

Tunnelling in Bimolecular Collisions

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I. Introduction

Although tunnelling in bimolecular reactions has been studied since the late 1920s, the importance of tunnelling in chemistry is still the subject of much misunderstanding. Just mentioning the question, "How much does curvature in an Arrhenius plot reflect the tunnelling contribution to the rate constant?" is likely to evoke much discussion and controversy. However, for very simple gas-phase reactions, particularly atom-diatom hydrogen-transfer reactions, many of the quantitative questions pertaining to tunnelling have been unravelled in the past few years through the use of modern theoretical reaction dynamics methods. Thus we now have a quantitative understanding of tunnelling processes for some simple reactions, and this understanding is rapidly extending to more complex reactions.

It is the purpose of this review to discuss these recent developments in the theory of tunnelling in bimolecular gas phase reaction dynamics. Since our emphasis will be on quantitative theories, much of this review will be concerned with atom-diatom H and D atom exchange reactions where the potential energy surfaces are well characterized, and where experimental measurements allow for a quantitative comparison between theory and experiment. We will, however, also discuss recent developments which have expanded our qualitative understanding of tunnelling, including the question of how tunnelling should be defined, the validity of the vibrationally adiabatic approximation when tunnelling is important, and the question of tunnelling times. The theories of tunnelling that will be discussed range from essentially exact quantum scattering methods to one-dimensional theories based on reaction path concepts. A special emphasis will be placed on the variational-transition-state-theory description of reaction dynamics since this provides one of the most meaningful ways to define tunnelling contributions to rate constants.

Almost all of our discussion will be devoted to H or D atom tunnelling in reactions with potential energy



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barriers. The importance of H atom tunnelling in recombination reactions with small or no barriers is a potentially important topic that is just starting to receive attention.¹ Tunnelling of atoms other than hydrogen isotopes has received very little attention in quantitative theoretical studies.² Electron tunnelling in gas-phase charge-transfer reactions has received some attention^{3,4} but is outside the scope of this review. Proton and hydride transfer reactions in the gas phase are usually not associated with substantial barriers, and thus tunnelling has received less attention here than in corresponding condensed-phase studies.⁵

A closely related review of tunnelling in *unimolecular* reactions can be found elsewhere in this journal edition.⁶ Other recent reviews that have touched upon tunnelling to some extent include reviews of variational-transition-state theory by Truhlar, Garrett, and co-workers,⁷⁻¹⁰ of accurate quantum reactive scattering calculations by Schatz¹¹ and by Connor,¹² of reduced di-

mensionality quantum methods by Bowman,¹³ of infinite-order sudden methods by Jellinek and Kouri,¹⁴ of semiclassical methods by Miller,¹⁵ and of the H₃ kinetics by Truhlar and Wyatt.¹⁶

To summarize the rest of this review, in the next section (section II) we define what we mean by tunnelling and use a simple model of reactive scattering to illustrate this definition and to indicate the very important relationship between tunnelling and vibrational adiabaticity. Section III then discusses recent exact and approximate theoretical studies of tunnelling using quantum-scattering methods, while section IV describes methods and applications based on reaction path models, including those used in connection with variational-transition-state theory, and section V describes path integral methods (and related methods) for describing tunnelling.

II. What is Tunnelling? A Simple Model of Tunnelling Dynamics

Although there is no unique definition of what one means by the term "tunnelling", in one dimensional problems the term "tunnelling" is usually taken to refer to reaction that takes place at energies less than the classical barrier energy.¹⁷ Above the classical barrier, deviation between quantum and classical reaction probabilities is generally called "non-classical reflection". This means that the "transmission coefficient" or "tunnelling factor" κ which is defined as the ratio of quantum to classical thermal rate constants actually measures both tunnelling and nonclassical reflection. At low temperatures, however, κ is dominated by "tunnelling" as defined above and thus the term "tunnelling factor" is appropriate.

In two or more dimensions, the above definitions of tunnelling and tunnelling factor need to be refined. In particular, it is not useful to define tunnelling as reaction that occurs at energies below the classical barrier energy because energy locked up in modes perpendicular to the reaction path makes the energy needed to surmount the effective barrier to reaction different from the classical barrier. Although there is no rigorous way to define this effective barrier, a commonly used assumption which underlies variational-transition-state theory (VTST) and other theories is to define this barrier in terms of vibrationally adiabatic potential curves which are generated by diagonalizing the Hamiltonian associated with motion perpendicular to the reaction path connecting reagents and products at each point along the reaction path. The technology associated with evaluating vibrationally adiabatic potentials has been discussed elsewhere,^{7-10,18-21} and often one finds that the important bottleneck in determining thermal rate constants is that associated with the vibrationally adiabatic ground-state (VAG) curve. We will denote the VAG barrier by V_a^G .

To be rigorous, we should note that the VTST prescription for locating the bottleneck is based on finding a free-energy maximum for either a canonical or microcanonical ensemble,¹⁸⁻²⁰ and the energy of this bottleneck equals V_a^G only in the limit of zero temperature or energy. However, for reactions involving transfer of a light atom (H or D), usually V_a^G is an excellent approximation to this free-energy barrier up to quite high temperatures or energies. We should also

note that if the VTST bottleneck is located at the potential surface saddle point, then VTST reduces to conventional transition state theory. There are many examples of where this does *not* happen.^{7-10,18-20}

If we accept the VTST definition of reaction bottleneck, then the logical way to measure tunnelling is via a transmission coefficient κ which is defined as

$$\kappa = k_{EQ}/k_{VTST} \quad (2.1)$$

where k_{EQ} is the exact quantum rate constant and k_{VTST} is that obtained from VTST treating reaction path motions classically but other modes quantum mechanically. According to the definition in eq 2.1, κ includes for all differences between the VTST and exact rate constants, and thus includes for both tunnelling and recrossing. At low temperatures, however, one expects that κ will primarily reflect the influence of tunnelling, and thus, just as in the one-dimensional case, it is reasonable to refer to it as a "tunnelling factor".

It may seem that use of the VTST rate constant as a reference by which tunnelling is defined is a rather specialized definition that may not describe reaction bottleneck behavior meaningfully in situations where motional time scales are inappropriate for perpendicular vibrational motions to be adiabatic, but in fact this is actually much more general than a simple consideration of adiabatic theory would indicate. Before discussing this point in a general sense, let us illustrate it numerically by considering the following two dimensional model of reaction dynamics. (References 22-23 describe similar models used in other applications.)

In this model we imagine that one of the coordinates in the problem is the reaction path coordinate s , and the other is a rotational angle γ . The Hamiltonian H is taken to be that appropriate for the coplanar interaction of an atom with a homonuclear diatomic molecule, taking the total angular momentum to be zero and assuming that stretch vibrational motion is adiabatic. In this case then, we find

$$H = P^2/2\mu + j^2/2I + V(s,\gamma) \quad (2.2)$$

where the first term refers to reaction path motion, the second refers to rotational motion, and the third is a coupling term which we take to be

$$V(s,\gamma) = B \sin^2 \gamma / \cosh^2 (s/L) \quad (2.3)$$

This represents an Eckart barrier in the s coordinate modulated by $\sin^2 \gamma$ such that the $\gamma = 0$ and π barriers vanish and the $\gamma = \pi/2, 3\pi/2$ barrier is B . Taking parameters roughly appropriate to H + H₂ ($\mu = 1224.7$ au, $I = 3600$ au, $B = 1.63$ eV and $L = 0.500 a_0$), we generate the vibrationally adiabatic potential curves given in Figure 1. Note that the rotorlike energy levels at $s = \pm\infty$ transform into oscillatorlike levels near $s = 0$. The VAG barrier is 0.11 eV. Notice especially that the oscillator period varies from ∞ at $s = \pm\infty$ to 2×10^{-14} s at $s = 0$, while the time needed for reaction to occur (roughly $2L/v$ where v is the velocity associated with an energy of 0.11 eV) is 1×10^{-14} s. Thus the time scales do not seem to be appropriate for vibrationally adiabatic behavior.

Figure 2 shows the results of exact quantum-scattering calculations (EQ) using this model, along with results from classical trajectories (CT), vibrationally adiabatic theory (VA), and rotational sudden (RS) ap-

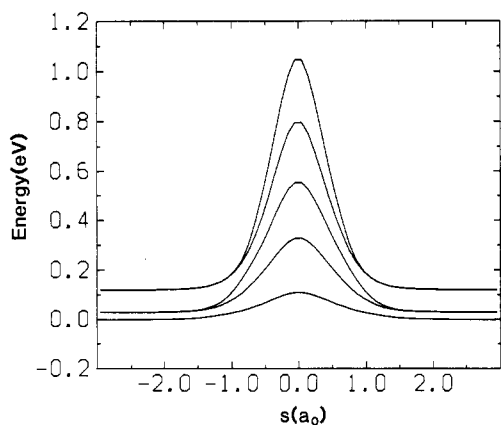


Figure 1. Vibrationally adiabatic potentials (in eV) as a function of the reaction path coordinate s (in a_0) for the lowest 5 states of the model Hamiltonian described in text.

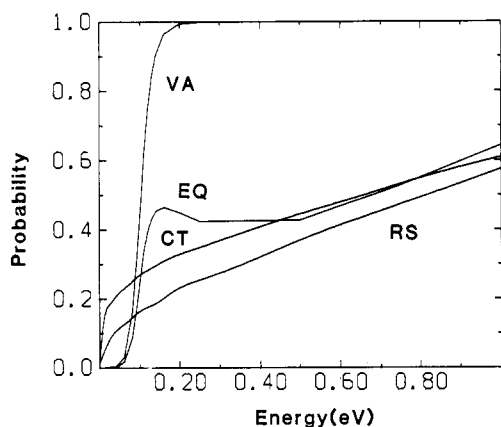


Figure 2. Reaction probability vs. reagent translational energy (in eV) for model described in text. EQ denotes the results from an accurate quantum scattering calculation, while CT denotes the corresponding classical trajectory probabilities; VA, the results of a quantum calculation using vibrationally adiabatic potentials; and RS, the results of using a quantum rotational sudden approximation.

proximations to the dynamics. (RS assumes that the rotor angle is fixed during the reaction and then averages over results from different orientations.) Plotted in Figure 2 is the total reaction probability P vs. reagent translational energy for reagents starting in the ground rotational state, and we see that the EQ results show a well-defined threshold at an energy which is very close to the VA threshold, and both are close to the VAG barrier. The CT and RS thresholds are by way of contrast at zero translational energy as one would expect given that the $\gamma = 0, \pi$ barrier is zero. Below threshold we find that the EQ and VA reaction probabilities are almost identical, while well above threshold the EQ probability merges in with the CT and RS results while the VA probability goes to unity.

Figure 2 graphically demonstrates that exact quantum dynamics is closely governed by the VAG threshold, thus supporting our contention that eq 2.1 provides a useful way to define tunnelling. This occurs even though the motional time scales seem to be inappropriate for VA theory to be right. Well above threshold, however, the CT and RS results are more accurate than VA for the initial state-resolved probability plotted in Figure 2. The agreement of EQ and VA probabilities for rotationally excited reagents (not shown) is much closer, however, and in fact the EQ cumulative proba-

bility (the sum of P over all initial states) is in excellent agreement (better than 1%) with VA over the entire energy range where the EQ probability is greater than 10^{-2} . The corresponding CT and RS cumulative probabilities are also accurate at high energies but retain the threshold error noted in Figure 2. Since it is the cumulative probability near threshold that determines thermal rate constants at typical temperatures (200–2000 K), the VA rate constants are thus in very good agreement with EQ while the CT and RS rate constants are not.

The apparent anomaly in time scales noted above has been discussed previously in an analysis of accurate quantum results for 3D $H + H_2$,²⁴ and recently it was the subject of a general study of time-delay behavior in reactive tunnelling by Abu-Salbi et al.²⁵ They examined the Eisenbud–Wigner^{26,27} time-delay matrix τ_{ij} for several models of reactive scattering, including an inverted harmonic oscillator potential and collinear $H + H_2$ and $D + H_2$ reactive collisions. τ_{ij} is related to the scattering matrix S_{ij} and its energy derivative dS_{ij}/dE by

$$\tau_{ij} = \text{Re}[-i\hbar S_{ij}^{-1} dS_{ij}/dE] \quad (2.4)$$

τ_{ij} had been studied in earlier calculations using collinear quantum methods,^{28–30} but the new result of Abu-Salbi et al. was that τ_{ij} exhibits a maximum at energies close to the VAG barrier which can be significantly larger than that estimated by simple arguments such as classical passage times. In addition they found that adiabatic behavior should arise if the period of internal motion is shorter than $(1/2\pi) \Delta\tau$ where $\Delta\tau$ is the barrier passage time. This was found to occur for both collinear $H + H_2$ and $D + H_2$ over a relatively wide range of energies near the VAG barrier. The same argument is less conclusive for 3D $H + H_2$, where the slower bend mode should be less adiabatic according to their arguments. However this bend mode was found to be highly adiabatic in the 3D $H + H_2$ calculations in ref 24. An alternative argument to resolve this time scale anomaly was given in ref 24 based on how the uncertainty principle constrains the minimum energy that a wave packet can have in each mode at the point that the barrier is crossed. Unfortunately it is hard to develop this argument for nonseparable systems in a way that rigorously leads to VAG bottleneck without invoking the VA approximation first.

If we ignore this time scale paradox, then the qualitative picture of tunnelling that appears from the discussion so far is one of somewhat deceptive simplicity. If tunnelling is dominant then vibrationally adiabatic theory always works well, and a relatively simple adiabatic theory estimate should be adequate to determine κ in eq 2.1, and hence the accurate rate constant from k_{VTST} . What we have left out of this discussion, however, is how curvature along the reaction path influences tunnelling. (The model used in Figure 1 and 2 leaves out curvature.) This point has been studied by several groups,^{31–36} and we will discuss the results of these studies in detail in section IV. Suffice it to say for now that eq 2.1 and the VAG threshold are still considered to be meaningful quantities when curvature is included, but the path along which tunnelling occurs has to be moved away from the steepest descents path in order to calculate accurate tunnelling factors. Of course, even

TABLE I. Collinear Exact Quantum Tunnelling Factors

reaction	β , deg	200 K	300 K	ref
H + BrH	89.3	36	5.3	42
H + BrD	89.0	12	3.0	42
Mu + H ₂ (LSTH)	77.0	71	7.7	45
H + H ₂ (PK2)	60.0	46	8.7	46-49
H + H ₂ (LSTH)	60.0	14	3.7	45
O + H ₂	46.7	60	9.4	54
Cl + DCl	19.0	14	5.0	55
Cl + HCl	13.6	93	16	55

the best of theories based on one dimensional paths is not perfect, but it is encouraging that the simple prescription based on adiabatic theory can be generalized to broad classes of reactions.

III. Quantum Scattering Studies of Reactive Collisions

Thanks to advances in scattering theory as well as to the availability of fast computers, it is now possible to calculate reaction rate constants for many atom-diatom reactions almost exactly for a given potential surface. Unfortunately, the only reaction for which the potential surface is known to "chemical accuracy" (~ 0.1 kcal/mol) is H + H₂, but at least for this reaction and its isotopomers one can quantitatively estimate rate constants for comparison with experiment. Even for reactions where the surface is not known accurately, exact results for a given surface allow for the study of tunnelling on that surface. Of course, the rate constants from a quantum scattering calculation do not by themselves indicate the importance of tunnelling, but by using eq 2.1 (or other theories³⁷⁻³⁹), one can determine the importance of tunnelling in these reactions.

We will begin our discussion of quantum scattering calculations by considering exact calculations done in one rather than three physical dimensions. Such calculations are much easier than three dimensional calculations and have been more extensively analyzed. We then discuss recent three-dimensional accurate quantum studies, followed by results from several approximate quantum methods. We will not go into the technology of these calculations since very detailed papers on that topic have appeared.^{40,41}

A. Collinear Exact Quantum Studies

Connor⁸ has extensively reviewed the collinear exact quantum studies of atom-diatom reactions. Here we restrict our discussion to those studies that specifically examined tunnelling and for which comparable three dimensional calculations have since been done.

Table I presents the tunnelling factors κ defined using eq 2.1 for several collinear reactions. The accurate results were taken from ref 42 (H + BrH, H + BrD using the surface of ref 43-44), ref 45 (Mu + H₂), ref 46-49 (H + H₂ on surface no. 2 of Ref 50 (denoted PK2)), ref 45 (H + H₂ on the surface of ref 51-53 (denoted LSTH)), ref 54 (O + H₂), and ref 55 (Cl + DCl, Cl + HCl), and many of the κ 's were previously tabulated by Garrett and Truhlar.³⁵ k_{VTST} in eq 1 was in all cases defined using the improved canonical variational theory (ICVT) of ref 18 (see refs 35 and 55). Mu in this table stands for muonium (μ^+e^-) which is an isotope of hydrogen with a mass of about $1/9$. The parameter β in the table stands for the kinematically

defined "skew" angle between reagent and product translational coordinates using a coordinate system that diagonalizes the kinetic energy. Mathematically, β is defined by

$$\beta = \tan^{-1} (m_B(m_A + m_B + m_C)/(m_A m_C))^{1/2} \quad (3.1)$$

where the atoms are labelled A, B, C with B being the atom which is exchanged during reaction, and m_i ($i = A, B, C$) is the mass of atom i . Physically, β provides a measure of the amount of reaction path curvature, with $\beta = 90^\circ$, corresponding to the light-heavy-light mass combination that minimizes curvature and $\beta = 0^\circ$ to the heavy-light-heavy combination that maximizes curvature.

The reactions in Table I have barriers of 5.5 kcal/mol (H + BrH (D)), 8.5 kcal/mol (Cl + HCl (DCl)), 9.1 kcal/mol (PK2), 9.8 kcal/mol (LSTH), and 12.5 kcal/mol (O + H₂). Evidently the κ values are not easily correlated with barrier height, and there is no straightforward correlation with β either. We will see later however that β does play an important role in determining the optimum tunnelling path.

Perhaps the most notable conclusion from Table I is how big the κ values actually are. The smallest tunnelling factor at 300 K is 3.0, meaning that tunnelling contributes 75% of the total rate constant. Tunnelling factors at 200 K range up to 93, meaning that 98.9% of the reaction rate constant is due to tunnelling. In addition, we note that tunnelling in the Br transfer reactions H + BrH and H + BrD is comparable in importance to that for the other reactions. Tunnelling does depend strongly on isotope, however, with the deuterated systems having κ 's that are often more than a factor of two smaller than their H-atom counterparts. As one might expect, the Mu + H₂ κ value is much larger than that for H + H₂, but here one has to note that the VAG barrier for Mu + H₂ is quite different in both location and shape from that for H + H₂, and thus the differences between these two reactions are due to a combination of mass-dependent effects that can both decrease and increase the κ values. This applies to a lesser extent to the other reactions, and as a result it is impossible to write down a simple analytical formula that explains all the results in Table I. There are, however, some very good numerical theories that can be used to describe the results in Table I in terms of tunnelling along one-dimensional paths, and we will discuss these in section IV.

B. Three-Dimensional Accurate Quantum Studies

The methods that have been used to date to determine accurate rate constants for atom-diatom reactions in three dimensions are all based on coupled-channel ("close-coupling") technology. The first calculations of this type were done on the H + H₂ reaction⁵⁶⁻⁶⁰ and used CC calculations in each arrangement channel followed by a matching procedure to construct globally acceptable scattering solutions. Recent calculations using this approach have considered H + H₂,⁶¹ D + H₂,⁶² H + D₂,⁶³ and Mu + H₂,⁶⁴ all on the LSTH potential surface. In all of these recent calculations, the coupled-states (CS) approximation⁶⁵⁻⁶⁷ was invoked. This method appears capable of generating results which are accurate to 20% under a variety of circumstances.

TABLE II. Three-Dimensional Tunnelling Factors

reaction	β , deg	200 K	300 K	ref
H + BrH	89.3	46.7	5.5	69
H + BrD	89.0	15	3.2	69
H + DH (PK2)	70.5	250	12	11
H + D ₂ (LSTH)	65.9	19	3.2	62
H + H ₂ (PK2)	60	556	23	59
H + H ₂ (LSTH)	60	83	6.9	61
O + DH	57.0		7.1	73
D + H ₂ (PK2)	54.7	303	17	11
D + H ₂ (LSTH)	54.7	68	6.7	62
O + D ₂	48.2		7.1	73
O + H ₂	46.7		19	73
O + HD	37.6		12	73
Cl + HCl	13.6	28	17	75

Since the LSTH potential surface for H₃ is also quite accurate, the rate constants from all of these recent CS calculations are in excellent agreement with experiment.^{45,46,48} Accurate calculations have also been done using CC (and related methods) on light-heavy-light reactions, where the matching is trivial.^{68,69}

Another accurate quantum approach that is especially well suited for describing tunnelling is the coupled-channel distorted wave (CCDW) method.⁷⁰⁻⁷² This uses perturbation theory to calculate the reactive cross sections and thus is only accurate at low energies or temperatures where reaction is truly a perturbation. Because it uses accurate nonreactive wave functions, it is, however, capable of determining essentially exact results in this perturbative limit, and the results of applications to H + H₂ are in fact in excellent agreement with matching based CC results.⁷⁰ Applications of the CS version of CCDW (denoted CSDW) have recently been made to O + H₂ (HD, D₂)⁷³ and Cl + HCl.^{74,75}

Table II summarizes the three-dimensional tunnelling factors that have been obtained to date in accurate calculations. (These results are adapted from ref 18-20, 35, 61, 66, 76, and 77). To the extent possible, the reactions listed in Table II correspond to reactions included in Table I, enabling a comparison of tunnelling factors in one and three dimensions. Simple adiabatic theory would predict that the main change in going from 1D to 3D is the addition of the bending zero point energy to the VAG barrier. Differences in tunnelling between 1D and 3D thus reflect how the bending energy varies along the reaction path, and if the bend force constant is independent of reaction path coordinate near the bottleneck, then the tunnelling factor will be independent of dimensionality. On the other hand, if the force constant peaks at the bottleneck then the 3D barrier will be "thinner" than 1D and the 3D tunnelling factor will be larger. In Tables I and II we see evidence for both possibilities, with κ for H + BrH and H + BrD approximately independent of dimension, and κ for H + H₂ larger in 3D than in 1D on both the PK2 and LSTH surfaces.

Table II also allows us to study the dependence of κ on isotope in some detail. In all cases one sees a tendency for κ values to be smaller for reactions involving D than H, and this applies both to the case that D is the atom transferred (primary isotope effect) and that it is not. Note also how strongly that κ depends on potential surface for H + H₂ and D + H₂. Table II indicates that the PK2 κ 's are larger than the LSTH κ 's by more than a factor of 3. This strong sensitivity to barrier shape adds significance to the excellent agree-

TABLE III. Rate Constants and Isotope Effects for H + H₂ and H + DH (PK2 Surface)

	200 K	300 K
Rate Constants (cm ³ /molecule s)		
H + H ₂	CS	1.6 (-17)
	VTST	2.9 (-20)
H + DH	CS	1.2 (-17)
	VTST	4.8 (-21)
Isotope Ratios (H + H ₂ /H + DH)		
	CS	13
	VTST	6.0
Activation Energies (kcal/mol)		
H + H ₂	CS	4.9
	VTST	8.7
H + DH	CS	5.4
	VTST	9.1
Preexponential Factors (cm ³ /molecule s)		
H + H ₂	CS	3.9 (-12)
	VTST	1.0 (-10)
H + DH	CS	9.2 (-13)
	VTST	3.7 (-11)

ment between theory and experiment that has been found for H + H₂ and D + H₂ on the LSTH surface.^{45,46,61}

The results in ref 76 can also be used to study the interplay between tunnelling and isotope effects. Let us consider the two reactions H + H₂ and H + DH, which differ only in the mass of the atom being transferred. Table III summarizes rate constants and isotope effects for these reactions as obtained from CS and VTST calculations on the PK2 surface. The table indicates that VTST (without tunnelling) only accounts for about 45% of the H + H₂/H + DH isotope ratio at both temperatures (4.6 from VTST versus 11 from CS at 300 K). Since it is customary in condensed-phase chemistry to discuss tunnelling contributions to isotope effects in terms of contributions from preexponential factors *A* and activation energies, *E_a*, values for these quantities (obtained by fitting an Arrhenius expression to the 200 and 300 K rate constants) are also included in Table III. The table indicates that both *A* and *E_a* contribute significantly to the isotope ratio, and that both quantities change significantly in going from VTST to CS. In accordance with simple intuition, the activation energy is lower for H + H₂ than for H + DH, and the difference between the two reactions is larger when tunnelling is included (CS values) than when it is not (VTST). Perhaps more significant, however, is how much *E_a* and *A* change in going from VTST to CS for each isotope. The change in *E_a* is 3.8 kcal/mol for H + H₂ and 3.7 kcal/mol for H + DH. Recalling that the PK2 saddle point energy is 9.1 kcal/mol, the table indicates why extreme caution should be used in relating measured activation energies to barrier heights. Notice also that the *A* factors decrease by large factors when tunnelling is included. This partially compensates the increase in rate constant expected from the decrease in activation energy, and since the decrease in *A* is isotope-dependent, it renders useless any attempt to interpret tunnelling as an effect which changes activation energies but not preexponential factors.

Another way to use accurate quantum rate constants is to fit the rate constants to transition-state-theory expressions which use simple one-dimensional reaction path formulas to describe tunnelling. This approach has recently been considered by Pacey⁷⁸ who used the

Eckart tunnelling factor⁷⁹ to derive apparent transition-state properties, including imaginary frequencies by comparison with CC rate constants for $H + H_2$.⁵⁹ This type of analysis is of relevance to the use of similar fits to experimental data to infer potential surface properties, and it indicates how to interpret Arrhenius plot curvature and temperature-dependent activation energies in terms of more fundamental dynamical features. As one might expect, the fitted parameters do not agree accurately with the saddle point properties of the surface used to generate the rate constants. Deviations between actual and fitted parameters could be related to the importance of tunnelling along paths which depart from the minimum energy path. (This point will be considered in greater detail in section IV.) Unfortunately, the Pacey comparison has not yet led to the development of improved parametrized formulas for relating potential surface properties to rate constants.

C. Approximate Quantum Calculations

In this section we examine the ability of approximate quantum mechanical calculations to describe tunnelling. The methods we consider are distinguished from the reaction path methods of Section IV in that they describe at least two degrees of freedom in a dynamically accurate way (i.e., are fully coupled) and they differ from the methods of the previous section in that they neglect some part of the potential energy coupling between different degrees of freedom. For atom-diatom reactions with collinear saddle points, all of the commonly used approximate methods have been designed to treat the collinear (stretching) degrees of freedom accurately so that effects of reaction path curvature should be accurately described. This leaves the internal angular (bending) degrees of freedom to be approximated (external rotational couplings are approximated using the CS method described earlier), and this has been done from two different points of view. One approach called the infinite order sudden approximation (IOSA) assumes that angular motion is slow and thus the internal bending angle is fixed during each collision.¹⁴ This is identical with the RS method described in Section II. The other approach which we call reduced dimensionality exact quantum (RDEQ) dynamics¹³ assumes that bending is adiabatic (the same as the VA method of Section II) and thus influences the active degrees of freedom only through the addition of a local bending eigenvalue at each value of the stretch coordinates. The RDEQ approach has also been developed in the context of reaction *surface* Hamiltonians,⁸⁰ and in view of the results of our model in section II, it would be expected to be more accurate than IOSA.

Another class of approximate quantum methods is based on the distorted-wave approximation. In contrast to the CCDW method of the previous section, here the nonreactive wave functions are approximated by neglecting potential couplings. Two commonly used approaches of this sort are the frozen molecule distorted wave (FMDW) method of Suck Salk and co-workers,^{81,82} and the vibrationally adiabatic distorted wave (VADW) method of Clary and Connor⁸³ and Tang, Choi, and co-workers.^{84,85} Normally these methods (especially FMDW) are not useful for quantitative rate constant estimates, but recent developments using VADW have

TABLE IV. Accurate and Approximate Tunnelling Factors for $D + H_2 \rightarrow DH + H$ (LSTH Surface)

T, K	accurate ^a	RDEQ ^b	IOSA ^c	VADW ^d	QCT ^e	MC ^f
200	68	63	176	195	68	60
300	6.4	7.0	17	8.9	11	6.7
400	2.8	3.5	6.2	3.5	4.8	3.2

^aReference 62. ^bReference 86. ^cReference 87. ^dReference 84. ^eReference 88. ^fReference 20 (there denoted ICVT/MCPVAG).

led to promising results as will be noted below.

Table IV presents κ values for the $D + H_2 \rightarrow DH + H$ reaction (LSTH potential surface) from all of the approximate quantum methods discussed so far,^{83,86-88} as well as from the accurate quantum calculations of the previous section. $D + H_2$ is actually the only reaction for which all of these methods have been applied, but the results in Table IV are representative of other comparisons between accurate and approximate quantum results that have been made.^{13,61,64,69,73} In particular, we note that the RDEQ results from ref 86 are in excellent agreement with the accurate values, while the IOSA κ values from ref 87 are high by factors of 2-3. The direction of the errors in IOSA is consistent with the results in Figure 2 where we found that IOSA overestimates the reaction probability in the threshold region. Pollak has proposed that one way to correct IOSA for this threshold error is to shift the IOSA cross sections upward in energy by the bending zero point energy which IOSA ignores.⁸⁹ He reports that this improves the agreement between IOSA and accurate rate constants. The reason for this is clear from Figure 2, although it should also be evident from that figure that it will not necessarily lead to an accurate description of tunnelling since the IOSA barrier does not have the same shape as the VAG barrier.

Considering now the VADW results in Table IV, we note that κ is too high at 200 K but becomes more accurate as T increases, becoming comparable to the RDEQ value at 400 K. This indicates that VADW is capable of modestly accurate results, which is a significant improvement over the results of earlier comparisons⁵⁹ using less sophisticated versions of VADW.

The sixth column in Table IV contains the κ values from quasiclassical trajectory (QCT) calculations.⁸⁸ Although it may seem somewhat out of place in a review of tunnelling to discuss classical results, we note in Table IV that the QCT κ values are in better agreement with the accurate values than some of the approximate quantum results. Actually, this surprising agreement between classical and quantum mechanics is the result of close to perfect cancellation between two opposing errors. The first is the absence of tunnelling, which tends to make the QCT rate constants too low, while the second is the absence of vibrationally adiabatic zero point energy constraints (noted in Figure 2) which tends to make the QCT rate constants too high.²⁴ Evidently it is only by accident that the results cancel as well as they do, and in fact there are systems where the QCT rate constants are known to be in poor agreement with accurate results in both positive⁶⁴ and negative⁷³ directions.

The overall conclusion of the comparisons in Table IV is that the RDEQ method is the most reliable of the approximate quantum methods for determining thermal rate constants for atom-diatom reactions with collinear reaction paths. Formulation and testing of the

method for more general classes of reactions still remains to be done, but even in its present state it has been of great use in studies of tunnelling and isotope effects in the $O + H_2 \rightarrow OH + H$ reaction,^{90,91} and a recent comparison of CSDW and RDEQ results for that reaction⁷³ confirms the expected accuracy of RDEQ in this application.

IV. Reaction Path Methods

The concept of using a one-dimensional reaction path to calculate tunnelling factors is an old one which dates to the beginnings of quantum mechanics. The work of Eckart⁷⁹ and of Bell⁹² are especially noteworthy in this regard since they both determined approximate solutions to one dimensional Schrodinger equations which have been used to interpret tunnelling behavior. An approximation to the Bell expression for κ known as the Wigner tunnelling factor⁹³ is also in widespread use.

These early attempts at developing one-dimensional tunnelling factors did not use rigorous theory to determine where the tunnelling path should be located, but it was commonly assumed that this path should be chosen as the minimum-energy path (MEP) between reagents and products. In recent years, however, the question of tunnelling paths has received more rigorous attention, beginning with the semiclassical S-matrix studies of collinear $H + H_2$ by Miller and coworkers.⁹⁴⁻⁹⁶ In these studies it was found that the primitive semiclassical S-matrix is determined at low energies by a single classical trajectory which follows a complex time contour which takes it through the "corner cutting" region of the potential energy surface. This behavior coincides with the results from collinear exact quantum calculations⁹⁷⁻⁹⁹ wherein the wavefunction is observed to maximize away from the MEP in the corner cutting region at energies where tunnelling is dominant.

One practical problem with using the complex trajectory approach to determining tunnelling probabilities is that it is computationally difficult to find the complex path in time that the trajectory should take to tunnel between reagents and products such that it satisfies both reagent and product boundary conditions. To circumvent this, a simpler (though less rigorous) approach to tunnelling was proposed by Marcus and Coltrin³¹ (MC) who used vibrationally adiabatic arguments to define a one dimensional path which follows the locus of outer vibrational turning points between reagents and products. A simple imaginary time contour is then sufficient to tunnel through the barrier. Table IV compares tunnelling coefficients obtained by Garrett et al.²⁰ using the MC path for $D + H_2$ with those from accurate results. The table indicates that the results are in excellent agreement with the accurate κ values, with the largest difference being only 14%. The relationship between the MC and complex trajectory approaches has been studied by Altkorn and Schatz,³⁶ who found that the MC path is a close approximation to the best purely imaginary time path that satisfies the semiclassical boundary conditions, and that this best imaginary time path is a very close approximation to the complex trajectory path of Miller and coworkers.

Truhlar, Garrett, and co-workers^{7-10,18-21,33-35,77,97} have extended this work on one-dimensional purely imaginary time reaction paths by developing several new methods for defining the paths and for calculating

TABLE V. Accurate and Approximate Transmission Coefficients for $H + H_2$, $D + H_2$, $H + HD$, and $H + DH$ (PK2 Surface)

T, K	W	SCTSAG	LAG	accurate
(A) $H + H_2 \rightarrow H_2 + H$ (Distinguishable Atoms)				
200	12	211	411	556
300	5.7	14	21	23
(B) $D + H_2 \rightarrow DH + H$				
200	10	82	173	303
300	5.2	8.1	13	17
(C) $H + DH \rightarrow HD + H$ (Distinguishable Atoms)				
200	7.8	243	258	250
300	4.1	14	12	12

transition probabilities from them. Three of these methods are in common use at present and are denoted SCTSAG, LCG, and LAG. The simplest is the small-curvature tunnelling semiclassical adiabatic ground-state (SCTSAG) method,³³ which treats curvature along the reaction path perturbatively and thus is most appropriate for large skew angle light-heavy-light reactions. For $H + H_2$, it is approximately equivalent to the MC approximation, though it recasts the tunnelling factor calculation in terms of tunnelling along the MEP with a coordinate dependent mass as opposed to tunnelling along the locus of outer turning points path with a constant mass. A related tunnelling factor has also been derived by Miller⁹⁸ using the reaction path Hamiltonian formulation⁹⁹⁻¹⁰³ that serves as the general theory by which the role of curvature in reaction dynamics is understood.

For many reactions, SCTSAG is superior to MC since it avoids unphysical loops in the tunnelling path that can arise from the MC prescription for constructing the path. In addition, SCTSAG is readily generalized to the treatment of polyatomics.⁹⁷ Its main defect arises in the treatment of large curvature reactions, where it often underestimates tunnelling. Table V compares SCTSAG and accurate tunnelling factors for several isotopes of the $H + H_2$ reaction at 200 and 300 K, using results derived from ref 76. Also included in the table are results from the Wigner method (labelled W) evaluated using the MEP potential. The table indicates that SCTSAG κ values are much closer to the accurate results than are the W results. For the large skew angle (70.5°) $H + DH$ reaction, the SCTSAG κ 's are also in excellent quantitative agreement with the accurate results. However the accuracy of SCTSAG deteriorates as the skew angle decreases, with the poorest results seen for the smallest skew angle reaction ($D + H_2$).

A method that has been developed for treating large curvature reactions (such as the heavy-light-heavy mass combination) is called LCG for large-curvature-ground-state method.³⁴ See also ref 104-107. This method uses a straight-line path that cuts the corner between reagents and products. The precise location of this path is determined by maximizing the tunnelling probability, and often it lies well inside the locus-of-outer-turning-points path. Applications of this method to the $Cl + HCl$ reaction¹⁰⁸ indicate generally good agreement with collinear exact quantum results, though there is a tendency to underestimate tunnelling at low temperatures.

The most general method for determining tunnelling probabilities that has been developed by Truhlar and co-workers is the least action ground-state (LAG) me-

thod.³⁵ This method calculates the tunnelling probabilities along a family of paths that spans the range from small to large curvatures, from this determines the optimum path for each energy, and then evaluates a thermally weighted average of the results to determine the overall tunnelling factor. Through this process, LAG becomes roughly equivalent to SCTSAG in the small-curvature limit, and to LCG in the large-curvature limit. Extensive comparisons of LAG rate constants with accurate quantum results in three dimensions have been done, and they indicate that LAG makes an average error of only 15%.⁷⁶ Tunnelling factors derived from this comparison are included in Table V under the "LAG" column, and we see that the results are comparable to SCTSAG for the small curvature H + DH reaction and are much more accurate than SCTSAG for the larger curvature H + H₂ and D + H₂ reactions.

Although the accuracy of the LAG method still needs to be tested in its application to more general classes of reactions, the success of the method to date represents a real triumph of reaction path methods for calculating tunnelling factors and thermal rate constants. Among the questions that still remain about its utilization are (1) its accuracy in describing tunnelling to and from vibrationally excited states (where LAG is replaced by the more general LA theory⁶⁹), (2) how to describe reactions which exhibit extensive recrossing at threshold (e.g., F + H₂⁷⁻¹⁰), and (3) whether LAG is quantitative for describing tunnelling when there is significant reaction path curvature in more than two coordinates (i.e., is the LAG choice of parametrized tunnelling paths still appropriate?)

V. Path Integral and Related Methods

Another approach to tunnelling in bimolecular collisions is based on the idea of directly evaluating the following formally exact expression for the thermal rate constant k ¹¹⁰⁻¹¹²

$$k(T) = Z_R^{-1} \int_0^\infty dt \operatorname{tr}[F e^{-(\beta/2 - it/\hbar)H} F e^{-(\beta/2 + it/\hbar)H}] \quad (5.1)$$

where F is the flux operator

$$F = \frac{1}{2} [\delta(s)(p_s/m) + (p_s/m)\delta(s)]. \quad (5.2)$$

In eq 5.2, p_s/m is the velocity operator for motions along the reaction path and δ is a Dirac delta function. Z_R in eq 5.1 stands for the reagent partition function and tr denotes "trace". Equation 5.1 can be derived in several ways, one of which was developed by Miller¹¹³ in his formulation of quantum-transition-state theory. A closely related semiclassical theory also developed by Miller^{113,114} will not be reviewed here. The technology associated with evaluating the trace in eq 5.1 is currently at a rather early stage of its development, so the types of applications considered so far are much less sophisticated than have been considered using the methods of sections III and IV of this review. The most accurate results generated to date with this approach have involved direct numerical evaluation of the trace using square integrable basis functions.¹¹⁵ Applications of this approach have so far been limited to collinear

H + H₂, where it has been found that the number of functions needed to generate converged results is comparable to the number needed to converge R -matrix theory results in applications to the same problem.¹¹⁶

A second approach to evaluating eq 5.1 is via path integrals.¹¹⁰⁻¹¹² Here it is important to distinguish between methods which treat all the degrees of freedom equivalently in evaluating the trace via path integrals vs. methods which explicitly set up path integrals only for motions along the reaction coordinate and use influence functionals to describe the rest.^{112,117,118} The first type of method has become popular in statistical mechanics,¹¹⁹⁻¹²³ but has so far not been useful in gas-phase dynamics problems because of computational difficulties.^{112,117} The second approach has seen more widespread use in gas-phase applications^{112,117} and is a computationally tractable approach, but its accuracy depends on the accuracy of the influence functionals used to describe effects arising from degrees of freedom not explicitly included in the calculation. At this point such influence functionals have only been developed for the case of linearly coupled harmonic oscillators perpendicular to the reaction path. This is what was used by Yamashita and Miller¹¹² in their study of the three-dimensional H + H₂ reaction using the reaction path Hamiltonian.⁹⁹⁻¹⁰⁰ They obtained a tunnelling factor at 300 K in good agreement with accurate quantum results on the PK2 surface (25 vs. 23). This result is consistent with previous studies,⁷⁷ which indicate that the neglect of anharmonicity is not very important for H + H₂. Thus this appears to be a promising approach to the determination of accurate quantum rate constants for reactions for which anharmonic effects are not important. An important challenge for future work will be to develop more powerful influence functional methods that allow for the treatment of anharmonicity in the motions of the perpendicular modes.

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