

Quantum Mechanical Tunnelling in Chemistry

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1 Introduction and Scope

One of the most unusual and interesting results of quantum mechanics is the prediction of tunnelling, *i.e.* the ability of a particle (or system of particles) to exist in, or pass through, a region of space where its total energy is less than its potential energy. According to classical mechanics, such a phenomenon is impossible, but in quantum mechanics it is a natural result of the probabilistic interpretation of wavefunctions, by which the states (position, momentum, energy, *etc.*) of atomic and molecular systems are specified. In view of this non-classical wave nature ascribed to particles, there is a certain logical inconsistency in using the classical word 'tunnelling' to describe the above phenomenon. The usage is universal, however, and seems to be entirely sensible in a probabilistic sense.

The physical importance and consequences of tunnelling have been recognized since the very earliest days of quantum mechanics. Hund¹ discussed the probability of intramolecular rearrangements *via* tunnelling in 1927, and the following year the importance of tunnelling in the decay of radioactive nuclei was described.² As early as 1932, Wigner³ discussed tunnelling with a view aimed at chemical kinetics; in the same year, the tunnelling mechanism responsible for the doubling of certain spectral bands of ammonia was clarified.⁴ Since these earliest days numerous experimental and theoretical studies have been performed to describe quantitatively the mechanisms and consequences of tunnelling in chemical systems.

In this article, we will review some of the areas in which tunnelling has been of significance over the years since its recognition. Several reviews and discussions of particular areas have appeared in the past. For example, Johnston⁵ and Caldin⁶ have provided reviews of various aspects of proton tunnelling in ordinary chemical reactions, and the significance of tunnelling to the understanding of the hydrogen bond has been well-described.⁷ The theory and certain

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¹ F. Hund, *Z. Physik*, 1927, **43**, 805.

² G. Gamow, *Z. Physik*, 1928, **51**, 204.

³ E. P. Wigner, *Z. phys. Chem. (Leipzig)*, 1932, **B19**, 203.

⁴ D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.*, 1932, **41**, 313.

⁵ H. S. Johnston, *Adv. Chem. Phys.*, 1961, **3**, 131.

⁶ E. F. Caldin, *Chem. Rev.*, 1969, **69**, 135.

⁷ See, for example, C. Haas and D. F. Hornig, *J. Chem. Phys.*, 1960, **32**, 1763; D. Hadzi, *J. Chem. Phys.*, 1961, **34**, 1445; G. M. Barrow, *Spectrochim. Acta*, 1960, **16**, 799.

experimental aspects of tunnelling methyl groups have been reviewed,⁸ and Löwdin⁹ has discussed tunnelling from a biological viewpoint. The view presented here will be less specific, with the aim toward stressing the unity of the phenomena together with the differences.

In order that the general features will be understood, we present in the next section an elementary theoretical discussion of tunnelling. Following this we shall move directly to a consideration of some chemical applications. We shall avoid tunnelling phenomena which lie principally in the realm of physics research, such as electron tunnelling through superconductor junctions.¹⁰

2 Theoretical Characteristics of Tunnelling

A. Free Particle Incident upon a Potential Barrier.—As a simple illustration we consider a particle of mass m moving in one dimension from left to right through a rectangular potential barrier. Two cases may be distinguished [see Figures 1(a) and 1(b)], depending upon whether the potential energy to the right

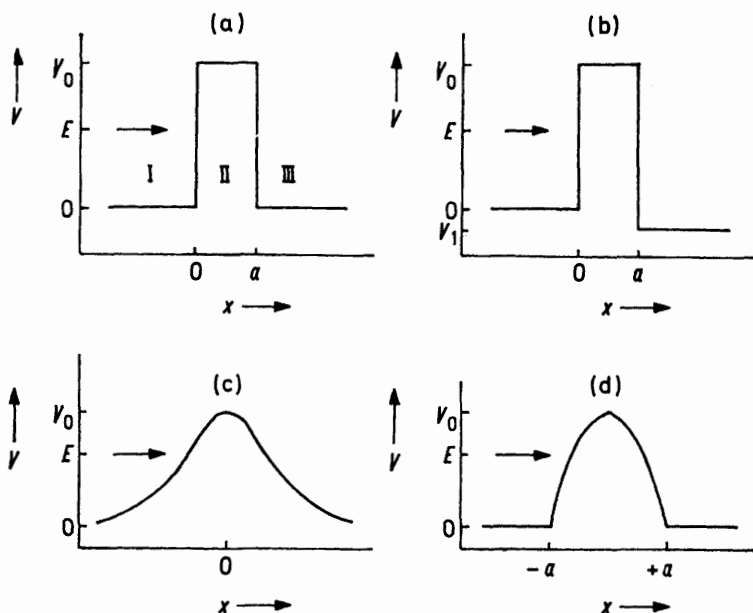


Figure 1 Simple one-dimensional potential barriers. Incident particle has energy E

⁸ C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, 1959, 31, 841.

⁹ P. O. Löwdin, *Adv. Quantum Chem.*, 1965, 2, 213.

¹⁰ J. Bardeen, *Phys. Rev. Letters*, 1961, 6, 57.

of the barrier is the same as, or different from, the potential energy on the left. These cases are termed symmetrical and unsymmetrical, respectively.

The solutions Ψ_i of Schrödinger's equation

$$\mathcal{H}\Psi = E\Psi \quad (1)$$

for either case are well-known,¹¹ and may be obtained by joining up functions for each of the regions I, II, and III so that Ψ_i and Ψ_i' are continuous at $x = 0$ and $x = a$. Solutions Ψ_i exist for both $E_i > V_0$ and $E_i < V_0$. If the transmission coefficient T is defined as the probability that a particle will tunnel through the barrier, the result is found to be¹¹ for the symmetrical case with $E < V_0$,

$$T = \frac{4k_1^2 k_2^2}{(k_1^2 + k_2^2)^2 \sinh^2 ak_2 + 4k_1^2 k_2^2} \quad (2)$$

In equation 2, $k_1 = \sqrt{2mE}/\hbar$ and $k_2 = \sqrt{2m(V_0 - E)}/\hbar$. For $E > V_0$, equation (2) applies if we replace k_2^2 by $-k_2'^2 = 2m(E - V_0)/\hbar^2$ and \sinh by \sin . To get some idea how the transmission coefficient depends upon the physical parameters we have plotted T in Figure 2 as a function of E for both a proton and deuteron incident upon a barrier of height 20 kcal mol⁻¹, and width 1 Å. This Figure indicates clearly that (a) tunnelling decreases markedly as V_0/E becomes large, and (b) that tunnelling decreases rapidly as the mass of the tunnelling particle increases. Further computations show a final feature, namely that tunnelling decreases rapidly as the width of the barrier increases. These are the chief characteristics of tunnelling which are expected to occur for all systems, even those having smoothed potential barriers rather than the square type in this example. While it is not shown in Figure 2, the transmission coefficient for particles having $E > V_0$ is not always unity, that is, there is a small probability of reflection above the barrier.

For the unsymmetrical case of Figure 1(b) an expression similar to equation (2) may be derived. As a first approximation equation (2) may be applied if it is multiplied by k_3/k_1 where $k_3 = \sqrt{2m(E - V_1)}/\hbar$. Thus as V_1 becomes more negative (for a fixed incident energy) the transmission coefficient increases. If V_1 is positive on the other hand, T decreases until eventually (when $E - V_1 \leq 0$) it goes to zero, that is, the probability of escaping to $x \gg a$ vanishes. These effects of the unsymmetrical barrier have often been overlooked in the past, but their importance has been particularly emphasized by Johnston *et al.*¹²

In general, tunnelling may be of significance in chemical phenomena when the wavefunction describing the tunnelling particle has a significant amplitude across the barrier region. Thus the de Broglie wavelength $\lambda = h/p$ provides a suitable qualitative measure for predicting *relative* tunnelling efficiencies. For particles of atomic mass 1, 2, 5, 10, 20, 50, and 100 having identical energies of 20 kcal mol⁻¹, the de Broglie wavelengths are 0.31, 0.22, 0.14, 0.097, 0.068,

¹¹ (a) L. Landau and E. Lifshitz, 'Quantum Mechanics', Addison-Wesley, Reading, Mass., 1958; (b) H. Eyring, J. Walter, and G. E. Kimball, 'Quantum Chemistry', John Wiley, New York, 1944; (c) D. Park, 'Quantum Theory', McGraw-Hall, New York, 1964.

¹² H. S. Johnston and J. Heicklen, *J. Phys. Chem.*, 1962, 66, 532.

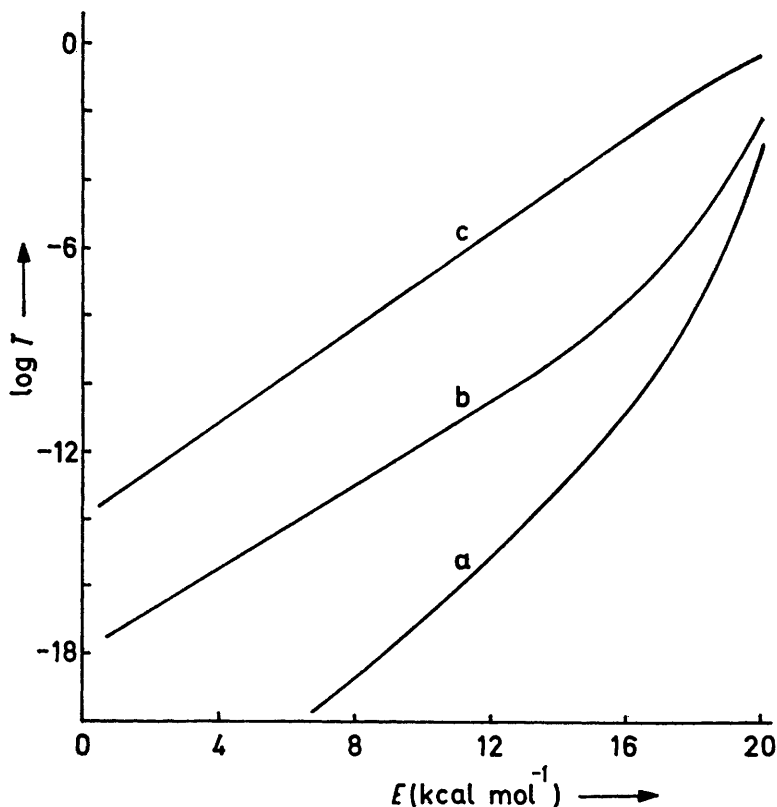


Figure 2 Transmission coefficient as a function of particle energy. Curves a and b are for deuteron and proton, respectively, incident upon rectangular barrier 20 kcal mol^{-1} high and 1 \AA wide. Curve c is for proton incident upon parabolic barrier of same height and base width

0.044 , and 0.031 \AA respectively. From these values it is clear that only the very lightest particles have a de Broglie wavelength comparable to the width of barriers in molecular systems ($\frac{1}{2}$ – 1 \AA). Nevertheless, tunnelling of heavier particles may still be observable if the barrier height is sufficiently low, or the barrier width sufficiently small.

Since the sharp-edged rectangular barrier is not a very realistic one for physical situations, other functional forms have been investigated. Figures 1(c) and 1(d) show two of those for which exact equations for the transmission coefficient exist. In Figure 1(c), the functional form is

$$V(x) = V_0/\cosh^2 \alpha x \tag{3}$$

and the transmission coefficient is given by¹³

¹³ See ref. 11 (a), p. 77.

$$T = \frac{\sinh^2(\pi k/\alpha)}{\sinh^2(\pi k/\alpha) + \cosh^2[(\pi/2)\sqrt{(8mV_0/\hbar^2\alpha^2) - 1}]} \quad (4)$$

when, as is typical, the square root term is greater than zero. In equation (4) $k = \sqrt{2mE/\hbar}$ and $E < V_0$. This symmetrical potential function is a special case of a more complicated function first investigated by Eckart.¹⁴

The potential in Figure 1(d) is an inverted parabola for $-a \leq x \leq +a$,

$$V(x) = V_0 \left(1 - \frac{x^2}{a^2} \right) \quad (5)$$

and $V(x) = 0$ otherwise. An exact calculation for the transmission coefficient yields¹⁵⁻¹⁷ for this case

$$T = \frac{1}{1 + \exp(\beta y)} \quad (6)$$

for all values of $E \geq 0$, where $y = 1 - E/V_0$ and $\beta = 2\pi^2 a \sqrt{2mV_0}/h$.

Each of the latter two potential functions of Figure 1 has been used rather extensively in practical applications. The potential of equation (5) has been particularly appealing because of its simplicity and the simple resulting expression for T given in equation (6). In Figure 2, equation (6) has been plotted for a proton incident upon a barrier having $V_0 = 20$ kcal mol⁻¹ and $2a = 1$ Å. The simplified Eckart potential of equation (3) and Figure 1(c) is undoubtedly more realistic than the parabolic form, however, particularly because of the absence of the discontinuities present at $x = \pm a$ in the latter function. Both of the barrier functions yield transmission coefficients having the same strong dependence upon E , V_0 , and barrier width, although the details differ quantitatively.

B. Bound Particle Tunnelling through Potential Barriers.—Here we consider bound particles which may exist in two or more potential energy minima separated by potential maxima. We show in Figure 3 one of the common potential functions of this form. Numerous types are encountered in physical problems, including functions having non-equivalent maxima and minima. In this section we shall merely consider the behaviour of a single particle of mass m moving in the double-minimum potential of Figure 3, but it is perhaps useful to mention that this potential is applicable to the inversion motion of the protons of ammonia.

The principal quantum mechanical feature of systems such as this is that all particle energies are not now available, *i.e.* Schrödinger's equation (equation 1) permits only certain energy states. For the double-minimum potential, the qualitative appearance of the lower-energy states has been shown in Figure 3.

¹⁴ C. Eckart, *Phys. Rev.*, 1930, **35**, 1303.

¹⁵ See ref. 11 (a), pp. 177—178.

¹⁶ R. P. Bell, *Proc. Roy. Soc.*, 1935, **A148**, 241.

¹⁷ R. P. Bell, *Trans. Faraday Soc.*, 1959, **55**, 1.

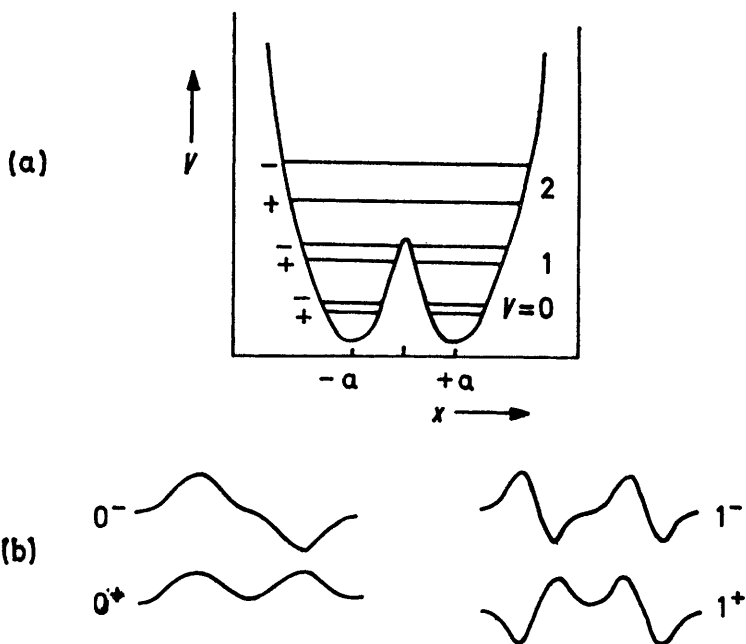


Figure 3 (a) Typical double-minimum potential; (b) qualitative forms of wavefunctions of lowest states

The characteristic feature is that below the barrier top the states occur as closely-spaced doublets. As the top of the barrier is approached the doublet spacing increases, and above the barrier the doublet structure finally disappears. Also shown in Figure 3 are the qualitative appearances of the eigenfunctions for the two lowest pairs of states. Note that the probability distribution (Ψ^2) is identical in the two equivalent wells, and is non-zero in the region of the barrier.

The question which must now be considered is what is meant precisely by *tunnelling* in such a system. Suppose we found by some measurement that at a certain time the particle existing in the potential of Figure 3 had an energy of $E_0^+(v = 0, + \text{ symmetry})$, and were asked where the particle was located. The acceptable answer is that there is a 50% probability that the particle existed in the region $x < 0$ at the time of the measurement; somewhat more approximately we might state that the particle has an equal probability of existing in either well. This answer is the proper one according to the interpretation of *stationary states*.

Suppose instead, that a measurement of position made at some time $t = 0$ showed positively that the particle was in the left-hand well with an energy of approximately $E_0^+ \sim E_0^-$. We ask now where the particle might be found at

$t > 0$. To answer this question it is necessary to utilize the concept of *non-stationary* states, since the certain presence of the particle in the left-hand well means it is not in any of the stationary states. Berry¹⁸ has described some of the general principles that must be considered. The simplest resulting view is that non-stationary states may be experimentally observed if the average lifetime of the state is long compared to the characteristic time involved in the particular measuring technique being used. For the particular case considered here, the most elementary theory¹⁹ leads to the conclusion that the particle tunnels between the left and right wells, represented by the non-stationary states $\Psi_0^+ + \Psi_0^-$ and $\Psi_0^+ - \Psi_0^-$, respectively, at a frequency

$$\nu_t = \frac{2(E_0^- - E_0^+)}{h} \quad (7)$$

Thus at the time $t = 1/\nu_t$ the particle is in the right well, while at $t = 2/\nu_t$ it is again back in the left well.

It is clear that the doublet separations provide a direct measure of the tunnelling rate or average lifetime of a non-stationary state of the particle. Much more sophisticated analyses have been performed,^{20,21} but this simple result is satisfactory for symmetrical barriers of the double-minimum type when the doublet spacings are small compared to the separation between states of different v .

For the free particle case it was found that the tunnelling probability might increase or decrease when the potential became unsymmetrical, depending upon whether the right-hand potential decreased or increased. For the bound particle case, the tunnelling rate usually decreases very markedly when any small asymmetry is introduced in the right-hand well. If, for example, the right-hand well is deepened by an amount equal to 1% of V_0 , the tunnelling rate may decrease by as much as a factor of 100. As shown by the computations of Somorjai and Hornig,²² this effect is caused not by any major change in the structure of the energy levels, but by the localization of the *stationary* state wavefunctions in either the left or right well. Thus in the case above, the lowest energy state Ψ_0 represents a particle largely localized in the slightly deeper right well, while in the next-lowest state Ψ_1 the particle is largely localized in the left-hand well. Then a particle definitely known to be in the left well at $t = 0$ will have a non-stationary state function of the form $\Psi_1 + c\Psi_0$ where $c^2 \ll 1$. This particle will eventually appear in the right well (state $\Psi_0 + c\Psi_1$) but it will take a time longer by a factor on the order of c^2 than that of the symmetrical case. This problem has been treated quantitatively by Brickmann and Zimmermann,^{21,23} who show, for example, that an offset of the minima of only 20 cm^{-1} in a double-minimum potential with a barrier of $\sim 6000 \text{ cm}^{-1}$ leads to a decrease in

¹⁸ R. S. Berry, *Rev. Mod. Phys.*, 1960, **32**, 447.

¹⁹ See, for example, C. H. Townes and A. L. Schawlow, 'Microwave Spectroscopy', McGraw-Hill, New York, 1955, Chap. 12.

²⁰ P. O. Löwdin, *Biopolymers Symp.*, 1964, **1**, 161.

²¹ J. Brickmann and H. Zimmermann, *J. Chem. Phys.*, 1969, **50**, 1608.

²² R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.*, 1962, **36**, 1980.

²³ J. Brickmann and H. Zimmermann, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 157.

ν_t of a factor of *ca.* 100. An expression for ν_t which is equivalent to Brickmann and Zimmermann's result in the limit of small asymmetry and small tunnelling is²⁴

$$\nu_t = \nu_t^0 \left[\frac{2\Delta E}{\sqrt{(\Delta E)^2 + 4(\Delta V)^2}} \right] \quad (8)$$

where ν_t^0 is the tunnelling rate for the limiting symmetrical potential, $2\Delta E = h\nu_t^0$ and ΔV is the difference in the energy of the minima. As an example, ν_t^0 might be $2 \times 10^{10} \text{ s}^{-1}$, which means $\Delta E \sim 1 \text{ cal mol}^{-1}$. If the minima differ by 1 kcal mol^{-1} ($\Delta V = 1000 \text{ cal mol}^{-1}$), the tunnelling rate is decreased by a factor of *ca.* 1×10^{-3} . It is evident that very serious errors may arise if a symmetrical function is utilized to approximate an unsymmetrical one in tunnelling calculations.

From the foregoing it is seen that the tunnelling properties in bound systems are adequately described if the energy level doublet separations are known. In principle these energy levels are obtained by solving equation (1) using an appropriate potential function $V(x)$ as in Figure 3. Very few exact analytic solutions are available, however, for realistic potentials. The best known is probably the symmetrical Manning potential²⁵

$$V(x) = A \operatorname{sech}^4 \frac{x}{2\rho} - B \operatorname{sech}^2 \frac{x}{2\rho} \quad (9)$$

where A , B , and ρ fix the precise size and shape of the function. Although an exact formal solution of equation (1) has been obtained using this function, no simple expression for the doublet spacing results.

Most attempts at relating the doublet spacings, ΔE_v , to the physical parameters (mass, barrier height, shape, and width) have used approximation methods of some type.^{4,26} The most commonly used method is the WKB approximation which was first applied to the double-minimum system by Dennison and Uhlenbeck.⁴ The general result given by this treatment is

$$\Delta E_v = \frac{h\nu}{\pi} \exp \left(- \frac{2}{\hbar} \int_0^{x_1} P_v dx \right) \quad (10)$$

where $P_v = \sqrt{2m(V - E_v)}$, ν is the (harmonic) oscillation frequency within each well, and x_1 is the value of x for which $E_v = V$ in the barrier region. This method shows clearly that ΔE_v is determined primarily by the area under the barrier, but is not greatly affected by its precise shape. The integral in equation (10) has been evaluated analytically for a few simple barrier shapes,^{4,9} but in general the problem has been treated numerically.

Recently we suggested an approximate expression²⁷ for the symmetric double-

²⁴ M. D. Harmony, to be published.

²⁵ M. F. Manning, *J. Chem. Phys.*, 1935, 3, 136.

²⁶ N. Rosen and P. M. Morse, *Phys. Rev.*, 1932, 42, 210; F. T. Wall and G. Glocker, *J. Chem. Phys.*, 1937, 5, 314.

²⁷ M. D. Harmony, *Chem. Phys. Letters*, 1971, 10, 337.

minimum potential which shows clearly the dependence of ΔE_0 upon the physical parameters, and which is expected to be valid for cases of small tunnelling (small ΔE_0) when each well is more or less parabolic (harmonic) in character. This equation

$$\Delta E_0/h = \frac{ah\alpha^{3/2}}{2m\pi^{5/2}} \exp(-\alpha a^2) \quad (11)$$

is independent of the precise shape *and* height of the barrier, but depends strongly upon the separation of the minima ($2a$), the mass (m), and the oscillator frequency (ν) in each well ($\alpha = 2\pi\nu m/\hbar$). Also, a maximum barrier height of $2\pi^2\nu^2 a^2 m$ is implied. Corrections to equation (11) to account for the barrier shape and height have been derived,²⁷ but the equation itself provides a useful semi-quantitative means for predicting ΔE_0 . In Figure 4 we have shown the variation of $\nu_t (= 2\Delta E_0/h)$ for both a proton and a deuteron as a function of the separation of the minima for a fixed value of the well force constants ($k = 4\pi^2\nu^2 m$).

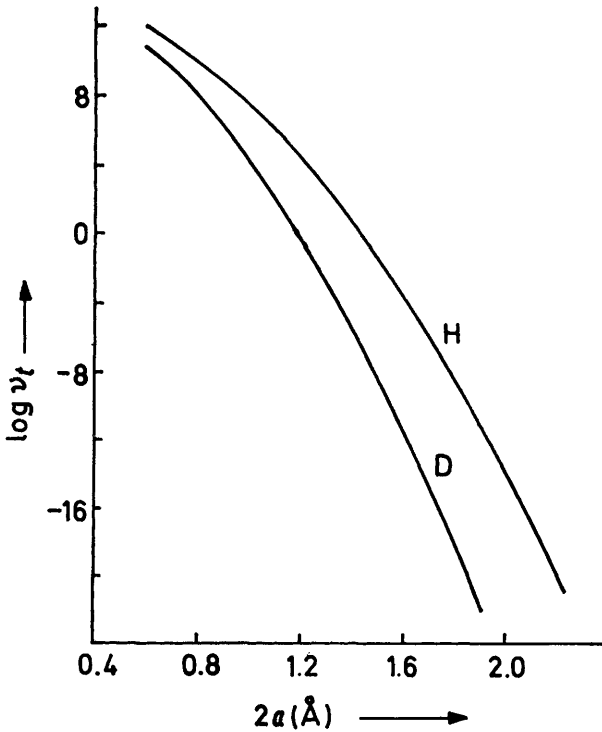


Figure 4 Dependence of tunnelling frequency upon the separation of the potential well minima (computed from equation 11) for a proton and a deuteron. $k = 3 \times 10^8$

Finally we should mention that numerical solutions for the energy level splittings may be obtained to any desired accuracy by using the matrix mechanics technique.^{22,28} There is, of course, a loss of simplicity in this type of computation, but it is recommended when the experimental data are sufficiently good to warrant the computational effort.

C. The Relationship between Bound- and Free-particle Tunnelling Cases.— The discussion in Section 2A was couched in terms of transmission probability, T , while that in Section 2B was in terms of tunnelling frequency, ν_t . We can, in fact, also state the properties of free-particle tunnelling in terms of a tunnelling frequency. This is done merely by multiplying T by the rate at which particles strike the barrier. Thus if ν_i particles/second strike the barrier (or equivalently, if a single oscillating particle strikes the barrier ν_i times/second), the tunnelling frequency is $\nu_t = \nu_i T$.

This suggests that bound-particle tunnelling might be treated by performing a free-particle tunnelling calculation using equations (4) or (6), for example, and then multiplying this by the oscillator frequency ν which is appropriate for the potential wells of interest. Although this seems a reasonable approach, it will generally lead to a serious underestimation of ν_t , particularly for symmetric potentials. In simple terms this is because for bound particles there is a kind of resonance between the two wells, so that each time the bound, oscillating particles in the left well strike the barrier they transmit a certain probability amplitude to the right well. This probability then builds up, since the particles are not free to escape to $x = +\infty$. On the other hand, this mechanism is not operable for the free particle, since once through the barrier the particles continue to $x = +\infty$. A more detailed discussion of this matter has been given recently.²³

3 Tunnelling in the Real World

In the real world of molecules and chemistry, the tunnelling of a single particle along a one-dimensional co-ordinate may seem a highly unlikely model to apply. Indeed, the real potential surfaces of molecules and molecule-aggregates are complicated and many-dimensional, and all the nuclei in the system are undergoing at least small oscillations. In many cases several nuclei must be undergoing large displacement motions. Still, it has proved to be possible to treat many real systems as judiciously selected one-dimensional problems. The validity of such one-dimensional models is normally judged by the extent of agreement with available experimental data. Unfortunately, since the many-dimensional problems are still impractical from a computational viewpoint, there has been little work performed for more than one-dimensional problems.²⁹

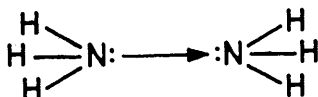
A few examples should show how real systems are turned into one-dimensional cases. An intra- or inter-molecularly hydrogen-bonded proton is a rather simple case.⁷ It clearly has stable equilibrium positions (wells) about which it under-

²² J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, 1962, **36**, 1914.

²⁹ T. R. Singh and J. L. Wood, *J. Chem. Phys.*, 1968, **48**, 4567.

goes small oscillations. To get from one stable well to another it must tunnel through a potential barrier following a path not really known in most cases, but assumed to be more or less along the lines representing the hydrogen bonds. Because, in general, the tunnelling proton is much lighter than the remainder of the system, only the motion of this single particle need be considered.

In many cases it is clear that several nuclei undergo simultaneous tunnelling. The umbrella inversion motion of the ammonia molecule provides a good illustration:



The protons move along a path similar to, but not identical with, the normal co-ordinate for the symmetrical (ν_2) bending mode. The potential energy as a function of the height of the pyramid is of the form of Figure 3, with the maximum corresponding to the planar configuration. Although all three protons move during the tunnelling motion (the nitrogen moves also to ensure that the centre of mass remains constant), the kinetic energy may be represented correctly by the motion of a single particle of *reduced* mass, μ .²⁸ Calculations show that

$$\mu \sim \frac{3(14)(1)}{14 + 3(1)}, \text{ or more approximately, } \mu \sim 3.$$

As a final example, consider the ordinary chemical reaction involving proton or hydrogen atom transfer. The potential surface here is indeed not simple, since even the most elementary treatment indicates that the energy surfaces must be considered to be a function of two bond distances, the one being broken and the other being formed. But according to ordinary transition state theory, there does exist a low-energy pathway, known as the classical reaction path, along which the proton may be considered to move. Actually this view is much too naïve, of course, and one should investigate other possible paths over the saddle point region which are energetically feasible.³⁰ Nevertheless we see again how, in an approximate way, a complicated motion is reduced to a simple one-dimensional problem. We will have more to say about the reaction path later.

4 Experimental Observation of Tunnelling

A. General Considerations.—As for most molecular phenomena, the existence of tunnelling is best detected by its effects upon various macroscopic or microscopic equilibrium and non-equilibrium properties which are measurable in the laboratory. The most direct and quantitative method is the spectroscopic observation of the doublet splitting of the stationary-state energy levels in a bound system such as ammonia. Thus the splittings of the $\nu = 0, 1,$ and 2 states of NH_3 (and its various deuteriated forms) have been observed by microwave

³⁰ H. S. Johnston and D. Rapp, *J. Amer. Chem. Soc.*, 1961, **83**, 1.

and i.r. spectroscopy, and the agreement of the observations with the double-minimum model²⁸ leads one to conclude that ammonia is indeed a tunnelling system. One might argue that these observations have nothing whatever to do with tunnelling, which is true in the sense that no rate phenomena were being observed, but unless some other quantum mechanical explanation of the doublet splittings can be deduced, the tunnelling conclusion is inevitable. In fact, there is other evidence for tunnelling in ammonia which is of a rate nature. The shifts of the rotation-inversion states of ammonia in a static electric field (Stark effect) are found to be second-order in the field strength ($\propto E^2$), which implies that the dipole moment of the molecule is effectively zero.³¹ This is reasonable only if the molecule is inverting very rapidly, as indeed it is ($\approx 10^{10} \text{ s}^{-1}$). In contrast, phosphine inverts by tunnelling very slowly (the doubling of $\approx 10^{-6} \text{ s}^{-1}$ has been too small to observe spectroscopically) and should exhibit a first-order Stark effect characteristic of a rigid non-planar symmetric rotor.

One of the earliest studies providing evidence for tunnelling involved the determination of thermodynamic functions (particularly the entropy) of molecules. Thus a calorimetric determination of the entropy of a molecule must agree with that evaluated by statistical mechanical means. It was found, for example, that agreement was possible for ethane only if, in the statistical theory, the torsional (harmonic vibrational) mode was replaced by a large amplitude mode which permitted tunnelling of methyl protons between three equivalent minima.³² As with ammonia, the characteristic feature of the energy levels for ethane is the presence of closely-spaced pairs of doublets below the barrier maxima.

For chemical reactions involving transfer of light nuclei such as protons or deuterons, the effects of tunnelling are shown by the reaction rate constants. Usually it is necessary to measure either the isotope effect ($k_{\text{H}}/k_{\text{D}}$) or the temperature dependence of the rate constant. The presence of appreciable tunnelling will usually lead to (a) greatly enhanced isotope effects,^{6,33} (b) non-linear Arrhenius plots,⁶ and (c) unexpectedly large differences in effective activation energies for H and D species.⁶ In practical cases, one or more of these phenomena may be observed, depending on the accuracy of the data, the temperature range studied, and, of course, the magnitude of the tunnelling.

Other measurements having the potential for detecting tunnelling include electron diffraction and n.m.r. The latter technique has particular advantages, since it has the possibility of distinguishing, *via* temperature-dependence studies, the rate at which molecules undergo intramolecular conversions. As an example, the n.m.r. spectrum of aziridine shows the ring protons to be all equivalent (even at low temperatures), indicating that the amino-proton is inverting fast on the n.m.r. time-scale. On the other hand, the spectrum of tetramethylaziridine³⁴ shows two pairs of non-equivalent methyl groups, indicating slow inversion.

³¹ D. K. Coles and W. E. Good, *Phys. Rev.*, 1946, **70**, 979; J. M. Jauch, *Phys. Rev.*, 1947, **72**, 715.

³² J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, 1936, **4**, 749.

³³ A. Warshel and A. Bromberg, *J. Chem. Phys.*, 1970, **52**, 1262; A. Bromberg and A. Warshel, *J. Chem. Phys.*, 1970, **52**, 5952.

³⁴ T. J. Bardos, C. Szantay, and C. K. Navada, *J. Amer. Chem. Soc.*, 1965, **87**, 5796.

The difficult problem is knowing whether the inversion is influenced by tunnelling or whether it is simply a classical process involving transfer *over* the barrier. As with the proton-transfer reactions, the isotope effect and temperature dependence should, in principle, permit tunnelling to be detected. In fact, in the tetramethylaziridine case, the reported value of $E_a(\text{H}) - E_a(\text{D}) = -3.3$ kcal is considerably larger than expected from zero-point energy differences, and consequently it seems likely that tunnelling is involved.

B. Intramolecular Tunnelling.—For a macroscopic sample of a substance A, which converts unimolecularly *via* a double-minimum potential to a substance B, the effective rate constant may be written³⁵

$$k_{\text{eff}} = \sum_i f(i) \nu_{\text{A} \rightarrow \text{B}}(i) \quad (12)$$

where $\nu_{\text{A} \rightarrow \text{B}}(i)$ is the reaction (isomerization) rate for species of energy ϵ_i , and $f(i)$ is the fraction of all molecules in any state ϵ_i as given by Boltzmann's energy distribution. The summation for all states above the top of the barrier reduces approximately to a single term of the classical Arrhenius form, $A \exp(-E_a/kT)$, where A is essentially one-half the classical vibrational frequency and E_a is the energy difference between the lowest state ($v = 0$) and the first state above the barrier. For states below the barrier top, $\nu_{\text{A} \rightarrow \text{B}}$ is replaced by the tunnelling frequency, ν_t , calculated by the methods of Section 2B, and the summation is carried out for all states v below the barrier maximum. In general it is clear that equation (12) does not lead to Arrhenius-type behaviour (linear $\ln k$ vs. $1/T$). In particular, if the ground-state tunnelling rate [$\nu_t(0)$] is large enough, k_{eff} will be essentially temperature independent at low temperature.

To illustrate equation (12) we have computed k_{eff} for *N*-H- and *N*-D-aziridine. The potential barrier V_0 is taken as 5000 cm^{-1} ($\approx 14 \text{ kcal mol}^{-1}$), and the other input data are: $\nu_t(0) = 180 \text{ s}^{-1}$, $\nu = 1200 \text{ cm}^{-1}$, $A = 10^{18} \text{ s}^{-1}$, and $E_a = 4800 \text{ cm}^{-1}$ for the $(\text{CH}_2)_2\text{NH}$ species; $\nu_t(0) = 1.8 \times 10^{-3}$, $\nu = 850$, $A = 0.7 \times 10^{18}$ and $E_a = 5100$ for the $(\text{CH}_2)_2\text{ND}$ species. The $\nu_t(0)$ values were obtained by using equation (11),²⁷ and the vibrational energy levels are assumed to be harmonic in behaviour. Tunnelling rates for the other states below the barrier top are obtained from the $\nu_t(0)$ values by assuming a factor of 30 increase for each succeeding state. Figure 5 shows the results of this computation. Note in particular the different high- and low-temperature behaviour. There is considerable uncertainty in these calculations, but the results do indicate that the $(\text{CH}_2)_2\text{NH}$ species probably inverts too fast to observe on the n.m.r. time scale, in agreement with experimental results. On the other hand, the $(\text{CH}_2)_2\text{ND}$ species rate should be observable by n.m.r., and perhaps the transition region between the low- and high-temperature behaviour may be accessible.

In the past several years a number of authors have discussed intramolecular conversions from both the classical Arrhenius and the tunnelling points of view.

³⁵ R. E. Weston, *J. Amer. Chem. Soc.*, 1954, 76, 2645.

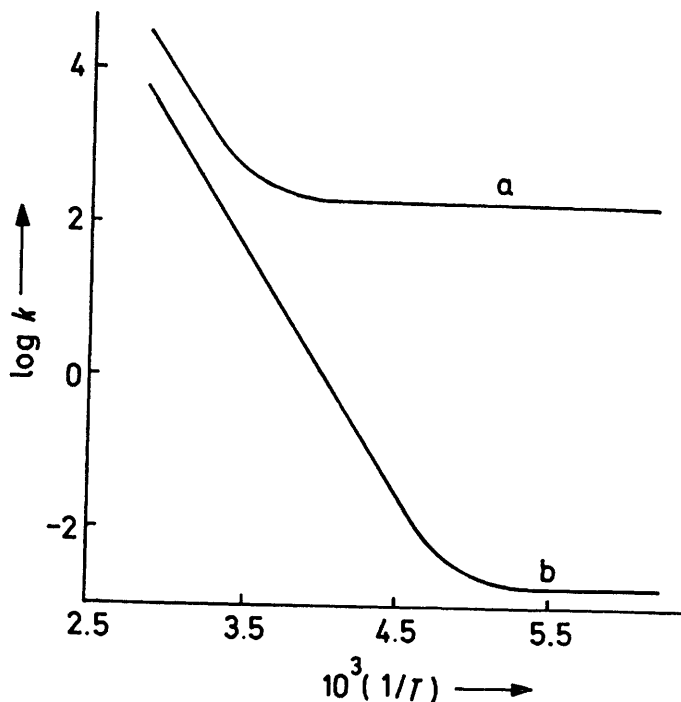


Figure 5 Effective rate constant for aziridine inversion as a function of temperature. Curve (a) is for $(\text{CH}_2)_2\text{NH}$ species, (b) for $(\text{CH}_2)_2\text{ND}$ species. See text for input data

Weston³⁶ and Koepl *et al.*³⁶ considered the rate of inversion of XY_3 -type species (including $\text{XY}_1\text{Y}_2\text{Y}_3$ forms) similar to ammonia. Using a method first devised by Costain and Sutherland³⁷ for obtaining an approximate double-minimum potential, these workers predicted the inversion rates for many pyramidal species. One of the principal interests was in ascertaining whether the asymmetric forms converted sufficiently slowly to show optical activity experimentally. From these studies it was shown that when $\text{X} = \text{P}$ or As , the conversions would be slow by either tunnelling through, or passage over, the barrier for a variety of Y groups, and hence the observed³⁸ optical activity in molecules of this type was verified.

Another interesting series of studies was provided by the experimental observation of the fluorine equivalence of PF_5 in n.m.r. studies.³⁹ Berry⁴⁰ first postulated

³⁶ G. W. Koepl, D. S. Sagatys, and G. S. Krishnamurthy, *J. Amer. Chem. Soc.*, 1967, **89**, 3396.

³⁷ C. C. Costain and G. B. M. Sutherland, *J. Phys. Chem.*, 1952, **56**, 321.

³⁸ K. Mislow, 'Introduction to Stereochemistry', Benjamin, New York, 1965.

³⁹ H. S. Gutowsky, A. D. McCall, and C. P. Slichter, *J. Chem. Phys.*, 1953, **21**, 279.

⁴⁰ R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 936.

a suitable mechanism for this involving a large amplitude internal motion following more or less the E' normal vibrational mode of this D_{3h} species. Later Holmes⁴¹ performed more extensive theoretical studies of a variety of related phosphorus species. The most startling result was that the tunnelling mechanism for PF_5 was found to be about as favourable as the classical over-the-top mechanism at room temperature even though the tunnelling particles (fluorine nuclei) are relatively heavy. The reasons for this seemingly anomalous result are that the barrier is not too high or wide, but more importantly the number of states below the barrier top is large (≈ 21). The latter fact permits a net tunnelling (summed over all the levels) which is appreciable, even though the ground state tunnelling frequency ($\approx 10^{-9} \text{ s}^{-1}$) is quite small. Muettterties⁴² has reviewed much of the recent experimental work on *fluxional* motions of the type shown for PF_5 . In view of the PF_5 results, it seems likely that tunnelling motions may be responsible for some of the observations of large amplitude intramolecular motions. However, it must be remembered that for sufficiently low and wide barriers the motions will most likely be dominated by passage over the barrier *via* the excited vibrational states.

As a final example, the molecular beam study of IF_7 by Kaiser *et al.*⁴³ is interesting. These workers found this species to be effectively non-polar at high temperatures and polar at low temperatures. One proposed explanation of this is that IF_7 undergoes a large amplitude motion of the double-minimum type, with only a few states below the barrier. At low temperature, the beam deflection measurements are dominated by the lowest states, which are polar, whereas at high temperature they are dominated by the states near to or above the barrier, which are effectively non-polar. Tunnelling may be playing a role here, but the data are not conclusive with respect to the detailed dynamical processes.

C. Intermolecular Tunnelling, Proton Transfer Reactions, etc.—In the simplest version of ordinary transition state theory of chemical kinetics, bimolecular reactions are postulated to occur by the passage of the reactants through some high energy *transition state* and then on to products. In this view, reactants must pass over a potential barrier to produce products. If tunnelling through the barrier is permitted, the true quantum mechanical rate constant is obtained by applying a correction factor, Γ , to the classical rate constant calculated with neglect of tunnelling:

$$k_{\text{QM}} = \Gamma k \quad (13)$$

To calculate Γ , one normally assumes that the reactants exist with a two-dimensional Maxwellian energy distribution, $P(E) = (1/kT) \exp(-E/kT)$. Then the quantum tunnelling correction for the one-dimensional reaction path is simply the sum over all energies of the transmission probabilities, $T(E)$ [weighted by $P(E)$], divided by the net transmission probability for the classical process:

⁴¹ R. R. Holmes, *Inorg. Chem.*, 1968, 7, 2229.

⁴² E. L. Muettterties, *Accounts Chem. Res.*, 1970, 3, 266.

⁴³ E. W. Kaiser, J. S. Muentner, and W. Klemperer, *J. Chem. Phys.*, 1970, 53, 53.

$$\Gamma = \frac{\int_0^{\infty} T(E)P(E) dE}{\exp(-V_0/kT)} \quad (14)$$

The denominator achieves the simple form because in the classical process the transmission probability vanishes unless $E > V_0$, when it is unity. The zero of energy in equation (14) is that of the reactants, and $T(E)$ is an expression of the form of equations (2), (4), or (6). In general, Γ does not have a simple temperature dependence, but is expected to approach unity at high temperatures. It is clear also that $\ln k_{QM}$ vs. $1/T$ will not, in general, produce a linear Arrhenius plot, although the quantum contribution to the slope ($d \ln \Gamma / d[1/T]$) will often not be large.

Equations (13) and (14) and the theory as outlined have been applied to a variety of chemical problems over the years, using primarily the parabolic and Eckart barriers for evaluation of $T(E)$. Two general approaches have been used: in the first method, experimental isotope effects [k_H/k_D , $E_a(D) - E_a(H)$, for example] are used to determine the height and width of the potential barrier,⁶ usually using the parabolic barrier because of its simplicity; in the second approach, the potential energy surface for the reacting system is determined by some independent theoretical method, such as that of Sato,⁴⁴ or a more sophisticated method such as used by Shavitt *et al.*⁴⁵ for $H + H_2$. A one-dimensional barrier (usually of the Eckart-type) is then fit to the computed reaction path, the tunnelling contributions are calculated, and the results are compared with experimental rate constants, activation energies, and isotope effects.

Caldin's⁶ recent review provides good coverage of the former method with respect to proton transfer reactions in liquid solution. Although the parabolic barrier is not very reasonable physically, and the interpretation of the width parameter ($2a$ in equation 5) is not entirely clear, the method has been useful in describing and correlating trends in barrier parameters for related reactions. It should be pointed out that in studies of this type it is usually assumed, either explicitly or implicitly, that the tunnelling co-ordinate and the parabolic barrier extend from reactant to product; that is, $x < -a$ corresponds to reactant and $x > a$ to product in Figure 1(d). Furthermore, the tunnelling mass has usually been taken to be 1, 2, or 3 a.u. for H, D, or T, respectively. Except for these assumptions (which will be discussed shortly), the principal objections one might have to these studies is the use of the parabolic barrier. It would be interesting to have some of these studies repeated using an Eckart barrier for comparison purposes.

Studies of the second type above have most often been concentrated on simple reactions such as $H + H_2$,^{30,46} or $CH_3 + H_2 \rightarrow CH_4 + H$.⁵ More recently, however, Warshel and Bromberg³³ have applied the method to both the initiation and propagation steps of the oxidation of dihydrophenanthrene. These studies

⁴⁴ S. Sato, *J. Chem. Phys.*, 1955, 23, 2465.

⁴⁵ I. Shavitt, R. M. Stephens, F. L. Minn, and M. Karplus, *J. Chem. Phys.*, 1968, 48, 2700.

⁴⁶ I. Shavitt, *J. Chem. Phys.*, 1968, 49, 4048; R. E. Weston, *J. Chem. Phys.*, 1959, 31, 892.

have left little doubt as to the necessity for tunnelling corrections, and in most cases the theoretical results have been in semi-quantitative agreement with experiment, although they are strongly dependent upon the detailed model. Considering the many uncertainties which exist, it was interesting that Warshel³³ was able to explain quantitatively a very large isotope effect by a large quantum tunnelling isotope effect of $\Gamma(\text{H})/\Gamma(\text{D}) = 11.84$.

In all of these studies, the principal uncertainties in determining Γ are caused by uncertainties in (a) proper barrier shape, (b) proper path for tunnelling, and (c) proper reduced mass. The most common assumptions of $m = 1$ a.u. for proton transfer, and that a single one-dimensional tunnelling path exists which leads from reactants to products, are undoubtedly too naïve. Some years ago, Johnston and Rapp³⁰ discussed the difficulties in separating out exactly such a path for even a collinear reaction of the form $\text{AH} + \text{B}$. Shavitt⁴⁶ has commented on this for the $\text{H} + \text{H}_2$ case also. Johnston and Rapp have suggested that the more proper tunnelling paths should be along lines of slope -45° on the usual AH vs. HB contour diagrams. These paths correspond essentially to H motion with the end groups motionless. Paths of this kind do not lead from reactant to product, and indeed it is usually found that these paths have potential energy minima far above those for reactants and products. These workers have suggested further that the tunnelling factors should be summed over all paths in the vicinity of the saddle point, which lends a two-dimensional character to the evaluation of Γ . Nevertheless, this modified method is still only an approximation of the real problem.

The proper reduced mass to use in the tunnelling calculations is intimately related to the tunnelling path. For proton transfer between infinitely heavy groups along the -45° paths, the proper reduced mass is $\frac{1}{2}$ a.u.⁴⁷ For the $\text{H} + \text{H}_2$ case, the corresponding asymmetrical stretching normal mode of linear H_3 would have a reduced mass of $\frac{1}{3}$ a.u. Most of the simple tunnelling computations⁴⁶ on $\text{H} + \text{H}_2$ (and isotopic variations) have used a reduced mass which corresponds to a path for which the kinetic energy of the three-particle system is diagonal from reactants to products. For this path the reduced mass for the $\text{H} + \text{H}_2$ reaction is $\frac{2}{3}$ a.u. In any real paths it is probably true that the reduced mass is not strictly constant over any extended range of reaction coordinate.

Recently there have been a number of papers describing the dynamics of the simple $\text{H} + \text{H}_2$ reactions in a detailed way.⁴⁸ These theoretical studies have pointed out clearly many of the inadequacies of the simple treatments, including the problems involving reaction paths and the one-dimensional assumption. This recent work has also avoided the arbitrary assumption of particular barrier shapes (such as Eckart or parabolic barriers) by using numerical solutions of

⁴⁷ T. E. Sharp and H. S. Johnston, *J. Chem. Phys.*, 1962, **37**, 1541.

⁴⁸ D. J. Diestler and V. McKoy, *J. Chem. Phys.*, 1968, **48**, 2951; D. G. Truhlar and A. Kuppermann, *J. Amer. Chem. Soc.*, 1971, **93**, 1840; R. A. Marcus, *J. Chem. Phys.*, 1966, **45**, 4493; E. M. Mortensen, *J. Chem. Phys.*, 1968, **48**, 4029.

Quantum Mechanical Tunnelling in Chemistry

Schrödinger's equation to obtain transmission probabilities for the 'real' potential barrier.

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