Physics 486 Discussion 10 – The Spherical Harmonics

Introduction: Angular Momentum Appears At Last

Last week you used the **3D** Schrödinger equation to solve a problem in (x,y,z) coordinates. Cartesian coordinates are perfectly suited to last week's particle-in-a-box, but in nature, systems tend to display cylindrical or spherical forms rather than rectangular ones. The particular system we are heading for is **the atom**, and clearly spherical coordinates are a much better way to describe the orbitals of atomic electrons! Here is the 3D Schrödinger equation :

$$\hat{H}\,\Psi(\vec{r}) = \hat{E}\,\Psi(\vec{r}) \qquad \text{where} \qquad \hat{H} = \frac{|\vec{p}|^2}{2m} + V(\vec{r}) = -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r})$$

and here are the gradient and the Laplacian in **spherical coordinates** :

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial \theta} + \frac{\hat{\phi}}{r\sin\theta}\frac{\partial}{\partial \phi} \quad \text{and} \quad \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\,.$$

For most of this class, we will restrict our attention to **central potentials**, where V depends only on the coordinate r, and so has spherical symmetry (i.e., looks the same from all angles). The electric potential $V(r) = -e/4\pi\varepsilon_0 r$ produced by the hydrogen nucleus and seen by the single electron in the hydrogen atom is a perfect example!

Now let's examine the $p^2 = -\hbar^2\nabla^2$ part of the Hamiltonian, and see how angular momentum appears.

In spherical coordinates, we can decompose momentum into two perpendicular pieces: a **radial component** p_r and an **angular component** p_Ω.:

$$\vec{p} = \vec{p}_r + \vec{p}_\Omega \qquad \text{with} \qquad \vec{p}_r \equiv \hat{r}\,p_r \quad \& \quad \vec{p}_\Omega \equiv \hat{\theta}\,p_\theta + \hat{\phi}\,p_\phi\,.$$

Since $\vec{p}_r$ and $\vec{p}_\Omega$ are perpendicular to each other,

$$p^2 = p_r^2 + p_\Omega^2\,.$$

It's time for a crucial observation. The **angular momentum** relative to the origin produced by a momentum vector $\vec{p}$ is $\vec{L} = \vec{r}\times\vec{p}$. The cross-product picks out the $\vec{p}$ component perpendicular to the radial vector $\vec{r}$, which is $\vec{p}_\Omega$, so the magnitude of the angular momentum is

$$L = r\,p_\Omega\,.$$

Thus, $p^2 = p_r^2 + p_\Omega^2$ can be written as follows:

$$\boxed{p^2 = p_r^2 + \frac{L^2}{r^2}}\,.$$

The angular components of momentum, p_θ and p_ϕ – and *only* the angular components— are now absorbed in L^2. Now compare the above decomposition of p^2 to the QM operator version of p^2 :

$$\begin{aligned} p^2 = -\hbar^2\nabla^2 &= -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[-\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \\ &= \qquad p_r^2 \qquad + \frac{1}{r^2}\left[\;L^2(\theta,\phi)\;\right] \end{aligned}$$

All of the angular dependence is in the second term, within the square brackets, so that *must* be L^2! It even has the factor of $1/r^2$ in front of it. ☺ The first term must therefore be p_r^2 (and indeed it has no dependence on θ or ϕ, perfect). Here, then, are the operators for the radial and angular pieces of p^2, and for L^2:

$$\hat{p}^2 = -\hbar^2\nabla^2 = \hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \quad \text{where} \quad \hat{p}_r^2 = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \quad \text{and} \quad \hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Problem 1 : Separation of Variables in Spherical Coordinates

Our goal today is to find the eigenstates of the Hamiltonian for **central potentials *V*(*r*)** using **spherical coordinates**, i.e. to solve for the functions $\psi_E(r,\theta,\phi)$ that satisfy :

$$\hat{H}\,\psi_E(r,\theta,\phi) = E\,\psi_E(r,\theta,\phi) \qquad \text{when} \qquad \hat{H} = \frac{\hat{p}^2}{2m} + V(r).$$

Using the decomposition of p^2 described in the introduction, the Hamiltonian is

$$2m\hat{H} = \hat{p}_r^2 + \frac{\hat{L}^2(\theta,\phi)}{r^2} + 2mV(r)$$

We will proceed via separation of variables, in two steps.

Separation #1: Separate the **radial** and **angular** dependences via $\psi(\vec{r}) = R(r)Y(\theta,\phi)$.

(a) Plug the form $\psi(\vec{r}) = R(r)Y(\theta,\phi)$ into the eigenvalue equation $2m\hat{H}\psi = 2mE\psi$ and obtain separated equations for $R(r)$ and $Y(\theta,\phi)$. Use whatever letter you like for your separation constant.

(b) The angular equation you obtained was hopefully

$$\frac{\hat{L}^2}{\hbar^2}Y(\theta,\phi) = \text{const}\cdot Y(\theta,\phi)$$

What are the units of $\hbar$? What are the units of the separation "const"? (Remember from class, there are *two* useful versions of the units of $\hbar$, pick the most useful one here [1].)

(c) Our "const" must be positive, since it is the eigenvalue of a positive quantity ($L^2/\hbar^2$) so let's call it λ^2. The previous part also tells us that it must be dimensionless. Our equation is now

$$\frac{\hat{L}^2}{\hbar^2}Y(\theta,\phi) = \lambda^2\,Y(\theta,\phi).$$

This is the eigen-equation for L^2! The functions $Y(\theta,\phi)$ we seek are the eigenfunctions of L^2, excellent! These are very important functions and we call them the **spherical harmonics**. It's now time for …

Separation #2: Separate the **polar** and **azimuthal** dependences via $Y(\theta,\phi) = T(\theta)F(\phi)$.

(c continued) Come up with separated equations for $T(\theta)$ and $F(\phi)$ respectively. Again, use any letter you like as your separation constant.

▶ When you apply the boxed expression above for L^2, don't expand the first term with the $\partial/\partial\theta$'s, it won't help.

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[1] Recap: $\hbar$ has units of (1) **angular momentum** and (2) **energy × time**, which are actually the same thing.

(d) Let's deal with the **azimuthal** part first, $F(\phi)$. Your separated equation for $F(\phi)$ should look like this :

$$F''(\phi) = \text{const} \cdot F(\phi)$$

Let's call that constant μ, giving us $F''(\phi) = \mu F(\phi)$. Write down the general solution of this equation

- when μ is positive, and
- when μ is negative.

(e) You must now impose a very important physical constraint on $F(\phi)$: since ϕ and $\phi + 2\pi n$ are physically the exact same angle, any function $F(\phi)$ representing a physical system must be **periodic with period 2π**. The function must obey the relation

$$F(\phi + 2\pi n) = F(\phi).$$

(If it doesn't, it will be a multivalued function, with different values at the exact same physical angle, and so it cannot represent anything physical.) Consider your general solutions from the previous part and figure out what constraints must you impose on the separation variable μ to satisfy $F(\phi + 2\pi n) = F(\phi)$? HINT: There are *two* constraints. One has to do with the sign of μ, and the other has to do with integers vs real numbers.

(f) The constraints you must impose are that $\mu = -m^2$ where m is an integer. Combining this with your general solution from part (d), you should get

$$\boxed{F(\phi) \sim e^{im\phi}} \quad \text{where } m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

If this is not what you obtained, check part (d) or ask your instructor.

(g) Now we turn to the **polar** function $T(\theta)$. Your separated equation from part (c) for $T(\theta)$ should be :

$$\left(m^2 - \lambda^2 \sin^2\theta\right) T(\theta) = \sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial T(\theta)}{\partial\theta}\right)$$

What a horrid equation. Fortunately Professeur Adrien-Marie Legendre has done the work for us. (We will do the derivation in next lecture). It turns out that this equation only has physically acceptable solutions when

- $\lambda^2 = l(l+1)$ where $l = 0, 1, 2, 3, \ldots$
- $|m| \le l$ i.e. where $m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l$

When these conditions are satisfied, the solutions $T(\theta)$ to the above equation are the **Associated Legendre Functions $P_l^m(\cos\theta)$**. When $\boldsymbol{m = 0}$, you get the regular **Legendre Polynomials $P_l(\cos\theta)$**. The relation between the two is explained rather well in Jain §11.4, have a look! Griffiths' table of the first few is on the left. When these θ-dependent functions are combined with our ϕ-dependent solutions $F(\phi) \sim \exp(im\phi)$, we get the full angular part of the energy eigenfunction. When normalized, the functions $Y_l^m(\theta, \phi) \sim P_l^m(\cos\theta)e^{im\phi}$ are called the **Spherical Harmonics**. Griffith's table of the first few of these is on the right.

Table 4.1: Some associated Legendre functions, $P_l^m(\cos\theta)$.

$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$
$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$	

Table 4.2: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm 3i\phi}$

To make sure we understand the significance of these spherical harmonics $Y_l^m(\theta,\phi) \sim P_l^m(\cos\theta)e^{im\phi}$, combine the eigenvalue equation for Y in part (c) with the requirement that $\lambda^2 = l(l+1)$. You will find that the spherical harmonic $Y_l^m(\theta,\phi)$ is an **eigenfunction of L^2 with eigenvalue _______**. (Fill in the blank, and be sure to check that your units make sense!)

(h) Thus, the quantum number l tells us about the state's total angular momentum. What about the quantum number m? Here is the operator for the angular momentum vector $\vec{L} = \vec{r}\times\vec{p} = \vec{r}\times(\hbar/i)\vec{\nabla}$ in spherical coords:

$$\frac{i}{\hbar}\vec{L} = \hat{\phi}\frac{\partial}{\partial\theta} - \frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial\phi}$$

Make a good sketch of the unit vectors $\hat{\phi},\hat{\theta},\hat{z}$ at a random point in space, then figure out the operator $L_z = \vec{L}\cdot\hat{z}$.

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Does the sketch at the bottom of the page help you to figure out the operator L_z? The answer is in the footnote[2]

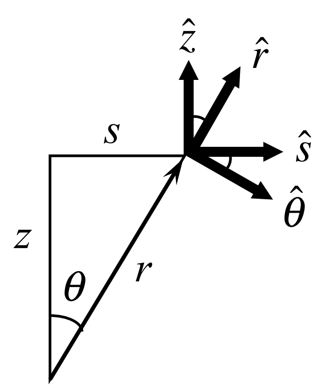
(i) Calculate $\hat{L}_z Y_l^m(\theta,\phi) \sim \hat{L}_z P_l^m(\cos\theta)e^{im\phi}$. You should find that the spherical harmonic $Y_l^m(\theta,\phi)$ is an **eigenfunction of L_z with eigenvalue _______**. (You fill in the blank, and check your units!)

(j) Now that you know what the spherical harmonics represent, have a look at the table on the previous page and try sketching a couple of them. Remember that Y is the angular part of a wavefunction so its probability density is Y^*Y.

(k) To obtain some more physical intuition, calculate the **probability current density** $\vec{j} = \mathrm{Re}\left[Y_l^{m*}\frac{\hat{\vec{p}}}{m}Y_l^m\right]$ for these angular wavefunctions. We will talk about this quantity in detail in lecture, but for now, just know that it describes the **flow** of probability represented by a wavefunction. $\rho = \psi^*\psi$ and $\vec{j} = \mathrm{Re}\left[\psi^*\left(\hat{\vec{p}}/m\right)\psi\right]$ in QM are the exact analogues of the charge density ρ and current density $\vec{j}$ in E&M, just replace "charge" with "probability". Calculate $\vec{j}$ for two examples: $(l, m) = (1, 0)$ and $(l, m) = (1, \pm 1)$. You will see the influence of the m quantum number and its association with L_z very clearly in your result for $\vec{j}$!

(l) Calculate the **commutator** $\left[\hat{L}^2, \hat{L}_z\right]$. What you find should be consistent with the fact that the spherical harmonics $Y_l^m(\theta,\phi)$ constitute a common set of eigenfunctions for both the operator $\hat{L}^2$ and the operator $\hat{L}_z$. The relevant principle was presented in lecture: operators that commute have a common set of eigenfunctions.

$\hat{\phi}$ points into the page



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[2] $\hat{L}_z = -i\hbar\,\partial/\partial\phi$