Chapter 14

Scattering Theory

Exercises

14.1 **(a)** The process is *inelastic* because the electronic state of atomic oxygen changes.

(b) The process is *elastic* because the initial and final states are the same.

(c) The process is *inelastic* because the vibrational state of HF changes.

(d) The process is *reactive* because a chemical reaction has occurred; the reactant HF is not retained in the product.

(e) The process is *elastic* because the initial and final states are the same.

Exercise: Characterize each of the following as elastic, inelastic or reactive:

$$\mathrm{O}(^3\mathrm{P}_2) + \mathrm{H}_2(v=0, j=0) \rightarrow \mathrm{O}(^3\mathrm{P}_1) + \mathrm{H}_2(v=0, j=0)$$

$$\mathrm{O}(^3\mathrm{P}_2) + \mathrm{H}_2(v=0, j=0) \rightarrow \mathrm{O}(^3\mathrm{P}_2) + 2\mathrm{H}(^2\mathrm{S})$$

14.2 For scattering by a one-dimensional potential energy barrier of finite width (Section 14.1), the continuity conditions for the wavefunction and its slope at $x = L$ are given by the last two equations in eqn 14.1.

$$A'\mathrm{e}^{\mathrm{i}k'L} + B'\mathrm{e}^{-\mathrm{i}k'L} = A''\mathrm{e}^{\mathrm{i}kL} + B''\mathrm{e}^{-\mathrm{i}kL} \quad \text{(i)}$$

$$\mathrm{i}k'A'\mathrm{e}^{\mathrm{i}k'L} - \mathrm{i}k'B'\mathrm{e}^{-\mathrm{i}k'L} = \mathrm{i}kA''\mathrm{e}^{\mathrm{i}kL} - \mathrm{i}kB''\mathrm{e}^{-\mathrm{i}kL} \quad \text{(ii)}$$

Multiplying (i) by ik and adding (ii) yields:

$$2\mathrm{i}kA'' \mathrm{e}^{\mathrm{i}kL} = \mathrm{i}kA'\mathrm{e}^{\mathrm{i}k'L} + \mathrm{i}k'A'\mathrm{e}^{\mathrm{i}k'L} + \mathrm{i}kB'\mathrm{e}^{-\mathrm{i}k'L} - \mathrm{i}k'B'\mathrm{e}^{-\mathrm{i}k'L}$$

or

$$A'' = \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k+k')A' + \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k-k')B'\mathrm{e}^{-2\mathrm{i}k'L} \text{(iii)}$$

Similarly, multiplying (i) by i*k* and subtracting (ii) yields:

$$2\mathrm{i}kB'' \mathrm{e}^{-\mathrm{i}kL} = \mathrm{i}kA'\mathrm{e}^{\mathrm{i}k'L} - \mathrm{i}k'A'\mathrm{e}^{\mathrm{i}k'L} + \mathrm{i}kB'\mathrm{e}^{-\mathrm{i}k'L} + \mathrm{i}k'B'\mathrm{e}^{-\mathrm{i}k'L}$$

or

$$B'' = \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k-k')A'\mathrm{e}^{2\mathrm{i}kL} + \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}(k+k')B'\mathrm{e}^{2\mathrm{i}kL}\mathrm{e}^{-2\mathrm{i}k'L} \text{(iv)}$$

Equations (iii) and (iv) can be written in matrix form as

$$\begin{pmatrix} A'' \\ B'' \end{pmatrix} = \frac{\mathrm{e}^{\mathrm{i}(k'-k)L}}{2k}\begin{pmatrix} k+k' & (k-k')\mathrm{e}^{-2\mathrm{i}k'L} \\ (k-k')\mathrm{e}^{2\mathrm{i}kL} & (k+k')\mathrm{e}^{2\mathrm{i}kL}\mathrm{e}^{-2\mathrm{i}k'L} \end{pmatrix}\begin{pmatrix} A' \\ B' \end{pmatrix}$$

from which we confirm the form of the matrix $\boldsymbol{Q}$ given in *Justification* 14.1.

14.3 From eqns 14.2 and 14.3a:

$$\begin{pmatrix} B \\ A'' \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} A \\ B'' \end{pmatrix}$$

If the particle is incident from the right of the one-dimensional barrier, then $A = 0$ (see Fig. 14.1 of the text). As a result:

$B = S_{12} B''$ $\quad$ $T = |S_{12}|^2$

$A'' = S_{22} B''$ $R = |S_{22}|^2$

14.4 Use eqn 14.15

$$\sigma = |f_k(\theta, \phi)|^2 = \sin^2\theta \cos^2\phi$$

Exercise: Proceed to evaluate the integral scattering cross-section σ_{tot}.

14.5 Use eqn 14.7:

$$\sigma_{\text{tot}} = \int_0^{\pi}\int_0^{2\pi} C \sin\theta \mathrm{d}\theta \mathrm{d}\phi$$

$$= C\left[\int_0^{\pi} \sin\theta \mathrm{d}\theta\right] \times \left[\int_0^{2\pi} d\phi\right]$$

$$= 4\pi C$$

Exercise: What scattering amplitude f_k corresponds to the above σ_{tot}? Within the Born approximation, find the potential that gives rise to this scattering amplitude.

14.6 We show in *Justification* 14.2 that in the limit $r \to \infty$, $\mathrm{e}^{\mathrm{i}kz}$ and $f_k\mathrm{e}^{\mathrm{i}kr}/r$ are each eigenfunctions of the hamiltonian with the same eigenvalue $k^2\hbar^2/2\mu$. Therefore, the total wavefunction has an asymptotic form given by the sum of $\mathrm{e}^{\mathrm{i}kz}$ and $f_k\mathrm{e}^{\mathrm{i}kr}/r$ with eigenvalue $k^2\hbar^2/2\mu$:

$$H(\mathrm{e}^{\mathrm{i}kz} + f_k\mathrm{e}^{\mathrm{i}kr}/r) = H\,\mathrm{e}^{\mathrm{i}kz} + H f_k\mathrm{e}^{\mathrm{i}kr}/r$$

$$= (k^2\hbar^2/2\mu)\,\mathrm{e}^{\mathrm{i}kz} + (k^2\hbar^2/2\mu)\, f_k\mathrm{e}^{\mathrm{i}kr}/r$$

$$= (k^2\hbar^2/2\mu)(\mathrm{e}^{\mathrm{i}kz} + f_k\mathrm{e}^{\mathrm{i}kr}/r)$$

14.7 The free-particle radial wave equation, eqn 14.23, is

$$\frac{\mathrm{d}^2 u_l^0}{\mathrm{d}r^2} + \left\{k^2 - \frac{l(l+1)}{r^2}\right\} u_l^0 = 0$$

(i) $u_l^0 = \hat{j}_0(kr) == \sin(kr)$; $l = 0$ implies $l(l+1)/r^2 = 0$

$$\frac{\mathrm{d}^2 u_l^0}{\mathrm{d}r^2} = \frac{\mathrm{d}^2 \sin(kr)}{\mathrm{d}r^2} = -k^2 \sin(kr)$$

Therefore

$$-k^2 \sin(kr) + \{k^2 - 0\} \sin(kr) = 0$$

(ii)

$$u_l^0 = \hat{j}_1(kr) = \frac{\sin(kr)}{kr} - \cos(kr)$$

$$\frac{\mathrm{d}\hat{j}_1(kr)}{\mathrm{d}r} = \frac{\cos(kr)}{r} - \frac{\sin(kr)}{kr^2} + k\sin(kr)$$

$$\frac{\mathrm{d}^2 \hat{j}_1(kr)}{\mathrm{d}r^2} = \frac{-k\sin(kr)}{r} - \frac{2\cos(kr)}{r^2} + \frac{2\sin(kr)}{kr^3} + k^2\cos(kr)$$

Therefore

$$-\frac{k\sin(kr)}{r} - \frac{2\cos(kr)}{r^2} + \frac{2\sin(kr)}{kr^3} + k^2\cos(kr)$$

$$+\left\{k^2 - \frac{2}{r^2}\right\}\left\{\frac{\sin(kr)}{kr} - \cos(kr)\right\} = 0$$

Exercise: Repeat the confirmation for the first three ($l = 0, 1, 2$) Riccati–Neumann functions.

14.8 The general relation between E and K is given in the equation proceeding eqn 14.51:

$$\hbar^2 K^2 = 2\mu(E + V_0)$$

Therefore

$$E = \frac{\hbar^2 K^2}{2\mu} - V_0$$

$$E_{\text{res}} = \frac{\hbar^2 K_{\text{res}}^2}{2\mu} - V_0$$

and, using eqn 14.62,

$$E_{\text{res}} = \frac{(2n+1)^2 \pi^2 \hbar^2}{8\mu a^2} - V_0$$

14.9 The relation between the mean lifetime τ of the resonance state and the full width at half-maximum Γ is given by eqn 14.75. If the full width at half-maximum expressed in cm^{-1} units is denoted Δ, then $\Gamma = hc\Delta$; therefore

$$\tau = \frac{\hbar}{hc\Delta} = (2\pi c\Delta)^{-1}$$

(a)

$$\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 0.05\ \text{cm}^{-1})^{-1}$$

$$= 1.1 \times 10^{-10}\ \text{s} = \underline{0.11\ \text{ns}}$$

(b)

$$\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 3.5\ \text{cm}^{-1})^{-1}$$

$$= 1.5 \times 10^{-12}\ \text{s} = \underline{1.5\ \text{ps}}$$

(c)

$$\tau = (2\pi \times 2.9979 \times 10^{10}\ \text{cm s}^{-1} \times 45\ \text{cm}^{-1})^{-1}$$

$$= 1.2 \times 10^{-13}\ \text{s} = \underline{0.12\ \text{ps}}$$

Exercise: If the mean lifetime of the resonance state is 10 fs, what would be the expected full width at half-maximum for the Breit–Wigner peak?

14.10 At scattering energy E_1, the total number of open channels is 11 + 6 + 16 = 33. Therefore, the scattering matrix is a 33 × 33 square matrix. The dimension is <u>33</u>.

Exercise: Explore how the dimension of the scattering matrix varies with the scattering energy. Take $J = 0$. Assume that only rotational levels in the ground vibrational states of BC, AB, and AC are open. Treat the rotational constants of the three diatomic molecules as equivalent.

14.11 We need to evaluate the integral on the right-hand side of eqn 14.102 assuming that the cumulative reaction probability $P(E)$ is independent of energy:

$$\int_0^\infty P(E)\mathrm{e}^{-E/kT}\mathrm{d}E = P\int_0^\infty \mathrm{e}^{-E/kT}\mathrm{d}E$$

$$= -PkT\mathrm{e}^{-E/kT}\Big|_0^\infty$$

$$= -PkT(0-1)$$

$$= PkT$$

Therefore the rate constant is directly proportional to the temperature.

14.12 The classical model of chemical reactivity yields a cumultive reaction probability of

$P(E) = 0 \quad 0 \le E < V_0$

$P(E) = 1 \quad V_0 \le E < \infty$

Therefore

$$k_\mathrm{r}(T) \propto \int_0^\infty P(E)\mathrm{e}^{-E/kT}\mathrm{d}E = \int_{V_0}^\infty \mathrm{e}^{-E/kT}\mathrm{d}E$$

$$= -kT\mathrm{e}^{-E/kT}\Big|_{V_0}^{\infty}$$

$$= kT\mathrm{e}^{-V_0/kT}$$

This has a form similar to the Arrhenius equation if we allow the pre-exponential factor A to be directly proportional to temperature and identify the activation energy E_a with $E_\mathrm{a}/RT = V_0/kT$ or, since $R = kN_\mathrm{A}$, $E_\mathrm{a} = N_\mathrm{A}V_0$.

14.13 According to eqn 14.103 and the discussion in Section 14.10, a pole in the scattering matrix (i.e. a resonance) will appear in each scattering matrix element. Therefore scattering cross-sections connecting all possible incoming and outgoing channels should have peaks at the same energy E_res with the same width Γ. In this case, the resonance which appears in the neutron–Te scattering process effects both the elastic scattering and non-elastic scattering processes and therefore the cross-sections show Breit–Wigner peaks at the same energy and of the same width.

Exercise: It is found experimentally that the scattering cross-sections have peaks at an energy of 2.3 eV with a width of 0.11 eV. Determine the resonance energy of the resonance state in the neutron–Te scattering process.

14.14 The scattering matrix $\boldsymbol{S}$ is often symmetric, $S_{ij} = S_{ji}$. (It is always symmetric when the scattering process has a property known as time-reversal invariance). The probability in general for a transition from incident channel i to final channel j is given by

$$P_{ji} = |S_{ji}|^2$$

Thus, for a two-channel scattering process with a symmetric scattering matrix,

$$P_{12} = |S_{12}|^2$$
$$= |S_{21}|^2$$
$$= P_{21}$$

consistent with the principle of microscopic reversibility.

Exercise: Give examples of scattering systems for which the principle of microscopic reversibility is not satisfied.

Problems

14.1 For Zone II (see Section 14.1), the potential energy is $V(x) = -V$ (rather than $+V$) and all solutions are oscillatory for positive energies:

$$\text{Zone II:}\ \psi = A'\mathrm{e}^{iKx} + B'\mathrm{e}^{-iKx} \quad K\hbar = \{2m(E+V)\}^{1/2}$$

Hence S can be constructed from eqn 14.3 by replacing k' in eqn 14.3c with K. The transmission probability for a particle incident from the left is given by $|S_{21}|^2$.

14.4. From Example 14.3

$$\sigma = \frac{4\mu^2 V_0^2/\hbar^4}{(\alpha^2 + 4k^2\sin^2\tfrac{1}{2}\theta)^2}$$

$$= \frac{4\mu^2 V_0^2}{\hbar^4\alpha^4(1+(4k^2/\alpha^2)\sin^2\tfrac{1}{2}\theta)^2}$$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = \frac{1}{(1+(4k^2/\alpha^2)\sin^2\tfrac{1}{2}\theta)^2}$$

(a) For zero energy, $k = 0$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = 1$$

independent of θ.

(b) For moderate energy ($k = \alpha/2$)

$$k^2/\alpha^2 = \tfrac{1}{4}$$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = \frac{1}{(1+\sin^2\tfrac{1}{2}\theta)^2}$$

(c) For high energy ($k = 10\alpha$)

$$k^2/\alpha^2 = 100$$

$$\frac{\sigma}{(2\mu V_0/\hbar^2\alpha^2)^2} = \frac{1}{(1+400\sin^2\tfrac{1}{2}\theta)^2}$$

Plots of the differential cross-section as a function of θ are shown in Fig. 14.1 for **(a)**, **(b)** and **(c)**. For $k >> \alpha$, σ falls off very rapidly as θ increases from 0 to $\pi/2$.

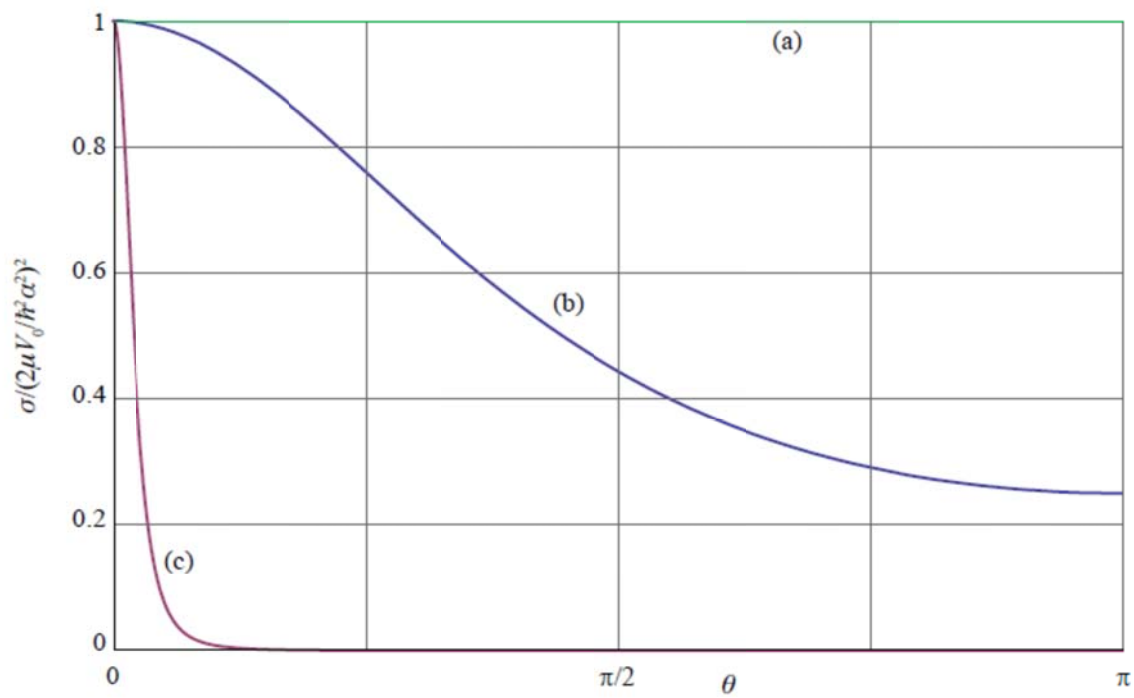

Figure 14.1 The differential cross-section for the Yukawa potential within the Born approximation for (a) zero energy ($k = 0$), (b) moderate energy ($k = \alpha/2$), and (c) high energy ($k = 10\alpha$).

Exercise: Compare the plots to those for $k = \alpha$ and $k = 20\alpha$.

14.7 To derive eqns 14.41 and 14.42, we begin with the equation following eqn 14.40

$$\frac{C_l}{r}\sin(kr - \tfrac{1}{2}l\pi + \delta_l) = i^l(2l+1)\frac{\sin(kr - \tfrac{1}{2}l\pi)}{kr} + f_l\frac{e^{ikr}}{r}$$

Since

$$\sin x = \frac{e^{ix} - e^{-ix}}{2i}$$

$$\frac{C_l}{r}\frac{\mathrm{e}^{\mathrm{i}(kr-\frac{1}{2}l\pi+\delta_l)}-\mathrm{e}^{-\mathrm{i}(kr-\frac{1}{2}l\pi+\delta_l)}}{2\mathrm{i}}=\frac{\mathrm{i}^l(2l+1)[\mathrm{e}^{\mathrm{i}(kr-\frac{1}{2}l\pi)}-\mathrm{e}^{\mathrm{i}(kr-\frac{1}{2}l\pi)}]}{2\mathrm{i}kr}+\frac{f_l\mathrm{e}^{\mathrm{i}kr}}{r}$$

Collect terms with a common factor of $\mathrm{e}^{-\mathrm{i}kr}$

$$\mathrm{e}^{-\mathrm{i}kr}\left\{-\frac{C_l}{r}\frac{\mathrm{e}^{\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{-\mathrm{i}\delta_l}}{2\mathrm{i}}\right\}=\mathrm{e}^{-\mathrm{i}kr}\left\{-\frac{i^l(2l+1)}{2\mathrm{i}kr}\mathrm{e}^{\frac{1}{2}\mathrm{i}l\pi}\right\}$$

Cancel common terms:

$$C_l\mathrm{e}^{-\mathrm{i}\delta_l}=\frac{\mathrm{i}^l(2l+1)}{k}$$

or

$$C_l=\frac{\mathrm{i}^l(2l+1)}{k}\mathrm{e}^{\mathrm{i}\delta_l}\quad\text{[eqn 14.41]}$$

Now collect terms with a common factor of $\mathrm{e}^{-\mathrm{i}kr}$

$$\mathrm{e}^{\mathrm{i}kr}\left\{\frac{C_l}{r}\frac{\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{\mathrm{i}\delta_l}}{2\mathrm{i}}\right\}=\mathrm{e}^{\mathrm{i}kr}\left\{\frac{\mathrm{i}^l(2l+1)\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}}{2\mathrm{i}kr}+\frac{f_l}{r}\right\}$$

Cancel common terms:

$$C_l\frac{\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{\mathrm{i}\delta_l}}{2\mathrm{i}}=\frac{\mathrm{i}^l(2l+1)\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}}{2\mathrm{i}k}+f_l$$

Use eqn 14.41:

$$\frac{\mathrm{i}^l(2l+1)\mathrm{e}^{\mathrm{i}\delta_l}}{k}\frac{\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}\mathrm{e}^{\mathrm{i}\delta_l}}{2\mathrm{i}} = \frac{\mathrm{i}^l(2l+1)\mathrm{e}^{-\frac{1}{2}\mathrm{i}l\pi}}{2\mathrm{i}k} + f_l$$

Because $\mathrm{e}^{\mathrm{i}\pi/2} = \mathrm{i}$, $\mathrm{e}^{\mathrm{i}\pi l/2} = \mathrm{i}^l$.

Therefore

$$\frac{(2l+1)\mathrm{e}^{2\mathrm{i}\delta_l}}{2\mathrm{i}k} = \frac{(2l+1)}{2\mathrm{i}k} + f_l$$

$$f_l = \frac{(2l+1)}{2\mathrm{i}k}(\mathrm{e}^{2\mathrm{i}\delta_l} - 1)$$

$$= \frac{(2l+1)}{k}\mathrm{e}^{\mathrm{i}\delta_l}\frac{(\mathrm{e}^{\mathrm{i}\delta_l} - \mathrm{e}^{-\mathrm{i}\delta_l})}{2\mathrm{i}}$$

$$= \frac{(2l+1)}{k}\mathrm{e}^{\mathrm{i}\delta_l}\sin\delta_l \quad \text{[eqn 14.42]}$$

Exercise: Derive eqn 14.49.

14.10

If $V(r) > 0$ for all r, then $\delta_l(E) < 0$.

If $V(r) < 0$ for all r, then $\delta_l(E) > 0$.

Note that if $V(r) = 0$, $\delta_l(E) = 0$ by definition.

If the potential is purely repulsive for all r, then, since the energy E of the particle is conserved in elastic scattering, the particle's kinetic energy is decreased as a result of scattering. The wavelength of the particle is therefore increased (recall $\lambda = h/p$), corresponding to a negative phase shift δ_l. (Recall that $\sin(kr + \delta)$ has a longer wavelength than $\sin kr$ if $\delta < 0$.)

Conversely, if the potential is purely attractive for all r, the particle is accelerated as it scatters. The increase in kinetic energy corresponds to a shortened wavelength and a positive phase shift δ_l.

Exercise: Sketch the form of the scattering wavefunctions for $V(r) > 0$, $V(r) = 0$, and $V(r) < 0$; qualitatively verify the above conclusions.

14.13

$$V(r) = \begin{cases} \infty & \text{if } r = 0 \\ V_0 & \text{if } 0 < r < a \\ 0 & \text{if } r \geq a \end{cases}$$

Consider energies $E > V_0$ and find δ_0.

At $r = 0$, $V(r) = \infty$ which implies $u_0(0) = 0$ for the radial wavefunction.

For $0 < r < a$, $V(r) = V_0 \quad (V_0 > 0)$

$$-\frac{\hbar^2}{2m}\frac{d^2u_0}{dr^2} + V_0u_0 = Eu_0 \quad \text{(centrifugal potential = 0)}$$

$$\frac{d^2u_0}{dr^2} + \frac{2m}{\hbar^2}(E - V_0)u_0 = 0$$

$$u_0(r) = A \sin k_1r + B \cos k_1r$$

$$k_1^2 = \frac{2m}{\hbar^2}(E - V_0)$$

For $r \geq a$, $V(r) = 0$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u_0}{\mathrm{d}r^2} = Eu_0$$

$$u_0(r) = C\sin kr + D\cos kr$$

$$k^2 = \frac{2mE}{\hbar^2}$$

As $r \to \infty$

$$u_0(r) = C\sin kr + D\cos kr$$

$$= E\sin(kr + \delta_0)$$

where

$$\tan\delta_0 = D/C$$

To find δ_0, we need to obtain an expression for D/C. We require that $u_0(r)$ and $(\mathrm{d}u_0/\mathrm{d}r)$ are continuous at $r = a$.

First, require $u_0(r)$ be continuous at $r = 0$. (We do not impose continuity of $(\mathrm{d}u_0/\mathrm{d}r)$ at $r = 0$ because $V(0) = \infty$.)

$$r = 0: \quad u_0(r = 0) = 0 = A\sin k_1 0 + B\cos k_1 0 = B$$

Therefore for $0 < r < a$, $u_0(r) = A\sin k_1 r$

$$r = a: \quad u_0(r = a) = A\sin k_1 a = C\sin ka + D\cos ka$$

$$\frac{\mathrm{d}u_0}{\mathrm{d}r}(r = a) = k_1 A\cos k_1 a = kC\cos ka - kD\sin ka$$

Divide the above two equations:

$$\frac{1}{k_1}\tan k_1 a = \frac{C\sin ka + D\cos ka}{kC\cos ka - kD\sin ka}$$

$$= \frac{\sin ka + (D/C)\cos ka}{k\cos ka - k(D/C)\sin ka}$$

$$= \frac{\sin ka + \tan\delta_0 \cos ka}{k\cos ka - k\tan\delta_0 \sin ka}$$

$$\frac{k}{k_1}\tan k_1 a\cos ka - \frac{k}{k_1}\tan k_1 a\tan\delta_0 \sin ka = \sin ka + \tan\delta_0\cos ka$$

$$\frac{k}{k_1}\tan k_1 a\cos ka - \sin ka = \tan\delta_0\left\{\cos ka + \frac{k}{k_1}\tan k_1 a\sin ka\right\}$$

$$\tan\delta_0 = \frac{(k/k_1)\tan k_1 a\cos ka - \sin ka}{(k/k_1)\tan k_1 a\sin ka + \cos ka}$$

with

$$\frac{k}{k_1} = \left(\frac{E}{E - V_0}\right)^{1/2}$$

Exercise: First, plot δ_0 as a function of E ($E > V_0$) for fixed V_0 and a. Second, for $E > V_0$, find an expression for the P-wave phase shift δ_1 for scattering off the same central potential and plot δ_1 as a function of energy.

14.16 The spherical square well potential is given in Section 14.5: $V = -V_0$ for $r \le a$ and $V = 0$ for $r > a$. We solve this problem by requiring that the radial solution $u_l(r)$ and its first derivative be continuous at $r = a$.

In the region $r \le a$, we have to solve the equation

$$\frac{\mathrm{d}^2 u_l}{\mathrm{d}r^2} + \left[K^2 - \frac{l(l+1)}{r^2}\right] u_l = 0$$

where

$$\hbar^2 K^2 = 2\mu(E + V_0)$$

The general solution is a linear combination of the Riccati–Bessel and Riccati–Neumann functions:

$$u_l(r) = A_l \hat{j}_l(Kr) + A_l' \hat{n}_l(Kr)$$

To ensure that $R(r) = u_l/r$ is finite at the origin, we require $u_l(0) = 0$. Since the Riccati–Neumann function $\hat{n}_l(z)$ behaves like z^{-l} as $z \to 0$, we must have $A_l' = 0$. Therefore, inside the well the solution is of the form

$$u_l(r) = A_l \hat{j}_l(Kr)$$

For $r > a$, the potential vanishes and u_l is the solution of the free-particle equation (which includes the $l(l+1)/r^2$ centrifugal potential term). We can immediately write down the solution as

$$u_l(r) = C_l \hat{j}_l(kr) + D_l \hat{n}_l(kr)$$

where, as usual, $E = k^2\hbar^2/2\mu$. The scattering phase shift δ_l is introduced via

$$C_l = B_l \cos \delta_l \quad D_l = B_l \sin \delta_l$$

so we can write

$$u_l(r) = B_l \cos \delta_l \hat{j}_l(kr) + B_l \sin \delta_l \hat{n}_l(kr)$$

We require that $u_l(r)$ and its first derivative be continuous at $r = a$. The continuity of the wavefunction requires that

$$A_l \hat{j}_l(Ka) = B_l \cos \delta_l \hat{j}_l(ka) + B_l \sin \delta_l \hat{n}_l(ka)$$

and the continuity of the first derivative requires that

$$KA_l \hat{j}_l'(Ka) = kB_l \cos \delta_l \hat{j}_l'(ka) + kB_l \sin \delta_l \hat{n}_l'(ka)$$

where the prime denotes the derivative with respect to r. Division of the above two equations results in the following complicated expression for the phase shift:

$$K\frac{\hat{j}_l'(Ka)}{\hat{j}_l(Ka)} = k\frac{\hat{j}_l'(ka) + \tan \delta_l \, \hat{n}_l'(ka)}{\hat{j}_l(ka) + \tan \delta_l \, \hat{n}_l(ka)}$$

or

$$\tan \delta_l = \frac{K\hat{j}_l'(Ka)\hat{j}_l(ka) - k\hat{j}_l(Ka)\hat{j}_l(ka)}{k\hat{j}_l(Ka)\hat{n}_l'(ka) - K\hat{j}_l'(Ka)\hat{n}_l(ka)}$$

From the above equation, for a given energy (and corresponding K and k), we can determine the phase shift δ_l.

Exercise: Write down the expression for δ_l for P-wave scattering by a spherical square-well potential.

14.19 Begin with the asymptotic expression (eqn 14.92) for the multichannel stationary scattering state

$$\Psi_{\alpha 0} \simeq \mathrm{e}^{\mathrm{i}k_{\alpha_0} z}\chi_{\alpha_0} + \sum_{\alpha} f_{\alpha\alpha_0}\frac{\mathrm{e}^{\mathrm{i}k_\alpha r_\mathrm{A}}}{r_\mathrm{A}}\chi_\alpha$$

The incident flux J_i is determined by the plane wave $\mathrm{e}^{\mathrm{i}k\alpha_0 z}$ which is the term containing all the (relative) initial kinetic energy. By analogy with the results in *Justification* 14.3, the magnitude of the incident flux is $k_{\alpha_0}\hbar/\mu$.

Likewise, by analogy with the result for J_r in *Justification* 14.3,

$$J_r = \frac{k\hbar\,|f_k|^2}{\mu r^2}$$

for the radial component of the flux density corresponding to $(f_k\mathrm{e}^{\mathrm{i}kr}/r)$, we have here

$$J_r = \frac{k_\alpha\hbar\,|f_{\alpha\alpha_0}|^2}{\mu r^2}$$

where we have equated r_A with r, the relative position.

Only J_r needs to be retained as $r \to \infty$ and we have focused on a single term α in the summation for ψ_{α_0}.

Following the argument in Section 14.3, we then have

$$dN_s = J_r r^2 \mathrm{d}\Omega$$

$$= \frac{k_\alpha \hbar |f_{\alpha\alpha_0}|^2}{\mu} \mathrm{d}\Omega$$

$$= \sigma_{\alpha\alpha_0} J_i \mathrm{d}\Omega$$

$$= \sigma_{\alpha\alpha_0} \frac{k_{\alpha_0} \hbar}{\mu} \mathrm{d}\Omega$$

and therefore

$$\sigma_{\alpha\alpha_0} = \frac{k_\alpha}{k_{\alpha_0}} |f_{\alpha\alpha_0}|^2$$

Exercise: Show in detail why χ_α and χ_{α_0} do not need to be considered in the above argument and also why we can treat each term α in the summation of eqn 14.92 individually.

14.22 (i) Model the cumulative reaction probability as $P(E) = \alpha \arctan(\beta E)$.

(a) In the limit $E \to 0$, $P = \alpha \arctan(0) = 0$, consistent with the model.

(b) At $E = V_0$, $P = \alpha \arctan(\beta V_0) = ½$.

(c) In the limit $E \to \infty$, $P = \alpha \arctan(\infty) = \alpha\pi/2 = 1$.

From condition (c), $\underline{\alpha = 2/\pi}$. Therefore, from condition (b),

$(2/\pi) \arctan(\beta V_0) = ½$

$\arctan(\beta V_0) = \pi/4$

$\beta V_0 = 1$ [since $\tan \pi/4 = 1$]

$\underline{\beta = 1/V_0}$

(ii) Model the cumulative reaction probability as $P(E) = 1 - \mathrm{e}^{-\alpha E}$.

(a) In the limit $E \rightarrow 0$, $P = 1 - 1 = 0$, consistent with the model.

(b) At $E = V_0$, $P = 1 - \mathrm{e}^{-\alpha V_0} = ½$

(c) In the limit $E \rightarrow \infty$, $P = 1 - 0 = 1$, consistent with the model.

From condition (b), $\mathrm{e}^{-\alpha V_0} = ½$ or $\underline{\alpha = (\ln 2)/V_0}$.

For part (ii), the temperature dependence of the rate constant predicted by eqn 14.102 is

$$k_\mathrm{r}(T) \propto \int_0^\infty P(E)\mathrm{e}^{-E/kT}\mathrm{d}E = \int_0^\infty (1 - \mathrm{e}^{-\alpha E})\mathrm{e}^{-E/kT}\mathrm{d}E$$

$$= \int_0^\infty \mathrm{e}^{-E/kT}\mathrm{d}E - \int_0^\infty \mathrm{e}^{-E(\alpha+1/kT)}\,\mathrm{d}E$$

$$= -kT\mathrm{e}^{-E/kT}\Big|_0^\infty + \frac{1}{\alpha + 1/kT}\mathrm{e}^{-E(\alpha+1/kT)}\Big|_0^\infty$$

$$= kT - \frac{1}{\alpha + 1/kT}$$

$$= kT - \frac{1}{(\ln 2/V_0) + (1/kT)}$$

$$= kT\left\{1 - \frac{1}{kT(\ln 2/V_0) + 1}\right\}$$

$$= kT\left\{1 - \frac{V_0}{kT\ln 2 + V_0}\right\}$$