Quantum Mechanics in Three Dimensions

Lecture 20

Physics 342
Quantum Mechanics I

Monday, March 24th, 2008

We begin our spherical solutions with the "simplest" possible case – zero potential. Aside from being uncommon, this allows us to clearly see the role of the various terms in the separation. From the solution regular at the origin, we can develop the infinite barrier cases, in which we consider the three-dimensional, spherically symmetric analogue of the infinite square well from one dimension.

20.1 The Radial Equation

When we combine the potential, which depends only on r with the angular "constant" $(-\ell\,(\ell+1))$, we obtain the ordinary differential equation for $R(r)$:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \ell\,(\ell+1) - \frac{2\,m\,r^2}{\hbar^2}\,(U(r)-E) = 0. \tag{20.1}$$

If we define $u(r) \equiv r\,R(r)$, then the above simplifies:

$$\boxed{-\frac{\hbar^2}{2\,m}\frac{d^2u}{dr^2} + \left(U(r) + \frac{\hbar^2\,\ell\,(\ell+1)}{2\,m\,r^2}\right)\,u = E\,u.} \tag{20.2}$$

Compare the term in parenthesis to the classical orbital effective potential we found last time:

$$U_{eff} = U(r) + \frac{p_\phi^2}{2\,m\,r^2}, \tag{20.3}$$

this is, in a sense "precisely" the same term we had there – if only we knew how to associate p_ϕ^2 with the numerator of the above, we could have written this down directly.

20.2 No Potential

Suppose we have in mind *no* explicit potential, i.e. $U(r) = 0$. Then we can solve the above for u – but what are the relevant boundary conditions? We pretty clearly want the wavefunction to go to zero as $r \longrightarrow 0$. Near the origin, we want the probability to be finite. Think of what this means for the radial wavefunction – the probability will be proportional to $R^* R r^2 dr$, and this is just $u^* u\, dr$ in our new notation, but then we want $u \longrightarrow 0$ (or, potentially, a non-zero constant) as $r \to 0$. The point is, $R(r) \sim 1/r$ is allowed, but no higher power.

Now we can return to the ODE (20.2) – written in standard form, this is

$$\frac{d^2 u}{dr^2} = \left(\frac{\ell(\ell+1)}{r^2} - \frac{2\,m\,E}{\hbar^2}\right) u, \tag{20.4}$$

and we define $k^2 \equiv \frac{2\,m\,E}{\hbar^2}$. Very "far" from the origin, where the constant term dominates, we recover a sinusoidal solution, $\cos(k\,r)$ and $\sin(k\,r)$ – and we suspect that the radial wavefunction is not normalizable – that comes as no surprise, since the Cartesian solution with zero potential was also not normalizable. Still, it is instructive to look at the solutions, if only in preparation for finite range. The solutions to the above ODE are spherical Bessel/Neumann functions (more explicitly, the $R(r)$ solutions are spherical Bessel functions, $u(r)$ gets multiplied by r):

$$u_\ell(r) = \alpha\, r\, j_\ell(k\,r) + \beta\, r\, n_\ell(k\,r). \tag{20.5}$$

These are related to the Bessel functions (and Bessel's equation, of course), and can be defined via:

$$j_p(x) = (-1)^p \left(\frac{1}{x}\frac{d}{dx}\right)^p \frac{\sin x}{x} \qquad n_p = -(-1)^p \left(\frac{1}{x}\frac{d}{dx}\right)^p \frac{\cos x}{x}. \tag{20.6}$$

We are interested in the asymptotic behavior here – both j_p and n_p reduce to cosine and sine as $r \to \infty$ as they must, and this is the source of the normalization issue. But near the origin, we have:

$$j_p(x \sim 0) = \frac{2^p\, p!}{(2\,p+1)!}\, x^p \qquad n_p(x \sim 0) = -\frac{(2\,p)!}{2^p\, p!}\, x^{-(p+1)}, \tag{20.7}$$

so the well-behaved solution near the origin is the j_p one[1].

[1] Compare with your electrodynamics experience – there, we cannot have a single solu-

Consider, for example, the $p = 0$ form, $j_0(k\,r) = \frac{\sin(k\,r)}{k\,r}$, this is finite close to $k\,r \sim 0$, as is clear from its Taylor expansion, $\frac{\sin(k\,r)}{k\,r} \sim \frac{k\,r + O((k\,r)^2)}{k\,r} \sim 1 + O(k\,r)$. While not normalizable, we can plot the wavefunction (the angular portions are unity) to get a sense for the eventual density. Working back to $R(r)$, we have:

$$R(r) = \frac{1}{r}\,u(r) = \alpha\,j_0(k\,r) \tag{20.8}$$

and this is plotted (with $\alpha = 1$) in Figure 20.1.

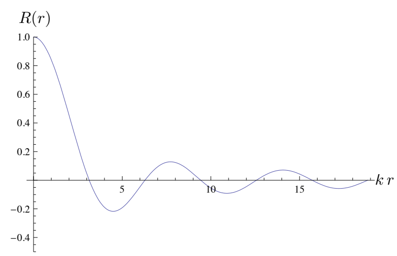

Figure 20.1: The zeroth spherical Bessel function – this gives the radial wavefunction for a free particle in spherical coordinates.

Spherical Bessel Functions

We quoted the result above, the differential equation (20.4) has solutions that look like $u_\ell(r) = \alpha\,r\,j_\ell(k\,r)$ (finite at the origin). But how could we develop these if we didn't know them already? Well, there's always Frobenius, that would be one way. We could also connect these special functions to simpler ones, as we did for the associated Legendre polynomials, for example. Here we consider yet another way to get the solutions – we can use an integral transform (like the Fourier transform, or Laplace transform) to simplify the ODE. What we will end up with is an integral form for the spherical Bessel functions.

tion to Laplace's equation that is well-behaved at both the origin and infinite. Here, the requirement is less stringent, we can allow *some* "explosive" behavior on either end, since the wavefunction, unlike **E** and **B**, is not the "observable" or at least, experimentally comparable object. In quantum mechanics, it is $R^*\,R$ that is important, and the requirement is that $R^*\,R\,r^2$ be integrable.

Our goal is to solve:

$$u'' - \left[\frac{\ell\,(\ell+1)}{r^2} - k^2\right] u = 0 \tag{20.9}$$

with $k^2 \equiv \frac{2\,m\,E}{\hbar^2}$ as usual. We make the ansatz:

$$u(r) = r^p \int e^{r\,x}\, f(x)\, dx \tag{20.10}$$

where p, $f(x)$ *and* the integration limits (x can be complex here) are to be determined by our solution. This is similar to our usual Frobenius ansatz, but with an integral rather than a sum. First we need the derivatives:

$$\begin{aligned} u'(r) &= p\, r^{p-1} \int e^{r\,x} f(x)\, dx + r^p \int x\, e^{r\,x}\, f(x)\, dx \\ u''(r) &= p\,(p-1)\; r^{p-2} \int e^{r\,x}\, f(x)\, dx + 2\, p\, r^{p-1} \int x\, e^{r\,x}\, f(x)\, dx \\ &\quad + r^p \int x^2\, e^{r\,x}\, f(x)\, dx. \end{aligned} \tag{20.11}$$

Now if we input this into the ODE, we get:

$$0 = r^{p-2} \int \left[p\,(p-1) - \ell\,(\ell+1) + 2\,x\,r\,p + \left(x^2 + k^2\right)\; r^2\right]\; e^{r\,x}\, f(x)\, dx. \tag{20.12}$$

The analogue of the Frobenius "indicial" equation is the r^0 portion of the above: $p\,(p-1) - \ell\,(\ell+1) = 0$ – this has solutions: $p = -\ell$ and $p = \ell + 1$. How should we choose between these? Think of the case $p = -\ell$ – then in front of the integral, we have $r^{-\ell-2}$ which, for $\ell > 0$ will lead to bad behavior at $r = 0$. If we take $p = \ell + 1$ for $\ell > 0$, we will have a vanishing term in front of the integral. So take $p = \ell + 1$. We are left with

$$\begin{aligned} 0 &= r^\ell \int f(x)\; \left[2\,(\ell+1)\; x + (x^2 + k^2)\, r\right]\; e^{r\,x}\, dx \\ &= r^\ell \int f(x)\; \left[2\,(\ell+1)\; x + (x^2 + k^2)\, \frac{d}{dx}\right]\; e^{r\,x}\, dx. \end{aligned} \tag{20.13}$$

Notice the replacement in the second line, $r \rightarrow \frac{d}{dx}$ acting on $e^{r\,x}$. This comes from the observation that $\frac{d}{dx}\, e^{r\,x} = r\, e^{r\,x}$.

We still don't know what our limits of integration are, nor do we have $f(x)$. All we have done so far is choose a value for p. Keep in mind that the choices we make: p, $f(x)$, and the integration path itself, all serve to limit our solution – we will not obtain the most general solution to (20.9).

We can use the product rule to rewrite our integral again:

$$\begin{aligned}0 &= r^\ell \int f(x) \left[2\,(\ell+1)\;x + (x^2+k^2)\,\frac{d}{dx}\right] e^{r\,x}\,dx \\ &= r^\ell \left\{\int f(x)\,(2\,(\ell+1)\;x)\;e^{r\,x}\,dx + \int \frac{d}{dx}\;\left[f(x)\left(x^2+k^2\right)\,e^{r\,x}\right]\,dx \right. \\ &\left. - \int e^{r\,x}\,\frac{d}{dx}\;\left[f(x)\,(x^2+k^2)\right]\,dx\right\}.\end{aligned} \tag{20.14}$$

Again in the interests of specialization – we could make the above zero by setting:

$$\begin{aligned}0 &= 2\,(\ell+1)\;x\,f(x) - \frac{d}{dx}\;\left[f(x)\,(x^2+k^2)\right] \\ 0 &= \int \frac{d}{dx}\;\left[f(x)\,(x^2+k^2)\,e^{r\,x}\right]\,dx\end{aligned} \tag{20.15}$$

there are other ways to get zero from the integral, but we are not currently interested in them. These two equations are enough to set the function $f(x)$ and at the same time, determine the integration region.

Taking the ODE first – from inspection, a good "guess" is $f(x) = (x^2+k^2)^q$, then:

$$2\,(\ell+1)\;x\,f(x) = \frac{d}{dx}\;\left[f(x)\left(x^2+k^2\right)\right] \longrightarrow q = \ell. \tag{20.16}$$

This gives us

$$\boxed{f(x) = \left(x^2+k^2\right)^\ell.} \tag{20.17}$$

With $f(x)$ in hand, we need to choose integration limits for the second equation in (20.15). Suppose we think of this as one-dimensional integration (for $x \in \mathbb{C}$, we could have in mind a complicated contour integral), then:

$$\left(x^2+k^2\right)\;e^{r\,x}\Big|_{x=x_0}^{x_f} = 0. \tag{20.18}$$

If we set $x_0 = -i\,k$, $x_f = i\,k$, then each endpoint vanishes separately. This suggests we take:

$$u(r) = r^{\ell+1} \int_{-i\,k}^{i\,k} e^{r\,x} \left(x^2 + k^2\right)^\ell \, dx. \tag{20.19}$$

This can be rewritten by taking $z = \frac{1}{i\,k}\,x$, then

$$u(r) = r \left(i\,k^\ell\right) (k\,r)^\ell \int_{-1}^{1} e^{i\,(k\,r)\,z} \left(1 - z^2\right)^\ell \, dz. \tag{20.20}$$

Now, the integral form of the spherical Bessel functions is:

$$j_\ell(x) = \frac{x^\ell}{2^{\ell+1}\,\ell!} \int_{-1}^{+1} e^{i\,x\,z} \left(1 - z^2\right)^\ell \, dz, \tag{20.21}$$

and noting that constants don't matter (since we will normalize the radial wavefunction at the end, anyway), we can write

$$\boxed{u_\ell(r) = A\,r\,j_\ell(k\,r)} \tag{20.22}$$

20.2.1 Spherical Barrier

We cannot extend the free particle range to infinity, but it is possible to cut off the spherical Bessel solutions at a particular point – we imagine a "perfectly confining" potential like the infinite square well, but w.r.t. the radial coordinate. This imposes a boundary condition – if we take

$$U(r) = \begin{cases} 0 & r \le R \\ \infty & r > R \end{cases} \tag{20.23}$$

then the free particle solutions described above have $u(r = R) = 0$, so as to match with the perfect zero outside the infinite (spherical) "well".

With the cut-off in place, the solutions are normalizable, we just integrate from $r = [0, R]$, which is more manageable than an infinite domain. But, we have to choose a value for k that makes $j_\ell(k\,R) = 0$ – the zeroes of the Bessel function are, like cosine and sine, finite in any given interval. The spacing is not so clean as simple trigonometric functions. If this were sine or cosine, we would just set $k\,R = n\,\pi$ or a half-integer multiple and be done. With the spherical Bessel functions, it is possible to find zero-crossings (and also to determine how many zero crossings are in an interval), but there is no obvious formula.

For the $\ell = 0$ case, we do, in fact, know the zero crossings, since $j_0(k\,r) = \frac{\sin(k\,r)}{k\,r}$, and $k\,R = n\,\pi$ for integer n gives zero. Then, the usual story: Our boundary condition has provided quantization of energy. Remember that we get E out of this process. The quantized $k = \frac{n\,\pi}{R} = \frac{\sqrt{2\,m\,E}}{\hbar}$ gives

$$E = \frac{\hbar^2\,n^2\,\pi^2}{2\,m\,R^2} \tag{20.24}$$

for integer n. Now, this is relatively uninteresting as a three-dimensional solution to Schrödinger's equation: There is no angular component since we solved with $\ell = 0$, and $Y_{00}(\theta, \phi) = \frac{1}{2\sqrt{\pi}}$ is the only available term. We have for $\ell = 0$, an n-indexed set of wavefunctions (normalized):

$$\psi(r, \theta, \phi) = \frac{\sin(\frac{n\,\pi}{R}\,r)}{\sqrt{2\,\pi\,R}\,r}. \tag{20.25}$$

This "ground state" (state with lowest energy) is spherically symmetric, it shares the symmetry of the potential itself (an idea to which we shall return).

In general, we can denote the n^{th} zero crossing of the ℓ^{th} spherical Bessel function as $\beta_{n\ell}$ The full spatial wavefunction reads:

$$\psi_{n\,\ell\,m}(r, \theta, \phi) = A_{n\,\ell}\,j_\ell\left(\frac{\beta_{n\,\ell}\,r}{R}\right)\,Y_\ell^m(\theta, \phi). \tag{20.26}$$

with normalization $A_{n\,\ell}$. The energy, then, is given by

$$k\,R = \beta_{n\,\ell} \longrightarrow E_{n\,\ell} = \frac{\hbar^2\,\beta_{n\,\ell}^2}{2\,m\,R^2} \tag{20.27}$$

and we can use this in the full time-dependent solution:

$$\Psi_{n\,\ell\,m}(r, \theta, \phi, t) = \psi_{n\,\ell\,m}(r, \theta, \phi)\,e^{-i\,\frac{E_{n\,\ell}\,t}{\hbar}}. \tag{20.28}$$

Each energy $E_{n\,\ell}$ is shared by the $2\ell + 1$ values of m that come with the angular solution.

In Figure 20.2, we see the probability density (unnormalized) for the $\ell = 0$ and $n = 1, 2, 3$ states (top row) and the densities for ψ_{11-1}, ψ_{110} and ψ_{111}

(trivially related to ψ_{11-1}). Keep in mind that our local density is, now $\psi^*_{n\,\ell\,m}\psi_{n\,\ell\,m}\,r^2\,\sin\theta$. Notice that as with the one-dimensional square well, the number of "nodes" in the r direction (top row) is directly related to the energy of the state.

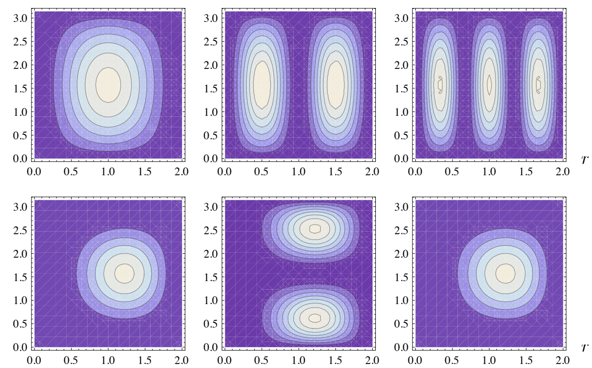

Figure 20.2: Probability densities ($\psi^*\,\psi\,r^2\,\sin\theta$ in this case) for ψ_{100}, ψ_{200}, ψ_{300} (top row) and ψ_{11-1}, ψ_{110}, ψ_{111} (bottom row). The horizontal axis of each plot is the radial direction, the vertical direction goes from 0 to π in θ.

20.3 Example of Similar Problem (PDE + BC)

Before we begin our onslaught – the Coulomb potential and Hydrogenic wavefunctions – let's review some of the other applications of our current techniques, just to highlight the familiarity of the procedure of solving the Schrödinger equation, even while its interpretation is new. First of all, we recognize that solving the PDE requires some boundary conditions – in the above infinite potential, we wanted regular solutions on the interior of the sphere of radius R. This is similar to solving Laplace's equation for the electrostatic potential inside and outside a distribution. Consider a sphere, if we are inside some spherically symmetric distribution of charge, and the origin $r = 0$ is enclosed, then solutions must go like r^p. If we are solving for the potential outside the distribution, where spatial infinity is included, we expect $V \sim r^{-p}$. All of this is in the name of boundary conditions. The same is true for quantum mechanical problems: Our domain of interest (or, in some cases, the energy scale of interest) defines the types of solution we accept physically.

Take a uniformly charged spherical shell with surface charge σ. We rotate the shell with angular velocity $\boldsymbol{\omega} = \omega\,\hat{z}$ (about the $\hat{z}$ axis). Our goal is to find the magnetic field, outside the sphere, say. Well, for $r \geq R$, we know that the magnetic vector potential satisfies:

$$\nabla^2\,\mathbf{A} = 0 \qquad \left(\frac{d\mathbf{A}^{out}}{dr} - \frac{d\mathbf{A}^{in}}{dr}\right)\bigg|_{r=R} = -\mu_0\,\mathbf{K}. \tag{20.29}$$

First, from the physical setup, we automatically know the surface current: $\mathbf{K} = \sigma\,\mathbf{v} = \sigma\,\omega\,R\,\sin\theta\,\hat{\boldsymbol{\phi}}$. So we know pretty quickly that $\mathbf{A} \sim \sin\theta\,\hat{\boldsymbol{\phi}}$. Now $\sin\theta$ is not one of your usual Legendre polynomial solutions to Laplace's equation, so there is something strange going on here. Suppose we take the ansatz: $\mathbf{A} = A(r,\theta)\,\hat{\boldsymbol{\phi}}$, then the vector Laplace equation reads:

$$0 = \nabla^2\,\mathbf{A} = (\nabla^2\,A)\hat{\boldsymbol{\phi}} + A\,\nabla^2\,\hat{\phi}. \tag{20.30}$$

The absence of Legendre polynomials comes as no surprise – we are not solving Laplace's equation (remember that $\nabla^2\,\hat{\boldsymbol{\phi}} \neq 0$, the spherical basis vectors are position dependent). One can easily (if tediously) calculate $\nabla^2\,\hat{\boldsymbol{\phi}} = -\frac{1}{r^2\,\sin^2\theta}\,\hat{\boldsymbol{\phi}}$, so the equation we are trying to solve looks like:

$$\nabla^2\,A - \frac{A}{r^2\,\sin^2\theta} = 0 \tag{20.31}$$

and this looks more like the Schrödinger equation. If we use our usual separation of variables, factoring $A(r,\theta)$ into $A(r,\theta) = A_r(r)\,A_\theta(\theta)$, then the above becomes

$$\frac{\frac{d}{dr}\left(r^2\,A_r'\right)}{A_r} + \left[\frac{1}{A_\theta\,\sin\theta}\,\frac{d}{d\theta}\left(\sin\theta\,\frac{dA_\theta}{d\theta}\right) - \frac{1}{\sin^2\theta}\right] = 0. \tag{20.32}$$

We can make our separation ansatz as before, with constant $\ell\,(\ell+1)$:

$$\begin{aligned} \frac{\frac{d}{dr}\left(r^2\,A_r'\right)}{A_r} &= \ell\,(\ell+1) \\ \left[\frac{1}{A_\theta\,\sin\theta}\,\frac{d}{d\theta}\left(\sin\theta\,\frac{dA_\theta}{d\theta}\right) - \frac{1}{\sin^2\theta}\right] &= -\ell\,(\ell+1). \end{aligned} \tag{20.33}$$

For the angular equation, we now need to solve:

$$\sin\theta\,\frac{d}{d\theta}\left(\sin\theta\,\frac{dA_\theta}{d\theta}\right) + \left(\ell\,(\ell+1)\,\sin^2\theta - 1\right)A_\theta = 0. \tag{20.34}$$

But that is very close to an equation we encountered in our development of Y_ℓ^m, think of [4.25]:

$$\sin\theta\,\frac{d}{d\theta}\left(\sin\theta\,\frac{dA_\theta}{d\theta}\right) + \left(\ell\,(\ell+1)\,\sin^2\theta - m^2\right) = 0. \tag{20.35}$$

This was solved by the associated Legendre function $P_\ell^m(\cos\theta)$ that makes up the θ dependence of the spherical harmonics. Comparing (20.34) to (20.35), we see that for our current purposes, we are interested in $m = \pm 1$ (it doesn't really matter which sign we choose, take $m = 1$). So the angular portion is $A_\theta(\theta) \sim P_\ell^1(\cos\theta)$. We can go further, though – the boundary condition

$$\left(A_r'^{out}(R)\, A_\theta^{out} - A_r'^{in}(R)\, A_\theta^{in}\right) = -\mu_0\,\sigma\,\omega\, R\,\sin\theta \tag{20.36}$$

suggests that we want $\ell = 1$ (the associated Legendre polynomials are order ℓ in $\sin\theta$ and $\cos\theta$). In fact, if we look up $P_1^1(\cos\theta) = \sin\theta$, just what we want. With $\ell = 1$ in hand, we can return to the radial equation:

$$\frac{\frac{d}{dr}\left(r^2\, A_r'\right)}{A_r} = \ell\,(\ell+1) = 2 \longrightarrow A_r(r) = \alpha\, r + \frac{\beta}{r^2}. \tag{20.37}$$

This second order differential equation has actually given us both the interior and exterior cases. For the interior, we set $\beta = 0$ so that the potential does not blow up at the origin. For the exterior, we set $\alpha = 0$ to get good behavior at $r \longrightarrow \infty$.

We can finish the whole job now:

$$\mathbf{A}^{out} = \frac{\alpha}{r^2}\, P_1^1(\cos\theta)\,\hat{\boldsymbol{\phi}} \qquad \mathbf{A}^{in} = \beta\, r\, P_1^1(\cos\theta)\,\hat{\boldsymbol{\phi}}, \tag{20.38}$$

and $P_1^1(\cos\theta) = \sin\theta$ (perfect). Just apply the boundary condition (20.36) and continuity ($\mathbf{A}^{out} = \mathbf{A}^{in}$)

$$\begin{gathered} -\frac{2\alpha}{R^3}\,\sin\theta - \beta\,\sin\theta = -\mu_0\,\sigma\,\omega\,R\,\sin\theta\,\hat{\boldsymbol{\phi}} \\ \frac{\alpha}{R^2} = \beta\, R \end{gathered} \tag{20.39}$$

to get $\alpha = \frac{1}{3}\,\mu_0\,\sigma\,\omega\,R^4$ and $\beta = \frac{1}{3}\,\mu_0\,\sigma\,\omega\,R$. The end result is

$$\mathbf{A}^{out} = \frac{\mu_0\,\sigma\,\omega\,R^4\,\sin\theta}{3\,r^2}\,\hat{\boldsymbol{\phi}} \qquad \mathbf{A}^{in} = \frac{1}{3}\,\mu_0\,\sigma\,\omega\,R\,r\,\sin\theta\,\hat{\boldsymbol{\phi}}. \tag{20.40}$$

Homework

Reading: Griffiths, pp. 136–145. Homework assigned in Lecture 19.