SCATTERING IN QUANTUM MECHANICS

Consider the unbound motion of a single quantum particle — or equivalently, reduced motion of two particles — in a central potential $V(r)^\star$ which vanishes for $r\to\infty$. A scattering solution of the Schrödinger equation

$$\hat{H}\,|\Psi\rangle \;=\; E\hat{\Psi} \quad \text{for} \quad \hat{H} \;=\; \frac{\hat{\mathbf{p}}^2}{2M} \;+\; V(\hat{r}) \tag{1}$$

is a solution whose wave function $\Psi(\mathbf{x})$ combines an incoming plane wave with an outgoing spherical wave. Or rather, $\Psi(\mathbf{x})$ combines an incoming plane wave with an outgoing spherical wave *at asymptotically large distances from the center*

$$\text{for } r\to\infty, \quad \Psi(r,\theta,\not\phi) \;=\; e^{ikz} \;+\; \frac{e^{ikr}}{r}\times f(\theta) \;+\; O(1/r^2), \tag{2}$$

$$k \;=\; \sqrt{2ME} \quad \langle\!\langle \text{in } \hbar=1 \text{ units} \rangle\!\rangle, \tag{3}$$

where I used the spherical symmetry of the problem to send the incoming wave in the $+z$ direction. The $f(\theta)$ in eq. (2) is called the *scattering amplitude*; it governs the scattering partial cross-section as

$$\frac{d\sigma}{d\Omega} \;=\; |f(\theta)|^2. \tag{4}$$

To see how this works, let's replace the exact eigenstate of the Hamiltonian with a wave packet

$$\Psi(\mathbf{x},t) \;=\; \int dk\, e^{-(k-k_0)^2/\alpha} \times \Psi_k(\mathbf{x}) \times e^{-itE(k)} \tag{5}$$

of narrow energy width

$$\Delta E \;=\; \frac{k_0}{M}\times\Delta k \;=\; \frac{k_0}{M}\times\frac{\sqrt{\alpha}}{2} \;\ll\; E(k_0) \quad \text{for } \alpha\to 0. \tag{6}$$

Assuming $\Psi_k(\mathbf{x})$ is as in eq. (2) with $f(\theta)$ approximately k-independent within the $k_0\pm\Delta k$

$\star$ For simplicity, in these notes I assume a central potential $v(r)$; generalizing to non-central potentials is fairly straightforward but uses much messier notations.

range, we end up with

$$\Psi(\mathbf{x},t) \;=\; \sqrt{4\pi\alpha}\,e^{-itE_0}\left(e^{ik_0z}\times e^{-\alpha(z-vt)^2}\;+\;\frac{e^{ik_0r}}{r}\,f(\theta)\times e^{-\alpha(r-vt)^2}\;+\;O(1/r^2)\right) \tag{7}$$

for $v = k_0/M$ being the particle's asymptotic speed. In the asymptotic past $t \to -\infty$, the expression inside $(\cdots)$ is dominated by the first term, which physically is the incoming plane wave packet. In the asymptotic future $t \to +\infty$, we have both the first term and the second term, the first term being the un-scattered plane wave continuing in the forward direction, while the second term is the scattered wave spreading out in all directions. Moreover, the un-scattered wave and the scattered wave exist in the non-overlapping regions

$$z \;=\; r\cos\theta \;=\; vt \;\pm\; \frac{1}{\sqrt{\alpha}} \quad \textit{versus} \quad r \;=\; vt \;\pm\; \frac{1}{\sqrt{\alpha}}\,, \tag{8}$$

$$\text{thus no overlap for} \quad vt \;\gg\; \frac{1}{1-\cos\theta}\times\frac{1}{\sqrt{\alpha}}\,. \tag{9}$$

We see that in the wave packet description, the plane-wave and the spherical-wave terms in the wave function (2) do not overlap at the same space at the same asymptotic time, so we may treat the two terms as separate non-interfering waves. Consequently, the particle flux $\mathbf{F}$ described by the wave function (2) splits into the incoming/un-scattered flux and the scattered flux,

$$\mathbf{F}_{\text{net}} \;=\; \mathbf{F}_{\text{in}} \;+\; \mathbf{F}_{\text{sc}} \tag{10}$$

and we do not have to worry about the interference terms in this flux. Specifically,

$$\mathbf{F}_{\text{in}} \;=\; |\Psi_{\text{in}}|^2\mathbf{k} \;=\; \mathbf{k} \tag{11}$$

while

$$\mathbf{F}_{\text{sc}} \;=\; |\Psi_{\text{sc}}|^2 k\mathbf{n}_r \;=\; \frac{|f(\theta)|^2}{r^2}\,k\,\mathbf{n}_r\,,$$

hence identifying the partial cross section as a net flow rate of scattered particles through area $r^2 d\omega(\theta,\phi)$ divided by the incoming flux, we end up with

$$\frac{d\sigma}{d\Omega} \;=\; |f(\theta)|^2. \tag{4}$$

Perturbation Theory

A common approach to finding the scattering solutions of the Schrödinger equation and hence the scattering amplitudes $f(\theta)$ is the perturbation theory. In the asymptotic past and in the asymptotic future, the particle is at large distances where $V(r) \approx 0$, so its energy is purely kinetic. Therefore, we take the un-perturbed Hamiltonian

$$\hat{H}_0 \;=\; \frac{\hat{\mathbf{p}}^2}{2M} \tag{12}$$

to be purely kinetic, while the potential $\hat{V} = V(\hat{r})$ acts as a perturbation.

Green's Function

The perturbation theory uses Green's functions

$$\hat{G}(E) \;=\; \frac{1}{E - \hat{H}_0} \tag{13}$$

of the un-perturbed Hamiltonian $\hat{H}_0$ and it's coordinate-space matrix elements

$$\langle \mathbf{x} | \, \hat{G}(E) \, | \mathbf{y} \rangle \;=\; \int \frac{d^3\mathbf{k}}{(2\pi)^3} \, e^{-i\mathbf{k}\cdot\mathbf{x}} \times \frac{1}{E \,-\, (\mathbf{k}^2/2M)} \times e^{+i\mathbf{k}\cdot\mathbf{y}}. \tag{14}$$

Unfortunately, for any real $E > 0$, the integrand here has a pole along the spherical shell $|\mathbf{k}| = \sqrt{2ME}$, so the integral needs to be regulated. In a way that should be familiar to this class, we are going to regulate it by moving E into the complex plane, thus two different Green's functions

$$G_+(E) \;=\; \frac{1}{E + i\epsilon - \hat{H}_0} \quad \text{and} \quad G_-(E) \;=\; \frac{1}{E - i\epsilon - \hat{H}_0}\,, \quad \text{both for } \epsilon \to +0. \tag{15}$$

Let's calculate their coordinate space matrix elements. Denoting $k_0 = \sqrt{2EM}$, we have

$$E \,\pm\, i\epsilon \;=\; \frac{k_0^2 \pm i\epsilon}{2M} \;=\; \frac{(k_0 \pm i\epsilon)^2}{2M} \tag{16}$$

and hence

$$G_\pm(E) \;=\; \frac{2M}{(k_0 \pm i\epsilon)^2 - \hat{\mathbf{p}}^2}\,. \tag{17}$$

Consequently,

$$\begin{aligned}
\langle\mathbf{x}|\,\hat{G}_\pm(E)\,|\mathbf{y}\rangle &= \int\frac{d^3\mathbf{k}}{(2\pi)^3}\,e^{-i\mathbf{k}\cdot\mathbf{x}}\times\frac{2M}{(k_0\pm i\epsilon)^2-k^2}\times e^{+i\mathbf{k}\cdot\mathbf{y}}\\
&= \frac{2M}{(2\pi)^3}\int\limits_0^\infty dk\int\limits_0^\pi d\theta\,k^2\times 2\pi\sin\theta\times\frac{1}{(k_0\pm i\epsilon)^2-k^2}\times\left(e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{y})}\;=\;e^{ikr\cos\theta}\right)\\
&\qquad\langle\!\langle\text{ where } r=|\mathbf{x}-\mathbf{y}| \text{ and } \theta \text{ is the angle between } \mathbf{k} \text{ and } \mathbf{x}-\mathbf{y}\,\rangle\!\rangle\\
&= \frac{2M}{4\pi^2}\int\limits_0^\infty dk\,\frac{k^2}{(k_0\pm i\epsilon)^2-k^2}\times\frac{e^{+ikr}-e^{-ikr}}{ikr}\\
&= \frac{2iM}{4\pi^2 r}\int\limits_{-\infty}^{+\infty} dk\,\frac{k\,e^{ikr}}{k^2-(k_0\pm i\epsilon)^2}\\
&= \frac{2iM}{4\pi^2 r}\oint\limits_\Gamma dk\,\frac{k\,e^{ikr}}{k^2-(k_0\pm i\epsilon)^2}
\end{aligned}\tag{18}$$

where Γ is a large semicircular contour in the complex plane. Since the e^{ikr} factor shrinks for $\operatorname{Im}k\to+\infty$, the semicircular arc should be above the real axis. Taking the contour integral by residue method, we get

$$\langle\mathbf{x}|\,\hat{G}_\pm(E)\,|\mathbf{y}\rangle \;=\; -\frac{M}{\pi r}\times\text{Residue}\left[\frac{k\,e^{ikr}}{k^2-(k_0\pm i\epsilon)^2}\right]\tag{19}$$

where the residue is taken at whichever pole happen to lie inside the integration contour — *i.e.*, above the real axis. Specifically:

- For the G_+, the poles are at $k_1=+(k_0+i\epsilon)$ and at $k_2=-(k_0+i\epsilon)$, with only the first pole being above the real axis. Consequently,

$$\begin{aligned}
\langle\mathbf{x}|\,\hat{G}_+(E)\,|\mathbf{y}\rangle &= -\frac{M}{\pi r}\;\text{Residue}\left[\frac{k\,e^{ikr}}{(k-(k_0+i\epsilon))(k+(k_0+i\epsilon))}\right]_{k=k_0+i\epsilon}\\
&= -\frac{M}{\pi r}\times\frac{e^{ir(k_0+i\epsilon}}{2}\\
&\xrightarrow[\epsilon\to+0]{}\; -\frac{M}{2\pi r}\times e^{+ik_0r}.
\end{aligned}\tag{20}$$

- For the G_-, the poles are at $k_1=+(k_0-i\epsilon)$ and at $k_2=-(k_0-i\epsilon)$, with only the second pole being above the real axis. Consequently,

$$\begin{aligned}\langle\mathbf{x}|\,\hat{G}_+(E)\,|\mathbf{y}\rangle \;&=\; -\frac{M}{\pi r}\,\text{Residue}\left[\frac{k\,e^{ikr}}{(k-(k_0-i\epsilon))(k+(k_0-i\epsilon))}\right]_{k=-k_0+i\epsilon}\\ &=\; -\frac{M}{\pi r}\times\frac{e^{ir(-k_0+i\epsilon}}{2}\\ &\xrightarrow[\epsilon\to+0]{}\; -\frac{M}{2\pi r}\times e^{-ik_0r}.\end{aligned}\tag{21}$$

Lippmann–Schwinger Series

Coming back to the perturbation theory, we look for a scattering eigenstate $|\Psi\rangle$ of the full Hamiltonian $\hat{H}=\hat{H}_0+\hat{V}$ by starting with a plane wave eigenstate $|\Psi_0\rangle$ of $\hat{H}_0$ for the same energy $E=k^2M$. Thus, we have $(E-\hat{H}_0)\,|\Psi_0\rangle=0$ and we look for $|\Psi\rangle$ such that

$$(E-\hat{H})\,|\Psi\rangle \;=\; (E-\hat{H}_0-\hat{V})\,|\Psi\rangle=0.\tag{22}$$

Consequently, for such a $|\Psi\rangle$ we would have

$$(E-\hat{H}_0)\big(|\Psi\rangle-|\Psi_0\rangle\big) \;=\; (E-\hat{H}_0)\,|\Psi\rangle \;=\; (E-\hat{H}_0-\hat{V})\,|\Psi\rangle \;+\; \hat{V}\,|\Psi\rangle \;=\; 0\;+\;\hat{V}\,|\Psi\rangle\,.\tag{23}$$

Now let's act with a Green's function $\hat{G}_\pm(E)$ on both sides of the equation: on the RHS we have

$$\hat{G}_\pm(E)\hat{V}\,|\Psi\rangle$$

while on the LHS we have

$$\hat{G}_\pm(E)\times(E-\hat{H}_0)\big(|\Psi\rangle-|\Psi_0\rangle\big) \;=\; \big(|\Psi\rangle-|\Psi_0\rangle\big),\tag{24}$$

thus

$$|\Psi\rangle \;-\; |\Psi_0\rangle \;=\; \hat{G}_\pm(E)\hat{V}\,|\Psi\rangle\tag{25}$$

and therefore

$$\big(1\;-\;\hat{G}_\pm(E)\hat{V}\big)\,|\Psi\rangle \;=\; |\Psi_0\rangle\,.\tag{26}$$

For a small (in some sense) perturbation $\hat{V}$, the operator on the LHS here has an inverse obtaining as a power series,

$$\left(1-\hat{G}_\pm(E)\hat{V}\right)^{-1} \;=\; 1 + \hat{G}_\pm(E)\hat{V} + \hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V} + \hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V} + \cdots, \tag{27}$$

hence the formal solution of eq. (26) is the Lippmann–Schwinger series

$$|\Psi\rangle \;=\; |\Psi_0\rangle \;+\; \hat{G}_\pm(E)\hat{V}\,|\Psi_0\rangle \;+\; \hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V}\,|\Psi_0\rangle \;+\; \cdots. \tag{28}$$

Usually, this series is summarized as

$$|\Psi\rangle \;=\; |\Psi_0\rangle \;+\; \hat{G}_\pm(E)\hat{T}_\pm(E)\,|\Psi_0\rangle \tag{29}$$

where $\hat{T}_\pm(E)$ is the Lippmann–Schwinger operator

$$\hat{T}_\pm(E) \;=\; \hat{V} + \hat{V}\hat{G}_\pm(E)\hat{V} + \hat{V}\hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V} + \hat{V}\hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V}\hat{G}_\pm(E)\hat{V} + \cdots. \tag{30}$$

Now let's look at the coordinate-space wavefunction of the perturbed state (29). We take the un-perturbed state $|\Psi_0\rangle$ to be the plane wave $|\mathbf{k}_0\rangle$, hence

$$\begin{aligned}\Psi(\mathbf{x}) \;&=\; e^{i\mathbf{k}_0\cdot\mathbf{x}} \;+\int\!d^3\mathbf{y}\;\langle\mathbf{x}|\,\hat{G}_\pm(E)\,|\mathbf{y}\rangle\times\langle\mathbf{y}|\,\hat{T}_\pm(E)\,|\mathbf{k}_0\rangle \\ &=\; e^{i\mathbf{k}_0\cdot\mathbf{x}} \;-\; \frac{M}{2\pi}\int\!d^3\mathbf{y}\,\frac{\exp\bigl(\pm ik_0|\mathbf{x}-\mathbf{y}|\bigr)}{|\mathbf{x}-\mathbf{y}|}\times\langle\mathbf{y}|\,\hat{T}_\pm(E)\,|\mathbf{k}_0\rangle\,.\end{aligned} \tag{31}$$

In the second factor under the integral here, every term in the series (30) for the $\hat{T}_\pm(E)$ operator has $\hat{V}$ as it's left-most factor, so we may write

$$\hat{T}_\pm(E) \;=\; \hat{V}\times(\text{other factors}) \tag{32}$$

and hence

$$\langle\mathbf{y}|\,\hat{T}_\pm(E)\,|\mathbf{k}_0\rangle \;=\; V(\mathbf{y})\times\langle\mathbf{y}|\,\text{other factors}\,|\mathbf{k}_0\rangle\,, \tag{33}$$

which becomes negligibly small for $\mathbf{y}$ outside the effective range of the potential $V(\mathbf{y})$. Consequently, for an asymptotically large $|\mathbf{x}|$ we may assume $|\mathbf{x}|\gg|\mathbf{y}|$ and hence in the first factor in the integrand of eq. (31)

$$|\mathbf{x}-\mathbf{y}| \;\approx\; |\mathbf{x}| \,-\, \mathbf{n}_x\cdot\mathbf{y} \quad\Longrightarrow\quad \frac{\exp\bigl(\pm ik_0|\mathbf{x}-\mathbf{y}|\bigr)}{|\mathbf{x}-\mathbf{y}|} \;\approx\; \frac{\exp(\pm ik_0|\mathbf{x}|)}{|\mathbf{x}|}\times\exp(\mp ik_0\mathbf{n}_x\cdot\mathbf{y}). \tag{34}$$

Plugging this formula into eq. (31), we find that

$$\text{for } |\mathbf{x}|\to\infty,\quad \Psi(\mathbf{x}) \;\approx\; e^{i\mathbf{k}_0\cdot\mathbf{x}} \;-\; \frac{M}{2\pi}\,\frac{\exp(\pm ik_0|\mathbf{x}|)}{|\mathbf{x}|}\times\int\! d^3\mathbf{y}\,\exp(\mp ik_0\mathbf{n}_x\cdot\mathbf{y})\times\langle\mathbf{y}|\,\hat{T}_\pm(E)\,|\mathbf{k}_0\rangle\,.$$

In particular, for the $\hat{G}_+(E)$ choice of the Green's function the second term here looks precisely like the divergent spherical wave of the scattering solution,

$$\text{for } |\mathbf{x}|\to\infty,\quad \Psi(\mathbf{x}) \;\approx\; e^{i\mathbf{k}_0\cdot\mathbf{x}} \;+\; \frac{\exp(+ik_0|\mathbf{x}|)}{|\mathbf{x}|}\times f(\mathbf{n}_x), \tag{35}$$

for the scattering amplitude

$$\begin{aligned} f(\mathbf{n}_x) \;&=\; -\frac{M}{2\pi}\int\! d^3\mathbf{y}\,\exp(\mp ik_0\mathbf{n}_x\cdot\mathbf{y})\times\langle\mathbf{y}|\,\hat{T}_+(E)\,|\mathbf{k}_0\rangle \\ &=\; -\frac{M}{2\pi}\times\bigl\langle\mathbf{k}'\bigr|\,\hat{T}_+(E)\,|\mathbf{k}_0\rangle \qquad (36)\\ \text{for } \mathbf{k}' \;&=\; k_0\mathbf{n}_x\,. \qquad (37) \end{aligned}$$

Of in conventional (MKSA or Gauss) units,

$$f(\theta) \;=\; -\frac{M}{2\pi\hbar^2}\,\bigl\langle\mathbf{k}'\bigr|\,\hat{T}_+(E)\,|\mathbf{k}_0\rangle \tag{38}$$

where θ is the angle between the initial particle directions of bk_0 and the final direction of $\mathbf{k}'$.

Born Approximation

Born series is the series for the matrix elements of the Lippmann–Schwinger operator (30). In momentum space, it looks like

$$\bigl\langle\mathbf{k}'\bigr|\,\hat{T}_+(E)\,|\mathbf{k}_0\rangle \;=\; \bigl\langle\mathbf{k}'\bigr|\,\hat{V}\,|\mathbf{k}_0\rangle + \int\!\frac{d^3\mathbf{k}_1}{(2\pi)^3}\,\bigl\langle\mathbf{k}'\bigr|\,\hat{T}_+(E)\,|\mathbf{k}_0\rangle\times\frac{2M}{(bk_0+i\epsilon)^2-\mathbf{k}_1^2}\times\langle\mathbf{k}_1|\,\hat{V}\,|\mathbf{k}_0\rangle + \cdots. \tag{39}$$

The Born approximations obtain by truncating this series to its first few terms. In particularly, the first Born approximation — often called *the Born approximation* — is simply the leading term in the series (39),

$$\langle \mathbf{k}' | \hat{T}_+(E) | \mathbf{k}_0 \rangle \;\approx\; \langle \mathbf{k}' | \hat{V} | \mathbf{k}_0 \rangle \tag{40}$$

and hence

$$f(\theta) \;=\; -\frac{M}{2\pi} \langle \mathbf{k}' | \hat{V} | \mathbf{k}_0 \rangle \;. \tag{41}$$

The matrix element here is simply the Fourier transform of the potential $V(\mathbf{y})$ to the momentum space,

$$\langle \mathbf{k}' | \hat{V} | \mathbf{k}_0 \rangle \;=\; \int d^3\mathbf{y}\, e^{-i\mathbf{k}'\cdot\mathbf{y}} \times V(\mathbf{y}) \times e^{+i\mathbf{y}\cdot\mathbf{k}_0} \;=\; \int d^3\mathbf{y}\, e^{-i\mathbf{q}\cdot\mathbf{y}} \times V(\mathbf{y}) \tag{42}$$

where $\mathbf{q} = \mathbf{k}' - \mathbf{k}_0$. In particular, for a spherically symmetric potential $V(r)$,

$$\begin{aligned} \langle \mathbf{k}' | \hat{V} | \mathbf{k}_0 \rangle \;&=\; \int_0^\infty dr_y\, r_y^2 \int_0^\pi d\theta_y\, 2\pi \sin\theta_y \times V(r_y) \times \exp(iqr_y \cos\theta_y) \\ &=\; \int_0^\infty dr_y\, r_y^2 v(r_y) \times \frac{4\pi \sin(qr_y)}{qr_y} \\ &=\; \frac{4\pi}{q} \int_0^\infty dr\, V(r) \times r \sin(qr), \end{aligned} \tag{43}$$

and therefore

$$f(\theta) \;=\; -\frac{2M}{\hbar^2 q} \int_0^\infty dr\, V(r) \times r \sin(qr) \tag{44}$$

$$\text{for } q \;=\; |\mathbf{k}' - \mathbf{k}| \;=\; \frac{\sqrt{2ME}}{\hbar} \times 2\sin(\theta/2). \tag{45}$$

Example:

For an example, consider the Yukawa potential — or equivalently, the screened Coulomb potential —

$$V(r) \;=\; \frac{A}{r}\times e^{-\kappa r}. \tag{46}$$

For this potential

$$\begin{aligned}\int_0^\infty dr\,V(r)\times r\sin(qr) \;&=\int_0^\infty dr\,Ae^{-\kappa r}\times \operatorname{Im} e^{iqr}\\ &=\;A\operatorname{Im}\int_0^\infty dr\;\exp(-r(\kappa-iq))\\ &=\;A\operatorname{Im}\frac{1}{\kappa-iq}\;=\;A\,\frac{q}{q^2+\kappa^2}\,,\end{aligned} \tag{47}$$

hence

$$f(\theta)\;=\;-\frac{2MA}{\hbar^2}\times\frac{1}{q^2+\kappa^2}\;=\;-\frac{2MA}{(\hbar\kappa)^2+4\mathbf{p}^2\sin^2(\theta/2)}\,. \tag{48}$$

In particular, for the un-screened Coulomb potential with $\kappa\to 0$ while $A=Z_1Z_2e^2$ (in Gauss units), we get

$$f(\theta)\;=\;-\frac{2MZ_1Z_2e^2}{4(M\mathbf{v})^2\sin^2(\theta/2)} \tag{49}$$

and therefore

$$\frac{d\sigma}{d\Omega}\;=\;\frac{Z_1^2Z_2^2e^4}{M_{\rm red}^2\mathbf{v}_{\rm rel}^4}\times\frac{1}{4\sin^4(\theta/2)}\,. \tag{50}$$

Note: Although this formula is based on the first Born approximation, it happens to be exact in Quantum Mechanics. Also, it happens to be in perfect agreement with the classical Rutherford formula for the Coulomb scattering!

The S Matrix and the Partial Wave Analysis

Beyond the Born approximation, we need to go back to the matrix elements of the Lippmann–Schwinger operator

$$\hat{T}_+(E) \;=\; \hat{V} + \hat{V}\hat{G}_+(E)\hat{V} + \hat{V}\hat{G}_+(E)\hat{V}\hat{G}_+(E)\hat{V} + \hat{V}\hat{G}_+(E)\hat{V}\hat{G}_+(E)\hat{V}\hat{G}_+(E)\hat{V} + \cdots. \quad (30)$$

The same Lippmann–Schwinger operator is also related to the S-matrix

$$\hat{S} \;=\; \mathbf{T}\text{-exp}\left(-i\int\limits_{-\infty}^{+\infty} dt\, e^{+it\hat{H}_0}\hat{V}e^{-it\hat{H}_0}\right), \quad (51)$$

or rather their respective matrix elements between eigenstates of the un-perturbed Hamiltonian $\hat{H}_0$ are related as

$$\langle f|\,\hat{S}\,|i\rangle \;=\; \langle f|i\rangle \;-2\pi i\delta(E_f - E_i)\times\langle f|\,\hat{T}_+(E_f = E_i)\,|i\rangle\,. \quad (52)$$

This relation obtains by formal integration of the Dyson series hiding in the time-ordered exponential, but I am not going to do it in these notes. Instead, I am going to use it as it is, and combine with the unitarity of the $\hat{S}$ operator.

Suppose the particles involved in the scattering are spinless, and the potential $V(r)$ is spherically symmetric. In this case, the complete Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$ commutes with the orbital angular momentum $\hat{\mathbf{L}}$, so the $\hat{S}$-operator also commutes with $\hat{\mathbf{L}}$. Consequently, we may use the simultaneous eigenstates of $\hat{\mathbf{L}}^2$, $\hat{L}_z$, and $\hat{H}_0$ to make a basis $|E,\ell,m\rangle$ of all the unbound states, and in that basis the S-matrix should be diagonal,

$$\hat{S}\,|E,\ell,m\rangle \;=\; C(E,\ell)\,|E,\ell,m\rangle \quad (53)$$

Furthermore, by unitarity of the S-matrix, all the coefficients $C(E,\ell)$ here should be unimodular, thus

$$\hat{S}\,|E,\ell,m\rangle \;=\; \exp\bigl(2i\delta_\ell(E)\bigr)\,|E,\ell,m\rangle \quad (54)$$

for some real *phase shifts* $\delta_\ell(E)$. Consequently,

$$\bigl\langle E',\ell',m'\bigr|\,\hat{S}\,|E,\ell,m\rangle \;=\; (2\pi)\delta(E'-E)\,\delta_{\ell',\ell}\delta_{m',m}\times e^{2i\delta_\ell(E)}, \quad (55)$$

which in light of eq. (52) translates to

$$\left\langle E,\ell',m'\right|\hat{T}_+(E)\left|E,\ell,m\right\rangle \;=\; \delta_{\ell',\ell}\delta_{m',m}\times\frac{e^{2i\delta_\ell(E)}-1}{-i}\,. \tag{56}$$

Furthermore, translating between the $|E,\ell,m\rangle$ basis and the momentum basis, we have

$$\langle E,\ell,m|\mathbf{k}\rangle \;=\; \frac{2\pi}{\sqrt{M\,|\mathbf{k}|}}\delta(E-\frac{\mathbf{k}^2}{2M})\times Y^*_{\ell,m}(\mathbf{n}_\mathbf{k}). \tag{57}$$

Consequently, for 2 momentum vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ of equal magnitudes $|\mathbf{k}_1|=|\mathbf{k}_2|=\sqrt{2ME}$ but different directions $\mathbf{n}_1\neq\mathbf{n}_2$, we have

$$\begin{aligned}\langle\mathbf{k}_2|\,\hat{T}_+(E)\,|\mathbf{k}_1\rangle \;&=\; \sum_{\ell,m}\langle\mathbf{k}_2|E,\ell,m\rangle\times\frac{e^{2i\delta_\ell(E)}-1}{-i}\times\langle E,\ell,m|\mathbf{k}_1\rangle\\ &=\; \frac{4\pi^2}{Mk}\sum_\ell\frac{e^{2i\delta_\ell(E)}-1}{-i}\times\sum_m Y_{\ell,m}(\mathbf{n}_2)Y^*_{\ell,m}(\mathbf{n}_1)\\ &=\; \frac{4\pi^2}{Mk}\sum_\ell\frac{e^{2i\delta_\ell(E)}-1}{-i}\times\frac{(2\ell+1)}{4\pi}P_\ell(\mathbf{n}_2\cdot\mathbf{n}_1)\\ &=\; -\frac{2\pi}{M}\sum_\ell\frac{e^{2i\delta_\ell(E)}-1}{2ik}\times(2\ell+1)P_\ell(\cos\theta)\end{aligned} \tag{58}$$

where θ is the angle between the directions of $\mathbf{k}_1$ and $\mathbf{k}_2$ and P_ℓ are the Legendre polynomials. Therefore, *in terms of the phase shifts $\delta_\ell(E)$, the scattering amplitude is*

$$f(\theta) \;=\; \sum_{\ell=0}^{\infty}\frac{e^{2i\delta_\ell(E)}-1}{2ik}\times(2\ell+1)P_\ell(\cos\theta). \tag{59}$$

The total cross-section also has a simple form in terms of the phase shifts. Indeed,

$$\sigma_{\rm tot} \;=\; \int\!d^2\Omega\,\frac{d\sigma}{d\Omega} \;=\; \int_0^\pi\!d\theta\,2\pi\sin\theta\times|f(\theta)|^2, \tag{60}$$

so for the scattering amplitude $f(\theta)$ expanded into partial waves according to eq. (59), — or more generally, as

$$f(\theta) \;=\; \sum_\ell C_\ell P_\ell(\cos\theta), \tag{61}$$

— we have

$$\begin{aligned}
\sigma_{\rm tot} &= \int_0^\pi d\theta\, 2\pi\sin\theta \times \sum_\ell\sum_{\ell'} C_\ell^* C_{\ell'} P_\ell(\cos\theta) P_{\ell'}(\cos\theta) \\
&= \sum_{\ell,l'} C_\ell^* C_{\ell'} \times 2\pi \int_{-1}^{+1} d\cos\theta\, P_\ell(\cos\theta) P_{\ell'}(\cos\theta) \\
&= \sum_{\ell,l'} C_\ell^* C_{\ell'} \times \frac{4\pi}{2\ell+1}\,\delta_{\ell,\ell'} \\
&= \sum_\ell \frac{4\pi}{2\ell+1}\,|C_\ell|^2.
\end{aligned} \tag{62}$$

In our case,

$$C_\ell \;=\; (2\ell+1)\times\frac{e^{2i\delta_\ell}-1}{2ik} \quad\Longrightarrow\quad |C_\ell|^2 \;=\; \frac{(2\ell+1)^2}{k^2}\times\sin^2\delta_\ell\,, \tag{63}$$

hence

$$\sigma_{\rm tot} \;=\; \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2(\delta_\ell). \tag{64}$$

Note the **optical theorem:** *the imaginary part of the forward scattering amplitude is related to the total cross-section as*

$$\sigma_{\rm tot} \;=\; \frac{4\pi}{k}\times{\rm Im}\, f(\theta=0). \tag{65}$$

Proof: For $\theta = 0$, all the Legendre polynomials $P_\ell(\cos\theta = 1)$ evaluate to 1. Consequently, eq. (59) for the forward amplitude evaluates to

$$f(\theta=0) \;=\; \sum_\ell \frac{e^{2i\delta_\ell}-1}{2ik}\times(2\ell+1) \;=\; \frac{1}{k}\sum_\ell(2\ell+1)\times\sin(\delta_\ell)e^{i\delta_\ell}, \tag{66}$$

and its imaginary part is

$$\operatorname{Im} f(\theta=0) \;=\; \frac{1}{k}\sum_{\ell}(2\ell+1)\times\sin^2\delta_\ell\,. \tag{67}$$

Comparing this formula to eq. (64) for the total cross-section, we immediately see the relation (65) between them. *Quod erat demonstrandum.*

Calculating the Phase Shifts

Now that we know what the phase shifts δ_ℓ are good for, let's learn how to calculate them. Our starting point the Schrödinger equation for the $|E,\ell,m\rangle$ states with wave-functions of the form

$$\Psi(r,\theta,\phi) \;=\; \psi_\ell(r)\times Y_{\ell,m}(\theta,\phi). \tag{68}$$

The radial wavefunctions $\psi_\ell(r)$ obey

$$-\frac{1}{2M}\left(\psi''(r)\,+\,\frac{2}{r}\psi'(r)\,-\,\frac{\ell(\ell+1)}{r^2}\psi(r)\right)\,+\,V(r)\psi(r)\;=\;E\psi(r), \tag{69}$$

or equivalently

$$(r\psi(r))''\,+\,\left(k^2\,-\,2MV(r)\,-\,\frac{\ell(\ell+1)}{r^2}\right)\times r\psi(r)\;=\;0. \tag{70}$$

In the total absence of the potential, the free solution of this equation that is non-singular at $r=0$ is the spherical Bessel function $\psi_\ell(r)=kj_\ell(kr)$, which at large distances $kr\gg\ell$ asymptotes to

$$r\psi_\ell(r)\;\longrightarrow\;(+i)^\ell e^{-ikr}\,+\,(-i)^\ell e^{+ikr}. \tag{71}$$

Physically, the first terms here is the (radial profile of the) convergent incoming wave while the second term is the (radial profile of the) divergent outgoing wave.

In presence of the potential, the solutions of the radial equations (70) would be more complicated, but at asymptotically large distances where

$$\text{both } 2MV(r) \text{ and } \frac{\ell(\ell+1)}{r^2} \ll k^2, \tag{72}$$

the radial profiles $r\psi_\ell(r)$ should always be combinations of incoming and outgoing waves, albeit with different relative phases,

$$r\psi_\ell(r) \longrightarrow \psi_{\text{incoming}}(r) + e^{2i\delta_\ell} \times \psi_{\text{outgoing}}(r), \tag{73}$$

or — once we multiply both terms by $e^{-i\delta_\ell}$, —

$$r\psi_\ell(r) \longrightarrow (+i)^\ell e^{-i\delta_\ell - ikr} + (-i)^\ell e^{+i\delta_\ell + ikr} = 2\sin\bigl(kr + \delta_\ell - \ell \times \tfrac{\pi}{2}\bigr). \tag{74}$$

In light of this formula, this is how one calculates the phase shifts for a potential scattering in QM:

1. Solve the radial Schrödinger equation (70) for the $\psi_\ell(r)$, subject to the boundary condition of no singularity at $r \to 0$.
2. Look at the asymptotic behavior of the solutions at large distances $r \to \infty$. The solutions must asymptote to

$$\psi_\ell(r) \xrightarrow[r\to\infty]{} \frac{\text{const}}{r} \times \sin\bigl(kr + \delta_\ell - \ell \times \tfrac{\pi}{2}\bigr) \tag{75}$$

for some real phase shifts δ_ℓ. And these are precisely the phase shifts we need to calculate the scattering amplitude $f(\theta)$ and the total cross-section.

Small hard sphere example

For an example of calculating the phase shifts, consider a hard sphere of a small radius $a \ll (1/k)$. By a hard sphere, the particle cannot penetrate the sphere at all, but there is nothing outside the sphere. In terms of the potential, the hard sphere is equivalent to

$$V(r) \;=\; \begin{cases} +\infty & \text{for } r < a, \\ 0 & \text{for } r > 0, \end{cases} \tag{76}$$

while in terms of the radial Schrödinger equation, it means the Dirichlet boundary condition $\psi_\ell(r = a) = 0$ at the sphere's edge, but outside the sphere ψ_ℓ obeys the free radial equation

$$(r\psi_\ell(r))'' \;+\; \left(k^2 \;-\; \frac{\ell(\ell+1)}{r^2}\right) \times r\psi_\ell(r) \;=\; 0. \tag{77}$$

A general solution of this equation is a linear combination of the regular and irregular spherical Bessel functions of order ℓ, thus up to an overall constant factor

$$\psi_\ell(r) \;=\; \cos\alpha_\ell \times j_\ell(kr) \;-\; \sin\alpha_\ell \times n_\ell(kr), \tag{78}$$

where α_ℓ obtains from the boundary condition $\psi_\ell = 0$ for $r = a$, thus

$$\cos\alpha_\ell \times j_\ell(ka) \;-\sin\alpha_\ell \times n_\ell(ka) \;=\; 0 \quad\Longrightarrow\quad \tan\alpha_\ell \;=\; \frac{j_\ell(ka)}{n_\ell(ka)}\,. \tag{79}$$

Asymptotically, at large distances $kr \gg 1, \ell$, the two spherical Bessel functions behave as

$$j_\ell(kr) \;\longrightarrow\; \frac{\sin(kr - \ell \times \frac{\pi}{2})}{kr}\,, \qquad n_\ell(kr) \;\longrightarrow\; -\frac{\cos(kr - \ell \times \frac{\pi}{2})}{kr}\,, \tag{80}$$

hence the radial wavefunctions of the form (78) become

$$\psi_\ell(r) \;\longrightarrow\; \frac{\sin(kr - \ell \times \frac{\pi}{2} + \alpha_\ell)}{kr}\,. \tag{81}$$

Comparing this equation to eq. (75) we immediately identify the phase shifts as

$$\delta_\ell \;=\; \alpha_\ell \;=\; \arctan\frac{j_\ell(ka)}{n_\ell(ka)}\,. \tag{82}$$

This formula applies to scattering off a hard sphere of any radius, but it becomes much simpler for small radii $ka \ll 1$. In this case, we may approximate the spherical Bessel functions by their low-radius limits, thus

$$j_\ell(ka) \;\approx\; \frac{(ka)^\ell}{(2\ell+1)!!}\,, \qquad n_\ell(ka) \;\approx\; -\frac{(2\ell-1)!!}{(ka)^{\ell+1}}\,, \tag{83}$$

and hence

$$\tan\delta_\ell \;\approx\; -\frac{(ka)^{2\ell+1}}{(2\ell-1)!!\,(2\ell+1)!!}\,. \tag{84}$$

In particular,

$$\tan\delta_0 \;\approx\; -(ka), \quad \tan\delta_1 \;\approx\; -\frac{(ka)^3}{3}\,, \quad \tan\delta_2 \;\approx\; -\frac{(ka)^5}{45}\,, \quad \ldots. \tag{85}$$

For small ka, all these phase shifts are small, and they are rapidly shrink with ℓ, so to a leading order we may approximate

$$\delta_0 \;\approx\; -ka, \quad \text{all other } \delta_\ell \;\approx\; 0. \tag{86}$$

Consequently,

$$\begin{aligned} \frac{e^{2i\delta_0}-1}{2ik} \;&\approx\; \frac{-2ika}{2ik} \;=\; -a, \\ \text{other } \frac{e^{2i\delta_\ell}-1}{2ik} \;&\approx\; 0, \end{aligned} \tag{87}$$

and therefore the scattering amplitude

$$f(\theta) \;\approx\; -a\times P_0(\theta) \;+\; 0 \;=\; -a\;\forall\theta. \tag{88}$$

This leads to the isotropic partial cross-section

$$\frac{d\sigma}{d\Omega} \;=\; a^2 \quad \text{in all directions} \tag{89}$$

and hence

$$\sigma_{\text{total}} \;=\; 4\pi a^2. \tag{90}$$

Note this total cross section is 4 times larger than the geometric cross section πa^2 of the hard sphere, but that's OK because the classical geometric scattering has no reason to work in the $ka \ll 1$ regime.