Physics 486 Discussion 11 – Spherical Harmonics

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 system we are heading for in particular is the atom, and clearly spherical coordinates are a much better way to describe the orbitals the electrons can occupy! So, here is the 3D Schrödinger equation:

\[
\hat{H} \Psi(\vec{r}) = \hat{E} \Psi(\vec{r}) \quad \text{where} \quad \hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r}) = -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r})
\]

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

\[
\vec{\nabla} = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{\partial}{r \partial \theta} + \hat{\phi} \frac{\partial}{r \sin \theta \partial \phi}
\]

\[
\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}.
\]

If these rather monstrous forms surprise or distress you, don’t worry, we will talk about it in lecture!

Our task is to find a procedure for obtaining the energy eigenstates of systems where the potential \(V(\vec{r})\) is best expressed in spherical coordinates. We will immediately concentrate on the simplest of all such potentials, central potentials, where \(V\) depends only on the coordinate \(r\) and so has perfect spherical symmetry (i.e., looks the same from all angles). The electric potential \(V(r) = -e/4\pi\epsilon_0 r\) produced by the hydrogen nucleus and seen by the single electron whose energy eigenstates we wish to calculate is a perfect example!

Let’s impose some structure on the \(p^2 = -\hbar^2 \nabla^2\) part of the Hamiltonian — that’s the complicated part!

In spherical coordinates, the momentum has a radial component \(p_r\) and a component perpendicular to \(p_r\) that we will call \(p_\Omega\). I’m using \(\Omega\) since it stands for solid-angle, and \(p_\Omega\) is composed of the angular components of momentum:

\[
\hat{p}_\Omega = \hat{\theta} p_\theta + \hat{\phi} p_\phi.
\]

Since \(p_r\) and \(p_\phi\) are perpendicular to each other,

\[
p^2 = p_r^2 + p_\Omega^2.
\]

Now one final 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 only the \(\vec{p}\) component perpendicular to the radial vector \(\vec{r}\), so the magnitude of angular momentum is \(L = r p_\Omega\). Thus, \(p^2 = p_r^2 + p_\Omega^2\) can be rewritten as

\[
p^2 = p_r^2 + \frac{L^2(\theta,\phi)}{r^2}
\]

where all the angular components — and only the angular components, \(p_\theta\) and \(p_\phi\) — are absorbed in \(L^2\).

Now compare this simple decomposition to the QM operator version:

\[
p^2 = -\hbar^2 \nabla^2 = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[ -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]

\[
= p_r^2 + \frac{1}{r^2} \left[ L^2(\theta, \phi) \right]
\]

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 \(\theta\) or \(\phi\). Here then are our radial and angular operators for the pieces of \(p^2\):

\[
\hat{\nabla} = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{\partial}{r \partial \theta} + \hat{\phi} \frac{\partial}{r \sin \theta \partial \phi}
\]

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

\[
\therefore \quad 2m \hat{H} = \frac{\hat{p}^2}{r^2} + \frac{\hat{L}^2(\theta, \phi)}{r^2} + 2mV(r) \quad \text{for a central potential } V(r)
\]

**Problem 1 : Separation of Variables**

Our goal is, as always, to “solve the Schrödinger equation”, i.e. to find the eigenstates of the Hamiltonian = the energy eigenstates of the system. Our central-potential Hamiltonian is \( \hat{H} = \frac{\hat{p}^2}{2m} + V(r) \) so we must find the eigenfunctions \( \hat{H} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \). We will do separation-of-variables on \( \psi(\vec{r}) \) in two stages.

(a) First, we will separate the radial and angular dependences. Take \( \psi(\vec{r}) = R(r)Y(\theta, \phi) \), plug that into the energy eigenvalue equation \( 2m \hat{H} \psi = 2mE \psi \) for a central potential \( V(r) \), 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

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

Here’s a small but important question: what are the units of \( \hbar \)? What are the units of the separation “const”?

(c) Our “const” must be positive, since it is the eigenvalue of a positive quantity \( L^2 / \hbar^2 \) so let’s call it \( \lambda^2 \).

The previous part tells us that it must also be dimensionless. Our equation is now

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

This is the **eigenvalue equation for angular momentum**. The functions \( Y(\theta, \phi) \) we seek are the eigenfunctions of \( L^2 \). This is a rather big deal! To proceed, we separate again: separate the polar and azimuthal dependences by taking \( Y(\theta, \phi) = T(\theta) F(\phi) \). Again, use any letter you like as your separation constant, and come up with separated equations for \( T(\theta) \) and \( F(\phi) \). NOTE: When you apply the boxed equation for \( L^2 \) above, don’t bother expanding the first term with the \( \partial / \partial \theta \)’s, it won’t help.

(d) Let’s deal with the azimuthal function first. Your separated equation for \( F(\phi) \) should look like this:

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

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

* when \( \mu \) is positive, and
* when \( \mu \) is negative.

(e) You must now impose a very important physical constraint on \( F(\phi) \): since \( \phi \) and \( \phi + 2\pi n \) are physically the exact same angle, any function \( F(\phi) \) representing a physical system must be periodic with period \( 2\pi \). 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 \( \mu \) to satisfy \( F(\phi + 2\pi n) = F(\phi) \)? HINT: There are **two** constraints. One has to do with the sign of \( \mu \), and the other has to do with integers vs real numbers.
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

$$F(\phi) \sim e^{im\phi}$$

where $m = 0, \pm 1, \pm 2, \pm 3, \ldots$

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

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

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

Aieeee, what a horrid equation. Fortunately Professeur Adrien-Marie Legendre has done the work for us. It turns out that this equation only has physically acceptable solutions when

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

When these conditions are satisfied, the solutions $T(\theta)$ to the above equation are the Associated Legendre Functions $P_l^m(\cos \theta)$. When $m = 0$, 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 $\theta$-dependent functions are combined with our $\phi$-dependent solutions $F(\phi) \sim e^{im\phi}$, 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>
<thead>
<tr>
<th>$l$</th>
<th>$P_1^1 = \sin \theta$</th>
<th>$P_2^3 = 15 \sin \theta (1 - \cos^2 \theta)$</th>
<th>$P_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$</th>
<th>$P_2^0 = \frac{1}{4} (3 \cos^2 \theta - 1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0$</td>
<td>$P_0^0 = \cos \theta$</td>
<td>$P_1^1 = 15 \sin \theta (1 - \cos^2 \theta)$</td>
<td>$P_2^3 = \frac{1}{2} \sin \theta (5 \cos^2 \theta - 1)$</td>
<td>$P_3^0 = \frac{1}{8} (5 \cos^2 \theta - 3 \cos \theta)$</td>
</tr>
<tr>
<td>$1$</td>
<td>$P_2^0 = 3 \sin^2 \theta$</td>
<td>$P_3^1 = \frac{1}{2} \sin \theta (5 \cos^2 \theta - 1)$</td>
<td>$P_4^3 = \frac{1}{2} \sin \theta (5 \cos^2 \theta - 3 \cos \theta)$</td>
<td>$P_5^0 = \frac{1}{4} (3 \cos^2 \theta - 1)$</td>
</tr>
</tbody>
</table>

Let’s make sure we understand the significance of these spherical harmonics $Y_l^m(\theta, \phi) \sim P_l^m(\cos \theta)e^{im\phi}$.

First, 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 $l(l+1)$. (Fill in the blank .. and be sure to check that your units make sense!)

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 $\vec{L} = \hat{r} \times \vec{p} = \hat{r} \times (\hbar i \vec{\nabla})$ in spherical coords:

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

Make a good sketch of the unit vectors $\hat{\phi}, \hat{\theta}, \hat{z}$ at a random point in space, then calculate the operator $L_z = \vec{L} \cdot \hat{z}$. Hint: the next page has a good sketch of the unit vectors if you need assistance.
Does the sketch on the left help you to figure out the operator $L_z$? The answer is ...

\[ \hat{L}_z = \frac{i}{\hbar} \frac{\partial}{\partial \phi} \]

(i) Calculate $\hat{L}_z Y^m_l(\theta, \phi) \sim \hat{L}_z P^m_l(\cos \theta) e^{im\phi}$. You should find that the spherical harmonic $Y^m_l(\theta, \phi)$ 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 $\vec{j}_l^m = \text{Re} \left[ Y_l^m e^* \hat{p}_m Y_l^m \right]$ for these angular wavefunctions. Try just 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 $L_z$ quite clearly!

(l) Calculate the commutator $[\hat{L}^2, \hat{L}_z]$. What you find should be consistent with the fact that the spherical harmonics $Y^m_l(\theta, \phi)$ constitute a common set of eigenfunctions for both the operator $\hat{L}^2$ and the operator $\hat{L}_z$. 

\[ \hat{L}_z = \frac{i}{\hbar} \frac{\partial}{\partial \phi} \]