Uniform Multidimensional Barrier Penetration

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Reflection phases in one dimension

Reflection from a barrier using comparison to a linear potential gives a reflection phase

\[ r = -i \]

while comparison to a parabolic potential gives reflection and transmission coefficients

\[ r = -ie^{-i\delta} \frac{1}{\sqrt{1 + e^{-2\theta}}} \]
\[ t = e^{-i\delta} \frac{e^{-\theta}}{\sqrt{1 + e^{-2\theta}}} \]

where \( \delta \) and \( \theta \) are computed from complex barrier-crossing dynamics.
The transition state

The transition state is a set of configurations dividing reactants from products. There are two approaches

- Classical (trajectories).
- Quantum (scattering operator).
The simplest nontrivial reaction

Most simple description is for a collinear reaction

\[ AB + C \rightarrow A + BC. \]

Dynamics in the two degrees of freedom are described by a potential with channels.
Periodic orbit dividing surfaces

provide a natural means of dividing reactants from products in two degrees of freedom [Pechukas (1976)].

Initially restricted to
- two degrees of freedom
- kinetic plus potential (time reversal symmetry).
In phase space

The PODS defines an invariant manifold whose stable manifold divides reactants from products.

Generalisations:

- Jaffé et al PRA 60, 3833 (1999); PRL 84, 610 (2000).
A quantisable formulation

We consider an ensemble of reacting molecules described in a section along the reacting channel

\[ \rho = \int_{\Sigma} f(q, p) \chi_R(q, p) \, dq \, dp = \langle \chi_R \rangle. \]

by the distribution \( f(q, p) \). The fraction of reacting molecules is then

A quantum formulation will give a similar expression for the probability of reaction, depending on the mode of vibration of the incoming molecules.
The scattering matrix

In quantum mechanics we can think in terms of waveguides.

\[ \Psi_{\text{in}} = \psi_n(x) e^{-iky} \]

\[ \Psi_{\text{out}} = \sum_m S_{mn} \varphi_m(y) e^{ikx} \]

Everything about quantum scattering is determined from the operator

\[ \hat{S}(E) : \mathcal{H}_R \to \mathcal{H}_P \]

with matrix elements \( S_{mn}(E) = \langle \varphi_m | \hat{S} | \psi_n \rangle \). Can be approximated using trajectories, real and complex [Miller and George (1972)].
The reaction operator

We will work instead with the reaction operator

\[ \hat{R}(E) = \hat{S}^\dagger(E)\hat{S}(E) \]

which maps

\[ \hat{R}(E) : \mathcal{H}_R \to \mathcal{H}_R. \]

From it, the probability of reaction for an incoming mode \( \psi_n(x) \) is

\[
\begin{align*}
    p_n &= \sum_{m} |S_{nm}(E)|^2 \\
    &= \sum_{m} |\langle \psi_n | \hat{S}(E) | \varphi_m \rangle|^2 \\
    &= \langle \psi_n | \hat{R}(E) | \psi_n \rangle \\
    &= \langle \hat{R}(E) \rangle
\end{align*}
\]

In Wigner-Weyl formalism this looks just like the classical formula

\[
p_n = \int_{\Sigma} W_n(q, p)W_\hat{R}(q, p) dq dp
\]

and we will indeed find that \( W_\hat{R}(q, p) \) is a fuzzy version of \( \chi_R(q, p) \).
Weyl symbol of $R(E)$

$Q$ or $P$

$E=0$

$Q$ or $P$

$E$
Scattering in one-dimension

The transmission coefficient $t$ is approximated semiclassically for $E < E_c$ by

$$t \simeq e^{-\theta}$$

where

$$2i\theta = \frac{1}{\hbar} \int p\,dq$$

is a complex action integral.
A multidimensional version

For energies below the barrier we may approximate

\[ \hat{R}(E) \sim \hat{T} = e^{-2\theta} \hat{T}_0 \]

where the tunnelling operator \( \hat{T}_0 \) is determined from the dynamics of a complex barrier-crossing periodic orbit [Creagh and Whelan (1999)].

An orbit beginning and ending on \( \Sigma_R \) is obtained using a contour in the complex time plane of the form
Below barrier

Above barrier
**Multidimensional uniformisation**

In analogy with the one-dimensional uniformisation

\[ T \sim e^{-2\theta} \rightarrow \frac{e^{-2\theta}}{1 + e^{-2\theta}} \]

we have the two-dimensional version

\[ \hat{R}(E) \sim \hat{\mathcal{T}}(E) \rightarrow \frac{e^{-2\theta} \hat{\mathcal{T}}_0(E)}{1 + e^{-2\theta} \hat{\mathcal{T}}_0(E)} = \frac{\hat{\mathcal{T}}(E)}{1 + \hat{\mathcal{T}}(E)} \]

Recalling that

\[ \hat{\mathcal{T}}|\varphi_k\rangle = e^{-2\theta} \Lambda^{k+1/2} |\varphi_k\rangle \]

we see that \( \hat{R}(E) \) effectively projects onto the subspace generated by modes \( |\varphi_k\rangle \) such that

\[ e^{-2\theta(E)} \Lambda^{k+1/2} \sim 1 \]

or less.
A useful representation

The primitive tunnelling operator is of the form

$$\hat{T}_0 = e^{-\hat{h}\tau_0/\hbar}$$

→ the evolution of a quadratic Hamiltonian $\hat{h}$ for an imaginary time $-i\tau_0$. It is well known how to calculate these.

By analogy with

$$\frac{e^x}{1 + e^x} = e^x - e^{2x} + \cdots = \frac{1}{2i} \int_C \frac{e^{\rho x}}{\sin \pi \rho} d\rho$$

we will write

$$\frac{\hat{T}}{1 + \hat{T}} = \frac{1}{2i} \int_C \frac{\hat{T}^\rho}{\sin \pi \rho} d\rho$$

Asymptotic contributions from

- saddle points (orbits with $h = e$)
- poles (integer $\rho$)

These coalesce at the boundary of the classically reacting region.
Asymptotic Wigner-Weyl representation

It is “well-known” that $\mathcal{T}_\rho$ is of the form

$$W_{\mathcal{T}_\rho} = \frac{e^{\lambda(e^\rho - 2h \tanh(\rho/2))}}{\cosh(\rho/2)}$$

in Wigner-Weyl representation, where $\lambda$ is a constant.

Coalescence of two saddles and the pole at $\rho = 0$ when $h = e$, which is the boundary of the reacting region.

Integral representation for $W_{\mathcal{R}}$ similar to

$$\frac{1}{2\pi i} \int_C \frac{e^{\rho^3/3 - x\rho}}{\rho} d\rho \simeq \text{AI}(x)$$

where $\text{AI}(x) = \int_x^\infty \text{Ai}(u) du$ with $x \sim h - e$. 
Conclusion

- We have a fairly complete description in quantum mechanical terms of the opening up of the classical transition state.

- This can be calculated using just the dynamics of a complex periodic orbit.

- The calculation is for now restricted to near-critical energies.

- Rotational dynamics not yet incorporated.