Phys 342 Lecture 30

If you are reading these lectures notes, then you might be surprised as to the upbeat salutation that I have at the beginning of each. Well, the reason for that is that I front-loaded my lectures, writing them several weeks ahead of where the course actually was. This lecture is the first that I am writing after Reed closed and the course went exclusively online. It's harder now to be upbeat, facing an indeterminant amount of time essentially stuck at home and futher uncertainty about higher education after that. Nevertheless, let's muster the intellectual strength we have, focusing on something we can control for once. Let's get back to learning quantum mechanics together, apart.

This week, we are studying the hydrogen atom whose Hamiltonian is:

$$\hat{H} = \frac{\hat{p}_r^2}{2m_e} + \frac{\hbar^2 \ell(\ell+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}, \text{ where } r \in [0,\infty) \text{ is}$$

the radius of the electron from the proton, ℓ is the angular momentum of the electron, and $\hat{p}_r$ is its radial linear momentum. For $\ell=0$, we had found the energy levels of the electron to be:

$$E_n = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} = -\frac{13.6\text{ eV}}{n^2}, \text{ where } n = 1,2,\ldots$$

is a natural number. Calculating the energy levels for $\ell \neq 0$ aren't much harder, but I point you to Griffith's and Schroeter for more details. In finding the energy levels, we had also found the wavefunction of the electron $\psi_n(r)$, in the n^{th} energy eigenstate. Properly, we had only identified the radial dependence of the wavefunction, as the Hamiltonian is only a function of the variable position of the electron from the proton, r. As this is a three-dimensional problem, we need the complete three-dimensional position dependence of the wave function, and not just that for radius.

Our strategy for proceeding will be the following. As we are working in spherical coordinates because of the radial symmetry of the Coulomb potential, we would like to express the wavefunction of the electron ψ in terms of some basis functions as:

$$\psi(r,\theta,\varphi) = \sum_{n,\ell,m} c_{n\ell m} \psi_n(r)\, Y_\ell^m(\theta,\varphi),$$

where $\psi_n(r)$ is the radial wavefunction we identified earlier, and $Y_\ell^m(\theta,\varphi)$ are orthonormal and complete functions defined on the unit sphere, where $\theta \in [0,\pi]$, the polar angle, and $\varphi \in [0,2\pi)$, the azimuthal angle about the sphere. That is, the Y_ℓ^m's form a complete basis for all functions defined on the sphere. This notion of a "function defined on the sphere" might be a bit unfamiliar, but it's not so out of left field as you might think. In particular, we live on the Earth, whose surface coordinates are defined by latitude (i.e., effectively a polar angle) and longitude (effectively an azimuthal angle). As the Y_ℓ^m functions are assumed to be orthonormal and complete, we can express the elevation at every point on the Earth's surface (at every latitude and longitude) as some appropriate linear combination of the Y_ℓ^m's.

The indices on these Y_ℓ^m's, which are called "spherical harmonics", should suggest that they encode information about the total angular momentum l, and z-component of angular momentum, m. Indeed, as the spherical harmonics are function of angles θ and ϕ, we know that angular momentum is the Hermitian operator that generates rotations. Thus, these spherical harmonics satisfy the eigenvalue equations:

$$L^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)$$

$$\hat{L}_z Y_l^m(\theta,\phi) = \hbar m Y_l^m(\theta,\phi).$$

That is, the $Y_l^m(\theta,\phi)$ functions are just precisely the angular momentum states $|l,m\rangle$ that we introduced abstractly last week.

Now, one way to proceed to actually determine the functional form of these $Y_l^m(\theta,\phi)$ functions is to write L^2 and $\hat{L}_z$ as operators in θ,ϕ space and then solve some nasty second-order differential equation. This is done in Griffiths and Schroeter, so I won't discuss it in these notes. Instead, I want to understand these operators a bit more concretely, and express the orthogonality in a useful way.

First, let's work to express $\hat{L}_z$ in the basis of θ,ϕ. Recall that the basis-independent definition of $\hat{L}_z$ is

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \text{ for the position and momentum operators.}$$

Now, we can write each of these operators in spherical coordinate basis. Recall that for positions x, y, z in spherical coordinates θ, ϕ with fixed $r=1$ they are

$$x = \sin\theta\cos\phi, \quad y = \sin\theta\sin\phi, \quad z = \cos\theta.$$

Additionally, the momenta are just the appropriate derivatives in position space:

$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$, and we can use the chain rule to express these derivatives in terms of θ, ϕ. The chain rule states that:

$$\frac{\partial}{\partial\theta} = \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\theta}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\theta}\frac{\partial}{\partial z} \quad \text{and} \quad \frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y}.$$

Note that we have written the derivatives of θ and ϕ in terms of derivatives of x and y (and z) and there is no ϕ dependence in z so it does not appear in $\partial/\partial\phi$. Additionally, angular momentum in the z-direction means that you are rotating in the x-y plane, with z fixed. So, we can ignore derivatives of z. So, we can solve:

$$\frac{\partial}{\partial\theta} = \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\theta}\frac{\partial}{\partial y} \quad \text{and} \quad \frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} \quad \text{for}$$

$\frac{\partial}{\partial x}$ and $\partial/\partial y$ and correspondingly solve for the linear momenta $\hat{p}_x$ and $\hat{p}_y$.

This is simply solving two linear equations, so I won't provide the details here. One finds:

$$\left(\frac{\partial y}{\partial\theta}\frac{\partial x}{\partial\phi} - \frac{\partial y}{\partial\phi}\frac{\partial x}{\partial\theta}\right)\frac{\partial}{\partial y} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial\theta} - \frac{\partial x}{\partial\theta}\frac{\partial}{\partial\phi} \quad \text{and}$$

$$\left(\frac{\partial x}{\partial \theta}\frac{\partial y}{\partial \phi} - \frac{\partial x}{\partial \phi}\frac{\partial y}{\partial \theta}\right)\frac{\partial}{\partial x} = \frac{\partial y}{\partial \phi}\frac{\partial}{\partial \theta} - \frac{\partial y}{\partial \theta}\frac{\partial}{\partial \phi}$$

Using the explicit form of the coordinates from earlier, we can evaluate all of the derivatives. We then find:

$$\frac{\partial}{\partial y} = \frac{\sin\phi}{\cos\theta}\frac{\partial}{\partial \theta} + \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial \phi}, \quad \frac{\partial}{\partial x} = \frac{\cos\phi}{\cos\theta}\frac{\partial}{\partial \theta} - \frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial \phi}$$

Next, we just multiply by the appropriate coordinates and take the difference:

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= -i\hbar\left[\sin\theta\cos\phi\left(\cancel{\frac{\sin\phi}{\cos\theta}\frac{\partial}{\partial \theta}} + \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right) - \sin\theta\sin\phi\left(\cancel{\frac{\cos\phi}{\cos\theta}\frac{\partial}{\partial \theta}} - \frac{\sin\phi}{\sin\theta}\right)\frac{\partial}{\partial \phi}\right]$$

$= -i\hbar\frac{\partial}{\partial \phi}$, which is exceptionally simple! We could have also just guessed this, but this provides a method for finding $\hat{L}_x$ and $\hat{L}_y$, too. For $\hat{L}_x$, for example, we fix x, and then use the chain rule to determine $\partial/\partial y$ and $\partial/\partial z$ in a similar fasion. You'll play around with that in homework.

Now, it is trivial to solve the eigenvalue eqnation for $\hat{L}_z$:

$$\hat{L}_z Y_\ell^m(\theta,\phi) = m\hbar Y_\ell^m(\theta,\phi) = -i\hbar\frac{\partial}{\partial \phi} Y_\ell^m(\theta,\phi),$$

which has solution $Y_\ell^m(\theta,\phi) = P_\ell^m(\cos\theta)\,e^{im\phi}$, where $P_\ell^m(\cos\theta)$ is just some other function of θ only. Note that $e^{im\phi}$ is periodic on $\phi \in [0, 2\pi)$, and m is any integer. Further, it is orthogonal for m, n, $m \neq n$ on $\phi \in [0, 2\pi)$:

$$\int_0^{2\pi} e^{im\phi} e^{-in\phi} d\phi = \frac{1}{i(m-n)} e^{i(m-n)\phi}\Big|_0^{2\pi} = 0.$$

To normalize it, we simply multiply by $\frac{1}{\sqrt{2\pi}}$ as:

$$\int_0^{2\pi} e^{im\phi} (e^{im\phi})^* d\phi = \int_0^{2\pi} d\phi = 2\pi.$$

Thus, the eigenfunctions, properly normalized, of $\hat{L}_z$ in spherical coordinates are:

$$\frac{1}{\sqrt{2\pi}} e^{im\phi}.$$

Next, we could derive in great detail L^2 as a differential operator and solve its eigenvalue equation, but it will turn out to be outside of linear, first-order, homogeneous that I know how to solve, so we'll spend the last few minutes today doing something else. What we are going to do is to just identify the functions $P_\ell^m(\cos\theta)$ from orthogonality, nothing else. Actually, it will turn out that this procedure is restricted to $m=0$, but can be generalized. Recall the integration measure of three-dimensions in spherical cooordinates:

$$\int dx\, dy\, dz = \int_0^\infty r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = \int_0^\infty r^2 dr \int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi.$$

We have already discussed techniques for identifying the orthonormal bases of radial coordinate r and azimuthal coordinate ϕ with different methods. Let's now identify an orthonormal basis $P_\ell^0(\cos\theta)$ for polar coordinate θ. Orthonormal here means that, for two total angular momenta ℓ, ℓ', we have

$$\int_0^\pi P_\ell^0(\cos\theta)\, P_{\ell'}^0(\cos\theta) \sin\theta\, d\theta = \delta_{\ell\ell'}.$$

Note, however, that it is nice to write the argument of this function as $\cos\theta = x$ because the integration measure over the polar angle is exactly as expressed in x: $\sin\theta \, d\theta = d(\cos\theta) = dx$. To construct these orthonormal functions, we will do what you always do when constructing an orthonormal basis: Gram-Schmit it!

For simplicity, let's assume that our basis are monomials of x: $1, x, x^2, x^3, \ldots$. So we start with "1" and normalize it:

$$\int_{-1}^{1} (1\cdot N)(1\cdot N)\, dx = N^2 \cdot 2, \quad \text{or} \quad N = \frac{1}{\sqrt{2}}.$$

So, our first function with $l = 0$ is

$$P_0^0(x) = \frac{1}{\sqrt{2}}.$$

Next, we take the function/monomial x and subtract its dot product with "1":

$$P_1^0(x) = N\left(x - \frac{1}{\sqrt{2}} \int_{-1}^{1} dx \, \frac{1}{\sqrt{2}} \cdot x\right) = Nx,$$

as x integrates to 0 on $[-1, 1]$.

Then, we find the normalization constant for this function to be:

$$1 = N^2 \int_{-1}^{1} dx\, x^2 = N^2 \left.\frac{x^3}{3}\right|_{-1}^{1} = N^2 \frac{2}{3}, \quad \text{or that } N = \sqrt{\frac{3}{2}}.$$

Thus, $P_1^0(x) = \sqrt{\frac{3}{2}}\, x$. Continuing, we take the monomial x^2 and subtract its dot products with P_1^0 and P_0^0:

$$P_2^0(x) = N\left(x^2 - \sqrt{\tfrac{3}{2}}\, x \cancelto{0}{\int_{-1}^{1} dx \sqrt{\tfrac{3}{2}}\, x \cdot x^2} - \frac{1}{\sqrt{2}} \int_{-1}^{1} dx \frac{1}{\sqrt{2}} x^2\right)$$

$$= N\left(x^2 - \frac{1}{2} \cdot \left.\frac{1}{3} x^3\right|_{-1}^{1}\right) = N\left(x^2 - \frac{1}{3}\right).$$

Then, we can normalized $P_2^0(x)$ as:

$$1 = N^2\int_{-1}^{1} dx\left(x^2-\frac{1}{3}\right)^2 = N^2\int_{-1}^{1} dx\left(x^4-\frac{2}{3}x^2+\frac{1}{9}\right)$$

$$= N^2\left(\frac{2}{5}-\frac{4}{9}+\frac{2}{9}\right) = \frac{8}{45}N^2, \text{ or that } N = \frac{\sqrt{45}}{2\sqrt{2}} = \frac{3}{2}\sqrt{\frac{5}{2}}$$

That is, $P_2^0(x) = \sqrt{\frac{5}{8}}\left(3x^2-1\right)$.

Now, we can continue, but I think you get the idea. These orthonormal polynomials we have constructed are identical to the Legendre polynomials we encounted in HW #1! So, apparently, these Legendre polynomials are vital for understanding angular momentum in three dimensions! Again, I said that this holds for $m=0$; if $m\neq 0$, the analysis changes slightly, but the idea ~~is~~ is the same. See Griffiths and Schroeter for more details if $m\neq 0$, and you'll play with it more in homework.