Chemical Reaction Dynamics

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Contents

I. INTRODUCTION

In these lectures, I will present an introduction to quantum scattering theory and to the quantum theory of chemical reaction rates, at a level that will hopefully be accessible to students with a good working knowledge of bound state quantum mechanics but little or no previous knowledge of continuum wave functions. In order to do this in four lectures, I will present the entire theory in the context of a simple one dimensional barrier transmission problem, and leave to further reading how the final result (Miller's flux-side correlation function expression for the reaction rate coefficient[1,2]) can be applied to more general reactions.

II. QUANTUM SCATTERING THEORY

A. Free particle eigenstates

The simplest possible continuum wave functions are the eigenstates of the free particle Hamiltonian

$$\hat{H}_0 = \frac{\hat{p}^2}{2m}. \tag{1}$$

Since $\hat{H}_0$ commutes with $\hat{p}$, its eigenstates can be chosen to be eigenstates of the momentum operator. Calling these eigenstates $|p\rangle$ and the momentum eigenvalues p, one has both

$$\hat{H}_0 |p\rangle = E |p\rangle \tag{2}$$

and

$$\hat{p} |p\rangle = p |p\rangle , \tag{3}$$

with $E = p^2/2m$.

It is straightforward to find the form of the momentum eigenstates in the position representation, where

$$\hat{p} = -i\hbar \frac{d}{dx} \tag{4}$$

and

$$\langle x|p\rangle = \phi_p(x) \tag{5}$$

convert Eq. (3) into a first order differential equation

$$-i\hbar \frac{d}{dx}\phi_p(x) = p\,\phi_p(x), \tag{6}$$

the solution of which is

$$\phi_p(x) \equiv \langle x|p\rangle = Ne^{+ipx/\hbar}. \tag{7}$$

Note that this also gives the form of the position eigenstates in the momentum representation,

$$\phi_p(x)^* \equiv \langle p|x\rangle = N^* e^{-ipx/\hbar}. \tag{8}$$

The normalization of the momentum eigenstates is a little tricky, because the normalization integral $\langle p|p\rangle$ is undefined. (In other words, the momentum eigenstate $|p\rangle$ is not a "proper" state vector in the space of square integrable functions in one dimension, and neither for that matter is the position eigenstate $|x\rangle$. Both are nevertheless extremely useful in quantum scattering theory as we are about to see.) The only way to make any sense of the situation is to recognize that the overlap integral between two different momentum eigenstates,

$$\begin{aligned}\langle p'|p\rangle &= \int_{-\infty}^{\infty} dx\, \phi_{p'}(x)^* \phi_p(x) \\ &= \int_{-\infty}^{\infty} dx\ \langle p'|x\rangle\, \langle x|p\rangle \\ &= |N|^2 \int_{-\infty}^{\infty} dx\, e^{-i(p'-p)x/\hbar},\end{aligned} \tag{9}$$

is proportional to a Dirac delta function (see Appendix A)

$$\delta(p'-p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx\, e^{-i(p'-p)x/\hbar}. \tag{10}$$

This suggests choosing $N = (2\pi\hbar)^{-1/2}$ in Eqs. (7) and (8), so that[3]

$$\langle x|p\rangle = (2\pi\hbar)^{-1/2} e^{+ipx/\hbar} \tag{11}$$

and

$$\langle p|x\rangle = (2\pi\hbar)^{-1/2} e^{-ipx/\hbar} \tag{12}$$

giving

$$\langle p'|p\rangle = \delta(p'-p). \tag{13}$$

The momentum eigenstates form a complete set of states because they are the *only* eigenstates of the free particle Hamiltonian H_0 (which does not support any bound states). This means that any state $|\psi\rangle$ of a one-dimensional system can be expanded in terms of the momentum eigenstates as

$$|\psi\rangle = \int_{-\infty}^{\infty} dp\ |p\rangle\, \langle p|\psi\rangle\,. \tag{14}$$

In the position representation this reads

$$\langle x|\psi\rangle = \int_{-\infty}^{\infty} dp\ \langle x|p\rangle \langle p|\psi\rangle\,, \tag{15}$$

or equivalently

$$\psi(x) = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dp\, e^{+ipx/\hbar}\psi(p). \tag{16}$$

Applying the Fourier inversion theorem to this gives

$$\psi(p) = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}\psi(x), \tag{17}$$

or equivalently

$$\langle p|\psi\rangle = \int_{-\infty}^{\infty} dx\ \langle p|x\rangle \langle x|\psi\rangle\,, \tag{18}$$

and taking this out of the momentum representation leaves

$$|\psi\rangle = \int_{-\infty}^{\infty} dx\ |x\rangle \langle x|\psi\rangle\,. \tag{19}$$

Thus the position eigenstates also form a complete set of states, and indeed setting $|\psi\rangle = |x'\rangle$ in Eq. (15) gives

$$\begin{aligned} \langle x|x'\rangle &= \int_{-\infty}^{\infty} dp\ \langle x|p\rangle \langle p|x'\rangle \\ &= \frac{1}{(2\pi\hbar)} \int_{-\infty}^{\infty} dp\, e^{-ip(x'-x)/\hbar} \\ &= \delta(x'-x). \end{aligned} \tag{20}$$

Equations (13), (14), (19) and (20) are the main results so far. They show that the momentum eigenstates $|p\rangle$ and the position eigenstates $|x\rangle$ each form a complete set of orthonormal states. These results are entirely analogous to those obtained in a discrete basis of "proper" square integrable state vectors such as the eigenstates $|n\rangle$ of a harmonic oscillator, in which one has the more familiar orthonormality condition

$$\langle n'|n\rangle = \delta_{n'n} \tag{21}$$

and the completeness relation

$$|\psi\rangle = \sum_{n=0}^{\infty} |n\rangle \langle n|\psi\rangle\,, \tag{22}$$

The only differences that arise in the momentum and position eigenstate bases are that the Kronecker delta in Eq. (21) becomes a Dirac delta function and the sum over states in Eq. (22) becomes an integral.

One other thing we shall need to know how to do is calculate the trace of an operator in these two bases. In a basis set of harmonic oscillator eigenstates, the trace of an operator $\hat{A}$ is

$$\mathrm{tr}\left[\hat{A}\right] = \sum_{n=0}^{\infty} \left\langle n|\hat{A}|n\right\rangle, \tag{23}$$

and this is independent of the force constant that is chosen for the harmonic oscillator because the transformation between any one (complete, orthonormal) basis and any other is a unitary transformation. In the momentum and position eigenstate bases, one can write either

$$\mathrm{tr}\left[\hat{A}\right] = \int_{-\infty}^{\infty} dp \left\langle p|\hat{A}|p\right\rangle, \tag{24}$$

or

$$\mathrm{tr}\left[\hat{A}\right] = \int_{-\infty}^{\infty} dx \left\langle x|\hat{A}|x\right\rangle, \tag{25}$$

both of which will again give the same result as can be seen from the following argument:

$$\begin{aligned}
\int_{-\infty}^{\infty} dp \left\langle p|\hat{A}|p\right\rangle &= \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \left\langle p|x\right\rangle \left\langle x|\hat{A}|x'\right\rangle \left\langle x'|p\right\rangle \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \, e^{-ip(x-x')/\hbar} \left\langle x|\hat{A}|x'\right\rangle \\
&= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \, \delta(x-x') \left\langle x|\hat{A}|x'\right\rangle \\
&= \int_{-\infty}^{\infty} dx \left\langle x|\hat{A}|x\right\rangle.
\end{aligned} \tag{26}$$

Exercise 1. Any operator $\hat{A}$ that acts on the space of square integrable functions in one dimension can be written in terms of the eigenstates $|n\rangle$ of a harmonic oscillator as

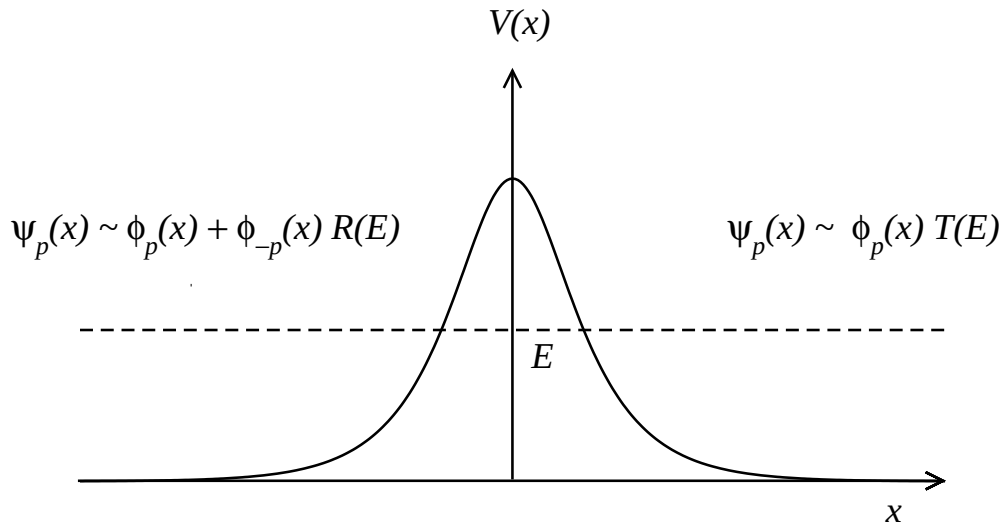
$$\hat{A} = \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} |n\rangle \left\langle n|\hat{A}|n'\right\rangle \langle n'|. \tag{27}$$

(a) Why is this? (b) Use this expression to show that Eq. (25) will give the same result as Eq. (23) for $\mathrm{tr}\left[\hat{A}\right]$.

B. Scattering eigenstates

Now consider a more general problem with a Hamiltonian of the form

$$\hat{H} = \hat{H}_0 + \hat{V} = \frac{\hat{p}^2}{2m} + V(\hat{x}), \tag{28}$$



in which the potential energy function $V(x)$ tends to zero as $x \to \pm\infty$. The scattering eigenstates of this problem are the solutions of the Schrödinger equation

$$\hat{H}\,|\psi_p\rangle = E\,|\psi_p\rangle \tag{29}$$

with $E = p^2/2m > 0$.

It is convenient to study these eigenstates in the position representation, where they become the wave functions $\psi_p(x) = \langle x|\psi_p\rangle$. As $x \to \pm\infty$, these wave functions must tend to linear combinations of $\phi_{\pm p}(x) = \langle x|\pm p\rangle = (2\pi\hbar)^{-1/2}e^{\pm ipx/\hbar}$, which are linearly independent solutions of the Schrödinger equation when $V(x) = 0$. The conventional way to specify these linear combinations is as shown above: $\psi_p(x \to -\infty)$ contains both an incident and a reflected component,

$$\psi_p(x \to -\infty) \sim \phi_p(x) + \phi_{-p}(x)R(E), \tag{30}$$

whereas $\psi_p(x \to \infty)$ contains a single transmitted component

$$\psi_p(x \to \infty) \sim \phi_p(x)T(E). \tag{31}$$

The reflection amplitude $R(E)$ and the transmission amplitude $T(E)$ can be obtained for any potential $V(x)$ by solving the Schrödinger equation in the interaction region. For example, in the trivial case where the potential is zero, the only solution of the Schrödinger equation that is compatible with both boundary conditions is $\psi_p(x) = \phi_p(x)$, giving $R(E) = 0$ and $T(E) = 1$.

Exercise 2. Consider the scattering from the potential energy barrier

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0, & 0 < x < a \\ 0, & x > a \end{cases} \tag{32}$$

in which $V_0 > 0$. Use the fact that $\psi_p(x)$ and $\psi_p'(x)$ must both be continuous at $x = 0$ and $x = a$ to obtain explicit expressions for the reflection amplitude $R(E)$ and the transmission amplitude $T(E)$ when $E = V_0$, and verify that your expressions satisfy

$$|R(E)|^2 + |T(E)|^2 = 1. \tag{33}$$

C. Flux and unitarity

Equation (33) shows that the reflection and transmission probabilities for the problem considered in exercise 2 sum to one ("unitarity"). This is a general result that can be shown to hold for any potential $V(x)$ and any scattering energy E as follows.

The flux (number of particles per unit time) passing through the point $x = s$ is given in quantum mechanics by the Heisenberg time derivative of the projection operator onto the subspace in which $x > s$, namely (see Appendix B)

$$\hat{F}(s) = \frac{i}{\hbar}\left[\hat{H}, h(\hat{x} - s)\right], \tag{34}$$

where

$$h(x - s) = \begin{cases} 1, & \text{if } x > s \\ 0, & \text{if } x < s \end{cases}. \tag{35}$$

For a Hamiltonian of the form in Eq. (28), it is straightforward (and therefore left as an exercise) to show that $\hat{F}(s)$ can be written in the position representation as

$$\hat{F}(s) = -\frac{i\hbar}{2m}\left\{\delta(x - s)\frac{d}{dx} + \frac{d}{dx}\delta(x - s)\right\}. \tag{36}$$

The flux through s for a general time-dependent wave function $\psi(x,t)$ is therefore

$$j(s,t) \equiv \langle\psi|\,\hat{F}(s)\,|\psi\rangle = -\frac{i\hbar}{2m}\left\{\psi(s,t)^*\frac{\partial\psi(s,t)}{\partial s} - \frac{\partial\psi(s,t)}{\partial s}^*\psi(s,t)\right\}, \tag{37}$$

and it is equally straightforward to show (another exercise) that this satisfies the quantum mechanical *continuity equation*

$$\frac{\partial}{\partial s}j(s,t) = -\frac{\partial}{\partial t}|\psi(s,t)|^2. \tag{38}$$

The most important implication of these equations is that the flux $j(s,t)$ will be a constant (independent of both s and t) when $\psi(s,t) = \psi(s,0)e^{-iEt/\hbar}$ is an eigenstate of the Hamiltonian (a stationary state). If this stationary state is a bound state its wave function $\psi(s,0)$ may be chosen to be real, and it follows from this that $j(s,t)$ will be identically zero for all s and t. So bound states do not contribute any flux, but scattering states do: inserting the scattering eigenstate $|\psi_p\rangle$ into Eq. (37), and choosing s to be in the asymptotic "product" region where the boundary condition in Eq. (31) applies, we obtain

$$\begin{aligned}
\langle\psi_p|\,\hat{F}(s)\,|\psi_p\rangle &= \langle p|\,\hat{F}(s)\,|p\rangle\,|T(E)|^2 \\
&= -\frac{i\hbar}{2m}\left\{\phi_p(s)^*\frac{d}{ds}\phi_p(s) - \phi_p(s)\frac{d}{ds}\phi_p(s)^*\right\}|T(E)|^2 \\
&= -\frac{i\hbar}{2m}\frac{1}{2\pi\hbar}\left\{e^{-ips/\hbar}\frac{d}{ds}e^{+ips/\hbar} - e^{+ips/\hbar}\frac{d}{ds}e^{-ips/\hbar}\right\}|T(E)|^2 \\
&= -\frac{i\hbar}{2m}\frac{1}{2\pi\hbar}\frac{2ip}{\hbar}|T(E)|^2 = \frac{1}{2\pi\hbar}\left(\frac{p}{m}\right)|T(E)|^2.
\end{aligned} \tag{39}$$

Had we chosen instead to place s in the asymptotic "reactant" region where the boundary condition in Eq. (30) applies, we would have obtained

$$\left\langle\psi_p|\hat{F}(s)|\psi_p\right\rangle = \frac{1}{2\pi\hbar}\left(\frac{p}{m}\right)\left(1 - |R(E)|^2\right). \tag{40}$$

And since the flux is independent of s for a stationary state, this completes the proof of Eq. (33).

Exercise 3. (a) Use Eqs. (28) and (34) to derive the expression for the flux operator in Eq. (36). (b) Derive the continuity equation in Eq. (38) from Eq. (37) and the time-dependent Schrödinger equation in the form

$$\frac{\partial}{\partial t}\psi(s,t) = -\frac{i}{\hbar}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial s^2} + V(s)\right]\psi(s,t).$$

(c) Verify the result in Eq. (40).

D. The scattering Green's function

The full scattering Schrödinger equation is

$$\hat{H}\,|\psi_p\rangle = \left(\hat{H}_0 + \hat{V}\right)|\psi_p\rangle = E\,|\psi_p\rangle\,. \tag{41}$$

Rearranging this gives

$$(E - \hat{H}_0)\,|\psi_p\rangle = \hat{V}\,|\psi_p\rangle\,, \tag{42}$$

which can be solved formally to give

$$|\psi_p\rangle = |\chi_p\rangle + \lim_{\epsilon\to 0}(E + i\epsilon - \hat{H}_0)^{-1}\hat{V}\,|\psi_p\rangle \tag{43}$$

where $|\chi_p\rangle$ satisfies the free particle Schrödinger equation

$$(E - \hat{H}_0)\,|\chi_p\rangle = 0. \tag{44}$$

In the language of linear second order differential equations, the first term on the right-hand side of Eq. (43) is a "complementary function" and the second is a "particular integral"; the $i\epsilon$ in this integral is a tiny embellishment that is needed to make the inverse of the operator $(E - \hat{H}_0)$ well defined (see exercise 4 below).

In the position representation, Eq. (43) becomes an integral equation for the scattering wave function $\psi_p(x) \equiv \langle x|\psi_p\rangle$,

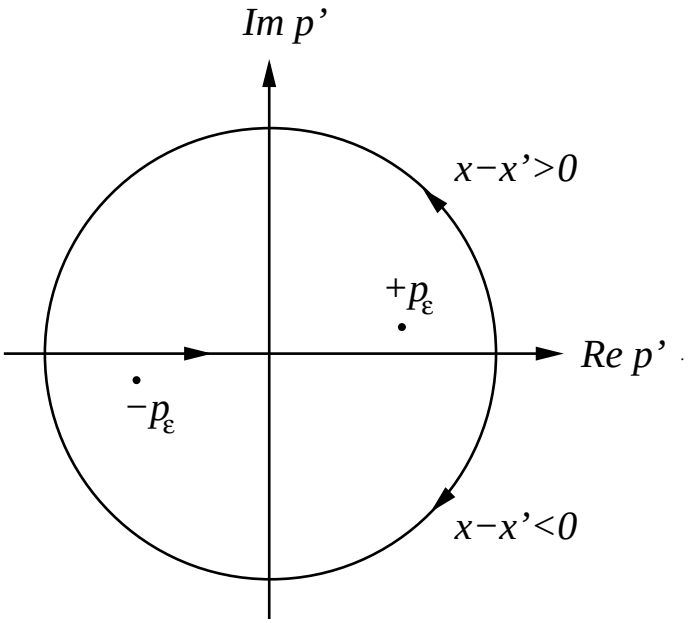
$$\psi_p(x) = \chi_p(x) + \int_{-\infty}^{\infty} dx'\, G_0^+(x,x')V(x')\psi_p(x'), \tag{45}$$

where

$$G_0^+(x,x') = \lim_{\epsilon\to 0}\langle x|\,(E + i\epsilon - \hat{H}_0)^{-1}\,|x'\rangle\,. \tag{46}$$

Letting $p_\epsilon = \sqrt{2m(E+i\epsilon)}$, and noting that $\hat{H}_0 = \hat{p}^2/2m$, one can evaluate this free particle Green's function as follows:

$$\begin{aligned}
G_0^+(x,x') &= \lim_{\epsilon\to 0}\langle x|\,(E + i\epsilon - \hat{H}_0)^{-1}\,|x'\rangle \\
&= \lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dp'\ \langle x|\,(E + i\epsilon - \hat{p}^2/2m)^{-1}\,|p'\rangle\,\langle p'|x'\rangle \\
&= \lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dp'\ \langle x|p'\rangle\,(p_\epsilon^2/2m - [p']^2/2m)^{-1}\,\langle p'|x'\rangle \\
&= \lim_{\epsilon\to 0}\frac{2m}{2\pi\hbar}\int_{-\infty}^{\infty} dp'\,\frac{e^{+ip'(x-x')/\hbar}}{(p_\epsilon^2 - [p']^2)} \\
&= -\lim_{\epsilon\to 0}\frac{m}{\pi\hbar}\int_{-\infty}^{\infty} dp'\,\frac{e^{+ip'(x-x')/\hbar}}{(p' - p_\epsilon)(p' + p_\epsilon)}.
\end{aligned} \tag{47}$$



For small positive ϵ, the poles in the integrand of Eq. (47) at $p' = \pm p_\epsilon = \pm\sqrt{2m(E+i\epsilon)}$ are shifted off the real integration axis into the first and third quadrants of the complex p' plane (see above). The integral is therefore well defined and can be evaluated using the residue theorem. When $x > x'$, the integration contour can be closed along a semicircle at infinity in the upper half of the complex plane, enclosing the simple pole at $p' = +p_\epsilon$. The semicircle does not make any contribution to the contour integral and the residue theorem gives

$$\begin{aligned} G_0^+(x,x') &= -\lim_{\epsilon\to 0}\frac{m}{\pi\hbar}2\pi i R(+p_\epsilon) = -\lim_{\epsilon\to 0}\frac{m}{\pi\hbar}2\pi i\frac{e^{+ip_\epsilon(x-x')/\hbar}}{2p_\epsilon} \\ &= -\lim_{\epsilon\to 0}\frac{im}{\hbar p_\epsilon}e^{+ip_\epsilon(x-x')/\hbar} = -\frac{im}{\hbar p}e^{+ip(x-x')/\hbar} \quad (x>x'), \end{aligned} \tag{48}$$

where $p = \lim_{\epsilon\to 0} p_\epsilon = \sqrt{2mE}$. When $x < x'$, the contour can be closed along a semicircle at infinity in the lower half of the complex plane (which again makes no contribution), and the residue theorem gives

$$\begin{aligned} G_0^+(x,x') &= +\lim_{\epsilon\to 0}\frac{m}{\pi\hbar}2\pi i R(-p_\epsilon) = -\lim_{\epsilon\to 0}\frac{m}{\pi\hbar}2\pi i\frac{e^{-ip_\epsilon(x-x')/\hbar}}{2p_\epsilon} \\ &= -\lim_{\epsilon\to 0}\frac{im}{\hbar p_\epsilon}e^{-ip_\epsilon(x-x')/\hbar} = -\frac{im}{\hbar p}e^{-ip(x-x')/\hbar} \quad (x<x'), \end{aligned} \tag{49}$$

where the initial sign change arises because the contour is now clockwise. So overall

$$G_0^+(x,x') = -\frac{im}{\hbar p}e^{+ip|x-x'|/\hbar} = -\frac{2\pi im}{p}\phi_{-p}(x_<)\phi_p(x_>), \tag{50}$$

where $\phi_{\pm p}(x) = (2\pi\hbar)^{-1/2} e^{\pm ipx/\hbar}$ and $x_<$ ($x_>$) is the lesser (greater) of x and x'.

The final stage of the argument is to substitute this back into Eq. (45) and to use the boundary conditions on $\psi_p(x)$ in Eqs. (30) and (31) to determine the homogeneous solution $\chi_p(x)$. As $x \to -\infty$, Eqs. (45) and (50) give

$$\begin{aligned}\psi_p(x \to -\infty) &\sim \chi_p(x) - \frac{2\pi i m}{p}\phi_{-p}(x)\int_{-\infty}^{\infty} dx'\, \phi_p(x')V(x')\psi_p(x') \\ &= \chi_p(x) - \frac{2\pi i m}{p}\phi_{-p}(x)\int_{-\infty}^{\infty} dx'\, \phi_{-p}(x')^* V(x')\psi_p(x'). \end{aligned} \tag{51}$$

Comparing this with Eq. (30), and noting that the coefficients of $\phi_p(x)$ and $\phi_{-p}(x)$ must be the same in both equations, fixes

$$\chi_p(x) = \phi_p(x) \tag{52}$$

and gives

$$R(E) = -\frac{2\pi i m}{p}\left\langle -p|\hat{V}|\psi_p\right\rangle. \tag{53}$$

Finally, as $x \to \infty$, Eqs. (45), (50) and (52) give

$$\begin{aligned}\psi_p(x \to \infty) &\sim \phi_p(x) - \frac{2\pi i m}{p}\phi_p(x)\int_{-\infty}^{\infty} dx'\, \phi_{-p}(x')V(x')\psi_p(x') \\ &= \phi_p(x) - \frac{2\pi i m}{p}\phi_p(x)\int_{-\infty}^{\infty} dx'\, \phi_p(x')^* V(x')\psi_p(x'), \end{aligned} \tag{54}$$

and comparing this with Eq. (31) gives

$$T(E) = 1 - \frac{2\pi i m}{p}\left\langle p|\hat{V}|\psi_p\right\rangle. \tag{55}$$

Exercise 4. The need for the $i\epsilon$ in Eq. (43) arises because the resolvent operator $(z - \hat{H}_0)^{-1}$ has a branch cut along the positive real z axis, on which $z = E$ is an eigenvalue of $\hat{H}_0$. Prove this by showing that when the real axis is approached from below, as it is in

$$G_0^-(x, x') = \lim_{\epsilon \to 0}\left\langle x\right| \left(E - i\epsilon - \hat{H}_0\right)^{-1} \left|x'\right\rangle, \tag{56}$$

one obtains a result that differs from the one in Eq. (50). (The reason why we have chosen to focus on $G_0^+(x, x')$ here is that it is consistent with the boundary conditions on $\psi_p(x)$ in Eqs. (30) and (31), whereas $G_0^-(x, x')$ is not; $\psi_p(x)$ is sometimes called $\psi_p^+(x)$ in the literature for this reason.)

E. Formal scattering theory

The free particle Green's function $G_0^+(x,x')$ in Eq. (50) is a position matrix element of the free particle Green's operator

$$\hat{G}_0^+(E) = \lim_{\epsilon\to 0}\left(E + i\epsilon - \hat{H}_0\right)^{-1}, \tag{57}$$

and one can clearly define an analogous operator for the full scattering problem:

$$\hat{G}^+(E) = \lim_{\epsilon\to 0}\left(E + i\epsilon - \hat{H}\right)^{-1}. \tag{58}$$

These two operators are related by the fact that $\hat{H} = \hat{H}_0 + \hat{V}$, which implies that

$$\hat{G}_0^+(E)^{-1} = \hat{G}^+(E)^{-1} + \hat{V}. \tag{59}$$

Pre-multiplying Eq. (59) by $\hat{G}^+(E)$ and post-multiplying by $\hat{G}_0^+(E)$ gives

$$\hat{G}^+(E) = \hat{G}_0^+(E) + \hat{G}^+(E)\hat{V}\hat{G}_0^+(E), \tag{60}$$

whereas pre-multiplying by $\hat{G}_0^+(E)$ and post-multiplying by $\hat{G}^+(E)$ gives

$$\hat{G}^+(E) = \hat{G}_0^+(E) + \hat{G}_0^+(E)\hat{V}\hat{G}^+(E). \tag{61}$$

These two equations are known as the *Lippmann-Schwinger equations*[4] for $\hat{G}^+(E)$.

In view of Eqs. (43) and (52), the free particle Green's operator $\hat{G}_0^+(E)$ provides a link between the scattering eigenstate $|\psi_p\rangle$ and the free particle (momentum) eigenstate $|p\rangle$:

$$|\psi_p\rangle = |p\rangle + \hat{G}_0^+(E)\hat{V}\,|\psi_p\rangle\,. \tag{62}$$

This can be solved to give $|\psi_p\rangle$ explicitly as

$$|\psi_p\rangle = \left[1 - \hat{G}_0^+(E)\hat{V}\right]^{-1}|p\rangle\,. \tag{63}$$

An alternative expression for $|\psi_p\rangle$ is obtained by noting that both

$$\left[1 + \hat{G}^+(E)\hat{V}\right]\left[1 - \hat{G}_0^+(E)\hat{V}\right] = 1, \tag{64}$$

and

$$\left[1 - \hat{G}_0^+(E)\hat{V}\right]\left[1 + \hat{G}^+(E)\hat{V}\right] = 1, \tag{65}$$

where Eq. (64) follows from Eq. (60) and Eq. (65) from Eq. (61); therefore

$$\left[1 - \hat{G}_0^+(E)\hat{V}\right]^{-1} = \left[1 + \hat{G}^+(E)\hat{V}\right] \tag{66}$$

and

$$|\psi_p\rangle = \left[1 + \hat{G}^+(E)\hat{V}\right]|p\rangle\,. \tag{67}$$

Note in passing that this expression implies that Eq. (55) can be written more symmetrically as

$$T(E) = 1 - \frac{2\pi i m}{p}\,\langle p|\,\hat{T}(E)\,|p\rangle \tag{68}$$

where $\hat{T}(E)$ is the *transition operator*[4]

$$\hat{T}(E) = \hat{V} + \hat{V}\hat{G}^+(E)\hat{V}. \tag{69}$$

Returning to Eq. (67), and recalling that $\hat{V} = \hat{H} - \hat{H}_0$ and $\hat{H}_0\,|p\rangle = E\,|p\rangle$, one finds that the following formal manipulations[1] give yet another expression for $|\psi_p\rangle$:

$$\begin{aligned}
|\psi_p\rangle &= \left[1 + \hat{G}^+(E)\hat{V}\right]|p\rangle \\
&= \left[1 - \hat{G}^+(E)(E - \hat{H})\right]|p\rangle \\
&= \lim_{\epsilon\to 0}\left[1 - (E + i\epsilon - \hat{H})^{-1}(E - \hat{H})\right]|p\rangle \\
&= \lim_{\epsilon\to 0}\left[1 - (E + i\epsilon - \hat{H})^{-1}(E + i\epsilon - \hat{H} - i\epsilon)\right]|p\rangle \\
&= \lim_{\epsilon\to 0}(i\epsilon)(E + i\epsilon - \hat{H})^{-1}\,|p\rangle \\
&= \lim_{\epsilon\to 0}(i\epsilon)(i\hbar)^{-1}\int_0^\infty dt\, e^{+i(E+i\epsilon-\hat{H})t/\hbar}\,|p\rangle \\
&= \lim_{\epsilon\to 0}\frac{\epsilon}{\hbar}\int_0^\infty dt\, e^{-\epsilon t/\hbar}e^{-i\hat{H}t/\hbar}e^{+iEt/\hbar}\,|p\rangle \\
&= \lim_{\epsilon\to 0}\frac{\epsilon}{\hbar}\int_0^\infty dt\, e^{-\epsilon t/\hbar}e^{-i\hat{H}t/\hbar}e^{+i\hat{H}_0 t/\hbar}\,|p\rangle \\
&= \lim_{\epsilon\to 0}\int_0^\infty dx\, e^{-x}e^{-i\hat{H}x/\epsilon}e^{+i\hat{H}_0 x/\epsilon}\,|p\rangle \\
&= \lim_{t\to\infty}\int_0^\infty dx\, e^{-x}e^{-i\hat{H}t/\hbar}e^{+i\hat{H}_0 t/\hbar}\,|p\rangle \\
&= \lim_{t\to\infty} e^{-i\hat{H}t/\hbar}e^{+i\hat{H}_0 t/\hbar}\,|p\rangle \\
&= \hat{\Omega}_+\,|p\rangle\,,
\end{aligned} \tag{70}$$

where $\hat{\Omega}_+$ is the *Møller operator*[4]

$$\hat{\Omega}_+ = \lim_{t\to\infty} e^{-i\hat{H}t/\hbar}e^{+i\hat{H}_0 t/\hbar}. \tag{71}$$

The physical interpretation of this result is that the scattering eigenstate $|\psi_p\rangle$ can be obtained by propagating the free-particle eigenstate $|p\rangle$ back into the infinite past under the influence of the free-particle Hamiltonian $\hat{H}_0$, and then propagating the result forward to time $t = 0$ under the influence of the full Hamiltonian $\hat{H}$.

An important implication of Eq. (70) is that the full scattering eigenstates are normalized in the same way as the free particle eigenstates:

$$\begin{aligned}\langle\psi_{p'}|\psi_p\rangle &= \langle p'|\,\hat{\Omega}_+^\dagger\hat{\Omega}_+\,|p\rangle \\ &= \lim_{t\to\infty}\langle p'|\,e^{-i\hat{H}_0t/\hbar}e^{+i\hat{H}t/\hbar}e^{-i\hat{H}t/\hbar}e^{+i\hat{H}_0t/\hbar}\,|p\rangle \\ &= \langle p'|p\rangle = \delta(p'-p).\end{aligned} \tag{72}$$

If the Hamiltonian $\hat{H}$ does not support any bound states, this implies by analogy with Eqs. (14) and (24) that any state $|\psi\rangle$ can be expanded in terms of the scattering eigenstates as

$$|\psi\rangle = \int_{-\infty}^{\infty} dp\;|\psi_p\rangle\,\langle\psi_p|\psi\rangle\,, \tag{73}$$

and that the trace of an operator $\hat{A}$ can be calculated as

$$\mathrm{tr}\left[\hat{A}\right] = \int_{-\infty}^{\infty} dp\;\langle\psi_p|\,\hat{A}\,|\psi_p\rangle\,. \tag{74}$$

If $\hat{H}$ *does* support some bound states $|\psi_b\rangle$, such that $\hat{H}\,|\psi_b\rangle = E_b\,|\psi_b\rangle$ with $\langle\psi_{b'}|\psi_b\rangle = \delta_{b'b}$ and $E_{b'}, E_b < 0$, these will be orthogonal to the scattering states as they are eigenstates of the same Hermitian operator with different eigenvalues (recall that $\hat{H}\,|\psi_p\rangle = E\,|\psi_p\rangle$ with $E = p^2/2m > 0$). It follows from this that each of the above equations will simply be augmented by a bound-state contribution:

$$|\psi\rangle = \sum_b |\psi_b\rangle\,\langle\psi_b|\psi\rangle + \int_{-\infty}^{\infty} dp\;|\psi_p\rangle\,\langle\psi_p|\psi\rangle\,, \tag{75}$$

and

$$\mathrm{tr}\left[\hat{A}\right] = \sum_b \langle\psi_b|\,\hat{A}\,|\psi_b\rangle + \int_{-\infty}^{\infty} dp\;\langle\psi_p|\,\hat{A}\,|\psi_p\rangle\,. \tag{76}$$

Note finally that, according to the argument in Eq. (72), the operator $\hat{\Omega}_+^\dagger\hat{\Omega}_+$ behaves like a unit operator when acting on any free particle eigenstate:

$$\hat{\Omega}_+^\dagger\hat{\Omega}_+\,|p\rangle = |p\rangle\,. \tag{77}$$

Since the free particle eigenstates are complete ($\hat{H}_0$ does not support any bound states), this implies that $\hat{\Omega}_+^\dagger \hat{\Omega}_+$ *is* a unit operator:

$$\hat{\Omega}_+^\dagger \hat{\Omega}_+ = 1. \tag{78}$$

If it were also true that $\hat{\Omega}_+ \hat{\Omega}_+^\dagger = 1$, then $\hat{\Omega}_+$ would be unitary. However, this is not true when the Hamiltonian $\hat{H}$ supports any bound states, as can be seen from the following argument:

$$\langle p| \hat{\Omega}_+^\dagger |\psi_b\rangle = \langle \psi_b| \hat{\Omega}_+ |p\rangle^* = \langle \psi_b|\psi_p\rangle^* = 0. \tag{79}$$

Since this is true for all $|p\rangle$, and the free particle eigenstates are complete, it implies that

$$\hat{\Omega}_+ \hat{\Omega}_+^\dagger |\psi_b\rangle = 0 \tag{80}$$

for all bound states $|\psi_b\rangle$, and it is immediately apparent from this that

$$\hat{\Omega}_+ \hat{\Omega}_+^\dagger \neq 1 \tag{81}$$

(in fact, $\hat{\Omega}_+ \hat{\Omega}_+^\dagger$ is just a projection operator onto the subspace of scattering eigenstates, as shown in exercise 5 below). An operator $\hat{\Omega}_+$ that satisfies Eqs. (78) and (81) is norm-preserving (or *isometric*), but it is not unitary.[4]

Exercise 5. Starting with Eq. (62) in the form $|p\rangle = \left[1 - \hat{G}_0^+(E)\hat{V}\right] |\psi_p\rangle$, and recalling that $\hat{V} = \hat{H} - \hat{H}_0$ and $\hat{H} |\psi_p\rangle = E |\psi_p\rangle$, show by following the steps in Eq. (70) that $|p\rangle = \Omega_+^\dagger |\psi_p\rangle$ where $\Omega_+^\dagger = \lim_{t\to\infty} e^{-i\hat{H}_0 t/\hbar} e^{+i\hat{H}t/\hbar}$. This implies that $\hat{\Omega}_+ \hat{\Omega}_+^\dagger |\psi_p\rangle = \hat{\Omega}_+ |p\rangle = |\psi_p\rangle$ for any $|\psi_p\rangle$, which in conjunction with Eq. (80) shows that $\hat{\Omega}_+ \hat{\Omega}_+^\dagger$ is a projection operator onto the subspace of scattering eigenstates; a simpler way to see this is to note that

$$\hat{\Omega}_+ \hat{\Omega}_+^\dagger = \hat{\Omega}_+ \hat{1}\, \hat{\Omega}_+^\dagger = \int_{-\infty}^{\infty} dp\, \hat{\Omega}_+ |p\rangle \langle p| \hat{\Omega}_+^\dagger = \int_{-\infty}^{\infty} dp\, |\psi_p\rangle \langle \psi_p| .$$

III. CHEMICAL REACTION RATE THEORY

A. The thermal rate coefficient

The one-dimensional barrier transmission problem illustrated in the figure on page 6 is the simplest possible model for a bimolecular chemical reaction, with the reactant asymptote at

$x \to -\infty$ and the product asymptote at $x \to \infty$. The exact quantum mechanical expression for the thermal rate coefficient of this "reaction" is

$$k(T) = \frac{1}{2\pi\hbar Q_r(T)} \int_0^\infty dE\, e^{-\beta E} N(E), \tag{82}$$

where $\beta = 1/(k_{\rm B}T)$. Here $Q_r(T)$ is the reactant partition function per unit length (it would become the partition function per unit volume for a reaction in three-dimensional space), which is given by elementary statistical mechanics as

$$Q_r(T) = \frac{1}{\Lambda(T)} = \left(\frac{2\pi m k_{\rm B} T}{h^2}\right)^{1/2} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}, \tag{83}$$

and $N(E)$ is the "cumulative reaction probability",[2] which in the present case of a one-dimensional barrier transmission problem is simply the barrier transmission probability

$$N(E) = |T(E)|^2 . \tag{84}$$

Exercise 6. Verify that $k(T)$ in Eq. (82) has the correct dimensions for a bimolecular (second order) rate coefficient in one-dimensional space, where "concentrations" are measured in terms of the number of particles per unit length.

B. Miller's trace formula

The flux-side correlation function formulation of Miller and co-workers[1,2] provides an extremely elegant (and entirely rigorous) way to calculate the rate coefficient in Eq. (82), and one that has a clear connection with the classical limit (and classical transition state theory). We shall therefore spend the next few sections working towards this formulation, beginning with the derivation of Miller's trace formula for the reaction rate.[1]

According to the analysis in Sec. II.D, the cumulative reaction probability $N(E)$ in Eq. (84) can be calculated from the steady-state flux through any point (or "dividing surface") $x = s$ as

$$N(E) = 2\pi\hbar \left(\frac{m}{p}\right) \langle\psi_p|\, \hat{F}\, |\psi_p\rangle , \tag{85}$$

where we have suppressed the dependence of the flux operator on s to simplify the notation [compare Eq. (85) with Eq. (39)]. Substituting Eq. (85) into Eq. (82) gives

$$k(T)Q_r(T) \;= \int_0^\infty dE\, \left(\frac{m}{p}\right) e^{-\beta E} \langle\psi_p|\, \hat{F}\, |\psi_p\rangle$$

$$= \int_0^\infty dE \left(\frac{m}{p}\right) \langle\psi_p| e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} |\psi_p\rangle , \tag{86}$$

where we have used the fact that $\hat{H}|\psi_p\rangle = E|\psi_p\rangle$ and chosen to split the Boltzmann operator symmetrically around the flux operator for later convenience.

We would now like to change the integration variable from energy to momentum in Eq. (86), so as to obtain an expression that more closely resembles an operator trace [see Eq. (24)]. The correct way to do this is to set $p = +\sqrt{2mE}$, which along with $dE = (p/m)dp$ gives

$$k(T)Q_r(T) = \int_0^\infty dp \, \langle\psi_p| e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} |\psi_p\rangle . \tag{87}$$

The steps from here to Miller's trace formula are a series of straightforward manipulations that begin by replacing $|\psi_p\rangle$ with $\hat{\Omega}_+ |p\rangle$:

$$\begin{aligned} k(T)Q_r(T) &= \int_0^\infty dp \, \langle p| \hat{\Omega}_+^\dagger e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} \hat{\Omega}_+ |p\rangle \\ &= \int_{-\infty}^\infty dp \, \langle p| \hat{\Omega}_+^\dagger e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} \hat{\Omega}_+ |p\rangle \, h(p) \\ &= \int_{-\infty}^\infty dp \, \langle p| \hat{\Omega}_+^\dagger e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} \hat{\Omega}_+ h(\hat{p}) |p\rangle \\ &= \mathrm{tr}\left[\hat{\Omega}_+^\dagger e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} \hat{\Omega}_+ h(\hat{p})\right] \\ &= \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2} \hat{\Omega}_+ h(\hat{p}) \hat{\Omega}_+^\dagger\right] . \end{aligned} \tag{88}$$

The physical interpretation of this result is that the rate coefficient can be obtained by correlating the thermal flux $e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}$ through the dividing surface at time $t = 0$ with the projection

$$\begin{aligned} \hat{\Omega}_+ h(\hat{p}) \hat{\Omega}_+^\dagger &= \lim_{t\to\infty} e^{-i\hat{H}t/\hbar} e^{+i\hat{H}_0 t/\hbar} h(\hat{p}) e^{-i\hat{H}_0 t/\hbar} e^{+i\hat{H}t/\hbar} \\ &= \lim_{t\to\infty} e^{-i\hat{H}t/\hbar} h(\hat{p}) e^{+i\hat{H}t/\hbar} \end{aligned} \tag{89}$$

onto states with positive momentum (which are incident on the potential from the reactant side) in the infinite past.[1]

C. A simpler projection operator

As it stands, Eq. (88) is already quite appealing. Since the trace can be evaluated in any convenient basis, we are no longer obliged to solve the Schrödinger equation for the scattering eigenstates $|\psi_p\rangle$ in order to calculate the reaction rate. And since the equation is

guaranteed to give the same result for any choice of dividing surface $x = s$, we can make this choice in such a way as to simplify the calculation (as will become apparent when we come on to consider the classical limit of the equation and its transition state theory approximation below). However, before we get on to these things, let us spend some time seeing if we can make Eq. (88) look even prettier than it already is.

The first step in this direction is to note that the projection operator $h(\hat{p})$ can be written equivalently as either[2]

$$h(\hat{p}) = \lim_{t\to\infty} e^{-i\hat{H}_0 t/\hbar} h(s-\hat{x}) e^{+i\hat{H}_0 t/\hbar}, \tag{90}$$

or

$$h(\hat{p}) = \lim_{t\to\infty} e^{+i\hat{H}_0 t/\hbar} h(\hat{x}-s) e^{-i\hat{H}_0 t/\hbar}, \tag{91}$$

for any choice of the dividing surface $x = s$. In other words, positive momentum states are those that evolve under the influence of the free particle Hamiltonian from the left of the dividing surface in the infinite past [Eq. (90)] to the right of the dividing surface in the infinite future [Eq. (91)]. This clearly makes good physical sense, and it can be shown to be correct by proving that the matrix elements of both sides of Eqs. (90) and (91) are the same. For example, Eq. (90) can be verified as follows.[2]

Choosing the position eigenstates as a basis, the matrix elements of $h(\hat{p})$ are simply

$$\langle x|\, h(\hat{p})\, |x'\rangle = \int_{-\infty}^{\infty} dp\ \langle x|p\rangle\, h(p)\, \langle p|x'\rangle = \frac{1}{2\pi\hbar}\int_0^{\infty} dp\, e^{+ip(x-x')/\hbar}. \tag{92}$$

To check that the right-hand side of Eq. (90) has the same matrix elements, we can begin by writing

$$\langle x|\, e^{-i\hat{H}_0 t/\hbar} h(s-\hat{x}) e^{+i\hat{H}_0 t/\hbar}\, |x'\rangle = \int_{-\infty}^{\infty} dx''\ \langle x|\, e^{-i\hat{H}_0 t/\hbar}\, |x''\rangle\, h(s-x'')\, \langle x''|\, e^{+i\hat{H}_0 t/\hbar}\, |x'\rangle\,. \tag{93}$$

This contains two free particle propagator matrix elements, which can be shown (see exercise 7 below) to be

$$\langle x|\, e^{-i\hat{H}_0 t/\hbar}\, |x''\rangle = \left(\frac{m}{2\pi i\hbar t}\right)^{1/2} e^{+im(x-x'')^2/(2\hbar t)}, \tag{94}$$

and

$$\langle x''|\, e^{+i\hat{H}_0 t/\hbar}\, |x'\rangle = \left(\frac{im}{2\pi\hbar t}\right)^{1/2} e^{-im(x''-x')^2/(2\hbar t)}. \tag{95}$$

Substituting these results into Eq. (93) and rearranging gives

$$\langle x|\, e^{-i\hat{H}_0 t/\hbar} h(s-\hat{x})\ e^{+i\hat{H}_0 t/\hbar}\, |x'\rangle = \frac{m}{2\pi\hbar t}\int_{-\infty}^{\infty} dx''\, e^{+im[(x-x'')^2-(x''-x')^2]/(2\hbar t)} h(s-x'')$$

$$= \frac{m}{2\pi\hbar t}\int_{-\infty}^{\infty} dx''\, e^{+im(x+x'-2x'')(x-x')/(2\hbar t)} h(s-x'')$$
$$= \frac{m}{2\pi\hbar t} e^{+im(x+x')(x-x')/(2\hbar t)} \int_{-\infty}^{s} dx'' e^{-imx''(x-x')/(\hbar t)}, \tag{96}$$

and changing the integration variable to $p = m(s-x'')/t$ converts this into

$$\begin{aligned}\langle x|\, e^{-i\hat{H}_0 t/\hbar} h(s-\hat{x}) e^{+i\hat{H}_0 t/\hbar}\, |x'\rangle &= e^{+im(x+x'-2s)(x-x')/(2\hbar t)} \frac{1}{2\pi\hbar}\int_0^{\infty} dp\, e^{+ip(x-x')/\hbar} \\ &= e^{+im(x+x'-2s)(x-x')/(2\hbar t)} \langle x|\, h(\hat{p})\, |x'\rangle\,. \end{aligned} \tag{97}$$

Hence

$$\lim_{t\to\infty} \langle x|\, e^{-i\hat{H}_0 t/\hbar} h(s-\hat{x}) e^{+i\hat{H}_0 t/\hbar}\, |x'\rangle = \langle x|\, h(\hat{p})\, |x'\rangle \tag{98}$$

(for all x, x' and s), and since the position eigenstate basis is complete this completes the proof of Eq. (90).

Of Eqs. (90) and (91), Eq. (90) is the more convenient for us, owing to the presence of the Møller operators $\hat{\Omega}_+$ and $\hat{\Omega}_+^\dagger$ in Eq. (89). Indeed combining Eqs. (89) and (90) gives

$$\begin{aligned}\hat{\Omega}_+ h(\hat{p}) \hat{\Omega}_+^\dagger &= \lim_{t\to\infty} e^{-i\hat{H}t/\hbar} e^{+i\hat{H}_0 t/\hbar} e^{-i\hat{H}_0 t/\hbar} h(s-\hat{x}) e^{+i\hat{H}_0 t/\hbar} e^{-i\hat{H}_0 t/\hbar} e^{+i\hat{H}t/\hbar} \\ &= \lim_{t\to\infty} e^{-i\hat{H}t/\hbar} h(s-\hat{x}) e^{+i\hat{H}t/\hbar}, \end{aligned} \tag{99}$$

and inserting this into Eq. (88) gives

$$k(T)Q_r(T) = \lim_{t\to\infty} \left[e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2}\, e^{-i\hat{H}t/\hbar} h(s-\hat{x}) e^{+i\hat{H}t/\hbar} \right]. \tag{100}$$

This is almost in the neatest possible form, but there is one more useful modification we can make to it, based on the observation that

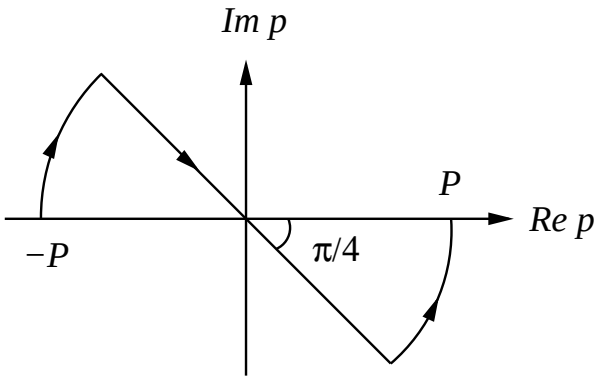
$$h(s-\hat{x}) = 1 - h(\hat{x}-s). \tag{101}$$

Since, from Eqs. (39) and (76)

$$\begin{aligned}\mathrm{tr}\left[e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2} \right] &= \sum_b \langle \psi_b|\, e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2}\, |\psi_b\rangle + \int_{-\infty}^{\infty} dp\, \langle \psi_p|\, e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2}\, |\psi_p\rangle \\ &= \sum_b e^{-\beta E_b} \langle \psi_b|\, \hat{F}\, |\psi_b\rangle + \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m} \langle \psi_p|\, \hat{F}\, |\psi_p\rangle = 0, \end{aligned} \tag{102}$$

the unit operator in Eq. (101) does not contribute to $k(T)Q_r(T)$, and we are left with

$$k(T)Q_r(T) = -\lim_{t\to\infty} \left[e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2}\, e^{-i\hat{H}t/\hbar} \hat{h} e^{+i\hat{H}t/\hbar} \right], \tag{103}$$



where

$$\hat{h} = h(\hat{x} - s) \tag{104}$$

and $\hat{F} = \frac{i}{\hbar}\left[\hat{H}, \hat{h}\right]$ is the Heisenberg time-derivative of $\hat{h}$.

Exercise 7. (a) Show that, for positive t, the integral

$$\begin{aligned} \langle x|\, e^{-i\hat{H}_0 t/\hbar}\, |x''\rangle &= \int_{-\infty}^{\infty} dp\, \langle x|p\rangle\, e^{-ip^2 t/2m\hbar}\, \langle p|x''\rangle \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp\, e^{-ip^2 t/2m\hbar + ip(x-x'')/\hbar} \\ &= \frac{1}{2\pi\hbar}\lim_{P\to\infty}\int_{-P}^{P} dp\, e^{-ip^2 t/2m\hbar + ip(x-x'')/\hbar} \end{aligned} \tag{105}$$

can be evaluated along the contour illustrated above to give the result in Eq. (94). (b) What is the appropriate contour for the integral in Eq. (95), assuming again that $t > 0$?

Exercise 8. Explain carefully why the sum and the integral in the last line of Eq. (102) both vanish.

D. Side-side, flux-side and flux-flux correlation functions

Equation (103) can be re-written as

$$k(T)Q_r(T) = -\lim_{t\to\infty} c_{fs}(-t), \tag{106}$$

where $c_{fs}(t)$ is a *flux-side* correlation function[2]

$$c_{fs}(t) = \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}\right]. \tag{107}$$

Since $\hat{F} = \dfrac{i}{\hbar}[\hat{H}, \hat{h}]$ is the Heisenberg time derivative of $\hat{h}$, one might expect this to be related to the following *side-side*

$$c_{ss}(t) = \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}(1-\hat{h})e^{-i\hat{H}t/\hbar}\right] \tag{108}$$

and *flux-flux*

$$c_{ff}(t) = \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}\right] \tag{109}$$

correlation functions, and indeed it is. Differentiating Eq. (107) with respect to t immediately gives

$$\frac{d}{dt}c_{fs}(t) = \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}\right] = c_{ff}(t), \tag{110}$$

and differentiating Eq. (108) with respect to t and rearranging gives

$$\begin{aligned}
\frac{d}{dt}c_{ss}(t) &= -\mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}\right] \\
&= -\mathrm{tr}\left[e^{-i\hat{H}t/\hbar}\hat{h}e^{+i\hat{H}t/\hbar}\, e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}\right] \\
&= -\mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}\, e^{-i\hat{H}t/\hbar}\hat{h}e^{+i\hat{H}t/\hbar}\right] = -c_{fs}(-t),
\end{aligned} \tag{111}$$

where we have used the fact that the Boltzmann operator $e^{-\beta\hat{H}/2}$ commutes with the evolution operators $e^{\pm i\hat{H}t/\hbar}$ and that one can cyclically permute the operators within a trace.

These same manipulations reveal that both $c_{ss}(t)$ and $c_{ff}(t)$ are real and even functions of t. For example,

$$\begin{aligned}
c_{ss}(t)^* = c_{ss}(-t) &= \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\, e^{-i\hat{H}t/\hbar}(1-\hat{h})e^{+i\hat{H}t/\hbar}\right] \\
&= \mathrm{tr}\left[e^{-\beta\hat{H}}\hat{h}\right] - \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\, e^{-i\hat{H}t/\hbar}\hat{h}e^{+i\hat{H}t/\hbar}\right] \\
&= \mathrm{tr}\left[e^{-\beta\hat{H}}\hat{h}\right] - \mathrm{tr}\left[e^{+i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}\, e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\right] \\
&= \mathrm{tr}\left[e^{-\beta\hat{H}}\hat{h}\right] - \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}\right] \\
&= \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{h}e^{-\beta\hat{H}/2}\, e^{+i\hat{H}t/\hbar}(1-\hat{h})e^{-i\hat{H}t/\hbar}\right] = c_{ss}(t),
\end{aligned} \tag{112}$$

and similarly for $c_{ff}(t)$. In view of Eq. (111), this implies that $c_{fs}(t)$ is a real and odd function of t, and combining this with Eqs. (106) and (110) gives

$$k(T)Q_r(T) = \lim_{t\to\infty}\frac{d}{dt}c_{ss}(t) = \lim_{t\to\infty}c_{fs}(t) = \int_0^\infty dt\, c_{ff}(t). \tag{113}$$

These final results were originally obtained by Miller *et al.*[2] in 1983. They are entirely rigorous, they apply equally well to more complicated reactions than the simple one-dimensional

model problem we have considered here, and they form the basis of all modern approaches to the calculation of chemical reaction rates.

Exercise 9. (a) Show that $c_{ss}(t)$ in Eq. (108) can be evaluated as

$$c_{ss}(t) = \int_s^\infty dx \int_{-\infty}^s dx' \left| \langle x' | \, e^{-i\hat{H}t_c/\hbar} \, |x\rangle \right|^2, \tag{114}$$

where $t_c = t - i\beta\hbar/2$. (b) Now consider the special case where $\hat{H} = \hat{H}_0$ and assume that $t > 0$ so that $\langle x' | \, e^{-i\hat{H}_0 t_c/\hbar} \, |x\rangle$ can be evaluated using Eq. (94). Show that in this case

$$c_{ss}(t) = \frac{m}{2\pi\hbar|t_c|} \int_s^\infty dx \int_{-\infty}^s dx' e^{-\beta m(x'-x)^2/(2|t_c|^2)}. \tag{115}$$

(c) Prove that, for $a > 0$,

$$\int_s^\infty dx \int_{-\infty}^s dx' \, e^{-a(x'-x)^2} = \frac{1}{2a}. \tag{116}$$

(d) Obtain closed-form expressions for $c_{ss}(t)$, $c_{fs}(t)$ and $c_{ff}(t)$ when $\hat{H} = \hat{H}_0$ and sketch the behaviour of these functions for t between $\pm 3\beta\hbar$. (e) Verify that the rate coefficient obtained from Eq. (113) agrees with that obtained from Eq. (82) in the special case of free particle motion.

IV. THE CLASSICAL LIMIT

A. Classical partition functions

There is a straightforward and well-defined procedure for obtaining the classical limit of a quantum mechanical trace expression such as the definition of $c_{fs}(t)$ in Eq. (107): One simply replaces the trace with a classical phase space average and all of the operators within the trace by the corresponding classical functions of positions and momenta.

For example, the classical (high temperature) limit of the partition function for a particle in a one-dimensional box of length a, which will be familiar from elementary statistical mechanics courses as

$$\begin{aligned} Q(T) \; &= \mathrm{tr}\left[e^{-\beta\hat{H}}\right] = \sum_{n=1}^\infty e^{-\beta E_n} = \sum_{n=1}^\infty e^{-\beta n^2\pi^2\hbar^2/(2ma^2)} \\ &\sim \int_0^\infty dn \, e^{-\beta n^2\pi^2\hbar^2/(2ma^2)} = \frac{1}{2}\left(\frac{2\pi m a^2}{\beta\pi^2\hbar^2}\right)^{1/2} = \frac{a}{2\pi\hbar}\left(\frac{2\pi m}{\beta}\right)^{1/2}, \end{aligned} \tag{117}$$

can be calculated more directly (without using the quantum mechanical energy levels) as

$$Q(T) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx\, e^{-\beta H(p,x)} \tag{118}$$

where

$$H(p,x) = \frac{p^2}{2m} + V(x) \tag{119}$$

with

$$V(x) = \begin{cases} 0, & 0 < x < a, \\ \infty, & x < 0,\ x > a. \end{cases} \tag{120}$$

Indeed substituting Eqs. (119) and (120) into Eq. (118) immediately gives

$$Q(T) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp \int_{0}^{a} dx\, e^{-\beta p^2/2m} = \frac{a}{2\pi\hbar}\left(\frac{2\pi m}{\beta}\right)^{1/2}. \tag{121}$$

B. Classical correlation functions

The classical analogue of the flux operator $\hat{F}$ in $c_{fs}(t)$ is given by Eq. (36) as

$$F(p,x) = \frac{1}{2m}\left\{\delta(x-s)p + p\,\delta(x-s)\right\} = \frac{p}{m}\delta(x-s), \tag{122}$$

and the classical analogue of the time-evolved side operator

$$e^{+i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar} = h\left[e^{+i\hat{H}t/\hbar}\hat{x}e^{-i\hat{H}t/\hbar} - s\right] \equiv h[\hat{x}(t) - s] \tag{123}$$

is clearly

$$h(p,x) = h[x_t - s], \tag{124}$$

where $x_t \equiv x_t(p,x)$ is obtained from p and x by solving the classical equations of motion

$$\dot{p}_t = -\frac{\partial H(p_t,x_t)}{\partial x_t} = -\frac{dV(x_t)}{dx_t} \tag{125}$$

and

$$\dot{x}_t = +\frac{\partial H(p_t,x_t)}{\partial p_t} = \frac{p_t}{m} \tag{126}$$

subject to the initial conditions $p_0 = p$ and $x_0 = x$. The classical limit of the rate coefficient of our model one-dimensional reaction is therefore given by Eq. (113) as

$$k^{\rm cl}(T)Q_r(T) = \lim_{t\to\infty} c_{fs}^{\rm cl}(t), \tag{127}$$

where $Q_r(T) = 1/\Lambda(T)$ is the same as in Eq. (83) and

$$\begin{aligned} c_{fs}^{\rm cl}(t) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx\, e^{-\beta H(p,x)}\frac{p}{m}\delta(x-s)h(x_t-s) \\ &\equiv \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dx_0\, e^{-\beta H(p_0,x_0)}\frac{p_0}{m}\delta(x_0-s)h(x_t-s). \end{aligned} \tag{128}$$

As in the quantum mechanical case, this classical flux-side correlation function is a real and odd function of t, and it can be obtained from the time derivative of a classical side-side correlation function

$$c_{ss}^{\rm cl}(t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dx_0\, e^{-\beta H(p_0,x_0)}h(x_0-s)\left[1-h(x_t-s)\right]. \tag{129}$$

For example, differentiating $c_{ss}^{\rm cl}(t)$ with respect to t and using Eq. (126) for $\dot{x}_t$ gives

$$\frac{d}{dt}c_{ss}^{\rm cl}(t) = -\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dx_0\, e^{-\beta H(p_0,x_0)}h(x_0-s)\frac{p_t}{m}\delta(x_t-s), \tag{130}$$

but in view of *Liouville's theorem* (see Appendix C)

$$dp_0\, dx_0 = dp_t\, dx_t, \tag{131}$$

and the fact that classical dynamics conserves the Boltzmann factor

$$e^{-\beta H(p_0,x_0)} = e^{-\beta H(p_t,x_t)}, \tag{132}$$

this can be written equivalently as

$$\begin{aligned} \frac{d}{dt}c_{ss}^{\rm cl}(t) &= -\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_t \int_{-\infty}^{\infty} dx_t\, e^{-\beta H(p_t,x_t)}h(x_0-s)\frac{p_t}{m}\delta(x_t-s) \\ &\equiv -\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dx_0\, e^{-\beta H(p_0,x_0)}h(x_{-t}-s)\frac{p_0}{m}\delta(x_0-s) \\ &= -c_{fs}^{\rm cl}(-t), \end{aligned} \tag{133}$$

which is clearly the classical analogue of Eq. (111).

Exercise 10. Use Eqs. (131) and (132) to prove that $c_{ss}^{\rm cl}(t)$ is a even function of t. It follows from this via Eq. (133) that $c_{fs}^{\rm cl}(t)$ is an odd function of t, and that the classical rate coefficient in Eq. (127) can therefore be calculated equivalently as

$$k^{\rm cl}(T)Q_r(T) = \lim_{t\to\infty}\frac{d}{dt}c_{ss}^{\rm cl}(t); \tag{135}$$

again just as in the quantum mechanical case in Eq. (113).

C. Classical transition state theory

The classical limit of the flux-side correlation function introduced above is clearly very similar to its quantum mechanical counterpart. Both are real and odd functions of t and both are independent of the location of the dividing surface in the limit as $t \to \infty$. However, there is one essential difference between the two that leads to a well-defined classical transition state theory: $c_{fs}^{\rm cl}(t)$ is *discontinuous* at $t = 0$ and tends to a non-zero value as $t \to 0$ from above. In particular, since within the integral in Eq. (128)

$$\begin{aligned}\lim_{t\to 0_+} \delta(x_0 - s)h(x_t - s) &= \lim_{t\to 0_+} \delta(x_0 - s)h(x_0 + p_0 t/m - s) \\ &= \lim_{t\to 0_+} \delta(x_0 - s)h(p_0 t/m) \\ &= \delta(x_0 - s)h(p_0), \end{aligned} \tag{136}$$

we have

$$\begin{aligned}\lim_{t\to 0_+} c_{fs}^{\rm cl}(t) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dx_0\, e^{-\beta H(p_0,x_0)} \frac{p_0}{m}\delta(x_0 - s)h(p_0) \\ &= \frac{1}{2\pi\hbar}\int_0^{\infty} dp_0\, \frac{p_0}{m} e^{-\beta p_0^2/2m} \int_{-\infty}^{\infty} dx_0\, e^{-\beta V(x_0)}\delta(x_0 - s) \\ &= \frac{1}{2\pi\beta\hbar} e^{-\beta V(s)}, \end{aligned} \tag{137}$$

and inserting this into Eq. (127) in place of $\lim_{t\to\infty} c_{fs}^{\rm cl}(t)$ gives the classical *transition state theory* result

$$k_{\rm cl}^{\rm TST}(T) = \frac{1}{Q_r(T)} \lim_{t\to 0_+} c_{fs}^{\rm cl}(t) = \frac{1}{2\pi\beta\hbar Q_r(T)} e^{-\beta V(s)} \equiv \frac{k_{\rm B}T}{h}\frac{1}{Q_r(T)} e^{-\beta V(s)}. \tag{138}$$

Note that:

(a) In undergraduate text books, the transition state theory rate coefficient is usually written as

$$k^{\rm TST}(T) = \frac{k_{\rm B}T}{h}\frac{Q_\ddagger(T)}{Q_r(T)} e^{-\Delta E_0^\ddagger/k_{\rm B}T}, \tag{139}$$

where $Q_r(T)$ is the partition function of the reactants (per unit volume in three dimensions or per unit length in one dimension), $Q_\ddagger(T)$ is the partition function of the transition state excluding the contribution from motion along the reaction coordinate, and $\Delta E_0^\ddagger$ is the difference in zero point energies between the reactants and the transition state. For the simple model reaction we are considering here, the reaction

coordinate is the only degree of freedom and so $Q_\ddagger(T) = 1$. And since there is no zero point energy in any mode orthogonal to the reaction coordinate, $\Delta E_0^\ddagger \equiv V(x^\ddagger)$ is simply the difference in potential energy between the reactant asymptote and the top of the reaction barrier at $x = x^\ddagger$ (the "transition state"). So Eq. (138) agrees with Eq. (139) when we set $s = x^\ddagger$, as it must (because the derivation of Eq. (139) assumes that the motion along the reaction coordinate is purely classical).

(b) With this choice of dividing surface, the transition state theory approximation in Eq. (138) will actually give the same result (for our model one-dimensional reaction) as the full classical rate in Eq. (127). This can be seen by setting $s = x^\ddagger$ in Eq. (128):

$$c_{fs}^{\rm cl}(t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_0 \int_{-\infty}^{\infty} dx_0\, e^{-\beta H(p_0,x_0)} \frac{p_0}{m} \delta(x_0 - x^\ddagger) h(x_t - x^\ddagger). \tag{140}$$

If p_0 is positive, a classical trajectory starting at the top of the reaction barrier will clearly evolve to the right of the barrier as time increases and so make a positive contribution to the integral in Eq. (140) for $t > 0$. However, if p_0 is negative, the trajectory will evolve to the left of the barrier and contribute nothing. For any positive time t, we can therefore replace the step function $h(x_t - x^\ddagger)$ in the integrand with a step function in the initial momentum,

$$\delta(x_0 - x^\ddagger) h(x_t - x^\ddagger) \to \delta(x_0 - x^\ddagger) h(p_0) \quad (t > 0). \tag{141}$$

Having done this, the same simplifications as in Eq. (137) give

$$c_{fs}^{\rm cl}(t > 0) = \frac{1}{2\pi\beta\hbar} e^{-\beta V(x^\ddagger)} \tag{142}$$

and therefore

$$k^{\rm cl}(T) = \frac{1}{Q_r(T)} \lim_{t\to\infty} c_{fs}^{\rm cl}(t) = \frac{1}{2\pi\beta\hbar Q_r(T)} e^{-\beta V(x^\ddagger)} \equiv \frac{k_{\rm B}T}{h} \frac{1}{Q_r(T)} e^{-\beta V(x^\ddagger)}. \tag{143}$$

(c) For any other choice of dividing surface, we will have $V(s) \le V(x^\ddagger)$, and therefore $e^{-\beta V(s)} \ge e^{-\beta V(x^\ddagger)}$ and [compare Eqs. (138) and (143)]

$$k_{\rm cl}^{\rm TST}(T) \ge k^{\rm cl}(T). \tag{144}$$

This *variational* aspect of transition state theory carries over to reactions with more degrees of freedom and enables one to find the optimum dividing surface by minimizing

the transition state theory rate (at least in principle; in practice this is quite difficult to do properly for reactions with more than a handful of degrees of freedom). The one peculiarity of the one-dimensional case is that the resulting optimized $k_{\rm cl}^{\rm TST}(T)$ is exactly equal to $k^{\rm cl}(T)$ (as shown above); this is not generally true for reactions with more degrees of freedom.

Exercise 11. Show by combining Eq. (138) with Eq. (83) that the optimum transition state theory rate coefficient can be written as

$$k_{\rm cl}^{\rm TST}(T) = \frac{1}{2}\,\langle|\dot{x}|\rangle\, e^{-\beta V(x^\ddagger)}, \tag{145}$$

where

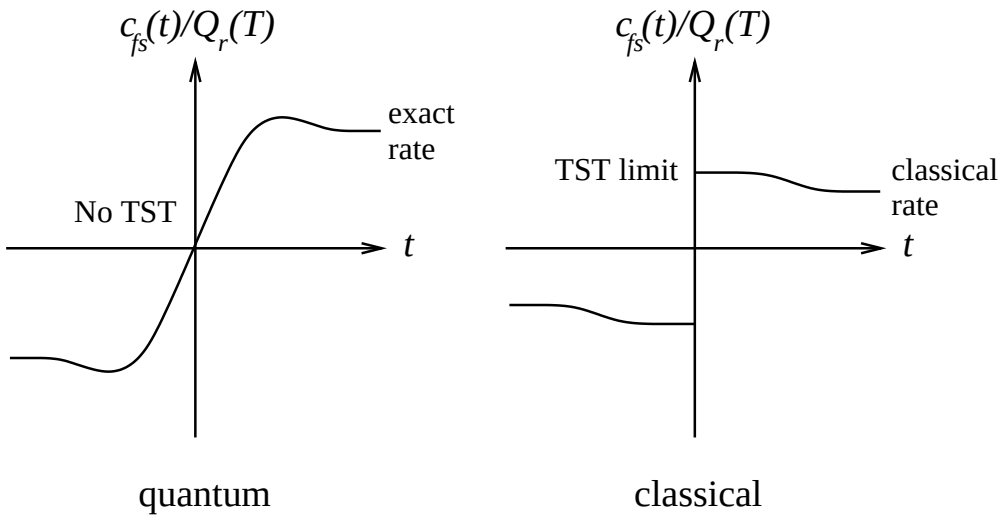
$$\frac{1}{2}\,\langle|\dot{x}|\rangle = \int_0^\infty dp\,\frac{p}{m}e^{-\beta p^2/2m} \Big/ \int_{-\infty}^\infty dp\, e^{-\beta p^2/2m} \tag{146}$$

is the thermal expectation value of the classical flux through the dividing surface and the factor of $e^{-\beta V(x^\ddagger)}$ is the probability that a thermal fluctuation will bring the classical system to the top of the reaction barrier.

D. Quantum transition state theory?

We have just seen that classical transition state theory is obtained by taking the short-time limit of the classical flux-side correlation function. This gives a well-defined approximation to the classical rate coefficient because $c_{fs}^{\rm cl}(t)$ is discontinuous at $t = 0$. However, one cannot do the same thing in quantum mechanics because the exact quantum mechanical $c_{fs}(t)$ is a real, odd, and *continuous* function of t (as you have shown for the case of free motion in exercise 9). Thus there is no true quantum mechanical analogue of classical transition state theory (see below).

The ubiquitous (and generally quite successful) use of transition state theory to calculate reaction rates in the classical limit and the need to allow for quantum mechanical zero point energy and tunneling effects in reactions involving hydrogen atoms have nevertheless led to the development of a number of transition state theory-like approximations to the quantum rate coefficient. The simplest of these is the undergraduate transition state theory expression in Eq. (139). For a multi-dimensional reaction, this expression assumes that the motion along the reaction coordinate is separable from the motion on the dividing surface



and treats the former classically and the latter quantum mechanically. It therefore includes zero point energy in the modes orthogonal to the reaction coordinate but it does not allow for tunneling through the reaction barrier. More sophisticated approximations remove the separability assumption and include the effect of tunneling, typically in such a way as to give the exact result for a parabolic barrier. We do not have the time to discuss these approximations here but some references to them are given in the further reading.[1,5,6] The starting point for the development of new approximations is the exact flux-side correlation function expression for the quantum rate coefficient in Eq. (113), which underlies most of the modern research into the theory and calculation of chemical reaction rates.

V. FURTHER READING

The material described in these lecture notes is based on two classic papers by Bill Miller, both of which indicate how the theory can be generalized to treat more complicated reactions than the simple one-dimensional model problem we have considered here:

1. W. H. Miller, *J. Chem. Phys.* **61**, 1823 (1974).

2. W. H. Miller, S. D. Schwartz and J. W. Tromp, *J. Chem. Phys.* **79**, 4889 (1983).

The two books I found most useful while preparing the lectures were:

3. P. A. M. Dirac, *The Principles of Quantum Mechanics*, 4th edition (OUP, 1958).

4. J. R. Taylor, *Scattering Theory* (Dover, 2000).

Three different attempts to construct a quantum mechanical version of transition state theory are presented in Sec. IV of Ref. 1 and in:

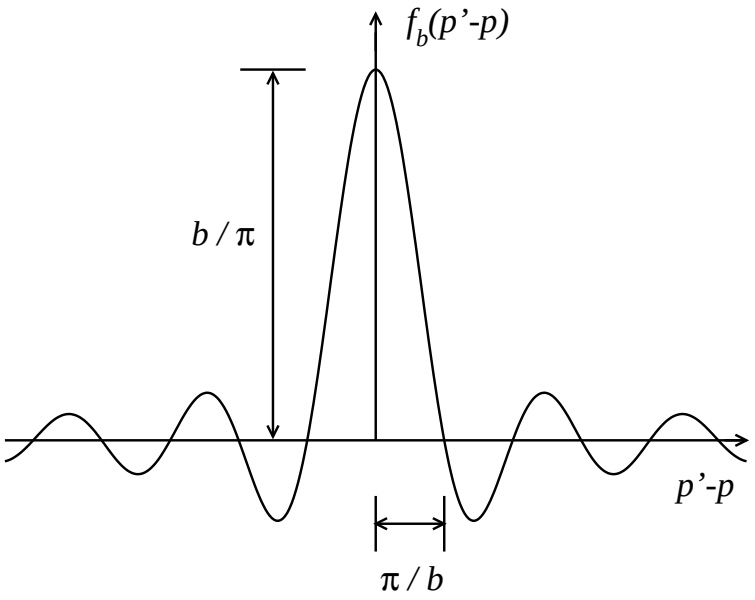
5. G. A. Voth, D. Chandler and W. H. Miller, *J. Chem. Phys.* **91**, 7749 (1989).

6. W. H. Miller, Y. Zhao, M. Ceotto and S. Yang, *J. Chem. Phys.* **119**, 1329 (2003).

And for what it is worth, my own preferred way to calculate chemical reaction rates (including quantum mechanical zero point energy and tunneling effects and allowing for recrossing of the transition state dividing surface) is described in the following two papers, both of which should be quite accessible to anyone who has understood these lecture notes:

7. I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **123**, 034102 (2005).

8. R. Collepardo-Guevara, I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **128**, 144502 (2008).



VI. APPENDICES

A. The Dirac delta function

The Dirac delta function $\delta(p'-p)$ in Eq. (10) is not a proper mathematical function,[3] but it can at least be written as a limit of something that is:

$$\begin{aligned}
\delta(p'-p) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx\, e^{-i(p'-p)x/\hbar} \\
&= \lim_{a\to\infty}\frac{1}{2\pi\hbar}\int_{-a}^{a} dx\, e^{-i(p'-p)x/\hbar} \\
&= \lim_{a\to\infty}\frac{1}{2\pi\hbar}\left[\frac{e^{-i(p'-p)x/\hbar}}{-i(p'-p)/\hbar}\right]_{-a}^{a} \\
&= \lim_{a\to\infty}\frac{1}{\pi}\frac{\sin(p'-p)a/\hbar}{(p'-p)} \\
&= \lim_{b\to\infty} f_b(p'-p), \qquad \text{(A1)}
\end{aligned}$$

where

$$f_b(p'-p) = \frac{1}{\pi}\frac{\sin(p'-p)b}{(p'-p)}. \qquad \text{(A2)}$$

This function is plotted above. It consists of a sharp peak centred on $p'=p$ with a height proportional to b and a width inversely proportional to b, along with a rapid oscillation with a period of $2\pi/b$ that extends to larger values of $|p'-p|$. In view of this, the delta function $\delta(p'-p) = \lim_{b\to\infty} f_b(p'-p)$ can be envisaged as an infinitely high and infinitely narrow

spike at $p' = p$ and nothing else, the period of the rapid oscillation having shrunk to zero in the limit as $b \to \infty$.

The area under $f_b(p' - p)$ remains well defined in this limit and can be calculated as follows:

$$\begin{aligned}\int_{-\infty}^{\infty} dp'\, \delta(p' - p) &= \lim_{b\to\infty} \frac{1}{\pi} \int_{-\infty}^{\infty} dp'\, \frac{\sin(p' - p)b}{p' - p} \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} dx\, \frac{\sin x}{x} \\ &= 1, \end{aligned} \tag{A3}$$

where we have made the substitution $x = (p' - p)b$ in the second line and evaluated a standard contour integral to get the third (exercise). In fact, the same argument shows more generally that, for any continuous function $f(p)$,

$$\begin{aligned}\int_{-\infty}^{\infty} dp'\, f(p')\delta(p' - p) &= \lim_{b\to\infty} \frac{1}{\pi} \int_{-\infty}^{\infty} dp'\, f(p')\frac{\sin(p' - p)b}{p' - p} \\ &= \lim_{b\to\infty} \frac{1}{\pi} \int_{-\infty}^{\infty} dx\, f(p + x/b)\frac{\sin x}{x} \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} dx\, f(p)\frac{\sin x}{x} = f(p). \end{aligned} \tag{A4}$$

This is one of the most important properties of the delta function and it is used in various places in the text [for example in Eq. (26)].

Another generalization of the argument in Eq. (A3) shows that, for any $\epsilon > 0$,

$$\int_{-\infty}^{p-\epsilon} dp'\, \delta(p' - p) = \lim_{b\to\infty} \frac{1}{\pi} \int_{-\infty}^{-b\epsilon} dx\, \frac{\sin x}{x} = 0, \tag{A5}$$

$$\int_{p-\epsilon}^{p+\epsilon} dp'\, \delta(p' - p) = \lim_{b\to\infty} \frac{1}{\pi} \int_{-b\epsilon}^{+b\epsilon} dx\, \frac{\sin x}{x} = 1, \tag{A6}$$

$$\int_{p+\epsilon}^{\infty} dp'\, \delta(p' - p) = \lim_{b\to\infty} \frac{1}{\pi} \int_{+b\epsilon}^{\infty} dx\, \frac{\sin x}{x} = 0, \tag{A7}$$

and thus that the integral of the delta function is a step function:

$$\int_{-\infty}^{p''} dp'\, \delta(p' - p) = h(p'' - p) = \begin{cases} 1, & \text{if } p'' > p \\ 0, & \text{if } p'' < p \end{cases}. \tag{A8}$$

We have also made extensive use of this result in these notes [for example in going from Eq. (128) to (129)].

B. The Heisenberg picture

In the text we have asserted that $\hat{F} = (i/\hbar)[\hat{H}, \hat{h}]$ is the Heisenberg time derivative of $\hat{h}$, and that $\lim_{t\to\infty} e^{-i\hat{H}t/\hbar} h(\hat{p}) e^{+i\hat{H}t/\hbar}$ is the projection onto states with positive momentum in the infinite past. These assertions are based on the Heisenberg picture of quantum mechanics, in which state vectors are regarded as time-independent and the time-dependence is transferred to the operators.

Consider a system with a time-independent Hamiltonian $\hat{H}$ and a state vector $|\psi(t)\rangle$ that satisfies the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \,. \tag{B1}$$

Assuming for simplicity that the state $|\psi(t)\rangle$ is normalized, the expectation value of an observable A corresponding to an operator without any explicit time dependence (such as the projection operator $\hat{A} = h(\hat{p})$) is given at time t by

$$A(t) = \langle\psi(t)| \hat{A} |\psi(t)\rangle \,. \tag{B2}$$

This is in the Schrödinger picture where the state $|\psi(t)\rangle$ evolves in time and the operator $\hat{A}$ remains constant.

However, since the Schrödinger equation in Eq. (B1) can be integrated to give

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\psi(0)\rangle \,, \tag{B3}$$

and therefore

$$\langle\psi(t)| = \langle\psi(0)| e^{+i\hat{H}t/\hbar}, \tag{B3}$$

one can equally well write

$$A(t) = \langle\psi| \hat{A}(t) |\psi\rangle \tag{B4}$$

where $|\psi\rangle \equiv |\psi(0)\rangle$ is now constant and

$$\hat{A}(t) = e^{+i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} \tag{B5}$$

changes with time. This is the Heisenberg picture, in which $\hat{A}(t)$ is the Heisenberg-evolved operator at time t. So for example

$$\lim_{t\to\infty} e^{-i\hat{H}t/\hbar} h(\hat{p}) e^{+i\hat{H}t/\hbar} = \lim_{t\to-\infty} e^{+i\hat{H}t/\hbar} h(\hat{p}) e^{-i\hat{H}t/\hbar} \tag{B6}$$

can be interpreted as the projection operator onto states with positive momentum ($h(\hat{p}) = 1$) in the infinite past ($t \to -\infty$). And since $\hat{H}$ commutes with the evolution operators $e^{\pm i\hat{H}t/\hbar}$, we can differentiate Eq. (B5) with respect to t to obtain

$$\begin{aligned}\frac{d}{dt}\hat{A}(t) &= \frac{i}{\hbar}e^{+i\hat{H}t/\hbar}\left[\hat{H}\hat{A} - \hat{A}\hat{H}\right]e^{-i\hat{H}t/\hbar} \\ &= \frac{i}{\hbar}e^{+i\hat{H}t/\hbar}\left[\hat{H},\hat{A}\right]e^{-i\hat{H}t/\hbar} \\ &= \frac{i}{\hbar}\left[\hat{H}, e^{+i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}\right] \\ &= \frac{i}{\hbar}\left[\hat{H},\hat{A}(t)\right], \end{aligned} \tag{B7}$$

thus confirming that $\hat{F}(t) = (i/\hbar)[\hat{H},\hat{h}(t)]$ is the Heisenberg time derivative of $\hat{h}(t)$ (at any time t including $t = 0$).

C. Liouville's theorem

We have made use of Liouville's theorem in Eq. (131). This theorem states that phase space volume is conserved in classical mechanics,

$$dp_0\, dx_0 = dp_t\, dx_t, \tag{C1}$$

or equivalently that the Jacobian of the dynamical transformation from (p_0, x_0) to (p_t, x_t) is unity:

$$J_t = \frac{\partial(p_t,x_t)}{\partial(p_0,x_0)} = \begin{vmatrix} \partial p_t/\partial p_0 & \partial x_t/\partial p_0 \\ \partial p_t/\partial x_0 & \partial x_t/\partial x_0 \end{vmatrix} = \left(\frac{\partial p_t}{\partial p_0}\right)\left(\frac{\partial x_t}{\partial x_0}\right) - \left(\frac{\partial x_t}{\partial p_0}\right)\left(\frac{\partial p_t}{\partial x_0}\right) = 1. \tag{C2}$$

Since it is evidently true that $J_0 = 1$, we can prove the theorem by showing that $\dot{J}_t = 0$ for all t, and this follows directly from Hamilton's equations of motion in Eqs. (125) and (126):

$$\begin{aligned}\dot{J}_t &= \left(\frac{\partial \dot{p}_t}{\partial p_0}\right)\left(\frac{\partial x_t}{\partial x_0}\right) + \left(\frac{\partial p_t}{\partial p_0}\right)\left(\frac{\partial \dot{x}_t}{\partial x_0}\right) - \left(\frac{\partial \dot{x}_t}{\partial p_0}\right)\left(\frac{\partial p_t}{\partial x_0}\right) - \left(\frac{\partial x_t}{\partial p_0}\right)\left(\frac{\partial \dot{p}_t}{\partial x_0}\right) \\ &= \left(\frac{\partial \dot{p}_t}{\partial p_0}\right)\left(\frac{\partial x_t}{\partial x_0}\right) - \left(\frac{\partial \dot{p}_t}{\partial x_0}\right)\left(\frac{\partial x_t}{\partial p_0}\right) - \left(\frac{\partial \dot{x}_t}{\partial p_0}\right)\left(\frac{\partial p_t}{\partial x_0}\right) + \left(\frac{\partial \dot{x}_t}{\partial x_0}\right)\left(\frac{\partial p_t}{\partial p_0}\right) \\ &= -\left(\frac{\partial H}{\partial x_t}\right)\left[\left(\frac{\partial x_t}{\partial p_0}\right)\left(\frac{\partial x_t}{\partial x_0}\right) - \left(\frac{\partial x_t}{\partial x_0}\right)\left(\frac{\partial x_t}{\partial p_0}\right)\right] \\ &\quad -\left(\frac{\partial H}{\partial p_t}\right)\left[\left(\frac{\partial p_t}{\partial p_0}\right)\left(\frac{\partial p_t}{\partial x_0}\right) - \left(\frac{\partial p_t}{\partial x_0}\right)\left(\frac{\partial p_t}{\partial p_0}\right)\right] \\ &= 0. \end{aligned} \tag{C3}$$