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Tunneling through a time-dependent barrier – a numerical study

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Abstract. We present a numerical investigation of quantum mechanical tunneling process in a double well potential with fluctuating barrier. The tunneling probability and rate are calculated for two cases in which (i) the height of the barrier is undergoing harmonic oscillation with frequency ω and (ii) the height of the barrier is undergoing random fluctuation with frequency ω. It is observed that in both cases, the quantum mechanical tunneling probability and rate exhibit a maximum as a function of the fluctuation frequency. The optimal frequency i.e. the frequency at which rate exhibits a maximum shows a strong isotopic mass effect.

Keywords. Time-dependent barrier; fluctuation frequency; tunneling rate.

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1. Introduction

Tunneling through a potential barrier is a very common occurance in many branches of physics and chemistry [1–3]. Proton, hydride ion or H-atom transfer reaction have long been associated with the purely quantum mechanical phenomenon of tunneling, the significance of which has often been recognised in the existence of a temperature independent reaction rate constant when $T \rightarrow 0$. Nevertheless, the idea that reaction rates are regulated by the ease with which quantum system can surmount potential barriers (which is fixed for all time) has become generally acceptable. The problem was then to tell that particles on one side of the barrier; whatever their energy (which may vary), will escape to the other. But one may be curious as to what happens if the potential barrier is not fixed for all time but itself varies with time. There are a host of circumstances in which the concept of time-dependent barrier might apply [4–7]. The potential barrier to the dissociation of a molecule, for example may depend on the geometrical position of atoms not directly involved in what may be simply the stretching of a chemical bond to destruction. Or, as much to the point, an insulating layer separating two semiconducting layers may be subject to a bias that effects the ease with which electrons can tunnel through it. Except, in the highly rarefied atmosphere prevailing in supersonic jets or molecular beams, chemical reaction usually occur in the presence of a medium, a material surrounding, with which the molecular species undergoing a chemical reaction interacts, however weak it may be.

The interaction with the surrounding medium may cause the barrier to fluctuate with time [8]. Indeed, environmental effects on rate processes in complex dynamical systems, such as biomolecules have received serious attention in recent years. The emphasis has been on the dynamics of escape over fluctuating barriers which could arise as a result of stochastic re-orientations of a bridge unit or stochastically interrupted electronic pathway as in proteins. So the fluctuating barrier can act as good model for proton or H atom transfer dynamics in biomolecules or proteins where the protonic pathway contains a flipping molecular unit [9,10].

The rate of particles crossing a potential barrier which fluctuates with time is of great interest in condensed phase processes such as diffusion and relaxation [11–13]. A recent study on the fluctuating barrier has revealed an interesting phenomenon in that the barrier crossing rate exhibits a resonance like behaviour at some intermediate fluctuation rate [14]. However, their calculation is strictly classical, with no quantum tunneling and might apply to the particles of a perfect gas enclosed in a one-dimensional box that itself encloses the potential barrier. Although the quantum tunneling problem in a fluctuating barrier has recently been studied by a number of authors [15,16], the implication of this phenomenon in the real world of quantum mechanics with more realistic potential barrier is not clear at all.

In this paper we present a quantum mechanical study of tunneling probability and rate of a particle in a double well potential, the barrier of which fluctuates with time. We consider both harmonic and random fluctuation of the barrier height and examine how the tunneling probability and rate of an incident wavepacket depend on the rate of fluctuation of the barrier height.

2. The model

The model hamiltonian employed in the present study is the one dimensional double well oscillator

$$H_0 = \frac{p^2}{2m} + K_0(1 - \mathrm{e}^{-x^2}) = \frac{p^2}{2m} + V(x), \tag{1}$$

where K_0 is the barrier height of the potential. For the present calculation it is chosen the value of 9.0 a.u. and mass is taken as 1836 a.u.

The initial state is prepared by the linear combination of two lowest degenerate double-well eigenstates. Let $\phi_1(x)$ and $\phi_2(x)$ be the two lowest eigenstates with energy E. Because $\phi_1(x)$ has even and $\phi_2(x)$ has odd parity, the linear combinations

$$\phi_\pm(x) = \frac{1}{\sqrt{2}}(\phi_1(x) \pm \phi_2(x)) \tag{2}$$

are 'localized' in the 'right' or the 'left' well. We have chosen the wavefunction which is localized in the left well.

In order to simulate the effect of the barrier fluctuation with time, we assume that the barrier height K_0 is now time-dependent. So the time-dependent potential becomes

$$V_h(x,t) = K_t(1 - \mathrm{e}^{-x^2}).$$

For the present study we have chosen the following two forms of K_t.

(i) $$K_t = K_0 + \Delta K \sin(\omega t), \tag{3}$$

(ii) $$K_t = K_0 + \Delta K R(t). \tag{4}$$

So the total Hamiltonian now becomes

$$H = \frac{p^2}{2m} + V(x) + V'(x,t) = H_0 + V'(x,t), \tag{5}$$

where $V'(x,t) = \Delta K \sin(\omega t)(1 - \mathrm{e}^{-x^2})$ or $\Delta K R(t)(1 - \mathrm{e}^{-x^2})$. ΔK is the size of the fluctuation in the barrier height and ω is the frequency of harmonic oscillation. We have modeled $R(t)$ by a sequence of random numbers of magnitudes between -1 and $+1$ generated at preselected discrete time steps. The size of the time steps then determine what may be called fluctuation frequency. Thus in our current model study, the time-dependent potential exercises (i) harmonic oscillation of the barrier height with time, (ii) random fluctuation with time. We study the tunneling probability and rate in both cases and in particular, investigate the influence of the fluctuation frequency ω on the tunneling probability and rate. The parameter of amplitude fluctuation ΔK is chosen the value 1.0 for both cases throughout the calculation.

3. The method

The time-dependent Schrödinger equation (TDSE) describing our system can be written down easily (we use atomic units throughout).

$$i\frac{\delta \Psi(x,t)}{\delta t} = [H_0 + V'(x,t)]\, \Psi(x,t). \tag{6}$$

We can employ the FGH method [17] to evaluate the eigenfunctions and eigenvalues of the unperturbed oscillator (H_0) giving

$$H_0|\Phi_i^0(x)\rangle = \epsilon_i^0|\Phi_i^0(x)\rangle, i = 1, 2, \cdots, \tag{7}$$

where N is the number of grid points used for representing $|\Phi_i^0\rangle$ in the co-ordinate space.

$$|\Phi_i^0\rangle = \sum_{i=1}^{N} |x_i\rangle \Delta x w_i^0. \tag{8}$$

w_i^0 in eq. (8) represent the values of the co-ordinate representative of the state function $|\Phi_i^0\rangle$ at the grid points, the values of which are obtained by the standard variational recipe. The FGH method, as shown by Adhikari *et al* [18,19] can be used to propagate the wave function on the same grid. Thus, when the perturbations produced by the randomly fluctuating well-depth is switched on, the state function $\Psi(x,t)$ is supposed to be given by

$$|\Psi(x,t)\rangle = \sum_{q=1}^{N} w_q(t)|x_q\rangle \Delta x. \tag{9}$$

The amplitudes $(w_i(t))$ are now time dependent quantities and their evolution equations can be easily obtained by invoking the Dirac–Frenkel time-dependent variational principle which demands that

$$\langle \delta\Psi(x,t)|H_0 + \frac{1}{2}(K_t - K_0)x^2 - i\frac{\delta}{\delta t}|\Psi(x,t)\rangle = 0. \tag{10}$$

Since $w_q(t)$s are the variational parameters of our model, eq. (7) easily leads us to (for arbitrary variations $\delta w_p(t)$) the evolution equations for the grid point amplitudes:

$$\begin{aligned}\dot{w}_p &= \frac{1}{i}\sum_{q=1}^{n_x} \Delta x \langle x_q|H|x_p\rangle \Delta x w_q(t) \\ &= \frac{1}{i}\sum_{q=1}^{n_x}\left[\langle x_q|H_0|x_p\rangle + \frac{1}{2}(K_t - K_0)\langle x_q|x^2|x_p\rangle\right] w_q(t).\end{aligned} \tag{11}$$

One can easily integrate these equations if the initial $(t = 0)$ values of the grid point amplitudes of $\Psi(x,t)$ are known with reasonable accuracy. Since H_0 is time-independent, its eigenstates can be easily obtained by the time-independent FGH method [17]. The matrix elements H_{pq} are easily evaluated by the standard FGH recipe. The tunneling probability $P^{\nu}_{\rm tun}$ from the νth state is computed by calculating the time-dependent probability of finding the system within the perimeters of the right well of the double well oscillator.

$$P^{\nu}_{\rm tun}(t) = \int_a^b |\Psi(x,t)|^2 {\rm d}x, \tag{12}$$

where the well-perimeters are defined by the points $x = a$ and b. In the discretized coordinate space used by us, the integration can be replaced by summation over the appropriate grid points

$$P^{\nu}_{\rm tun}(t) = \sum_{i=m}^{n} |w_{i\nu}(t)|^2, \tag{13}$$

where m is the leftmost grid point and n the rightmost grid point on the perimeter of the well. The slopes of the plots of $\ln P^{\nu}_{\rm tun}(t)$ against t give us the tunneling rate constants $(k^{\nu}_{\rm tun})$ while $P^{\nu}_{\rm tun}(t = T)$ itself yields the tunneling probability at a particular time T.

4. Results and discussion

Let us first consider the model where the barrier height of the double well oscillator undergoes harmonic oscillation with time and examine what kind of influence the oscillation has on the tunneling probability and rate.

Figure 1 displays the profile of the tunneling probability $P_{\rm tun}(T)$ of the oscillator after the lapse of a fixed time ($T = 10$ fs) as a function of the oscillation frequency. From the figure it is seen that the tunneling probability show a parabolic dependence (with a maximum) on the oscillation frequency i.e. with frequency it first increases, reaches a

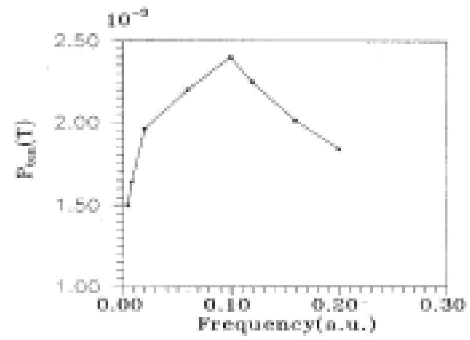

Figure 1. Plots of tunneling probability $P_{\rm tun}$ (T) versus oscillation frequency when the barrier height undergoes harmonic oscillation.

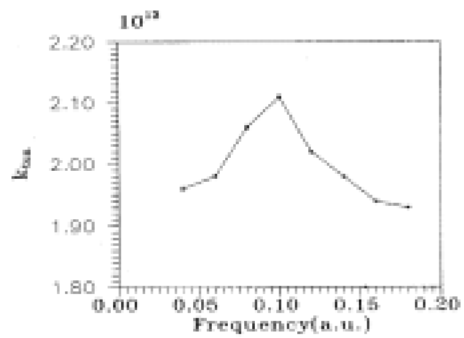

Figure 2. Plots of tunneling rate $K_{\rm tun}$ versus oscillation frequency when the barrier height undergoes harmonic oscillation.

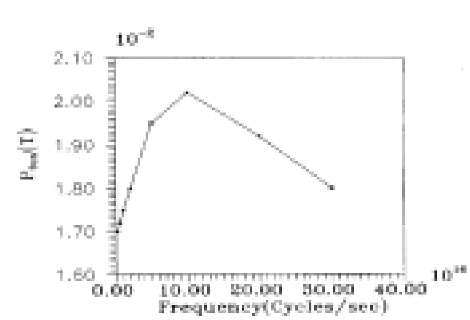

Figure 3. Plots of tunneling probability $P_{\rm tun}$ (T) versus fluctuation frequency when the barrier height undergoes random fluctuation.

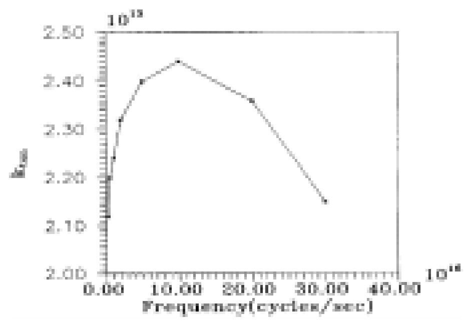

Figure 4. Plots of tunneling rate constants $k_{\rm tun}$ versus fluctuation frequency when the barrier height undergoes random fluctuation.

maximum value and then decreases. We have calculated the tunneling rate constant from the slope of the plots of $\ln P_{\rm tun}(t)$ against time for different values of oscillation frequency. In figure 2, the computed tunneling rate constant $k_{\rm tun}$ is shown as a function of oscillation frequency. The rate constant, like tunneling probability also shows a parabolic dependence on oscillation frequency.

Now we turn our attention to a more realistic model where the barrier height of the oscillator undergoes random fluctuation with time. In figures 3 and 4 we have plotted the tunneling probability and rate, respectively, as functions of random fluctuation frequency of the well-depth. As in the case of harmonic oscillation of the barrier height, the tunneling probability and rate in randomly fluctuating case also shows a parabolic dependence on fluctuation frequency.

Now we try to explain this phenomenon of maximum tunneling probability and rate as a function of oscillation or fluctuation frequency of barrier fluctuation that is observed in our quantum mechanical study. At very low frequencies, the particles see an effectively static barrier during their traversal and the tunneling probability and rate is low and it corresponds to the value of oscillator with fixed barrier height. At very high frequencies a particle sees many cycles of oscillation of the modulation potential. The particle sees, therefore, an effective potential of average height K_0. So the tunneling probability and rate again attains the value of that of oscillator with static barrier height. The phenomenon of maximum tunneling probability and rate as a function of fluctuation frequency may arise as a result of two primarily competing processes that counterbalance each other and result in a maximum value for the tunneling probability as well as rate. Following Ge *et al* [16] we assume that the barrier tunneling probability $P(\omega)$ can be written as the product of two separate probabilities

$$P(\omega) = P_A(\omega) P_B(\omega). \tag{14}$$

$P_A(\omega)$ is associated with the primary process for the tunneling particle to absorb a single quanta $\hbar\omega$. This probability is obviously a decreasing function of ω because it is more difficult for the particle to absorb a high energy quanta than allow energy one for a reasonably smooth potential barrier. The second process is identified as the barrier transmission process for the particle with the total energy $E = E_0 + \hbar\omega$, where E_0 is the initial kinetic energy of the particle. Obviously this transmission probability $P_B(\omega)$ is an increasing function of ω. The optimal frequency to yield the maximum tunneling probability or rate is the combined result of two opposing processes; the process of absorbing one quanta $\hbar\omega$ and the process of tunneling through the barrier with increased total energy of $E_0 + \hbar\omega$. The compromise between the two yields the optimal frequency $\omega_{\max}$ to give the maximum tunneling probability and rate.

The observed maximum in our computed tunneling rate constant as a function of the fluctuation frequency of the well-depth bears a resemblance with a novel resonant behaviour predicted by Doering and Gadoua [14] in diffusion over a fluctuating barrier. They observe that for slow variation the average barrier crossing time is the average of times required to cross over each instantaneous barrier, while for very fast variation, it is just the time required to cross the average barrier. In the intermediate regime, the crossing process becomes strongly correlated with potential fluctuation and the crossing rate exhibits a maximum at a resonant fluctuation frequency. It is interesting to note that in our case, the process of transfer is not thermally activated; yet the appearance of a resonant frequency where tunneling rate is maximum indicates that stochastic resonance may be exhibited in purely quantum processes. The signature of these processes may be found in electron transfer rates across fluctuating bridgehead in biomolecules. Thus Goychuk *et al* [10] find maximum in their calculated bridge assisted transfer rate in a protein molecule as a function of noise frequency, just as we have found the tunneling rate to pass through a maximum in a zero temperature model problem that may be assumed to mimick electron transfer between two equivalent sites.

As it is mentioned earlier, fluctuating barrier can act as a good model for proton or H atom transfer dynamics. It is worthwhile to study in this context, the isotopic mass effect on the optimal frequency (the frequency at which the maxima occur). We carry out the calculations of tunneling rate at different random fluctuation frequencies with two different masses that correspond to the mass of deuterium ($m = 367$ a.u.) and tritium ($m = 5408$ a.u.). We have calculated the optimal frequency from the plot of tunneling rate versus fluctuation frequency. The optimal frequency obtained is now plotted as a function of mass in figure 5. From the figure it is seen that with increase in mass the optimal frequency increases. This is physically understandable since the tunneling process involves large amplitude motion of H atom, the displacement of a larger mass causes the shift in the optimal frequency.

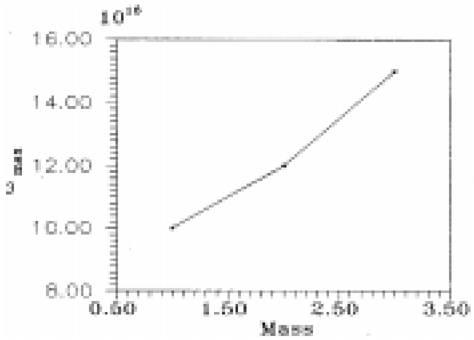

Figure 5. Optimal frequency versus mass profile of the oscillator having randomly varying barrier height.

5. Conclusion

Numerical experiments with a double-well oscillator having time-dependent barrier height (undergoing harmonic oscillation or random fluctuation) reveal interesting features in its tunneling behaviour. The tunneling probability and rate passes through a maximum when plotted as a function of fluctuation frequency of the barrier. The maximum in the tunneling rate appears as a result of competition between two opposing processes; the process of absorption of one quanta and the process of transmission through the barrier. The optimal frequency shows a strong isotopic mass effect.

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