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CLASSICAL S-MATRIX THEORY OF REACTIVE TUNNELING: LINEAR H + H_2 COLLISIONS*

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ABSTRACT

Complex-valued classical trajectories (computed by direct numerical integration of Hamilton's equations) are found for linear reaction collisions of H + H_2 → H_2 + H (on the Porter-Karplus potential surface) at collision energies for which all ordinary real trajectories are non-reactive, and from such trajectories classical S-matrix elements are constructed. This analytically continued classical-limit theory is seen to be an accurate description of reactive tunneling for the H + H_2 system. At each collision energy there is only one classical trajectory that contributes to the reaction, so that various features of the reaction dynamics are easily illucidated by looking specifically at this one trajectory. It is also shown how a Boltzmann average of the reaction probability can be carried out semiclassically, and this leads to an interesting relation between the imaginary part of the time increment of the complex-valued trajectory at a given energy and the absolute temperature at which this is the dominant energy in the Boltzmann average: $\mathrm{Im}(t_2-t_1) = -\frac{1}{2}\hbar/(kT)$. It is seen, for example, that for $T \lesssim 1000°K$ the dominant energy region is below the classical threshold, i.e., in the tunneling region.

I. INTRODUCTION

The utility of classical trajectory methods for describing the dynamics of molecular collisions (such as A + BC, the simplest non-trivial example) is well-known, reactive and non-reactive (energy transfer) processes having been studied[1]. The usefulness of a classical (as opposed to quantum) description lies in the fact that, given the intermolecular potential, the dynamics can then always be treated exactly (i.e., numerically) by integration of the classical equations of motion (e.g., Hamilton's equations). The shortcoming of such classical treatments is, of course, that real molecules obey quantum, not classical mechanics.

In the last few years, however, it has been shown[2-4], both formally and with specific examples, how numerically computed[5] classical trajectories for a complex collision system can be used semiclassically to construct the classical limit approximation to probability amplitudes for transitions between individual quantum states of the collision partners. Since classical mechanics is used to construct probability <u>amplitudes</u> (i.e., S-matrix elements) rather than probabilities themselves, the quantum superposition principle is properly incorporated in the theory, and it appears that this is often the chief contribution of quantum mechanics to the dynamics of molecular collisions; i.e., although quantum effects can be quite prominent, they are all essentially a consequence of quantum superposition.

A particularly interesting and important aspect of this "classical S-matrix" theory is the ability to extend (i.e., analytically continue) classical mechanics in such a way as to describe <u>classically forbidden</u>

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collision phenomena. By "classically forbidden" one does not mean that the transition is forbidden by any conservation law or selection rule, but simply that ordinary classical mechanics does not lead to the transition. The most familiar example of such a process is one-dimensional tunneling of a particle through a potential energy barrier, the WKB approximation for the tunneling being the analytic continuation of classical mechanics[6]. The importance of this aspect of classical S-matrix theory is due to the fact that thermal energy kinetic phenomena often have significant, and sometimes dominant contributions from classically forbidden transitions, and ordinary trajectory methods are obviously not capable of describing such processes. This is in contrast to the case of classically allowed processes for which ordinary trajectory methods give average collision properties quite well, with classical S-matrix theory primarily adding an oscillatory interference structure that is largely quenched out by any averaging over initial or final quantum states[7]. The ability to describe classically forbidden phenomena, therefore, may actually be the most important practical contribution of classical S-matrix theory.

Quite recently it has been shown[2f] how this analytic continuation of classical mechanics for systems with several degrees of freedom can actually be accomplished by direct numerical integration of the classical equations of motion through classically inaccessible regions of phase space; the coordinates and momenta, and the time also, become complex-valued for these analytically continued trajectories, but this is seen to be completely consistent with the semiclassical description. Application to linear non-reactive A + BC collisions (vibrational excitation) gave excellent agreement with exact quantum

mechanical transition probabilities, and there seemed to be no limit to the "forbiddenness" of a transition that could be accurately described.

This paper presents results of analytically continued classical S-matrix theory applied to linear reactive $H + H_2$ collisions below the classical threshold; i.e., complex-valued classical trajectories are found which go from $H + H_2$ to $H_2 + H$ at collision energies for which all ordinary (i.e., real) trajectories are non-reactive, and from such trajectories classical S-matrix elements are constructed[8]. Since the quantum nature of the $H + H_2$ reaction should be as prominent as for any chemical reaction, it is of considerable interest to see how well a semiclassical theory is able to describe it. It is collision energies in the vicinity of the classical threshold, too, that are most important for thermal energy kinetics and for which ordinary trajectory methods are poorest[9,10].

Section II first summarizes the general results of classical S-matrix theory as they pertain to the present system and discusses some of the details of how the appropriate complex-valued trajectories are found. In Section III it is shown how a Boltzmann average of the reaction probability over translational energy can be carried out semiclassically, and from this steepest descent approximation there emerges an interesting relation between the imaginary time increment of the trajectory and the temperature: $\mathrm{Im}(t_2-t_1) = -\frac{1}{2}\hbar\beta$, $\beta = (kT)^{-1}$. In the Appendix it is shown that this approximation for the temperature dependent reaction probability also has an interesting interpretation in terms of a transition state-like expression; i.e., it is possible to identify the imaginary part of the classical action with an "entropy of activation".

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Numerical results for the ground state to ground state reactive transition are presented and discussed in Section IV; agreement with quantum mechanical values calculated for this same Porter-Karplus[11] potential surface is seen to be quite good. Also interesting is the fact that there is just one complex-valued trajectory that contributes to the reaction at each energy and that it is symmetric about the symmetric H-H-H configuration; some of these trajectories are shown in Section IV for different collision energies.

It should be clear intuitively that the classically forbidden process being described in this paper is what one means by the term "reactive tunneling". The description of reactive tunneling that results from classical S-matrix theory, however, is quite different from the usual treatments[12] that rely on an approximate reduction of the A + BC → AB + C reaction to one-dimensional motion in some effective potential, with the tunneling aspect of the problem then being handled by one-dimensional tunneling formulas. Any such reduction of the problem to one-dimensional motion is an inherent dynamical approximation to which the concept of reactive tunneling should not be tied; i.e., in such a treatment one can never be sure what features of the result are due to tunneling and which are due to the dynamical approximations necessary to reduce the problem to a one-dimensional one. Classical S-matrix theory thus allows one to define the concept of reactive tunneling precisely, within the framework of exact dynamics. This question of "what is tunneling" in systems with more than one degree of freedom is discussed more fully in Section V.

II. SUMMARY OF CLASSICAL S-MATRIX THEORY FOR CLASSICALLY FORBIDDEN REARRANGEMENT PROCESSES.

A. General Formulation

The expressions for the classical S-matrix that pertain to the linear reactive systems

$$A + BC \rightarrow AB + C$$

have been given in detail by Rankin and Miller[2e]. Since the Porter-Karplus[11] potential surface being employed for $H + H_2$ is such that the asymptotic vibrational potential for the diatomic molecule is a Morse potential, even these details of the formulation in reference 2e can be carried over directly to the present case. All equations below are written for the present situation for which there is just one internal (quantized) degree of freedom, but the more general expressions are obvious generalizations.

To summarize the general formulation briefly, let (R^a, P^a) and (r^a, p^a) denote the Cartesian coordinates and momenta for the translational and vibrational degrees of freedom, respectively, for arrangement a (A + BC), and (R^c, P^c) and (r^c, p^c) the similar variables for arrangement c (AB + C); a simple linear transformation[2e] relates the variables in the two arrangements. It is also necessary to introduce the action-angle variables[13] (n^a, q^a) for the vibrational degree of freedom of arrangement a, and the analogous variables (n^c, q^c) for arrangement c; n^a and q^a are expressible[2e] in terms of r^a and p^a, and vice-versa, and similarly for the variables of arrangement c. The F_2-type generator[14] for the $(r^a, p^a) \longleftrightarrow (n^a, q^a)$ canonical transformation is denoted by $f_2(r^a, n^a)$, an explicit expression for which is given in reference 2e

for the case of a Morse vibrational potential.

In the asymptotic regions before and after collision the action variable of the vibrational degree of freedom (the classical analog of the vibrational quantum number) is required by the semiclassical quantum condition to be an integer. The transition probability for the $n_1^a \rightarrow n_2^c$ reactive transition is then given by

$$P_{n_2^c, n_1^a} = |S_{n_2^c, n_1^a}|^2 \tag{2.1}$$

where the classical S-matrix element is

$$S_{n_2^c, n_1^a} = \left[- \frac{\partial^2 \phi(n_2^c, n_1^a)}{\partial n_2^c \, \partial n_1^a} \Big/ 2\pi i\hbar \right]^{\frac{1}{2}} \times \exp[i\phi(n_2^c, n_1^a)/\hbar] , \tag{2.2}$$

$\phi(n_2^c, n_1^a)$ being the classical action integral along the reactive trajectory determined by the double-ended boundary conditions $n^a(t) = n_1^a$, $t \rightarrow -\infty$, and $n_2^c(t) = n_2^c$, $t \rightarrow +\infty$. (The boundary conditions are discussed in more detail in Section IIB.) The action integral ϕ is given explicitly by[2e]

$$\phi(n_2^c, n_1^a) = P_1^a R_1^a + f_2(r_1^a, n_1^a) - P_2^c R_2^c - f_2(r_2^c, n_2^c) + \int_{t_1}^{t_2} dt \; 2T \; , \tag{2.3}$$

where T is the kinetic energy, expressed in the variables of arrangement a

$$2T = P^a(t) \dot{R}^a(t) + p^a(t) \dot{r}^a(t),$$

or equivalently[2e] in the variables of arrangement c

$$2T = P^c(t) \dot{R}^c(t) + p^c(t) \dot{r}^c(t) \; .$$

If there is more than one trajectory which satisfies the appropriate double-ended boundary conditions, then Equation (2.2) is a sum of terms, one for each such trajectory.

To find the trajectory (or trajectories) that satisfies this nonlinear boundary value problem it is convient to introduce the classical trajectory function (cf. the classical deflection function of elastic scattering[15]) $n_2^c(q_1^a, n_1^a)$, the final vibrational quantum number in arrangement c for the classical trajectory which begins in arrangement a with initial conditions q_1^a and n_1^a. (Initial values for the translational coordinate and momentum are always determined implicitly by those of the internal degrees of freedom, energy conservation, and the scattering boundary condition: R_1^a = large, $P_1^a = -\left\{2\mu_a\left[E-\varepsilon_a(n_1^a)\right]\right\}^{\frac{1}{2}}$, where E is the total energy, $\varepsilon_a(n_1^a)$ is the semiclassical eigenvalue function for the vibrational degree of freedom, and μ_a is the translational reduced mass for arrangement a.) The trajectory related to the $n_1^a \rightarrow n_2^c$ transition is thus found by finding the root of the equation.

$$n_2^c(q_1^a, n_1^a) = n_2^c \quad . \tag{2.4}$$

[To keep the rotation concise we use the same symbol for the integer vibrational quantum number n_2^c and the classical trajectory function $n_2^c(q_1^a, n_1^a)$. Written without arguments, n_1^a and n_2^c denote integer vibrational quantum numbers; written with arguments, $n_2^c(q_1^a, n_1^a)$ is the final quantum number in arrangement c, not necessarily integral, that results from the classical trajectory beginning in arrangement a with initial conditions q_1^a and n_1^a. For the ground state to ground state reactive transition, for example, Equation (2.4) is an equation for

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q_1^a and reads: $n_2^c(q_1^a, 0) = 0.$] Also, the pre-exponential factor in Equation (2.2) is more conveniently (and equivalently) expressed in terms of the classical trajectory function:

$$\frac{\partial^2 \phi(n_2^c, n_1^a)}{\partial n_2^c \, \partial n_1^a} = \left[\frac{\partial n_2^c(q_1^a, n_1^a)}{\partial q_1^a}\right]^{-1} , \qquad (2.5)$$

with q_1^a evaluated at the root of Equation (2.4).

The $n_1^a \rightarrow n_2^c$ transition is classically forbidden if there is no value of q_1^a (at the given total energy) in its entire $(0,2\pi)$ interval for which Equation (2.4) is satisfied; e.g., it might be that all the trajectories at this energy and in this initial vibrational state are non-reactive. There will in general, however, be complex values of q_1^a for which Equation (2.4) is satisfied. Along such a trajectory with complex initial conditions all the coordinates and momenta become complex-valued, and the action integral in Equation (2.3) thus acquires an imaginary part. If there is just one trajectory that contributes significantly to the $n_1^a \rightarrow n_2^c$ transition (as is true for the present case), then Equations (2.1)-(2.5) give the reactive transition probability as

$$P_{n_2^c, n_1^a} = \left(2\pi \left|\frac{\partial n_2^c(q_1^a, n_1^a)}{\partial q_1^a}\right|\right)^{-1} \exp\left[-2\mathrm{Im}\phi(n_2^c, n_1^a)/\hbar\right] ; \quad (2.6)$$

i.e., the transition probability is, apart from the classical Jacobian factor, an exponentially decreasing function of the imaginary part of the classical action along that trajectory which leads to the transition. This exponential damping of the transition probability is the characteristic

feature of classically forbidden processes and the reason for use of the term "tunneling"; i.e., Equation (2.6) is the appropriate generalization of the one dimensional WKB tunneling formula[6] (which is also an exponential function of the imaginary part of the classical action along the tunneling trajectory) to systems of several interacting degrees of freedom.

Except for the fact that we are now considering a rearrangement process, the situation is essentially the same as in our previous study[2f] of classically forbidden transitions in non-reactive A + BC collisions[16]. One significant difference is that it is now not possible (even in principle) to find the complex roots of Equation (2.4) by extrapolating the function from its classically allowed region (for such a region does not exist), so that it is imperative that one be able to numerically integrate the equations of motion with complex initial conditions.

B. Calculational Procedure

More specifically, for the $n_1^a \rightarrow n_2^c$ reactive transition one seeks a classical trajectory with initial conditions in arrangement a (A + BC)

$$n_1^a = \text{specified integer} \tag{2.7a}$$

$$q_1^a = \text{anything} \tag{2.7b}$$

$$P_1^a = -\left\{ 2\mu_a \left[E - \varepsilon_a(n_1^a) \right] \right\}^{\frac{1}{2}} \tag{2.7c}$$

$$R_1^a = \text{real and large} \quad , \tag{2.7d}$$

and final conditions in arrangement c (AB + C)

$$n_2^c = \text{specified integer} \tag{2.8a}$$

$$q_2^c = \text{anything} \tag{2.8b}$$

$$P_2^c = + \left\{ 2\mu_c \left[E - \varepsilon_c(n_2^c) \right] \right\}^{\frac{1}{2}} \tag{2.8c}$$

$$R_2^c = \text{real and large} \quad . \tag{2.8d}$$

For a classically forbidden process q_1^a and q_2^c will be complex, and in addition the time increment $(t_2 - t_1)$ must also be complex; i.e., one has $\mathrm{Re}(t_2 - t_1) \to +\infty$, but $\mathrm{Im}(t_2 - t_1)$ is some finite value that is determined by the boundary conditions in Equations (2.7) and (2.8).

The practical problem, therefore, is to find the trajectory with these double-ended boundary conditions. The first method employed was, as before[2f], to integrate from the initial asymptotic region [with the initial conditions in Equation (2.7)] forward in time, and from the final asymptotic region [with the final conditions in Equation (2.8)] backward in time, choosing q_1^a and q_2^c iteratively so that all the coordinates and momenta are equal at some intermediate point.

For the initial branch, for example, the time is first incremented from t_1 to $\bar{t}_1$,

$$\bar{t}_1 = t_1 - i \, \mathrm{Im} q_1^a / \varepsilon_a'(n_1^a) \quad ; \tag{2.9}$$

just as before[2f], this time increment is taken to make $\bar{q}_a \equiv q_a(\bar{t}_1)$ real, so that the oscillator is more localized in configuration space. The time is then incremented in the purely real direction until the translational turning point (the time at which $\mathrm{Re}\ P_a = 0$) is passed; from here the time increment is chosen complex in order to "pull" the trajectory to the symmetric line $r_a = r_c$. To see how this can be accomplished, let

$$f(t) \equiv r_a(t) - r_c(t) \quad ; \tag{2.10}$$

$f(t)$ is thus complex, and one wishes to integrate to that time at which $f(t) = 0$. For t near t_K,

$$f(t) \simeq f_K + \dot{f}_K(t-t_K) \quad , \tag{2.11}$$

where $f_K = f(t_K)$ and $\dot{f}_K = \dot{f}(t_K)$, so that the time increment

$$t_{K+1} - t_K = - f_K/\dot{f}_K \tag{2.12}$$

would make $f_{K+1} \simeq 0$ <u>provided</u> the RHS of Equation (2.12) is not so large as to invalidate the linear approximation to $f(t)$ in Equation (2.11); in addition the <u>magnitude</u> of the complex time increment must not be larger than that allowed by the accuracy requirement of the numerical integrater[17]. If $|\Delta t|$ is the magnitude of time increment allowed by the numerical integrater ($|\Delta t|$ is chosen automatically[17]), therefore, one chooses the complex time increment as

$$t_{K+1} - t_K = -(f_K/\dot{f}_K) \quad \text{Min}\left(1, \frac{|\Delta t|}{|f_K/\dot{f}_K|}\right) \quad . \tag{2.13}$$

This algorithm , in conjunction with our variable step-size numerical integrater[17], very efficiently integrates to the time at which $f(t) = 0$.

One preceeds analogously for the final branch of the trajectory, integrating to its translational turning-point and then "pulling" it to the symmetric $r_a = r_c$ line as above, by choice of the complex time increment. One linear combination of the four coordinates and momenta from the initial and final branches is thus continuous, at this intermediate point, q_1^a and q_2^c are adjusted iteratively to make two other linear combination of the coordinates and momenta continuous, and energy

conservation then insures that the fourth linear combination is continuous, so that the two branches form one complete trajectory.

Although the above double-ended procedure worked quite well, we found that it was actually possible to integrate "straight through" from the initial to final asymptotic regions. One begins the initial branch of the trajectory as described above, integrates with real time increments to the translational turning point, and then instead of simply "pulling" the trajectory to the symmetric line, one "pulls" it all the way into arrangement c; i.e., one integrates to the time at which Re $r_c = r_o$, the equilibrium H_2 value. From here one then increments the time in the real direction. At the end of the trajectory in the final asymptotic region the translational coordinate R_c will not necessarily be real, but can be made so by a final pure imaginary time increment

$$\Delta t = -i\mu_c (\mathrm{Im}\ R_2^c) / P_2^c \quad ;$$

it is this condition (i.e., R_1^a, R_2^c real) that uniquely fixes $\mathrm{Im}(t_2 - t_1)$.[18]

This latter "straight through" procedure considerably simplifies the calculation, for there is only the <u>one</u> variable q_1^a to adjust iteratively to satisfy the boundary conditions of Equations (2.7)-(2.8), whereas the double-ended method of integration requires that one adjust both q_1^a and q_2^c iteratively; i.e., the number of variables in the non-linear "matching equations" is cut in half by the "straight through" procedure. The classical S-matrix is, of course, invariant to how one goes about finding the appropriate trajectory; to provide numerical checks, in fact, the transition probabilities presented in Section IV were calculated both ways, with identical results.

Numerical accuracy of the results was checked by successively increasing R_{max} (the value of the translational coordinate at which the trajectories were begun and terminated) and decreasing the error parameter for the numerical integrater until the transition probabilities were unchanged to the number of significant figures reported. Only an ordinary error parameter ($\epsilon \simeq 10^{-5}$) was necessary to achieve this level of accuracy.

C. Symmetry of the Trajectory

There is one particularly interesting feature that arises for a symmetrical reactive system such as $H + H_2$; the following remarks also apply to the more general system $A + BA \rightarrow AB + A$ for $A \neq B$. If there is only one trajectory that contributes significantly to a particular symmetric transition (i.e., $n_1^a = n_2^c$), then this trajectory must itself be symmetric; i.e., the trajectory from the initial asymptotic region to the symmetric A-B-A configuration is related to the trajectory from the symmetric configuration to the final asymptotic region simply by time reversal.

To see that this must be true, suppose there exists an unsymmetric trajectory that satisfies the boundary conditions in Equations (2.7) and (2.8) with $n_1^a = n_2^c$. Since the trajectory is not symmetric, the time reversed trajectory is different from the original one but still satisfies the boundary conditions of Equations (2.7) and (2.8). (This is because arrangements a (A + BA) and c (AB + A) are dynamically equivalent.) Furthermore, the contribution to the classical S-matrix of this trajectory is identical to the original one.

If an unsymmetric trajectory contributes to the transition, therefore, then there must be a second trajectory (the time-reversed trajectory of

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the original) that contributes equally. Thus if only one trajectory is found (as is the case for the ground state to ground state $H + H_2$ reaction), it means that the time reversed trajectory is identical to the original one, i.e., that the trajectory is symmetric. QED.

A direct quantitative check on the symmetry of the trajectory is possible by noting that time reversal implies the replacement $R \rightarrow R$, $P \rightarrow -P$, $r \rightarrow r$, $p \rightarrow -p$ for the Cartesian variables, but it is easy to show from the expressions in Reference 2e that the replacement for the action-angle variables is $n \rightarrow n$, $q \rightarrow -q$. Since the final values of the original trajectory are the initial values of the time-reversed trajectory, which by symmetry is identical to the original trajectory, one sees that the initial and final angle variables of the original trajectory must be related by

$$q_2 + q_1 = 2\pi N \quad ,$$

where N is any integer. This was indeed observed to be true for the present case.

III. TEMPERATURE AVERAGING AND ITS RELATION TO IMAGINARY TIME

Before discussing the numerical results for $H + H_2$ collisions, it is interesting to see how a Boltzmann temperature average over translational energy is related to certain features of the dynamics. With the usual definition $\beta = (kT)^{-1}$ the thermally averaged transition probability is

$$\bar{P}(T) = \beta \int_0^\infty dE \exp(-\beta E) P(E) \quad , \tag{3.1}$$

where here E denotes the initial translational energy and P(E) is a transition probability of the form in Equation (2.6), i.e.,

$$P(E) = J(E) \exp\left[-2\mathrm{Im}\phi(E)/\hbar\right] \quad , \tag{3.2}$$

J(E) being the square root of a Jacobian factor; the quantum number indices for P(E) have been omitted since they are not involved in the present discussion, but it should be understood that we are considering the average over initial translational energy of a specific $n_1^a \rightarrow n_2^c$ transition. Since Equation (3.2) is being used for the transition probability, it is also clear that we are assuming the transition to be classically forbidden in the energy region of interest.

Equation (3.1) thus becomes

$$\overline{P}(T) = \beta \int_0^\infty dE\, J(E) \exp\left[-\beta E - 2\,\mathrm{Im}\phi(E)/\hbar\right] \quad , \tag{3.3}$$

which is precisely of the form for which a steepest descent approximation[19] to the integral is useful. This approximation gives the following approximate expression

$$\int dx\, g(x)\, e^{-f(x)/\hbar} \simeq \left[\frac{2\pi\hbar}{f''(x_o)}\right]^{\frac{1}{2}} g(x_o)\, e^{-f(x_o)/\hbar} \quad , \tag{3.4}$$

where x_o is the position of a local minimum of f(x), i.e.,

$$f'(x_o) = 0 \quad . \tag{3.5}$$

[Equations (3.4) and (3.5) will also be recognized as the method of stationary phase for the case that the "phase" is pure imaginary.] Applying this approximation to Equation (3.3) gives

$$\overline{P}(T) = P(E)\, \beta\left[\frac{\pi\hbar}{\mathrm{Im}\phi''(E)}\right]^{\frac{1}{2}} \exp(-\beta E) \quad , \tag{3.6}$$

where $E = E(\beta)$ is the particular value defined implicitly by the equation

$$-\tfrac{1}{2}\hbar\beta = \mathrm{Im}\phi'(E) \quad . \tag{3.7}$$

It is well-known[20], however, that the energy derivative of the classical action integral gives the time increment for the trajectory, so that if $\tau(E)$ is the imaginary part of the total time increment of the trajectory,

$$\tau(E) \equiv \mathrm{Im}(t_2 - t_1) = \mathrm{Im}\phi'(E) \quad , \tag{3.8}$$

then Equation (3.7) becomes

$$\tau(E) = -\tfrac{1}{2}\hbar\beta \quad . \tag{3.9}$$

The imaginary part of the time increment for the appropriate complex-valued trajectory at a particular energy is thus seen to be directly related to the temperature at which this energy makes the dominate contribution to the temperature average. A similar relation between imaginary time and $\hbar\beta$ has been seen to arise in other applications of classical-limit theory[21].

Using Equations (3.7) and (3.8) and replacing β by $(kT)^{-1}$ it follows that

$$\mathrm{Im}\phi''(E) = \tfrac{1}{2}\hbar(kT)^{-2}\left[\frac{dE}{d(kT)}\right]^{-1} \quad ,$$

so that the thermally averaged transition probability takes the simple form

$$\overline{P}(T) = P(E)\left[2\pi\,\frac{dE}{d(kT)}\right]^{\frac{1}{2}} \exp(-E/kT) \quad , \tag{3.10}$$

$E = E(T)$ being determined by Equation (3.7).

In the course of calculating $P(E)$ for a sequence of energies E it is thus possible to generate $\overline{P}(T)$ simultaneously with essentially no increase in labor. This is true because at each energy E one had at hand $\tau(E)$, the imaginary past of the time increment for the appropriate trajectory. As E is varied in calculating $P(E)$, the following parametric equationsthus map out $\overline{P}(T)$ simultaneously:

$$\overline{P} = P(E) \left[2\pi / \frac{d(kT)}{dE} \right]^{\frac{1}{2}} \exp(-E/kT) \quad , \tag{3.11}$$

for the temperature

$$kT = \tfrac{1}{2}\hbar / |\tau(E)| \quad . \tag{3.12}$$

The Appendix discusses some other implications of this semiclassical treatment of the temperature averaged reaction probability.

IV. DISCUSSION OF RESULTS

A. Reaction Probabilities

Figures 1 and 2 show the ground state to ground state ($n_1^a = n_2^c = 0$) reaction probability in the energy region below the classical threshold as a function of the relative collision energy E_o; the corresponding numerical values are given in Table I. Also listed in Table I are the imaginary part of the classical action for the appropriate trajectory at each energy, the absolute temperature T related to E_o by Equation (3.7), and the Boltzmann averaged transition probability for this temperature. The calculations were carried out by the procedure described in Section II, and as evidenced by Figure 1, there is no difficulty at all in describing transitions that are "extremely forbidden".

0 0 0 0 3 8 0 0 8 6 9

Also shown in Figures 1 and 2 are the quantum mechanical reaction probabilities calculated for this same Porter-Karplus[11] potential surface by Diestler[22] (crosses) and by Wu and Levine[23] (circles). The strictly classical reaction probability[24] is also included in Figure 2, and it is seen that for $E_o < 0.21$ eV all ordinary trajectories are non-reactive. The agreement with Diestler's[22] value far below the classical threshold is almost exact, but in the energy region just below the classical threshold (as best seen in Figure 2) the two quantum mechanical calculations differ somewhat, lying on either side of the classical S-matrix results. Although it is thus not possible to assess the precise degree of accuracy of the semicalssical values, it is clear nevertheless that the analytic continuation of classical mechanics within the framework of classical S-matrix theory correctly describes at least the major features of reactive tunneling in this system. It will be most interesting to see just how precise the semiclassical theory is, but this must await a resolution of the quantum discrepancy[25].

B. Coordinate Trajectories

As discussed in Section II, there is only one complex-valued trajectory that contributes to the ground state to ground state reaction probability at each energy, so that various features of the reaction dynamics can be illucidated by observing it. As has been discussed before[2f], however, for complex-valued trajectories of a system with more than one degree of freedom there is a certain degree of arbitrariness in the trajectory due to the arbitrariness of the path in the complex time plane along which one increments the time from t_1 to t_2, with $\mathrm{Re}(t_2-t_1) \to +\infty$, $\mathrm{Im}(t_2-t_1)$ finite. For a system with only one degree offreedom a

"physically unique" trajectory is fairly obvious: one chooses the time path so that the coordinate is always real, and this choice determines a unique trajectory. With more than one degree of freedom, however, it is not possible to choose the time path to keep all coordinates real, and there thus appears to be no "physically unique" trajectory. One should keep in mind, of course, that the desirability of a "physically unique" coordinate trajectory is purely for interpretational convenience, for the classical S-matrix elements themselves are invariant to the choice of the time path[26].

Although the choice of time path described in Section II was for computational convenience, the coordinate trajectories that result appear to be quite physically reasonable; i.e., it appears that the coordinate trajectory does not change drastically with different "reasonable" choices of the time path. Figure 3 shows the real part of the coordinate trajectory for the ground state to ground state reaction at two different collision energies. As discussed in Section II, these trajectories are rigorously symmetric with regard to reflection about the bisector of the angle between the two asymptotic channels of the potential surface. The "kink" in the low energy trajectory just as it begins to tunnel is obviously an artifact of the particular way the time path has been chosen, and it is clear that it could be eliminated by a modified choice of the time path.

The most interesting feature of the reactive trajectories is the degree to which they "cut the corner", the higher energy (0.20 eV) trajectory passing the symmetric H-H-H point at an interatomic distance of 1.86 a_o, with the corresponding value for the lower energy (0.02 eV)

0 0 0 0 0 8 0 0 0 7 0

trajectory being 1.95 a_o; for comparison the interatomic distance of the saddle point is 1.70 a_o. This observation that the appropriate reactive trajectory "cuts the corner" more as the collision energy is reduced is similar to that of other workers[27-30] who, in addition, observe typical trajectories to move inside the saddle point as the energy is increased above the classical threshold.

C. Temperature Averaging

As discussed in Section III, it is quite easy to obtain the temperature average over translational energy for a given $n_1^a \rightarrow n_2^c$ transition essentially simultaneously with the calculation of the energy dependent transition probability.

Figure 4 shows the temperature-energy steepest descent relation of Equation (3.7); i.e., for a given temperature Figure 4 shows the translational energy that is the dominate contributer to the average over translational energy. For T = 300°K, for example, the dominate energy region is near E_o = 0.15 eV. For temperatures below 1000°K, therefore, Figure 4 shows that the dominate energy region is below the classical threshold, a fact that again points out the importance of classically forbidden processes to low energy kinetic phenomena.

The thermally averaged ground state to ground state reaction probability as calculated from Equation (3.10) is shown in Figure 5. Since the development in Section III is strictly valid only if the dominant energy is below the classical threshold, the reaction probability in Figure 5 should only be valid for temperatures below about 1000°K. The extrapolation to a probability of 1 at ∞ temperature, however, appears to be quite smooth. One will note the lack of linearity of the log $\bar{P}(T)$

versus 1/T plot in Figure 5 that shows the degree of departure from a pure Arrhenius form for temperatures below 1000°K; the limiting slope above T = 1000°K leads to an activation energy of about 0.27 eV.

V. CONCLUDING REMARKS: WHAT IS TUNNELING?

In conclusion we would like to discuss briefly our thoughts on what should be meant by the term "reactive tunneling", or even simply "tunneling", for dynamical systems of more than one degree of freedom.

The term "tunneling" presumably originated in the treatment of one dimensional barrier penetration problems[6]; if the energy is less than the barrier height, then the reaction is said to proceed by tunneling. In one dimension, therefore, the energetic criterion is identical to the dynamic criterion; i.e., if the particle has sufficient energy to surmount the barrier, then classical dynamics will indeed carry the particle over the barrier, for in one dimension dynamics is completely determined by energy conservation.

With more than one degree of freedom this ceases to be true; i.e., energy conservation alone does not determine the dynamics, and certain processes may be energetically possible but dynamically impossible. For the linear $H + H_2$ collision on the Porter-Karplus surface, for example, the barrier height is 0.396 eV, the vibrational energy of ground state H_2 is 0.273 eV, so that the reaction is energetically possible classically for a collision energy above the classical energetic threshold

$$E(\text{energetic threshold}) = 0.12 \text{ eV} \quad .$$

Classical dynamics, however, shows that there are no (real) reactive trajectories for collision energies below a dynamic threshold

E(dynamic threshold) $\simeq$ 0.21 eV ;

i.e., the energetic and dynamic threshold, which are identical for one dimensional systems can be quite different for systems with several degrees of freedom, as they are for H + H_2.

Wu and Levine[23] have implicitly used the energetic criterion in reference to tunneling, but our feeling is that tunneling relates to dynamics and that the dynamic criterion is the more meaningful one; i.e., tunneling is something that does not take place via classical dynamics. Thus Wu and Levine[23] comment that since the reaction probability is very small for collision energies below the energetic threshold of 0.12 eV, there is no significant amount of tunneling in the linear H + H_2 reaction. According to classical dynamics, however, all reaction below the dynamic threshold of 0.21 eV is tunneling, so that there is a great deal of reactive tunneling for this system.

Reactive tunneling, of course, emerges quite naturally in classical S-matrix theory as simply a particular kind of classically forbidden transition, i.e., a transition for which the action integral along the appropriate classical trajectory has an imaginary part. Indeed, it is this fact, that the resulting classical S-matrix element has an exponential damping factor due to the imaginary part of the classical action, that most strongly suggests this use of "tunneling" in relation to classical dynamics.

Acknowledgment

We are happy to acknowledge very helpful discussions with Dr. Jimmie D. Doll concerning this work.

APPENDIX: TRANSITION STATE INTERPRETATION OF THE THERMALLY AVERAGED REACTION PROBABILITY

The temperature dependent reaction probability given by Equation (3.10) of Section III has the form (omitting pre-exponential factors)

$$\bar{P}(T) \sim \exp\left[-E/kT - 2\,\mathrm{Im}\phi(E)/\hbar\right] , \tag{A1}$$

where $E = E(T)$ is the function of temperature determined implicitly by

$$(kT)^{-1} = -\,2\mathrm{Im}\phi'(E)/\hbar , \tag{A2}$$

$\phi(E)$ being the classical action for the appropriate classical trajectory.

The transition state form for the thermally averaged reaction probability is[31]

$$\bar{P}(T) \sim \exp(-A/kT) , \tag{A3}$$

where A is the "free energy of activation " and in general temperature dependent; from Equation (A1) one thus identifies A(T) as

$$A(T) = E + 2kT\ \mathrm{Im}\phi(E)/\hbar , \tag{A4}$$

with $E = E(T)$ given by Equation (A2). S, the "entropy of activation", is defined by the thermodynamic relation[32]

$$S(T) = -\frac{\partial A}{\partial T} , \tag{A5}$$

and from Equation (A4) this is

$$S(T) = -\,E'(T) - \frac{2kT}{\hbar}\,\mathrm{Im}\phi'(E)\,E'(T) - 2k\,\mathrm{Im}\phi(E)/\hbar \quad ;$$

Equation (A2) shows that the first two terms cancel, giving

$$S(T) = -2k\phi \mathrm{Im}\,(E)/\hbar \quad , \tag{A6}$$

with $E = E(T)$ from Equation (A2). Taking advantage of Equation (A6), the "free energy" of Equation (A4) is also seen to be given by

$$A(T) = E(T) - T\,S\,(T) \quad , \tag{A7}$$

the standard thermodynamic relation[32], where $E(T)$ given by Equation (A2) is thus seen to be the "energy of activation".

The temperature dependent reaction probability thus has the transition state form

$$\overline{P}(T) \sim \exp(S/k)\,\exp(-E/kT) \quad , \tag{A8}$$

but where the "activation energy" E and "entropy of activation" S are temperature dependent, defined by Equations (A2) and (A6), respectively. These definitions of $E(T)$ and $S(T)$, too, are purely dynamical quantities; it would be interesting to explore in detail the circumstances under which they can be adequately described by statistical approximations to dynamics.

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17. See Appendix D of Ref 2f.

18. Asymptotic time increments such as this do not change the quantum numbers and do not contribute to the classical action integral of Eq. (2.3), and they actually need not be taken in practice. The reason for this is that the quantity of interest (see Section III) is not the total time increment but the time delay δt,

$$\delta t \equiv \frac{d}{dE} \phi(P_2 n_2, P_1 n_1; E) \quad ,$$

where ϕ is here expressed as a function of all the momenta of the system. For fixed n_1 and n_2, P_1 and P_2 are the functions of E given by Eqs. (2.7c) and (2.8c), and ϕ is a generator of the F_4-type (see Ref. 14), so that this becomes

$$\delta t = \frac{\partial \phi}{\partial P_2} \frac{\partial P_2}{\partial E} + \frac{\partial \phi}{\partial P_1} \frac{\partial P_1}{\partial E} + \frac{\partial \phi}{\partial E} = -\mu R_2/P_2 + \mu R_1/P_1 + (t_2 - t_1) \quad ,$$

where (t_2-t_1) is the actual time increment for the trajectory. As $Re(t_2-t_1) \to +\infty$, δt is obviously finite, and if asymptotic imaginary time increments are taken so that R_1 and R_2 are real, then one has the convenient relation

$$Im(\delta t) = Im(t_2 - t_1) \quad .$$

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TABLE I: Ground State to Ground State Reaction Probability for $H + H_2$

E_o(eV)[a]	Imϕ[b]	T(°K)[c]	$P_{o,o}^{R}$[d]	$\langle P_{o,o}^{R} \rangle$[e]
0.02	11.84	32	2.28×10^{-11}	-
0.03	10.16	44	6.59×10^{-10}	1.85×10^{-12}
0.04	8.860	57	8.98×10^{-9}	1.96×10^{-11}
0.05	7.794	70	7.64×10^{-8}	1.40×10^{-10}
0.07	6.107	99	2.27×10^{-6}	4.20×10^{-9}
0.09	4.798	134	3.20×10^{-5}	8.14×10^{-8}
0.11	3.735	176	2.75×10^{-4}	1.08×10^{-6}
0.13	2.850	230	1.65×10^{-3}	1.12×10^{-5}
0.14	2.460	264	3.64×10^{-3}	3.47×10^{-5}
0.15	2.102	303	7.52×10^{-3}	9.93×10^{-5}
0.16	1.772	350	1.47×10^{-2}	2.73×10^{-4}
0.17	1.468	408	2.74×10^{-2}	7.22×10^{-4}
0.18	1.190	483	4.88×10^{-2}	1.89×10^{-3}
0.19	0.9367	579	8.43×10^{-2}	4.70×10^{-3}
0.20	0.7076	715	1.42×10^{-1}	1.15×10^{-2}
0.21	0.5031	917	2.36×10^{-1}	2.69×10^{-2}
0.22	0.3247	1269	3.95×10^{-1}	7.94×10^{-2}
0.23	0.1754	2009	6.76×10^{-1}	1.25×10^{-1}

a. The initial translational energy.

b. The imaginary part of the classical action integral of Eq. (2.3) along the appropriate complex-valued trajectory.

c. The absolute temperature that is related to translational energy E_o by the steepest descent relation in Eq. (3.9); the graphical

TABLE I - continued

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representation of the E_o versus T relation is shown in Figure 4.

d. The ground state to ground state reaction probability as given by Eq. (2.6) and shown in Figures 1 and 2.

e. The Boltzmann average of the energy dependent reaction probability for the corresponding temperature T, as defined by Equation (3.1) and shown in Figure 5.

FIGURE CAPTIONS

1. Reaction probability for the ground state (i.e., vibrational quantum number equal to zero) to ground state $H + H_2 \rightarrow H_2 + H$ reaction, as a function of the relation collision energy E_o. Corresponding numerical values are given in Table I. The crosses and circles show the quantum mechanical values calculated by Diestler[22] and Wu and Levine[23], respectively, for this same Porter-Karplus[11] potential surface.

2. Same as Figure 1, but a more detailed picture of the energy region just below the classical threshold. The broken line is the purely classical reaction probability[24] for the same potential surface.

3. Coordinate trajectories for collision energies E_o = 0.20 eV (dotted line) and E_o 0.02 eV (dash-dot line). For reference, the dashed line is the "reaction coordinate" (i.e., the path of minimum potential energy) and the cross is the saddle point. R_a and r_a are the real parts of the complex translational and vibrational coordinate , respectively, of arrangement a (A + BC). As discussed in Section IVB, the "kink" in the lower energy trajectory (dash-dot line) is undoubtedly an artifact of the particular way the path of integration in the complex time plane was chosen.

4. The energy-temperature relation determined by the steepest descent condition of Eq. (3.7) or (3.9); corresponding numerical values are given in Table I. For a given temperature the corresponding energy is the one that makes the dominant contribution to the Boltzmann average of the reaction probability for that temperature. For T = 300°K,

for example, collision energies in the vicinity of $E_o \simeq 0.15$ eV make the most significant contribution to the Boltzmann average.

5. The temperature dependent reaction probability $\overline{P}(T)$ given by Eq. (3.10) for the ground state to ground state $H + H_2$ reaction. The semi-classical treatment of Section III is only valid in the present case for $T \lesssim 1000°K$, so that the dashed part of the curve is simply an extrapolation to unit probability at infinite temperature. Corresponding numerical values are given in Table I.

0 0 0 0 3 8 0 0 0 7 3

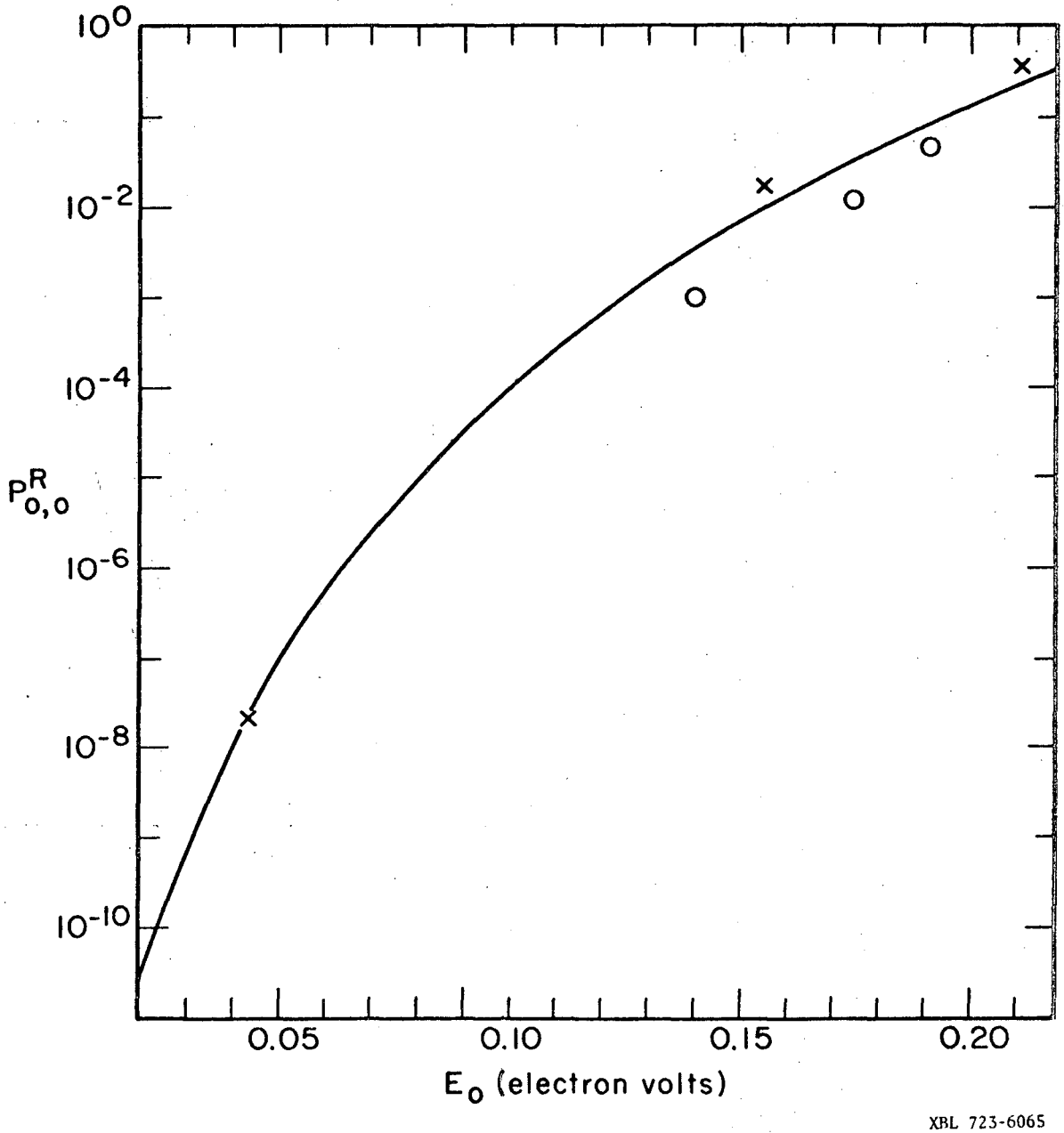

Fig. 1

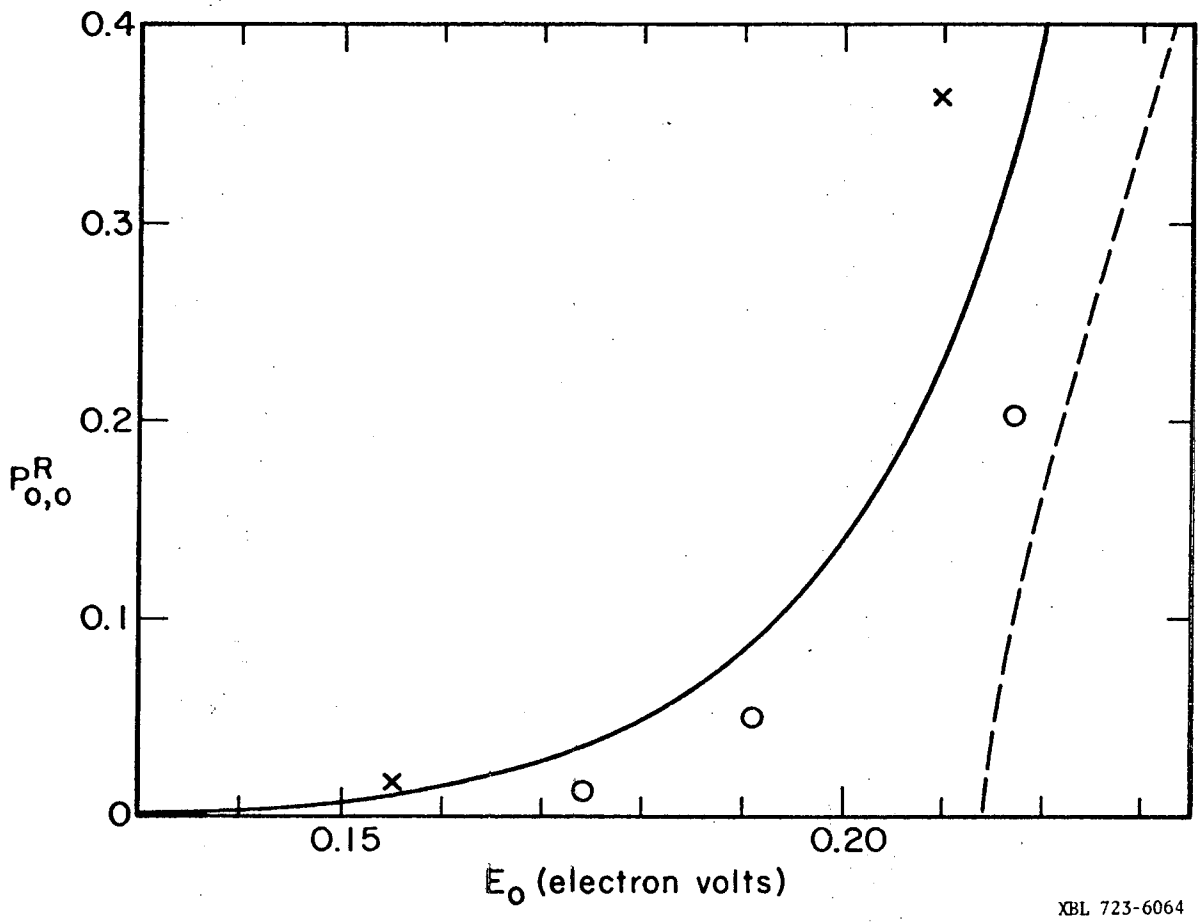

Fig. 2

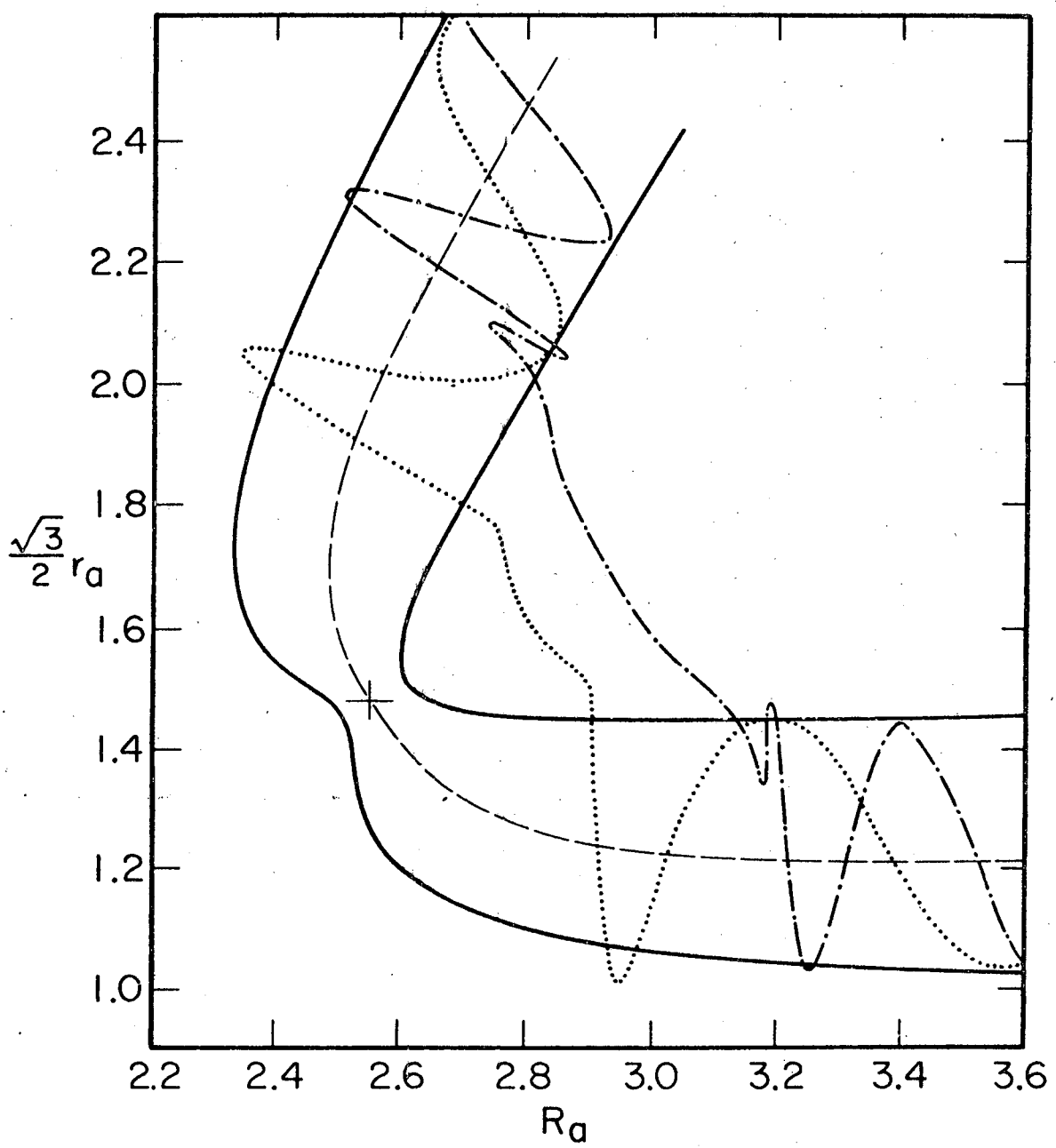

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Fig. 3

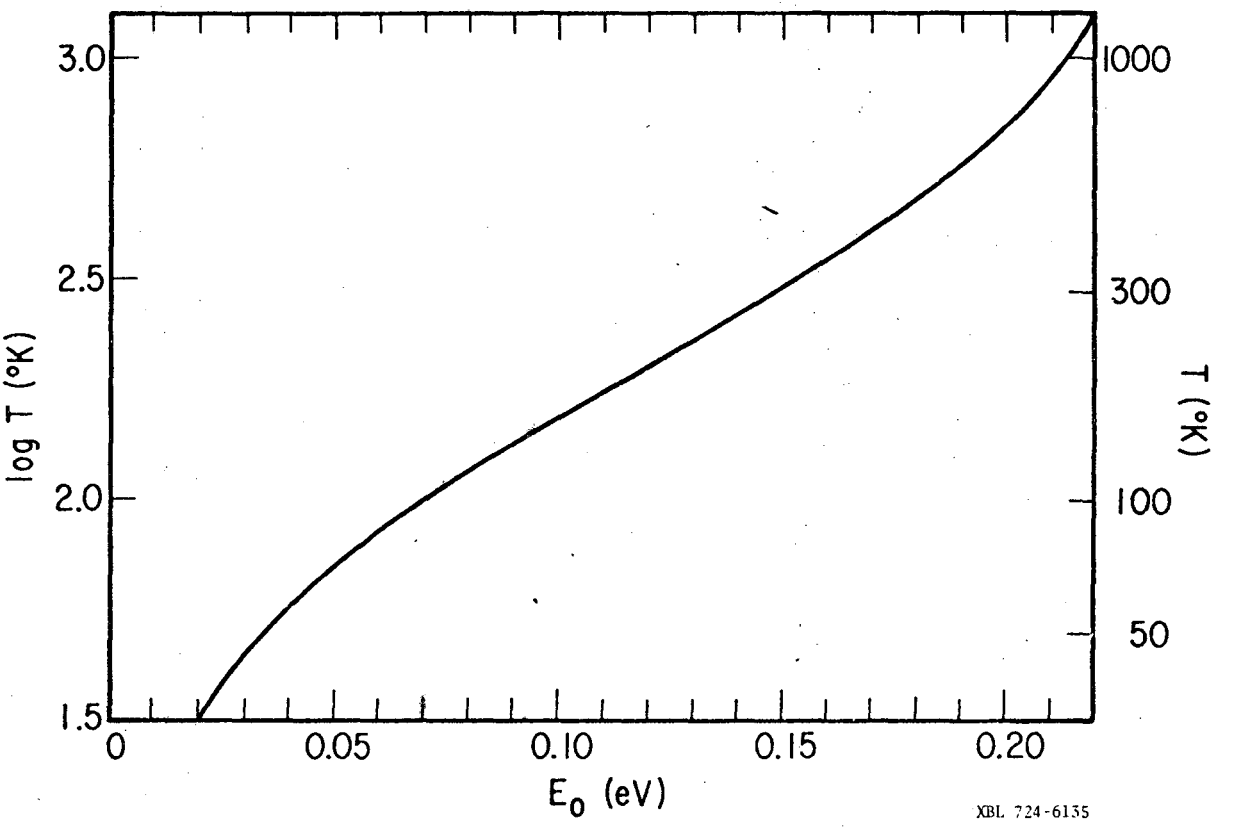
3.0
2.5
2.0
1.5
log T (°K)
0
0.05
0.10
0.15
0.20
E_0 (eV)
1000
300
100
50
T (K°)
XBL 724-6135

Fig. 4

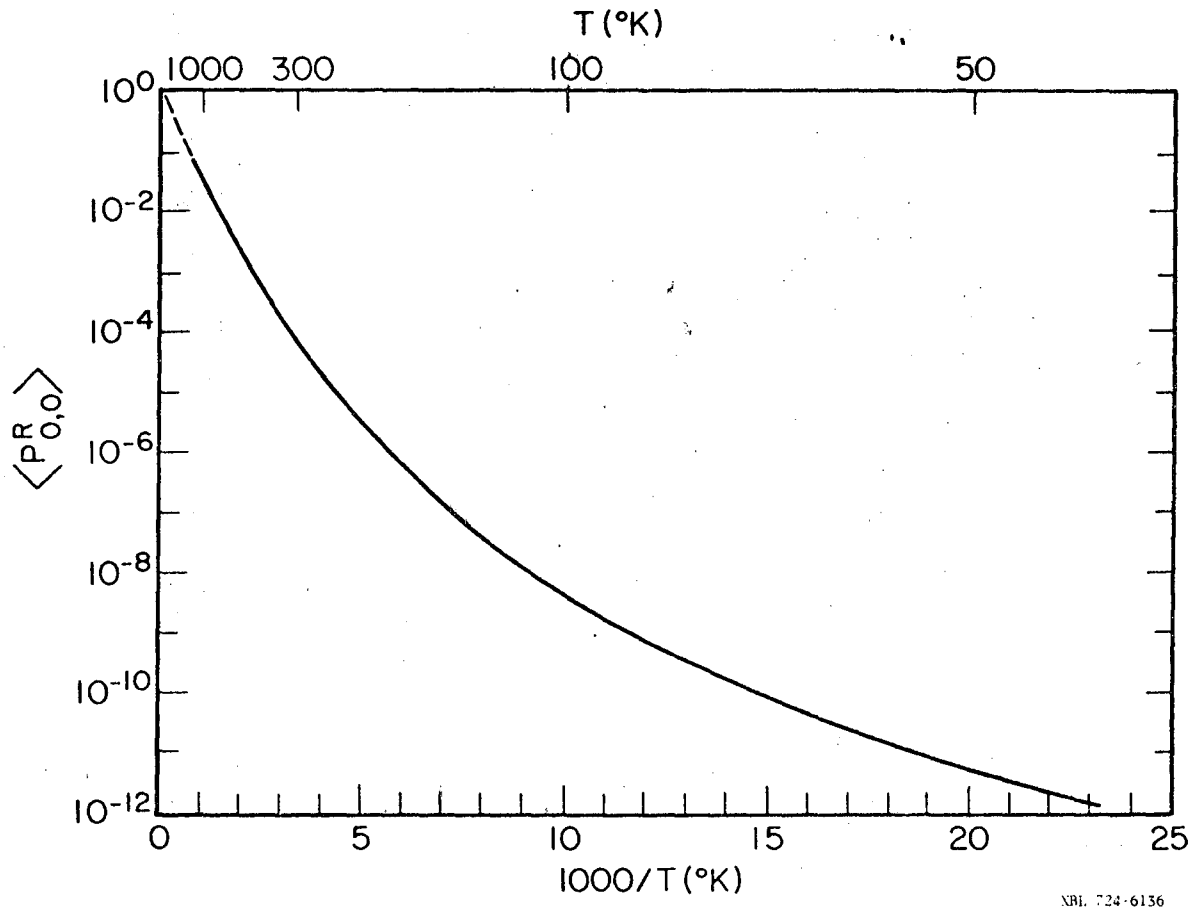
T (°K)
1000
300
100
50
10^{0}
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
$\langle P^{R}_{0,0} \rangle$
0
5
10
15
20
25
1000/T (°K)
XBL 724-6136

Fig. 5

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