

# Quantum Scattering Dynamics

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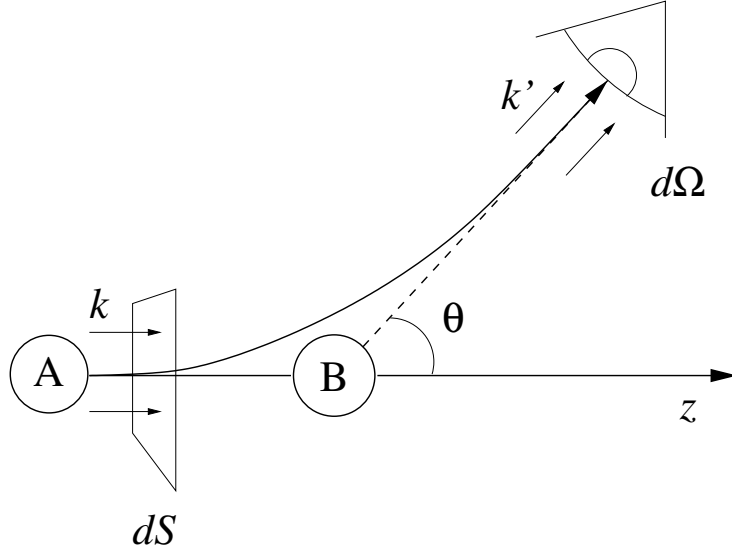
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# 1 Elastic Scattering

## 1.1 Experimental observables

Consider a collision between two structureless ( $^1S$ ) atoms A and B:



The experimental observables are the differential cross section (DCS)

$$\frac{d\sigma(E)}{d\Omega} = \frac{\text{scattered flux per unit solid angle}}{\text{incident flux per unit area}}, \quad (1)$$

and the integral cross section (ICS)

$$\sigma(E) = \int \frac{d\sigma(E)}{d\Omega} d\Omega = 2\pi \int_0^\pi \frac{d\sigma(E)}{d\Omega} \sin\theta d\theta, \quad (2)$$

where

$$E = \frac{\hbar^2 k^2}{2\mu} = \frac{\hbar^2 (k')^2}{2\mu}, \quad (3)$$

and

$$\mu = \frac{m_A m_B}{m_A + m_B}. \quad (4)$$

In eq. (2), we have exploited the cylindrical symmetry of the collision to eliminate the integral over the azimuthal angle  $\phi$  (where  $d\Omega = \sin\theta d\theta d\phi$ ). The fact that  $k^2 = (k')^2$  in eq. (3) arises because the scattering is *elastic*, so the initial and final relative kinetic energies are the same. Note also that both  $\sigma(E)$  and  $d\sigma(E)/d\Omega$  have the dimensions of area.

## 1.2 The flux density

In order to calculate the DCS in eq. (1) quantum mechanically, we must first work out how to calculate the fluxes (number of particles per unit time) in the numerator and denominator. This can be done<sup>1</sup> by considering the rate of change of the probability of finding the A+B system in a finite volume  $V$ :

$$\begin{aligned} \frac{dP_V(t)}{dt} &= \frac{d}{dt} \int_V |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} \\ &= \int_V \Psi^* \dot{\Psi} + \dot{\Psi}^* \Psi d\mathbf{r} \\ &= 2\text{Re} \int_V \Psi^* \dot{\Psi} d\mathbf{r}, \end{aligned} \quad (5)$$

where  $\mathbf{r}$  is the vector between the atoms A and B. Since the wavefunction  $\Psi(\mathbf{r}, t)$  satisfies the time-dependent Schrödinger equation

$$i\hbar \dot{\Psi} = H\Psi = \left(-\frac{\hbar^2}{2\mu} \nabla^2 + V\right) \Psi, \quad (6)$$

and the potential  $V(r)$  is real, this simplifies to

$$\begin{aligned} \frac{dP_V(t)}{dt} &= 2\text{Re} \left[ \frac{1}{i\hbar} \int_V \Psi^* \left(-\frac{\hbar^2}{2\mu} \nabla^2 + V\right) \Psi d\mathbf{r} \right] \\ &= \text{Re} \left[ \frac{i\hbar}{\mu} \int_V \Psi^* \nabla^2 \Psi d\mathbf{r} \right]. \end{aligned} \quad (7)$$

If we now integrate by parts (using Green's theorem), we can reduce the volume integral to a surface integral over the surface  $S$  of  $V$ :

$$\frac{dP_V(t)}{dt} = \text{Re} \left[ \frac{i\hbar}{\mu} \left( \int_S \Psi^* \nabla \Psi \cdot d\mathbf{S} - \int_V \nabla \Psi^* \cdot \nabla \Psi d\mathbf{r} \right) \right]$$

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<sup>1</sup>W. H. Miller, Charles Coulson Summer School Lecture Notes, 1996.

$$\begin{aligned}
&= -\text{Re} \int_S \Psi^* \frac{\mathbf{p}}{\mu} \Psi \cdot d\mathbf{S} \\
&= - \int_S \mathbf{j}(\mathbf{r}, t) \cdot d\mathbf{S},
\end{aligned} \tag{8}$$

where  $\mathbf{p} = -i\hbar\nabla$  is the momentum operator and  $\mathbf{j}(\mathbf{r}, t)$  is the *flux density*

$$\mathbf{j}(\mathbf{r}, t) = \text{Re} \left[ \Psi(\mathbf{r}, t)^* \frac{\mathbf{p}}{\mu} \Psi(\mathbf{r}, t) \right]. \tag{9}$$

(The minus sign in eq. (8) arises because if there is a net *outward* flux through  $S$ , so that  $\int_S \mathbf{j}(\mathbf{r}, t) \cdot d\mathbf{S} > 0$ , then the probability of finding the system in  $V$  will decrease with increasing  $t$ .)

Note that:

- (a) The flux density  $\mathbf{j}(\mathbf{r}, t)$  in eq. (9) has the dimensions of a probability density,  $\rho(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi(\mathbf{r}, t)^* \Psi(\mathbf{r}, t)$ , times a velocity,  $\mathbf{v} = \mathbf{p}/\mu$ . However, in quantum mechanics, the flux density is not simply the probability density times the velocity as it is in classical mechanics.
- (b) If  $\Psi(\mathbf{r}, t)$  has the trivial time-dependence  $\Psi(\mathbf{r}, t) = \Psi(\mathbf{r})e^{-iEt/\hbar}$  then both the probability density and the flux density are independent of  $t$ ; the *steady state flux* is  $\mathbf{j}(\mathbf{r}) = \text{Re} [\Psi(\mathbf{r})^* (\mathbf{p}/\mu) \Psi(\mathbf{r})]$ .
- (c) If  $\Psi(\mathbf{r})$  is real then (since  $\mathbf{p} = -i\hbar\nabla$ )  $\mathbf{j}(\mathbf{r}) = 0$ . Hence scattering theory *requires* complex wavefunctions.

*Exercises:*

- 1.1** If  $\Psi(\mathbf{r}) = e^{+ikz}$  and  $d\mathbf{S} = \hat{\mathbf{z}} dx dy = \hat{\mathbf{z}} dS$ , where  $\hat{\mathbf{z}}$  is a unit vector in the  $z$  direction, show that

$$\mathbf{j}(\mathbf{r}) \cdot d\mathbf{S} = \frac{\hbar k}{\mu} dS.$$

- 1.2** If  $\Psi(\mathbf{r}) = \frac{e^{+ikr}}{r} f(\theta)$  and  $d\mathbf{S} = \hat{\mathbf{r}} r^2 \sin\theta d\theta d\phi = \hat{\mathbf{r}} r^2 d\Omega$ , where  $\hat{\mathbf{r}}$  is a unit vector in the radial direction, show that

$$\mathbf{j}(\mathbf{r}) \cdot d\mathbf{S} \stackrel{r \rightarrow \infty}{\sim} \frac{\hbar k}{\mu} |f(\theta)|^2 d\Omega.$$

### 1.3 The scattering amplitude

Combining the results of these two exercises, it follows that if we can find a solution of the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \quad (10)$$

subject to the boundary condition

$$\Psi(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} e^{+ikz} + \frac{e^{+ikr}}{r} f(\theta), \quad (11)$$

then we can calculate the DCS in eq. (1) as

$$\begin{aligned} \frac{d\sigma(E)}{d\Omega} &= \frac{(\text{scattered flux into } d\Omega)/d\Omega}{(\text{incident flux through } dS)/dS} \\ &= \frac{(\hbar k/\mu)|f(\theta)|^2 d\Omega/d\Omega}{(\hbar k/\mu) dS/dS} \\ &= |f(\theta)|^2, \end{aligned} \quad (12)$$

and the ICS in eq. (2) as

$$\sigma(E) = 2\pi \int_0^\pi |f(\theta)|^2 \sin\theta d\theta. \quad (13)$$

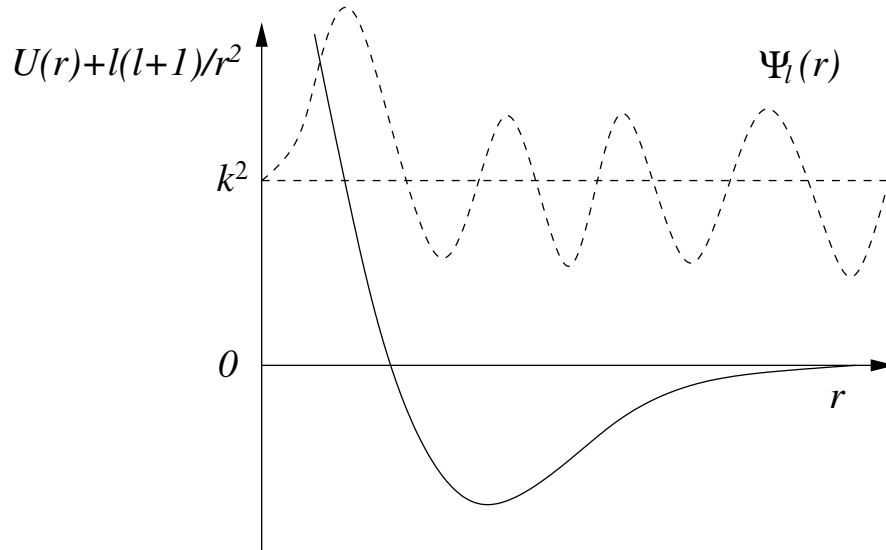
The function  $f(\theta)$  in eq. (11) is called the *scattering amplitude*; it is independent of the azimuthal angle  $\phi$  because of the cylindrical symmetry of the problem, and it has the dimensions of a length.

### 1.4 Partial wave phase shifts

The Hamiltonian

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r) = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{l}^2}{2\mu r^2} + V(r) \quad (14)$$

in eq. (10) commutes with  $\hat{l}^2$  and  $\hat{l}_z$ , so both  $l$  and  $m_l$  are conserved (constants of the motion). Furthermore, since the boundary condition in eq. (11) has cylindrical symmetry, we only have to consider solutions of the Schrödinger equation with  $m_l = 0$ .



These solutions have the general form

$$\Psi_l(\mathbf{r}) = \frac{1}{r} \psi_l(r) P_l(\cos \theta), \quad (15)$$

where  $\psi_l(r)$  satisfies the radial Schrödinger equation

$$\left[ \frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - U(r) \right] \psi_l(r) = 0, \quad (16)$$

with  $k^2 = 2\mu E/\hbar^2$  and  $U(r) = 2\mu V(r)/\hbar^2$ .

The behaviour of the radial wavefunction  $\psi_l(r)$  is sketched above.  $\psi_l(r)$  must be regular at the origin because of the factor of  $1/r$  in eq. (15),

$$\psi_l(r \rightarrow 0) \sim 0, \quad (17)$$

and (assuming that  $U(r)$  tends to zero faster than  $1/r$  as  $r \rightarrow \infty$ , which will certainly be true for atom-atom collisions)  $\psi_l(r)$  must tend asymptotically to a linear combination of  $\sin(kr)$  and  $\cos(kr)$  (or equivalently of  $e^{+ikr}$  and  $e^{-ikr}$ ). The coefficients in this linear combination are related by the boundary condition at the origin in eq. (17), which fixes one of the two independent

parameters that are needed to specify the solution of the second-order differential equation in eq. (16). It is convenient to choose the remaining parameter to be a *phase shift*,  $\eta_l$ , and to write the asymptotic ( $r \rightarrow \infty$ ) form of  $\psi_l(r)$  as

$$\psi_l(r \rightarrow \infty) \sim \sin(kr - l\pi/2 + \eta_l). \quad (18)$$

The reason for this choice is as follows. If the potential  $V(r)$  were zero, eq. (16) would be

$$\left[ \frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} \right] \psi_l(r) = 0. \quad (19)$$

This equation has two linearly-independent solutions, the Riccati-Bessel functions<sup>2</sup>  $\hat{j}_l(kr)$  and  $\hat{y}_l(kr)$ , but only one of these [ $\hat{j}_l(kr)$ ] is regular at the origin. Hence, for  $V(r) = 0$ ,  $\psi_l(r)$  is proportional to  $\hat{j}_l(kr)$ , and the asymptotic form of this function as  $r \rightarrow \infty$  is  $\hat{j}_l(kr) \sim \sin(kr - l\pi/2)$ . The phase shift  $\eta_l$  in eq. (18) therefore reflects the effect of the *potential* on the asymptotic form of  $\psi_l(r)$ , whereas the phase shift of  $-l\pi/2$  comes from the centrifugal barrier. Attractive potentials lead to positive phase shifts and repulsive potentials to negative phase shifts, as shown in exercise 1.6 below.

*Exercises:*

**1.3** Assuming that the potential  $V(r)$  is less singular than  $1/r^2$  as  $r \rightarrow 0$ , show that eqs. (16) and (17) imply  $\psi_l(r \rightarrow 0) \sim Cr^{l+1}$  for some constant  $C$ .

**1.4** Show that the boundary condition in eq. (18) can be written equivalently as

$$\psi_l(r \rightarrow \infty) \sim C_l \left[ e^{-i(kr - l\pi/2)} - e^{+i(kr - l\pi/2)} S_l \right],$$

where  $C_l = \frac{i}{2} e^{-i\eta_l}$  and  $S_l = e^{2i\eta_l}$ .

**1.5** Show that the s-wave ( $l = 0$ ) phase shift for the square-well potential

$$V(r) = \begin{cases} -V_0, & 0 \leq r < a, \\ 0, & a \leq r, \end{cases}$$

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<sup>2</sup>M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions (Dover, New York, 1965), Chapter 10.

is given by

$$\eta_0(k) = \arctan\left(\frac{k}{k'} \tan k'a\right) - ka,$$

where  $(k')^2 = 2\mu[E + V_0]/\hbar^2$ .

**1.6** Consider the scattering by a potential  $\lambda V(r)$  that depends on a multiplicative strength parameter  $0 \leq \lambda \leq 1$ ; i.e.,

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} - \lambda U(r)\right]\psi_l^\lambda(r) = 0,$$

subject to

$$\psi_l^\lambda(r \rightarrow 0) \sim 0,$$

and

$$\psi_l^\lambda(r \rightarrow \infty) \sim \sin(kr - l\pi/2 + \eta_l^\lambda).$$

Differentiate the first of these equations with respect to  $\lambda$ , pre-multiply by  $\psi_l^\lambda(r)$ , and integrate over  $r$  to show that

$$\int_0^R \psi_l^\lambda U \psi_l^\lambda dr = \left[ \psi_l^\lambda \frac{\partial^2 \psi_l^\lambda}{\partial r \partial \lambda} - \frac{\partial \psi_l^\lambda}{\partial r} \frac{\partial \psi_l^\lambda}{\partial \lambda} \right]_{r=0}^{r=R},$$

and hence, using the two boundary conditions, deduce that

$$\eta_l \equiv \eta_l^{\lambda=1} = -\frac{1}{k} \int_0^1 \left( \int_0^\infty \psi_l^\lambda U \psi_l^\lambda dr \right) d\lambda.$$

[It follows from this result (and the reality of  $\psi_l^\lambda(r)$ ) that a purely attractive potential  $V(r) \leq 0$  will give rise to a positive phase shift and a purely repulsive potential to a negative phase shift. Furthermore, it can be seen that the phase shift  $\eta_l$  goes to zero in the limit as the scattering energy  $E$  (and hence  $k$ ) goes to infinity.]

## 1.5 Partial wave expansion of $e^{+ikz}$

In order to make a connection between eq. (11) and eq. (15), and hence relate the scattering amplitude  $f(\theta)$  to the partial wave phase shifts  $\eta_l$ , we first need to determine the partial wave expansion of the incident plane wave  $e^{+ikz}$ .



This can be done<sup>3</sup> by expanding  $e^{+ikz}$  as in eq. (15),

$$e^{+ikz} \equiv e^{+ikr \cos \theta} = \frac{1}{r} \sum_{l=0}^{\infty} \phi_l(r) P_l(\cos \theta), \quad (20)$$

making the substitution  $x = \cos \theta$ , and using the orthogonality relation of the Legendre polynomials

$$\int_{-1}^1 P_l(x) P_{l'}(x) dx = \frac{2}{2l+1} \delta_{ll'}, \quad (21)$$

to extract the expansion coefficient  $\phi_l(r)$  as

$$\phi_l(r) = \frac{2l+1}{2} \int_{-1}^1 P_l(x) r e^{ikrx} dx. \quad (22)$$

All we need in eq. (11) is the asymptotic ( $r \rightarrow \infty$ ) form of  $\phi_l(r)$ , which can be obtained by integrating eq. (22) by parts and using the fact that  $P_l(\pm 1) = (\pm 1)^l$ :

$$\begin{aligned} \phi_l(r) &= \frac{2l+1}{2ik} \left\{ [P_l(x) e^{+ikrx}]_{-1}^1 - \int_{-1}^1 P_l'(x) e^{+ikrx} dx \right\} \\ &= \frac{2l+1}{2ik} [e^{+ikr} - (-1)^l e^{-ikr}] + O(1/r) \\ &= \frac{2l+1}{k} i^l \sin(kr - l\pi/2) + O(1/r). \end{aligned} \quad (23)$$

Hence

$$e^{+ikz} \underset{r \rightarrow \infty}{\sim} \sum_{l=0}^{\infty} \frac{2l+1}{kr} i^l \sin(kr - l\pi/2) P_l(\cos \theta). \quad (24)$$

*Aside:* This argument only gives the  $r \rightarrow \infty$  limit of  $e^{+ikz}$ . However, it is easy to generalize the result to all  $r$ . Since the plane wave  $e^{+ikz}$  is a solution of the Schrödinger equation in eq. (10) with the potential  $V(r)$  set equal to zero,  $\phi_l(r)$  must be a solution of eq. (19). Since this solution must also be regular at the origin, this implies that  $\phi_l(r) = C \hat{j}_l(kr)$ , where  $\hat{j}_l(kr)$  is the regular Riccati-Bessel function and  $C$  is a constant of proportionality. Finally, since

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<sup>3</sup>M. S. Child, *Molecular Collision Theory* (Dover, New York, 1996), Chapter 3.

the asymptotic ( $r \rightarrow \infty$ ) form of  $\hat{j}_l(kr)$  is  $\hat{j}_l(kr) \sim \sin(kr - l\pi/2)$ , eq. (23) fixes the constant  $C$  as  $(2l + 1)i^l/k$ . Hence eq. (24) generalizes to

$$e^{+ikz} = \sum_{l=0}^{\infty} (2l + 1)i^l j_l(kr) P_l(\cos \theta), \quad (25)$$

where  $j_l(kr) = \hat{j}_l(kr)/kr$ .

## 1.6 Integral and differential cross sections

Inserting in eq. (24) into eq. (11), and re-expanding  $\sin(kr - l\pi/2)$  in terms of exponentials, we obtain

$$\begin{aligned} \Psi(\mathbf{r}) \quad r \xrightarrow{\sim} \infty \quad & \frac{e^{+ikr}}{r} \cdot \left[ f(\theta) + \sum_{l=0}^{\infty} \frac{(2l + 1)}{2ik} P_l(\cos \theta) \right] \\ & - \frac{e^{-ikr}}{r} \cdot \sum_{l=0}^{\infty} \frac{(2l + 1)e^{il\pi}}{2ik} P_l(\cos \theta), \end{aligned} \quad (26)$$

whereas expanding  $\Psi(\mathbf{r})$  as

$$\Psi(\mathbf{r}) = \sum_{l=0}^{\infty} A_l \Psi_l(\mathbf{r}) \quad (27)$$

and using eqs. (15) and (18) gives

$$\begin{aligned} \Psi(\mathbf{r}) \quad r \xrightarrow{\sim} \infty \quad & \frac{e^{+ikr}}{r} \cdot \sum_{l=0}^{\infty} \frac{A_l e^{-il\pi/2+i\eta_l}}{2i} P_l(\cos \theta) \\ & - \frac{e^{-ikr}}{r} \cdot \sum_{l=0}^{\infty} \frac{A_l e^{+il\pi/2-i\eta_l}}{2i} P_l(\cos \theta). \end{aligned} \quad (28)$$

Equating the coefficients of  $e^{-ikr}/r$  in eqs. (26) and (28) gives

$$A_l = \frac{(2l + 1)e^{+il\pi/2+i\eta_l}}{k}, \quad (29)$$

and substituting this back into eq. (28) and equating the coefficients of  $e^{+ikr}/r$  gives

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l + 1) P_l(\cos \theta) (e^{2i\eta_l} - 1). \quad (30)$$

This is a major result, as it relates the scattering amplitude  $f(\theta)$ , and hence the differential and integral cross sections defined in Section 1.1, directly to the partial wave phase shifts  $\eta_l$ . The DCS is given by eq. (12) as  $|f(\theta)|^2$ , and the ICS can be obtained from eq. (13):

$$\begin{aligned}
\sigma(E) &= 2\pi \int_0^\pi |f(\theta)|^2 \sin \theta \, d\theta \\
&= \frac{\pi}{2k^2} \sum_{l=0}^{\infty} \sum_{l'=0}^{\infty} (2l+1)(2l'+1) (e^{-2i\eta_l} - 1) (e^{+2i\eta_{l'}} - 1) \\
&\quad \times \int_0^\pi P_l(\cos \theta) P_{l'}(\cos \theta) \sin \theta \, d\theta \\
&= \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l,
\end{aligned} \tag{31}$$

where we have used the orthogonality relation of the Legendre polynomials [eq. (21)] to obtain the bottom line.

*Exercises:*

**1.7** Use the identity  $P_l(1) = 1$  to derive the *optical theorem*

$$\sigma(E) = \frac{4\pi}{k} \text{Im } f(0).$$

**1.8** In the hard-sphere model of a collision between two atoms, the potential  $V(r)$  is infinite for  $r \leq d$  and zero for  $r > d$ , where  $d$  is the collision diameter. The classical cross section for this model is  $\sigma_{\text{cl}}(E) = \pi d^2$ , independent of the collision energy  $E$ . Show that the quantum mechanical cross section is exactly 4 times larger than this in the limit as  $E \rightarrow 0$ , where only the  $l = 0$  partial wave contributes to eq. (31). Why don't any other partial waves contribute in this limit?

## 1.7 The scattering matrix

Equations (30) and (31) can be written equivalently in terms of the *scattering matrix*  $S_l \equiv S_l(E)$  introduced in exercise 1.4,

$$S_l = e^{+2i\eta_l}, \tag{32}$$

as

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) (S_l - 1) \quad (33)$$

and

$$\sigma(E) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) |S_l - 1|^2 \quad (34)$$

respectively. Furthermore, it follows from exercise 1.4 that  $S_l$  can be computed directly (without first calculating  $\eta_l$ ) by solving the radial Schrödinger equation in eq. (16) subject to the boundary condition in eq. (17) and

$$\psi_l(r \rightarrow \infty) \sim v^{-1/2} e^{-i(kr-l\pi/2)} - v^{-1/2} e^{+i(kr-l\pi/2)} S_l, \quad (35)$$

where  $v = \hbar k / \mu$  is the asymptotic speed of the collision. This radial wavefunction differs from that in eq. (18) by a constant factor of  $-2iv^{-1/2} e^{+i\eta_l}$ , but this factor is immaterial because the problem is *homogeneous* (i.e., if  $\psi_l(r)$  is a solution of eqs. (16) and (17) then so is  $\lambda\psi_l(r)$  for any constant  $\lambda$ ). The speed factors of  $v^{-1/2}$  in eq. (35) flux-normalize the incoming and outgoing waves and have been included for later convenience.

The advantage of eqs. (33) and (34) over the corresponding phase shift formulae is that they generalize in a straightforward way to multichannel (inelastic and reactive) problems, where  $S_l(E)$  becomes a unitary matrix  $\mathbf{S}^J(E)$ . For example, the scattering amplitude for a state-to-state transition in an atom-diatom collision is given (in the helicity representation where  $k$  is the projection of  $j$  along  $\mathbf{k}$  and  $k'$  the projection of  $j'$  along  $\mathbf{k}'$ ) by

$$f_{v'j'k' \leftarrow vjk}(\theta) = \frac{1}{2ik_{vj}} \sum_{J=0}^{\infty} (2J+1) d_{k'k}^J(\theta) \left( S_{v'j'k',vjk}^J - \delta_{v'v} \delta_{j'j} \delta_{k'k} \right) \quad (36)$$

and the integral cross section by

$$\sigma_{v'j'k' \leftarrow vjk}(E) = \frac{\pi}{k_{vj}^2} \sum_{J=0}^{\infty} (2J+1) \left| S_{v'j'k',vjk}^J - \delta_{v'v} \delta_{j'j} \delta_{k'k} \right|^2, \quad (37)$$

where  $J$  is the conserved *total* angular momentum quantum number and  $d_{k'k}^J(\theta)$  is a reduced rotation matrix element. Since  $d_{00}^J(\theta) = P_J(\cos \theta)$ , eq. (36) is a straightforward generalization of eq. (33), and eq. (37) is the corresponding generalization of eq. (34). We shall return to discuss how to compute the scattering matrix  $\mathbf{S}^J(E)$  in Lecture 3.

## 2 Scattering “Theory”

### 2.1 S-wave potential scattering

In this Lecture we shall derive some of the central results of scattering theory in the simple context of s-wave ( $l = 0$ ) potential scattering. These results all generalize in a straightforward way to higher partial waves ( $l > 0$ ) by replacing  $\sin kr$  and  $\cos kr$  with the appropriate Riccati-Bessel functions [ $\hat{j}_l(kr)$  and  $\hat{y}_l(kr)$ ]. They also generalize to multichannel (inelastic and reactive) scattering problems.

The radial Schrödinger equation for s-wave potential scattering is

$$(E - H)\psi = 0, \quad (1)$$

where

$$H = H_0 + V = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r), \quad (2)$$

and we would like to solve this equation subject to eq. (1.17)

$$\psi(r \rightarrow 0) \sim 0, \quad (3)$$

and eq. (1.35)

$$\psi(r \rightarrow \infty) \sim v^{-1/2} e^{-ikr} - v^{-1/2} e^{+ikr} S(E), \quad (4)$$

where  $k^2 = 2\mu E/\hbar^2$  and  $v = \hbar k/\mu$ .

### 2.2 Free particle eigenstates

The eigenstates of the radial kinetic energy operator  $H_0 = p^2/2\mu$  that satisfy the boundary condition in eq. (3) are

$$\langle r|p\rangle = (2/\pi\hbar)^{1/2} \sin(pr/\hbar), \quad (5)$$

where the normalization constant has been chosen such that

$$\begin{aligned} \langle r|r'\rangle &= \int_0^\infty dp \langle r|p\rangle \langle p|r'\rangle \\ &= \frac{2}{\pi\hbar} \int_0^\infty dp \sin(pr/\hbar) \sin(pr'/\hbar) \\ &= \frac{1}{\pi} \int_0^\infty d\kappa [\cos \kappa(r - r') - \cos \kappa(r + r')] \\ &= \delta(r - r') - \delta(r + r'). \end{aligned} \quad (6)$$

Since  $r$  and  $r'$  are radial variables,  $r'$  cannot equal  $-r$ , and the second of the delta functions in eq. (6) can therefore be dropped to leave

$$\langle r|r'\rangle = \int_0^\infty dp \langle r|p\rangle \langle p|r'\rangle = \delta(r - r'); \quad (r, r' > 0). \quad (7)$$

A slight generalization of eq. (6) that we shall need below is that the coordinate matrix elements of any operator of the form  $f(H_0)$  are given by

$$\begin{aligned} \langle r|f(H_0)|r'\rangle &= \int_0^\infty dp \langle r|p\rangle f(p^2/2\mu) \langle p|r'\rangle \\ &= \frac{1}{\pi} \int_0^\infty d\kappa f(\hbar^2\kappa^2/2\mu) [\cos \kappa(r - r') - \cos \kappa(r + r')] \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty d\kappa f(\hbar^2\kappa^2/2\mu) [\cos \kappa(r - r') - \cos \kappa(r + r')], \end{aligned} \quad (8)$$

where we have used the fact that the integrand is an even function of  $\kappa$  to obtain the bottom line. Equation (6) is a special case of eq. (8) in which the operator  $f(H_0) = 1$  (the identity operator).

*Exercises:*

**2.1** Use the definition of  $\langle r|p\rangle$  in eq. (5) to show that

$$\langle p|p'\rangle = \int_0^\infty dr \langle p|r\rangle \langle r|p'\rangle = \delta(p - p'); \quad (p, p' > 0).$$

**2.2** Given that  $H_0|p\rangle = (p^2/2\mu)|p\rangle$  and that  $1 = \int_0^\infty dp |p\rangle \langle p|$ , show that the spectral representation

$$f(H_0) = \int_0^\infty dp |p\rangle f(p^2/2\mu) \langle p|$$

is valid for any function  $f(x)$  that can be expanded as a power series in  $x$ . (When  $f(x)$  is a rational function that can become singular at certain values of  $x$  we have to proceed a bit more carefully, as discussed in the following section.)

### 2.3 Integral equation formulation

The radial Schrödinger equation in eq. (1) can be re-written as an inhomogeneous equation

$$(E - H_0)\psi = V\psi, \quad (9)$$

and solved formally to give

$$\psi = \phi + (E - H_0)^{-1}V\psi, \quad (10)$$

where  $\phi$  satisfies the homogeneous equation

$$(E - H_0)\phi = 0. \quad (11)$$

In the coordinate representation, eq. (10) becomes an *integral equation* for the radial wavefunction  $\psi(r)$ ,

$$\psi(r) = \phi(r) + \int_0^\infty dr' G_0(r, r')V(r')\psi(r'), \quad (12)$$

where

$$G_0(r, r') = \langle r | (E - H_0)^{-1} | r' \rangle. \quad (13)$$

However, in order to complete this formulation, we still have to specify (i) how to choose the homogeneous solution  $\phi(r)$  and (ii) how to compute the Green's function matrix element  $G_0(r, r')$ . As we shall see, the answers to both of these questions are intimately associated with the boundary conditions on  $\psi(r)$  in eqs. (3) and (4).

Let us begin by considering the evaluation of  $G_0(r, r')$ . Since the operator  $(E - H_0)^{-1}$  is singular for positive real energies, we should be wary about using eq. (8). Nevertheless, if we go ahead and apply this equation we obtain

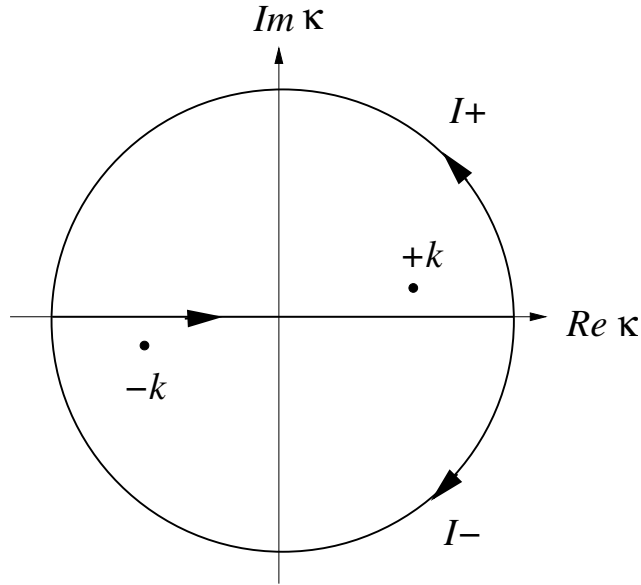
$$\begin{aligned} G_0(r, r') &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\kappa \frac{\cos \kappa(r - r') - \cos \kappa(r + r')}{E - \hbar^2 \kappa^2 / 2\mu} \\ &= \frac{\mu}{\pi \hbar^2} \int_{-\infty}^{\infty} d\kappa \frac{\cos \kappa(r - r') - \cos \kappa(r + r')}{k^2 - \kappa^2} \\ &\equiv c(|r - r'|) - c(r + r'), \end{aligned} \quad (14)$$

where

$$\begin{aligned}
 c(x) &= \frac{\mu}{\pi\hbar^2} \int_{-\infty}^{\infty} d\kappa \frac{\cos \kappa x}{k^2 - \kappa^2} \\
 &= \frac{\mu}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\kappa \frac{e^{+i\kappa x} + e^{-i\kappa x}}{k^2 - \kappa^2},
 \end{aligned} \tag{15}$$

with  $x \geq 0$ .

The integral in eq. (15) does not converge for real energies  $E = \hbar^2 k^2 / 2\mu$ , because the integrand diverges when  $\kappa = \pm k$ . This is precisely the difficulty we were anticipating. The standard way to avoid the problem is to replace  $E$  with  $E \pm i\epsilon$ , where  $\epsilon$  is a small but finite positive constant. In particular, if we choose the replacement  $E \rightarrow E + i\epsilon$ , the poles of the integrand will be shifted off the real integration axis and into the first and third quadrants of the complex  $\kappa$ -plane:



For finite  $\epsilon$ , the integral in eq. (15) can therefore be evaluated using the residue theorem, with the closed semi-circular contour  $I_+$  ( $I_-$ ) being used to reduce the integral involving  $e^{+i\kappa x}$  ( $e^{-i\kappa x}$ ) to  $+2\pi i$  ( $-2\pi i$ ) times the residue



of the pole at  $\kappa = +k$  ( $-k$ ):

$$c(x) = \frac{\mu}{2\pi\hbar^2} \left[ 2\pi i \frac{e^{+ikx}}{(-2k)} - 2\pi i \frac{e^{+ikx}}{(2k)} \right] = -\frac{i\mu}{\hbar^2 k} e^{+ikx}. \quad (16)$$

Combining this result with eq. (14), recalling that  $v = \hbar k/\mu$ , and taking the limit as  $\epsilon \rightarrow 0$  after having evaluated the integral, we obtain

$$\begin{aligned} G_0(r, r') &= \lim_{\epsilon \rightarrow 0} \langle r | (E + i\epsilon - H)^{-1} | r' \rangle \\ &= -\frac{i}{\hbar v} e^{+ik|r-r'|} + \frac{i}{\hbar v} e^{+ik(r+r')} \\ &= -\frac{i}{\hbar v} \left[ e^{+ik(r_>-r_<)} - e^{+ik(r_>+r_<)} \right] \\ &= -\frac{2}{\hbar v} \sin(kr_<) e^{+ikr_>}, \end{aligned} \quad (17)$$

where  $r_<$  ( $r_>$ ) is the lesser (greater) of  $r$  and  $r'$ . Hence the replacement  $E \rightarrow E + i\epsilon$  leads to an *outgoing-wave* ( $e^{+ikr_>}$ ) Green's function  $G_0(r, r')$ .

The final stage of the argument is to substitute eq. (17) back into eq. (12) and use the boundary conditions in eqs. (3) and (4) to determine the homogeneous solution  $\phi(r)$ . As  $r \rightarrow 0$  we obtain

$$\psi(r \rightarrow 0) \sim \phi(r) - \frac{2}{\hbar v} \sin kr \int_0^\infty dr' e^{+ikr'} V(r') \psi(r'), \quad (18)$$

which in view of eq. (3) implies that  $\phi(r \rightarrow 0) \sim 0$ . Hence  $\phi(r) = A \sin kr$ , where the constant  $A$  can be determined by examining the asymptotic form of  $\psi(r)$  as  $r \rightarrow \infty$ :

$$\psi(r \rightarrow \infty) \sim \frac{A}{2i} (e^{+ikr} - e^{-ikr}) - \frac{2}{\hbar v} e^{+ikr} \int_0^\infty dr' \sin(kr') V(r') \psi(r'). \quad (19)$$

Comparing the coefficient of  $e^{-ikr}$  in this equation with that in eq. (4) gives  $A = -2iv^{-1/2}$ , and therefore

$$\phi(r) = -2iv^{-1/2} \sin kr. \quad (20)$$

Finally, substituting this value of  $A$  back into eq. (19) and comparing the coefficient of  $e^{+ikr}$  with that in eq. (4), we obtain an integral representation

for the scattering matrix:

$$\begin{aligned} S(E) &= 1 + \frac{i}{\hbar} \int_0^\infty dr' \phi(r') V(r') \psi(r') \\ &= 1 - \frac{i}{\hbar} \int_0^\infty dr' \phi(r')^* V(r') \psi(r'), \end{aligned} \quad (21)$$

where we have used the fact that  $\phi(r)$  is purely imaginary (see eq. (20)) in the second line.

*Exercises:*

- 2.3** Show that the replacement  $E \rightarrow E - i\epsilon$  in eq. (15) leads to an incoming-wave Green's function of the form

$$G_0(r, r') = -\frac{2}{\hbar v} \sin(kr_<) e^{-ikr_>},$$

i.e., to the complex conjugate of eq. (17).

- 2.4** Show further that this incoming-wave Green's function is inconsistent with the boundary conditions on  $\psi(r)$  in eqs. (3) and (4); i.e., that if the incoming-wave Green's function is used then no choice of the homogeneous solution  $\phi(r)$  can be made so as to satisfy both boundary conditions.

## 2.4 Time-independent scattering theory

### 2.4.1 Green's operators

The outgoing-wave Green's function  $G_0(r, r')$  in eq. (17) can be regarded as a coordinate matrix element of a free-particle Green's *operator*

$$G_0(E) = (E + i\epsilon - H_0)^{-1}, \quad (22)$$

where the limit as  $\epsilon \rightarrow 0$  is implied in the sense of eq. (17). Similarly, we can define an analogous Green's operator for the full potential scattering problem:

$$G(E) = (E + i\epsilon - H)^{-1}. \quad (23)$$

These two Green's operators are clearly related by the fact that  $H = H_0 + V$ , which implies that

$$G_0(E)^{-1} = E + i\epsilon - H_0 = (E + i\epsilon - H) + V = G(E)^{-1} + V. \quad (24)$$

Pre-multiplying eq. (24) by  $G(E)$  and post-multiplying by  $G_0(E)$  gives

$$G(E) = G_0(E) + G(E)VG_0(E), \quad (25)$$

whereas pre-multiplying by  $G_0(E)$  and post-multiplying by  $G(E)$  gives

$$G(E) = G_0(E) + G_0(E)VG(E). \quad (26)$$

Equation (25) (or equivalently eq. (26)) is known as the *Lippmann-Schwinger equation* for  $G(E)$ .

### 2.4.2 The Born series

The integral equation in eq. (12) can be written in terms of  $G_0(E)$  as

$$|\psi\rangle = |\phi\rangle + G_0(E)V|\psi\rangle, \quad (27)$$

and the integral expression for  $S(E)$  in eq. (21) is

$$S(E) = 1 - \frac{i}{\hbar} \langle \phi | V | \psi \rangle. \quad (28)$$

Equation (27) can be solved formally to give

$$|\psi\rangle = [1 - G_0(E)V]^{-1} |\phi\rangle, \quad (29)$$

and substituting this into eq. (28) gives

$$S(E) = 1 - \frac{i}{\hbar} \langle \phi | V [1 - G_0(E)V]^{-1} |\phi\rangle. \quad (30)$$

If we now expand the inverse in eq. (29) as a binomial series,  $(1 - x)^{-1} = 1 + x + x^2 + \dots$ , we obtain

$$|\psi\rangle = |\phi\rangle + G_0(E)V|\phi\rangle + G_0(E)VG_0(E)V|\phi\rangle + \dots, \quad (31)$$

and the corresponding expansion in eq. (30) gives

$$S(E) = 1 - \frac{i}{\hbar} \langle \phi | V | \phi \rangle - \frac{i}{\hbar} \langle \phi | V G_0(E) V | \phi \rangle + \dots \quad (32)$$

Equation (31) is known as the *Born series* for the scattering wavefunction  $|\psi\rangle$ , and eq. (32) is the Born series for the scattering matrix. The terms in both series are straightforward to calculate in the coordinate representation, where the third term in eq. (32) (for example) becomes

$$\langle \phi | V G_0(E) V | \phi \rangle = \int_0^\infty dr \int_0^\infty dr' \phi(r)^* V(r) G_0(r, r') V(r') \phi(r'), \quad (33)$$

with  $G_0(r, r')$  given in eq. (17) and  $\phi(r)$  in eq. (20).

However, since the binomial expansion  $(1 - x)^{-1} = 1 + x + x^2 + \dots$  only converges for  $|x| < 1$ , the Born series does not always converge. It is most likely to converge if the potential  $V(r)$  is “weak” and the scattering energy  $E$  is “large”, in which case the *Born approximation*

$$S(E) \simeq 1 - \frac{i}{\hbar} \langle \phi | V | \phi \rangle \quad (34)$$

is likely to dominate. This is invariably the case in neutron scattering (where  $V$  is weak), and often the case in high-energy electron scattering (where  $E$  is large). However, the Born series nearly always *diverges* for thermal-energy atomic and molecular collisions.

### 2.4.3 The transition operator

A better way to proceed for molecular collision problems is therefore to abandon the Born series and concentrate instead on the exact *transition operator*

$$T(E) = V[1 - G_0(E)V]^{-1} \quad (35)$$

that appears in eq. (30), in terms of which the S matrix can be calculated as

$$S(E) = 1 - \frac{i}{\hbar} \langle \phi | T(E) | \phi \rangle. \quad (36)$$

A more convenient expression for  $T(E)$  can be obtained by using eq. (24) to eliminate  $G_0(E)$  from eq. (35) in favour of the full scattering Green's operator  $G(E)$ :

$$\begin{aligned}
T(E) &= V[1 - G_0(E)V]^{-1} \\
&= V[1 - G_0(E)V]^{-1}[1 - G_0(E)V + G_0(E)V] \\
&= V + V[1 - G_0(E)V]^{-1}G_0(E)V \\
&= V + V[G_0(E)^{-1} - V]^{-1}V \\
&= V + VG(E)V.
\end{aligned} \tag{37}$$

This is an expression for  $T(E)$  in terms of  $G(E)$ , but it can easily be inverted to obtain an expression for  $G(E)$  in terms of  $T(E)$ . If we post-multiply both sides of eq. (37) by  $G_0(E)$  and use the Lippmann-Schwinger equation in eq. (25) we obtain

$$T(E)G_0(E) = V[G_0(E) + G(E)VG_0(E)] = VG(E), \tag{38}$$

and using this to replace  $VG(E)$  with  $T(E)G_0(E)$  in eq. (26) gives

$$G(E) = G_0(E) + G_0(E)T(E)G_0(E). \tag{39}$$

This equation will be used as the starting point for deriving a time-dependent wavepacket formula for  $S(E)$  in the following section.

## 2.5 Time-dependent scattering theory

The above equations can be taken into the time domain by noting that

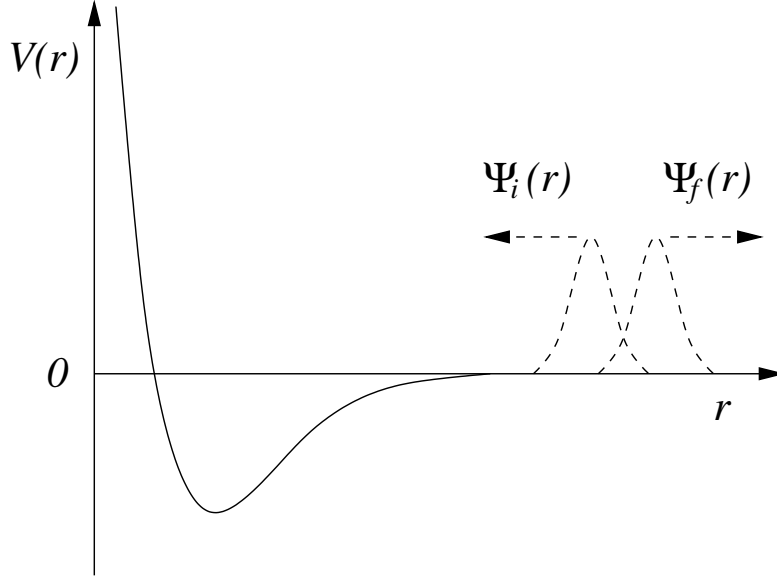
$$\int_0^\infty dt e^{+i(E+i\epsilon-H)t/\hbar} = \left[ \frac{e^{+i(E+i\epsilon-H)t/\hbar}}{i(E+i\epsilon-H)/\hbar} \right]_0^\infty = i\hbar(E+i\epsilon-H)^{-1}, \tag{40}$$

and therefore

$$G(E) = (E+i\epsilon-H)^{-1} = -\frac{i}{\hbar} \int_0^\infty dt e^{+i(E+i\epsilon-H)t/\hbar}, \tag{41}$$

where the  $+i\epsilon$  now plays the role of a convergence factor for the integral over (positive)  $t$ .

As an application of eq. (41), consider a matrix element of  $G(E) - G_0(E)$  between two localized (square integrable) wavepackets  $|\psi_i\rangle$  and  $|\psi_f\rangle$  that lie beyond the range of the interaction potential:



$$\langle \psi_f | G(E) - G_0(E) | \psi_i \rangle = -\frac{i}{\hbar} \int_0^\infty dt e^{+iEt/\hbar} [C(t) - C_0(t)], \quad (42)$$

where

$$C(t) = \langle \psi_f | e^{-i(H-i\epsilon)t/\hbar} | \psi_i \rangle \equiv \langle \psi_f(0) | \psi_i(t) \rangle, \quad (43)$$

and (similarly)

$$C_0(t) = \langle \psi_f | e^{-i(H_0-i\epsilon)t/\hbar} | \psi_i \rangle. \quad (44)$$

According to eq. (39), the matrix element on the left-hand side of eq. (42) can be written equivalently as

$$\begin{aligned} \langle \psi_f | G(E) - G_0(E) | \psi_i \rangle &= \langle \psi_f | G_0(E) T(E) G_0(E) | \psi_i \rangle \\ &= \int_0^\infty dr \int_0^\infty dr' \int_0^\infty dr'' \int_0^\infty dr''' \\ &\times \psi_f(r)^* G_0(r, r') \langle r' | T(E) | r'' \rangle G_0(r'', r''') \psi_i(r'''), \end{aligned} \quad (45)$$

where  $G_0(r, r')$  is given by eqs. (17) and (20) as

$$G_0(r, r') = -\frac{i}{\hbar} \phi(r_<) \phi^+(r_>), \quad (46)$$

with

$$\phi(r) = \phi^-(r) - \phi^+(r), \quad (47)$$

and

$$\phi^\pm(r) = v^{-1/2} e^{\pm ikr}. \quad (48)$$

Now from the expression for  $T(E)$  in eq. (37), we know that the matrix element  $\langle r' | T(E) | r'' \rangle$  will only be non-zero if both  $r'$  and  $r''$  lie within the range of the potential, whereas  $\psi_f(r)$  and  $\psi_i(r''')$  in eq. (45) are only non-zero (by construction) if  $r$  and  $r'''$  lie beyond the potential. Hence  $r$  is the greater of  $r'$  and  $r''$ , and  $r'''$  is the greater of  $r''$  and  $r'''$ , and the integrand in eq. (45) becomes

$$+\frac{1}{\hbar^2} \psi_f(r)^* \phi^+(r) \phi(r')^* \langle r' | T(E) | r'' \rangle \phi(r'') \phi^-(r''')^* \psi_i(r'''),$$

where we have used the fact that  $\phi(r')$  is purely imaginary and  $\phi^-(r''')$  is the complex conjugate of  $\phi^+(r''')$ . Integrating over all four radial variables therefore gives

$$\langle \psi_f | G(E) - G_0(E) | \psi_i \rangle = \frac{1}{\hbar^2} \langle \psi_f | \phi^+ \rangle \langle \phi | T(E) | \phi \rangle \langle \phi^- | \psi_i \rangle, \quad (49)$$

which when combined with eqs. (36) and (42) gives the scattering matrix  $S(E)$  as

$$S(E) = 1 - \frac{1}{\langle \psi_f | \phi^+ \rangle \langle \phi^- | \psi_i \rangle} \int_0^\infty dt e^{+iEt/\hbar} [C(t) - C_0(t)] \quad (50)$$

where the correlation functions  $C(t)$  and  $C_0(t)$  are defined in eqs. (43) and (44).

Equation (50) shows that the scattering matrix  $S(E)$  can be calculated at all energies by propagating the initial wavepacket  $|\psi_i\rangle$  forwards in time under the influence of the full Hamiltonian  $H$  (to give  $C(t)$ ) and the free-particle Hamiltonian  $H_0$  (to give  $C_0(t)$ ). The multichannel generalization of this equation<sup>4</sup> provides one of the most promising modern methods for calculating state-to-state reactive scattering matrix elements, as we shall discuss further in Lecture 4.

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<sup>4</sup>See: W. H. Miller, *Advan. Chem. Phys.* 25 (1974) 69; Section III.A

*Exercises:*

**2.5** Use the Lorentzian representation of the delta function,

$$\delta(x) = \frac{1}{\pi} \lim_{\epsilon \rightarrow 0} \frac{\epsilon}{x^2 + \epsilon^2},$$

to obtain an expression for the microcanonical density operator  $\delta(E - H)$  in terms of the imaginary part of the outgoing-wave Green's operator  $G(E) = (E + i\epsilon - H)^{-1}$ .

**2.6** Find a time-dependent expression analogous to that in eq. (41) for the incoming-wave Green's operator  $G(E) = (E - i\epsilon - H)^{-1}$ .

**2.7** Show that if the final wavepacket  $|\psi_f\rangle$  is localized at larger  $r$  than the initial wavepacket  $|\psi_i\rangle$  then eq. (50) can be simplified to

$$S(E) = \frac{\langle \phi^+ | \psi_i \rangle}{\langle \phi^- | \psi_i \rangle} - \frac{1}{\langle \psi_f | \phi^+ \rangle \langle \phi^- | \psi_i \rangle} \int_0^\infty dt e^{+iEt/\hbar} C(t),$$

whereas if  $|\psi_f\rangle$  is localized at smaller  $r$  than  $|\psi_i\rangle$  then

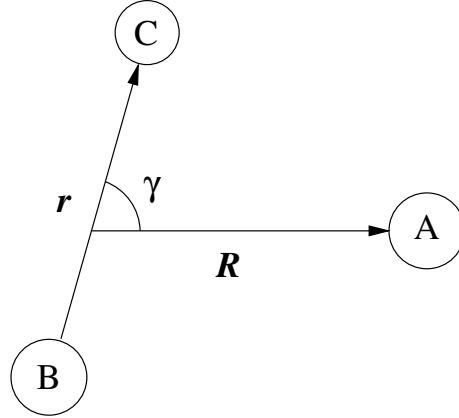
$$S(E) = \frac{\langle \psi_f | \phi^- \rangle}{\langle \psi_f | \phi^+ \rangle} - \frac{1}{\langle \psi_f | \phi^+ \rangle \langle \phi^- | \psi_i \rangle} \int_0^\infty dt e^{+iEt/\hbar} C(t).$$



### 3 Inelastic Scattering

#### 3.1 Close-coupled equations

Now consider a collision between a structureless ( $^1S$ ) atom A and a structureless ( $^1\Sigma$ ) diatomic molecule BC:



The Hamiltonian in the centre-of-mass frame is

$$H = -\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 + h(\mathbf{r}) + V(R, r, \gamma), \quad (1)$$

where

$$h(\mathbf{r}) = -\frac{\hbar^2}{2\mu_r}\nabla_r^2 + v(r). \quad (2)$$

In eq. (1),  $\mu = m_A m_{BC}/m_{ABC}$  is the reduced mass of the collision, and  $V(R, r, \gamma)$  is the interaction potential between the atom and the diatomic molecule. In eq. (2),  $\mu_r = m_B m_C/m_{BC}$  is the diatomic reduced mass and  $v(r)$  is the diatomic potential. Combining both equations gives

$$H = -\frac{\hbar^2}{2\mu} \frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{l}^2}{2\mu R^2} - \frac{\hbar^2}{2\mu_r} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{j}^2}{2\mu_r r^2} + V(R, r, \gamma), \quad (3)$$

where  $\hat{l}^2$  is the squared orbital angular momentum operator associated with the rotation of the vector  $\mathbf{R}$ ,  $\hat{j}^2$  is the squared rotational angular momentum operator associated with the rotation of the vector  $\mathbf{r}$ , and  $V(R, r, \gamma) =$

$V(R, r, \gamma) + v(r)$  is the full triatomic interaction potential. Two preliminary observations will be useful before we consider how to solve  $H\Psi = E\Psi$ .

The first is that, since the Hamiltonian  $H$  in eq. (3) commutes with  $\hat{J}^2 = (\hat{l} + \hat{j})^2$  and  $\hat{J}_z = \hat{l}_z + \hat{j}_z$ , the total angular momentum quantum number  $J$  and the projection quantum number  $M$  are both conserved. The eigenstates of  $\hat{J}^2$  and  $\hat{J}_z$  can be formed by coupling  $Y_{lm_l}(\hat{\mathbf{R}}) \equiv Y_{lm_l}(\Theta, \Phi)$  with  $Y_{jm_j}(\hat{\mathbf{r}}) \equiv Y_{jm_j}(\theta, \phi)$  to obtain

$$\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = \sum_{m_j m_l} Y_{lm_l}(\hat{\mathbf{R}}) Y_{jm_j}(\hat{\mathbf{r}}) \langle jm_j, lm_l | JM \rangle, \quad (4)$$

where  $\langle jm_j, lm_l | JM \rangle$  is a vector-coupling coefficient<sup>5</sup> and the sums over  $m_j \in [-j, j]$  and  $m_l \in [-l, l]$  are restricted by the requirement that  $M = m_j + m_l$ . The functions  $\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$  in eq. (4) are simultaneous eigenfunctions of the commuting operators  $\hat{J}^2$ ,  $\hat{J}_z$ ,  $\hat{l}^2$  and  $\hat{j}^2$ ,

$$\begin{aligned} \hat{J}^2 \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= \hbar^2 J(J+1) \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \\ \hat{J}_z \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= \hbar M \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \\ \hat{l}^2 \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= \hbar^2 l(l+1) \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \\ \hat{j}^2 \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) &= \hbar^2 j(j+1) \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}), \end{aligned} \quad (5)$$

and they are normalized such that

$$\int d\hat{\mathbf{R}} \int d\hat{\mathbf{r}} \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})^* \mathcal{Y}_{j'l'}^{J'M'}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = \delta_{JJ'} \delta_{MM'} \delta_{jj'} \delta_{ll'}. \quad (6)$$

Equations (5) are especially convenient because both  $\hat{l}^2$  and  $\hat{j}^2$  appear in eq. (3).

The second observation is that at long range, as  $R \rightarrow \infty$ , the interaction potential  $V(R, r, \gamma)$  between the atom and the diatomic molecule tends to zero. Hence eq. (1) *separates* at large  $R$  into

$$H \stackrel{R \rightarrow \infty}{\sim} -\frac{\hbar^2}{2\mu} \nabla_R^2 + h(\mathbf{r}), \quad (7)$$

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<sup>5</sup>R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).

where  $h(\mathbf{r})$  is the diatomic Hamiltonian. Assuming that the collision energy is not too high, we need only concern ourselves with the bound states of this Hamiltonian, which are given by

$$\Psi_{vjm_j}(\mathbf{r}) = \frac{1}{r} \phi_{vj}(r) Y_{jm_j}(\hat{\mathbf{r}}), \quad (8)$$

where  $\phi_{vj}(r)$  satisfies the radial Schrödinger equation

$$\left[ -\frac{\hbar^2}{2\mu_r} \frac{d^2}{dr^2} + \frac{j(j+1)}{2\mu_r r^2} + v(r) \right] \phi_{vj}(r) = E_{vj} \phi_{vj}(r), \quad (9)$$

and may be normalized such that

$$\int_0^\infty dr \phi_{vj}(r)^* \phi_{v'j'}(r) = \delta_{vv'}. \quad (10)$$

Combining these two observations, we see that the solutions  $\Psi^{JM}$  of the time-independent Schrödinger equation

$$H\Psi^{JM} = E\Psi^{JM} \quad (11)$$

can conveniently be expanded as

$$\Psi^{JM}(\mathbf{R}, \mathbf{r}) = \frac{1}{Rr} \sum_{v'j'l'} \psi_{v'j'l'}^{JM}(R) \mathcal{Y}_{j'l'}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \phi_{v'j'}(r), \quad (12)$$

where only the radial expansion coefficients  $\psi_{v'j'l'}^{JM}(R)$  remain to be determined. Substituting eq. (12) into eq. (11), pre-multiplying by

$$\frac{2\mu}{\hbar^2} \frac{1}{Rr} \phi_{vj}(r)^* \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})^*,$$

and integrating over  $\hat{\mathbf{R}}$  and  $\mathbf{r}$  with the help of eqs. (6) and (10), we obtain a set of *close-coupled equations* for these expansion coefficients:

$$\left[ \frac{d^2}{dR^2} + k_{vj}^2 - \frac{l(l+1)}{R^2} \right] \psi_{vj}^{JM}(R) = \frac{2\mu}{\hbar^2} \sum_{v'j'l'} V_{vj, v'j'l'}^{JM}(R) \psi_{v'j'l'}^{JM}(R), \quad (13)$$

where

$$k_{vj}^2 = \frac{2\mu}{\hbar^2} [E - E_{vj}], \quad (14)$$

and

$$V_{vj, v'j'l'}^{JM}(R) = \int d\hat{\mathbf{R}} \int d\hat{\mathbf{r}} \int dr \phi_{vj}(r)^* \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})^* V(R, r, \gamma) \mathcal{Y}_{j'l'}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \phi_{v'j'}(r). \quad (15)$$

Several comments about these equations are now in order:

- (a) Channels  $vjl$  with internal energies  $E_{vj} \gg E$  are strongly classically forbidden, and therefore make a negligible contribution to the wavefunction. Hence, in a practical calculation, the expansion in eq. (12) can be truncated to a finite number ( $N$ ) of channels.
- (b) With this truncation, eq. (13) becomes a straightforward matrix generalization of eq. (1.16),

$$\left[ \frac{d^2}{dR^2} + k^2 - \frac{l(l+1)}{R^2} - U(R) \right] \psi(R) = 0, \quad (16)$$

where  $k^2$  and  $l(l+1)$  are diagonal matrices with diagonal elements  $k_{vj}^2$  and  $l(l+1)$ ,  $U(R) = 2\mu V(R)/\hbar^2$  is a full ( $N \times N$ ) matrix with elements  $2\mu V_{vj'l, v'j'l'}^{JM}(R)/\hbar^2$ , and  $\psi(R)$  is a column vector with elements  $\psi_{vj'l}^{JM}(R)$ .

- (c) The potential matrix  $V(R)$  is manifestly hermitian from eq. (15). Furthermore, it can be shown that its matrix elements are both (i) real and (ii) independent of  $M$ , neither of which is quite so obvious from eq. (15). Hence  $V(R)$  and  $U(R)$  will be assumed to be real and symmetric matrices and we shall drop all reference to the  $M$  quantum number in what follows.
- (d) In view of the  $1/R$  factor in eq. (12), the boundary condition on  $\psi(R)$  at the origin is

$$\psi(R \rightarrow 0) \sim 0. \quad (17)$$

If there were only one radial equation ( $N = 1$ ), this would be sufficient to determine  $\psi(R)$  to within a multiplicative constant  $\lambda$ , as discussed in Lecture 1. However, for  $N$  coupled radial equations, there are  $N$  linearly-independent solutions of eq. (16) that satisfy the boundary condition in eq. (17), as illustrated in exercise 3.2 below.

- (e) It is convenient to collect these solutions together as the columns of an ( $N \times N$ ) regular solution *matrix*,  $\Psi(R)$ , which satisfies

$$\left[ \frac{d^2}{dR^2} + k^2 - \frac{l(l+1)}{R^2} - U(R) \right] \Psi(R) = 0, \quad (18)$$

subject to

$$\Psi(R \rightarrow 0) \sim 0, \quad (19)$$

these two equations only being sufficient to determine  $\Psi(R)$  to within a post-multiplicative constant matrix  $\Lambda$  by virtue of the homogeneity of the problem.

- (f) The arbitrariness in the choice of  $\Lambda$  can be removed by specifying the boundary condition on  $\Psi(R)$  as  $R \rightarrow \infty$ , which we shall take to be a direct matrix generalization of eq. (1.35):

$$\Psi(R \rightarrow \infty) \sim I(R) - O(R)S, \quad (20)$$

where  $I(R)$  and  $O(R)$  are diagonal matrices of incoming and outgoing waves with diagonal elements that satisfy

$$\begin{aligned} I_{vjl}(R \rightarrow \infty) &\sim k_{vj}^{-1/2} e^{-i(k_{vj}R - l\pi/2)} \\ O_{vjl}(R \rightarrow \infty) &\sim k_{vj}^{-1/2} e^{+i(k_{vj}R - l\pi/2)}, \end{aligned} \quad (21)$$

and  $S$  is a complex *scattering matrix* with elements  $S_{vjl, v'j'l'}^J(E)$ . [Note that we have chosen here to use normalization factors of  $k_{vj}^{-1/2}$  rather than  $v_{vj}^{-1/2}$ , where  $v_{vj} = \hbar k_{vj}/\mu$ . This turns out to be more convenient for some of the things we are about to do.]

- (g) Rather than choosing  $I(R)$  and  $O(R)$  to have the forms in eq. (21) for all  $R$ , and therefore to be solutions of

$$\left[ \frac{d^2}{dR^2} + k^2 \right] \begin{Bmatrix} I(R) \\ O(R) \end{Bmatrix} = 0, \quad (22)$$

it is better to choose them to be solutions of eq. (18) with the interaction potential  $U(R)$  set equal to zero:

$$\left[ \frac{d^2}{dR^2} + k^2 - \frac{l(l+1)}{R^2} \right] \begin{Bmatrix} I(R) \\ O(R) \end{Bmatrix} = 0. \quad (23)$$

In view of the asymptotic forms in eq. (21), this fixes  $I_{vjl}(R)$  and  $O_{vjl}(R)$  as

$$\begin{aligned} I_{vjl}(R) &= k_{vj}^{-1/2} \hat{h}_l^-(k_{vj}R) \\ O_{vjl}(R) &= k_{vj}^{-1/2} \hat{h}_l^+(k_{vj}R), \end{aligned} \quad (24)$$

where  $\hat{h}_l^\pm(x) = -\hat{y}_l(x) \pm i\hat{j}_l(x)$ . The advantage of these equations is that they allow eq. (20) to be used as soon as the interaction potential matrix elements are negligible, whereas the asymptotic forms in eq. (21) are only valid once the centrifugal potential  $l(l+1)/R^2$  can also be ignored. Since the elements of  $U(R)$  typically decay much faster than  $1/R^2$  (e.g., the dipole-induced dipole and dispersion interactions between A and BC decay like  $1/R^6$ ), this is a worthwhile thing to do.

*Exercises:*

- 3.1** Use equations (1) to (12) to verify eq. (13).
- 3.2** By diagonalizing the  $(2 \times 2)$  coupling matrix or otherwise, construct 2 independent solutions of the 2 coupled equations

$$\begin{bmatrix} \psi_a''(R) \\ \psi_b''(R) \end{bmatrix} = \begin{bmatrix} -2 & 1 \\ 1 & -2 \end{bmatrix} \begin{bmatrix} \psi_a(R) \\ \psi_b(R) \end{bmatrix},$$

both of which are regular at the origin. (The condition for the two solutions,  $\psi_1$  and  $\psi_2$ , to be independent is that the determinant of the corresponding wavefunction matrix,

$$|\Psi(R)| = \begin{vmatrix} \psi_{a1}(R) & \psi_{a2}(R) \\ \psi_{b1}(R) & \psi_{b2}(R) \end{vmatrix},$$

does not vanish identically for all  $R$ . The determinant *may* however vanish at certain isolated values of  $R$ : does yours?)

- 3.3** The Wronskian of the incoming and outgoing waves  $I(R)$  and  $O(R)$  is

$$\Omega(R) = I(R)O'(R) - I'(R)O(R),$$

where the primes denote differentiation with respect to  $R$ . Use eq. (23) to show that  $\Omega(R)$  is independent of  $R$ , and hence (using eq. (21)) show that  $\Omega(R) = +2i$ . (Hint: Since  $I(R)$ ,  $O(R)$ ,  $\Omega(R)$ ,  $k^2$ , and  $l(l+1)$  are all diagonal matrices, this is just a scalar calculation.)

## 3.2 The log derivative method

We have shown in the last section that, for each conserved value of  $J$ , the atom-diatom inelastic scattering problem can be reduced to solving a set of close-coupled equations of the form

$$\Psi''(R) = W(R)\Psi(R), \quad (25)$$

where the real and symmetric coupling matrix  $W(R)$  is given by eq. (18) as

$$W(R) = U(R) + \frac{l(l+1)}{R^2} - k^2 \quad (26)$$

and the wavefunction matrix  $\Psi(R)$  satisfies the boundary conditions in eqs. (19) and (20). Close-coupled equations with this same generic form also arise in *all* other inelastic scattering problems.

The log derivative method<sup>6</sup> is a stable and efficient method for solving these equations. It is based on the *log derivative matrix*  $Y(R) = d \ln \Psi(R)/dR$ , which is defined at all  $R$  for which the wavefunction matrix is non-singular by the matrix Riccati transformation

$$\Psi'(R) = Y(R)\Psi(R). \quad (27)$$

Differentiating this equation throughout with respect to  $R$ , and using eq. (25) to eliminate  $\Psi''(R)$ , we obtain a non-linear differential equation for  $Y(R)$  known as the matrix Riccati equation:

$$Y'(R) = W(R) - Y(R)^2. \quad (28)$$

Since this equation is first-order, the solution  $Y(R)$  is uniquely determined for all  $R$  once an appropriate initial value has been specified, and this initial value is uniquely determined by the boundary condition at the origin in eq. (19).

For example, in inelastic atom-diatom scattering problems, the eigenvalues of the coupling matrix  $W(R)$  typically become very large and positive at small  $R$  due both to the centrifugal potential  $l(l+1)/R^2$  and to the repulsive

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<sup>6</sup>B. R. Johnson, *J. Comput. Phys.* 13 (1973) 445.

nature of the short-range interaction potential. Under these circumstances, it is legitimate to neglect the derivative  $Y'(R)$  on the left-hand side of eq. (28) to obtain the WKB initial value

$$Y(R_i) \simeq +W(R_i)^{\frac{1}{2}}, \quad (29)$$

where  $R_i$  lies in the strongly classically forbidden region and the choice of a positive square root corresponds to a wavefunction that increases exponentially with increasing  $R$  (in accordance with eq. (19)). In practice, eq. (29) can be evaluated by diagonalizing  $W(R_i)$  with an orthogonal transformation matrix  $C(R_i)$  to give a diagonal matrix  $w(R_i)$  of positive eigenvalues,

$$C(R_i)^T W(R_i) C(R_i) = w(R_i), \quad (30)$$

and then computing  $Y(R_i)$  as

$$Y(R_i) \simeq C(R_i) w(R_i)^{\frac{1}{2}} C(R_i)^T. \quad (31)$$

This initial value is clearly a real and symmetric matrix, and it follows from eq. (28) and the symmetry of  $W(R)$  that  $Y(R)$  will remain real and symmetric for all  $R$ .

Once  $Y(R_i)$  has been initialized using eq. (31), we can use any one of a number of log derivative propagation methods<sup>7</sup> to integrate eq. (28) from  $R_i$  to  $R_f$ , where  $R_i$  lies in the classically forbidden region and  $R_f$  lies beyond the range of the interaction potential. With  $Y(R_f)$  in hand, we can then combine eqs. (20) and (27) to obtain

$$[I'(R_f) - O'(R_f)S] = Y(R_f)[I(R_f) - O(R_f)S], \quad (32)$$

and solve this equation for the  $S$  matrix:

$$S = [Y(R_f)O(R_f) - O'(R_f)]^{-1}[Y(R_f)I(R_f) - I'(R_f)]. \quad (33)$$

It is also possible to obtain a more symmetrical expression for  $S$  by using the Wronskian of  $I(R_f)$  and  $O(R_f)$  derived in exercise 3.3,

$$I(R_f)O'(R_f) - I'(R_f)O(R_f) = +2i, \quad (34)$$

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<sup>7</sup>See, e.g., D. E. Manolopoulos, J. Chem. Phys. 85 (1986) 6425.



to eliminate  $I'(R_f)$  from eq. (33) as follows:

$$\begin{aligned}
S &= [YO - O']^{-1}[YI - I'] \\
&= O^{-1}[Y - O'O^{-1}]^{-1}[Y - I'I^{-1}]I \\
&= O^{-1}[Y - O'O^{-1}]^{-1}[Y - O'O^{-1} + O'O^{-1} - I'I^{-1}]I \\
&= O^{-1}I + O^{-1}[Y - O'O^{-1}]^{-1}[O'O^{-1} - I'I^{-1}]I \\
&= O^{-1}I + O^{-1}[Y - O'O^{-1}]^{-1}O^{-1}[IO' - I'O] \\
&= O^{-1}I + 2i O^{-1}[Y - O'O^{-1}]^{-1}O^{-1}, \tag{35}
\end{aligned}$$

where we have made repeated use of the fact that  $I$ ,  $O$ ,  $I'$  and  $O'$  are all diagonal matrices and therefore commute. Hence eq. (33) can be written equivalently as

$$S = A(R_f) + 2i B(R_f)[Y(R_f) - C(R_f)]^{-1}B(R_f), \tag{36}$$

where the diagonal matrices  $A(R_f)$ ,  $B(R_f)$  and  $C(R_f)$  are defined by

$$\begin{aligned}
A(R_f) &= O(R_f)^{-1}I(R_f) \\
B(R_f) &= O(R_f)^{-1} \\
C(R_f) &= O'(R_f)O(R_f)^{-1}, \tag{37}
\end{aligned}$$

and all reference to  $I'(R_f)$  has been eliminated. We shall use eqs. (33) and (36) to prove the unitarity and symmetry of the  $S$  matrix in the following section.

*Exercises:*

- 3.4** Assuming that the elements of the interaction potential  $U(R)$  are less singular than  $1/R^2$  as  $R \rightarrow 0$ , show that eqs. (18), (19) and (27) imply

$$Y(R \rightarrow 0) \sim \frac{l+1}{R},$$

which is manifestly real and symmetric like eq. (31).

- 3.5** By considering the single-channel (scalar) case for simplicity, and writing  $W(R)$  as  $W(R) = P(R)^2/\hbar^2$ , use eq. (28) to obtain the first two terms in a power series expansion of  $\hbar Y(R)$  in  $\hbar$ , and hence comment on the validity of eq. (29).

### 3.3 Unitarity and symmetry of the $S$ matrix

One of the nicest features of the log derivative method is that it leads to an exactly unitary and symmetric  $S$  matrix. In order to show this, we shall begin by supposing that no closed channels are retained in the coupled-channel expansion, so that all the  $k_{vj}$ 's in eq. (21) are real. The diagonal matrices  $I(R_f)$  and  $O(R_f)$  are then simply complex conjugates, and since  $Y(R_f)$  is real eq. (33) gives

$$S^* = [Y(R_f)I(R_f) - I'(R_f)]^{-1}[Y(R_f)O(R_f) - O'(R_f)] = S^{-1}. \quad (38)$$

But since  $Y(R_f)$  is also symmetric, and  $A(R_f)$ ,  $B(R_f)$  and  $C(R_f)$  are all diagonal, it is immediately apparent from eq. (36) that

$$S^T = S. \quad (39)$$

Combining these two results gives

$$S^\dagger = (S^T)^* = S^* = S^{-1}, \quad (40)$$

which proves that a real and symmetric log derivative matrix  $Y(R_f)$  leads to a unitary [eq. (40)] and symmetric [eq. (39)]  $S$  matrix.

If some closed channels *are* retained in the coupled-channel expansion, then we can write eq. (36) out in block-matrix notation as

$$\begin{aligned} \begin{bmatrix} S_{oo} & S_{oc} \\ S_{co} & S_{cc} \end{bmatrix} &= \begin{bmatrix} A_{oo} & 0 \\ 0 & A_{cc} \end{bmatrix} \\ &+ 2i \begin{bmatrix} B_{oo} & 0 \\ 0 & B_{cc} \end{bmatrix} \begin{bmatrix} Y_{oo} - C_{oo} & Y_{oc} \\ Y_{co} & Y_{cc} - C_{cc} \end{bmatrix}^{-1} \begin{bmatrix} B_{oo} & 0 \\ 0 & B_{cc} \end{bmatrix}, \end{aligned} \quad (41)$$

from which it is clear that the open-channel submatrix  $S_{oo}$  of  $S$  can be calculated as

$$S_{oo} = A_{oo} + 2iB_{oo}([Y - C]^{-1})_{oo}B_{oo}. \quad (42)$$

We shall leave it as an exercise to show that

$$([Y - C]^{-1})_{oo} = [\tilde{Y}_{oo} - C_{oo}]^{-1}, \quad (43)$$

where the effective open-channel log derivative matrix  $\tilde{Y}_{oo}$  is given by

$$\tilde{Y}_{oo} = Y_{oo} - Y_{oc}[Y_{cc} - C_{cc}]^{-1}Y_{co}, \quad (44)$$

and therefore that  $S_{oo}$  can be calculated using a formula with an identical structure to eq. (36):

$$S_{oo} = A_{oo} + 2iB_{oo}[\tilde{Y}_{oo} - C_{oo}]^{-1}B_{oo}. \quad (45)$$

Now it follows from eq. (21) that if  $k_{vj}$  is purely imaginary,  $k_{vj} = +i\kappa_{vj}$ , then  $C_{vjl}(R) = O'_{vjl}(R)O_{vjl}(R)^{-1}$  will tend to  $-\kappa_{vj}$  as  $R \rightarrow \infty$ , which is purely real. Hence the matrix  $C_{cc}$  in eq. (44) is real and diagonal, and  $\tilde{Y}_{oo}$  is therefore real and symmetric in view of the reality and symmetry of the full log derivative matrix  $Y$ . Thus an identical argument to that given above shows that the open-channel submatrix  $S_{oo}$  of  $S$  will be unitary and symmetric regardless of whether or not there are any closed channels.

Physically, the unitarity of the (open-channel)  $S$  matrix ensures that the incoming and outgoing fluxes in eq. (20) are equal, or that the “total number of particles in the system is conserved”, while the symmetry of  $S$  ensures that the flux scattered from channel  $vjl$  to channel  $v'j'l'$  is equal to that scattered in the reverse direction.

*Exercise:*

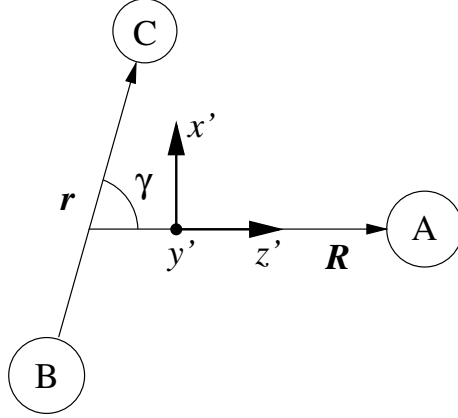
**3.6** Use the block-matrix identity

$$\begin{bmatrix} M_{oo} & M_{oc} \\ M_{co} & M_{cc} \end{bmatrix} \begin{bmatrix} (M^{-1})_{oo} \\ (M^{-1})_{co} \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix},$$

to verify eq. (43). (Hint: Write the identity out as two separate matrix equations and then eliminate  $(M^{-1})_{co}$ .)

### 3.4 The helicity representation ...

Two remaining issues that we have not addressed are (i) how to evaluate the potential energy matrix elements in eq. (15) and (ii) how to calculate integral and differential cross sections for inelastic scattering. Both of these issues are simplified by transforming to the so-called *helicity representation*, and indeed we have already stated the equations for integral and differential cross sections in this representation in Lecture 1.



The helicity representation revolves around the molecule-fixed  $(x'y'z')$  axes shown above, which can be obtained by rotating the laboratory-fixed  $(x, y, z)$  axes through the Euler angles  $\Omega = (\Phi, \Theta, \Psi)$ , where  $\Theta$  and  $\Phi$  are the polar and azimuthal angles of the vector  $\mathbf{R}$  and  $\Psi$  is a final rotation around  $\mathbf{R}$  to bring  $\mathbf{r}$  into the  $x'z'$  plane.

The advantage of choosing the molecule-fixed  $z'$  axis to lie along  $\mathbf{R}$  is that the projection of the orbital angular momentum  $m'_l$  on this axis is zero, and hence the molecule-fixed projections of  $j$  and  $J$  are the same:  $m'_j = M' = k$ . Therefore, both  $m'_j$  and  $m'_l$  are determined once the *helicity* quantum number  $k$  has been specified, and it follows from this that the molecule-fixed axes analogue of eq. (4) does not involve any summation. I.e.,

$$\mathcal{Y}_{jl}^{JM'}(\hat{\mathbf{R}}', \hat{\mathbf{r}}') = \sum_{m'_j m'_l} Y_{lm'_l}(\hat{\mathbf{R}}') Y_{jm'_j}(\hat{\mathbf{r}}') \langle jm'_j, lm'_l | JM' \rangle, \quad (46)$$

becomes simply

$$\begin{aligned} \mathcal{Y}_{jl}^{Jk}(\hat{\mathbf{R}}', \hat{\mathbf{r}}') &= Y_{l0}(\hat{\mathbf{R}}') Y_{jk}(\hat{\mathbf{r}}') \langle jk, l0 | Jk \rangle \\ &= Y_{l0}(\Theta', \Phi') Y_{jk}(\theta', \phi') \langle jk, l0 | Jk \rangle \\ &= Y_{l0}(0, 0) Y_{jk}(\gamma, 0) \langle jk, l0 | Jk \rangle, \end{aligned} \quad (47)$$

where we have referred to the above diagram to obtain the final line (e.g., to note that the polar and azimuthal angles of  $\mathbf{r}$  relative to the molecule-fixed axes are  $\gamma$  and 0 respectively).

The functions  $\mathcal{Y}_{jl}^{Jk}(\hat{\mathbf{R}}', \hat{\mathbf{r}}')$  in eq. (47) are related to the functions  $\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$  in eq. (4) by the fact that the molecule-fixed and laboratory-fixed axes, which define both the primed and unprimed coordinates and the quantization directions for  $k$  and  $M$ , differ by a rotation through the Euler angles  $\Omega = (\Phi, \Theta, \Psi)$ . Hence, according (e.g.) to eq. (3.121) of Zare, we have

$$\mathcal{Y}_{jl}^{Jk}(\hat{\mathbf{R}}', \hat{\mathbf{r}}') = \sum_M \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) D_{Mk}^J(\Omega), \quad (48)$$

and therefore also

$$\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = \sum_k \mathcal{Y}_{jl}^{Jk}(\hat{\mathbf{R}}', \hat{\mathbf{r}}') D_{kM}^J(-\Omega) = \sum_k \mathcal{Y}_{jl}^{Jk}(\hat{\mathbf{R}}', \hat{\mathbf{r}}') D_{Mk}^J(\Omega)^*, \quad (49)$$

where  $D_{Mk}^J(\Omega)$  is a Wigner rotation matrix element. Combining this with eq. (47), and noting that

$$Y_{l0}(0, 0) = \left( \frac{2l+1}{4\pi} \right)^{1/2}, \quad (50)$$

we find that  $\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$  can be written equivalently as

$$\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) = \sum_k C_{kl}^{Jj} \mathcal{Y}_{jk}^{JM}(\gamma, \Omega), \quad (51)$$

where

$$C_{kl}^{Jj} = \left( \frac{2l+1}{2J+1} \right)^{1/2} \langle jk, l0 | Jk \rangle \equiv (-1)^{j-k} \langle jk, J-k | l0 \rangle \quad (52)$$

and

$$\mathcal{Y}_{jk}^{JM}(\gamma, \Omega) = \left( \frac{2J+1}{4\pi} \right)^{1/2} Y_{jk}(\gamma, 0) D_{Mk}^J(\Omega)^*. \quad (53)$$

Equation (51) is a key result, because it relates the angular basis functions  $\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$  of the orbital angular momentum representation (in which the quantum number  $l$  is specified) to the basis functions  $\mathcal{Y}_{jk}^{JM}(\gamma, \Omega)$  of the helicity representation (in which  $k$  is specified in place of  $l$ ). Indeed one can show further that, for given values of  $J$  and  $j$ , the coefficient  $C_{kl}^{Jj}$  in eq. (52) is an element of an *orthogonal* transformation matrix between the two representations, so that eq. (51) can be inverted to give

$$\mathcal{Y}_{jk}^{JM}(\gamma, \Omega) = \sum_l C_{kl}^{Jj} \mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}}). \quad (54)$$

*Exercise:*

**3.7** Use the second expression for  $C_{kl}^{Jj}$  in eq. (52) and the orthogonality relations of the vector-coupling coefficients (Zare, eqs. (2.8) and (2.9))

$$\sum_{m_1 m_2} \langle jm | j_1 m_1, j_2 m_2 \rangle \langle j_1 m_1, j_2 m_2 | j' m' \rangle = \delta_{jj'} \delta_{mm'}$$

and

$$\sum_{jm} \langle j_1 m_1, j_2 m_2 | jm \rangle \langle jm | j_1 m'_1, j_2 m'_2 \rangle = \delta_{m_1 m'_1} \delta_{m_2 m'_2},$$

to show that

$$\sum_k C_{kl}^{Jj} C_{k'l'}^{Jj} = \delta_{ll'}$$

and

$$\sum_l C_{kl}^{Jj} C_{k'l}^{Jj} = \delta_{kk'},$$

i.e., that the matrix  $C^{Jj}$  is orthogonal.

### 3.5 ... and (one of) its applications

The theory in Section 3.1 was developed exclusively in the orbital angular momentum representation, where the functions  $\mathcal{Y}_{jl}^{JM}(\hat{\mathbf{R}}, \hat{\mathbf{r}})$  are used as angular basis functions. However, since the helicity representation is only an orthogonal transformation away, there is no reason why one should not use this instead as the primary representation.

There are in fact several good reasons for doing so, including the fact (which we have touched on but not proved) that it simplifies the calculation of differential inelastic (and also reactive) scattering cross sections. It also leads to a useful angular momentum decoupling approximation (the *coupled-states* or *centrifugal-sudden* approximation), which simplifies calculations by reducing the number of coupled equations that have to be solved.

Unfortunately, we shall not have time to cover these topics in this lecture (see, e.g., Child<sup>8</sup> and Pack<sup>9</sup> for more details if you are interested). However,

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<sup>8</sup>M. S. Child, *Molecular Collision Theory*, Chapter 6.

<sup>9</sup>R. T. Pack, *J. Chem. Phys.* 60 (1974) 633.

we can at least quickly demonstrate the utility of the helicity representation by using it to evaluate the interaction potential matrix elements in eq. (15).

Substituting eq. (51) (twice) into eq. (15), expanding  $\mathcal{Y}_{jk}^{JM}(\gamma, \Omega)$  as in eq. (53), and noting that the integrals over the angular coordinates  $\hat{\mathbf{R}}$  and  $\hat{\mathbf{r}}$  can be written in terms of  $\gamma$  and  $\Omega$  as

$$\int d\hat{\mathbf{R}} \int d\hat{\mathbf{r}} = \int_0^\pi \sin \gamma d\gamma \int d\Omega, \quad (55)$$

we obtain

$$V_{vj, v'j'l'}^{JM}(R) = \sum_{kk'} C_{kl}^{Jj} V_{vjk, v'j'k'}^{JM}(R) C_{k'l'}^{Jj}, \quad (56)$$

where the potential matrix elements in the helicity representation are given by

$$\begin{aligned} V_{vj, v'j'k'}^{JM}(R) &= \int_0^\infty dr \int_0^\pi \sin \gamma d\gamma \\ &\times \phi_{vj}(r)^* Y_{jk}(\gamma, 0)^* V(R, r, \gamma) Y_{j'k'}(\gamma, 0) \phi_{v'j'}(r) \\ &\times \frac{2J+1}{4\pi} \int d\Omega D_{Mk}^J(\Omega) D_{Mk'}^J(\Omega)^*. \end{aligned} \quad (57)$$

But since the integral over the Euler angles can now be evaluated using the orthogonality relation of the rotation matrices (Zare eq. (3.113)),

$$\int d\Omega D_{Mk}^J(\Omega) D_{Mk'}^J(\Omega)^* = \frac{8\pi^2}{2J+1} \delta_{kk'}, \quad (58)$$

we see that the potential is actually *diagonal* in the helicity quantum number:

$$\begin{aligned} V_{vj, v'j'k'}^{JM}(R) &= 2\pi \delta_{kk'} \int_0^\infty dr \int_0^\pi \sin \gamma d\gamma \\ &\times \phi_{vj}(r)^* Y_{jk}(\gamma, 0)^* V(R, r, \gamma) Y_{j'k}(\gamma, 0) \phi_{v'j'}(r). \end{aligned} \quad (59)$$

This is clearly one advantage of the helicity representation over the orbital angular momentum representation, since the potential is certainly *not* diagonal in  $l$  (see eq. (56)). Furthermore, it follows from eq. (59) (and the fact that the vibrational wavefunctions  $\phi_{vj}(r)$  can be chosen to be real) that the potential energy matrices in both representations are indeed (i) real and (ii) independent of  $M$ , as stated in Section 3.1.