Lecture 2

Approaches to barrier penetration in phase space

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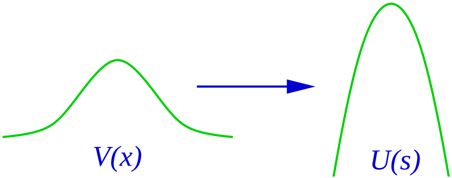
Method II: comparison equations

Given a barrier potential $V(x)$, look for a coordinate transformation

$$x \to s(x) \qquad \psi(x) \to \varphi(s) = \left(x'(s)\right)^{1/2} \psi(x(s))$$

which transforms the Schrödinger equation into a “similar” solvable one

$$-\frac{\hbar^2}{2m}\varphi''(s) - U(s)\varphi(s) = \mathcal{E}\varphi(s).$$



This works (approximately) provided we choose $s(x)$ so that

$$p\mathrm{d}x = w\mathrm{d}s, \quad p = \sqrt{2m(E - V(x))}, \quad w = \sqrt{2m(\mathcal{E} - U(s))}.$$

In a region where $V(x)$ and $U(s)$ have the same turning point structure, the transformation $x \to s$ can be made smooth.

Observation: The Schrödinger equation for the inverted harmonic oscillator

$$-\frac{1}{2}\varphi''(s) - \frac{1}{2}s^2\varphi(s) = \mathcal{E}\varphi(s)$$

is in terms of parabolic cylinder functions

$$\varphi(s) = aD_{\mathcal{E}-\frac{1}{2}}\left(\sqrt{2}s\right) + bD_{\mathcal{E}-\frac{1}{2}}\left(-\sqrt{2}s\right).$$

From the known asymptotics of these functions we deduce that

$$t \approx \frac{\mathrm{e}^{-\theta-\mathrm{i}\delta}}{\sqrt{1+\mathrm{e}^{-2\theta}}} \qquad \text{and} \qquad r \approx \frac{-\mathrm{i}\mathrm{e}^{-\mathrm{i}\delta}}{\sqrt{1+\mathrm{e}^{-2\theta}}}$$

where

$$\delta(E) = \frac{\theta}{\pi}\log\left|\frac{\theta}{\pi\mathrm{e}}\right| + \arg\Gamma\left(\frac{1}{2} - \mathrm{i}\frac{\theta}{\pi}\right)$$

The comparison method is attractive because it demands nothing beyond differential equations but is restricted to (a) Hamiltonians of type kinetic + potential (b) one dimension.

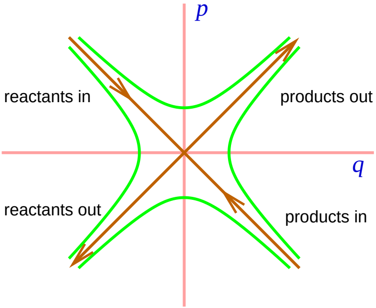
Method III: transformations in phase space

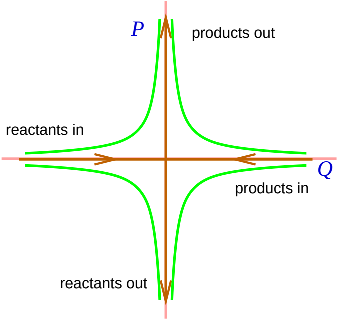
In classical mechanics it is common to use the canonical transformation

$$\begin{pmatrix} Q \\ P \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} q \\ p \end{pmatrix}$$

to swap between the Hamiltonians

$$H = \frac{1}{2}p^2 - \frac{1}{2}q^2 \qquad \leftrightarrow \qquad H = -QP$$





Suggests using, as a model for barrier penetration,

$$\begin{aligned}\hat{H} &= -\frac{1}{2}\left(\hat{Q}\hat{P}+\hat{P}\hat{Q}\right)\\ &= -\hat{Q}\hat{P}+\frac{1}{2}[\hat{Q},\hat{P}]\\ &= -\hat{Q}\hat{P}+\frac{\mathrm{i}\hbar}{2}.\end{aligned}$$

In a representation where

$$\hat{P}\psi(Q)=\frac{\hbar}{\mathrm{i}}\psi'(Q)$$

the Schrödinger equation $\hat{H}\psi=\mathcal{E}\psi$ becomes

$$-\frac{\hbar}{\mathrm{i}}\left(Q\psi'(Q)+\frac{1}{2}\psi(Q)\right)=\mathcal{E}\psi(Q)$$

This first-order ODE is very easily solved!

- Nonnenmacher and Voros J. Phys. A **30**, 295 (1997).
- Colin de Verdière and Parisse Commun. PDE. **19**, 1535 (1994).
- Creagh, Nonlinearity **18**, 2089 (2005).
- Waalkens et al, Nonlinearity **21**, R1 (2008).

For example, if we define

$$\psi(Q) = \int U(Q, q)\Psi(q)\mathrm{d}q$$

where

$$U(Q, q) = \frac{1}{\sqrt{2\pi \mathrm{i}\hbar}}\sqrt{\frac{\partial^2 F}{\partial Q \partial q}}\mathrm{e}^{\mathrm{i}F(Q,q)/\hbar}, \quad F(Q, q) = \frac{1}{2}\left(Q^2 - 2qQ + q^2\right)$$

defines a unitary operator quantising $(q, p) \to (Q, P)$ then it is easily seen that (exercise!)

$$\hat{H}\Psi(q) = \frac{1}{2}\left(\hat{p}^2 - \hat{q}^2\right)$$

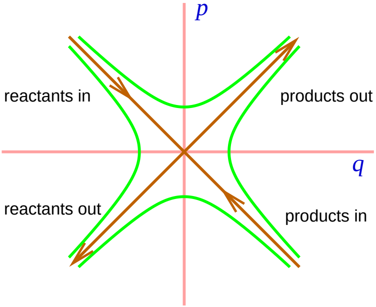
transforms to

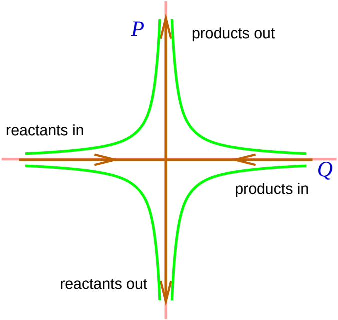
$$\hat{H}\psi(Q) = -\frac{1}{2}\left(\hat{Q}\hat{P} + \hat{P}\hat{Q}\right)\psi(Q).$$

Two fundamental solutions are

$$\psi_+(Q) = \Theta(Q)\,Q^{-1/2-\mathrm{i}\mathcal{E}/\hbar} \quad \text{and} \quad \psi_-(Q) = \psi_+(-Q)$$

respectively representing waves incident on the two sides of the barrier:

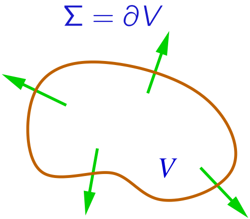




But how do we get information about tunnelling from this solution???

Generalised flux

It will help to be able to measure flux across surfaces in phase space, and not just in configuration space.



$$p_V = \langle \Psi | \hat{P}_V | \Psi \rangle$$

Ehrenfest's theorem: $\dfrac{\mathrm{d}p_V}{\mathrm{d}t} = \dfrac{1}{i\hbar} \langle \Psi | [\hat{P}_V, \hat{H}] | \Psi \rangle \equiv \langle \Psi \, /\!/_{\Sigma} \Psi \rangle$

In general we will define the flux across the surface Σ to be

$$F_\Sigma(\Psi) = \langle \Psi \, /\!/_{\Sigma} \Psi \rangle.$$

In the special case $\hat{H} = \frac{1}{2m}\hat{p}^2 + U(q)$ and $\hat{P}_V \Psi(q) = \Theta(q - q_0)\Psi(q)$ then

$$\begin{aligned} \frac{1}{\mathrm{i}\hbar}[\hat{P}_V, \hat{H}] &= \frac{1}{2m}\frac{1}{\mathrm{i}\hbar}[\hat{P}_V, \hat{p}^2] \\ &= \frac{1}{2m}\left(\Theta'(q - q_0)\hat{p} + \hat{p}\Theta'(q - q_0)\right) \\ &= \frac{1}{2m}\left(\delta(q - q_0)\hat{p} + \hat{p}\delta(q - q_0)\right) \end{aligned}$$

so, in one dimension,

$$\begin{aligned} F_\Sigma(\Psi) &= \langle \Psi \, //_\Sigma \Psi \rangle \\ &= \frac{1}{2m}\left[\Psi^*(q_0)(-i\hbar\Psi'(q_0)) + (-i\hbar\Psi'(q_0))^*\Psi(q_0)\right] \\ &= \frac{\hbar}{2im}\left[\Psi^*(q_0)\Psi'(q_0) - \Psi'^*(q_0)\Psi(q_0)\right] \end{aligned}$$

and in more dimensions (exercise!)

$$F_\Sigma(\Psi) = \int_\Sigma \mathbf{j} \cdot \mathrm{d}s, \qquad \mathbf{j} = \frac{\hbar}{2i}\left(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*\right)$$

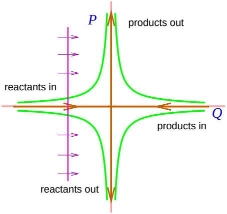
Exercise: For $\hat{H} = -\frac{1}{2}(\hat{Q}\hat{P} + \hat{P}\hat{Q})$, show that the state

$$\psi_-(Q) = \Theta(-Q)(-Q)^{-1/2 - \mathrm{i}\mathcal{E}/2}$$

is normalised so as to have unit incoming flux from the left.

Solution: Choose

$$\hat{P}_V \psi(Q) = \Theta(Q - Q_0)\psi(Q), \quad Q_0 < 0.$$



Then

$$\begin{aligned} \frac{1}{\mathrm{i}\hbar}[\hat{P}_V, \hat{H}] &= -\frac{1}{2\mathrm{i}\hbar}\Big(Q[\Theta(Q - Q_0), \hat{P}] + [\Theta(Q - Q_0), \hat{P}]Q\Big) \\ &= -Q\delta(Q - Q_0) \end{aligned}$$

and

$$\langle \psi /\!/_{\Sigma} \psi \rangle = \int -Q\delta(Q - Q_0)|\psi_-(Q)|^2 \mathrm{d}Q = -Q_0|(-Q_0)^{-1/2 - \mathrm{i}\mathcal{E}/2}|^2 = 1.$$

Exercise: Get the outgoing fluxes.

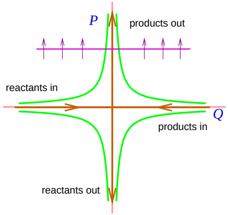
Solution: Here we need to measure flux across a momentum. Fourier transform the wavefunction

$$\begin{aligned}
\varphi(P) &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}QP/\hbar}\psi_-(Q)\mathrm{d}Q \\
&= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{0} (-Q)^{-1/2-\mathrm{i}\mathcal{E}/\hbar}\mathrm{e}^{-\mathrm{i}QP/\hbar}\mathrm{d}Q \\
&= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{|P|}{\hbar}\right)^{-1/2+\mathrm{i}\mathcal{E}/\hbar}\int_{0}^{\infty} q^{-1/2-\mathrm{i}\mathcal{E}/\hbar}\mathrm{e}^{\mathrm{i}\sigma q}\mathrm{d}q, \quad \sigma = \mathrm{sgn}(P) \\
&= \frac{1}{\sqrt{2\pi}}\mathrm{e}^{\sigma\pi\mathcal{E}/2\hbar}\Gamma\left(\frac{1}{2}-\frac{\mathrm{i}\mathcal{E}}{\hbar}\right)|P|^{-1/2+\mathrm{i}\mathcal{E}/\hbar}\times\hbar^{-\mathrm{i}\mathcal{E}/\hbar}\mathrm{e}^{\mathrm{i}\sigma\pi/4}
\end{aligned}$$

Notice

$$|\varphi(P)|^2 = \frac{\mathrm{e}^{\sigma\pi\mathcal{E}/\hbar}}{2\pi}\left|\Gamma\left(\frac{1}{2}-\frac{\mathrm{i}\mathcal{E}}{\hbar}\right)\right|^2\frac{1}{|P|} = \frac{\mathrm{e}^{\sigma\pi\mathcal{E}/\hbar}}{\mathrm{e}^{\pi\mathcal{E}/\hbar}+\mathrm{e}^{-\pi\mathcal{E}/\hbar}}\frac{1}{|P|}$$

Upwards flux: let the projection operator $\hat{P}_V$ act on $\varphi(P)$ according to



$$\hat{P}_V \varphi(P) = \Theta(P_0 - P)\varphi(P), \qquad P_0 > 0$$

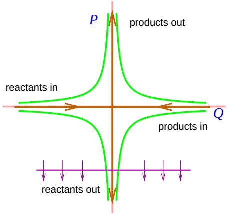
Then

$$\begin{aligned} \frac{1}{i\hbar}[\hat{P}_V, \hat{H}] &= -\frac{1}{2i\hbar}\Big([\Theta(P_0 - P), \hat{Q}]P + P[\Theta(P_0 - P), \hat{Q}]\Big) \\ &= P\delta(P - P_0) \end{aligned}$$

and

$$\langle \psi \, /\!/_{\Sigma} \psi \rangle = P_0 |\varphi(P_0)|^2 = \frac{e^{\pi\mathcal{E}/\hbar}}{e^{\pi\mathcal{E}/\hbar} + e^{-\pi\mathcal{E}/\hbar}}.$$

Similarly, the downwards flux (across $P_0 < 0$)) is



$$\langle \psi \, /\!/_{\Sigma} \psi \rangle = -P_0 |\varphi(P_0)|^2 = \frac{e^{-\pi\mathcal{E}/\hbar}}{e^{\pi\mathcal{E}/\hbar} + e^{-\pi\mathcal{E}/\hbar}}.$$

Technicalities

For a detailed calculation of **amplitides** (or the scattering matrix, including phase information) it is necessary to investigate more fully the nature of the transformation

$$\Psi(x) \quad \xrightarrow{\hat{U}} \quad \psi(Q)$$

$$\downarrow \quad \text{Solve } \hat{H} = \tfrac{1}{2}(\hat{Q}\hat{P} + \hat{P}\hat{Q})$$

$$S = \begin{pmatrix} r & t \\ t & r \end{pmatrix} \text{ for } \Psi(x) \quad \xleftarrow[\hat{U}^\dagger]{} \quad S' = \begin{pmatrix} r' & t' \\ t' & r' \end{pmatrix} \text{ for } \psi(Q)$$

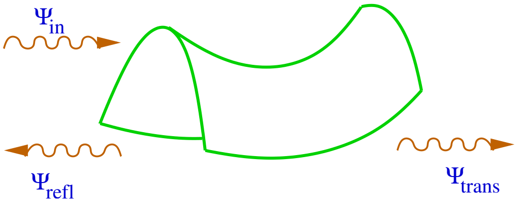
(see, for example, Waalkens et al, Nonlinearity **21** (2008) R1).

For transmission and reflection **probabilities**, on the other hand, which are measured invariantly by **fluxes**, the details of this transformation are not needed, except to note that (Creagh, Nonlinearity **18** (2005) 2089)

$$\theta = \frac{1}{2i\hbar}\oint p\,\mathrm{d}x \qquad \longleftrightarrow \qquad -\frac{\pi\mathcal{E}}{\hbar}.$$

Higher-dimensional barriers

The advantage of the phase-space version of the comparison method is that it generalises to higher-dimensional barriers.



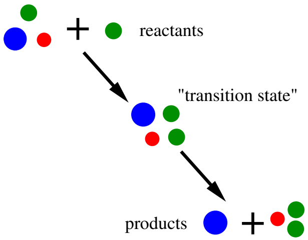
The starting point is a multidimensional version of

$$H(x, p) \qquad \longleftrightarrow \qquad QP$$

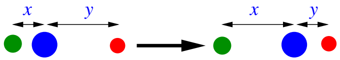
(the **normal form** transformation).

The transition state

The transition state is a set of configurations dividing reactants from products.

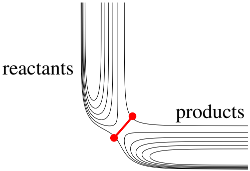


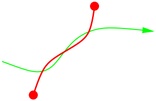
For a collinear reaction



$$AB + C \rightarrow A + BC$$

the classical transition state is identified with a periodic-orbit dividing surface, or PODS [eg, Pollak, Child and Pechukas,(1979)],

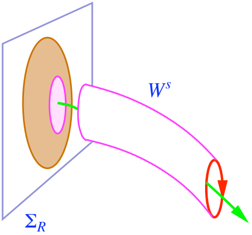


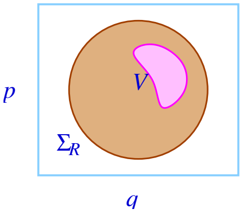
(eliminates multiple crossings ).

Phase space geometry

The PODS has a stable manifold W^s which divides reactants from products.

- Jaffé et al PRA **60**, 3833 (1999); PRL **84**, 610 (2000).
- Uzer et al, Nonlinearity **15**, 957 (2002).





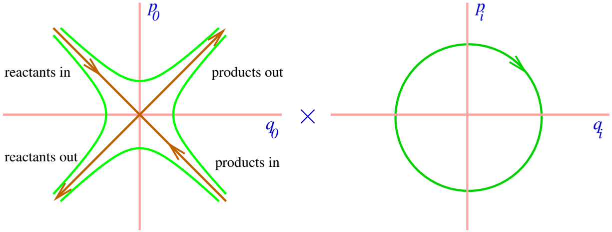
Reacting fraction

$$p_f = \int_V f(q,p)\,\mathrm{d}q\mathrm{d}p = \int_{\Sigma_R} \chi_V(q,p) f(q,p)\,\mathrm{d}q\mathrm{d}p = \langle \chi_V \rangle$$

The classical normal form

[Uzer et al, Nonlinearity **15**, 957 (2002)]

$$H = \frac{\lambda}{2}(p_0^2 - q_0^2) + \sum_{i=1}^{d} \omega_i (q_i^2 + p_i^2) + \mathrm{h.o.t.}$$



With $I = (q_0^2 - p_0^2)/2$ and $H_0(q,p) = \sum_{i=1}^{d} \omega_i (q_i^2 + p_i^2) + \mathrm{h.o.t.}$ then

$$\begin{aligned} H(q_0, p_0, q, p) &= -\lambda I + H_0(q,p) + I H_1(q,p) + I^2 H_2(q,p) + \cdots \\ &= H(q,p,I) \end{aligned}$$

The quantum normal form

$$\hat{H} = -\lambda \hat{I} + H_0(\hat{q}, \hat{p}) + \hat{I} H_1(\hat{q}, \hat{p}) + \hat{I}^2 H_2(\hat{q}, \hat{p}) + \cdots = H(\hat{q}, \hat{p}, \hat{I}),$$

where

$$\hat{I} = \frac{1}{2} \left(\hat{q}_0^2 - \hat{p}_0^2 \right)$$

and

$$[\hat{I}, \hat{q}] = 0 = [\hat{I}, \hat{p}]$$

Stationary states:

$$\Psi_{\mathcal{I},k}(q_0, q) = \psi_{\mathcal{I}}(q_0) \varphi_{\mathcal{I},k}(q),$$

where

$$\hat{I} \psi_{\mathcal{I}}(q_0) = \mathcal{I} \psi_{\mathcal{I}}(q_0)$$

and

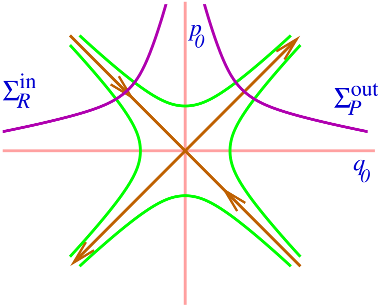
$$H(\hat{q}, \hat{p}, \mathcal{I}) \varphi_{\mathcal{I},k}(q) = E_k(\mathcal{I}) \varphi_{\mathcal{I},k}(q).$$

Transmission rate of NF scattering states

Relabel states using $E_k(\mathcal{I}) = E \Rightarrow \mathcal{I} = \mathcal{I}_k(E)$,

$$\Psi_{E,k}(q_0, q) = \psi_{\mathcal{I}_k(E)}(q_0)\varphi_{\mathcal{I}_k(E),k}(q).$$

Then (despite $\langle \varphi_{E,k} | \varphi_{E,k'} \rangle \neq \delta_{kk'}$),



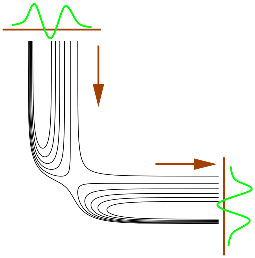
$$\langle \Psi_{E,k} /\!/_{\Sigma_R^{\mathrm{in}}} \Psi_{E,k} \rangle = \delta_{kk'}$$

$$\langle \Psi_{E,k} /\!/_{\Sigma_P^{\mathrm{out}}} \Psi_{E,k} \rangle = T_k(E)\delta_{kk'}$$

$$T_k(E) = \frac{\mathrm{e}^{-2\pi\mathcal{I}/\hbar}}{1 + \mathrm{e}^{-2\pi\mathcal{I}/\hbar}} \qquad \text{with} \qquad \mathcal{I} = \mathcal{I}_k(E)$$

An operator for uniform transmission probablities

Identify a basis



$$|k\rangle \sim \Psi_{E,k}(q_0, q)$$

for the space $\mathcal{H}_R^{\text{in}}(E)$ incoming states subject to the inner product

$$\langle k|k'\rangle \equiv \langle \Psi_{E,k} \, //_{\Sigma_R^{\text{in}}} \Psi_{E,k'}\rangle = \delta_{kk'}.$$

Transmission probabilities from $\langle k|\hat{\mathcal{R}}|k\rangle$, where

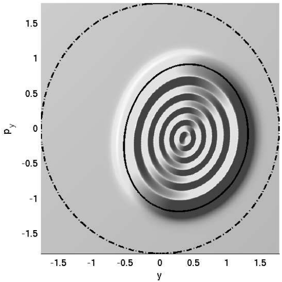
$$\begin{aligned} \hat{\mathcal{R}}(E) &= \sum_k \frac{\mathrm{e}^{-2\pi\mathcal{I}_k(E)/\hbar}}{1+\mathrm{e}^{-2\pi\mathcal{I}_k(E)/\hbar}} \, |k\rangle\langle k| \\ &= \frac{\mathrm{e}^{-2\pi\hat{h}/\hbar}}{1+\mathrm{e}^{-2\pi\hat{h}/\hbar}} = \frac{\hat{\mathcal{T}}(E)}{1+\hat{\mathcal{T}}(E)} \end{aligned}$$

where $\hat{h} = \sum_k \mathcal{I}_k(E) \, |k\rangle\langle k|$ and $\hat{\mathcal{T}}(E) = \mathrm{e}^{-2\pi\hat{h}/\hbar}$.

This operator can be related to the scattering matrix

$$S = \begin{pmatrix} r & t \\ t & r \end{pmatrix} \qquad \hat{\mathcal{R}} \sim t^\dagger t$$

and can be represented in phase space using the **Wigner-Weyl** correspondence:



$$E > E_{\text{barrier}}$$

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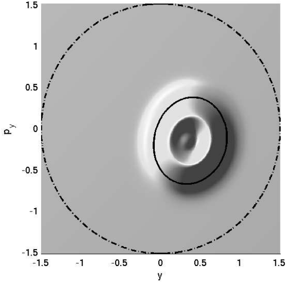

$$E \gtrapprox E_{\text{barrier}}$$

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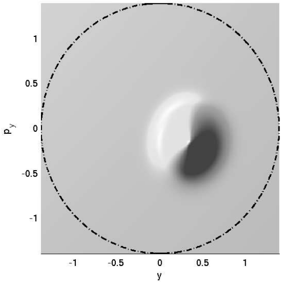

$$E \lessapprox E_{\text{barrier}}$$

Conclusion

• A variety of methods are available to treat barrier-transmission problems.

• All of them are useful

• Phase-space based methods are particularly powerful in dealing with multidimensional problems.