More Scattering: the Partial Wave Expansion

Michael Fowler 1/17/08

Plane Waves and Partial Waves

We are considering the solution to Schrödinger's equation for scattering of an incoming plane wave in the *z*-direction by a potential localized in a region near the origin, so that the total wave function beyond the range of the potential has the form

$$\psi\left(r,\theta,\varphi\right) = e^{ikr\cos\theta} + f\left(\theta,\varphi\right)\frac{e^{ikr}}{r}.$$

The overall normalization is of no concern, we are only interested in the *fraction* of the ingoing wave that is scattered. Clearly the outgoing current generated by scattering into a solid angle $d\Omega$ at angle θ, φ is $\left|f\left(\theta,\varphi\right)\right|^2 d\Omega$ multiplied by a velocity factor that also appears in the incoming wave.

Many potentials in nature are spherically symmetric, or nearly so, and from a theorist's point of view it would be nice if the experimentalists could exploit this symmetry by arranging to send in spherical waves corresponding to different angular momenta rather than breaking the symmetry by choosing a particular direction. Unfortunately, this is difficult to arrange, and we must be satisfied with the remaining azimuthal symmetry of rotations about the ingoing beam direction.

In fact, though, a full analysis of the outgoing scattered waves from an ingoing plane wave yields the same information as would spherical wave scattering. This is because a plane wave can actually be written as a *sum over spherical waves*:

$$e^{i\vec{k}.\vec{r}} = e^{ikr\cos\theta} = \sum_l i^l(2l+1)j_l(kr)P_l(\cos\theta)$$

Visualizing this plane wave flowing past the origin, it is clear that in spherical terms the plane wave contains both incoming *and* outgoing spherical waves. As we shall discuss in more detail in the next few pages, the real function $j_l(kr)$ is a standing wave, made up of incoming and outgoing waves of equal amplitude.

We are, obviously, interested only in the outgoing spherical waves *that originate by scattering from the potential*, so we must be careful not to confuse the pre-existing outgoing wave components of the plane wave with the *new* outgoing waves generated by the potential.

The radial functions $j_l(kr)$ appearing in the above expansion of a plane wave in its spherical components are the *spherical Bessel functions*, discussed below. The azimuthal rotational symmetry of plane wave + spherical potential around the direction of the ingoing wave ensures that the angular dependence of the wave function is just $P_l(\cos\theta)$, not $Y_{lm}\left(\theta,\varphi\right)$. The coefficient

$i^l(2l+1)$ is derived in Landau and Lifshitz, §34, by comparing the coefficient of $(kr\cos\theta)^n$ on the two sides of the equation: as we shall see below, $(kr)^n$ does not appear in $j_l(kr)$ for l greater than n, and $(\cos\theta)^n$ does not appear in $P_l(\cos\theta)$ for l less than n, so the *combination* $(kr\cos\theta)^n$ only occurs once—in the nth term, and the coefficients on both sides of the equation can be matched. (To get the coefficient right, we must of course specify the normalizations for the Bessel function—see below—and the Legendre polynomial.)

Mathematical Interval: The Spherical Bessel and Neumann Functions

The plane wave $e^{i\vec{k}\cdot\vec{r}}$ is a trivial solution of Schrödinger's equation with zero potential, and therefore, since the $P_l(\cos\theta)$ form a linearly independent set, each term $j_l(kr)P_l(\cos\theta)$ in the plane wave series must be itself a solution to the zero-potential Schrödinger's equation. It follows that $j_l(kr)$ satisfies the zero-potential radial Schrödinger equation:

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

The standard substitution $R_l(r)=u_l(r)/r$ yields

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

For the simple case $l=0$ the two solutions are $u_0(r)=\sin kr,\ \cos kr$. The corresponding radial functions $R_0(r)$ are (apart from overall constants) the zeroth-order *Bessel* and *Neumann* functions respectively.

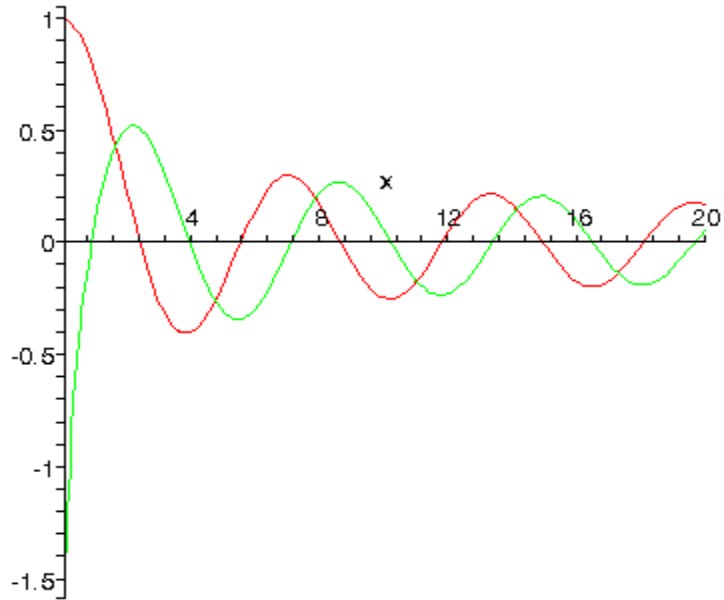The standard normalization for the zeroth-order Bessel function is

$$j_0(kr)=\frac{\sin kr}{kr},$$

and the zeroth-order Neumann function

$$n_0(kr)=-\frac{\cos kr}{kr}.$$

Note that the Bessel function is the one well-behaved at the origin: it could be generated by integrating out from the origin with initial boundary conditions of value one, slope zero.

Here is a plot of $j_0(kr)$ and $n_0(kr)$ from $kr = 0.1$ to 20:

For nonzero l, near the origin is $R_l(r) \sim r^l$ or $\sim r^{-(l+1)}$. The well-behaved $\sim r^l$ solution is the Bessel function, the singular function the Neumann function. The standard normalizations of these functions are given below.

Here are $j_5(kr)$ and $j_{50}(kr)$:
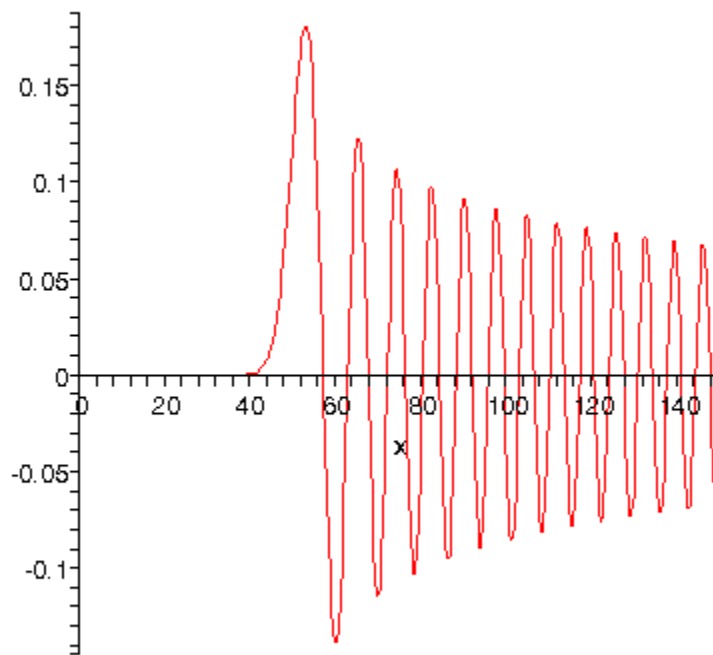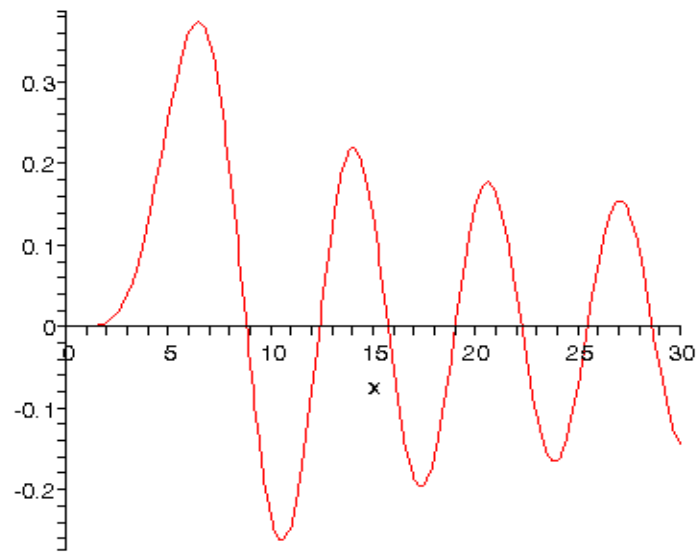
Detailed Derivation of Bessel and Neumann Functions
This subsection is just here for completeness. We use the dimensionless variable $\rho = kr$.

To find the higher l solutions, we follow a clever trick given in Landau and Lifshitz (§33).

Factor out the ρ^l behavior near the origin by writing

$$R_l = (\rho)^l \, \chi_l(\rho).$$

The function $\chi_l(\rho)$ satisfies

$$\frac{d^2}{d\rho^2} \chi_l(\rho) + \frac{2(l+1)}{\rho} \frac{d}{d\rho} \chi_l(\rho) + \chi_l(\rho) = 0.$$

The trick is to differentiate this equation with respect to ρ:

$$\frac{d^3}{d\rho^3} \chi_l(\rho) + \frac{2(l+1)}{\rho} \frac{d^2}{d\rho^2} \chi_l(\rho) + \left(1 - \frac{2(l+1)}{\rho^2}\right) \frac{d}{d\rho} \chi_l(\rho) = 0.$$

Writing purely formally $\frac{d}{d\rho} \chi_l(\rho) = \rho \chi_{l+1}(\rho)$, the equation becomes

$$\frac{d^2}{d\rho^2} \chi_{l+1}(\rho) + \frac{2(l+2)}{\rho} \frac{d}{d\rho} \chi_{l+1}(\rho) + \chi_{l+1}(\rho) = 0.$$

But this *is* the equation that $\chi_{l+1}(\rho)$ must obey! So we have a *recursion formula* for generating *all* the $j_l(\rho)$ from the zeroth one: $\chi_{l+1}(\rho) = \frac{1}{\rho} \frac{d}{d\rho} \chi_l(\rho)$, and $j_l(\rho) = (\rho)^l \chi_l(\rho)$, up to a normalization constant fixed by convention.

In fact, the standard normalization is

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho} \frac{d}{d\rho}\right)^l \left(\frac{\sin \rho}{\rho}\right).$$

Now

$$(\sin \rho)/\rho = \sum_0^\infty (-1)^n \, \rho^{2n} / (2n+1)!$$

This is a sum of only *even* powers of ρ. It is easily checked that operating on this series with $\left(\frac{1}{\rho} \frac{d}{d\rho}\right)^l$ can never generate any negative powers of ρ. It follows that $j_l(\rho)$, written as a power series in ρ, has leading term proportional to ρ^l. The coefficient of this leading term can be found by applying the differential operator to the series for $(\sin \rho)/\rho$,

$$j_l(\rho) \sim \frac{\rho^l}{(2l+1)!!} \quad \text{as } \rho \to 0.$$

This r^l behavior near the origin is the usual well-behaved solution to Schrödinger's equation in the region where the centrifugal term dominates.

Note that the small ρ behavior is *not* immediately evident from the usual presentation of the $j_l(\rho)$'s, written as a mix of powers and trigonometric functions, for example

$$j_1(\rho) = \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho}, \quad j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin \rho - \frac{3\cos \rho}{\rho^2}, \quad \text{etc.}$$

Turning now to the behavior of the $j_l(\rho)$'s for *large* ρ, from

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(\frac{\sin \rho}{\rho}\right)$$

it is evident that the dominant term in the large ρ regime (the one of order $1/\rho$) is generated by differentiating *only* the trigonometric function at each step. Each such differentiation can be seen to be equivalent to multiplying by (-1) and subtracting $\pi/2$ from the argument, so

$$j_l(\rho) \to \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right) \quad \text{as } \rho \to \infty.$$

These $j_l(\rho)$, then, are the physical partial-wave solutions to the Schrödinger equation with zero potential. When a potential is turned on, the wave function near the origin is still $\sim \rho^l$ (assuming, as we always do, that the potential is negligible compared with the $l(l+1)/\rho^2$ term sufficiently close to the origin). The wave function beyond the range of the potential can be found numerically in principle by integrating out from the origin, and in fact will be like $j_l(\rho)$ above *except* that there will be an extra phase factor, called the "phase shift" and denoted by δ) in the sine. The significance of this is that in the far region, the wave function is a linear combination of the Bessel function *and* the Neumann function (the solution to the zero-potential Schrödinger equation singular at the origin). It is therefore necessary to review the Neumann functions as well.

As stated above, the $l = 0$ Neumann function is

$$n_0(\rho) = -\frac{\cos \rho}{\rho},$$

the minus sign being the standard convention.

An argument parallel to the one above for the Bessel functions establishes that the higher-order Neumann functions are given by:

$$n_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \left(-\frac{\cos\rho}{\rho}\right).$$

Near the origin

$$n_l(\rho) \sim \frac{(2l-1)!!}{\rho^{l+1}} \text{ as } \rho \to 0$$

and for large ρ

$$n_l(\rho) \to -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right) \text{ as } \rho \to \infty,$$

so a function of the form $\frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2} + \delta\right)$ asymptotically can be written as a linear combination of Bessel and Neumann functions in that region.

Finally, the spherical *Hankel* functions are just the combinations of Bessel and Neumann functions that look like outgoing or incoming plane waves in the asymptotic region:

$$h_l(\rho) = j_l(\rho) + in_l(\rho), \quad h_l{}^*(\rho) = j_l(\rho) - in_l(\rho),$$

so for large ρ,

$$h_l(\rho) \to \frac{e^{i(\rho - l\pi/2)}}{i\rho}, \quad h_l{}^*(\rho) \to -\frac{e^{-i(\rho - l\pi/2)}}{i\rho}.$$

The Partial Wave Scattering Matrix

Let us imagine for a moment that we could just send in a (time-independent) spherical wave, with θ variation given by $P_l(\cos\theta)$. For this l^{th} partial wave (dropping overall normalization constants as usual) the radial function far from the origin for zero potential is

$$j_l(kr) \to \frac{1}{kr}\sin\left(kr - \frac{l\pi}{2}\right) = \frac{i}{2k}\left(\frac{e^{-i(kr - l\pi/2)}}{r} - \frac{e^{+i(kr - l\pi/2)}}{r}\right).$$

If now the (spherically symmetric) potential is turned on, the only possible change to this standing wave solution in the faraway region (where the potential is zero) is a phase shift δ:

$$\sin\left(kr - \frac{l\pi}{2}\right) \to \sin\left(kr - \frac{l\pi}{2} + \delta_l(k)\right).$$

This is what we would find on integrating the Schrödinger equation out from nonsingular behavior at the origin.

But in practice, the ingoing wave is given, and *its phase cannot be affected by switching on the potential*. Yet we must still have the solution to the same Schrödinger equation, so to match with the result above we multiply the whole partial wave function by the phase factor $e^{i\delta_l(k)}$. The result is to put *twice* the phase change onto the outgoing wave, so that when the potential is switched on the change in the asymptotic wave function must be

$$\frac{i}{2k}\left(\frac{e^{-i(kr-l\pi/2)}}{r} - \frac{e^{+i(kr-l\pi/2)}}{r}\right) \to \frac{i}{2k}\left(\frac{e^{-i(kr-l\pi/2)}}{r} - \frac{S_l(k)e^{+i(kr-l\pi/2)}}{r}\right).$$

This equation introduces the *scattering matrix*

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

which must lie on the unit circle $|S| = 1$ to conserve probability—the outgoing current must equal the ingoing current. If there is no scattering, that is, zero phase shift, the scattering matrix is unity.

It should be noted that when the radial Schrödinger's equation is solved for a nonzero potential by integrating out from the origin, with $\psi = 0$ and $\psi' = 1$ initially, the real function thus generated differs from the wave function given above by an *overall* phase factor $e^{i\delta_l(k)}$.

Scattering of a Plane Wave

We're now ready to take the ingoing plane wave, break it into its partial wave components corresponding to different angular momenta, have the partial waves individually phase shifted by l-dependent phases, and add it all back together to get the original plane wave plus the scattered wave.

We are only interested here in the wave function far away from the potential. In this region, the original plane wave is

$$e^{i\vec{k}\cdot\vec{r}} = e^{ikr\cos\theta} = \sum_l i^l(2l+1)j_l(kr)P_l(\cos\theta) = \sum_l i^l(2l+1)\frac{i}{2k}\left(\frac{e^{-i(kr-l\pi/2)}}{r} - \frac{e^{+i(kr-l\pi/2)}}{r}\right)P_l(\cos\theta).$$

Switching on the potential phase shifts factor the outgoing wave:

$$\frac{e^{+i(kr-l\pi/2)}}{r} \quad \rightarrow \quad \frac{S_l(k)e^{+i(kr-l\pi/2)}}{r}$$

The actual *scattering* by the potential is the *difference* between these two terms. The complete wave function in the far region (including the incoming plane wave) is therefore:

$$\psi(r,\theta,\varphi) = e^{ikr\cos\theta} + \left(\sum_l (2l+1)\frac{(S_l(k)-1)}{2ik}P_l(\cos\theta) \right)\frac{e^{ikr}}{r}.$$

The i^l factor cancelled the $e^{-il\pi/2}$. The -1 in $(S_l(k)-1)$ is there because zero scattering means $S=1$. Alternatively, it could be regarded as subtracting off the outgoing waves already present in the plane wave, as discussed above. There is no φ-dependence since with the potential being spherically-symmetric the whole problem is azimuthally-symmetric about the direction of the incoming wave.

It is perhaps worth mentioning that for scattering in just one partial wave, the outgoing current is equal to the ingoing current, whether there is a phase shift or not. So, if switching on the potential does not affect the total current scattered in any partial wave, how can it cause any scattering? The point is that for an ingoing *plane wave* with zero potential, the ingoing and outgoing components have the right relative phase to add to a component of a plane wave—a tautology, perhaps. But if an extra phase is introduced into the outgoing wave *only*, the ingoing + outgoing will *no longer give a plane wave*—there will be an extra outgoing part proportional to $(S_l(k)-1)$.

Recall that the scattering amplitude $f(\theta,\varphi)$ was defined in terms of the solution to Schrödinger's equation having an ingoing plane wave by

$$\psi(r,\theta,\varphi) = e^{ikr\cos\theta} + f(\theta,\varphi)\frac{e^{ikr}}{r}.$$

We're now ready to express the scattering amplitude in terms of the partial wave phase shifts (for a spherically symmetric potential, of course):

$$f(\theta,\varphi) = f(\theta) = \sum_l (2l+1)\frac{(S_l(k)-1)}{2ik}P_l(\cos\theta) = \sum_l (2l+1)f_l(k)P_l(\cos\theta)$$

where

$$f_l(k) = \frac{1}{k}e^{i\delta_l(k)}\sin\delta_l(k)$$

is called the *partial wave scattering amplitude*, or just the *partial wave amplitude*.

So the total scattering amplitude is the sum of these partial wave amplitudes:

$$f(\theta) = \frac{1}{k}\sum_l (2l+1)e^{i\delta_l(k)}\sin\delta_l(k)P_l(\cos\theta).$$

The total scattering cross-section

$$\sigma = \int |f(\theta)|^2 d\Omega$$

$$= 2\pi\int_0^\pi |f(\theta)|^2\sin\theta d\theta$$

$$= 2\pi\int_0^\pi \left|\frac{1}{k}\sum_l (2l+1)e^{i\delta_l(k)}\sin\delta_l(k)P_l(\cos\theta)\right|^2 \sin\theta d\theta$$

and the normalization of the Legendre polynomials

$$\int_0^\pi P_l^2(\cos\theta)\sin\theta d\theta = \frac{2}{2l+1}$$

gives

$$\sigma = 4\pi\sum_{l=0}^\infty (2l+1)|f_l(k)|^2 = \frac{4\pi}{k^2}\sum_{l=0}^\infty (2l+1)\sin^2\delta_l.$$

So the total cross-section is the sum of the cross-sections for each l value. This does *not* mean, though, that the differential cross-section for scattering *into a given solid angle* is a sum over separate l values—the different components interfere. It is only when *all* angles are integrated over that the orthogonality of the Legendre polynomials guarantees that the cross-terms vanish.

Notice that the maximum possible scattering cross-section for particles in angular momentum state l is $(4\pi/k^2)(2l+1)$, which is *four times* the classical cross section for that partial wave impinging on, say, a hard sphere! (Imagine semiclassically particles in an annular area: angular momentum $L=rp$, say, but $L=\hbar l$ and $p=\hbar k$ so $l=rk$. Therefore the annular area corresponding to angular momentum "between" l and $l+1$ has inner and outer radii l/k and $(l+1)/k$ and therefore area $\pi(2l+1)/k^2$.) The quantum result is essentially a diffractive effect, we'll discuss it more later.

It's easy to prove the *optical theorem* for a spherically-symmetric potential: just take the imaginary part of each side of the equation

$$f(\theta) = \frac{1}{k}\sum_l (2l+1)e^{i\delta_l(k)}\sin\delta_l(k)P_l(\cos\theta)$$

at $\theta = 0$, using $P_l(1) = 1$,

$$\text{Im} f(\theta = 0) = \frac{1}{k} \sum_l (2l+1) \sin^2 \delta_l(k)$$

from which the optical theorem $\text{Im} f(0) = k\sigma/4\pi$ follows immediately.

It's also worth noting what the unitarity of the lth partial wave scattering matrix $S_l^\dagger S_l = 1$ implies for the partial wave amplitude $f_l(k) = \frac{1}{k} e^{i\delta_l(k)} \sin \delta_l(k)$. Since $S_l(k) = e^{2i\delta_l(k)}$, it follows that

$$S_l(k) = 1 + 2ikf_l(k).$$

From this, $S_l^\dagger S_l = 1$ gives:

$$\text{Im} f_l(k) = k|f_l(k)|^2.$$

This can be put more simply:

$$\text{Im} \frac{1}{f_l(k)} = -k.$$

In fact,

$$f_l(k) = \frac{1}{k(\cot \delta_l(k) - i)}.$$

Phase Shifts and Potentials: Some Examples

We assume in this section that the potential can be taken to be zero beyond some boundary radius b. This is an adequate approximation for all potentials found in practice *except* the Coulomb potential, which will be discussed separately later.

Asymptotically, then,

$$\begin{aligned}
\psi_l(r) &= \frac{i}{2k} \left(\frac{e^{-i(kr - l\pi/2)}}{r} - \frac{e^{2i\delta_l(k)} e^{+i(kr - l\pi/2)}}{r} \right) \\
&= \frac{e^{i\delta_l(k)}}{kr} \sin\left(kr + \delta_l(k) - l\pi/2\right) \\
&= \frac{e^{i\delta_l(k)}}{kr} \left(\sin(kr - l\pi/2) \cos \delta_l(k) + \cos(kr - l\pi/2) \sin \delta_l(k) \right).
\end{aligned}$$

This expression is only exact in the limit $r \to \infty$, but since the potential can be taken zero beyond $r = b$, the wave function must have the form

$$\psi_l(r) = e^{i\delta_l(k)}\left(\cos\delta_l(k) j_l(kr) - \sin\delta_l(k) n_l(kr)\right)$$

for $r > b$.

(The $-$ sign comes from the standard convention for Bessel and Neumann functions—see earlier.)

The Hard Sphere
The simplest example of a scattering potential:

$$V(r) = \infty \quad \text{for} \quad r < R,$$
$$V(r) = 0 \quad \text{for} \quad r \geq R.$$

The wave function must equal zero at $r = R$, so from the above form of $\psi_l(r)$,

$$\tan\delta_l(k) = \frac{j_l(kR)}{n_l(kR)}.$$

For $l = 0$,

$$\tan\delta_0(k) = -\frac{(\sin kR)/kR}{(\cos kR)/kR} = -\tan kR,$$

so $\delta_0(k) = -kR$. This amounts to the wave function being effectively moved over to begin at R instead of at the origin:

$$\frac{\sin kr}{kr} \to \frac{\sin k(r+\delta)}{kr} = \frac{\sin k(r-R)}{kr}$$

for $r > R$, of course $\psi = 0$ for $r < R$.

For higher angular momentum states at low energies ($kR \ll 1$),

$$\tan\delta_l(k) = \frac{j_l(kR)}{n_l(kR)} \approx -\frac{(kR)^l/(2l+1)!!}{(2l-1)!!/(kR)^{l+1}} = -\frac{(kR)^{2l+1}}{(2l+1)\left((2l-1)!!\right)^2}.$$

Therefore at low enough energy, only $l = 0$ scattering is important—as is obvious, since an incoming particle with momentum $p = \hbar k$ and angular momentum $l\hbar$ is most likely at a distance l/k from the center of the potential at closest approach, so if this is much greater than R, the phase shift will be small.

The Born Approximation for Partial Waves

From the definition of $f(\theta,\varphi)$

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + f(\theta,\varphi)\frac{e^{ikr}}{r}$$

and

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int d^3r' e^{-i\vec{k}_f\cdot\vec{r}'}V(\vec{r}')\psi_{\vec{k}}(\vec{r}')$$

recall the Born approximation amounts to replacing the wave function $\psi_{\vec{k}}(\vec{r}')$ in the integral on the right by the incoming plane wave, therefore ignoring rescattering.

To translate this into a partial wave approximation, we first take the incoming $\vec{k}$ to be in the z-direction, so *in the integrand* we replace $\psi_{\vec{k}}(\vec{r}')$ by

$$e^{ikr'\cos\theta} = \sum_l i^l (2l+1) j_l(kr') P_l(\cos\theta').$$

Labeling the angle between $\vec{k}_f$ and $\vec{r}'$ by γ,

$$e^{-i\vec{k}_f\cdot\vec{r}'} = \sum_l (-i)^l (2l+1) j_l(kr') P_l(\cos\gamma).$$

Now $\vec{k}_f$ is in the direction (θ,φ) and $\vec{r}'$ in the direction (θ',φ'), and γ is the angle between them. For this situation, there is an *addition theorem for spherical harmonics*:

$$P_l(\cos\gamma) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}^*(\theta',\varphi') Y_{lm}(\theta,\varphi).$$

On inserting this expression and integrating over θ',φ', the nonzero m terms give zero, in fact the only nonzero term is that with the same l as the term in the $\psi_{\vec{k}}(\vec{r}')$ expansion, giving

$$f(\theta) = -\frac{2m}{\hbar^2}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)\int_0^{\infty} r^2 dr V(r)\left(j_l(kr)\right)^2$$

and remembering

$$f(\theta) = \frac{1}{k}\sum_l (2l+1)e^{i\delta_l(k)}\sin\delta_l(k)P_l(\cos\theta)$$

it follows that for small phase shifts (the only place it's valid) the partial-wave Born approximation reads

$$\delta_l(k) \approx -\frac{2mk}{\hbar^2}\int_0^\infty r^2 dr V(r)\left(j_l(kr)\right)^2.$$

Low Energy Scattering: the Scattering Length

From

$$f_l(k) = \frac{1}{k\left(\cot\delta_l(k) - i\right)},$$

the $l = 0$ cross section is

$$\sigma_{l=0} = \frac{4\pi}{k^2\left|\cot\delta_0(k) - i\right|^2}.$$

At energy $E \to 0$, the radial Schrödinger equation for $u = r\psi$ away from the potential becomes $d^2u/dr^2 = 0$, with a straight line solution $u(r) = C(r-a)$. This must be the $k \to 0$ limit of $u(r) = C'\sin\left(kr + \delta_0(k)\right)$, which can only be correct if δ_0 is itself linear in k for sufficiently small k, and then it must be $\delta_0(k) = -ka$, a being the point at which the extrapolated external wavefunction intersects the axis (maybe at negative r!) So, as k goes to zero, the cot term dominates in the denominator and

$$\sigma_{l=0}(k \to 0) = 4\pi a^2.$$

The quantity a is called the *scattering length*.

Integrating the zero-energy radial Schrödinger equation out from $u(r) = 0$ at the origin for a weak (spherical) square well potential, it is easy to check that a is positive for a repulsive potential, negative for an attractive potential.

Repulsive potential, zero-energy wave function (so it's a *straight line* outside of the well!):

Scattering Length for Square Well

Potential ——— Tangent ——— Wavefunction

Attractive potential:

Scattering Length for Square Well
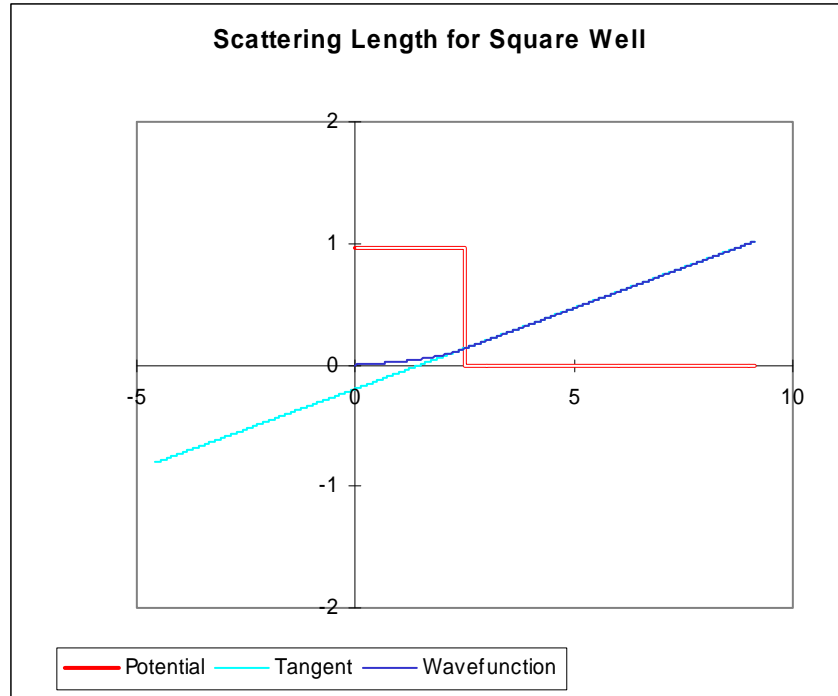
Potential ——— Tangent ——— Wavefunction
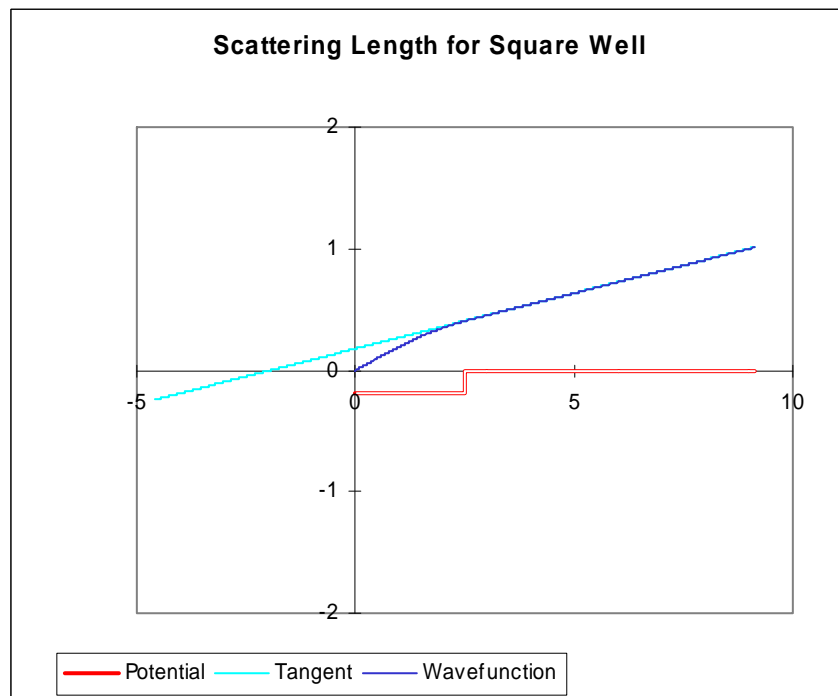
On increasing the strength of the repulsive potential, still solving for the zero-energy wave function, a tends to the potential wall—here's the zero-energy wavefunction for a barrier of height 6:

Scattering Length for Square Well
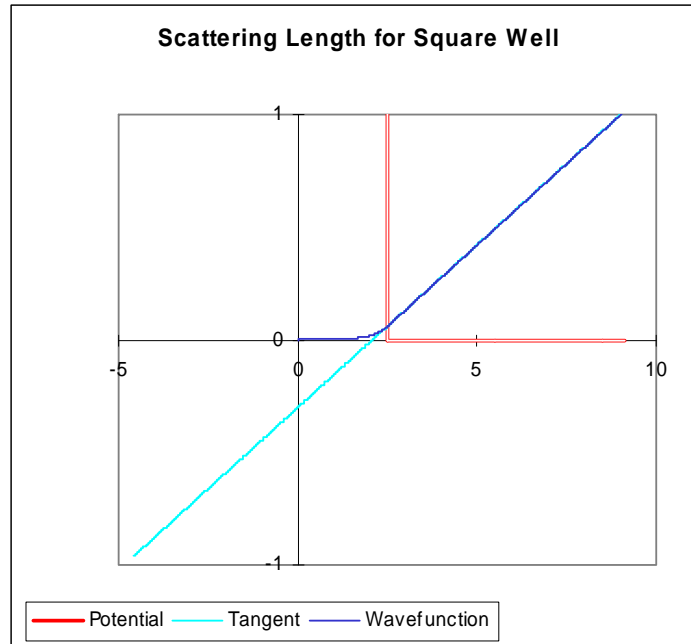
 For an infinitely high barrier, the wave function is pushed out of the barrier completely, and the hard sphere result is recovered: scattering length *a*, cross-section $4\pi a^2$.

On increasing the strength of the *attractive* well, if there is a phase change greater that $\pi/2$ within the well, *a* will become positive. In fact, right at $\pi/2$, *a* is infinite!

Scattering Length for Square Well
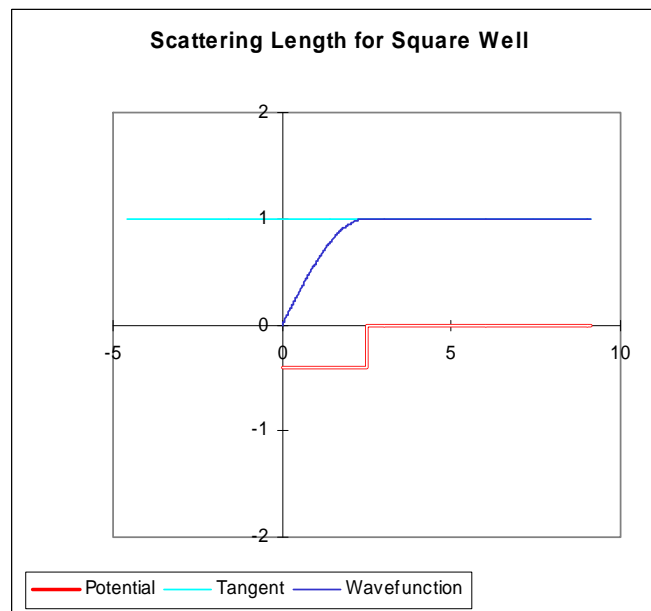
And a little more depth to the well gives a *positive* scattering length:

Scattering Length for Square Well
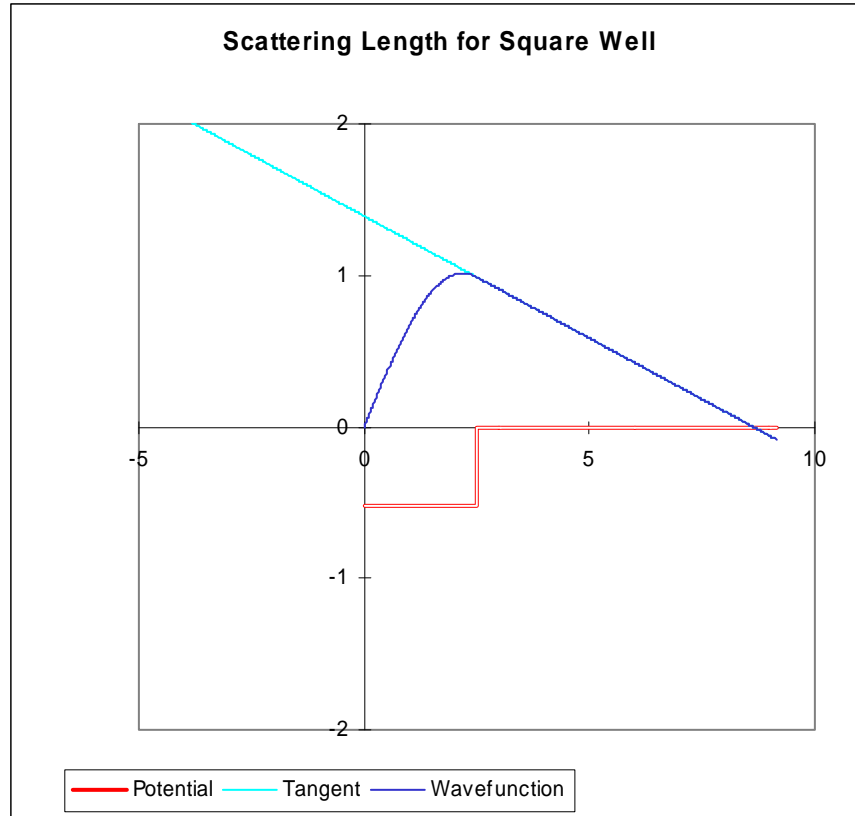
In fact, a well deep enough to have a positive scattering length will also have a bound state. This becomes evident when one considers that the depth at which the scattering length becomes infinite can be thought of as formally having a zero energy bound state, in that although the wave function outside is not normalizable, it is equivalent to an exponentially decaying function with infinite decay length. If one now deepens the well a little, the zero-energy wave function inside the well curves a little more rapidly, so the slope of the wave function at the edge of the well becomes negative, as in the picture above. With this slightly deeper well, we can now *lower* the energy slightly to negative values. This will have little effect on the wave function inside the well, but make possible a fit at the well edge to an exponential decay outside—a genuine bound state, with wave function $\sim e^{-\kappa r}$ outside the well.
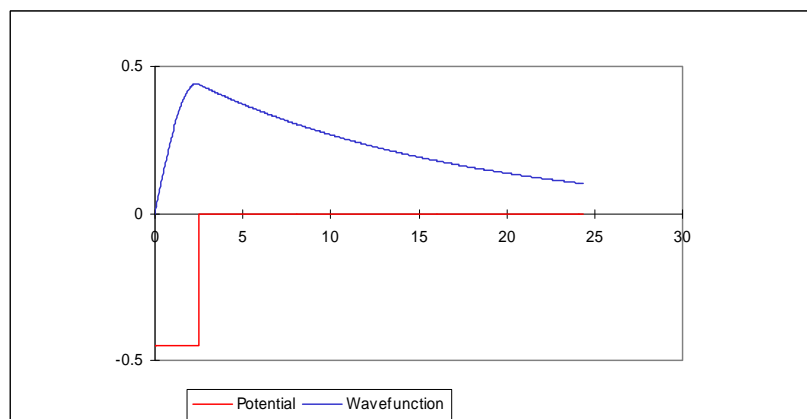
If the binding energy of the state is really low, the zero-energy scattering wave function inside the well is almost identical to that of this very low energy bound state, and in particular the logarithmic derivative at the wall will be very close, so $\kappa \cong 1/a$, taking a to be much larger than the radius of the well.

This connects the large scattering length to the energy of the weakly bound state,

$$\text{B. E. } = \hbar^2 k^2 / 2m = \hbar^2 / 2ma^2.$$

(Sakurai, p 414.)

Wigner was the first to use this to estimate the binding energy of the deuteron from the observed cross section for low energy neutron-proton scattering.