Identification of multidimensional semiclassical tunneling paths

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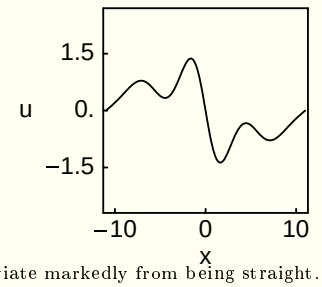
Introduction

Many reaction rates in physics and chemistry are determined by quantum mechanical tunneling below a classically insurmountable barrier. In the semiclassical approximation, the tunneling transmission probability is determined by the action integral

$$K = \int |p|\, dq \qquad (1)$$

along the tunneling path. The latter is easy to identify in one-dimensional problems as the straight line path below the barrier, but in systems with several degrees of freedom it can deviate markedly from being straight. As a further complication, oscillations transverse to the reaction coordinate can be excited in multidimensional systems.



If reactant and product regions of configuration space are separated by a saddle point in a multidimensional potential, the path of steepest descent from the saddle is regarded as the "reaction path" in chemistry (see, eg., [1]). However, it is also well known that the tunneling integral taken along that path severely underestimates the tunneling probability. The true tunneling path tends to lie on the concave side of the reaction path ("corner cutting"). In the absence of transverse excitation, it can be identified as the configuration space projection of an imaginary-time complex periodic orbit. How best to include the effects of the transverse modes is still a hotly debated topic in reaction rate theory.

I will here demonstrate that normal form theory allows a decoupling of the degrees of freedom and permits an identification of the tunneling path in the absence and in the presence of transverse excitation.

Tunneling in multiple degrees of freedom

We assume that the saddle point is unstable in one degree of freedom, which is the reaction coordinate, and stable in all others. The optimal tunneling path is easy to identify if the different degrees of freedom decouple, as in the Hamiltonian

$$H = \frac{\lambda}{2}(p_x^2 - x^2) + \frac{\omega_y}{2}(p_y^2 + y^2) + \frac{\omega_z}{2}(p_z^2 + z^2)\ . \qquad (2)$$

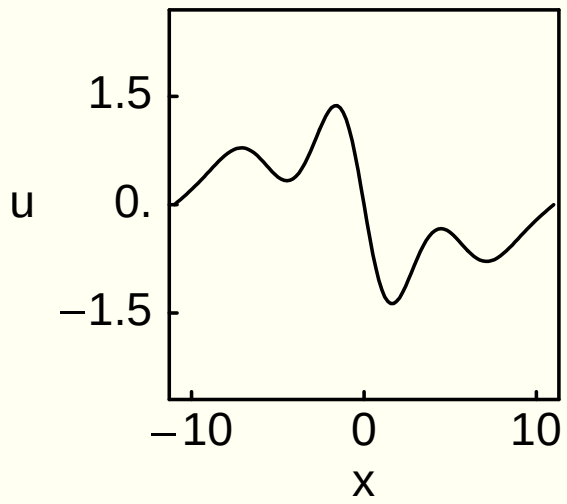
Here x represents the reaction coordinate and y and z are transverse coordinates. In this case, the optimum tunneling path can be found by setting the transverse coordinates to their equilibrium values $y = p_y = z = p_z = 0$, which reduces the problem to one degree of freedom. The tunneling integral can then be computed from the reduced problem in the usual way.

In general, a multidimensional dynamical system is non-separable. However, if its Hamiltonian is expanded in a multidimensional power series around an equilibrium point, normal form theory (see, eg., [2]) allows one to construct a coordinate transformation that puts the Hamiltonian into a separable form up to an arbitrarily high finite order. The high-order remainder that has not been brought into normal form is then neglected.

Tunneling paths

Once the tunneling path has been determined in normal form coordinates, it can be transformed to laboratory coordinates. The tunneling path thus found coincides with the projection of the periodic tunneling orbit into the configuration space.

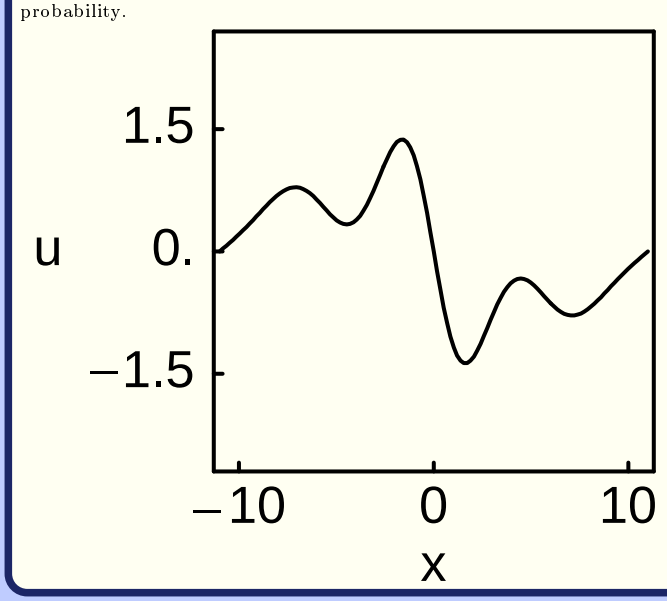
This is here illustrated for the dynamics of an electron under the combined influences of two identical Coulomb centers and a homogeneous electric field. This system has been used as a simple model for the ionization of a H_2^+ molecular ion by a laser field [3]. In the example shown, the Coulomb centers are located at $x = z = 0, y = \pm 1$ a.u. The external field strength is 0.77 a.u., and the field makes an angle of 84.3 degrees with the molecular axis. For these parameter values the reaction path is highly curved.



Tunneling action

Freezing the transverse degrees of freedom to equilibrium reduces the normal form Hamiltonian to a one-dimensional tunneling Hamiltonian given as a power series in the tunneling action. This series can be inverted to obtain the action as a function of energy.

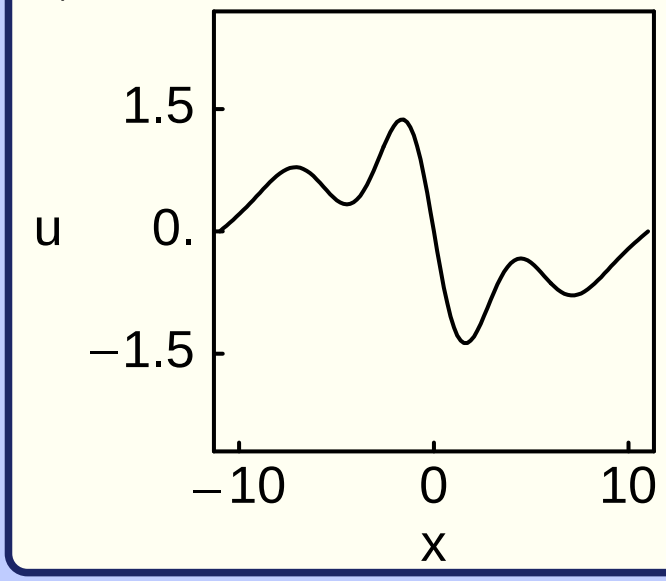
In practice, the power series for the action converges only very close to the saddle. By means of a Padé transform, however, useful values for the tunneling action can still be computed even far below the saddle point energy. It can then be observed how with increasing order the normal-form result converges to the action of the periodic tunneling orbit, whereas the action along the steepest-descent "reaction path" is markedly larger and thus significantly underestimates the tunneling probability.



Transverse frequencies

In a similar manner, the frequencies of the transverse normal modes can be computed from the terms in the normal form Hamiltonian that are quadratic in the transverse coordinates.

In the figure, solid lines denote frequencies of the linearized motion around the periodic tunneling orbit. Dashed lines indicate frequencies obtained from a normal form calculation of order 4, 8, 12 or 16, respectively.



Effects of transverse modes

The optimal tunneling paths described above were calculated under the assumption that there is no excitation of the transverse degrees of freedom. In practice, however, the transverse modes will always be excited at least to their zero-point oscillations. The normal form approach to tunneling lends itself easily to an inclusion of transverse vibrations: It allows to construct a complete set of action coordinates that are conserved under the truncated dynamics. They can be set to arbitrary non-zero values if the corresponding nonlinear normal modes are excited. Then, as before, the normal form yields the energy as a power series in the tunneling action, which can be inverted to obtain the action as a function of energy.

References

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[3] A. D. Bandrauk and H. Z. Lu: *Phys. Rev. A* **62** (2000), 053406