem. Phys. Letters. 7:525-532.

[17] Miller, W. H. 1974. Classical S-Matrix in Molecular Collisions. Adv. Chem. Phys. 30:77-136, and references cited therein.

[18] Examples of application of the formalism, in the "stationary phase form" to reaction rates are given in the references cited below. [An example of an application in the "integral form" is given in Marcus, R. A., and Coltrin, M. E. 1977. A New Tunneling Path for Reactions such as $H+H_2 \rightarrow H_2+H$. J. Chem. Phys. 70:xxx.] Chapman, S., Garret, B. C., and Miller, W. H. 1975. Semiclassical Transition State Theory for Nonseparable Systems: Application to the Collinear $H+H_2$ Reaction. J. Chem. Phys. 63:2710-2716. Shuskin, A. I., and Ovchinnikova, M. Ya. 1975. Tunneling Effect in Proton Transfer Reactions. Theoret. Exp. Chem. (Engl. Transl.) 11:374-382; Stine, J. R. and Marcus, R. A. 1974. Semiclassical S-Matrix Theory for a Compound State Resonance in the Reactive Collinear $H+H_2$ Collision. Chem. Phys. Letters 29:575-579.

[19] Corben, H. C. and Stehle, P. 1964. Classical Mechanics. John Wiley, New York, Second ed.; M. Born, The Mechanics of the Atom. F. Ungar Publ. Co., New York, 1960; R. A. Marcus, On the Analytical Mechanics of Chemical Reactions. Classical Mechanics of Linear Collisions. 1966. J. Chem. Phys. 45:4500.

[20] Marcus, R. A., Chemical and Electrochemical Electron-Transfer Theory. 1964. Annu. Rev. Phys. Chem. 15:155-196.