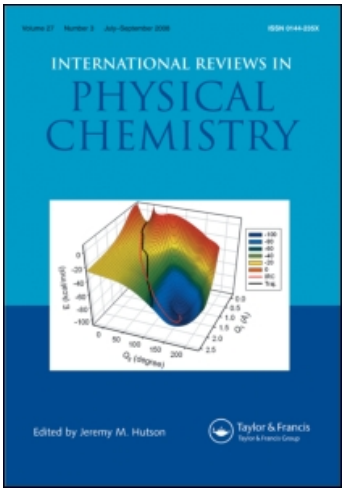


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# Tunnelling time and tunnelling dynamics

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The concept of 'tunnelling time' in the context of quantum particle tunnelling is reviewed. Various suggestions of linking the tunnelling dynamics with a characteristic time (real or complex) like the phase time, barrier interaction time (bounce time), presence time, etc. are analysed. A simple but fully quantal method of defining and estimating a real tunnelling time is examined in a variety of situations. The recently proposed idea of interpreting 'tunnelling time' as the cavity lifetime of a particle is also explored. We emphasize that proton or H-atom transfer reactions in double or triple wells offer systems in which the signature of the tunnelling time should be recognizable not just indirectly through the tunnelling splitting of spectral lines, but by following the relaxation dynamics of the subsystem that the proton or H atom leaves by tunnelling.



## Contents



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## 1. Introduction

Particle tunnelling is a purely quantum mechanical phenomenon involving over-barrier reflection and under-barrier penetration. It has aroused interest ever since the foundations of quantum mechanics were laid. Tunnelling was first used by Fermi in explaining the mechanism of alpha decay in radioactive atoms. Viewed as a dynamical event, it is very natural to try to associate a characteristic time with tunnelling – the so-called 'tunnelling time' – which was first put forward by MacColl [1]. Since then the idea of tunnelling being described by a characteristic tunnelling time has been debated, analysed and discussed in the literature [2–9]. These discussions do not seem to converge to a single or a simple conclusion – rather several points of view appear to emerge. One of these is that the very concept of tunnelling time is meaningless, there being no quantum mechanical operator ($\hat{T}$) for time ($t$) and that the use of such a concept could lead to a violation of the principle of causality and afford the possibility of superluminal communication [10–12]. Another view asserts that tunnelling time is not an observable, but the distribution of tunnelling times is. A third viewpoint assumes that the concept of tunnelling time need not be abandoned altogether and looks for schemes for computing and interpreting tunnelling time meaningfully. It is important, however, to be able to compute tunnelling time meaningfully and recognize its signature in suitable observables, if any. The present review is an attempt to capture the essential features of these schemes, especially in the context of chemical reactions, spectroscopy and molecular physics.

Tunnelling can be unambiguously defined only for one-dimensional barrier traversal problems. Classically, the transmission probability is zero at energies lower than the barrier energy. Quantum mechanics, however, predicts non-zero transmission probabilities even at energies below the barrier energy [13]. In one-dimensional problems, therefore, tunnelling may be taken to represent the passage of the system across a barrier at energies below the barrier energy. Such a passage may be viewed as a reaction by tunnelling. Generally, chemical reactions involve motion of nuclei on multidimensional potential energy surfaces through an activated state situated at the top of the barrier. If the PES has been obtained by solving the Schrödinger equation (SE) under the Born–Oppenheimer (BO) approximation exactly and the subsequent nuclear dynamics also solved quantum mechanically, all contributions due to tunnelling are automatically included in the computed results. One can then define the tunnelling factor $\kappa(\tau)$ to be equal to the ratio of $k_{\text{exact}}(\tau)$ and $k_{\text{VTST}}(\tau)$ where $k_{\text{VTST}}(\tau)$ represents the rate constant predicted by the variational transition state theory [14]. It has been shown that $\kappa(\tau) \gg 1$ in many simple atom transfer reactions of the type $\text{A} + \text{BC} \Rightarrow \text{AB} + \text{C}$. Although $k_{\text{VTST}}(\tau)$ is computed on the basis of a number of approximations, the ratio of $k_{\text{exact}}$ and $k_{\text{VTST}}$ may reflect, among other things, the tunnelling contribution to the rates of simple atom transfer reactions [14–16].

Experimentally, the presence of curvature in the Arrhenius plots of reaction rate constants has usually been taken to confirm the presence of tunnelling. Such curvatures are very difficult to detect in Arrhenius plots for gas phase reactions. The situation in condensed phase reactions is different, for not only have such curvatures been detected in many reactions in condensed phases at low temperatures ($T < 100\,\mathrm{K}$), the occurrence of a temperature-independent part of the rate constant has been confirmed as $T \to 0\,\mathrm{K}$. Very accurate theoretical calculations have, however, demonstrated how important the tunnelling contribution can be to reaction rates, even in simple gas phase reactions at low temperatures.

Classically the rate constant $k$ at a temperature $T$ can be expressed as

$$k = A \int_0^\infty g(\varepsilon) e^{-\varepsilon/k_B T}\, d\varepsilon \tag{1}$$

where $A$ represents the collision frequency, $k_B$ is the Boltzman constant and $g(\varepsilon)$ is an energy dependent barrier transparency factor (classically $g(\varepsilon) = 1$, if $\varepsilon \geq V_0$ and $g(\varepsilon) = 0$ if $\varepsilon < V_0$, $V_0$ being the barrier height). The integration over $\varepsilon$ then leads to the expression for the Arrhenius rate constant, $k_{\mathrm{classical}} = Ae^{-V_0/K_B T}$. For the simple reaction $D + H_2 \to HD + H$, $k_{\mathrm{classical}}$ at low temperatures turns out to be zero ($k_{\mathrm{classical}} \approx 10^{-426}$) whereas full quantum mechanical calculations lead to $k_{\mathrm{tunnelling}} \sim 18$ [15]. The theoretical results demonstrate emphatically that simple gas phase atom transfer reactions at low temperatures are dominated by tunnelling. The analysis of condensed phase reactions is more difficult as the environment couples to the reaction system and plays an important role, depending on the temperature.

Theoretical analysis of condensed phase reactions suggests that the behaviour of the rate constant depends strongly on the temperature regime [17–20]. In the high-temperature regime (regime III), the classical Arrhenius behaviour is noted. In this regime, both the medium and the reaction system behave classically. In the intermediate-temperature regime (regime II) the transfer of an atom (a particle) across the barrier is treated quantum mechanically, while the medium is allowed to respond classically. The result is an expression for the rate constant that grows exponentially with temperature

$$k_{\mathrm{II}} = k_0 e^{aT}. \tag{2}$$

When the temperature is further lowered, both the atom transfer process and the response of the environment are to be treated quantum mechanically. Two types of behaviour emerge as $T \to 0\,\mathrm{K}$. It is the intermolecular vibrations that determine the type of response. If only local modes are excited the plot of $\ln K$ versus $T$ results in a plateau. On the other hand, if the continuum of phonon modes of the surroundings couple to the reactive mode, the rate constants reveal an exponential dependence on high powers of temperature (($k_I = k_0 e^{\gamma T^n}$, $4 \leq n \leq 8$) [20a,b]. We have so far restricted our attention to atom transfer reactions in atom–diatom systems where tunnelling seems to contribute rather significantly to the reaction rate at low temperatures where non-classical behaviour of the rate constant as a function of temperature manifests itself quite clearly. Since a rate process is involved, the question of 'time characteristics' of the tunnelling

contribution naturally crops up. There are examples in the literature where a unimolecular decomposition at low temperatures seems to occur purely by tunnelling although the reactants and products are separated by a fairly large barrier. The elimination of an $H_2$ molecule from a 2, 2 dimethyl ethane cation with the formation of 2, 2 dimethyl ethylene cation is a typical example [20b]. The reactant cation is thus metastable and has a finite lifetime ($\tau$) which is just the inverse of the tunnelling reaction rate constant, $k_{\text{tunnelling}}$. The question of defining, interpreting and computing tunnelling time in the context of a rate process therefore becomes imperative and significant.

## 2. Signatures of tunnelling dynamics

Experimental determination of 'tunnelling time' is extremely difficult. One usually infers about 'tunnelling time' characterizing a process indirectly. Thus, tunnelling often leaves its signature in the spectroscopic properties of a molecule. Proton or H-atom transfer reactions have long been explored in the context of tunnelling [21]. A common spectral signature of tunnelling here lies in the tunnel-splitting of spectral lines in double or triple wells. If an energy barrier exists along the reaction coordinate of the proton transfer path, and it takes place at energies below the barrier, the mechanism must involve quantum mechanical tunnelling. In large molecules, the motion of the proton is coupled to the motion of many atoms, and the potential surface on which the proton tunnels is multidimensional in the majority of cases. The dynamics of multidimensional tunnelling and the characteristic time associated with the motion under the barrier, if any, have not been fully understood as yet. Experimentally, laser spectroscopic techniques have opened up a number of avenues of probing the dynamics of tunnelling on multidimensional surfaces and constructing the surfaces. The majority of the tunnelling systems studied belong to the class of molecules in which the proton or the H atom moves in a symmetric double well potential (SDWP).

The well-known signature of tunnelling in these systems lies in the presence of the so-called tunnelling doublet (figure 1) or tunnelling splitting. These splittings have been experimentally determined by measuring the laser-induced fluorescence excitation spectrum, resonance enhanced multiphoton ionization spectroscopy, hole burning UV spectroscopy, or by IR-UV double resonance spectroscopy [23–27]. If proton transfer occurs in a symmetric double well, the electronic spectrum provides only the difference in the tunnel doublet splitting between the upper and lower electronic states ($\Delta_\nu - \Delta_0$, in figure 1). Accurate estimates of $\Delta_0$ can be obtained by measuring rotational transitions between $0_+$ and $0_-$ levels by microwave or submillimetre spectroscopy. IR-UV double resonance spectroscopy has also been used to determine tunnelling splitting [27]. Time-resolved spectroscopic techniques, specially, the ultrafast femtosecond pump and probe technique, are very powerful tools for determining the rate of proton transfer reactions in the gas or condensed phases. The kinetic data leads to mapping of the PES on which the proton transfer takes place [27].

Tropolone (TRN) is one of the most extensively studied symmetric doublewell proton-transfer systems, for which the ground and excited state tunnelling splitting have been accurately determined [28, 29]. The magnitude of the tunnelling splitting

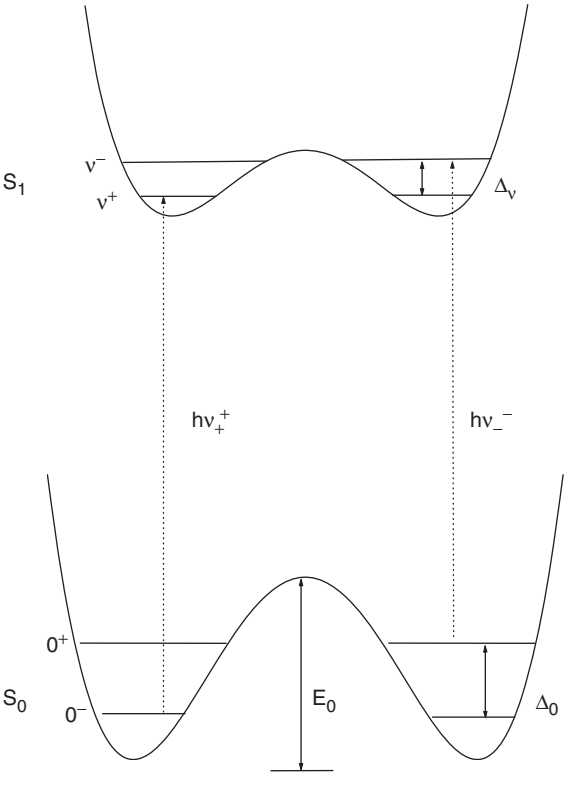


Figure 1. Schematic representation of tunnel splitting.



remarkably depends on the excited vibronic state. In fact, experimental $\Delta_\nu$ values of TRN have led to the classification of vibrational modes into three distinct categories [9]:

(a) tunnelling suppressing modes (e.g $\nu_{11}$, $\nu_{25}$ and $\nu_{26}$);
(b) tunnelling promoting modes (e.g $\nu_{13}$ and $\nu_{14}$);
(c) modes inert to tunnelling (e.g $\nu_{12}$).

The modes (a), (b) must be responsible in some ways in reshaping the barrier height and the distance through which the proton travels. How do they affect the time spent by the proton or H atom under the barrier? There is no direct experimental evidence to answer this question. One can, however, invoke the Fermi Golden rule and show that the 'tunnelling time', if it is there, would be inversely proportional to the square of the tunnelling splitting.

Tunnelling splitting has also been known to be affected by the substitution in different positions of the seven-member ring system of TRN. In a low-barrier symmetric tunnelling system (like TRN), substitution in an asymmetric position could localize the proton in one of the wells rather easily and strongly, leading to quenching of tunnelling. Substitution in a symmetric position (with respect to the tunnelling system) may cause electron withdrawal through the $\sigma$ bonding network thereby strengthening the intramolecular hydrogen bond and decreasing the tunnelling barrier height.

Apart from the indirect evidence through tunnelling splitting the dynamical features of tunnelling, tunnelling time and their effects on the properties of the interacting subsystems (double or triple wells) have not been studied systematically. As the proton on the H atoms moves through the barrier from subsystem A to subsystem B (well-A to well-B), it spends a certain amount of time under the barrier. What happens to the subsystem A or B, during the interval? How does the 'tunnelling time' affect the dynamics of relaxation of the subsystems? It appears that new experiments must be designed to probe these questions and answer unambiguously whether 'tunnelling time' has a definite signature of its own on the properties (observables) of the system. In order to analyse the results of such experiments it is necessary to have a well-defined scheme for computing tunnelling time in a specific context.

## 3. The concept of tunnelling time

We may take the simple stand that 'tunnelling time' is just the temporal difference between two events–the particle impinging on the barrier and the particle coming out of the barrier. The task of computing tunnelling time then boils down to observing the two events, recording the times and measuring the difference. The first problem is that 'time' in quantum mechanics is not represented by an operator. It enters quantum mechanics in the guise of a parameter. The second problem is that the systems are microscopic and measurements are quantum measurements capable of demolishing the tunnelling state under consideration. The question of the operation of the uncertainty principle in 'time measurements' on microscopic systems therefore assumes a significance in the context of tunnelling time analysis. In what follows we briefly review different suggestions relating to and interpretations of tunnelling time ($\tau$) which range from the rather simple to the more sublime ways of handling the problem.



### 3.1. *Uncertainty and tunnelling time*

The first candidate for a measure of the tunnelling time relates to the time–energy uncertainty principle. Let us now consider the tunnelling configuration in figure 2, wherein a particle of mass $m$ and energy $E$ tunnels through a barrier of height $V_0$ ($V_0 > E$) and width $a$. The process is thus characterized by an energy defect $\Delta E = (V_0 - E)$. We may assume that the particle, during a short time interval $\Delta\tau$

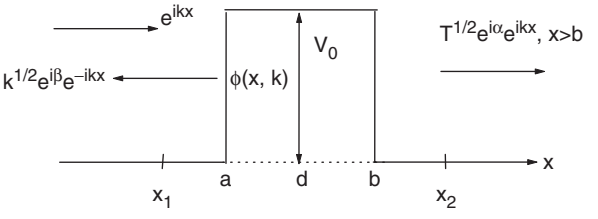


Figure 2. Rectangular opaque barrier $V(x)$.

(tunnelling duration), recovers the energy defect $\Delta E$ through quantum fluctuations, where $\Delta E$ and $\Delta\tau$ are related by the time–energy uncertainty principle:

$$\Delta E \Delta\tau \sim \hbar. \tag{3}$$

Equation (3) then leads to an estimate of the 'tunnelling time' $\Delta\tau \simeq \hbar/(V_0 - E)$. The particle seems to travel a distance $a$ in time $\Delta\tau$ with a 'tunnelling velocity' $vt = a/\Delta\tau = a(V_0 - E)/\hbar$. The simple interpretation of tunnelling time implies that $v_t$ would increase linearly with $a$ and any tunnelling velocity, low and high, would be achievable. That implies the possibility of superluminal communication and a breakdown of causality [30, 31]. The argument has been used by critics to demolish the very idea of tunnelling being associated with a characteristic time $\Delta\tau$. We will return to this aspect later in the review and reexamine the issue from a different angle.

### 3.2. *Dwell time ($\tau_D$) as a measure of tunnelling time*



It appears quite straightforward to ask the question 'What is the time spent by the tunnelling particle under the barrier'. Dwell time ($\tau_D$) is an estimate of precisely the time spent under the barrier assuming that the spatial extension and shape of the barrier is known along with the features of the wavepacket that describes the particle [32]. To be precise, let us consider a one-dimensional scattering configuration for a particle with fixed energy ($E$) as displayed in figure 2, for a rectangular opaque barrier $V(x)$.

For a rectangular barrier of height $V_0$ and width $d(=b-a)$, the transmission probability of a particle ($T(k)$) with momentum $\hbar k$ is [2, 4]

$$\begin{aligned} T(k) &= \frac{4k^2\kappa^2}{D} \\ &= 1 - R(k) \end{aligned} \tag{4}$$

where $R(k)$ is the reflection probability, and $D = 4k^2\kappa^2 + k_0^2 \sinh^2(\kappa d)$ and $V_0 - E = \hbar^2(k_0^2 - k^2)/2m = \hbar^2\kappa^2/2m$ [32]. Let the particle be described by the wavepacket $\psi(x,t)$. The probability of finding the particle in a definite region of space $(x_1, x_2)$ at time $t$ is given by

$$P(x_1, x_2; t) = \int_{x_1}^{x_2} |\psi(x,t)|^2 \, \mathrm{d}x. \tag{5}$$

The time spent by the particle in the given region of space $(x_1, x_2)$ is then obtained by integrating the probability $P(x,t)$ over time:

$$\tau_D(x_1, x_2) = \int_0^\infty \mathrm{d}t P(x_1, x_2; t) \tag{6}$$

$$= \int_0^\infty \mathrm{d}t \int_{x_1}^{x_2} |\psi(x,t)|^2 \, \mathrm{d}x. \tag{7}$$

Decomposing the packet into its scattering components, we have

$$\psi(x,t) = \int \frac{\mathrm{d}k}{2\pi}\phi(k)\psi(x,k)e^{(-i\hbar k^2 t)/2m}, \tag{8}$$

which is ploughed back into the definition of $\tau_D$ through the definition of $P(x_1, x_2, t)$ to obtain, after integration over time has been carried out, an expression for the so-called dwell time:

$$\tau_{\mathrm{D}}(x_1,x_2) = \int \frac{\mathrm{d}k}{2\pi}|\phi(k)|^2 \frac{1}{v(k)}\int_{x_1}^{x_2}\mathrm{d}x|\psi(x,k)|^2 \tag{9}$$

where $v(k)$ $(=\hbar k/m)$ represents the incoming particle flux. If we note that $|\phi(k)|^2/2\pi$ is the probability distribution of an arbitrary initial wavepacket over the wavenumbers $(k)$, we immediately get a dwell time for the particle with momentum $\hbar k$ [32]:

$$\bar{\tau}_{\mathrm{D}}(x_1,x_2,k) = \frac{1}{v(k)}\int_{x_1}^{x_2}\mathrm{d}x/\psi(x,k)|^2. \tag{10}$$

The dwell time is thus the average time that the particle in the scattering state $\psi(x, k)$ spends in a definite region of space $(x_1, x_2)$. When averaging is done over all the scattering channels that become open for the measurement, we get an average dwell time $\bar{\tau}_{\mathrm{D}}(x_1, x_2)$. If we use $x_1 = a$, and $x_2 = b$ in equation (10) we get an estimate of the dwell time, that is, the time spent by the particle under the barrier during the course of tunnelling. The dwell time is very closely related to what has been known as the phase time or time-delay characterizing the tunnelling process. The idea is to identify a typical feature of the wavepacket just as it impinges on the barrier and look for the delay in the appearance of the same feature on the other side of the barrier.



### 3.3. *Delay time (phase time) as a measure of tunnelling time*

Let us start by considering $\tau_{\mathrm{D}}(x_1, x_2, k)$ of equation (10). If $x_1 = a$, and $x_2 = b$ we get an estimate of the time spent just under the barrier – the dwell time $(\bar{\tau}_{\mathrm{D}}(a, b, k))$. Could it not be accepted as a measure of tunnelling time? One problem with $\bar{\tau}_{\mathrm{D}}(a, b, k)$ is that it averages over the total incoming flux without caring to take into account the fraction of the incident particles that get reflected and the fraction that ultimately get transmitted. $\tau_{\mathrm{D}}$ therefore has contributions both from the transmitted as well as the reflected components of the flux. Transmission and reflection being mutually exclusive events, the following relation must hold [2]:

$$\tau_{\mathrm{D}} = T(k)\tau_{\mathrm{t}} + R(k)\tau_{\mathrm{r}} \tag{11}$$

where $T(k) = 1 - R(k)$ is the transmission probability, $R(k)$ the probability of reflection, $\tau_t$ is the time spent by the transmitted particles under the barrier, and $\tau_r$ is counterpart for the reflected particles.

Let us consider a wavepacket sharply peaked around $k$ hitting the barrier (figure 2) and try to follow the motion of the peak of the packet ($x_p(t)$) which, we suppose, will be dominated by a few Fourier components of the form $T(k)^{\frac{1}{2}} \exp i\{\alpha(k) + kx_p - E(k)t/h\}$. Using the stationary phase approximation [33] we have [2, 4]

$$\frac{d\alpha}{dk} + x_p(t) - \frac{1}{\hbar}\frac{dE}{dk} \cdot t = 0. \tag{12}$$

Let us note that the tunnelling causes a spatial as well as a temporal delay. The spatial delay is measured by $\delta\tau = \alpha' = d\alpha/dk$ while the temporal delay is given by

$$\begin{aligned} \delta\tau &= \hbar \frac{d\alpha}{dE} \\ &= \frac{1}{v(k)}\frac{d\alpha}{dk} \\ &= v(k)^{-1}\alpha'. \end{aligned} \tag{13}$$

$v(k)$ is the group velocity given by

$$v(k) = \frac{1}{\hbar}\frac{dE}{dk} = \frac{\hbar k}{m}.$$

A delay time (a phase time) for the tunnelling process can now be defined for the transmitted particles [33]:

$$\tau_t(x_1(x < a), x_2(x > b), k) = \frac{1}{v(k)}[x_2 - x_1 + \alpha'(k)]. \tag{14}$$

A delay time can similarly be associated with the reflected particles:

$$\tau_r(x_1, x_2, k) = \frac{1}{v(k)}[-2x_1.\beta'(k)], \tag{15}$$

$\beta$ being the appropriate phase shift. If the tunnelling process distorts the packet, following $x_p$ is not an entirely acceptable way of describing the tunnelling dynamics. Furthermore, the phase times just defined are meaningful only when $a - x_1$ and $x_2 - b$ are much larger than the spatial width of the packet. The wavepacket based approach is beset with numerous difficulties. Büttiker and Landauer [34] emphasized that an incoming peak or centroid does not get transformed into the transmitted peak or centroid in any physically causative sense. The composition of the wavepacket affects

the computed delay time. The high energy components of the packet may have energies above the barrier. In that event the concept of delay time being a measure of the tunnelling time loses meaning. It has been argued that the barrier may act as an accelerator speeding up the propagation [2, 4].

### 3.4. *Barrier interaction time (traversal time) as a measure of tunnelling time*

**3.4.1. Bohm trajectory based interpretation.** Let us suppose that we have somehow determined a set of dynamic paths, $x(t)$, found the time spent by each path under the barrier and averaged over all such paths. The result is a traversal time which one may be tempted to equate with the tunnelling time. As to the calculation of the paths, we may use the Bohm approach [35], the Feynman path integral method [36] or the Wigner function [37] based approach.

In the Bohm approach articulated by Leavens and Aers [35a], we take $\psi = Re^{iS/\hbar}$ ($R$, $S$ real) and obtain $S$ as a solution of the Hamilton–Jacobi equation for a potential $V(x)$ modified by a quantum potential

$$V_{\mathrm{Q}} = -\frac{\hbar^2}{2m} R^{-1} \frac{\partial^2 R}{\partial x^2}$$

with $R^2$ determined by the density variation of a set of quantum particles following the paths with velocity

$$v = m^{-1} \partial S / \partial x. \tag{16}$$

The time spent under the barrier (between $x = a$, $b$) is defined by

$$\tau_{\mathrm{ab}}^{\mathrm{cl}} = \int_0^t \mathrm{d}t' \theta_B(x(t')) \tag{17}$$

where

$$\begin{aligned} \theta_{\mathrm{B}} &= 1, \quad a < x < b \\ &= 0, \quad \text{otherwise.} \end{aligned}$$

It has been argued that the velocity under the barrier evaluated as proposed has contributions both from the transmitted and reflected stream, and there are suggestions for extracting a velocity applicable to the transmitted beam only [35b]. The Bohm trajectory velocity for an eigenstate of $\hat{H}$ is always directed in the direction of the particle flux.

**3.4.2. Path integral interpretation.** If the right-hand side of equation (17) is averaged with a weight $\exp[iS(x(t))/\hbar]$, where $S$ is the action associated with the path $x(t)$, then $\tau_{\mathrm{ab}}$ can be expressed as a functional derivative of the logarithm of the Feynman amplitude with respect to the potential

$$\tau_{\mathrm{ab}} = i\hbar \int_0^t \mathrm{d}t' \int_B \mathrm{d}x \frac{\partial \ln \langle x_1, t' | x_0, 0 \rangle}{\partial V}. \tag{18}$$

As a measure of the barrier traversal time, $\tau_{ab}$ suffers from the difficulty that it is complex.

Sokolovsky and Conor [38] adapted the path integral approach to the wavepacket analysis and proposed that the traversal time should be given by

$$\tau_{\mathrm{ab}} = \langle \phi_I | t_{\mathrm{ab}}^{\mathrm{cl}} | \phi_T \rangle \tag{19}$$

where $\phi_I$ and $\phi_T$ are the initial and the final states, respectively. For a square potential barrier Fertig [39] made use of the path decomposition of Auerbach and Kivelson [40] and introduced a propagator $G(x_1, x_0, E)$ that represents the amplitude of tunnelling between two points on the opposite sides of the barrier $(x_0, x_1)$, with energy $E$. After summing over the Feynman trajectories that spend precisely an amount of time $\tau$ inside the barrier, the average traversal time is given by

$$\langle \tau \rangle = \frac{\int_0^\infty G_\tau(E, x_1, x_0)\tau \, \mathrm{d}\tau}{\int_0^\infty \mathrm{d}\tau G_\tau(E, x_1, x_0)}. \tag{20}$$



Once again $\langle \tau \rangle$ turns out to be complex. The complex barrier traversal time is not the characteristic of the Feynman approach alone.

Pollak and Miller [41] and Pollak [42] showed that the collision time may be interpreted as the time average of the flux–flux correlation function. This interpretation leads quantum mechanically to a complex time of which the real part ($\tau_R$) coincides with the usual definition given by Smith [32a]. The imaginary part ($\tau_I$) where

$$\tau_I = \mathrm{Im}\left[ -\frac{i\hbar}{t_E} \left( \frac{\partial t_E}{\partial E} \right) \right] \tag{21}$$

has been shown to be identical, in the semiclassical limit, to the imaginary time associated with tunnelling ($t_E$ is the complex transmission coefficient). There are others [43] who advocate that the barrier interaction is characterized by one real and one imaginary time. The beauty of the mathematical schemes not withstanding, one feels a certain amount of unease with two sets of tunnelling times. In a proton tunnelling reaction, for example, how would the imaginary and the real parts of the traversal time affect the overall rate? Would they have separately recognizable signatures?

**3.4.3. Wigner function based approach.** For a stationary barrier traversal problem, the Wigner function based approach seeks to determine a set of phase-space trajectories by demanding that the Wigner function remains constant along these trajectories which satisfy Hamiltons's equation with a modified potential. These trajectories can be used to compute a tunnelling time for stationary scattering [44]. The Wigner function, however, fails to satisfy Liouville's theorem globally [45].

### 3.5. *Modulated barrier interaction time as a measure of tunnelling time*

Let us assume that tunnelling takes place across a barrier of height ($V_0$) that has superimposed on it an oscillatory component, let us say, of small amplitude (figure 3). At very low frequency of oscillation, the particle incident on the barrier sees only a very small part of the modulation cycle. In other words, it sees, so to say, the static barrier. At low modulation frequency, therefore, the particle interacts with the barrier effectively adiabatically. As the modulation frequency increases, eventually a critical frequency is reached when the particle gets affected by a large part of the modulation cycle or even by more than one such cycle. The adiabatic picture then breaks down. The inverse of the critical frequency ($\omega_c^{-1}$), at which large deviation from adiabatic behaviour starts appearing, indicates approximately the length of time ($\tau_c$) during which the particle has interacted with the barrier. $\tau_c$ can therefore be used as a measure of the 'tunnelling time'. For an opaque rectangular barrier of static height $V_0$, width $d$ and particle mass $m$, this approach yields [4, 34a], for frequencies that are not too high,

$$\tau = \frac{(dm)}{\hbar k} \tag{22}$$

where $\hbar k$ is the imaginary momentum under the barrier. If the WKB approximation is valid, $\tau_{WKB}$ for the same problem would be

$$\tau_{WKB} = \int_{\text{barrier}} \mathrm{d}x \frac{m}{\hbar k(x)}. \tag{23}$$

$\tau_{WKB}$ has often been termed the bounce time in the literature. It is possible to encounter a situation where there is a long region where free propagation is possible and a rather

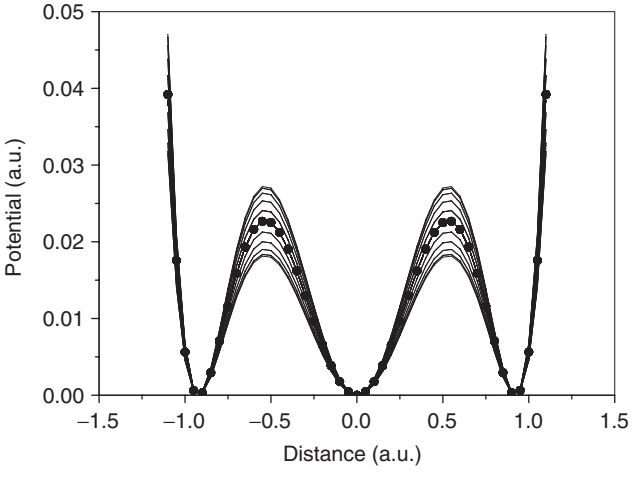


Figure 3. Fluctuating barrier of height $V_0$.

short region containing the barrier. If the WKB approximation holds it is possible to show that [46]

$$\tau = (\tau_P^2 + \tau_B^2)^{\frac{1}{2}} \tag{24}$$

where $\tau_P$ is the classical transit time in the region with $V < E$ and $\tau_B$ is the barrier traversal time given by $\tau_{WKB}$ of equation (23). Going back to equation (22), we note that the oscillating barrier produces particles that have gained or lost one or more modulation quanta, $\pm nh\omega_m$, where $\omega_m$ is the modulation frequency. The adiabatic behaviour breaks down when these new particles (components of the wavepacket) differ in phase or amplitude, from transmission at the pre-absorption or pre-emission energy. The $\tau$ of equation (22) simply measures this energy dependence of the transmission independent of the form of modulation (barrier height, location, width, etc.). It has been shown that

$$\tau = \hbar \left| \left\{ \frac{\partial^2 t_E / \partial E^2}{\partial t_E / \partial E} \right\} \right| \tag{25}$$

where $t_E$ is the ratio of the wavefunction at the far end of the interval to that of incident wave at the front. The modulated barrier approach of Bütikker and Landauer [4, 34] has the important ingredient of clock-based approaches to the problem of defining or estimating tunnelling time. The basic idea is to couple the tunnelling process to another dynamical or time-dependent event which serves as the clock. It would be worthwhile therefore to analyse the quantum clock-based approaches to tunnelling time.



### 3.6. *Quantum clock-based estimate of tunnelling time*

Let us refer to figure 4 in which a particle has a clock attached to it while it tunnels through the barrier ($V_0$) of width $x_2 - x_1 = \Delta x$. The particle is a quantum particle and the clock is a quantum clock. If one registers the difference in the positions in the hand of the clock as it impinges on the barrier ($x = x_1$) and leaves it ($x = x_2$) the difference

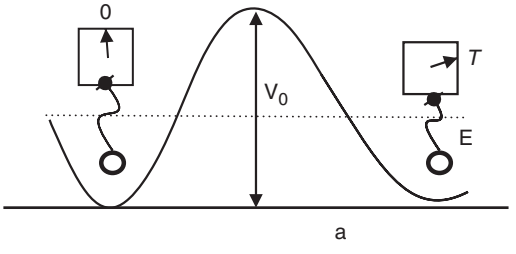


Figure 4. Quantum clock.

may be taken to define the duration of tunnelling [47–50]. The point to note is that *the expectation of the difference in the positions* of the hand of the clock is a quantum entity that relates naturally to the time taken by the particle to travel through the distance $\Delta x = x_2 - x_1$. If the particle is a free one, the momentum eigenstate $e^{ikx}$ describes it as it moves to the right with the mass $m$ and energy $E$ (figure 4). The phase accumulated in traversing the same distance $\Delta x$ in the potential free region ($V = 0$) is $\delta E = k\Delta x = (2mE)^{1/2}\Delta x$, ($\hbar = 1$). If we consider the attached clock, the phase difference is $\delta(E+\varepsilon)$ where $\varepsilon$ is the energy shift due to the coupling between the clock and the particle (tunnelling system). Assuming $\varepsilon \ll E$

$$\begin{aligned}\delta(E+\varepsilon) &= \delta(E) + \varepsilon\delta'(E)\\ &= x + \varepsilon\frac{1}{2}\left[\frac{\Delta x}{(2mE)^{\frac{1}{2}}}\right].2m\\ &= k\Delta x + \varepsilon\frac{m\Delta x}{(2mE)^{\frac{1}{2}}}\\ &= k\Delta x + \varepsilon\frac{\Delta x}{v} \quad \text{since } \frac{m}{(2mE)^{\frac{1}{2}}} = \frac{1}{v}\\ &= k\Delta x + \varepsilon\tau\end{aligned} \tag{26}$$

where $\tau$ is the analogue of the 'classical time' taken in traversing the length $\Delta x$, $v$ being the velocity of the particle during transit through the region $x_1 \to x_2$ [10].

Let us now consider the case where $x_1 = 0$, $x_2 = a$, and there is a square potential barrier of constant height $V > 0$ between $0 < x < a$. The phase shift is given by [10]

$$\delta(E) = \arctan\left[\frac{(\alpha^2 - \beta^2)}{2\alpha\beta\tanh(\beta a)}\right] \tag{27}$$

where $\alpha$, $\beta$ are phase factors of the wavefunctions in different regions of space as detailed below:

$$\begin{aligned} x < 0; &\quad \psi(x) = e^{i\alpha x} + A_1 e^{-i\alpha x}\\ 0 < x < a; &\quad \psi(x) = a_2 e^{\beta x} + a_3 e^{-\beta x}\\ x > a; &\quad \psi(x) = Be^{i\alpha x}.\end{aligned} \tag{28}$$

$\delta'(E)$ then leads to $\tau$, the tunnelling time (traversal time between $0 < x < a$) given by

$$\tau = \frac{2m[\alpha(\beta^2 - \alpha^2)a + (\beta^2 + \alpha^2)/2\alpha\beta](\sinh 2\alpha\beta)}{(\alpha^2 + \beta^2)^2\cosh^2\beta a - (\beta^2 - \alpha^2)^2}. \tag{29}$$

The previously derived expression for $\tau$ (free particle) is recovered from equation (29) by setting $V = 0$, $\beta = i\alpha$ and $\tau = ma/\alpha = a/v$. It has been demonstrated [10] that for $E = V/2$, $\tau \to 0$ as $a \to 0$. However, for small $a$, $\tau$ is $> 0$ demonstrating the fact that the barrier has slowed the particle down ($v_{\text{underbarrier}} < v_{\text{outside}}$).

In the special case of a barrier described by a delta-function potential with $a^2V$ remaining constant even as $a \to 0$ and $V \to \infty$, equation (29) predicts $\tau = 0$ in the corresponding limiting situation. Even for an array of delta-function potentials, $\tau = 0$ has been predicted [12]. In the opposite limit $a \to \infty$, $\tau \to 1/\sqrt{E(V-E)}$ so that the effective under-barrier velocity $v_{ub} = a[E(V-E)]^{\frac{1}{2}}$. $v_{ub}$ can, in principle, increase without limit, even exceeding the velocity of light ($c$) and thus unfolding the spectre of violation of causality. However, as argued by Davies [10] we are here measuring only the time difference and not the departure and arrival times of the particle from one side of the barrier to the other. In the absence of the latter information, superluminal signalling and the associated question of physically violating causality do not simply arise, at least as long as we are dealing with energy eigenstates. For wavepackets, the analysis has not yet been convincingly done by anyone. The stationary phase method encounters certain difficulties here. Recently, Bernardini [51] has suggested that the multiple peak decomposition technique [52] can be used within the framework of the stationary phase method to obtain an estimate of the tunnelling time when wavepackets are used. The standard tunnelling phase time or the scattering phase time allow the possibility of a superluminal interpretation for the peak of the transmitted wave.

In this context it is worth recalling the superluminal phenomena, observed in tunnelling experiments with photons and evanescent electromagnetic waves [54–57]. Olkhovsky *et al*. [57] suggested a simple way of understanding the problem in terms of a reshaping of the pulse, with attenuation. The later parts of the incoming pulse are preferentially attenuated in a way that makes the outgoing peak appear shifted toward earlier times even though it is nothing but a part of the forward tail of the incident pulse.



### 3.7. *Tunnelling time via presence time formalism*

A self-adjoint time operator is not defined in the standard formulation of quantum mechanics. The existence of such an operator, it was argued by Pauli [58], would imply an unbounded energy spectrum. Nevertheless, there has been various attempts to construct time operators and develop formalisms for estimating arrival times within the framework of quantum mechanics [58–60]. The average presence time for a spatial wavepacket $\psi(x, t)$, in terms of a time-operator based approach, at the position $x$, is given by (assuming that the integrals involved exist)

$$\langle t(x) \rangle = \frac{\int_{-\infty}^{+\infty} |\psi(x,t)|^2 t \, dt}{\int_{-\infty}^{+\infty} |\psi(x,t)|^2 \, dt}. \tag{30}$$

The tunnelling time through a barrier can be easily estimated by computing the local value of the operator defined above [61]. Such estimates agree well with those provided by the 'arrival time' method of Leon *et al*. [61]. It has been shown that the numerically computed tunnelling time of electronic wavepackets in nanostructures is sensitive to the finite size of the incident wavepacket [62]. The presence time method, however, has been shown to yield results that are equivalent to what has been obtained by the standard methods for very long wavepackets [63], and that it enables us to calculate the

tunnelling time for wavepackets of arbitrary shape and length. The tunnelling time for such a packet is simply the average of the standard phase times over the energy components.

In view of its performance, we would like to elaborate on the method of calculation of tunnelling time via presence time formalism. The integrals in equation (30) can be converted to integrals over energy easily, if only scattering states with positive momenta are considered. Under such conditions, the energy wavepacket is related to the spatial packet $\psi(x, t)$ as

$$\phi(x, E) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{+\infty} \psi(x, t) e^{iEt/\hbar} \, \mathrm{d}t. \tag{31}$$

The average presence time is then given by

$$\langle t(x) \rangle = \frac{1}{N} \int_0^{\infty} \phi^*(x, E) \left\{ -i/\hbar \frac{\partial}{\partial E} \right\} \phi(x, E) \mathrm{d}E \tag{32}$$

where the normalization factor $N$ is defined as follows

$$N = \int_0^{\infty} \left| \phi(x, E) \right|^2 \mathrm{d}E. \tag{33}$$

If $\phi(x, E)$ is assumed to be a continuous, differentiable and square integrable function of energy, and $\phi(x, 0) = 0$, then $-i\hbar(\partial/\partial E) = \hat{T}$ is a hermitian operator and our interest is to compute $\langle T(x) \rangle$. Now, the energy wavepacket may be assumed to be peaked at $x_0$, at $t = 0$ with a spatial width $\Delta x$ and moving to the right in free space. Then

$$\phi(x, E) = g(E) e^{ik(x - x_0)} \tag{34}$$

$g(E)$ being the normalized weight function peaked at $E = E_0$, with an energy width $\Delta E$, and wavenumber $k(E) = \sqrt{2mE}/\hbar$. If we now go back to equation (32) with $\phi(x, E)$ of equation (34) we have [63],

$$\left\langle \hat{T} \right\rangle = \frac{1}{N} \int_0^{\infty} g^2(E) [\tau_{\mathrm{cl}}(x, E) - i\tau_g(E)] \mathrm{d}E \tag{35}$$

where $\tau_{\mathrm{cl}}(x, E)$ is the classical time that a particle with velocity $\sqrt{2mE}/m$ takes to travel through the distance $(x - x_0)$, i.e.

$$\tau_{\mathrm{cl}}(x, E) = m(x - x_0)/\sqrt{2mE} \tag{36}$$

while $\tau_g(E)$ is the partial energy derivative of the weight function $g(E)$, i.e.

$$\tau_g(x, E) = \hbar \frac{\partial \ln g(E)}{\partial E}. \tag{37}$$

Turning our attention to propagation of the spatial wavepacket in space with a rectangular barrier of width $a$ and height $V_0$, placed between $x=0$ and $x_2$, the tunnelling time $\tau$ would just be the difference between the expectation values of $T(x)$ at $x=a$ with and without the barrier being present (specific and correct choice of phases are assumed). It is straightforward now to show that the tunnelling time for a general wavepacket of finite width is just the Buttiker time (longitudinal characteristic time) $\tau_x$ averaged over the energy weighted by the probability density in the energy representation at $x \geq L$. Similar results have been obtained by others in the momentum representation.

### 3.8. *Tunnelling time, Hartman effect and superluminality*

We have already encountered how a simple minded estimate of tunnelling time through the time–energy uncertainty relation leads to a paradoxical situation admitting to the possibility of superluminal propagation. In fact, a large part of the confusion and controversy concerning the very idea of tunnelling time centres round the Hartman effect [65] or the Hartman–Fletcher effect [66]. Hartman started by writing down the solution of the time-dependent Schrödinger equation of the tunnelling system as an integral over the energy of stationary states weighted by a Gaussian momentum distribution function. The integral over energy extends from $0 \rightarrow \infty$. The regime $E > V_0$ (barrier height) accounts for the non-tunnelling contributions while the region $E < V_0$ represents tunnelling components. Hartman showed [65] that for thin barriers, the transmitted packet has essentially the same form as the incident packet and its delay is greater than the time taken by the packet to traverse a distance equal to the barrier width. As the barrier thickness increases the peak of the transmitted packet shifts to slightly higher energy and the delay time becomes independent of the thickness and shorter than the 'free space delay' for equal length. For very thick barriers the under-barrier components are suppressed so that the propagating above-barrier components begin to dominate resulting in an increase of delay time. It can be shown that for $E = V_0/2$, the group delay is $\tau_g = 2\tanh(\kappa L)/\kappa v$. In the limit $\kappa L \rightarrow \infty$, the limiting group delay $\tau_{g\infty}$ for all $E$ is given by $\tau_{g\infty} = 2/\kappa v$ which is independent of the barrier width, $L$. If the group delay is accepted as the transit time across the length $L$, the particle is implied to travel with a group velocity ($v_g$)

$$v_g = \frac{L}{\tau_g}.$$

Since $\tau_g$ saturates as $L$ increases, $v_g$ increases with length, $L$. Since $L$ can increase without limit, $v_g$ can grow to exceed the speed of light in vacuum. The Hartman effect is also displayed by the dwell time ($\tau_d$), that is as $\kappa L \rightarrow \infty$

$$\tau_d \rightarrow \tau_{d\infty} = \frac{2}{\kappa v}\left(\frac{E}{V_0}\right).$$

Recently, the Hartman effect has been reanalysed [8, 67]. It has been claimed that the group delay in tunnelling is *not* a transit time at all. In reality, it represents a 'lifetime' and must not be used to assign a speed of barrier traversal. In that case, the question of superluminality in tunnelling becomes irrelevant. The reanalysis asserts that the origin

of the Hartman effect lies in the presence of stored energy within the barrier. The group delay ($\tau_g$) is proportional to the stored energy and it saturates as the stored energy saturates. The delay, under quasi-static conditions, is just the lifetime of stored energy leaking out at both ends of the barrier [67].

### 3.9. *A simple route to tunnelling time*

Let us consider a particle of mass $m$ moving in a systematic double well potential as the tunnelling system. The equation of motion is

$$\begin{aligned} i\hbar\frac{\partial\psi(x,t)}{\partial t} &= \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+v(x)\right]\psi(x,t) \\ &= H_0\psi(x,t). \end{aligned} \tag{38}$$

Let us consider an initial state $\psi(x,0)=\phi(x)$ localized entirely in one of the two equivalent wells (say the left well, L). The stationary states of $H_0$ satisfy the eigenvalue equation

$$H_0\chi_n(x)=E_n\chi_n(x), \quad 0,1,2,\ldots \tag{39}$$

$\chi_n$ can be exploited as an orthogonal basis and $\psi(x,t)$ expanded in terms of $\chi_n$:

$$\psi(x,t)=\sum_{n=0}^{\infty}C_n(t)\chi_n(x)e^{-iE_nt/\hbar} \tag{40}$$

where $c_n=\langle\chi_n|\psi(x,t)\rangle$. $\psi(x,t)$ of equation (40) may be used in equation (38) leading to the evolution equation for the superposition amplitudes $c_n(t)$, which can be solved. Once $c_n(t)$ are known, we can compute any quantity of interest at any time. Let us suppose that equation (38) has been solved and we have at our disposal the instantaneous quantum averages $\langle x\rangle$ and $\langle p_x\rangle$. Let the idealized width of the barrier separating the two equivalent wells be $l_0$ (figure 5). We may now define an average barrier interaction time ($\tau_{av}$) as

$$\begin{aligned} \tau_{av} &= \frac{l_0}{\frac{d}{dt}\overline{\langle x(t)\rangle}} \simeq \frac{l_0}{\overline{\langle v(t)\rangle}} \\ &= \frac{ml_0}{\overline{\langle p_x(t)\rangle}} \end{aligned} \tag{41}$$

where $\overline{\langle x(t)\rangle}$, $\overline{\langle p_x(t)\rangle}$ denote the time-averaged velocity and momentum of the tunnelling particle.

$\tau_{av}$ is manifestly real. The question that naturally arises at this point concerns the contribution of the intrinsic decay time $\tau_d$ of the initially localized state (wavepacket) to

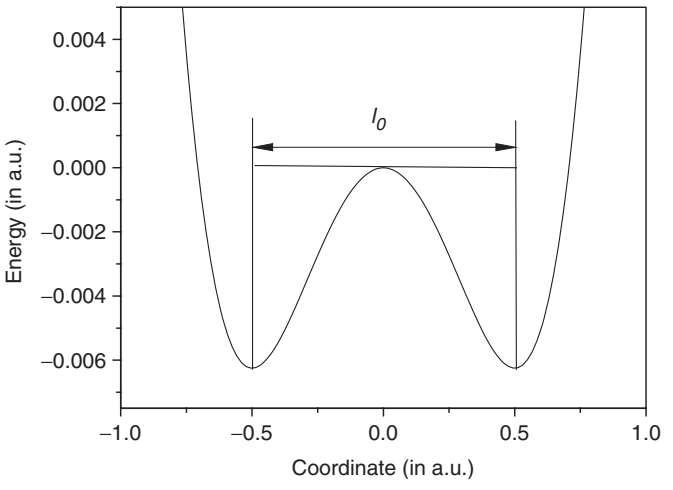


Figure 5. Symmetric double well.



the computed barrier interaction time $\tau_{av}$. We assume that $\tau_{av}$ can be resolved into a sum of $\tau_d$ and $\tau_b$, where $\tau_b$ is the barrier-traversal time and $\tau_d$ is the intrinsic decay time [68]:

$$\tau_{av} = \tau_d + \tau_b. \tag{42}$$

An independent estimate of $\tau_b$ is provided by the energy spread $\Delta E$ of the wavepacket where $\Delta E = \{\langle H^2\rangle - \langle H\rangle^2\}^{1/2}$ which immediately defines the decay time $\tau_d$ for the packet as

$$\tau_d = \frac{\hbar}{\Delta E}. \tag{43}$$

Since $H$ is the hamiltonian of the tunnelling system, the barrier parameters enter into the calculation of $\tau_d$ through the hamiltonian $H$. The computation of $\tau_{av}$, on the other hand, requires one to follow the instantaneous average position $\langle x(t)\rangle$ or momentum $\langle p_x\rangle$ of the particle throughout the course of evolution including the passage through the barrier. The barrier acts like an experimental device observing the packet and causes a delay ($\tau_b$). We propose that this delay $\tau_b = \tau_{av} - \tau_d$ is the barrier crossing time. We have shown previously that $\tau_b$ closely follows the WKB estimates of the barrier crossing time [68]. Depending upon the energy of the particle, the WKB method, however, may sense a width of the barrier (separation between two classical turning points at energy $E$) that is very different from the idealized width $l_0$ that we propose to use ($l_0$ is fixed by the geometry). The difference may manifest itself in $\tau_{WKB} < \tau_b$. Thus, for the Eckart potential $V(x) = V_0/\cosh^2(ax)$ with $V_0 = 0.03$ a.u., $a = 2.54$ a.u., if we consider the evolution of a wavepacket initially localized at $x = -3.773$ a.u. with energy equal to 0.00015 a.u. moving under the action of the Hamiltonian $-(\hbar^2/2m)(\partial^2/\partial x^2) + v(x)$ (figure 6). The tunnelling trajectory, $\langle x\rangle$, is shown in figure 7. The average tunneling

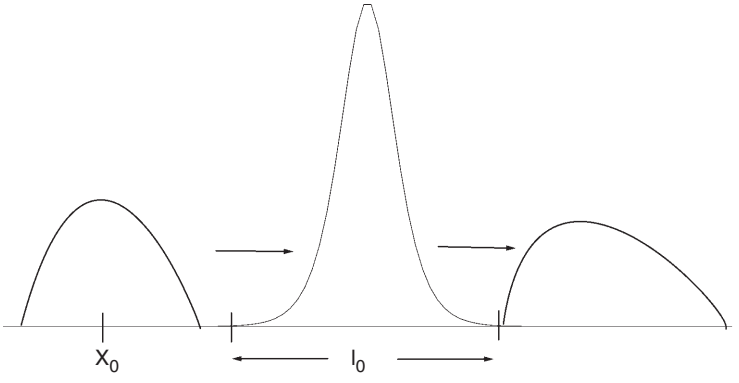


Figure 6. Eckart potential.

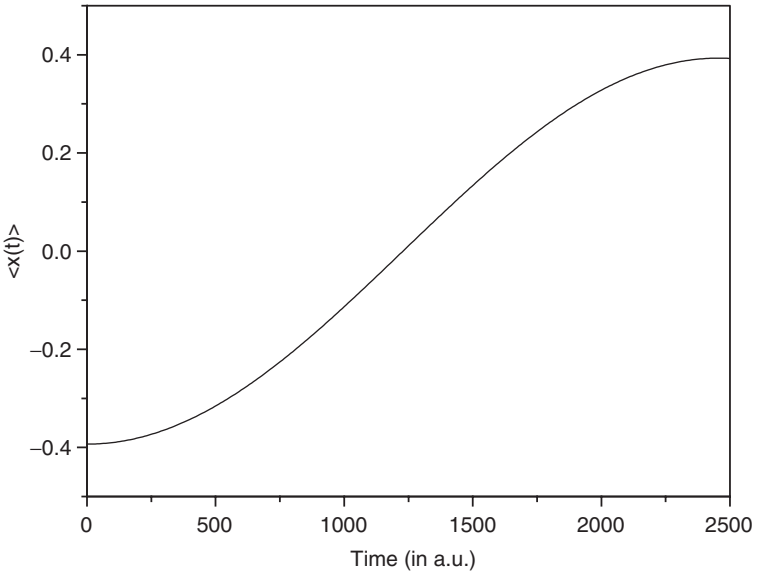


Figure 7. The tunnelling trajectory.



velocity $\langle v \rangle$ turns out to be $0.266 \times 10^{-3}$ a.u. The idealized barrier width ($l_0$) is 4.20 a.u. in our model and that leads to $\tau_{av} = 1.69 \times 10^4$ a.u. of time. If we subtract the intrinsic decay time $\tau_d$ of the packet which is $1.171 \times 10^4$ a.u. we are left with a barrier traversal time $\tau_b = 0.5190 \times 10^4$ a.u. of time. For the same case, a WKB estimate of $\tau_b^{WKB}$ is $0.3989 \times 10^4$ a.u. of time. A part of the difference between our estimate of $\tau_b$ and $\tau_b^{WKB}$ certainly comes from the difference in barrier width sensed by the WKB compared to the value of $l_0$ used by us [68]. The same scheme may be applied to tunnelling in a double-well potential.

In figure 8, a symmetrical double well based tunnelling system with a barrier height of $V_0$ and width of $2a$ is displayed. The ground tunnelling doublet ($\psi_0^{\pm}$) can be described as superpositions of the states $\psi_L$ and $\psi_R$ localized in the left and

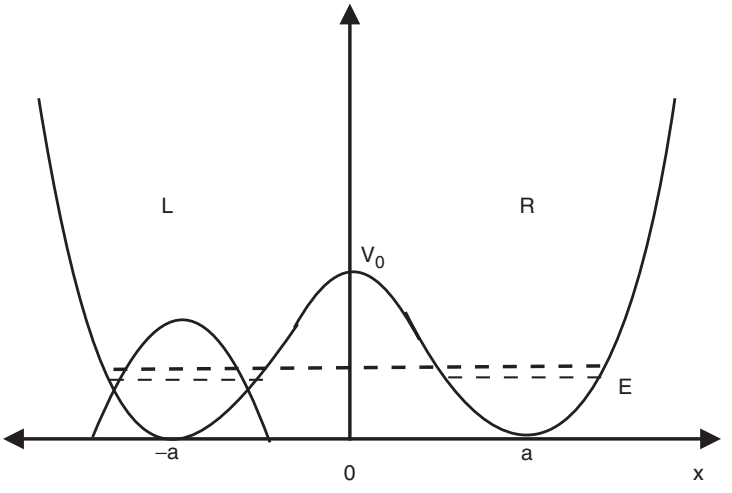


Figure 8. The symmetric double-well potential.



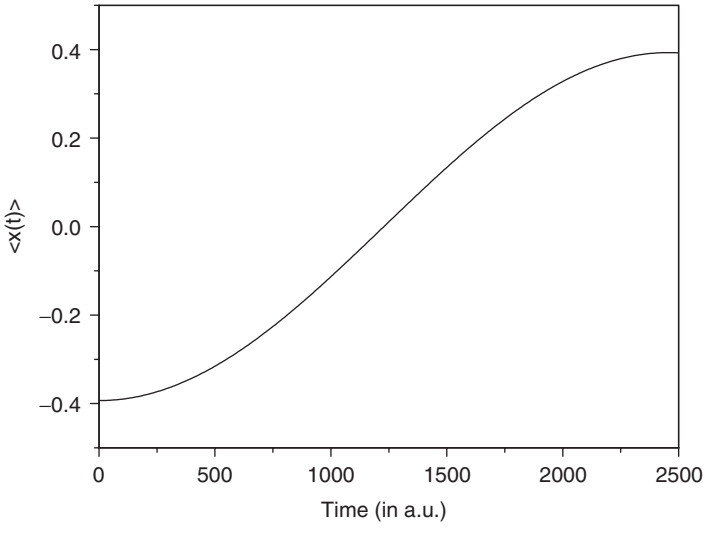


Figure 9. The tunnelling trajectory.

right wells, respectively, $\psi_0^{\pm} = (1/\sqrt{2})(\psi_L + \psi_R)$, with energy $E_0^{\pm}$. The tunnelling splitting is $\Delta E_0^{\pm} = (E_0^- - E_0^+)$. The tunnelling rate is proportional to $(\Delta E_0^{\pm})^2$ and the tunnelling time $\tau \propto \Delta E_0^{\pm})^{-2}$.

The tunnelling trajectory, for an initially localized state with energy $-0.00166$ a.u. is depicted in figure 9 and the volume of the phase space accessed by the tunnelling 'particle' is shown in figure 10. The semiclassical estimate of the barrier crossing time ($\tau_{SC}$) and $\tau_b$ of our model are compared in table 1.

In general, $\tau_b$ increases with a decrease in tunnelling splitting in a symmetrical double-well potential as expected. Recently, Maji and Bhattacharyya [69] investigated

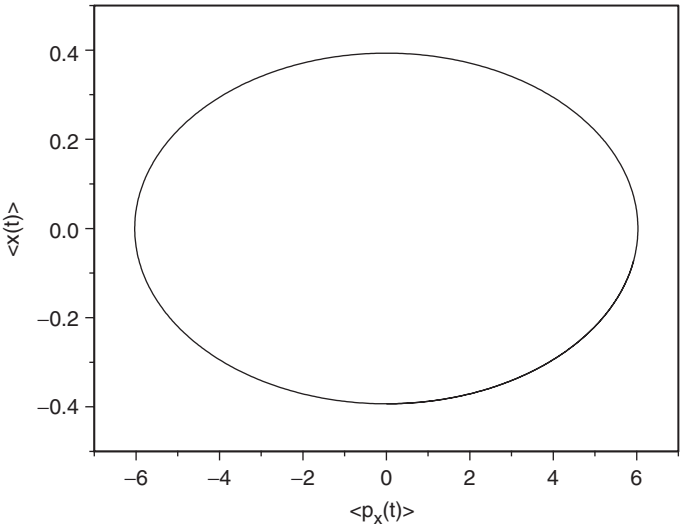


Figure 10. The quantum phase space in symmetric double-well potential.

Table 1. Energy dependence of $\tau_{av}$, $\tau_b$ and $\tau_{SC}$ in SDWP.

| Energy of the tunnelling state (in a.u.) | Velocity $\langle\bar{v}\rangle$ (in a.u.) | Tunnelling time $\tau_{av}$ (in a.u.) | $\tau_d$ Energy variance (in a.u.) | Barrier crossing time $\tau_b =$ $\tau_{av} - \tau_d$ (in a.u.) | Barrier crossing time $\tau_{SC}$ (a.u.) calculated by the WKB method |
|---|---|---|---|---|---|
| −0.0016634 | $3.88546 \times 10^{-4}$ | 2364.1 | 248.97 | 2115.2 | 2074.1 |
| −0.00083919 | $3.95659 \times 10^{-4}$ | 2321.1 | 324.19 | 1996.9 | 1972.0 |
| −0.00076848 | $4.28395 \times 10^{-4}$ | 2143.7 | 373.22 | 1770.5 | 1925.0 |



the behaviour of $\tau_{av}$ in symmetric triple-well systems. It has been demonstrated that in a perturbation produced by coupling a triple-well tunnelling system to a harmonic mode, $\tau_{av}$ generally decreases as the coupling strength increases. In the weak coupling regime, however, a tunnelling delay may appear ($\tau_{av}$ increases). A periodically varying well-depth was shown [68] to lead to an enhancement of the tunnelling duration ($\tau_{av}$) in triple wells and create a 'resonance-like' suppression of tunnelling at a critical frequency ($\omega_c$) of oscillation.

Mondal *et al*. [68] investigated how $\tau_{av}$ responds to change in $\omega$ of a generalized time-dependent double well potential $V(x, t) = bx^4 - a(1 + \lambda_a \sin \omega t)x^2 + \lambda_b x$. It was shown that $\tau_{av}$ passes through a well-defined minimum at $\omega = \omega_c$. It appears that $\omega_c$ demarcates the high and low frequency regimes in much the same way as $\omega = \hbar\kappa/md$ in the Landauer–Buttiker theory. It would be interesting to probe if $\tau_{av}^0 = \omega_c^{-1}$ of Mondal *et al*. [68] is related in some way to the Landauer–Buttiker tunnelling time. There are many other questions concerning $\tau_{av}$, $\tau_b$ and $\tau_d$ that need further careful exploration although $\tau_{av}$ or $\tau_b$ do not appear to lead to any obvious contradiction. It appears to be more like the (group) delay time or the semiclassical bounce time, rather than the 'lifetime' of the stored energy leaking out from the barrier at both ends (67).

## 4. Postscript

The various prescriptions for computing tunnelling time and various interpretations of tunnelling delay continue to present a confused picture. Tunnelling of a quantum particle is an attribute of its wave nature. Just like matter waves, electromagnetic waves or acoustic waves too, display the phenomenon of 'classical tunnelling' and experiments on 'tunnelling time' available in the literature have been mostly on tunnelling of an electromagnetic wave as it encounters an electromagnetic barrier. The present review has been restricted to matter waves that follow the Schrödinger equation. Whether the very concept of 'tunnelling time' is an experimentally testable construct for massive-particle tunnelling can only be decided by experiments. It is in this context that proton, or hydrogen atom transfer reactions could be important. If the relaxation dynamics of the subsystem from which the hydrogen atom or the proton moves out can be followed during the time of its barrier traversal, a signature of tunnelling time can identified. The tunnelling of an electron from a metal through an insulator similarly raises the possibility of following the dynamics of the image charge on the metal surface spreading out after the electron leaves the metal surface into the insulator by tunnelling. These experiments are hard to perform and even harder to analyse. The resolution of all controversies and debates concerning 'tunnelling time' for particles (non-zero rest mass) depends on the outcome of such experiments. Till then, newer ideas would continue to be proposed, older ideas continue to be sharpened.



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