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IMPORTANCE OF NON-SEPARABILITY IN QUANTUM MECHANICAL TRANSITION STATE THEORY*

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Abstract

A discussion of classical transition state theory shows that the fundamental dynamical assumption in transition state theory is that the reaction mechanism is "direct", and for reactions with activation barriers it is reasoned that this is a good approximation for the threshold of the reactive cross section. Examples are presented which show that this is indeed true within the framework of classical mechanics. Analogous comparisons that have been made quantum mechanically, however, show transition state theory to be significantly poorer than in the classical case, and it is argued that this is a result of the fact that the conventional quantum mechanical version of transition state theory involves the assumption that motion along some reaction coordinate is separable from that of the other degrees of freedom. (This separability approximation is known to be poor in the threshold region.) It is then shown how a more general definition of quantum mechanical transition state theory can be constructed, which does not necessitate the assumption of separability, and sample calculations show this to be in good agreement with (exact) quantum scattering theory.

I. INTRODUCTION.

The transition state theory[1] of chemical kinetics has without a doubt provided the most useful phenomenological framework for parameterizing rate constants for a wide variety of chemical reactions. Recently,[2-7] however, there has been interest in investigating the dynamical basis of transition state theory and trying to learn the extent to which it provides a quantitative description of rate constants for elementary bimolecular reactions.

One of the practical motivations for this recent direction of research is the recognition that for (chemical reactions with significant activation energy) transition state theory describes the threshold region of the reactive cross section quite well, and this[8] is the energy regime most important for determining the thermal rate constant. Since the threshold region is often described rather poorly by classical trajectory methods[9]--which are useful for describing many other aspects of the dynamics of simple chemical reactions--transition state theory is an important complement to trajectory methods. (It is interesting that an analogous complementarity also exists experimentally: the "modern" methods of chemical kinetics--e.g., crossed molecular beams, infrared chemiluminescence, various laser techniques, etc.--provide dynamical information about reactions which have little or no activation energy (or at energies significantly above any threshold), but it is difficult to extract information about the threshold behavior of the reactive cross section from such measurements. More traditional kinetics methodology--i.e., determination of the rate constant as a function of temperature--on the other hand, provides a sensitive measure of the threshold region (but essentially only this).)

Although it is apparent from the physical assumptions inherent in transition state theory (*vide infra*) that it *should* describe the threshold region accurately, the most detailed comparisons[10] of conventional transition state theory with "exact" results from quantum scattering calculations have shown it to be poor at moderate and low temperatures. This disappointing result seems to be a consequence of the fact that an assumption of separability of motion along a reaction coordinate is inextricably bound up in the usual quantum mechanical version of transition state theory, and separability has been seen in a variety of calculations to be a poor approximation in the threshold region. If transition state theory is to provide a quantitative description of the reactive cross section in the threshold region (and thus the rate constant), it must therefore be applied quantum mechanically, because quantum effects are important at threshold, but without assuming the reaction dynamics to be separable.

The weakness of the separability approximation in conventional transition state theory was recognized quite clearly by Johnston and Rapp[11] a number of years ago, and they proposed ways of trying to overcome it. While not rigorous or accurate quantitatively, these early attempts at dealing with non-separability in transition state theory were important in identifying this feature as a crucial weakness.

This Account first reviews the dynamical basis of transition state theory within the framework of classical mechanics, emphasizing the "fundamental assumption" on which it is based. Examples are presented showing that in a classical world transition state theory is an excellent approximation in the threshold region. It is then shown how a quantum mechanical version of transition state theory can be constructed which escapes the necessity of assuming separability. Results of calculations based on this theory are seen to be in good agreement with (exact) quantum mechanical scattering theory.

II. CLASSICAL TRANSITION STATE THEORY AND THE 'FUNDAMENTAL ASSUMPTION'

As Wigner[12] emphasizes, transition state theory is a model essentially based on classical mechanics. (The validity of classical mechanics to describe the nuclear dynamics is Wigner's[12] assumption number two; his first assumption is use of the Born Oppenheimer approximation to separate electronic and nuclear motion and the assumption that only one potential energy surface is involved in the reaction.) To gain a feeling for the dynamical approximations inherent in transition state theory it is therefore useful first to discuss classical transition state theory before considering a quantum mechanical version of it.

If the reactants are in a Boltzmann distribution of their internal states and relative translation, then the classical rate constant is a Boltzmann average of the flux of reactive trajectories through a surface which divides reactants from products. More precisely, the expression for the exact rate constant in classical mechanics is[13]

$$k_{b\leftarrow a}(T) = Q_a^{-1}\, h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\; e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}\; \delta[f(\underset{\sim}{q})]\; \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m\; \chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q}), \tag{1}$$

where $\beta = (kT)^{-1}$, $(\underset{\sim}{p},\underset{\sim}{q}) = (p_i,q_i)$, $i = 1, \ldots, F$ are the momenta and coordinates of the system with F degrees of freedom, Q_a is the partition function per unit volume of the non-interacting reactants, $H(\underset{\sim}{p},\underset{\sim}{q})$ is the total Hamiltonian for the system, and $f(\underset{\sim}{q})$ is a function of the coordinates which defines the <u>dividing surface</u> via Eq. (2),

$$f(\underset{\sim}{q}) = 0 \quad ; \tag{2}$$

δ is the Dirac delta function (the factor $\delta(f(\underset{\sim}{q}))$ in Eq. (1) converts the "volume" imtegral over all F coordinates into a "surface" integral over

F-1 coordinates), and $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ is the <u>characteristic</u> <u>function</u> for reaction. The definition of $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ is that

$$\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q}) = 1 \tag{3}$$

if the trajectory determined by the phase point $(\underset{\sim}{p},\underset{\sim}{q})$ is reactive in the a(A + BC) → b(AB + C) direction, and is zero otherwise.

It is illustrative to write out Eq. (1) more explicitly for the simplest possible example, a collinear A + BC → AB + C reaction. F = 2 in this case, and the two coordinates can be chosen to be r and R, which denote the relative B-C vibrational coordinate and the distance from A to the center of mass of BC, respectively; p and P are the momenta conjugate to r and R. The function f(r,R) which corresponds to choosing the dividing surface far out in the reactant region--surface S_1 in Fig. 1--is

$$f(r,R) = R_{max} - R \tag{4}$$

It is then not hard to see that Eq. (1) becomes

$$k_{b\leftarrow a} = Q_a^{-1}\, h^{-2} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dP\, \left(-\frac{P}{\mu}\right) e^{-\beta H(P,R,p,r)}\, \chi_{b\leftarrow a}(P,R,p,r)\ , \tag{5}$$

with $R = R_{max}$ and where μ is the reduced mass for the A - BC translational motion. If R_{max} is sufficiently large, the Hamiltonian is given by its asymptotic form

$$\lim_{R\to\infty} H(p,R,p,r) = \frac{P^2}{2\mu} + h(p,r) \quad ,$$

where h(p,r) is the vibrational Hamiltonian for the isolated BC molecule;

also, it is clear that trajectories beginning on this surface with $P > 0$ cannot be reactive in the $a \rightarrow b$ direction. Thus if the translational energy E_t is introduced,

$$E_t = \frac{P^2}{2\mu} \quad ,$$

Eq. (5) takes on its more conventional form

$$k_{b\leftarrow a} = Q_a^{-1} \left(\frac{kT}{h}\right) h^{-1} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dp \int_{0}^{\infty} d(\beta E_t)\, e^{-\beta E_t}\, e^{-\beta h(p,r)} \chi_{b\leftarrow a}(P,R,p,r), \quad (6)$$

with

$$R = R_{max}$$

$$P = -\sqrt{2\mu E_t} \quad .$$

Eq. (6) is the standard expression for which a Monte Carlo trajectory calculation[9] is often carried out: the variables r, p, and E_t are chosen randomly from their appropriate distributions and trajectories run to see whether $\chi_{b\leftarrow a}(P,R,p,r)$ is 1 (a reactive trajectory) or 0 (a non-reactive trajectory).

It is not necessary, however, to choose the dividing surface in the reactant region as was done above. Eq. (1) is, in fact, rigorously independent of the particular choice of dividing surface;[2] it is only necessary that the surface be one through which all reactive trajectories must pass. Fig. 1 shows two other possible choices, surfaces S_2 and S_3. This independence of the choice of dividing surface is a consequence of the classical continuity equation (i.e., Liouville's Theorem); this theorem states that if the surface defined by the equation

$$f(\underset{\sim}{q}) \;=\; 0$$

is a <u>closed</u> surface and if the <u>distribution function</u> $\rho(\underset{\sim}{p},\underset{\sim}{q})$ is constant along a classical trajectory, then

$$\int d\underset{\sim}{p} \int d\underset{\sim}{q} \;\; \rho(\underset{\sim}{p},\underset{\sim}{q}) \;\; \delta[f(\underset{\sim}{q})] \;\; \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m \;=\; 0 \quad ; \qquad (7)$$

in words, Eq. (7) states that the steady-state flux through a closed surface is zero. Eq. (1) corresponds to the distribution function

$$\rho(\underset{\sim}{p},\underset{\sim}{q}) = e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})} \; \chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q}) \quad ; \qquad (8)$$

conservation of total energy implies that $H(\underset{\sim}{p},\underset{\sim}{q})$ is constant along a trajectory, and it is clear from the definition of $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ that it also is (if the trajectory determined by $(\underset{\sim}{p},\underset{\sim}{q})$ is reactive at one time it obviously cannot be otherwise at another time), so that the distribution function in Eq. (1), Eq. (8), satisfies the condition of the theorem. Furthermore, it is clear that in Fig. 1 surfaces S_1 and S_3, for example, can be made into one <u>closed</u> surface by joining them with segments at infinity. By the classical continuity equation, the flux through this <u>closed</u> surface is zero. Since no flux passes through the pieces of the surface at infinity, this means that the flux <u>into</u> the closed surface through S_1 must be equal to the flux <u>out of</u> the closed surface through S_3, or equivalently, that the flux in the <u>reactive direction</u> through S_1 must be equal to the flux in the <u>reactive direction</u> through S_3. This argument is clearly valid for any surface which divides reactant and product space and thus proves the assertion that Eq. (1) is independent of the particular dividing surface.

The stage is now set to introduce the "fundamental assumption" of transition state theory (Wigner's[12] third assumption). The goal is to eliminate the characteristic function $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ from Eq. (1), and therefore the need to determine the complete classical dynamics of the system (i.e., to compute classical trajectories), and this is done in the following way. The "fundamental assumption" is that if the dividing surface is chosen in the appropriate place, then any trajectory which crosses it in the reactive direction is indeed a reactive trajectory, i.e., that it does not subsequently re-cross the surface and become non-reactive. Put another way, it is the assumption that the dividing surface is one which no trajectory crosses more than once. Whenever this assumption is true, transition state theory is exact (within the world of classical mechanics presently being considered).[6a]

Framed more quantitatively, suppose surface S_3 in Fig. 1 is chosen as the one through which one assumes no trajectory passes more than once. (It is clear that surfaces S_1 and S_2 would be poor candidates for such a surface). It is then convenient to choose the two coordinates to be s and u as depicted in Fig. 1, and the dividing surface S_3 then corresponds to the following function f(s,u),

$$f(s,u) \quad = \quad s \qquad ; \tag{9}$$

i.e., s = 0 defines surface S_3. Eq. (1) for the <u>exact</u> classical rate constant then reads

$$k_{b\leftarrow a} = Q_a^{-1}\, h^{-2} \int_{-\infty}^{\infty} dp_s \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp_u \; e^{-\beta H(p_s,s,p_u,u)} \left(\frac{p_s}{m_s}\right) \chi_{b\leftarrow a}(p_s,s,p_u,u) \tag{10}$$

with s = 0. The "fundamental assumption" of transition state theory corresponds to the replacement

$$\chi_{b\leftarrow a}(p_s,s,p_u,u) \longrightarrow h(p_s) \quad , \tag{11}$$

where h(x) is the step-function:

$$h(x) = \begin{matrix} 1, & x > 0 \\ 0, & x < 0 \end{matrix} \quad ;$$

i.e., it is assumed that if the trajectory has positive momentum in the reactive direction at the dividing surface, then it is indeed reactive in the a→b direction. Since the total Hamiltonian is of the form

$$H(p_s,s,p_u,u) = \frac{p_s^{\,2}}{2m_s} + \frac{p_u^{\,2}}{2m_u} + V(s,u) \quad , \tag{12}$$

where V(s,u) is the potential energy surface, Eq. (10) becomes

$$k_{b\leftarrow a} = Q_a^{-1} \; [h^{-1} \int_{-\infty}^{\infty} dp_s \; h(p_s) \; \frac{p_s}{m_s} \; e^{-\beta p_s^{\,2}/2m_s}]$$

$$\times \; [h^{-1} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du \; e^{-\beta[\frac{p_u^{\,2}}{2m_u} + V(0,u)]}$$

$$= \frac{kT}{h} \; \frac{Q^{\ddagger}}{Q_a} \; e^{-\beta V_o} \quad , \tag{13}$$

where $V_o = V(0,0)$ and $Q^{\ddagger}$ is the classical partition function of the "activated complex", the system with one degree of freedom removed:

$$Q^{\ddagger} = h^{-1} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du \; e^{-\beta[\frac{p_u^2}{2m_u} + V(0,u) - V(0,0)]} \quad . \qquad (14)$$

By invoking Eq. (11), the "fundamental assumption" of transition state theory, all explicit reference to classical dynamics (i.e., to the characteristic function $\chi_{b\leftarrow a}$) is therefore eliminated, and one recognizes Eq. (13) as the usual expression for the rate constant in transition state theory.[1]

In concluding this discussion of classical transition state theory it is interesting to note how different this dynamical view of transition state theory ála Wigner[12] is from other presentations which refer to the following "mechanism"

$$A + BC \rightleftharpoons (ABC)^{\ddagger} \longrightarrow AB + C \qquad (15)$$

to derive Eq. (13). It is often implied that some sort of equilibrium between reactants and "activated complexes" is responsible for the ratio of partition functions that appear in Eq. (13). This in turn suggests that transition state theory should perhaps be most applicable if A and BC form a collision complex that lives for many vibrational periods. (Recall the desire in the early days of transition state theory for the $H + H_2$ potential surface to have a well at the top of the barrier). The discussion in the above paragraphs show, on the contrary, that the fundamental assumption of transition state theory is that the mechanism is "direct", that all trajectories move right across the dividing surface and do not return. This assumption of "straight-through" dynamics is essentially the opposite to that of a long-lived collision complex, for the latter would result in trajectories which re-cross the dividing surface many times and thus invalidate the "fundamental assumption".

III. ACCURACY OF CLASSICAL TRANSITION STATE THEORY

Before considering quantum mechanical transition state theory, it is useful to look at the accuracy of classical transition state theory, i.e., the validity of the "fundamental assumption" that no trajectories cross the dividing surface more than once, that the reaction dynamics is "direct". Thus consider a simple collinear reaction such as $H + H_2 \rightarrow H_2 + H$ with the dividing surface chosen as the symmetric line (surface S_3 in Fig. 1). It also simplifies matters to consider the microcanonical version of transition state theory, which corresponds to a fixed total energy E rather than a fixed temperature T: The dimensionless function N(E) is defined by

$$N(E) = 2\pi\hbar\ h^{-F} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\ \ \delta[E-H(\underset{\sim}{p},\underset{\sim}{q})]\ \delta[f(\underset{\sim}{q})]\ \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}/m\ \ \chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q}) \quad , \tag{16}$$

in terms of which it is easy to see that the rate constant in Eq. (1) is given by

$$k_{b\leftarrow a} = Q_a^{-1}\ (2\pi\hbar)^{-1} \int_0^\infty dE\ e^{-\beta E}\ N(E) \quad . \tag{17}$$

The transition state approximation to N(E) corresponds to replacing $\chi_{b\leftarrow a}$ in Eq. (16) by the approximation in Eq. (11).

N(E) is clearly zero for $E < V_o$, V_o being the position of the saddle point in the potential energy surface, for no classical trajectory can be reactive unless it has enough energy to go over the barrier. For total energies E only slightly above the barrier it is not hard to conclude that the transition state approximation for N(E) will be exact,[6a] i.e., there will be no trajectories which cross the dividing surface more than once. To see this, imagine beginning a trajectory on the symmetric line with a total energy only slightly above the saddle point; the trajectory will begin slowly, pick up speed as it runs down the hill toward products, and clearly not return. At sufficiently high energy, on the other hand, it is clear that there will be trajectories which rebound back across the symmetric line and thus invalidate the "fundamental assumption".

Since the transition state approximation to N(E) begins correctly at the classical threshold V_o, the primary question in classical transition state theory is how high above V_o can E be increased and it still be true that there are no re-crossing trajectories. Pechukas and McLafferty[6a] have made an ingenius contribution to answering this question by discovering a simple geometrical criterion for finding a critical energy below which the transition state approximation to N(E) is exact. Another approach to investigating this question is the "experimental" one of simply comparing the exact N(E) function, determined by carrying out classical trajectory calculations, with the transition state approximation to N(E).

Figure 2 shows such a comparison[14,15] of the exact and the transition state approximation for N(E) as a function of total energy for the collinear H + H_2 reaction. As expected, at low energy--up to about 0.3 eV above the barrier height in this case--the transition state approximation is essentially exact, i.e., there are no trajectories at these energies that re-cross the symmetric line. At higher energies, however, there do exist trajectories that rebound back across so that the transition state approximation to N(E) is too large.

Figure 3 shows a similar comparison[14,15] for the three-dimensional $H + H_2$ reaction, the exact N(E) being evaluated by Monte Carlo trajectory calculations. Again one sees that transition state theory is essentially exact for energies up to about 0.3 eV above the barrier, and even when it begins to fail it is in much less error than in the collinear case; at 1 eV above the barrier the transition state approximates to N(E) is only 10% too large.

The above relation between the collinear and three-dimensional $H + H_2$ reaction (both with the same Porter-Karplus[16] potential energy surface) illustrates a feature which one expects to be general, namely that other things being equal, the fundamental assumption of transition state theory is better the higher the dimensionality of the system. This is understood qualitatively in that fewer trajectories, having departed from the dividing surface towards products, are able to find their way back in the higher dimensional phase space; i.e., they are more likely to get "lost" and not return.

IV. TOWARDS A QUANTUM TRANSITION STATE THEORY

The previous sections have shown that within the realm of classical mechanics transition state theory describes the threshold region of the reactive cross section quite accurately. This success of classical transition state theory is somewhat hollow, however, because quantum effects are important in the threshold region, particularly so if the reactive dynamics involves light atoms (i.e., H atom transfer). The task, then, is to implement the "fundamental assumption" of transition state theory in a fully quantum mechanical framework.

There are several reasons for believing that the assumption of "direct dynamics" through the saddle point region is valid for the threshold region also in a quantum mechanical theory. The streamlines of flux computed by Kuppermann et al.[17] for the H + H_2 reaction, for example, show "straight-through" dynamics at low energy, even in the tunneling regime below the classical threshold. (At higher energies, though, the streamlines develop "whirlpool effects", corresponding to re-crossing classical trajectories.) Similarly, the semiclassical calculations of George and Miller[18] show complex-valued classical trajectories which tunnel "straight-through" the saddle point region.

The first step in constructing a quantum version of transition state theory is to write the exact quantum mechanical expression for the rate constant (assuming a Boltzmann distribution of reactants). This can be expressed in a number of ways, but the form most useful for present purposes is one[7] which is the direct analog of the classical expression in Eq. (1),

$$k_{b\leftarrow a}(T) = Q_a^{-1}\, \mathrm{tr}[e^{-\beta H}\, \delta(f)\, \frac{\partial f}{\partial q}\cdot \underset{\sim}{p}/m\, \mathcal{P}] \quad , \tag{18}$$

where "tr" means a quantum mechanical trace, the quantum analog of a classical phase space average; H, $f(\underset{\sim}{q})$, and $\underset{\sim}{p}$ all have their same meanings as in Eq. (1) except that they are now quantum mechanical operators. The projection operator $\mathcal{P}$ is the quantum analog of the characteristic function $\chi_{b\leftarrow a}$ in Eq. (1), and it is given explicitly by[7]

$$\mathcal{P} = \lim_{t\to-\infty} e^{iHt/\hbar}\, h(-P)\, e^{-iHt/\hbar} \quad , \tag{19}$$

P being the momentum operator conjugate to R. The appearance of the quantum mechanical evolution operator, $e^{-iHt/\hbar}$, in $\mathcal{P}$ shows that it is the factor which contains all the quantum scattering dynamics, analogous to the dynamical content of the classical function $\chi_{b\leftarrow a}$. In words, $\mathcal{P}$ projects onto all states that have evolved in the infinite past from reactants.

As in the classical case, one can show[7] that the exact quantum rate constant in Eq. (18) is independent of the specific choice of the dividing surface. Quantum transition state theory is thus defined in a manner analogous to the classical case: A specific choice is made for the dividing surface (e.g., surface S_3 in Fig. 1), and then the "dynamical factor" $\mathcal{P}$ is approximated by invoking the fundamental assumption of transition state theory. Analogous to Eq. (11), one makes the replacement

$$\mathcal{P} \rightarrow h(p_s) \quad ;$$

this approximate projection operator projects onto all states that have positive momentum in the s-direction, and it is the "fundamental assumption" that positive momentum in the s-direction at the dividing surface implies evolution from reactants in the infinite past.

This approach[7] to quantum mechanical transition state theory thus gives the rate constant as

$$k_{b\leftarrow a} = Q_a^{-1}\ \mathrm{tr}[e^{-\beta H}\ \delta(s)\ \frac{p_s}{m_s}\ h(p_s)] \quad . \tag{20}$$

If one does introduce the assumption that the Hamiltonian is <u>separable</u> in s and u coordinates,

$$H \;=\; h_s + h_u + V_o \quad , \tag{21}$$

then it is easy to show[7] that the conventional expression for the rate constant results

$$k_{b\leftarrow a} = \Gamma \frac{kT}{h} \frac{Q^{\ddagger}}{Q_a} e^{-\beta V_o} \quad , \tag{22}$$

where $Q^{\ddagger}$ is the quantum mechanical partition function of the "activated complex"

$$Q^{\ddagger} = \underset{u}{\mathrm{tr}}(e^{-\beta h_u}) \quad , \tag{23}$$

and Γ is a one-dimensional tunneling coefficient,

$$\Gamma = 2\pi\hbar\beta \; \underset{s}{\mathrm{tr}}[e^{-\beta h_s} \delta(s) \frac{p_s}{m_s} h(p_s)] \quad . \tag{24}$$

The assumption of separability of the Hamiltonian, however, one knows to be a poor approximation in the threshold region where quantum effects are important. One manifestation of this is the "corner-cutting" effect that has been seen in a number of different kinds of calculations for the $H + H_2$ reaction:[17-19] at low energies in the threshold region the tunneling from reactants to products "cuts the corner", going through the side of the barrier rather than directly under the saddle point itself. Other evidence for the breakdown of the separability approximation is the poor agreement that Eq. (22) gives with the exact quantum scattering calculations of Truhlar and Kuppermann.[10]

To make a fair test of the "fundamental assumption" of transition state theory in the quantum mechanical case one thus needs to evaluate

Eq. (20) without incorporating any kind of assumption of separability. This is a considerably more difficult task, however, because the Boltzmann operator $e^{-\beta H}$ does not now factor into separate one-dimensional operators.

A first step toward evaluating Eq. (20) without assuming separability has been made[20,21] by introducing a semiclassical approximation for the Boltzmann operator and evaluating the trace within the semiclassical limit; no assumptions involving separability, however, were made. In addition to simplifying the calculation, the semiclassical limit of Eq. (20) leads to a very interesting physical picture of the non-separable tunneling dynamics; the interested reader should consult refs. 20 and 21.

Figure 4 shows the comparison of the "exact" function N(E), obtained from quantum scattering calculations,[22] to that obtained by this semiclassical evaluation[21] of Eq. (20), again for the collinear $H + H_2$ reaction. Also shown is the result for N(E) given by conventional (i.e., separable) transition state theory with a one-dimensional tunneling correction.[10,23] The comparison of the corresponding rate constants as a function of temperature, obtained from the functions N(E) via Eq. (17), is shown in Fig. 5.

The results in Figures 4 and 5 show quite clearly the degree to which the separability approximation fails in the threshold region. They also show that once non-separability is taken properly into account, quantum mechanical transition state theory provides an accurate description of the threshold region and thus the rate constant.

V. CONCLUSIONS AND PROGNOSIS

Although one should be wary of drawing too many conclusions from only one example, a few seem safe. For the threshold region of a simple chemical reaction it does seem that the "fundamental assumption" of transition state theory is accurate quantum mechanically, as it is classically, provided the separability approximation is not introduced to simplify the quantum calculation. Since the effects of non-separability, and quantum effects in general, are probably more prominent in the collinear $H + H_2$ reaction discussed in the previous sections than in any real chemical reaction, it indeed provides a severe test. Thus the generalized definition of quantum mechanical transition state theory is seen to be a useful and accurate one (although there are some subtle ambiguities[7] not discussed here).

For the future one needs to explore other ways of evaluating Eq. (20) and to investigate the effects that non-separability might have for real chemical reactions; e.g., are they neglible except perhaps for H-atom transfer reactions. Even more interesting is the question of how one can define transition state models for chemical reactions which do not have a single saddle point separating reactants and products. Suppose, for example, the triatomic molecule A-B-C has a stable potential well with two different saddle point regions leading to either AB + C or A + BC. The A + BC collision would then likely lead to a collision complex (if the reactions is not too endo- or exothermic) which would invalidate the simple version of the "fundamental assumption" of transition state theory. By considering two dividing surfaces, however, drawn through the two saddle point regions, it may be possible to develop a transition state model by assuming the flux through each of the two surfaces individually is direct. Also of importance is the extent to which transition state models can be developed for describing non-adiabatic reactions,[24] i.e., chemical reactions involving more than one potential energy surface.

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15. The functions actually plotted in Figs. 2 and 3 are the ratio of N(E), the reactive flux, to the incident flux (or flux per unit area for the 3D case). These ratios have the more physically meaningful interpretation of an average reaction probability in the collinear case (Fig. 2) and an average reaction cross section in the 3D case (Fig. 3).

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18. T. F. George and W. H. Miller, *J. Chem. Phys.* **56**, 5722; **57**, 2458 (1972).

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20. W. H. Miller, *J. Chem. Phys.* **62**, 1899 (1975).

21. S. Chapman, B. C. Garrett, and W. H. Miller, *J. Chem. Phys.* **63**, 2710 (1975).

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23. There are a variety of prescriptions considered in ref. 10 for how to calculate the one-dimensional tunneling co-efficient Γ in the conventional

quantum mechanical version of transition state theory. That plotted in Figure 5 is the "vibrationally adiabatic zero curvature" model which is perhaps most justifiable theoretically. Other prescriptions tried in ref. 10 give no better results.

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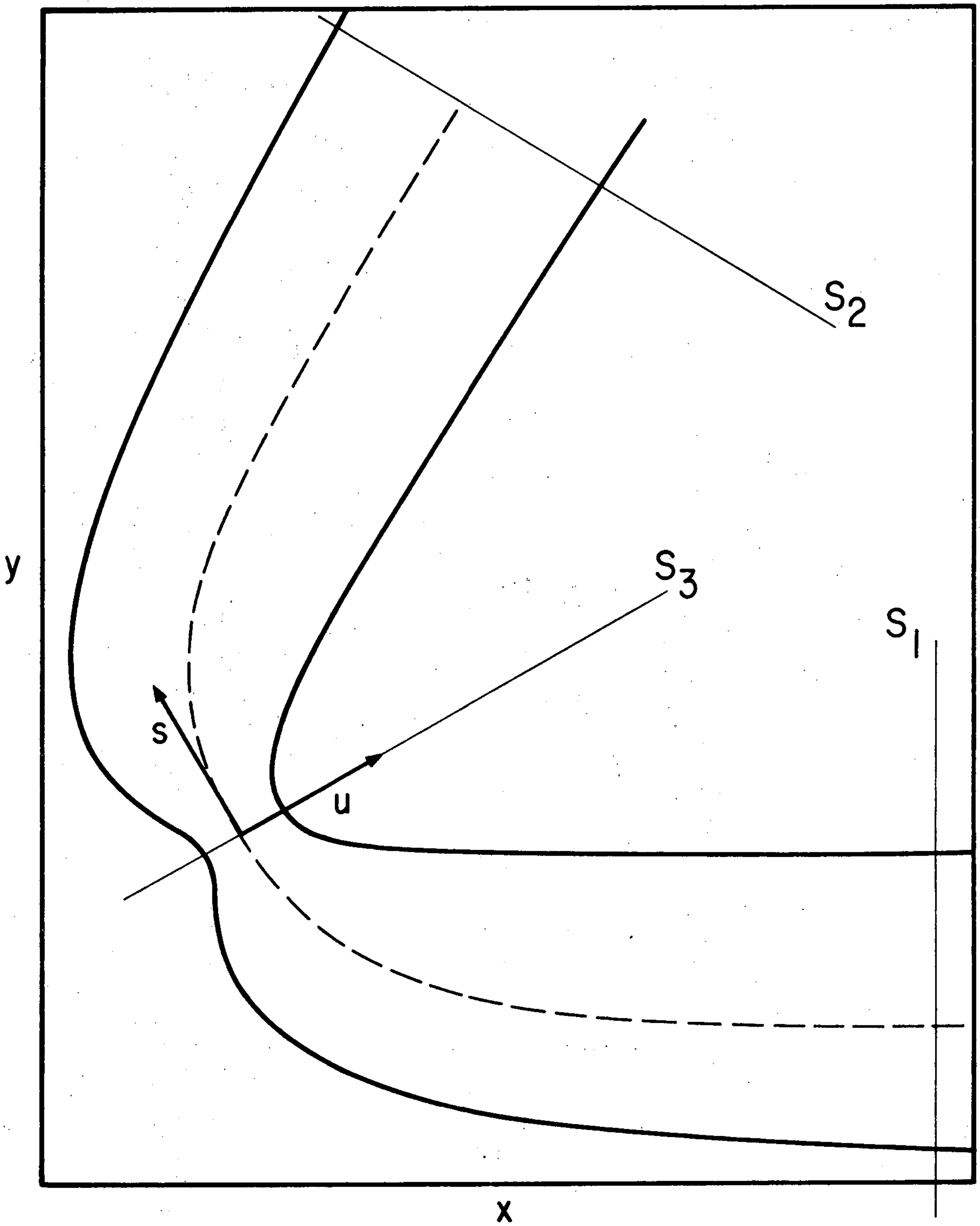
FIGURE CAPTIONS

1. Sketch of a collinear potential energy surface for a symmetric $A + BC \rightarrow AB + C$ reaction (i.e., $A \equiv C$). x and y are mass weighted, or "skewed" coordinates that diagonalize the kinetic energy: $x = R(\mu/M)^{1/2}$, $y = r(m/M)^{1/2}$, where R and r are the translational and vibrational coordinates, respectively, and μ and m the corresponding reduced masses [$m = BC/(B+C)$, $\mu = A(B+C)/(A+B+C)$]. M is any arbitrary mass, and the classical kinetic energy is $\frac{1}{2} M(\dot{x}^2 + \dot{y}^2)$. s and u are the linear combinations of x and y which diagonalize the potential energy at the saddle point. S_1, S_2, and S_3 indicate the "surfaces" which are referred to in the text.
2. Reaction probability for the collinear $H + H_2$ reaction on the Porter-Karplus potential surface from a microcanonical classical trajectory calculation (CL DYN) and microcanonical classical transition state theory (CL TST), as a function of total energy above the barrier height. (1 eV = 23.06 kcal/mole).
3. Same as in Figure 1, except that $\sigma(E)$ is the microcanonical reactive cross section for the three dimensional $H + H_2$ reaction.
4. The function N(E), defined by Eq. (16), for the collinear $H + H_2 \rightarrow H_2 + H$ reaction, as a function of total energy E_0 above the ground state of H_2. (In this energy regime N(E) is simply the ground state to ground state reaction probability.) QM SCAT denotes the (exact) result of quantum scattering theory (ref. 22), and SEP TST is that of conventional (i.e., separable) transition state theory with a one dimensional tunneling correction (refs. 10, 23). NON-SEP TST is the result based on a semiclassical evaluation of Eq. (20) (ref. 21), the generalized transition state theory that takes account of non-separability.

5. Rate constant as a function of temperature for the collinear $H + H_2 \rightarrow H_2 + H$ reaction; the labels have the same meaning as in Fig. 4. These results were calculated by Eq. (17) with the N(E) functions in Fig. 4.



XBL 744-6034

Figure 1

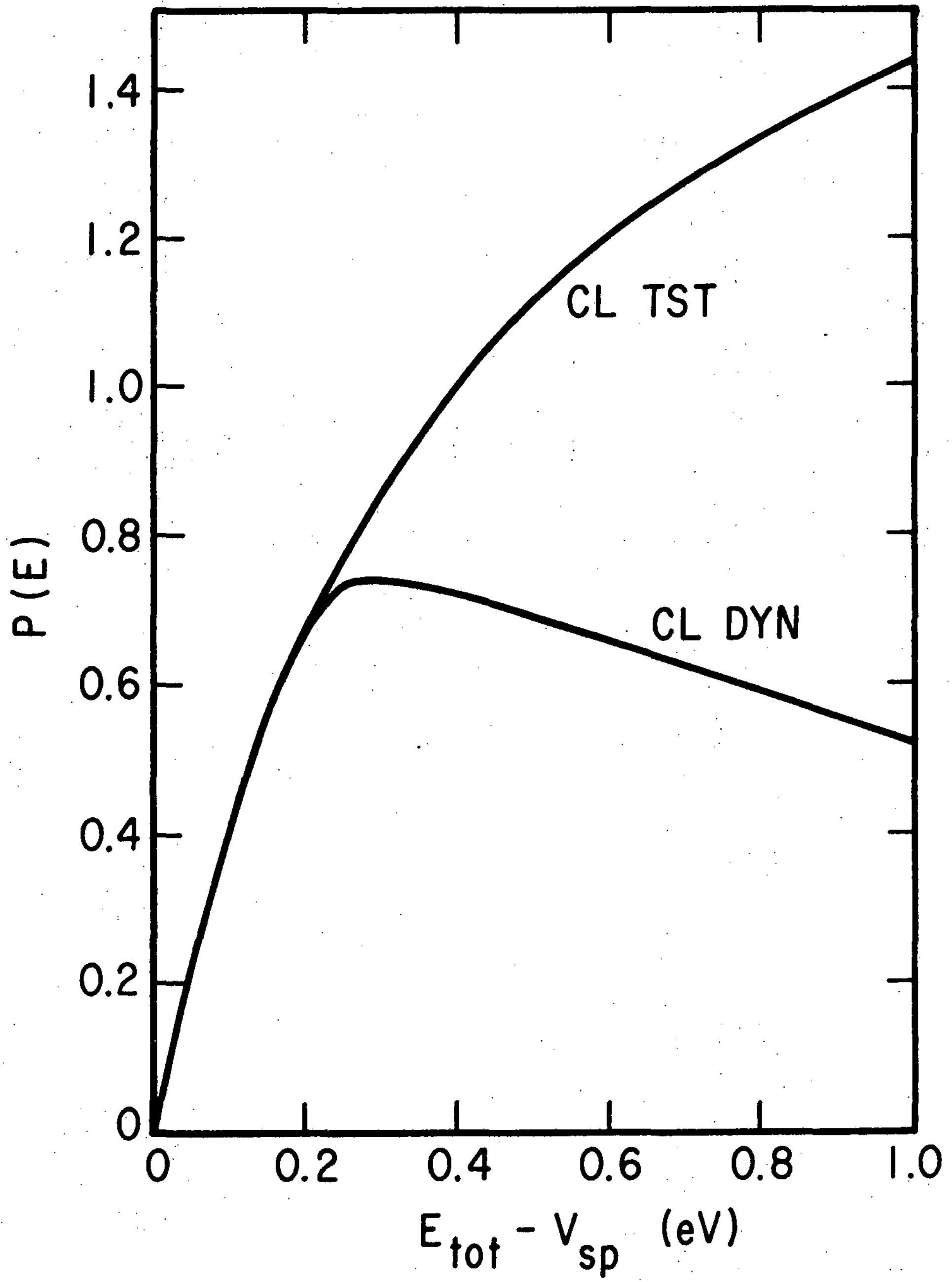


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Figure 2

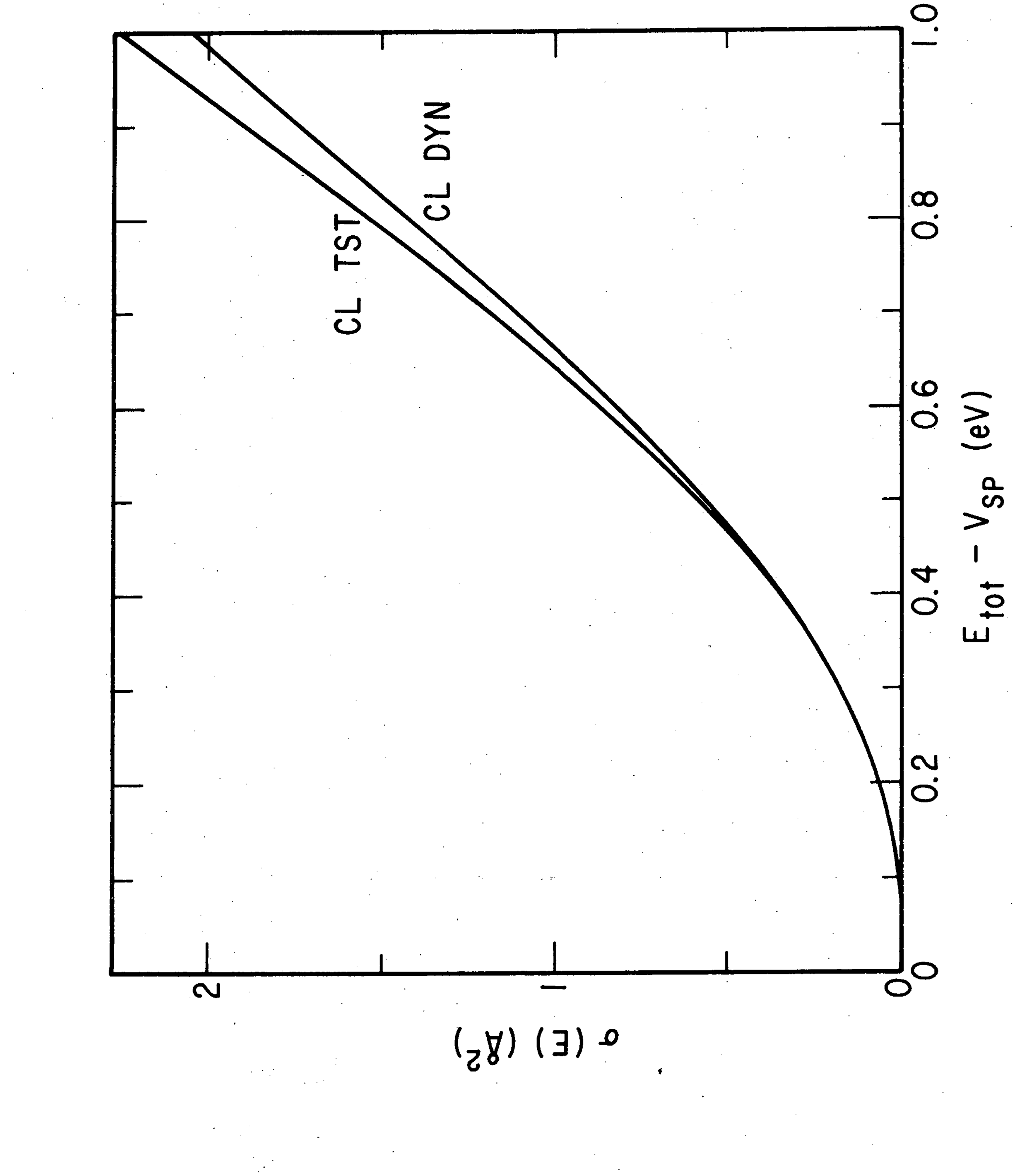

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Figure 3

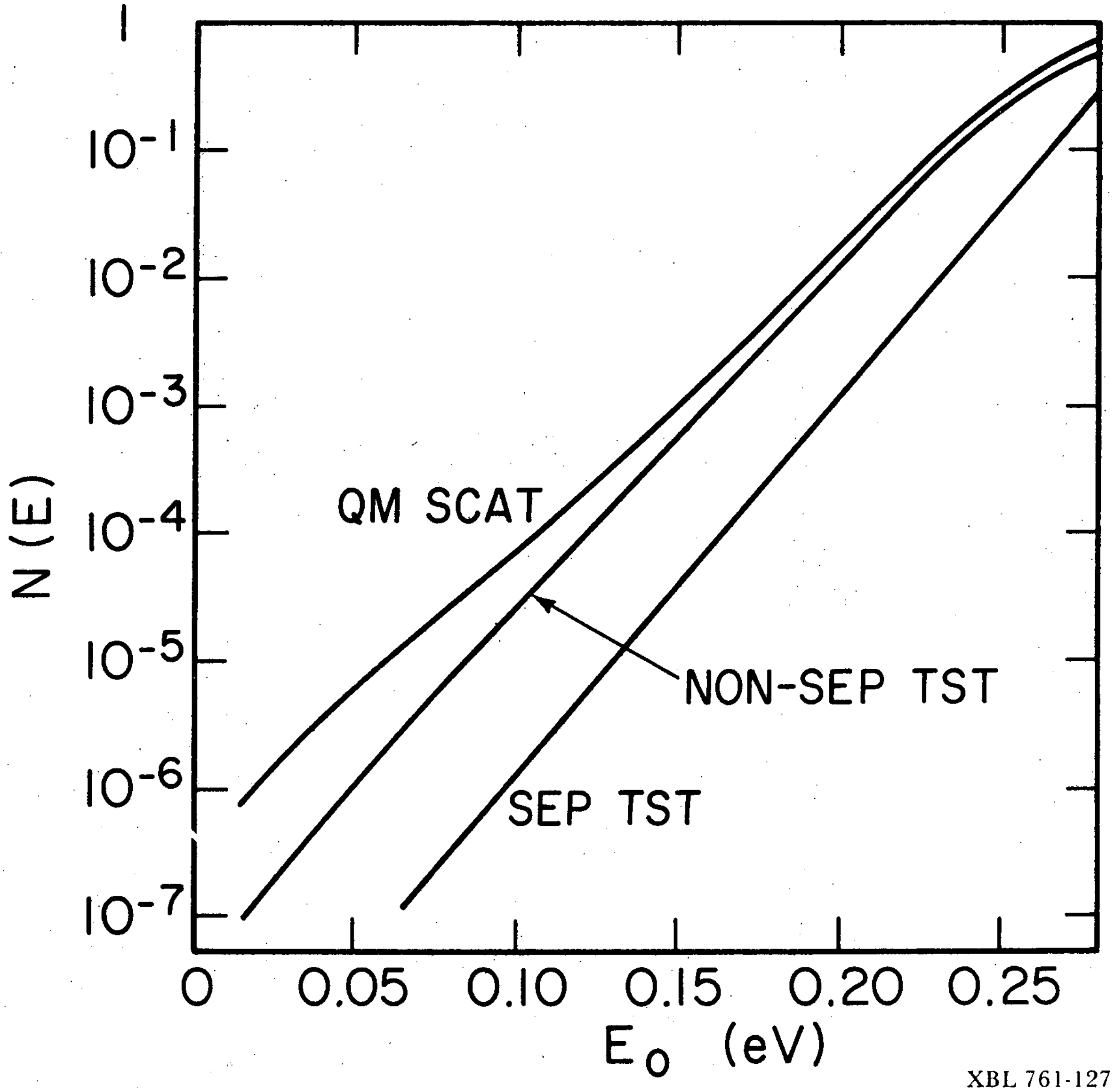
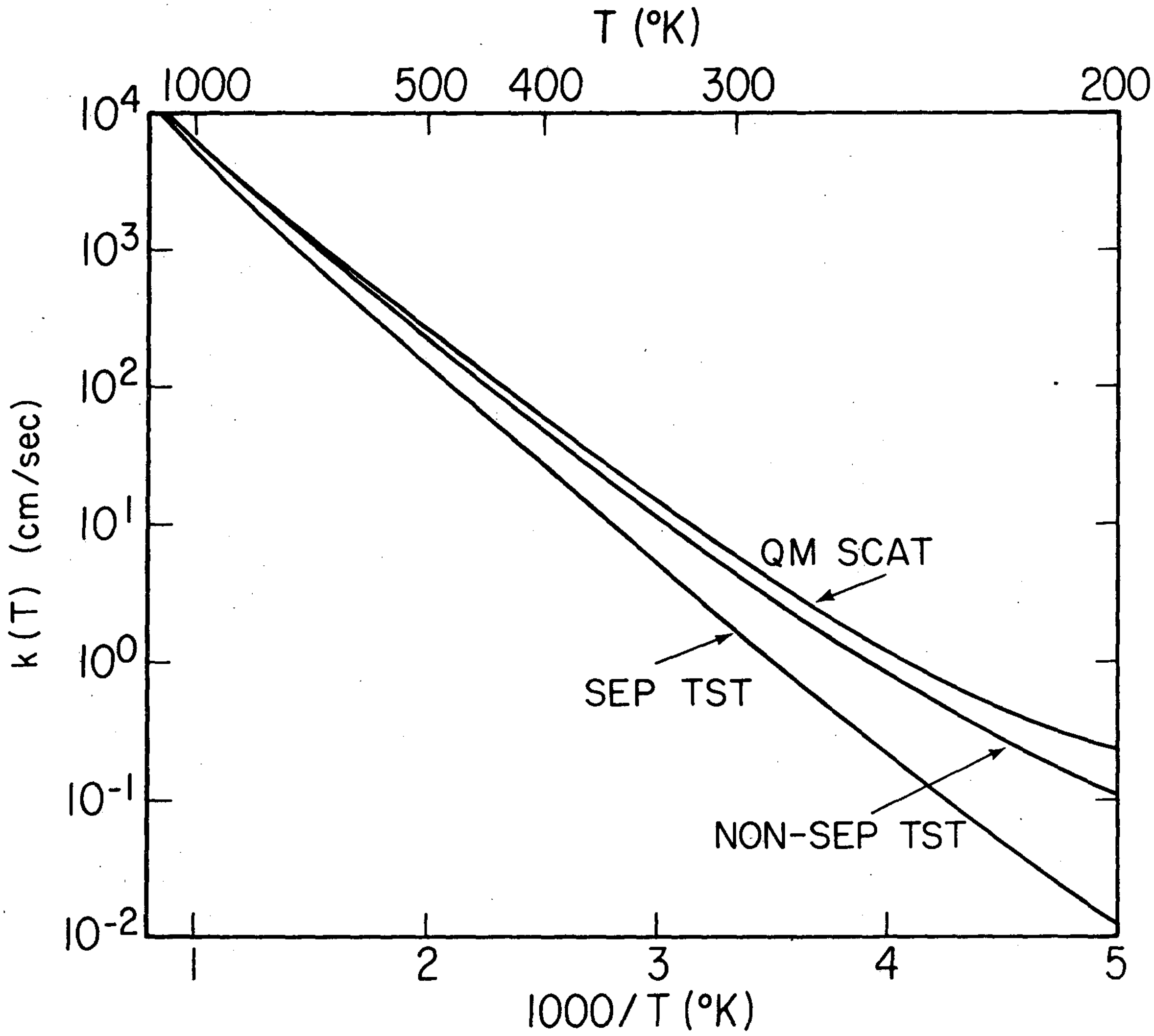

1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
N (E)
QM SCAT
NON-SEP TST
SEP TST
0
0.05
0.10
0.15
0.20
0.25
E_0 (eV)
XBL 761-127

Figure 4



XBL 761-128

Figure 5