Notes for Lecture 17

Partial wave analysis

In the previous lecture we have defined the asymptotic wave function for a scattering wave function and identified the scattering amplitude $f(\theta)$ as the key part of that wave function. Now, we study one important way how it can be calculated.

17.1 Rotational symmetry

As we discussed in the previous lecture, the system has the full rotational symmetry, if the scattering target and the probing beam form a closed system. This means that the angular momentum is conserved. In classical mechanics, the angular momentum of the problem is determined by the impact parameter b and the initial speed v_i, as $L = mv_i b$, which is conserved during the scattering. However, we emphasized how important quantum mechanics is for this topic—and so we should ask what does the angular momentum conservation mean in quantum mechanics?

Since it means that the total Hamiltonian commutes with the total angular momentum, it follows that we must be able to simultaneously diagonalize the Hamiltonian, $\hat{L}^2$, and $\hat{L}_z$. Therefore, $Y_{lm}(\theta, \phi)$ must be an Hamiltonian eigenstate. This is so, since Y_{lm} has a unique set of eigenvalues[1] (l, m) corresponding to $(\hat{L}^2, \hat{L}_z)$.

Therefore, we can write a Hamiltonian eigenstate as

$$\psi(\vec{r}) = R(r) Y_{lm}(\theta, \phi) \tag{17.1}$$

[1] So, there is no degeneracy involved. If there was a degeneracy associated with the symmetry, then we must form a general linear combination of degenerate states, and solve the problem to find the right coefficients of the linear combination.

and solve for $R(r)$. The differential equation that is satisfied by the radial wave function $R(r)$ is given in the most convenient form by Eq. T4.37, in terms of

$$u(r) \equiv rR(r) \tag{17.2}$$

satisfies a one dimensional time-independent Schrödinger equation with the *effective potential*, which is the sum of the real potential and the centrifugal term, $l(l+1)\hbar^2/(2mr^2)$.

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right)u = Eu \qquad l = 0, 1, 2, ... \tag{17.3}$$

17.2 Free particle state as angular momentum eigenstate

Before we discuss anything, let us emphasize that the solutions that we will discuss now apply not only to the globally free Hamiltonian case, but also to a *locally* free Hamiltonian case, i.e., in a certain radial segment of space, if the potential happens to be zero/constant or negligible there.

We have learned sometime ago how symmetric the free particle Hamiltonian is. Routinely, one writes the free particle wave function as a plane wave. This is such a sensible and easy thing to do. From the symmetry point of view, writing down the free particle wave function as a plane wave amounts to paying full attention to the translational symmetry. Since the free particle Hamiltonian has the full translational invariance, momentum and energy are compatible, and so energy eigenstates can be taken as momentum eigenstates: since $\exp(i\vec{k}\cdot\vec{x})$ is a *non-degenerate* momentum eigenfunction, and since momentum and Hamiltonian commute, it is automatically a Hamiltonian eigenstate.

Now, we turn our attention to the fact that the free Hamiltonian has the full rotational invariance[2] as well. The case is very analogous to the translation case, in that, as we saw in the last section, an "angular momentum eigenstate," i.e. a simultaneous eigenstate of $\hat{L}^2$ and $\hat{L}_z$ is automatically a Hamiltonian eigenstate. However, notice a difference. In the momentum case, the energy of a free particle is determined completely by the momentum, while, in the angular momentum case, the energy of a free particle cannot be determined completely by the angular momentum: as Eq. 17.3 shows, the energy is the sum of the angular momentum part (the centrifugal term $L^2/(2mr^2)$ that represents the rotational kinetic energy) plus the "radial kinetic energy," plus V. So, even when $V = 0$, we do not yet know what the total energy is,

[2]We consider the orbital degrees of freedom only, ignoring the spin degrees of freedom.

just by knowing what L is! Thus, the free particle problem is rather non-trivial in the spherical coordinates. We need to solve

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2}u = Eu \qquad l = 0, 1, 2, \ldots \tag{17.4}$$

However, the solution to this equation is well-known. It is given by

$$R(r) = \frac{u(r)}{r} = c_1\, j_l(kr) + c_2\, n_l(kr) \qquad c_2 = 0 \text{ if the origin is included} \tag{17.5}$$

with $k = \sqrt{2mE}/\hbar$, as before, and j_l and n_l are the so-called *spherical Bessel functions*, some of whose useful properties are listed here.

$$j_l(x) \longrightarrow \frac{x^l}{(2l+1)!!} \qquad x \longrightarrow 0 \tag{17.6}$$

$$n_l(x) \longrightarrow -\frac{(2l-1)!!}{x^{l+1}} \qquad x \longrightarrow 0 \tag{17.7}$$

$$j_l(x) \longrightarrow \frac{1}{x}\cos\left[x - \frac{(l+1)\pi}{2}\right] \qquad x \longrightarrow \infty \tag{17.8}$$

$$n_l(x) \longrightarrow \frac{1}{x}\sin\left[x - \frac{(l+1)\pi}{2}\right] \qquad x \longrightarrow \infty \tag{17.9}$$

where $(2l+1)!! \equiv (2l+1)(2l-1)\cdots 5\cdot 3\cdot 1$ and $(-1)!! \equiv 1$.

$$j_0(x) = \frac{\sin x}{x}, \qquad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}, \qquad j_2(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3}{x^2}\cos x \tag{17.10}$$

$$n_0(x) = -\frac{\cos x}{x}, \quad n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}, \quad n_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x}\right)\cos x - \frac{3}{x^2}\sin x \tag{17.11}$$

$$j_l(x) \equiv (-x)^l\left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x} \qquad n_l(x) \equiv -(-x)^l\left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x} \tag{17.12}$$

Spherical Hankel functions of the first kind and the second kind are defined respectively as

$$h_l^{(1)}(x) \equiv j_l(x) + i\, n_l(x) \qquad \longrightarrow \frac{1}{x}(-i)^{l+1}e^{ix} \quad \text{for } x \longrightarrow \infty \tag{17.13}$$

$$h_l^{(2)}(x) \equiv j_l(x) - i\, n_l(x) \qquad \longrightarrow \frac{1}{x}(i)^{l+1}e^{-ix} \quad \text{for } x \longrightarrow \infty \tag{17.14}$$

Note that the superscript with parenthesis here has *nothing* to do with perturbation.

As noted above, $R(r)$ cannot contain $n_l(kr)$ if the origin is included, since $n_l(kr)$ is not normalizable[3] if $l \geq 1$ and $n_l(kr)$ is simply not a good solution for the *full* Schrödinger equation[4], i.e. the three dimensional Schrödinger equation, if $l = 0$. As a result: **the important "boundary condition" to remember is**[5]

$$u(r) = rR(r) \to 0 \quad \text{if } r \to 0 \qquad\qquad \text{if } V(r) \text{ is regular at the origin} \tag{17.15}$$

where "regular" means $V(r)r^2 \to 0$ as $r \to 0$, so that $V(r)$ is less singular than the centrifugal term and can be ignored near the origin. Qualitatively, one can consider this boundary condition as being caused by the infinite potential energy at $r = 0$ contributed by the centrifugal term.

17.3 Partial wave analysis of a plane wave

From what we have learned so far, we now know how to write the wave function in free space as an angular momentum eigenfunction.

To appreciate what we just learned, we examine the following **Rayleigh's formula**:

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \tag{17.16}$$

[3]This is a bit subtle point. The relevant normalizability here is the "Dirac-delta-function normalizability," as the normalization of eigenstates with continuous eigenvalues is given by $\langle k \,|\, k' \rangle = \delta(k - k')$, where k and k' are eigenvalues, which are wave numbers in the current case. It is easy to think about this "Dirac-delta-function normalizability" as follows. (1) Consider the volume (or length in the case of the radial equation alone) $\mathcal{V}$ to be large but finite. (2) If an eigenfunction can be normalized to the volume $\int d^3\vec{r}\,|\psi|^2 = \mathcal{V}$, with only a numerical normalization constant for ψ, then it is "Dirac-delta-function normalizable." Using this simple criterion, one can easily see that $n_l(kr)$ with $l > 0$ is not Dirac-delta-function normalizable, since it diverges at $r = 0$ to give an infinite norm *locally*: i.e. $\int_0^a dr\, n_l(kr) \sim \int_0^a dr\, r^{-2l}$ is infinite for any small finite a.

[4]This is a *much more* subtle point. Why would a legitimate, and Dirac-delta-function normalizable, solution to the radial equation *not* a good solution to the full Schrödinger equation? Let us see. Here, we are concerned with $n_0(kr) = -\cos(kr)/(kr)$, and, so if we assume that $R(r) = c_1 j_0(kr) + c_2 n_0(kr)$ with $c_2 \neq 0$, then near $r = 0$, we get $R(r) \sim 1/r$. Note that this represents the behavior of the full three dimensional wave function, since the angular part is constant ($l = 0$). [At this point, note that just because $R(r)$ "blows up" does *not* mean that it is not allowed. In the current example, $R(r)$ blows up at the origin, but still $\int d^3\vec{r}\,|R(r)|^2 = \int dr r^2 d\Omega\,|R(r)|^2$ is finite for a finite volume integral, and the local probability, $\propto r^2|R(r)|^2 dr$, remains finite. The point here is that just because $R(r)$ blows up at $r = 0$ does not mean that it breaks the Dirac-delta-normalizability.] Now, the free particle Schrödinger equation is $\nabla^2\psi = -k^2\psi$. With $\psi \propto R(r) \sim 1/r$, and the well-known identity $\nabla^2(1/r) = -4\pi\delta(\vec{r})$, we get $\nabla^2\psi \sim \delta(\vec{r})$, which cannot be equal to $-k^2\psi$! Why did this happen? It is because the radial equation results from the use of the spherical coordinate system, which introduces a singularity at the origin.

[5]The lengthy discussions in the previous two footnotes are, in fact, a rigorous derivation of this important boundary condition.

where $P_l(\cos\theta)$ is the Legendre polynomial. The proof of this formula can be looked up in a mathematical physics book. Here, we discuss the physics of it. Some notable points of this formula are the following.

1. The wave function e^{ikz} does not have any angular momentum value $\hat{L}_z = \hat{L}_\phi \doteq -i\hbar\frac{\partial}{\partial\phi}$, since it does not depend on ϕ ($\because z = r\cos\theta$). This is why only $P_l(\cos\theta) \propto Y_{l,0}$ (cf. Eqs. T4.32 and T4.27) terms appear and no terms with $Y_{l,m}$ ($m \neq 0$) appear.
2. $n_l(kr)$ does not appear because of Eq. 17.15.
3. At large distance $r \to \infty$, partial wave term for each l value corresponds to a *standing wave* when observed locally, since j_l is a cosine function (Eq. 17.9).

The last point is expressed in a more analytic manner in the following expression, using Eqs. 17.13,17.14.

$$e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1)\, \frac{h_l^{(1)}(kr) + h_l^{(2)}(kr)}{2}\, P_l(\cos\theta) \tag{17.17}$$

$$\to \sum_{l=0}^{\infty} \frac{2l+1}{2ikr} \left(e^{ikr} - (-1)^l\, e^{-ikr}\right) P_l(\cos\theta) \qquad r\to\infty \tag{17.18}$$

So, each l-th partial wave is a standing wave at large distance, since there is an equal amount of outgoing wave (e^{ikr}) and incoming wave (e^{-ikr}).

It may seem curious then how it is possible that a plane wave, which is definitely not a standing wave, can be decomposed into a series of standing waves. This should not be a mystery at all[6]. Consider the first two standing wave components, note the position-dependent relative phase differences between the two standing waves due to the P_l functions, and you will be able to convince yourself that, yes, the result is a moving[7], not a standing, wave.

It is very important to note that *each* l-th partial wave in the above three equations is an eigenstate of the free particle Hamiltonian by itself. This is of course due to **the angular momentum conservation**, as we discussed above.

[6] By the same token, note that (1) when you combine two states such as an s state and a p state, each of which does not have any electric dipole moment, you get a state that *has* a dipole moment, and (2) when you combine stationary states, you can create a wave packet state whose probability density sloshes back and forth, while the probability density of any stationary state is ... stationary!

[7] Here, by "moving" what we mean is that the wave function has a finite momentum $\hbar\vec{k}$, or, more pointedly, the probability current (HW 5.4) = $|A|^2\hbar k\vec{e}_3/m$ for Ae^{ikz}. Any wave function that we consider in this lecture corresponds to a stationary state, and its probability density function is time-independent. However, for a standing wave, the probability current is zero, as well.

17.4 Partial wave analysis—phase shift

Now, we turn to the partial wave analysis in a general situation, in the presence of a potential energy, $V(r)$. We consider only one l-th partial wave. It helps to consider the problem in the following manner. First, assume that there is no potential. Then, slowly turn on the potential energy to the full value. What would happen to the original wave function? It is hard to say what would have happened to the wave function for small r values—that requires a detailed solution to the Schrödinger equation. However, it is quite possible to describe the behavior of the wave function at large r based on the angular momentum conservation and **the unitarity, or the particle conservation**. Namely, consider the fact that each l-th partial wave describes an incoming spherical wave and an outgoing spherical wave. Physically, one can visualize this as particles converging to the origin and then bouncing off of the origin. When this occurs, it is clear that the total number of particles must be conserved: what goes in must comes out! For this reason, we can write down the l-th partial wave at large r as

$$\frac{2l+1}{2ikr}\left(e^{2i\delta_l}\,e^{ikr} - (-1)^l\,e^{-ikr}\right)P_l(\cos\theta) \qquad\qquad r\to\infty \tag{17.19}$$

which is valid in general for r much greater than the range of the potential. Here, the only change in the l-th partial wave is the phase shift by $2\delta_l$ (where 2 is included by convention). The extra factor that the system acquires due to interaction is often defined with symbol S, as

$$S_l(k) \;\equiv\; e^{2i\delta_l} \tag{17.20}$$

and the **unitarity condition** corresponds to the condition $|S_l(k)| = 1$. The unitarity or the particle conservation means that the phase shift is the only change possible, as the outgoing wave cannot be reduced or magnified in intensity. Why did the incoming wave not change at all by the potential energy? It is because the potential energy scatters *out* the incoming wave. In other words, in Eq. 16.9, the scattering created only an outgoing spherical wave component. The complete wave function that can be equated to Eq. 16.9 is then given by

$$\psi(r,\theta) \;\approx\; A\sum_l \frac{2l+1}{2ikr}\left(e^{2i\delta_l}\,e^{ikr} - (-1)^l\,e^{-ikr}\right)P_l(\cos\theta) \qquad r\to\infty \tag{17.21}$$

Now, we are ready to make the connection between the phase shifts δ_l's and $f(\theta)$ of Eq. 16.9. If we subtract Eq. 17.18 times A from Eq. 17.21, then we must get $Af(\theta)e^{ikr}/r$, since Eq. 17.21 must be identical with Eq. 16.9.

$$A\sum_l \frac{2l+1}{2ikr}\left(e^{2i\delta_l}\,e^{ikr} - e^{ikr}\right)P_l(\cos\theta) = A\frac{f(\theta)}{r}e^{ikr}$$

Defining

$$f(\theta) = \sum_{l=0}^{\infty}(2l+1) f_l(k) P_l(\cos\theta) \quad (17.22)$$

we get[8]

$$f_l(k) = \frac{e^{2i\delta_l}-1}{2ik} = \frac{S_l(k)-1}{2ik} = \frac{e^{i\delta_l}\sin\delta_l}{k} \quad (17.23)$$

which means

$$f(\theta) = \sum_{l=0}^{\infty}\frac{2l+1}{k}e^{i\delta_l}\sin\delta_l\,P_l(\cos\theta) \quad (17.24)$$

and the differential crossection is given by

$$\frac{d\sigma}{d\Omega} = \sum_{l,l'}(2l+1)(2l'+1)\,f_l f_{l'}^*\,P_l(\cos\theta)P_{l'}(\cos\theta) \quad (17.25)$$

Integrating over $d\Omega = d(\cos\theta)d\phi$ and using

$$\int_{-1}^{1} dx P_l(x)P_{l'}(x) = \frac{2}{2l+1}\delta_{l,l'} \quad (17.26)$$

we get

$$\sigma = 4\pi\sum_l(2l+1)|f_l(k)|^2 = \frac{4\pi}{k^2}\sum_l(2l+1)\sin^2\delta_l \quad (17.27)$$

Note that all physics comes down to the phase shift δ_l, in this picture!

17.5 Partial wave analysis—intermediate region

Let us consider what we have accomplished so far. In Section 17.2, we have written down the most general solution when $V(r) = 0$. In Section 17.3, we examined how a plane wave state can be described in terms of those general solutions. In Section 17.4, we examined how the scattering wave function (Eq. 16.9) for *any* finite ranged potential problem can be expressed in terms of partial waves and their phase shifts *for large* r. Notice that phase shifts must be calculated in order to complete the solution. In order to do so, we now need to reduce r and trace how the wave function changes as we do so. We must go all the way to those r values where the potential energy is large, in order to calculate $\delta_l(k)$ values. As we try to do so, it is very convenient

[8] In the textbook notation, $a_l = f_l$.

to know the form of wave function for the *intermediate region*, where the potential energy itself remains negligible, but the centrifugal term is not.

So, the problem in the intermediate region is still that of a free particle, in the sense of Section 17.2, and we just need to express the radial functions in terms of spherical Bessel/Neumann functions or spherical Hankel functions (Section 17.2). The guiding principle is that we already know the wave function in its asymptotic form (Eq. 16.9 or, equivalently, Eq. 17.21), and we need to replace the e^{ikr}/r part of the wave function with an appropriate Hankel function using its known asymptotic limit (Eq. 17.13, which implies that $e^{ikr}/r \to k h_l^{(1)}/(-i)^{l+1}$ as r decreases while $V(r)$ remains negligible. Using, this and Eqs. 17.16, 17.22, we get

$$\begin{aligned}
\psi(r,\theta) &\approx A\left(e^{ikz} + \frac{f(\theta)}{r}e^{ikr}\right) && (16.9)\\
&= A\sum_l i^l(2l+1)\left(j_l(kr) + f_l(k)\frac{k\,h_l^{(1)}(kr)}{i^l(-i)^{l+1}}\right)P_l(\cos\theta)\\
&= A\sum_{l=0}^{\infty} i^l(2l+1)\left(j_l(kr) + ikf_l(k)h_l^{(1)}(kr)\right)P_l(\cos\theta) && (17.28)
\end{aligned}$$

So, this is the general form of the wave function in the intermediate region, where the phase shift information is contained in $f_l(k)$, through Eq. 17.23.

17.6 Example—hard sphere

Now, the final necessary step in solving a scattering problem is to go all the way to small r values, for which the potential energy is significant, and calculate δ_l values.

Here we consider a simple example. We consider the same potential energy that we considered in the last lecture, but now treated with quantum mechanics.

$$V(r) = \begin{cases} 0 & r > R \\ \infty & r < R \end{cases} \qquad (16.4)$$

In this case, Eq. 17.28 is valid for any $r > R$. All there is left for us to do is to apply the boundary condition that $\psi(r,\theta) = 0$ at $r = R$, since the potential energy becomes infinite there. This condition, along with the orthogonality of Legendre polynomials, leads to

$$j_l(kR) + ikf_l(k)h_l^{(1)}(kR) = 0$$

which means

$$f_l(k) = \frac{i\, j_l(kR)}{k\, h_l^{(1)}(kR)} \tag{17.29}$$

which is the phase shift information that we sought! With this information, our problem is solved, and, e.g., the total cross section is given as

$$\sigma = \frac{4\pi}{k^2} \sum_l (2l+1) \left| \frac{j_l(kR)}{h_l^{(1)}(kR)} \right|^2 \tag{17.30}$$

Although this result is useful, considering the low energy limit ($kR \to 0$) is enlightening. In this case, considering the $x \to 0$ limit of spherical Bessel/Hankel functions (Section 17.2), we get

$$f_l(k) = -\frac{(kR)^{2l}}{(2l+1)\left\{(2l-1)!!\right\}^2} R \tag{17.31}$$

Now, if we consider $f(\theta)$ (Eq. 17.22), then we see that f_0 gives a dominant contribution, having the smallest power of kR. Thus,

$$f(\theta) \approx f_0(k) = -R \tag{17.32}$$

So, in the low energy limit, we have

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \approx R^2 \tag{17.33}$$

and the total cross section is given by

$$\sigma = 4\pi R^2 \qquad\qquad kR \to 0 \tag{17.34}$$

This surprising result can be interpreted as the wave "hugging" the sphere all around, and "feeling the entire surface area." Perhaps this is not surprising since we are considering a quantum limit (i.e., low energy limit) any way. What is surprising is that even when we go to the high energy limit, we do *not* recover the classical result. The total cross section is given in that case by (cf., a homework problem)

$$\sigma = 2\pi R^2. \qquad\qquad kR \to \infty \tag{17.35}$$

This is due to the so-called "shadow scattering."