

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