Introduction to Time-Independent Scattering Theory

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Contents

1 Reaction Rate and Cross Section

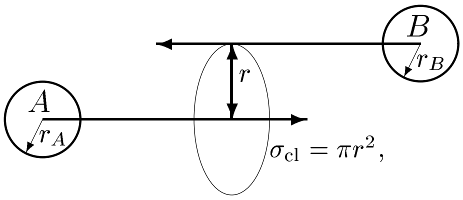
Consider a chemical reaction between reactants A and B, forming products C and D:

$$A + B \xrightarrow{k(T)} C + D. \tag{1}$$

The temperature-dependent rate of product formation is given by:

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = k(T)[A][B], \tag{2}$$

where $[\,\cdot\,]$ is in units of inverse volume, so $k(T)$ is in units of volume per time. In the classical hard-sphere model, reaction in assumed to occur when two particles collide. The scattering cross section σ_{cl} for two hard spherical particles A and B moving at relative velocity $\mathbf{v} = \mathbf{v}_A - \mathbf{v}_B$ is defined as shown below:



where $r = r_A + r_B$. The kinetic theory of gases provides the machinery to derive collision rates, mean free paths etc. for ideal gases. The *reactive scattering cross section* (σ) for reactants A and B is defined such that only collisions that lead to formation of $C + D$ contribute to the cross section. The connection between $k(T)$ and σ is given by:

$$k(T) = \langle v\sigma \rangle = \int_0^\infty \mathrm{d}v\ \sigma(E)P(v)v^2, \tag{3}$$

where $\langle\,\cdot\,\rangle$ denotes an expectation value, v is the relative velocity: $v = |\mathbf{v}_A - \mathbf{v}_B|$, scattering energy $E = \frac{1}{2}\mu v^2$ and

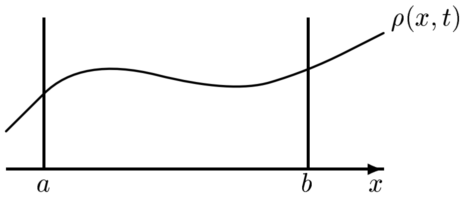
$$P(v) = \frac{e^{-E/kT}}{\int \mathrm{d}v\ v^2 e^{-E/kT}}, \tag{4}$$

represents Maxwell's relative velocity distribution. Notice that like the classical cross section σ is in units of area, but that the reactive cross section differs from the classical cross section in that it is no longer independent of scattering energy.

Scattering processes are usually divided into *inelastic*, *elastic* and *reactive* processes. In inelastic scattering events, the collision partners A and B exchange momentum only, and the internal structure of the colliding particles is conserved, as in ideal gases for instance. During inelastic scattering events, the colliding particles may exchange energy. Examples are spin-flip collisions or collision-induced vibrational relaxation. In reactive scattering events particles can be exchanged, like in chemical reactions. In principle, cross sections for these processes can be computed quantum mechanically. In this course we focus on the quantum mechanical description of elastic scattering processes.

2 Flux

Consider a 1-particle probability density function $\rho(r,t)$ in a 1-D region $[a,b]$:



The chance P_{ab} to find the particle in $[a,b]$ is given by:

$$P_{ab}(t) = \int_a^b \mathrm{d}x\ \rho(x,t). \tag{5}$$

The *flux* $j(x)$ through a point is defined via the change in time of the probability P_{ab}:

$$\dot{P}_{ab}(t) \quad = \quad \int_a^b \mathrm{d}x\ \dot{\rho}(x,t) \equiv j(a) - j(b), \tag{6}$$

where the dot denotes the time-derivative d/dt.

Similarly we can regard the 1-particle density $\rho(\mathbf{r},t)$ in three dimensions. The chance P to find the particle in some volume V of space is given by:

$$P_V(t) = \iiint\limits_V \rho(\mathbf{r},t)\mathrm{d}V, \tag{7}$$

where dV denotes the volume element. In Cartesian coordinates we have $dV = dxdydz$. The flux $\mathbf{j}$ through a point is a quantity with a direction and a magnitude, i.e. it is a vector. It is defined by:

$$\dot{P}_V(t) = \iiint\limits_V \dot{\rho}(\mathbf{r},t)\mathrm{d}V \equiv \iint\limits_S \mathbf{j}\cdot\vec{n}\ \mathrm{d}S = \oiint\limits_S \mathbf{j}\cdot\mathrm{d}\mathbf{S} \tag{8}$$

where S is the surface enclosing V and $\vec{n}$ the unit vector normal to the local surface. So the change in probability of finding a particle in some region V is given by integration over all flux normal to the surface S enclosing V. Next, we develop an expression for quantum mechanical flux associated with the wave function, but before we continue we need the following theorem from vector calculus:

Green's symmetrical theorem:

$$\iiint_V (\phi\nabla^2\psi) - \psi\nabla^2\phi)\ \mathrm{d}V = \oint\!\!\oint_S (\phi\nabla\psi - \psi\nabla\phi)\cdot \mathrm{d}\mathbf{S} \tag{9}$$

proof: for the proof we need Gauss' theorem, which relates a volume integral to a surface integral[Sch]:

$$\iiint_V \nabla\cdot\mathbf{a}\ \mathrm{d}V = \oint\!\!\oint_S \mathbf{a}\cdot\mathrm{d}\mathbf{S}. \tag{10}$$

First write the vector function **a** as a scalar function multiplied by the divergence of another scalar function:

$$\mathbf{a} = \phi\nabla\psi. \tag{11}$$

Using Eq. (11) we get:

$$\nabla\mathbf{a} = \nabla(\phi\nabla\psi) = (\nabla\phi)\cdot\nabla\psi + \phi\nabla^2\psi. \tag{12}$$

Now, substitute Eq. (12) into Eq. (10) once as it is, and once with the arguments ϕ and ψ exchanged. Subtracting the two results yields:

$$\begin{aligned}\iiint_V (\nabla\phi)\cdot\nabla\psi + \phi\nabla^2\psi)\mathrm{d}V - \iiint_V (\nabla\psi)\cdot\nabla\phi + \psi\nabla^2\phi)\mathrm{d}V \\ = \oint\!\!\oint_S (\phi\nabla\psi)\cdot\mathrm{d}\mathbf{S} - \oint\!\!\oint_S \psi\nabla\phi\cdot\mathrm{d}\mathbf{S} \\ \iiint_V (\phi\nabla^2\psi - \psi\nabla^2\phi)\ \mathrm{d}V = \oint\!\!\oint_S (\phi\nabla\psi - \psi\nabla\phi)\cdot\mathrm{d}\mathbf{S}. \quad \square\end{aligned} \tag{13}$$

The quantum mechanical probability density is given by:

$$\rho = |\psi|^2 = \psi^*\psi, \tag{14}$$

where ψ is the wave function, which obeys the Schrödinger equation:

$$i\hbar\dot{\psi} \quad = \quad \hat{H}\psi. \tag{15}$$

The time derivative of ρ is given by:

$$\begin{aligned}\dot{\rho} &= \frac{d}{dt}(\psi^*\psi) = \dot{\psi}^*\psi + \psi^*\dot{\psi} \\ &= \frac{i}{\hbar}\hat{H}\psi^*\psi - \frac{i}{\hbar}\psi^*\hat{H}\psi \\ &= \frac{-i}{\hbar}(\psi^*\hat{H}\psi - \psi\hat{H}\psi^*),\end{aligned} \tag{16}$$

where we used $\dot{\psi} = -i/\hbar \hat{H}\psi$ in the second line. The Hamiltonian for two colliding particles in the center-of-mass frame is effectively a 1-particle Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r}), \tag{17}$$

where μ is the reduced mass and $V(\mathbf{r})$ is the inter particle potential. Substituting $\hat{H}$ into Eq. (16) gives:

$$\begin{aligned} \dot{\rho} &= \frac{i}{\hbar}\frac{\hbar^2}{2\mu}\left(\psi^*[\nabla^2 + V(\mathbf{r})]\psi - \psi[\nabla^2 + V(\mathbf{r})]\psi^*\right) \\ &= \frac{i\hbar}{2\mu}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*), \end{aligned} \tag{18}$$

where we used in the second line that $V(\mathbf{r})$ is real so that $\psi^* V(\mathbf{r})\psi$ is also real. We now compute the change in density and apply Green's symmetrical theorem:

$$\begin{aligned} \dot{P}_V(t) &= \iiint\limits_V \dot{\rho}\ \mathrm{d}V = \frac{i\hbar}{2\mu}\iiint\limits_V (\psi^*\nabla^2\psi - \psi\nabla^2\psi^*)\ \mathrm{d}V \\ &= \frac{i\hbar}{2\mu}\oiint\limits_S (\psi^*\nabla\psi - \psi\nabla\psi^*)\cdot \mathrm{d}\mathbf{S}. \end{aligned} \tag{19}$$

Comparing this with Eq. (8) we define:

$$-\mathbf{j} \equiv \frac{i\hbar}{2\mu}(\psi^*\nabla\psi - \psi\nabla\psi^*) = -\frac{\hbar}{\mu}\Im[\psi^*\nabla\psi] \tag{20}$$

where we introduced the minus sign in our definition to make sure that positive flux causes a decrease in density in volume V, and we used that $z - z^* = 2i\Im[z]$ for any complex z. So the quantum mechanical flux $\mathbf{j}$ is given by:

$$\boxed{\mathbf{j}(\mathbf{r},t) = \frac{\hbar}{\mu}\Im[\psi^*(\mathbf{r},t)\nabla\psi(\mathbf{r},t)].} \tag{21}$$

Since the Hamiltonian (Eq. 17) does not depend on time, energy is conserved and the wave function may be written as:

$$\psi(\mathbf{r},t) = e^{-iEt/\hbar}\psi(\mathbf{r}), \tag{22}$$

where E is the total energy of the system, and $\psi(\mathbf{r})$ obeys the time-independent Schrödinger equation:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{23}$$

Substituting Eq. (22) into Eq. (21), we find that the flux is also time-independent:

$$\mathbf{j} = \frac{\hbar}{\mu}\Im[\psi^*(\mathbf{r},t)\nabla\psi(\mathbf{r},t)] \tag{24}$$

$$= \frac{\hbar}{\mu}\Im[e^{iEt/\hbar}\psi^*(\mathbf{r})\nabla e^{-iEt/\hbar}\psi(\mathbf{r})] \tag{25}$$

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{\mu}\Im[\psi^*(\mathbf{r})\nabla\psi(\mathbf{r})]. \tag{26}$$

3 Free Particles

In this section we discuss properties of eigenfunctions of the time-independent free-particle Hamiltonian $\hat{H}_0$:

$$\hat{H}_0 = \frac{-\hbar^2}{2\mu}\nabla^2. \tag{27}$$

The time-independent eigenfunctions are plane waves:

$$\begin{aligned} \hat{H}_0|\psi_{\mathbf{k}}\rangle &= E|\psi_{\mathbf{k}}\rangle = \frac{\hbar^2 k^2}{2\mu}|\psi_{\mathbf{k}}\rangle & (28) \\ \psi_{\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ik_x r_x}e^{ik_y r_y}e^{ik_z r_z}. & (29) \end{aligned}$$

where $\mathbf{k}$ is the *wave vector*. The flux associated with plane waves is readily computed using Eq. (21):

$$\begin{aligned} \mathbf{j} &= \frac{\hbar}{\mu}\Im[\psi^*\nabla\psi] & (30) \\ \begin{pmatrix} j_x \\ j_y \\ j_z \end{pmatrix} &= \frac{\hbar}{\mu}\Im\begin{pmatrix} e^{-ik_x r_x}e^{-ik_y r_y}e^{-ik_z r_z}\frac{d}{dx}e^{ik_x r_x}e^{ik_y r_y}e^{ik_z r_z} \\ e^{-ik_x r_x}e^{-ik_y r_y}e^{-ik_z r_z}\frac{d}{dy}e^{ik_x r_x}e^{ik_y r_y}e^{ik_z r_z} \\ e^{-ik_x r_x}e^{-ik_y r_y}e^{-ik_z r_z}\frac{d}{dz}e^{ik_x r_x}e^{ik_y r_y}e^{ik_z r_z} \end{pmatrix} & (31) \\ &= \frac{\hbar}{\mu}\Im\begin{pmatrix} ik_x \\ ik_y \\ ik_z \end{pmatrix} & (32) \\ \mathbf{j} &= \frac{\hbar\mathbf{k}}{\mu}. & (33) \end{aligned}$$

The plane waves have a well-defined momentum $\mathbf{p}$:

$$\begin{aligned} \hat{\mathbf{p}}|\psi_{\mathbf{k}}\rangle &= -i\hbar\nabla e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}|\psi_{\mathbf{k}}\rangle & (34) \\ &= \mathbf{p}|\psi_{\mathbf{k}}\rangle. & (35) \end{aligned}$$

In polar coordinates, the Hamiltonian reads:

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\hat{\mathbf{l}}^2}{2\mu r^2}, \tag{36}$$

where $\hat{\mathbf{l}}$ is the angular momentum operator acting on the polar angles (θ, φ) given by $\hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. The commutation relations for components of $\hat{\mathbf{l}}$ follow from Heisenberg's canonical commutation relations for $\hat{r}$ and $\hat{p}$ and are given by:

$$[\hat{l}_i, \hat{l}_j] = i\hbar\sum_k \hat{l}_k\epsilon_{ijk}, \tag{37}$$

where ϵ_{ijk} is the Levi-Cevita tensor which is 1 for ϵ_{xyz} and cyclic permutations of the indices, -1 for acyclic permutations of x, y and z, and zero otherwise.

Proof: using

$$\begin{aligned}\hat{l}_k &= (\hat{\mathbf{r}} \times \hat{\mathbf{p}})_k = \sum_{ij} \hat{r}_i \hat{p}_j \epsilon_{ijk} && (38)\\ [\hat{r}_i, \hat{p}_j] &= i\hbar\delta_{ij} && (39)\\ [\hat{r}_i, \hat{r}_j] &= [\hat{p}_i, \hat{p}_j] = 0. && (40)\end{aligned}$$

we get:

$$\begin{aligned}[\hat{l}_i, \hat{l}_j] = \sum_{mm'nn'} & \epsilon_{mni}\epsilon_{m'n'j}[\hat{r}_m\hat{p}_n, \hat{r}_{m'}\hat{p}_{n'}] \\ = & \sum_{mm'nn'} \epsilon_{mni}\epsilon_{m'n'j}\hat{r}_{m'}[\hat{r}_m\hat{p}_n, \hat{p}_{n'}] - [\hat{r}_{m'}, \hat{r}_m\hat{p}_n]\hat{p}_{n'} \\ = & \sum_{mm'nn'} \epsilon_{mni}\epsilon_{m'n'j} \\ & \times \hat{r}_{m'}([\hat{r}_m, \hat{p}_{n'}]\hat{p}_n - \hat{r}_m[\hat{p}_{n'}, \hat{p}_n]) - (\hat{r}_m[\hat{r}_{m'}, \hat{p}_n] - [\hat{r}_m, \hat{r}'_m]\hat{p}_n)\hat{p}_{n'} \\ = & \; i\hbar \sum_{mm'nn'} \epsilon_{mni}\epsilon_{m'n'j}(\hat{r}_{m'}\hat{p}_n\delta_{n'm} - \hat{r}_m\hat{p}_{n'}\delta_{m'n}) \\ = & \; i\hbar(\sum_{m'nn'} \epsilon_{n'ni}\epsilon_{n'jm'}\hat{r}_{m'}\hat{p}_n - \sum_{mnn'} \epsilon_{nim}\epsilon_{nn'j}\hat{r}_m\hat{p}_{n'}) \\ = & \; i\hbar(\sum_{m'n}[\delta_{nj}\delta_{im'} - \delta_{nm'}\delta_{ij}]\hat{r}_{m'}\hat{p}_n - \sum_{mn'}[\delta_{in'}\delta_{mj} - \delta_{ij}\delta_{mn'}]\hat{r}_m\hat{p}_{n'}) \\ = & \; i\hbar(\hat{r}_i\hat{p}_j - \hat{r}_j\hat{p}_i) = i\hbar(\hat{\mathbf{r}} \times \hat{\mathbf{p}})_k = i\hbar \sum_k \hat{l}_k\epsilon_{ijk},\end{aligned}$$

where we used the commutator property $[a, bc] = b[a, c] - [b, a]c$ and the property of the Levi-Cevita tensor $\sum_i \epsilon_{ijk}\epsilon_{ilm} = \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}$. □

Using Eqs. (37-40) we also get:

$$[\hat{\mathbf{l}}^2, \hat{l}_z] = [\hat{\mathbf{r}}, \hat{\mathbf{l}}] = 0, \tag{41}$$

and furthermore we have:

$$[\hat{H}, \hat{\mathbf{l}}] = [\hat{H}, \hat{l}_z] = 0. \tag{42}$$

Using the commutation relations Eq. (37) the spectrum of simultaneous eigenfunctions of $\hat{\mathbf{l}}^2$ and $\hat{l}_z$ can be derived:

$$\begin{aligned}\hat{\mathbf{l}}^2|lm\rangle &= \hbar^2 l(l+1)|lm\rangle && (43)\\ \hat{l}_z|lm\rangle &= \hbar m|lm\rangle. && (44)\end{aligned}$$

If we now write the total wave function as a product of a radial function $\phi_l(r)$ and angular functions $|lm\rangle$, and let the Hamiltonian H_0 work on this product, we get:

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\hat{\mathbf{l}}^2}{2\mu r^2}\right]\phi_l(r)|lm\rangle = \left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]\phi_l(r)|lm\rangle,$$

so the Schrödinger equation for the radial function can be written as:

$$\left[\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2} + \frac{2\mu E}{\hbar^2}\right]\phi_l(r) = 0, \tag{45}$$

where we recognize the term $2\mu E/\hbar^2 = k^2$. Now substitute $x \equiv kr$, so $d/dr = kd/dx$, and write $\phi_l(\mathbf{r}) \equiv f_l(kr)$, we get:

$$\left[\frac{1}{x}\frac{d}{dx}x - \frac{l(l+1)}{x^2} + 1\right] f_l(x) = 0, \tag{46}$$

applying the substitution $f_l(x) \equiv g_l(x)/x$, and multiplying the resulting equation with x from the right gives:

$$\left[\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2} + 1\right] g_l(x) = 0. \tag{47}$$

The solutions for $l = 0$ are very simple:

$$g_0(x) = \begin{cases} \sin(x) \\ \cos(x) \end{cases} \quad \text{and } f_0(x) = \begin{cases} j_0(x) = \frac{\sin(x)}{x} \\ y_0(x) = \frac{\cos(x)}{x}. \end{cases} \tag{48}$$

The solutions j_0 and y_0 are spherical 0^{th} order Bessel functions of the first and second kind[A&S]. In the following exercises we will show that the general solutions to Eq. (46) are given by Spherical Bessel functions of l^{th} order.

Exercise 1: Show that Eq. (46) is equivalent with the standard differential equation:

$$x^2 f_n'' + 2xf' + [x^2 - n(n+1)]f_n = 0, \tag{49}$$

by using the identity:

$$\frac{1}{x}\frac{d^2}{dx^2}x = \frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}. \tag{50}$$

Show that the f_n obey the following recursion relations:

$$1 \quad : \quad \frac{2n+1}{x} f_n = f_{n-1} + f_{n+1} \tag{51}$$

$$2 \quad : \quad (2n+1)f_n' = nf_{n-1} - (n+1)f_{n+1}. \tag{52}$$

Exercise 2: Prove the following recursion relation using Eqs. (51) and (52):

$$f_{n+1} = \left[\frac{n}{x} - \frac{d}{dx}\right] f_n. \tag{53}$$

Exercise 3: Derive the general equation:

$$f_n = (-1)^n x^n \left[\frac{1}{x}\frac{d}{dx}\right]^n f_0. \tag{54}$$

Exercise 4: Show that for large x:

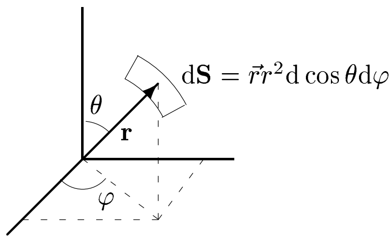
$$j_n(x) \cong \frac{\sin(x - \frac{n\pi}{2})}{x} \tag{55}$$

$$y_n(x) \cong \frac{\cos(x - \frac{n\pi}{2})}{x}. \tag{56}$$

Hint: prove this for j_0 and y_0 and use Eq.(54).

Finally, we derive an expression for the radial flux in spherical coordinates for some direction $\Omega = (\theta, \varphi)$. Recall Eq. (8). The radial flux $j_r \mathrm{d}\Omega$ in some direction is given by:

$$j_r \mathrm{d}\Omega = \mathbf{j} \cdot \mathrm{d}\mathbf{S}, \tag{57}$$



where $\mathrm{d}\mathbf{S}$ reads:

$$\mathrm{d}\mathbf{S} = \vec{r}r^2 \mathrm{d}\cos\theta \mathrm{d}\phi \equiv \vec{r}r^2 \mathrm{d}\Omega. \tag{58}$$

Using Eq. (26) we get:

$$j_r \mathrm{d}\Omega = \frac{\hbar}{\mu} \Im[\psi^* \nabla \psi] \cdot \vec{r} r^2 \mathrm{d}\Omega \tag{59}$$

$$= \frac{\hbar}{\mu} \Im[\psi^* (\vec{r} \cdot \nabla) \psi] r^2 \mathrm{d}\Omega \tag{60}$$

The inner product $\vec{r} \cdot \nabla$ gives:

$$\vec{r} \cdot \nabla = \sum_i \vec{r}_i \frac{\partial}{\partial r_i} = \sum_i \frac{r_i}{r} \frac{\partial}{\partial r_i} \tag{61}$$

$$= \sum_i \frac{\partial r_i}{\partial r} \frac{\partial}{\partial r_i} = \frac{\partial}{\partial r}. \tag{62}$$

Here we used that:

$$\frac{\partial}{\partial r} \mathbf{r} = \frac{\partial}{\partial r} r \vec{r} = \vec{r} \tag{63}$$

$$\text{so} \quad \frac{\partial r_i}{\partial r} = \vec{r}_i = \frac{r_i}{r}. \tag{64}$$

Substitution into Eq. (60) gives:

$$j_r \mathrm{d}\Omega = \frac{\hbar}{\mu}\Im[\psi^* \frac{\partial}{\partial r}\psi] r^2 \mathrm{d}\Omega. \tag{65}$$

Since $j_l(kr)$ and $y_l(kr)$ are real it they both have zero flux. However the Hankel functions $h_l^{(1)}(kr)$ and $h_l^{(2)}(kr)$ have the following definition and asymptotic behavior:

$$h_l^{(1)} = j_l + iy_l \cong -i(kr)^{-1} e^{i(kr - l\frac{\pi}{2})} \tag{66}$$

$$h_l^{(2)} = j_l - iy_l \cong i(kr)^{-1} e^{-i(kr - l\frac{\pi}{2})}. \tag{67}$$

The radial flux associated with these functions is given by:

$$j_r[h_l^{(1)}] = \frac{\hbar}{k\mu} \tag{68}$$

$$j_r[h_l^{(2)}] = \frac{-\hbar}{k\mu}, \tag{69}$$

which is why they are also referred to as *outgoing* and *incoming* functions respectively. Compare this with the flux of the plane waves [Eq. (33)]. It is common to use Hankel functions as a basis for description of radial time-independent scattering wave functions.

4 The Partial Wave Expansion

We now look for a way to express the plane waves [Eq. (29)] in terms of radial and angular functions. Choose $\vec{k}$ as z-axis, so the angles θ and φ are the polar and azimuthal angle of $\mathbf{r}$ with respect to the $\vec{k}$-axis system. Now, $\psi_{\mathbf{k}}(\mathbf{r})$ may be expanded as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{ikr\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{lm}(kr) Y_{lm}(\theta,\varphi), \tag{70}$$

where $Y_{lm} \equiv \langle\theta,\varphi|lm\rangle$ form a complete basis for square integrable functions on the sphere, and the $A_{lm}(kr)$ are r-dependent expansion coefficients. Using that:

$$\mathbf{k}\cdot\mathbf{r} = kr\cos\theta, \tag{71}$$

we see that $\psi_{\mathbf{k}}(\mathbf{r})$ is actually independent of φ, and hence $m = 0$. Using:

$$Y_{l0}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta), \tag{72}$$

we get:

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} a_l(kr) P_l(\cos\theta), \tag{73}$$

where the P_l are ordinary Legendre polynomials[A&S] and

$$a_l(kr) = A_{lm}(kr)\sqrt{\frac{2l+1}{4\pi}}\delta_{m0}. \tag{74}$$

The Legendre polynomials are orthogonal:

$$\langle P_l | P_{l'} \rangle \quad = \quad \int_{-1}^{1} P_l^*(z) P_{l'}(z) \mathrm{d}z = \delta_{ll'} \frac{2}{2l+1}. \tag{75}$$

The $P_l(z)$ are generated by the following recursion relation:

$$\begin{aligned} P_0(z) &= 1 & (76)\\ P_1(z) &= z & (77)\\ P_{l+1}(z) &= z\frac{2l+1}{l+1}P_l(z) - \frac{l}{l+1}P_{l-1}(z). & (78) \end{aligned}$$

To find expressions for $a_l(kr)$, we project Eq. (73) with $P_{l'}$:

$$\begin{aligned} &\int_{-1}^{1} \mathrm{d}(\cos\theta) P_{l'}(\cos\theta) e^{ikr\cos\theta} \\ &= \sum_{l=0}^{\infty} \int_{-1}^{1} \mathrm{d}(\cos\theta) a_l(kr) P_l'(\cos\theta) P_l(\cos\theta), \end{aligned} \tag{79}$$

which gives the expression:

$$a_l(x) \quad = \quad \frac{2l+1}{2} \int_{-1}^{1} \mathrm{d}z \; P_l(z) e^{ixz}. \tag{80}$$

For $l = 0$, this integral is very simple:

$$a_0(x) = i\frac{\sin x}{x} = i j_0(x). \tag{81}$$

In fact, it is easy to show that:

$$a_l(x) = i^l (2l+1) j_l(x). \tag{82}$$

Proof: Take the derivative of a_l with respect to x to obtain the recursion:

$$\begin{aligned} \frac{d}{dx}a_l(x) &= -i\frac{2l+1}{2}\int_{-1}^{1} \mathrm{d}z \; z P_l(z) e^{ixz} \\ &= i\frac{2l+1}{2}\left(\int_{-1}^{1} \mathrm{d}z \; \frac{l+1}{2l+1} P_{l+1} e^{ixz} + \int_{-1}^{1} \mathrm{d}z \; \frac{l}{2l+1} P_{l-1} e^{ixz}\right) \\ \frac{2}{2l+1} a_l' &= i\frac{l}{2l+1}\frac{2}{2(l-1)+1} a_{l-1} + i\frac{l+1}{2l+1}\frac{2}{2(l+1)+1} a_{l+1}, \end{aligned} \tag{83}$$

where we used Eq. (78). It is easy to show that:

$$\frac{i^{-l}}{2l+1} a_l' \quad = \quad \frac{l}{2l+1}\left[\frac{i^{-(l-1)}}{2(l-1)+1} a_{l-1}\right] - \frac{l+1}{2l+1}\left[\frac{i^{-(l+1)}}{2(l+1)+1} a_{l+1}\right] \tag{84}$$

which is the recursion relation for spherical Bessel functions Eq. (52). □

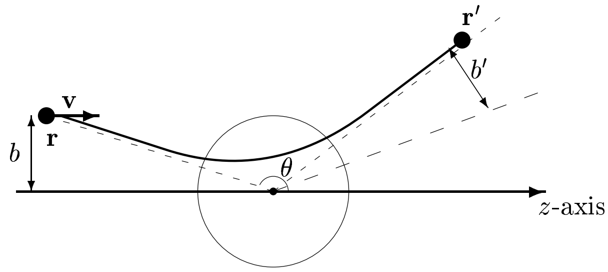
So the plane waves can be expressed in terms of the *partial wave expansion*:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l(2l+1)j_l(kr)P_l(\cos\theta) \tag{85}$$

$$= \sum_{l=0}^{\infty} \frac{i^l(2l+1)}{2}[h_l^{(1)}(kr) + h_l^{(2)}(kr)]P_l(\cos\theta). \tag{86}$$

5 Elastic Scattering

Consider a classical particle moving with a velocity $\mathbf{v}$, scattering of a spherical potential $V(r)$ with impact parameter b as indicated in the picture.



The conserved classical angular momentum is given by:

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} = \mu\mathbf{r} \times \mathbf{v}. \tag{87}$$

We may express the initial and final components l_x and l'_x in terms of the impact parameter b:

$$l_x = \mu r v \sin\theta = \mu v b \tag{88}$$

$$l'_x = \mu r' v' \sin\theta' = \mu v' b' \tag{89}$$

Since angular momentum is conserved, we have $l_x = l'_x$ and from conservation of kinetic energy we get $v = v'$, implying $b = b'$.

The quantum mechanical radial Hamiltonian for this problem is given by:

$$H = -\frac{\hbar^2}{2\mu} r \frac{d^2}{dr^2} r + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r). \tag{90}$$

The discussion that follows is valid for potentials that fulfill the following conditions [Tay]:

$$V(r) \xrightarrow{r\to\infty} \mathcal{O}(r^{-3-\varepsilon}), \text{ with } \varepsilon > 0 \tag{91}$$

$$V(r) \xrightarrow{r\to 0} \mathcal{O}(r^{-3/2+\varepsilon}), \text{ with } \varepsilon > 0, \tag{92}$$

and $V(r)$ must be continuous everywhere, except possibly at a finite number of singularities. These conditions are always met for collisions involving neutral molecules or atoms, and in collisions where one of the particles is charged. Notice however, that collisions between charged particles are excluded by the first condition since the Coulomb potential has $1/r$ behavior. With these conditions, the wave function can in the long range be written as a linear combination of incoming and outgoing spherical waves:

$$\begin{aligned}\psi(\mathbf{r}) &\cong \frac{i}{2k}\sum_l (2l+1)i^l\left[\frac{e^{-i(kr-l\frac{\pi}{2})}}{r} - \frac{e^{i(kr-l\frac{\pi}{2})}}{r}S_l(k)\right]P_l(\cos\theta) \quad (93)\\ &= \frac{1}{2}\sum_l i^l(2l+1)[h_l^{(2)} + h_l^{(1)}S_l(k)]P_l(\cos\theta). \quad (94)\end{aligned}$$

The coefficients $S_l(k)$ form the S-matrix or *scattering matrix*. The S-matrix contains all information that can be obtained from a scattering experiment. We will not prove here that the conditions are necessary for Eq. (93) to be valid. In stead we make some remarks on the S-matrix. If we compare Eq. (93) with the asymptotic form of the plane wave expansion Eq. (86), we see that if $V(r)$ is zero everywhere we have $S_l(k) = 1$. Furthermore we notice that since there are no sources of flux, the total flux must be zero even if $V(r) \neq 0$. This implies the very strict condition that S is unitary and:

$$|S_l(k)| = 1. \quad (95)$$

We may rewrite Eq. (93) by defining the T-matrix as follows:

$$T \equiv 1 - S, \quad (96)$$

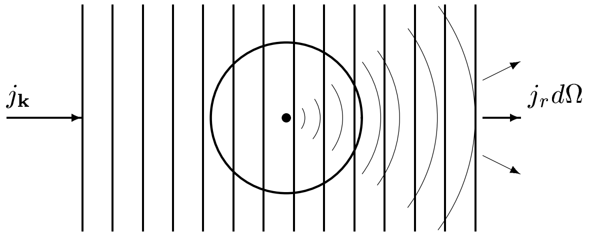
so that Eq. (93) becomes:

$$\begin{aligned}\psi(\mathbf{r}) &\cong \frac{i}{2k}\sum_l (2l+1)i^l\left[\frac{e^{-i(kr-l\frac{\pi}{2})}}{r} - \frac{e^{i(kr-l\frac{\pi}{2})}}{r} + i^{-l}T_l(k)\frac{e^{ikr}}{r}\right]P_l(\cos\theta)\\ &= e^{i\mathbf{k}\cdot\mathbf{r}} + \left[\frac{i}{2k}\sum_l (2l+1)T_l(k)P_l(\cos\theta)\right]\frac{e^{ikr}}{r} \quad (97)\\ &\equiv e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta,\varphi)\frac{e^{ikr}}{r}, \quad (98)\end{aligned}$$

where we defined $f(\theta, \varphi)$ in the last line. The angle φ is redundant here, but we re-introduced it for sake of completeness. The wave function in the long range [Eq. (98)] can thus be written as the sum of an unperturbed plane wave having flux of magnitude $j_{\mathbf{k}} = \hbar k/\mu$ in direction $\vec{k}$ and a term with a radial flux $j_r d\Omega$ that depends on the polar angles (θ, φ) (see figure below). The *differential cross section* is defined as:

$$\frac{d\sigma}{d\Omega} \equiv \frac{j_r}{j_{\mathbf{k}}} = \frac{|f(\theta,\varphi)|^2\hbar k/\mu}{\hbar k/\mu} = |f(\theta,\varphi)|^2, \quad (99)$$

where we used Eq. (33) and Eq. (65) to compute $j_{\mathbf{k}}$ and j_r respectively.



The total cross section is obtained by integration over θ and ϕ:

$$\sigma = \int \mathrm{d}\Omega \frac{d\sigma}{d\Omega} = \int_{-1}^{1} \int_{0}^{2\pi} |f(\theta,\varphi)|^2 \,\mathrm{d}\cos\theta \mathrm{d}\varphi. \tag{100}$$

Note that the conventional notation $d\sigma/d\Omega$ is in fact erroneous since σ does not really depend on Ω (it is defined by a determined integral), which means that the derivative $d\sigma/d\Omega = 0$. The notation is used for historical reasons. The total cross section is computed using the expression for $f(\theta,\varphi)$:

$$\begin{aligned} \sigma &= \int_{-1}^{1} \int_{0}^{2\pi} |f(\theta,\varphi)|^2 \,\mathrm{d}\cos\theta \mathrm{d}\varphi \\ &= \frac{2\pi}{4k^2} \sum_{ll'} \int_{-1}^{1} (2l+1)(2l'+1) T_l^*(k) T_{l'}(k) P_l(\cos\theta) P_{l'}(\cos\theta) \mathrm{d}\cos\theta \\ &= \frac{\pi}{k^2} \sum_{l} (2l+1) |T_l(k)|^2. \end{aligned} \tag{101}$$

This equation is often written in the form:

$$\sigma = \frac{4\pi}{k^2} \sum_{l} (2l+1) \sin^2 \delta_l(k), \tag{102}$$

this is easily obtained by recognizing that any function obeying Eq. (95) may be written as:

$$S_l(k) = e^{2i\delta_l(k)}, \tag{103}$$

so that:

$$T_l(k) = 1 - \left(e^{i\delta_l(k)}\right)^2 = -2ie^{i\delta_l(k)} \sin \delta_l(k). \tag{104}$$

The conditions given in (91) and further ensure that the sum in Eq. (102) converges. This may be compared with the classical case [Eq. (89)] where particles with higher angular momentum correspond with a larger effective impact parameter and thus smaller interaction with the potential.

6 The Log-Derivative Method

We derive a recursive method to handle a one-dimensional scattering problem numericaly. Consider the radial Schrödinger equation [see also Eq. (45)]:

$$\left[\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2} - \frac{2\mu E}{\hbar^2}V(r) + k^2\right]\phi_l(r) = 0. \tag{105}$$

The boundary conditions are given by:

$$\begin{aligned} \phi_l(0) &= 0 & (106)\\ \phi_l(r) &\xrightarrow{r\to\infty} h_l^{(2)}(kr) + h_l^{(1)}(kr)S_l(k). & (107) \end{aligned}$$

If we make the following definitions:

$$\begin{aligned} \phi_l(r) &\equiv \frac{1}{r}\chi_l(r) & (108)\\ W_l(r) &\equiv \frac{l(l+1)}{r^2} + \frac{2\mu E}{\hbar^2}V(r) - k^2, & (109) \end{aligned}$$

Eq. (105) can be rewritten in the form of the following differential equation:

$$\chi_l''(r) = W_l(r)\chi_l(r), \tag{110}$$

subject to the boundary conditions:

$$\begin{aligned} \chi_l(0) &= 0 & (111)\\ \chi_l(r) &\xrightarrow{r\to\infty} -u_l(r) + v_l(r)S_l(k), & (112) \end{aligned}$$

where we defined $u_l(r) \equiv -rh_l^{(2)}(kr)$ and $v_l(r) \equiv rh_l^{(1)}(kr)$. Now, write the derivative of $\chi_l(r)$ in terms of the log-derivative matrix $Y(r)$:

$$\chi_l'(r) \equiv Y_l(r)\chi_l(r). \tag{113}$$

Using Eq. (112), we can find a formal expression for the S-matrix. In the long-range we have:

$$\begin{aligned} -u_l'(r) + v_l'(r)S_l(k) = Y(r)[-u_l(r) + v_l(r)S_l(k)] & \quad (114)\\ S_l(k) = [v_l'(r) - Y_l(r)v_l(r)]^{-1}[u_l'(r) - Y_l(r)u_l(r)]. & \quad (115) \end{aligned}$$

So, to compute the S-matrix we now need the Y-matrix. Using (113) we have:

$$\begin{aligned} Y_l &= \chi_l'\chi_l^{-1} & (116)\\ Y_l' &= \chi_l''\chi_l^{-1} + \chi_l'[\chi_l^{-1}]' = W_l + Y_l\chi_l\frac{d\chi_l^{-1}}{d\chi_l}\chi_l' & (117)\\ &= W_l - Y_l\chi_l\chi_l^{-2}Y\chi_l & (118)\\ Y_l'(r) &= W_l(r) - Y_l^2(r). & (119) \end{aligned}$$

Solving the nonlinear differential equation (119) is thus equivalent to solving the 2nd order equation (110). We now derive a recursion relation for Y_l. Suppose we found a solution $\psi(r)$ to the problem (110) on some range $[r', r'']$. Define the *invariant imbedding matrix* $L(r', r'')$ such that:

$$\begin{bmatrix} \chi_l'(r') \\ \chi_l'(r'') \end{bmatrix} = \begin{pmatrix} L_1(r', r'') & L_2(r', r'') \\ L_3(r', r'') & L_4(r', r'') \end{pmatrix} \begin{bmatrix} -\chi_l(r') \\ \chi_l(r'') \end{bmatrix}. \tag{120}$$

It is easy to see that the matrix L is in fact independent of the boundary conditions, provided a solution exists. So $L(r', r'')$ can be determined by finding two linear independent solutions $\psi^{\pm}$ on $[r', r'']$ which fulfill the following boundary conditions:

$$\psi^{\pm}(r') = \begin{cases} 0 \\ 1 \end{cases} \qquad \psi^{\pm}(r'') = \begin{cases} 1 \\ 0 \end{cases} . \tag{121}$$

Notice that the solution to (110-112) on $[r', r'']$ can be written as a linear combination of ψ^+ and ψ^-. Expanding Eq. (120) we get:

$$\chi_l'(r') = -L_1(r', r'')\chi_l(r') + L_2(r', r'')\chi_l(r'') \tag{122}$$

$$\chi_l'(r'') = -L_3(r', r'')\chi_l(r') + L_4(r', r'')\chi_l(r''). \tag{123}$$

Multiply Eq. (122) with $\chi_l^{-1}(r')$, and Eq. (123) with $\chi_l^{-1}(r'')$:

$$\chi_l'(r')\chi_l^{-1}(r') = -L_1(r', r'') + L_2(r', r'')\chi_l(r'')\chi_l^{-1}(r') \tag{124}$$

$$\chi_l'(r'')\chi_l^{-1}(r'') = -L_3(r', r'')\chi_l(r')\chi_l^{-1}(r'') + L_4(r', r'') \tag{125}$$

from Eqs. (124) and (113) we get:

$$\chi_l(r')\chi_l^{-1}(r'') = [Y_l(r') + L_1(r', r'')]^{-1} L_2(r', r'') \tag{126}$$

substitution into (125) and using (113) again gives a recursion relation for the Y_l:

$$Y_l(r'') = L_4(r', r'') - L_3(r', r'')[Y_l(r') + L_1(r', r'')]^{-1} L_2(r', r''). \tag{127}$$

This recursion relation is the basis for several types of log-derivative algorithms. We will not derive an actual algorithm here, but in stead refer to some literature[Joh][Mru][Man].

7 Summary of Notation and Literature

$\mathbf{v}$	vector or vector function
v_i	vector elements, $i \in (x, y, z)$
$\vec{v}$	unit vector in the direction of $\mathbf{v}$
v	length: $v = \|\mathbf{v}\|$
$\hat{A}$	scalar operator
$\hat{\mathbf{a}}$	vector operator

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