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Maximum tunneling velocities in symmetric double well potentials

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ABSTRACT

We consider coherent tunneling of one-dimensional model systems in non-cyclic or cyclic symmetric double well potentials. Generic potentials are constructed which allow for analytical estimates of the quantum dynamics in the non-relativistic deep tunneling regime, in terms of the tunneling distance, barrier height and mass (or moment of inertia). For cyclic systems, the results may be scaled to agree well with periodic potentials for which semi-analytical results in terms of Mathieu functions exist. Starting from a wavepacket which is initially localized in one of the potential wells, the subsequent periodic tunneling is associated with tunneling velocities. These velocities (or angular velocities) are evaluated as the ratio of the flux densities versus the probability densities. The maximum velocities are found under the top of the barrier where they scale as the square root of the ratio of barrier height and mass (or moment of inertia), independent of the tunneling distance. They are applied exemplarily to several prototypical molecular models of non-cyclic and cyclic tunneling, including ammonia inversion, Cope rearrangement of semibullvalene, torsions of molecular fragments, and rotational tunneling in strong laser fields. Typical maximum velocities and angular velocities are in the order of a few km/s and from 10 to 100 THz for our non-cyclic and cyclic systems, respectively, much faster than time-averaged velocities. Even for the more extreme case of an electron tunneling through a barrier of height of one Hartree, the velocity is only about one percent of the speed of light. Estimates of the corresponding time scales for passing through the narrow domain just below the potential barrier are in the domain from 2 to 40 fs, much shorter than the tunneling times.

1. Introduction

The time it takes for a particle to tunnel through a barrier is a topic that has attracted considerable interest already in the early days of quantum mechanics [1–3]. Closely related is the problem of the corresponding tunneling velocity. Despite of its fundamental nature as well as its apparent simplicity, this question is still controversially discussed and a correct interpretation of tunneling is sometimes hampered by the absence of a unique definition of the tunneling time [4,5]. Some seemingly sensible definitions, e.g. the group delay, even lead to the predictions of velocities exceeding the speed of light [6]. This effect of superluminality, known as the Hartman effect [7], was also claimed to be detectable in microwave experiments [8]. However, in more recent work it was suggested that this paradox does not violate relativity because the group delay time should not be interpreted as a transit time [9,5].

In this article, in contrast to the often used model of incoming free particles hitting a barrier and exiting freely [4,5], and also in contrast with the hot topic of bound particles which dissociate or ionize through the time-dependent potential barrier induced by ultrashort intense laser fields (see e.g. Ref. [10]), we study the case of coherent tunneling in a symmetric double well potential, i. e. tunneling between bound states [1]. Specifically, we consider the deep tunneling regime of some model systems. Here, the two delocalized wavefunctions of the lowest doublet of eigenstates with tunneling splitting ΔE can be superimposed with equal or opposite amplitudes thus forming two wavefunctions which are localized in one of the potential wells or the other, say either in the left or right one. These superposition states are not stationary. As a consequence, for example the left wavefunction will tunnel from the left potential well to the right one, and back, within tunneling time $\tilde{\tau} = h/\Delta\tilde{E}$. This well-known definition was derived by Hund, already in 1927 [1]. To the best of our knowledge, however, the related topic of tunneling velocities $\tilde{v}$ during tunneling in the deep tunneling regime of symmetric double well potentials (assuming initial preparation as one of the superposition states which is localized e.g. in the left potential well) has not yet been

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considered in the literature. (The tilde notation (like $\tilde{\tau}$) refers to times, coordinates and velocities in terms of SI units; alternatively, for comprehensive derivations of the results we shall apply some convenient scalings of these variables, from SI to dimensionless units. The scaled variables will be written without tilde. The systems' parameters such as the mass m of the tunneling particle, the barrier height V_B of the double well potential and the positions $\pm x_0$ of the minima are also written without tilde.) The purpose of this paper is to derive a simple analytical expression which allows to estimate the maximum tunneling velocity, $\max \tilde{v}$, in this regime, in terms of few characteristic parameters such as m and V_B. Moreover, we shall compare the maximum tunneling velocity with the time-averaged one, $\text{avg}\, \tilde{v} = 2x_0/(\tilde{\tau}/2)$.

Our derivation of the maximum tunneling velocity, $\max \tilde{v}$, in systems with double well potentials will be restricted here to simple models of coherent tunneling along some coordinate $\tilde{x}$ which describes a (one-dimensional) path from the left potential well via the potential barrier V_B to the right potential well. For convenience and for symmetry reasons, the position of the barrier will be defined as $\tilde{x} = 0$, and the minima of the left and right potential wells are located at $-x_0$ and $+x_0$, respectively. For this class of systems, the derivation will be rather general, that means we shall consider tunneling of systems with mass m along non-cyclic Cartesian paths as well as systems with moments of inertia I along cyclic (angular or torsional) paths. For the corresponding velocities or angular velocities, we shall use the definition $\tilde{v} = \tilde{j}/\tilde{\rho}$ where $\tilde{\rho}$ and $\tilde{j}$ are the quantum mechanical probability densities and flux densities of the systems, depending on the coordinate $\tilde{x}$ and time $\tilde{t}$ which corresponds to analogous relations in classical mechanics and fluid dynamics [5,11]. Alternatively, this definition can also be obtained directly from the time-dependent Schrödinger equation (TDSE) and the polar representation of the wave function [12,13]. We shall show that the maximum value of $\tilde{v}$ is obtained just below the barrier, at $\tilde{x} = 0$. This implies a challenge because it is known that both the probability density $\tilde{\rho}(0)$ and the flux density $\tilde{j}(0)$ decrease exponentially when the barrier height V_B increases [14]. The limiting ratio of these two quantities is thus a priori unclear, and we shall particularly address the question whether $\tilde{v}$ is bounded or not. This question is in fact also motivated by the intriguing Hartman effect, as outlined above [6–8]. In order to answer this question, we shall take a risk by carrying out non-relativistic quantum dynamics simulations of the tunneling processes in terms of representative wavepackets which are obtained as solutions of the related TDSE. If the solutions of this approach would point to maximum tunneling velocities which approach the velocity of light, as reported for some cases of tunneling of free particles through potential barriers [8], the present approach would have to be replaced by a relativistic one. Once we have determined the maximum tunneling velocity $\max \tilde{v}$, we shall also address the related question of the time $\tilde{t}_B = x_0/(5 \max \tilde{v})$ for passing through the "most difficult part of the tunneling", that means through the domain from ca. $-x_0/10$ to $+x_0/10$ just below the top of the barrier. Moreover, we shall compare $\tilde{t}_B$ with the tunneling time $\tilde{\tau}$. It will also be illuminating to compare the ratio $\tilde{t}_B/\tilde{\tau}$ with the ratio of the time-averaged and maximum tunneling velocities, $\text{avg}\, \tilde{v}/\max \tilde{v}$.

The results which we shall derive below should be important for applications to many systems with symmetric double wells in chemistry and physics. For example, F. Hund in his fundamental paper [1] investigated tunneling from one enantiomer to the opposite one, with application to the torsional (cyclic) dynamics of H_2O_2. Below we shall consider complementary prototypical examples of molecules which may tunnel in cyclic symmetric double well potentials by torsional motions of two fragments about a connecting axis [15–19]. Alternatively, we shall also consider molecules which exhibit non-cyclic tunneling - the prototypical examples are tunneling of ammonia and semibullvalene along the coordinates which describe inversion [17,20] and Cope rearrangement [21–24], respectively. In the context of this work, Refs. [17,24] are of special importance because they present not only the nuclear probability densities but also the first nuclear flux densities during tunneling in symmetric double well potentials, in the deep tunneling regime. Finally, we point to the possible applications of rotational tunneling of molecules in external fields, induced by non-resonant interaction with laser fields through anisotropic polarizability [25–30]. Very intense and short laser pulses are used to effectively align molecules, where the molecule-field interaction leading to laser–induced molecular alignment is given by a trigonometric potential energy function. This intimately connects to the general case of a pendulum in quantum mechanics [31,32] for which the quantum dynamics of tunneling has recently been studied semi-analytically [33]. Note that stationary pendular states can be expressed in terms of Mathieu functions [34]. Although not analytically given, there is a substantial body of literature on their asymptotic properties [35–37].

The article is organized as follows: In Section 2, we introduce a generic Hamiltonian which allows to consider tunneling of non-cyclic as well as cyclic symmetric double well systems. The employed Hamiltonian depends on a single dimensionless action parameter β which combines the effect of several system parameters, i. e., the mass m or moment of inertia I, the barrier height V_B and width of the potential x_0. For this system, an expression for the potential is derived in Section 3 which is valid for sufficiently large values of β and which is compared with a Mathieu model of pendular states. In Section 4, the tunneling dynamics of the lowest doublet in this potential is analyzed, and an analytic expression for the maximum tunneling velocity is found. Finally, in Section 5 we discuss these results, with reference to various applications. We shall also consider the consequences for the times $\tilde{t}_B$ which the systems need to pass through the domain just below the barrier, together with the ratios $\tilde{t}_B/\tilde{\tau}$ and $\text{avg}\, \tilde{v}/\max \tilde{v}$. Section 5 also has some conclusions.

2. Model system and scaling properties

2.1. Non-cyclic model

Let us consider the case of a non-cyclic quantum system with mass m tunneling along the coordinate $\tilde{x}$. The corresponding Hamiltonian is

$$\widetilde{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \tilde{x}^2} + \widetilde{V}(\tilde{x}). \tag{1}$$

The symmetric double well potential $\widetilde{V}(\tilde{x})$ has its barrier centered at $\tilde{x} = 0$ with barrier height

$$V_B := \widetilde{V}(0) - \widetilde{V}(x_0), \tag{2}$$

and with minima at $\tilde{x} = \pm x_0$.

The eigenfunctions $\tilde{\psi}_n(\tilde{x})$ and eigenenergies $\widetilde{E}_n$ with quantum numbers $n = 0, 1, 2, \ldots$, are obtained as solutions of the time-independent Schrödinger equation (TISE)

$$\widetilde{H}\tilde{\psi}_n(\tilde{x}) = \widetilde{E}_n\tilde{\psi}_n(\tilde{x}). \tag{3}$$

The model is thus characterized by three parameters, the mass m, the barrier height V_B and width parameter x_0. For the subsequent applications, it is convenient to introduce scaled, dimensionless variables $x = \tilde{x}/x_0$ and $E = \widetilde{E}/V_B$, i.e. the length and the energy are measured in terms of x_0 and V_B.

Accordingly, we set $\widetilde{V}(\tilde{x}) = \widetilde{V}(x_0 x) = V_B V(x)$, thus defining a scaled potential $V(x)$ with minima at $x = \pm 1$, and barrier height