Appendix A: Partial Wave Analysis

This Appendix describes the method of **partial wave analysis**, which can be used to solve 3D scattering problems with *spherically symmetric* scattering potentials. Such a potential, $V(r)$, depends only on the radial distance $r = \sqrt{x^2+y^2+z^2}$ and not on direction. This typically describes a situation where a point particle or spherically-symmetric object sits at the coordinate origin, $\mathbf{r} = 0$, and is bombarded by incident particles.

A1. SPHERICAL WAVES

We begin by considering "exterior" solutions to the Schrödinger wave equation. Far from the scatterer, where $V(r) \rightarrow 0$, the Schrödinger wave equation can be rearranged into

$$\left(\nabla^2 + k^2\right)\psi(\mathbf{r}) = 0, \quad \text{where } \; k = \sqrt{2mE/\hbar^2}. \tag{A.1}$$

This partial differential equation is called the **Helmholtz equation**. We emphasize that E plays the role of a tunable parameter, and is not an eigenvalue in an eigenproblem. For the moment, we will not specify the boundary conditions, and look instead for a general set of solutions for a given E (and hence k).

In spherical coordinates (r, θ, ϕ), the Helmholtz equation has the explicit form

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + k^2\psi(r,\theta,\phi) = 0. \tag{A.2}$$

There is a standard procedure for solving this. The first step is to perform a separation of variables, and look for solutions of the form

$$\psi(r,\theta,\phi) = A(r)Y_{\ell m}(\theta,\phi), \tag{A.3}$$

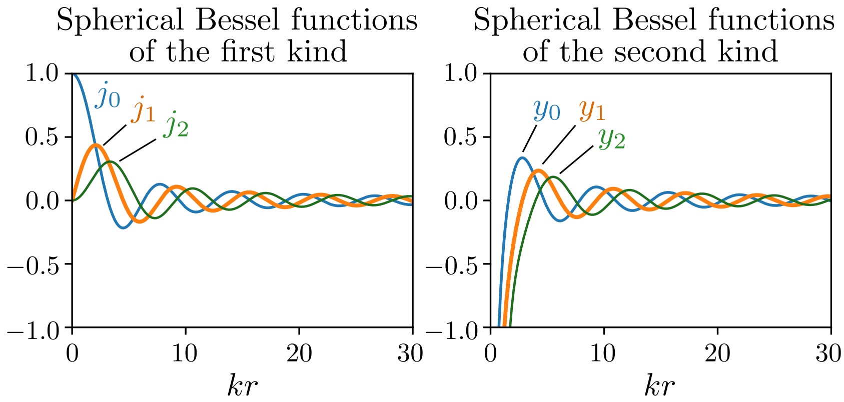
where $A(r)$ is a function to be determined and $Y_{\ell m}(\theta, \phi)$ is a special function known as a spherical harmonic. Spherical harmonics are functions designed specifically to represent the angular dependence of solutions with definite angular momenta. In the context of quantum mechanics, ℓ and m are the quantum numbers representing the total angular momentum and the z-component of the angular momentum. It can be shown that the indices ℓ and m must be integers satisfying $\ell \geq 0$ and $-\ell \leq m \leq \ell$, in order for $Y_{\ell m}(\theta, \phi)$ to be periodic in ϕ and regular at the poles of the spherical coordinate system.

After plugging in this form for $\psi(r, \theta, \phi)$, the Helmholtz equation reduces to the following ordinary differential equation, which is a variant of the Bessel equation:

$$\frac{d}{dr}\left(r^2\frac{dA}{dr}\right) + \Big[k^2r^2 - \ell(\ell+1)\Big]A(r) = 0, \quad \ell \in \mathbb{Z}_0^+. \tag{A.4}$$

Note that m drops out of the equation. Thus, $A(r)$ depends on ℓ, but *not* on m.

The ordinary differential equation has two linearly independent real solutions, $j_\ell(kr)$ and $y_\ell(kr)$, which are called **spherical Bessel functions**. Most scientific computing packages provide functions to calculate these; Scientific Python, for example, has `scipy.special.spherical_jn` and `scipy.special.spherical_yn`. Some spherical Bessel functions are plotted below:



Note that the y_ℓ functions diverge at $kr \rightarrow 0$. This does not bother us, for we are interested in solutions defined in the exterior region, away from the coordinate origin.

For large values of the input, the spherical Bessel functions have the limiting forms

$$\begin{aligned} j_\ell(kr) &\overset{kr\rightarrow\infty}{\longrightarrow} \frac{\sin(kr - \frac{\ell\pi}{2})}{kr} \\ y_\ell(kr) &\overset{kr\rightarrow\infty}{\longrightarrow} -\frac{\cos(kr - \frac{\ell\pi}{2})}{kr}. \end{aligned} \tag{A.5}$$

Since we are interested in incoming and outgoing spherical waves, it is convenient to define

$$h_\ell^\pm(kr) = j_\ell(kr) \pm i y_\ell(kr). \tag{A.6}$$

This complex function is called a **spherical Hankel function** of the first kind ($+$) or second kind ($-$). It solves the same differential equation, but has the limiting form

$$h_\ell^\pm(kr) \overset{kr\rightarrow\infty}{\longrightarrow} \pm\frac{\exp\left[\pm i(kr - \frac{\ell\pi}{2})\right]}{ikr}. \tag{A.7}$$

Using it, we can write down a solution to the Helmholtz equation, in the form

$$\Psi_{\ell m}^\pm(\mathbf{r}) = h_\ell^\pm(kr)\, Y_{\ell m}(\theta,\phi). \tag{A.8}$$

This describes a spherical wave that is outgoing ($+$) or incoming ($-$), and that has a definite angular momentum described by the quantum numbers ℓ and m.

Because the Helmholtz equation is linear, any linear combination of spherical waves, with various values of (ℓ, m), is also a solution:

$$\psi(\mathbf{r}) = \sum_{\pm} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell m}^\pm \Psi_{\ell m}^\pm(\mathbf{r}). \tag{A.9}$$

It can be shown that the spherical waves form a complete solution basis. In other words, any solution to the 3D Helmholtz equation within the exterior region can be written in the above form, for some choice of complex coefficients $c_{\ell m}^\pm$. (By the way, these spherical waves are appropriately normalized so that the flux associated with each term is directly proportional to $|c_{\ell m}^\pm|^2$.)

A2. THE SCATTERING MATRIX

For a given scattering problem, the exterior wavefunction is described by the complex numbers $\{c^+_{\ell m}\}$ and $\{c^-_{\ell m}\}$. These two sets of coefficients cannot, however, be independent of each other. For fixed $V(\mathbf{r})$ and E, suppose there is an incoming spherical wave with definite angular momentum, say $c^-_{\ell m} = 1$ for some choice of (ℓ, m). After striking the scatterer, the quantum particle bounces back out to infinity, and the outgoing wavefunction is some superposition of outgoing spherical waves with a variety of angular momenta, described by certain coefficients $\{c^+_{\ell' m'}\}$.

Thus, for each choice of incoming wave with definite angular momentum, there is a corresponding set of outgoing-wave coefficients. Since the Schrödinger wave equation is linear, the principle of superposition states that linear combinations of scattering solutions are also valid solutions—i.e., solutions to the Schrödinger wave equation for the same $V(\mathbf{r})$ and E. So if we supply an *arbitrary* set of incoming coefficients $\{c^-_{\ell m}\}$, the outgoing coefficients must be determined by a linear relation of the form

$$c^+_{\ell m} = \sum_{\ell' m'} S_{\ell m, \ell' m'}\, c^-_{\ell' m'}. \tag{A.10}$$

To make the notation cleaner, we rewrite this as

$$c^+_\mu = \sum_\nu S_{\mu\nu}\, c^-_\nu, \tag{A.11}$$

where each μ or ν denotes a pair of angular momentum quantum numbers (ℓ, m), called a **scattering channel**. The matrix S is called a **scattering matrix**. Knowing $V(\mathbf{r})$ and E, we can calculate S, and knowing S we can determine the outgoing wavefunction produced by any set of incoming waves.

Thus far, we have not specified how the "incoming" and "outgoing" waves are related to the "incident" and "scattered" waves of a scattering experiment. We now consider an incident plane wave, $\psi_i(\mathbf{r}) = \Psi_i \exp(i\mathbf{k}_i \cdot \mathbf{r})$, where $|\mathbf{k}_i| = k$. This introduces an important complication: relative to the coordinate origin, a plane wave is neither purely "incoming" nor "outgoing"! In fact, there is a mathematical identity stating that

$$\begin{aligned} e^{i\mathbf{k}_i\cdot\mathbf{r}} &= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} 4\pi j_\ell(kr) e^{i\ell\pi/2}\, Y^*_{\ell m}(\hat{\mathbf{k}}_i)\, Y_{\ell m}(\hat{\mathbf{r}}) \\ &= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} 2\pi \left[h^+_\ell(kr) + h^-_\ell(kr)\right] e^{i\ell\pi/2}\, Y^*_{\ell m}(\hat{\mathbf{k}}_i)\, Y_{\ell m}(\hat{\mathbf{r}}). \end{aligned} \tag{A.12}$$

Here, $\hat{\mathbf{k}}_i$ denotes the angular components (in spherical coordinates) of the incident wave-vector $\mathbf{k}_i$, while $\hat{\mathbf{r}}$ likewise denotes the angular components of the position vector $\mathbf{r}$. Eq. (A.12) informs us that the incident plane wave can be decomposed into a superposition of incoming and outgoing spherical waves, with the wave coefficients

$$c^\pm_{i,\ell m} = 2\pi e^{i\ell\pi/2}\, Y^*_{\ell m}(\hat{\mathbf{k}}_i)\; \Psi_i. \tag{A.13}$$

As described in Chapter 0, the total wavefunction in a scattering problem is the sum of the incident wavefunction $\psi_i(\mathbf{r})$ and the scattered wavefunction $\psi_s(\mathbf{r})$. The latter must be a superposition of only outgoing spherical waves; let us denote the coefficients by $c^+_{s,\ell m}$. The scattering matrix relation can then be re-written as

$$c^+_\mu = c^+_{i,\mu} + c^+_{s,\mu} = \sum_{\mu\nu} S_{\mu\nu} c^-_{i,\nu} \tag{A.14}$$

$$\Rightarrow \quad c^+_{s,\ell m} = 2\pi \sum_{\ell' m'} \Big(S_{\ell m,\ell' m'} - \delta_{\ell\ell'}\delta_{mm'} \Big) e^{i\ell'\pi/2}\, Y^*_{\ell' m'}(\hat{\mathbf{k}}_i)\; \Psi_i. \tag{A.15}$$

Using this, the scattered wavefunction can be written as

$$\begin{aligned} \psi_s(\mathbf{r}) &= \sum_{\ell m} c^+_{s,\ell m} h^+_\ell(kr)\, Y_{\ell m}(\hat{\mathbf{r}}) \\ &= \Psi_i \sum_{\ell m} \sum_{\ell' m'} 2\pi \Big(S_{\ell m,\ell' m'} - \delta_{\ell\ell'}\delta_{mm'} \Big) e^{i\ell'\pi/2}\, Y^*_{\ell' m'}(\hat{\mathbf{k}}_i)\; h^+_\ell(kr)\, Y_{\ell m}(\hat{\mathbf{r}}). \end{aligned} \tag{A.16}$$

Taking the large-r expansion of the spherical Hankel functions yields

$$\psi_s(\mathbf{r}) \overset{r\rightarrow\infty}{\longrightarrow} \Psi_i \frac{e^{ikr}}{r} \left[\frac{2\pi}{ik} \sum_{\ell m} \sum_{\ell' m'} \Big(S_{\ell m,\ell' m'} - \delta_{\ell\ell'}\delta_{mm'} \Big)\, e^{-i(\ell-\ell')\pi/2}\, Y^*_{\ell' m'}(\hat{\mathbf{k}}_i)\; Y_{\ell m}(\hat{\mathbf{r}}) \right]. \tag{A.17}$$

The quantity in square brackets is precisely what we call the scattering amplitude:

$$f(\mathbf{k}_i \rightarrow k\hat{\mathbf{r}}) = \frac{2\pi}{ik} \sum_{\ell m} \sum_{\ell' m'} \Big(S_{\ell m,\ell' m'} - \delta_{\ell\ell'}\delta_{mm'} \Big)\, e^{-i(\ell-\ell')\pi/2}\, Y^*_{\ell' m'}(\hat{\mathbf{k}}_i)\; Y_{\ell m}(\hat{\mathbf{r}}). \tag{A.18}$$

A3. SPHERICALLY SYMMETRIC SCATTERING POTENTIALS

Generally, the scattering matrix needs to be calculated numerically. The process is greatly simplified if the scattering potential is spherically symmetric, i.e. $V(\mathbf{r}) = V(r)$. In that case, angular momentum is conserved, so an incoming spherical wave with angular momentum quantum numbers (ℓ, m) must scatter exclusively into an outgoing spherical wave with the same (ℓ, m). This means that the scattering matrix components have the form

$$S_{\ell m,\ell' m'} = s_{\ell m}\, \delta_{\ell\ell'}\, \delta_{mm'}. \tag{A.19}$$

The scattering amplitude then simplifies to

$$f(\mathbf{k}_i \rightarrow k\hat{\mathbf{r}}) = \frac{2\pi}{ik} \sum_{\ell m} \Big(s_{\ell m} - 1 \Big)\, Y^*_{\ell m}(\hat{\mathbf{k}}_i)\; Y_{\ell m}(\hat{\mathbf{r}}). \tag{A.20}$$

Our task is now to obtain the $s_{\ell m}$'s. The procedure is very similar to what we already went through in Section A1. The total wavefunction satisfies the Schrödinger wave equation, which can be written in spherical coordinates as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + K^2(r)\psi(r,\theta,\phi) = 0, \tag{A.21}$$

where

$$K^2(r) = \sqrt{\frac{2m\big[E - V(r)\big]}{\hbar^2}}. \tag{A.22}$$

This is similar to the Helmholtz equation, but with the constant k^2 replaced by a function $K^2(r)$. In scattering channel (ℓ, m), the solution has the form

$$\psi(r,\theta,\phi) = A(r)\, Y_{\ell m}(\theta,\phi). \tag{A.23}$$

Upon substitution into the Schrödinger wave equation, we find that $A(r)$ must satisfy

$$\frac{d}{dr}\left(r^2 \frac{dA}{dr}\right) + \Big[K^2(r)\, r^2 - \ell(\ell+1)\Big] A(r) = 0, \quad \ell \in \mathbb{Z}_0^+. \tag{A.24}$$

As before, the equation for $A(r)$ does not involve m; hence, the scattering matrix components do not depend on m, and can be written as simply

$$s_{\ell m} \;=\; s_\ell. \tag{A.25}$$

For any given $V(r)$, we can solve the second-order ordinary differential equation numerically by supplying two boundary conditions at $r = 0$, integrating up to a large value of r, and matching to the exterior solution

$$A(r) \;\overset{r\rightarrow\infty}{\longrightarrow}\; c_\ell^- h_\ell^-(kr) + c_\ell^+ h_\ell^+(kr) = c_\ell^- \Big(h_\ell^-(kr) + s_\ell h_\ell^+(kr)\Big). \tag{A.26}$$

The value of s_ℓ can then be extracted.

To simplify the problem even further, let the scattering potential take the form of a spherical potential well of radius R and depth U:

$$V(r) = \begin{cases} -U & \text{for } \; r < R, \\ \;\;0 & \text{otherwise.} \end{cases} \tag{A.27}$$

We will take $U > 0$, so that the potential is attractive. (The interested reader can work through the repulsive case, $U < 0$. The process is almost the same as what is presented below, except that for some values of E, the wave inside the scatterer becomes evanescent.) Now, the Schrödinger wave equation in the interior region reduces to the Helmholtz equation, but with k replaced with

$$q = \sqrt{2m(E+U)/\hbar^2}. \tag{A.28}$$

Note that $q \in \mathbb{R}^+$ for $E > 0$, since we have assumed that $U > 0$. The elementary solutions for $A(r)$ in the interior region are $j_\ell(qr)$ and $y_\ell(qr)$. However, we must exclude the latter, since they diverge at $r = 0$. (When we got to a similar point in Section A1, we did not exclude the spherical Bessel functions of the second kind, because at the time we were concerned with solutions in the exterior region.) We thus arrive at a solution of the form

$$A(r) = \begin{cases} \alpha_\ell\, j_\ell(qr), & r \le R \\ c_\ell^- \Big(h_\ell^-(kr) + s_\ell h_\ell^+(kr)\Big) & r \ge R. \end{cases} \tag{A.29}$$

So far, the values of α_ℓ, c_ℓ^-, and s_ℓ remain unknown. To proceed, we match the wavefunction and its derivative at the boundary $r = R$:

$$\begin{aligned} \alpha_\ell\, j_\ell(qR) &= c_\ell^- \Big(h_\ell^-(kR) + s_\ell h_\ell^+(kR)\Big) \\ \alpha_\ell\, q j_\ell'(qR) &= c_\ell^-\, k\Big(h_\ell^{-\prime}(kR) + s_\ell h_\ell^{+\prime}(kR)\Big). \end{aligned} \tag{A.30}$$

Here, j_ℓ' denotes the derivative of the spherical Bessel function, and likewise for $h_\ell^{\pm\prime}$. Taking the ratio of these two equations eliminates α_ℓ and c_ℓ^-:

$$\frac{q j_\ell'(qR)}{j_\ell(qR)} = k\frac{h_\ell^{-\prime}(kR) + s_\ell h_\ell^{+\prime}(kR)}{h_\ell^-(kR) + s_\ell h_\ell^+(kR)}. \tag{A.31}$$

With a bit of rearrangement, this becomes

$$s_\ell = -\frac{k h_\ell^{-\prime}(kR) j_\ell(qR) - q h_\ell^-(kR) j_\ell'(qR)}{k h_\ell^{+\prime}(kR) j_\ell(qR) - q h_\ell^+(kR) j_\ell'(qR)}. \tag{A.32}$$

The numerator and denominator are complex conjugates of one another, since j_ℓ is real and $(h_\ell^+)^* = h_\ell^-$. Hence,

$$s_\ell = e^{2i\delta_\ell}, \quad \text{where}\;\; \delta_\ell = \frac{\pi}{2} - \arg\Big[k h_\ell^{+\prime}(kR) j_\ell(qR) - q h_\ell^+(kR) j_\ell'(qR)\Big]. \tag{A.33}$$

In other words, the scattering matrix component is a pure phase factor. This is actually a consequence of energy conservation. Since the scattering matrix does not couple different angular momentum channels (due to the spherical symmetry), the incoming flux and outgoing flux in each channel must be equal. Hence, the only thing the scattering potential can do is to shift the phase of the outgoing spherical wave component in each channel.

Once we find δ_ℓ, we can compute the scattering amplitude

$$f(\mathbf{k}_i \rightarrow k\hat{\mathbf{r}}) = \frac{2\pi}{ik} \sum_{\ell=0}^{\infty} \big(e^{2i\delta_\ell} - 1\big) \sum_{m=-\ell}^{\ell} Y_{\ell m}^*(\hat{\mathbf{k}}_i)\, Y_{\ell m}(\hat{\mathbf{r}}). \tag{A.34}$$

This can be simplified with the aid of the following addition theorem for spherical harmonics:

$$P_\ell(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell m}^*(\hat{\mathbf{r}}_1) Y_{\ell m}(\hat{\mathbf{r}}_2). \tag{A.35}$$

where $P_\ell(\cdots)$ denotes a Legendre polynomial. We finally obtain

$$\boxed{\begin{aligned} f(\mathbf{k}_i \rightarrow k\hat{\mathbf{r}}) &= \frac{1}{2ik} \sum_{\ell=0}^{\infty} \big(e^{2i\delta_\ell} - 1\big)\big(2\ell+1\big)\, P_\ell(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{r}}) \\ \delta_\ell &= \frac{\pi}{2} - \arg\Big[k h_\ell^{+\prime}(kR)\, j_\ell(qR) - q h_\ell^+(kR)\, j_\ell'(qR)\Big] \\ k = |\mathbf{k}_i| &= \sqrt{2mE/\hbar^2}, \;\; q = \sqrt{2m(E+U)/\hbar^2}. \end{aligned}} \tag{A.36}$$

This result for the scattering amplitude depends upon two variables: (i) E, the particle energy (which is conserved), and (ii) $\Delta\theta = \cos^{-1}(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{r}})$, the **deflection angle** (i.e., the angle between the direction of incidence and the direction into which the particle is scattered).