

Multidimensional Quantum Tunneling: Direct Instanton Calculation with Application to Polyatomic Molecules

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Abstract. Multidimensional tunneling appears in many problems at nano scale. The high dimensionality of the potential energy surface (e.g. many degrees of freedom) poses a great challenge in both theoretical and numerical description of tunneling. Numerical simulation based on Schrödinger equation is often prohibitively expensive. We propose an accurate, efficient, robust and easy-to-implement numerical method to calculate the ground state tunneling splitting based on imaginary-time path integral (*'instanton'* formulation). The method is genuinely multi-dimensional and free from any additional *ad hoc* assumptions on potential energy surface. It enables us to calculate the effects of all coupling modes on the tunneling degree of freedom without loss. We also review in this paper some theoretical background and survey some recent work from other groups in calculating multidimensional quantum tunneling effects in chemical reactions.

Key words: Quantum tunneling; path integral; chemical reaction.

1 Introduction

Tunneling describes the phenomena that particles pass through potential energy barrier with negative kinetic energy. It originates from the wave nature of quantum mechanics where a wave cannot be completely confined in a bounded region by any finite potential. It will leak out eventually. From corpuscle perspective, however, the tunneling behavior is rather bizarre and has far-reaching implications. The characteristic length for wave mechanics is the particle's de Broglie wavelength $\lambda = h/\sqrt{2mE}$. For an electron it is 18 Å

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at the energy of 10kJ/mol and 0.5 Å for hydrogen H(protium). Therefore at nano-scale when the de Broglie wavelength cannot be ignored, the wave/corpuscle duality nature of matter forces one to cooperate with this ‘non-classical’ tunneling behavior.

Quantum tunneling found its very early application in nuclear physics, soon after the discovery of the wave nature of particles. There has been considerable interest in tunneling in condensed matter physics, both in theory and applications. Most of it concerns electron tunneling since it has longer de Broglie wave length therefore greater tunneling effects. The examples include Cooper pair tunneling in super-conductor, tunneling transistor in semi-conductor, scanning tunneling microscopy, to name a few. For the past two and half decades, tunneling of macroscopic degrees of freedom has been studied intensively after the proposal of Leggett in [20]. A prototype example is magnetic flux tunneling in superconducting quantum interface devices (SQUIDS). One of the central theme in these studies is the many-body effects and the influence of environment on the behavior of tunneling degree of freedom. Of particular interest is the survival (or lost) of quantum mechanical behavior in the quantum-classical transition (the ‘decoherence’ problem). For this purpose, field theory based method (path integral) has become quite popular. Compared with wave function description of Schrödinger, path integral has the advantage in handling many degrees of freedom (many dimensions), in both theoretical study and real life computation. Reduction to effective few-body model can also be done in a relatively easy way (see, for example, [41] for details).

In chemistry and biochemistry, the importance of tunneling in electron transfer has been established after the work of Marcus. Recently hydrogen tunneling in proton transfer has attracted much attention in chemical reaction, in both theory and experiments, where the proton transfer is at the heart of acid-based reactions. It has been found tunneling play an important role at low and even moderate temperature. For some recent experimental discoveries, see [17,32] and series of reviews in [31].

In classical theory, the chemical reaction is conveniently described by reaction pathway(s) on a potential energy surface (PES). PES describes interaction among nuclei and is obtained after the Born-Oppenheimer approximation to separate the fast electronic motion and slow nuclear motion. Usually, the dimension (number of degrees of freedom) of PES is very large. For a molecule of M atoms, the dimension of PES is $d = 3M - 6$. By assuming the nuclear motion being classical, the reaction pathway is solved from Newtonian dynamics on PES. Since Newtonian dynamics is based on trajectories, the realization is relatively cheap (algebraic against d). When considering quantum mechanical behavior, this is no longer the case. The full quantum mechanical behavior can certainly be determined if one solves Schrödinger equation with PES $V(\mathbf{x})$ directly. But since there are d independent variables, the computational cost is $\mathcal{O}(N^d)$ where N is the number of basis functions in each dimension. It is prohibitively expensive beyond small d and N . Various approximation schemes have been developed. Semi-classical approximation of WKB type has been a major tool to handle the situation. However, since complete WKB approximation works only for 1D, in practice one still has to enforce various additional *ad hoc* assumptions on potential to reduce the number of dimensions. It is hard to justify these

assumptions.

WKB approximation can be generalized to multi-dimensions by path integral method. In particular, for the ground state calculation, the so-called ‘instanton’ formulation was developed in quantum field theory. Recently there have appeared many works using instanton to study chemical reaction on high dimensional PES. However, some fundamental difficulties exist in the application of instanton. Most of the computations do not fully exploit the multi-dimension nature of instanton and resort to 1D calculation after further *ad hoc* assumptions at some intermediate step. This makes the calculation results less reliable. In this work, we present an accurate and efficient numerical scheme to deal with one of the basic tunneling phenomena, tunneling splitting in multidimensional double well potential. Compared to other approaches, our method avoids any additional *ad hoc* assumptions on potential energy surface and can deal with any DOF which makes it attractive in realistic computation.

In the following sections, theoretical background will be introduced (both direct WKB and path integral approaches). Some of the recent numerical works on quantum tunneling calculation in chemical reaction base on instanton approach will be discussed after that. We propose our new numerical scheme to solve the problem of tunneling splitting followed by some computational results. The conclusion will be drawn in the final section.

2 Theoretical background

2.1 WKB

In this section, we give a very brief review of the theoretical background of the semi-classical description of quantum tunneling. For more details, we refer to [19].

After Born-Oppenheimer approximation, one reaches the potential energy surface $V(\mathbf{x})$. For the nuclear motion, one has either the time-dependent Schrödinger equation for the wave function $\Phi(\mathbf{x})$

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi = -\frac{\hbar^2}{2}\Delta_{\mathbf{x}}\Psi + V(\mathbf{x})\Psi. \quad (2.1)$$

Here and after we use mass-weighted coordinates; therefore \hbar is indeed a rescaled Planck constant. Or for a system at total energy E , one solves the stationary state Schrödinger equation

$$\hat{H}\psi = -\frac{\hbar^2}{2}\Delta_{\mathbf{x}}\psi + V(\mathbf{x})\psi = E\psi. \quad (2.2)$$

WKB semi-classical approximation looks for the wave function of the form

$$\psi = \exp(iW/\hbar), \quad (2.3)$$

where W admits following semi-classical expansion

$$W = W_0 + \hbar W_1 + \dots. \quad (2.4)$$

The first two equations are

$$|\nabla W_0(\mathbf{x})|^2 = 2(E - V(\mathbf{x})), \tag{2.5}$$

$$\nabla W_0(\mathbf{x}) \cdot \nabla W_1(\mathbf{x}) = \frac{i}{2} \Delta W_0(\mathbf{x}). \tag{2.6}$$

If the system has just a single DOF, the above equation can be solved trivially:

$$W_0(x) = \pm \int \sqrt{2(E - V(x))} dx. \tag{2.7}$$

One can easily see that for the region where the total energy E is larger than potential energy $V(x)$ (classically allowed), $\psi(x)$ is indeed a wave $\psi = e^{\pm \frac{i}{\hbar} \int p(x) dx}$ where $p(x)$ is the local momentum $p(x) = \sqrt{2(E - V(x))}$ that is real. However when the total energy E is lower than the potential energy $V(x)$ which is classically forbidden since kinetic energy is negative, ψ behaves like the exponential function $\psi(x) = e^{\pm \frac{1}{\hbar} \int \sqrt{2|E - V(x)|} dx}$ (or a wave with imaginary momentum $p(x)$ in another word). This exponentially small but non-vanishing property characterizes the semi-classical behavior of the particle under the potential barrier.

In 1D, the WKB wave function takes the general form

$$\psi = C_1 p^{-1/2} \exp\left(\frac{i}{\hbar} \int p dx\right) + C_2 p^{-1/2} \exp\left(-\frac{i}{\hbar} \int p dx\right), \tag{2.8}$$

where the local momentum is $p(x) = \sqrt{2(E - V(x))}$. This form holds for both classically allowed and forbidden waves. Indeed, classically forbidden wave can be regarded as an analytical continuation of a classically allowed wave into imaginary momentum. Of course the above general solution breaks down at the so-called turning point(s) where $E = V(x)$ thus $p(x) = 0$. One needs some connection formula to match classically allowed with forbidden wave functions. For the one-dimensional case, using Stokes lines emanating from turning point (isolated or finite many coalescent) one can do analytical continuation to match non-uniform asymptotic expansions in different sections.

The generalization of 1D solutions to multi-dimensional non-separable potential is non-trivial. Eq. (2.5) is now integrated along characteristics up to caustics which is now a manifold that cannot be calculated *a priori* (in contrast to 1D turning points). The form of the WKB wave function in classically forbidden region is difficult to determine. In the seminal work [1], the concept of ‘most probable escape path’ (MPEP) was introduced to simplify the construction of W_0 in this region. The idea is that in the forbidden region, $W_0(\mathbf{x})$ is purely imaginary and that $iW_0(\mathbf{x}) = \sqrt{2(V(\mathbf{x}) - E)}$ should be integrated along a ‘real’ characteristic. By the exponential property, one should concentrate on the tube around the path that minimizes $\int_{\mathcal{P}} \sqrt{2(V(\mathbf{x}) - E)}$. However, this is actually a free boundary problem with boundary condition (turning points) included in the path \mathcal{P} . Some very crude approximations are needed in practice to find \mathcal{P} . The connection problems are

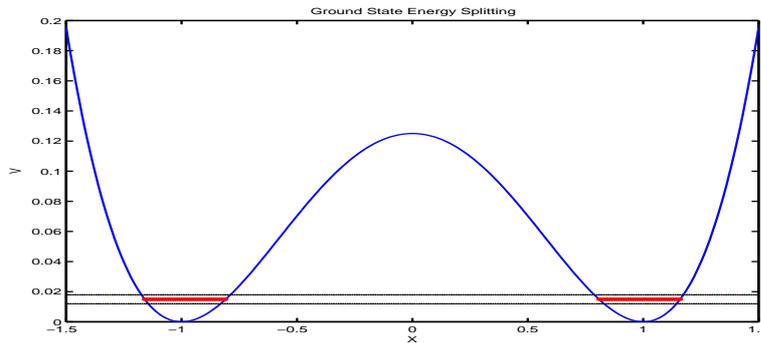


Figure 1: Ground state energy splitting by tunneling in 1D.

yet to be solved in a satisfactory way. The exception is $E = 0$ which means the tunneling out of the bottom of the well. We shall see later that this is closely related to the imaginary time path integral approach ('instanton').

One of the basic problems in quantum tunneling is the symmetric double-well potential problem. Classically, a particle stays in one well if its energy is not high enough. However, when considering quantum mechanical behavior, the particle will tunnel through the potential barrier even at zero temperature. The two 'localized' wave functions have exponentially small overlap which cause the tunneling and then the two original degenerated ground state energy will split into two levels with exponentially small difference. The resulting two lowest states will have opposite parity. This tunneling splitting has wide and vital implications in quantum field theory, phase transition, chemical isomerization reaction, among others.

Schematically, it is illustrated in Fig. 1.

Again for the 1D potential $V(x)$ this problem can indeed be solved nicely by standard WKB calculation ([19]). Tunneling splitting is given by:

$$\Delta_0 = \frac{\hbar\omega}{\pi} \exp\left(-\frac{1}{\hbar} \int_{-a'}^{a'} \sqrt{2(V(x) - E)} dx\right), \quad (2.9)$$

where E is single well energy level (not necessarily ground state) and $\pm a'$ are two (symmetric) inner turning points associated with E . $\omega = \sqrt{V''(a)}$ where $\pm a$ are local minima of $V(x)$ can be thought as attempting frequency of the particle in one well with energy E . This formula has been a workhorse for almost all tunneling splitting calculations. As said, to generalize it to multi-dimensions needs great effort.

2.2 Instanton

We now turn to the path integral formalism (see *e.g.*, [11, 30] for more details). For the description of a quantum system with many degrees of freedom, this is the most versatile tool.

Instead of solving for the wave function from the Schrödinger equation (either stationary or time-dependent), the path integral solves for the propagator (Green's function) of Eq. (2.1):

$$G(\mathbf{x}, t; \mathbf{y}, 0) = \langle \mathbf{y} | e^{-iHt/\hbar} | \mathbf{x} \rangle. \tag{2.10}$$

The critical step is to express the propagator as a path integral:

$$G(\mathbf{x}, t; \mathbf{y}, 0) = \int_{\mathbf{y},0}^{\mathbf{x},t} \exp(iS[\mathbf{u}(s)]/\hbar) \mathcal{D}\mathbf{u}, \tag{2.11}$$

where $\mathcal{D}\mathbf{u}$ is understood as summation over all the paths that connect two end-points $\mathbf{u}(0) = \mathbf{y}$, $\mathbf{u}(t) = \mathbf{x}$. $S[\mathbf{u}]$ is the classical action defined via the classical Lagrangian:

$$S[\mathbf{u}] = \int_0^t \mathcal{L}(\mathbf{u}, \dot{\mathbf{u}}, t') dt' = \int_0^t \left(\frac{1}{2} \dot{\mathbf{u}}^2 - V(\mathbf{u}) \right) dt'.$$

The path integral is most effective in the semi-classical regime where the action $S \gg \hbar$. It is then evaluated by the stationary phase method. Heuristically, because of the fast oscillation of the phase, the dominant contribution to the integral should come from the stationary point of the phase which is now a path $\mathbf{u}(t)$ that satisfies the Euler-Lagrange equation,

$$\frac{\delta S}{\delta \mathbf{u}} = -\ddot{\mathbf{u}}(t) - \nabla V(\mathbf{u}(t)) = 0, \tag{2.12}$$

with boundary conditions

$$\mathbf{u}(0) = \mathbf{y}, \quad \mathbf{u}(t) = \mathbf{x}. \tag{2.13}$$

This is nothing but the equation for the classical Newtonian trajectory. Higher order terms are included by formal Taylor's expansion of $S[\mathbf{u}]$. Usually, one stops at the second-order term which will be integrated by Gaussian integration. Some special treatment is necessary if it is singular. This is indeed what we shall encounter later. Quantum fluctuation around the classical path is thus given. In this way, the path integral bridges quantum description and the classical one.

Barrier tunneling (we do not consider the dynamical tunneling here) is classically forbidden and the kinetic energy of the system is negative. Formally, the momenta can be thought of as analytically continued into complex value. They are assumed to be purely imaginary and the imaginary-time path integral is therefore used to describe the process ([7]). This scheme indeed follows the seminal work of [1] in multidimensional WKB. There is however criticism on this assumption, especially in the so-called 'mixed tunneling' (see [38]). More complicated 'phase-space' tunneling can be found in *e.g.*, [9]. However, this 'imaginary-time' path integral is probably still the most practical tool to study the ground state behavior in tunneling of a system with large number of DOF and the whole 'Euclidean field' theory has been built on it.

After transforming $t \rightarrow \tau = it$, the (imaginary-time) propagator now reads

$$G_E(\mathbf{x}, \tau; \mathbf{y}, 0) = \langle \mathbf{x} | e^{-H\tau/\hbar} | \mathbf{y} \rangle = \int e^{-S_E[\mathbf{u}]/\hbar} \mathcal{D}\mathbf{u}, \tag{2.14}$$

where $S_E[\mathbf{u}]$ is now the Euclidean action defined as:

$$S_E[\mathbf{u}] = \int \mathcal{L}_E(\mathbf{u}, \dot{\mathbf{u}}, \tau') d\tau' = \int \left(\frac{1}{2} \dot{\mathbf{u}}^2(\tau) + V(\mathbf{u}(\tau)) \right) d\tau. \quad (2.15)$$

This path integral can be evaluated by the steepest decent method for functional integration when $S_E \gg \hbar$. The dominant contribution comes from the path $\bar{\mathbf{u}}$ that minimizes S_E . It satisfies

$$\frac{\delta S_E}{\delta \mathbf{u}} = \ddot{\mathbf{u}}(\tau) - \nabla V(\mathbf{u}(\tau)) = 0, \quad (2.16)$$

with appropriate boundary conditions. For ground state tunneling, we are interested in the trajectory that connects two local minima of the potential V , \mathbf{x}_L and \mathbf{x}_R . Therefore the boundary conditions are naturally

$$\mathbf{u}(\tau \rightarrow -\infty) = \mathbf{x}_L, \mathbf{u}(\tau \rightarrow +\infty) = \mathbf{x}_R. \quad (2.17)$$

This solution $\bar{\mathbf{u}}$ is termed *instanton* (or *kink*) [7] after the work of Polyakov, 't Hooft and Coleman in field theory. Indeed, before that it had already appeared in the work of Langer [18] in the study of phase transition in statistical physics. The instanton can be viewed as a classical trajectory in the up-side down potential $U(\mathbf{x}) = -V(\mathbf{x})$. The particle would spend most of the time near two local minima of V and traverses quickly crossing the potential barrier. The imaginary time τ is indeed linked to the temperature by $\tau = \hbar\beta = \hbar/(k_B T)$ where T is the absolute temperature and k_B the Boltzmann constant. The ground state is the zero temperature limit.

It is not hard to see that along instanton path one has

$$\frac{1}{2} \dot{\bar{\mathbf{u}}}^2 = V(\bar{\mathbf{u}}), \quad (2.18)$$

which means the total energy $E = 0$. Consequently,

$$S_0 := S_E[\bar{\mathbf{u}}] = \int_{-\infty}^{\infty} \dot{\bar{\mathbf{u}}}^2 d\tau = \int_{-\infty}^{\infty} 2V(\bar{\mathbf{u}}(\tau)) d\tau = \int_0^L \sqrt{2V} ds, \quad (2.19)$$

where s is the intrinsic coordinate of the instanton path and L is its total length in configuration space. One can see here the link with MPEP approach in [1]. The advantage here is that since $E = 0$ one avoids the very complicated problems associated with turning points.

Formally, one would include the second-order expansion term of $S_E[\mathbf{u}]$ around $\bar{\mathbf{u}}$ and evaluate it by Gaussian integration. Let $\mathbf{u}(\tau) = \bar{\mathbf{u}}(\tau) + \mathbf{v}(\tau)$ where $\mathbf{v} = \mathbf{v}(\tau)$ is the fluctuation around instanton path $\bar{\mathbf{u}}$. One has

$$\begin{aligned} S_E[\mathbf{u}] &= S_E[\bar{\mathbf{u}} + \mathbf{v}] \\ &= S_E[\bar{\mathbf{u}}] + \frac{1}{2} \langle \mathbf{v}, \mathcal{H}(\bar{\mathbf{u}}) \mathbf{v} \rangle + \mathcal{O}(|\mathbf{v}|^3), \end{aligned}$$

where \mathcal{H} is the Hessian of S_E :

$$\mathcal{H}(\mathbf{u}) = \frac{\delta^2 S_E}{\delta \mathbf{u}^2} = -\frac{\partial^2}{\partial \tau^2} \mathbb{I} + D^2 V(\mathbf{u}). \tag{2.20}$$

In (2.20), \mathbb{I} is the $d \times d$ identity matrix and $D^2 V$ is the Hessian of V . The expansion gives

$$\begin{aligned} G_E(\mathbf{x}, \tau; \mathbf{y}, 0) &= \int e^{-S_E[\mathbf{u}]/\hbar} \mathcal{D}\mathbf{u} \\ &= \int e^{-S_E[\bar{\mathbf{u}}]/\hbar - \frac{1}{2\hbar} \langle \mathbf{v}, \mathcal{H}(\bar{\mathbf{u}}) \mathbf{v} \rangle} \mathcal{D}\mathbf{v} \\ &= e^{-S_E[\bar{\mathbf{u}}]/\hbar} \int e^{-\frac{1}{2\hbar} \langle \mathbf{v}, \mathcal{H}(\bar{\mathbf{u}}) \mathbf{v} \rangle} \mathcal{D}\mathbf{v}. \end{aligned} \tag{2.21}$$

The integral over $\mathcal{D}\mathbf{v}$ is done by Gaussian integration where one expands the operator $\mathcal{H}(\bar{\mathbf{u}})$ in its complete set of eigen-basis ϕ_n (\mathbf{v} obeys the homogeneous boundary condition):

$$\mathbf{v}(\tau) = \sum_{n \geq 0} c_n \phi_n(\tau), \tag{2.22}$$

and the integration is transformed to

$$\mathcal{D}\mathbf{v} = \mathcal{N} \prod_{n \geq 0} dc_n. \tag{2.23}$$

Formally, one obtains

$$\begin{aligned} \int e^{-\frac{1}{2\hbar} \langle \mathbf{v}, \mathcal{H}(\bar{\mathbf{u}}) \mathbf{v} \rangle} \mathcal{D}\mathbf{v} &= \mathcal{N} \int \exp\left(-\frac{1}{2\hbar} \sum_{n \geq 0} \lambda_n c_n^2\right) \prod_{n \geq 0} dc_n \\ &= \mathcal{N} (\det(\mathcal{H}(\bar{\mathbf{u}})))^{-1/2} e^{-S_E[\bar{\mathbf{u}}]}, \end{aligned} \tag{2.24}$$

where \mathcal{N} is some global renormalization factor to be fixed at the end of computation as a common practice in formal path integral manipulation.

However, it can be shown that the operator $\mathcal{H}(\bar{\mathbf{u}})$ has a zero eigen-value; therefore the integral in Eq. (2.24) is not defined. Indeed, $\dot{\bar{\mathbf{u}}}(\tau)$ is the eigen-vector associated with the zero eigen-value of $\mathcal{H}(\bar{\mathbf{u}})$. To see this, one simply differentiates Eq. (2.16) and by noticing the boundary conditions for \mathbf{v} ask for $\tau \rightarrow \pm\infty$. This zero mode comes from the translational invariance of the instanton motion.

The definition of prefactor therefore must be modified accordingly. One needs to single out $\int dc_0$ (which is associated with the zero mode) and transform it to the integration over the position of the center of the instanton. For details, we refer to [7]. After some work (which also has multiple instanton and harmonic approximation of well bottom to take care of), it can be concluded that the ground state energy level splitting is given by

$$\Delta_0 = 2\hbar \left(\frac{S_0}{2\pi\hbar}\right)^{1/2} \left(\frac{\det'(\mathcal{H}(\bar{\mathbf{u}}))}{\det(\mathcal{H}(\mathbf{x}_L))}\right)^{-1/2} e^{-S_0/\hbar}, \tag{2.25}$$

where \det' is the determinant with the zero eigen-value removed.

For the 1D symmetric double-well potential $V(x)$ as in the previous section, the prefactor in Eq. (2.25) can be evaluated and it can be shown that this result matches the standard WKB calculation in Eq. (2.9) (by a factor of $\sqrt{e/\pi}$ which is attributed to the harmonic approximation for the ground state in the instanton rather than the linear connection in Eq. (2.9)). To prove it, one associates $\det(-\partial_\tau^2 + W(\tau))$ (from homogeneous boundary value problem) with the Jacobi field that is given by the solution of initial value problem of the following 2nd-order ODE:

$$\begin{aligned} (-\partial_\tau^2 + W(\tau))f(\tau) &= 0, \\ f(\tau_a) &= 0, \\ \partial_\tau f(\tau_a) &= 1. \end{aligned} \tag{2.26}$$

More specifically, it can be shown ([7], [21]) that

$$\frac{\det(-\partial_\tau^2 + W_1(\tau) - z)}{\det(-\partial_\tau^2 + W_2(\tau) - z)} = \frac{f_1(\tau_b)}{f_2(\tau_b)}, \tag{2.27}$$

where the f_i solve the Jacobi field Eqs. (2.26) with $W(\tau) = W_i(\tau) - z$. By using Eq. (2.18) in 1D, one can indeed get asymptotic behavior of the instanton trajectory $u(\tau)$ (now a scalar function) for $\tau \rightarrow \infty$ since $V(x)$ is approximated by a harmonic potential near the bottom. For more details, see [7].

The advantage of Eq. (2.25) is that it avoids completely the use of turning points and the formula holds for arbitrary dimensions. However, the price to pay is that the computation of the functional determinants is extremely difficult. This is indeed the bottleneck of the application of the instanton. Most of the current instanton based computations resort to 1D formula after finding the instanton path by some further *ad hoc* assumptions on the potential. Some adiabatic or weak coupling assumption make it possible to separate the longitudinal motion from the transverse motion. However, it is not satisfying. In this work, we are able to compute the prefactor in Eq. (2.25) in an accurate and efficient way. This enables us to study the genuine multi-dimensional effects in a much more accurate way.

Remark 2.1. The instanton action is termed Agmon distance in some of the mathematical literature. The leading order behavior (exponential factor $e^{-S_0/\hbar}$) of the splitting was proved rigorously by Simon in [34] and Helffer & Sjostrand in [14] independently in 80's. For the prefactor, see the recent work by Helffer & Nier in [15].

We next survey some of the existing instanton based calculation on multi-dimensional tunneling effects in molecular reactions. Before that, some discussion of other relevant approaches to include the tunneling effect in reaction dynamics is appropriate.

The oldest one belongs to Wigner, which assumes the tunneling take place at the classical transition state that is the saddle point on PES. Therefore the calculation reduces

to the tunneling through the top of the classical Minimal Energy Path (MEP) which is a 1D problem (in the reaction coordinate). This over-simplified hybridization approach works only for very high temperatures and is fundamentally flawed for low temperature where the quantum effect is more critical. A number of methods have since appeared to include the tunneling effect in a more systematical way.

Along the approach of MEP, there has been developed the so-called ‘small curvature tunneling approximation’ (or ‘slow-flip’, ‘adiabatic’) by assuming that the motion in the reaction coordinate (longitudinal mode) is much slower than the transverse modes. An effective 1D potential $V(s)$ along the reaction coordinate (with mass renormalization) is established. However, this is valid only in very limited situations. For details, see *e.g.*, [22, 25, 40]. Indeed, tunneling along MEP without mass renormalization has been used in a number of cases as first trial approximation.

The above ‘adiabatic’ approximation certainly fails in the tunneling in heavy-light-heavy tri-atomic system, for example hydrogen transfer in Oxygen-Hydrogen-Oxygen. The light atom moves much faster. For this ‘large curvature tunneling’ approximations (or ‘fast-flip’, ‘sudden’, ‘straight line’) have been developed. It assumes the tunneling occurs ‘suddenly’ and along a straight line between turning points.

Based on the above straight line tunneling model, Makri & Miller in [24] developed a method to calculate tunneling splitting which is very influential. It is built upon the real-time path integral for the potential well region and straight line tunneling between turning points (therefore Eq. (2.9) can be used directly). In this way, it avoids any usage of analytical continuation to the complex plane which would otherwise result in a much more complicated algorithm. It is not hard to see the situation where the straight line approximation breaks down. Some improvements have been suggested in *e.g.*, [13], with some success.

Benderskii *et al.* in [3] pioneered using instanton to study 2D quantum tunneling. To find the instanton trajectory which is the zero temperature limit, they started from finite temperature and by solving finite period minimization problem with increasing period (decreasing temperature) they found the instanton trajectory. The prefactor is factorized as a product of longitudinal factor and transverse one. Standard 1D splitting is employed for the longitudinal factor. Stability parameters (eigen-values of monodromy matrix) are sought for every finite temperature in order to calculate the transverse factor. The method works only for 2D and is very limited in practical usage.

In a series of papers [35–37] which leads eventually to a software package named ‘DOIT’ (dynamics of instanton tunneling), Smedarchina *et al.* simplified the prefactor calculation of Benderskii [3] by assuming that the potential is vibrational adiabatic. They reached a renormalized effective 1D potential for the calculation of transverse factor. However, for tunneling path they use classical MEP. Some additional parameter fits for the effective 1D potential are performed in order to match experimental results when calculating the tunneling splitting.

Benderskii *et al.* developed the so-called ‘perturbative instanton approximation’ method in [5]. It assumes that the coupling between the longitudinal motion and transverse vi-

bration is weak enough (compared with the transverse frequency) to admit a series of perturbation expansions. However, the validity of this assumption is in question for some realistic problems.

Tautermann *et al.* in [39] performed minimization of $\int \sqrt{2V}$ in configuration space directly in order to find the tunneling path connecting two local minima, The splitting is calculated by a 1D splitting formula. after some rather crude curve fitting of the 1D potential (a degree 6 polynomial) along the tunneling path.

Milnikov and Nakamura recently presented the first genuine multi-dimensional instanton calculation without additional *ad hoc* assumption on transverse mode coupling ([26, 27]). The path is calculated by direct minimization of Euclidean action in configuration space. The novelty of their approach is to use a variant of Jacobi fields as in Eqs. (2.26) and (2.27) to compute the prefactor. One needs to integrate an IVP for an ODE system for matrices from $-\infty$ to ∞ . Some of their parameters in the system become singular.

Finally we want to mention that another basic problem that deals with decay of a metastable state by quantum tunneling out of a potential well can also be studied under instanton formulation ([7]). There, the instanton (now the so-called *bounce*) \mathbf{u}_B is a periodic trajectory starting from local minimum of the potential well and runs at the exiting point. Apart from a zero eigen-value, the Hessian $\mathcal{H}(\mathbf{u}_B)$ now has one negative eigen-value which contributes to the decay. The bounce is thus not a minimum of the Euclidean action but rather a ‘saddle point’. The decay rate can be defined in a way similar to Eq. (2.25) by a certain analytical continuation procedure of the negative mode of $\mathcal{H}(\mathbf{u}_B)$.

3 Numerical method

We present an simple yet accurate method to compute the tunneling splitting Δ_0 . Firstly the instanton trajectory is found in an accurate and efficient way. We then calculate the prefactor directly.

3.1 Instanton trajectory

As commonly assumed in all the current work, there is only one instanton trajectory. It is valid for the double-well potential where there is only one saddle point of PES. As discussed, the instanton solution minimizes Euclidean action. Very naturally, one tries some minimization methods. Since the Hessian $\mathcal{H}(\bar{\mathbf{u}})$ is singular (or nearly singular in practice), the Newton type methods are not expected to work well. We find the following gradient descent approach accurate and efficient.

The instanton trajectory is computed by solving the non-linear gradient system

$$\begin{aligned} \frac{\partial \mathbf{u}}{\partial t} &= F(\mathbf{u}) := -\frac{\delta S_E}{\delta \mathbf{u}} \\ &= \frac{\partial^2 \mathbf{u}}{\partial \tau^2} - \nabla V(\mathbf{u}), \end{aligned} \tag{3.1}$$

with $\mathbf{u}(\tau \rightarrow -\infty) = \mathbf{x}_L$, $\mathbf{u}(\tau \rightarrow \infty) = \mathbf{x}_R$ for the steady state as $t \rightarrow \infty$. This is nothing but a 1D reaction-diffusion system.

For time advancing, we would like to have large time steps. Both the semi-implicit and linear implicit Euler scheme have been used and they offer comparable numerical results. They can be written as

$$\mathbf{u}_{k+1} = \mathbf{u}_k + \Delta t_k \delta \mathbf{u}_k, \tag{3.2}$$

$$(I - \Delta t_k A(\mathbf{u}_k)) \delta \mathbf{u}_k = F(\mathbf{u}_k), \tag{3.3}$$

where for the semi-implicit scheme $A(\mathbf{u}) = \partial_\tau^2$ and for the linear implicit scheme $A(\mathbf{u}) = \delta F / \delta \mathbf{u} = \partial_\tau^2 - D^2V(\mathbf{u})$.

For the linear implicit scheme, one can adopt the following residual based adaptive time step control([10, 16]):

1. Given \mathbf{u}_k and Δt_k , if $\|F(\mathbf{u}_{k+1})\| > \|F(\mathbf{u}_k)\|$, replace Δt_k by a new value

$$\Delta t_k^{new} = \frac{|(\delta \mathbf{u}_k, F(\mathbf{u}_k) - \delta \mathbf{u}_k)|}{2\|\delta \mathbf{u}_k\| \|F(\mathbf{u}_{k+1}) - \delta \mathbf{u}_k\|} \Delta t_k$$

and repeat for solving $\delta \mathbf{u}_k$ until success.

2. If success, set for next step

$$\Delta t_{k+1} = \frac{\|F(\mathbf{u}_k)\|}{\|F(\mathbf{u}_{k+1})\|} \Delta t_k$$

and repeat step 1 for $\mathbf{u}_{k+1} \mapsto \mathbf{u}_{k+2}$.

The advantage of it is superlinear convergence and globalization in minimization. The drawback is that one needs to evaluate (or approximate) the Hessian $\mathcal{H}(\mathbf{u})$ and solve a linear system which is non-tridiagonal. For the semi-implicit scheme, no information from $\mathcal{H}(\mathbf{u})$ is needed and only tri-diagonal systems are to be solved at every time step. However, it has only first order convergence.

‘Spatial’ discretization (in τ) in Eq. (3.1), is handled by the standard 2nd-order central finite difference scheme. The infinite domain in τ is truncated to $[-K, K]$. The simplest estimates can give $K \sim \ln(10^m) / \omega_1$ where ω_1 is the square root of the smallest eigenvalue of $D^2V(\mathbf{x}_L)$ (slowest vibration frequency in the bottom of the well) if one wants $\|\bar{\mathbf{u}}(K)\| \sim 10^{-m}$. This comes from Eq. (2.18) and by noticing the harmonic approximation

of $V(\mathbf{x})$ at the bottom of the well. This truncation introduces slight regularization to the Hessian in practice.

For initial condition, several different choices have been tried and the method is insensitive to it.

We want to point out that for realistic problems (complicated PES), the most expensive step is to compute (approximately) $\mathcal{H}(\mathbf{u})\delta\mathbf{u}$. Nevertheless, we found computing the instanton path is of no more difficulty than finding the transition pathway in classical transition state theory. This is to the contrary of the common belief as expressed in [3, 26, 35–37, 39]. It is certainly superior to the direct solution method for Schrödinger equations of which the computational cost is exponential against the DOF. Even for very high-dimensional PES, full resolution of the instanton trajectory is practical.

3.2 Prefactor

Computing prefactor in multi-dimensions is indeed a formidable task. This very fact prevent the wide application of instanton. Most of the existing work bypassed it by resorting to 1D splitting formula in one way or another. Some rather *ad hoc* assumptions on the potential are necessary for this purpose alone which makes the calculations less reliable.

The functional determinants (indeed the ratio between them)

$$\frac{\det(\mathcal{H}(\mathbf{x}_L))}{\det'(\mathcal{H}(\bar{\mathbf{u}}))} = \frac{\det(-\partial_\tau^2\mathbb{I} + D^2V(\mathbf{x}_L))}{\det'(-\partial_\tau^2\mathbb{I} + D^2V(\bar{\mathbf{u}}))} \quad (3.4)$$

cannot be computed in an straightforward way (say, by computing the spectrum directly). Although it can be reformulated into Jacobi field as implemented in [26, 27], numerically, that is not an appealing approach, in our opinion.

We offer an efficient and robust algorithm to calculate Eq. (3.4) by using thermodynamic integration. The method is based on the following theorem ([12]).

Theorem 3.1. *Let H, G be two symmetric positive definite matrices. Then*

$$\frac{\det H}{\det G} = \exp\left(\varepsilon^{-1} \int_0^1 Q(\alpha) d\alpha\right), \quad (3.5)$$

where

$$Q(\alpha) = \mathbb{E}(\langle \mathbf{q}, (H - G)\mathbf{q} \rangle). \quad (3.6)$$

The expectation is taken with respect to the invariant measure of the stochastic process

$$\dot{\mathbf{q}} = -\nabla V^\alpha(\mathbf{q}) + \sqrt{2\varepsilon}\dot{W}(t), \quad (3.7)$$

where

$$V^\alpha(\mathbf{q}) = \frac{1}{2}\langle \mathbf{q}, ((1 - \alpha)H + \alpha G)\mathbf{q} \rangle \quad (3.8)$$

and \dot{W} is a white noise with δ covariance in both space and time:

$$\langle \dot{W}(x, t) \dot{W}(y, s) \rangle = \delta(x - y) \delta(s - t).$$

In practice, $Q(\alpha)$ is evaluated by time averaging:

$$Q(\alpha) = \frac{1}{T} \int_0^T \langle \mathbf{q}, (H - G)\mathbf{q} \rangle dt \tag{3.9}$$

for sufficient large T by the ergodicity of \mathbf{q} .

Noticing that $\mathcal{H}(\bar{\mathbf{u}})$ has one zero eigenvalue which should be removed from the determinant, we have therefore $G = \mathcal{H}(\bar{\mathbf{u}}) + \mathbf{u}_1 \otimes \mathbf{u}_1$ where $\mathbf{u}_1 = \dot{\bar{\mathbf{u}}} / \|\dot{\bar{\mathbf{u}}}\|$ is the normalized zero-eigenvector. Then

$$\frac{\det(\mathcal{H}(\mathbf{x}_L))}{\det'(\mathcal{H}(\bar{\mathbf{u}}))} = \frac{\det(\mathcal{H}(\mathbf{x}_L))}{\det(G)}$$

and $\mathcal{H}(\mathbf{x}_L)$ and G are now SPD and the above algorithm can be applied.

Now Eq. (3.7) takes the specific form

$$\frac{\partial \mathbf{q}}{\partial t} = \frac{\partial^2 \mathbf{q}}{\partial \tau^2} + \alpha(D^2V(\mathbf{x}_L) - D^2V(\bar{\mathbf{u}}) - \mathbf{u}_1 \otimes \mathbf{u}_1)\mathbf{q} + \sqrt{2\varepsilon}\dot{W}, \tag{3.10}$$

which is a linear variable coefficient stochastic PDE. For simplicity, the standard finite difference discretization in τ is used following the calculation of instanton in previous section. Although the coefficient matrix in RHS of Eq. (3.10) appears to be full because of the $\mathbf{u}_1 \otimes \mathbf{u}_1$ term, the matrix-vector product of RHS can nevertheless be realized at a cost of $\mathcal{O}(d^2M + dM) = \mathcal{O}(d^2M)$.

In simulating Eq. (3.10) one can use either explicit or implicit time advancing scheme. For fine mesh in τ , implicit scheme is preferred for larger time step in t . Then iterative linear solvers should be used. Both explicit and implicit schemes have been implemented with comparable outcomes.

The integrations in Eq. (3.5) and Eq. (3.9) are computed by quadratures using the mid-point rule.

We have following remarks:

1. From the numerical viewpoint, boundary value problems are more appealing than initial value problems. Therefore, it is better to compute Eq. (3.4) from BVP than to solve the Jacobi field as in [26, 27].
2. For simplicity, we use $\bar{\mathbf{u}}$ as computed from previous section which has uniform mesh in τ space. However, this is not necessarily the most efficient way in general since the action of instanton is rather concentrated in a small τ region. For a better efficiency, one could use a non-uniform or even adaptive mesh when solving for the instanton trajectory. Since computing the instanton trajectory is normally the cheaper step, another strategy is to fully resolve the instanton trajectory using fine mesh and re-interpolate it using for example arclength of instanton path in configuration

space (see for example [29]). In any case, it results in a non-uniform mesh for \mathbf{q} in Eq. (3.10). It should be handled by finite element discretization in τ . The scheme is currently under consideration.

3. For the tunneling decay problem (*bounce*), the prefactor in the tunneling decay rate can be calculated in a similar fashion. However, solving the bounce trajectory needs some extra work since it is no more a minimization problem. We have developed a so-called ‘Quantum String Method’ for locating the ‘saddle point’ of $S_E[\mathbf{u}]$ which gives the bounce. For the numerical treatment of bounce and decay rate using the quantum string method, with the application in SQUIDS, see [28].

4 Numerical results

We report numerical results for 2D calculation for the purpose of demonstration and preliminary comparison. For the 2D Schrödinger equation, very accurate low lying eigenvalues can be calculated by pseudo-spectral discretization (termed ‘Discrete Variable Representation’ in the computational chemistry literature). These results can serve as benchmarks for various approximation schemes. For large DOF, usually only experimental measurements are available for comparison. There is danger in assessing an approximation method based on this kind of comparison because the underlying PES may not be good enough. Good agreements with experimental results may not necessarily indicate good approximation and vice versa. There are examples in the past that demonstrate this.

For our method, one can see there is no obstacle to generalize it to higher dimensions. The work is currently undergoing and the result will be reported subsequently.

4.1 Separable potential

We consider a toy model

$$V(x, y) = \frac{1}{8}((x + y)^2/2 - 1)^2 + \frac{\omega^2}{4}(x - y)^2, \quad (4.1)$$

with $\omega=8$ which comes from a rotation of the separable potential $V = \frac{1}{8}(x^2 - 1)^2 + \frac{\omega^2}{2}y^2$. The instanton is just a straight line and splitting $\Delta_0 = 12$ from 1D calculation. Our instanton calculation gives $\Delta_0 = 12.12$ which compares very well with the exact value. The exact Euclidean action $S_0 = 2/3$ while from our calculation $S_0 = 0.6676$. The calculation uses 128 mesh points in τ domain $[-15, 15]$. For stochastic process simulation we use the one-step Euler forward method with $\Delta t = 0.002$ and the time averaging in Eq. (3.9) is taken over 2×10^5 steps. The quadrature in Eq. (3.5) is by the mid-point rule with $\Delta\alpha = 1/40$ and ε is set to be 1.

This result is comparable in accuracy with the similar separable model test in Milnikov [26]. However, it is much simpler since there is neither a matrix ODE to be solved nor a singular parameters involved as in [26].

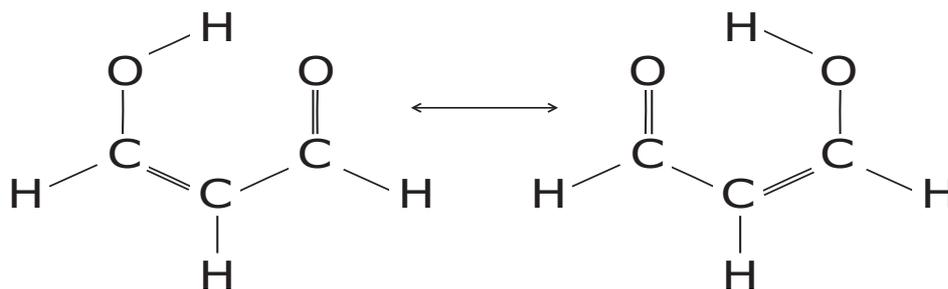


Figure 2: Hydrogen transfer in Malonaldehyde molecule.

4.2 Non-separable potential

4.2.1 Symmetric coupling PES

We consider the following non-separable Hamiltonian

$$H = -\frac{\hbar^2}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{8} (x^2 - 1)^2 + \frac{\omega^2}{2} \left(y + \frac{\gamma}{\omega^2} (x^2 - 1) \right)^2. \quad (4.2)$$

This potential is a simplified model for hydrogen transfer in the isomerization of Malonaldehyde which is depicted in Fig. 2. It has an intramolecular hydrogen bond $\text{O} - \text{H} \cdots \text{O}$ where the tunneling of a hydrogen atom between two oxygen atoms causes the splitting in the vibrational energy level. This is a prototype for transfer in hydrogen-bond systems. Numerically, this simple model serves as a benchmark for multi-dimensional tunneling calculation (see *e.g.*, [3, 6, 24, 38]).

In this 2D PES Eq. (4.2), x represents roughly the motion of hydrogen atom transfer from O to O which is modeled by symmetric double-well potential. It is coupled symmetrically with the motion of $\text{O}-\text{C}-\text{C}-\text{C}-\text{O}$ skeleton that is represented by y . γ is the coupling constant between tunneling and non-tunneling modes and ω is the frequency of frame vibration. This is a reduction from full 21D PES for a 9-atom molecule. The parameters have been obtained by Bosch *et al.* in [6] as $\omega = 0.48$, $\gamma = 0.39$, $\hbar = 0.1$. One of the characteristic features of this reaction is the coupling of proton transfer degree of freedom and intramolecular modes. The multi-dimensionality of this model lies in the reorganization of the skeleton during the hydrogen transfer.

Different tunneling paths have been sought in the past and tunneling splitting calculated. In Fig. 3 we plot the PES and the instanton path computed by our method. It can be seen clearly that the tunneling path lies between two extreme limits: straight line and MEP, as we discussed before. This tunneling shows a genuinely multidimensional effect. Indeed, it can be thought of as a compromise between tunneling length and barrier height. For MEP, the particle travels through longer distance but lower barrier. For a straight line the particle travels through much shorter distance but at the cost of higher potential barrier. The optimal path, instanton, which minimizes the action, lies in between. As one can observe, the path demonstrates a large ‘corner cutting’ behavior which was suggested

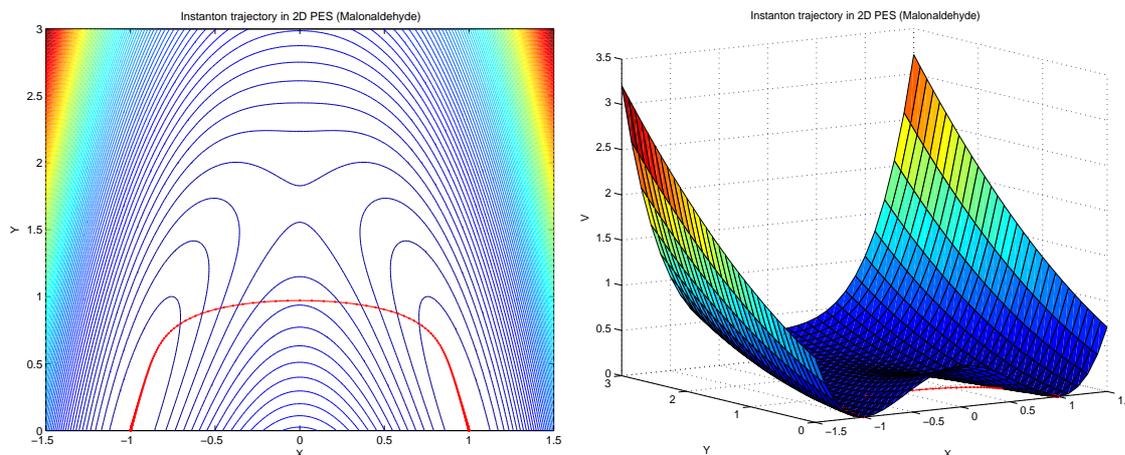


Figure 3: 2D PES and instanton trajectory for Malonaldehyde. Left: contour plot, right: surface.

in [23] by Marcus & Coltrin as a generic feature of multidimensional tunneling. It is not easy to separate various modes; therefore a unified approach is desired.

Direct diagonalization of the 2D Schrödinger operator using pseudo-spectral discretization gives $\Delta_0 = 10.6\text{cm}^{-1}$ ([6]). Our calculation shows $\Delta_0 = 10.27\text{cm}^{-1}$ which is in perfect agreement with the quantum value. We use $M=256$ mesh points in the truncated τ domain $[-30, 30]$. The initial \mathbf{u} is a straight line and convergence of the instanton path is achieved in 16 steps when using the linear implicit scheme with time step adaptivity, while in 327 steps using the semi-implicit scheme with fixed $\Delta t = 0.5$. Both were stopped when $\|F(\mathbf{u})\| < 10^{-6}$. Other initial values have been tried resulting in the same instanton path (with different number of steps however). For stochastic process simulation we use the one-step Euler forward method with $\Delta t = 2\text{E-}3$ and the time averaging in Eq. (3.9) is taken over 2×10^5 steps. The quadrature in Eq. (3.5) is by the mid-point rule with $\Delta\alpha = 1/40$ and ε is set to be 1. For comparison, Benderskii *et al.* in [3] gives $\Delta_0 = 13\text{cm}^{-1}$ using their instanton algorithm. Using a slightly different PES (different parameter fit), Makri & Miller in [24] calculated $\Delta_0 = 2.8\text{cm}^{-1}$ (exact quantum value for their PES is 11.9cm^{-1}). Both MEP and straight line tunneling give the estimation one or two orders of magnitude smaller ([6]).

From spectroscopy experiments, it has been measured that Δ_0 is about 21.6cm^{-1} actually. The discrepancy is attributed to the over-simplification of the above 2D PES. However for full 21D semi-empirical PES, rather contradictory results of Δ_0 have been obtained from different semi-classical calculations. Milnikov in [26] calculated $\Delta_0 = 57.7\text{cm}^{-1}$ using the semi-empirical PES from [33] while it was calculated, by using Makri-Miller method, that $\Delta_0 = 21.8\text{cm}^{-1}$ in [33]. The coupling with *ab initio* PES calculation also depends strongly on the *ab initio* computational levels it employs ([8,27]). It will be very interesting to see how our method performs on full PES.

Next we give some computational results for different sets of parameters and show the

Table 1: Tunneling splitting in symmetric coupling potential.

(ω, γ, \hbar)	(a) (0.5, 0.25, 0.04)	(b) (0.8, 0.32, 0.04)	(c) (1.5, 1.125, 0.04)	(d) (0.6, 0.2, 0.08)
Δ_Q	5.73E-9	1.49E-8	1.75E-8	1.19E-4
Δ_i	6.19E-9	1.64E-8	1.97E-8	1.42E-4
Δ_{ib}	6.4E-9	1.7E-8	2.0E-8	1.46E-4
Δ_{LSLA}	5.8E-9	1.6E-8	2.9E-8	1.16E-4
Δ_{MM}	2.31E-9	0.73E-8	0.00437E-8	1.61E-4
Δ_{EMM}	6.80E-9	1.03E-8	3.74E-8	1.90E-4
Δ_{SUD}	0.016E-9	0.12E-8	2.0E-14	0.22E-4
Δ_{MEP}	0.015E-9	0.016E-8	0.19E-8	0.10E-4

comparison in Table 1. The contour plots and instanton trajectories are in Fig. 4.

The datum are taken from [13, 38] except our computation Δ_i . Δ_Q is Δ_0 from exact quantum calculation. Δ_{ib} is the instanton calculation taken from [38] attributed to method of Benderskii [3]. Δ_{LSLA} is from an interesting algorithm from [38]. It computes approximately the 2D WKB wave function. The potential is assumed to be locally separable and linear near the intersection point of two caustics lines. Therefore a 1D linear connection formula (using the Airy function as usual) can be used when crossing them. Δ_{MM} is by the Makri-Miller model as in [24] and Δ_{EMM} is from an extended Makri-Miller method in [13]. Finally, Δ_{SUD} and Δ_{MEP} stand for sudden approximation and tunneling along MEP (without potential renormalization).

From the plots, we can see that in case (a) the tunneling path is much closer to a straight line, thus the Makri-Miller method performs reasonably well. The case (c) is much closer to the adiabatic limit and the M-M method gives very bad result, as expected, while primitive MEP tunneling gives its best performance here. Both primitive sudden and MEP approximation give Δ_0 one or two orders lower in magnitude. Our instanton algorithm consistently out-performs the old instanton calculations as well as all the others. The performance of LSLA depends strongly on the validity of its assumption on the potential and it is very difficult to assess it *a priori*. To implement it one needs to compute the classical wave by doing Huygens type wave propagation which is not feasible in more than 2D (there is yet no implementation beyond 2D).

4.2.2 Anti-symmetric coupling PES

We take

$$V(x, y) = \frac{1}{8}(x^2 - 1)^2 + \frac{\omega^2}{2}\left(y - \frac{\gamma x}{\omega^2}\right)^2. \quad (4.3)$$

This potential is also used in modeling Malonaldehyde. Here it describes the coupling between H transfer mode (x coordinate) and C—O stretching mode (y coordinate). We

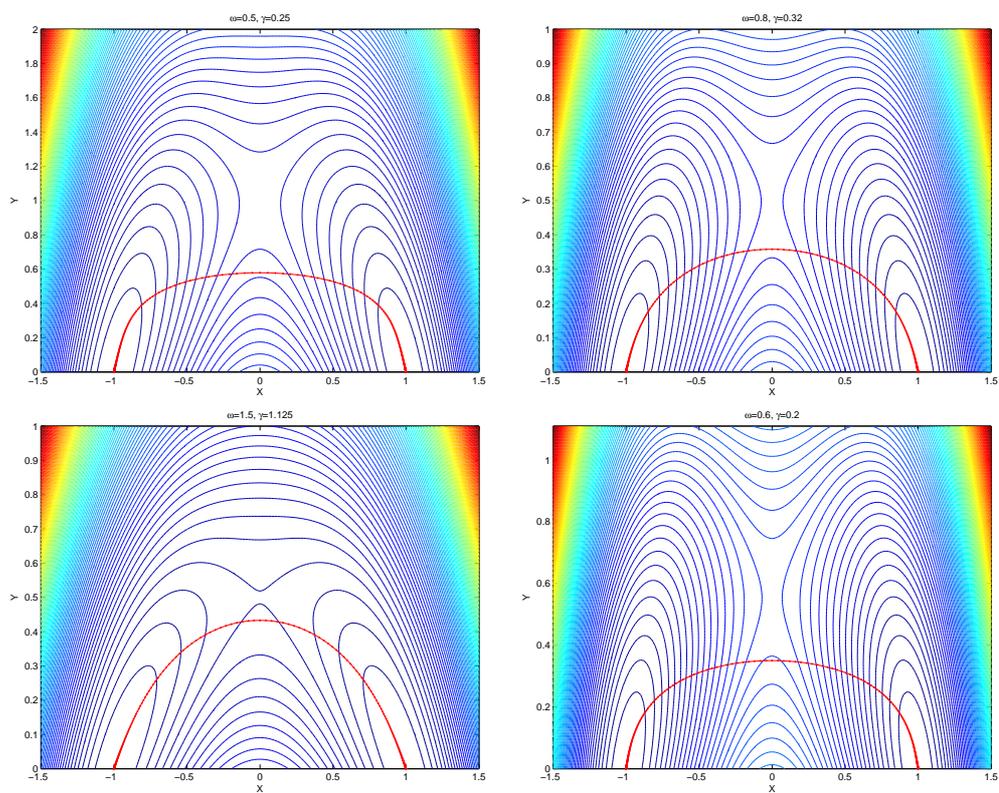


Figure 4: 2D symmetric coupling PES and instanton with the parameters as in (a), (b), (c) and (d) from Table 1.

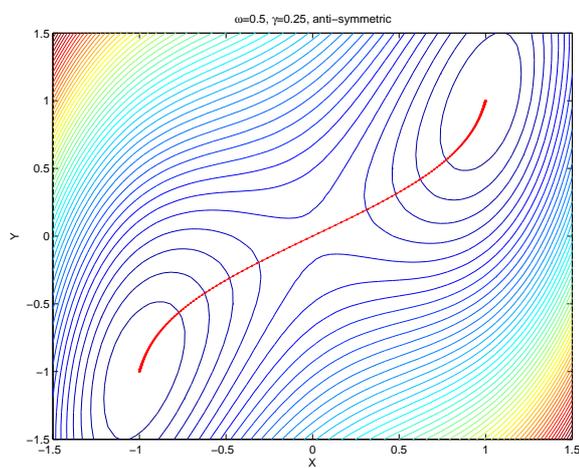


Figure 5: 2D anti-symmetric PES and instanton, anti-symmetric PES, $\omega = 0.5$, $\gamma = 0.25$.

take $\omega = 0.5$, $\gamma = 0.25$, $\hbar = 0.04$. From quantum calculation $\Delta_0 = 1.4\text{E-}10$ ([38]). Our instanton calculation gives $\Delta_0 = 1.5\text{E-}10$. The PES and instanton are plotted in Fig. 5.

5 Conclusion

In summary, we have developed a new method to calculate ground state tunneling splitting based on the path integral instanton formulation. The main feature is an efficient scheme to compute the tunneling path by using gradient flow and prefactor by using thermodynamic integration which is a stochastic method. Both instanton path and prefactor in the splitting are computed in a highly accurate and efficient way. Some preliminary comparison using hydrogen tunneling models demonstrated the effectiveness of the method. Compared with other approaches, this method is genuinely multi-dimensional without additional *ad hoc* assumptions on the potential (mode coupling and/or adiabaticity). Thus it includes the effects from all the modes coupled to tunneling degree of freedom without over-simplification. This shall give us a better understanding of the quantum tunneling in molecular reactions. The method is easy to implement and suitable for realistic problems with large number of degrees of freedom.

The algorithm is undergoing further development for better efficiency. Calculation based on full dimensional PES is also being carried out and will be reported subsequently.

There are shortcomings of the instanton approach. One of the most prominent one is that instanton is based on imaginary-time formulation. Therefore it cannot account for the behavior of positive kinetic energy. Hence, generalization to finite temperature requires some nontrivial analytic continuation into complex time. It is currently under investigation.

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