Python activities - PHY456
Rotation and Superposition of Spherical Harmonics

Federico Duque Gomez (Python code by Vijay Shankar)

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1 Introduction

Recall that the operators of angular momentum L^2 and L_z in coordinate representation have the form

$$\langle \mathbf{r} | L^2 | \mathbf{r}' \rangle = \mathcal{L}^2 \delta(\mathbf{r} - \mathbf{r}') \tag{1}$$

and

$$\langle \mathbf{r} | L_z | \mathbf{r}' \rangle = \mathcal{L}_z \delta(\mathbf{r} - \mathbf{r}'), \tag{2}$$

where we have introduced the differential operators

$$\mathcal{L}^2 \equiv -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan\theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \tag{3}$$

and

$$\mathcal{L}_z \equiv -i\hbar \frac{\partial}{\partial \phi}. \tag{4}$$

The *spherical harmonics*, $Y_l^m(\theta, \phi)$, are eigenfunctions of $\mathcal{L}^2$ and $\mathcal{L}_z$. They form a complete and orthonormal set of functions so any complex-valued function of θ and ϕ can be expressed as a linear combination of spherical harmonics. For these reasons they play a very important role in the description of angular momentum and rotations in real space.

The Python program for this activity allows you to represent spherical harmonics (and their superpositions) in three dimensions and apply an arbitrary rotation to them. Any rotation in three dimensional (real) space can be described by a set of three angles (α, β, γ), called *Euler angles*. This activity will help you understand how rotations of complex-valued functions (specifically, spherical harmonics) are performed according to some given Euler angles. In the course we have used another way of describing rotations using an "angle and axis" parametrization, where instead of three angles we specify the direction of a unit vector and the angle of the rotation around this axis. The connection between these two parametrizations is not easy in general but this activity will help you visualize how to relate them. Additionally, we will look at an interesting application of superposition of spherical harmonics to construct real-valued atomic orbitals.

2 Euler rotations

Let us go back to classical mechanics for a moment and consider a rigid body in 3D, described by three orthogonal **space-fixed** axes $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$. As their name implies, these axes will not change when we rotate the object. Now imagine that we have three additional orthogonal axes $(\hat{\mathbf{x}}', \hat{\mathbf{y}}', \hat{\mathbf{z}}')$ embedded in the rigid body, which we will call **body-fixed** axes. These new axes are aligned with the body-fixed ones before the rotation but they will rotate with the object, so that their orientation with respect to the rigid body remains the same. The description of an arbitrary rotation according to the three *Euler angles* (α, β, γ) corresponds to a decomposition of such rotation in three steps. First, rotate the object around the *space-fixed* axis $\hat{\mathbf{z}}$ counterclockwise by an angle α, which also results in a rotation of the body-fixed axes; next, rotate the object around the "new" *body-fixed* axis $\hat{\mathbf{y}}'$ counterclockwise by an angle β, which once again changes the orientation of the body-fixed axes; finally, rotate the object around the axis $\hat{\mathbf{z}}'$ counterclockwise by an angle γ. Using rotation matrices we can perform these operations on a cartesian 3D vector multiplying by the matrix

$$\mathbf{R}(\alpha, \beta, \gamma) \equiv \mathbf{R}_{z'}(\gamma)\mathbf{R}_{y'}(\beta)\mathbf{R}_{z}(\alpha). \tag{5}$$

It turns out that this rotation can be rewritten in terms of rotations around the *space-fixed* axes only,

$$\mathbf{R}(\alpha, \beta, \gamma) = \mathbf{R}_{z}(\alpha)\mathbf{R}_{y}(\beta)\mathbf{R}_{z}(\gamma). \tag{6}$$

For a proof and useful diagrams see section 3.3 of Sakurai's book (J. J. Sakurai, *Modern Quantum Mechanics - Revised Edition*, Addison Wesley (1994)). This expression is easier to translate to rotation operators, in terms of angular momentum operators L_z and L_y, namely

$$U[\mathbf{R}(\alpha, \beta, \gamma)] = e^{-\frac{i}{\hbar}\alpha L_z} e^{-\frac{i}{\hbar}\beta L_y} e^{-\frac{i}{\hbar}\gamma L_z}. \tag{7}$$

3 Real-valued superpositions of spherical harmonics and atomic orbitals

Recall that the hydrogen atom wavefunctions can be written as

$$\Phi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_l^m(\theta, \phi), \tag{8}$$

where $R_{n,l}(r)$ is some *real* radial function. The hydrogen atom wavefunctions are usually called *atomic orbitals* and superpositions of them for the same n but different l and m are called *hybrid* orbitals. These *orbitals* are useful to explain qualitatively the geometrical structure of atomic bonding.

Here we will only look at superpositions of spherical harmonics with the same l. This type of superposition is useful to construct real-valued hybrid orbitals. Atomic orbitals (8) are in general complex functions because of the spherical harmonic part. Can we form a superposition of complex-valued spherical harmonics to get real-valued ones? The answer is yes and the reason is simple. Recall the property

$$(Y_l^m(\theta, \phi))^* = (-1)^m Y_l^{-m}(\theta, \phi). \tag{9}$$

Clearly the functions

$$\frac{1}{\sqrt{2}} \left(Y_l^m(\theta, \phi) + (-1)^m Y_l^{-m}(\theta, \phi) \right) \tag{10}$$

and

$$\frac{i}{\sqrt{2}} \left(Y_l^m(\theta, \phi) - (-1)^m Y_l^{-m}(\theta, \phi) \right) \tag{11}$$

are real and orthonormal. Consequently, for given l the complete set of orthonormal functions $Y_l^m(\theta, \phi)$ (for $m = -l, ..., l$), which are in general complex-valued, can be replaced the real-valued functions (10) and (11) for $m = l, ..., 0$.

4 Implementation in Python

The Python implementation for this activity is in the attached script *rotate_spherical_harmonic.py*. In the program we define the function **rotate** (line 80) to rotate a single spherical harmonic and **rotate_vector** (line 112) to rotate a superposition of spherical harmonics with the same l. Both use an additional function **rotation_matrices** (line 141), which creates the rotation matrices (of dimension $(2l + 1) \times (2l + 1)$) for a given l in the basis of spherical harmonics. For plotting we use the function **plot_spherical_harmonic** (line 12).

5 Try it!

Open the script *rotate_spherical_harmonic.py* from the Python Shell and run it.[1] The program will prompt you to select if you want to plot a single spherical harmonic $Y_l^m(\theta,\phi)$ (option 1) or a linear superposition of spherical harmonics with the same l, $\sum_{m=l}^{-l} c_m Y_l^m(\theta,\phi)$, (option 2). If you enter 1, you will be asked to specify the values of l and m and then the three Euler angles; if you enter 2, you have to specify first the value of l and the complex coefficients c_m of the superposition for each m starting with $m = l$ and going down to $m = -l$, followed by the Euler angles of the rotation. When entering a complex number for the coefficients c_m use "j" for the imaginary number $\sqrt{-1}$. For example, you can write "5.0 + 6.8 j" or "7.0j"; if no real part is specified the program will assume it is simply a real number. The input must be some number; for instance, do not enter "pi/2", use "1.57" instead.

The program plots the angular distribution of the absolute value of $Y_l^m(\theta,\phi)$ (or a linear superposition) before and after the rotation in two separate windows, Figure 1 and Figure 2 respectively. If you consider the position vector of each point on the surface with respect to the origin, the magnitude of such vector corresponds to the absolute value of the spherical harmonic (or linear superposition) for the angles (θ,ϕ) of the position vector. The color of the surface represents the sign of the **real part**: red means that $\mathrm{Re}\,[Y_l^m(\theta,\phi)] > 0$ while blue means that $\mathrm{Re}\,[Y_l^m(\theta,\phi)] < 0$. Note that the axes in the plots, labeled by X, Y and Z, correspond to the *space-fixed* axes $(\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}})$ in our previous discussion.

Depending on the computer you are using, the program can take some time to run. To speed it up reduce the number of points in the grid $Ngrid$ (line 57), but keep in mind that for less dense grids the borders between regions of different color might look jagged. Another important remark is that when plotting superpositions of spherical harmonics the program sometimes returns a warning "Converting a masked element to nan"; we think this warning is harmless so ignore it, but tell us if you find any problem.

5.1 Plotting a single spherical harmonic

We can start with some simple examples to get a sense of how the different spherical harmonics look. Run the code for a few different values of l and m; at this point we will not be worried about the rotation, so use any set of angles. Try to answer the following questions by looking at the output of the code:

- What happens with the color and the shape as we increase l for fixed $m = 0$?
- What happens with the color and the shape as we increase l for $m = l$?
- For fixed l describe what happens when we change m from 0 to l.
- What happens when you change the sign of m?

Are your observations consistent with the analytical expressions for the spherical harmonics?

5.2 Rotating a single spherical harmonic

Now we will try some rotations! From Eq. (7) it is clear it is very simple to specify rotations around the Y or Z axes. Try a few of them to make sure you get what you expect.

How about rotations around the X axis? Suppose we want to rotate $Y_{l=1}^{m=0}(\theta,\phi)$ around the X axis by $\pi/2$, how would you choose the Euler angles? One first guess could be $(\alpha = -\pi/2, \beta = \pi/2, \gamma = 0)$, which in the language of Eq. (7) corresponds to no rotation around Z followed by a rotation around Y by $\pi/2$ (as if Y was the X axis) and finally a rotation by $-\pi/2$ around Z (which would take Y to the X axis). Try it! Is the output correct? It seems to be right but try now to apply the same rotation $(\alpha = -\pi/2, \beta = \pi/2, \gamma = 0)$ to $Y_{l=2}^{m=1}(\theta,\phi)$. It does not seem to work in this case, right? What is wrong? For $(l = 1, m = 0)$ the spherical harmonic is cylindrically

[1] If you don't know how to use the Python Shell or you have not installed a Python distribution in your computer, visit the compwiki web site **http://compwiki.physics.utoronto.ca** where you can find extensive information about how to install and use Python.

symmetric around Z so no rotation around this axis is required initially, but this is not true for $(l = 2, m = 1)$ so clearly we must perform some initial rotation around Z. After a moment of though you conclude that this initial rotation should be by an angle $\gamma = \pi/2$. If you try the new Euler angles $(\alpha = -\pi/2, \beta = \pi/2, \gamma = \pi/2)$ you should get the right answer. Why $\gamma = \pi/2$? Intuitively, you will look for a rotation that "counteracts" the effect of the final rotation around Z so it should be the same angle as α but opposite sign. Although this argument works here, you will not expect it to hold for every rotation. After all, if it was true that $\gamma = -\alpha$, then why bother to have three Euler angles instead of two, α and β? Nevertheless, we would expect some relation between α and γ. In fact you can prove that if the rotation is around an axis forming an angle ϕ_{axis} with Z, the angles α and γ are related according to

$$\alpha - \gamma = 2\phi_{\text{axis}} - \pi. \tag{12}$$

See, for instance, Wu-Ki Tung, *Group Theory in Physics*, World Scientific (1985), p. 99.

What we just sketched is a useful method to determine the Euler angles if you are given the direction of some axis and the angle of rotation around it. Notice that all the spherical harmonics depend on the azimuthal angle ϕ only through $e^{im\phi}$ so only the phase is affected by this angle; therefore, the *shape* of our plots for all the spherical harmonics is cylindrically symmetric around Z, although the coloring can change as we move around this axis due to the phase. First determine what combination of rotations, around Y first and then around Z, gives you the right rotation of the *body-fixed* angle $\hat{\mathbf{z}}'$ (ignoring the dependence of the original spherical harmonic around Z). This will give you the correct angles β and α. Then, use (12) to find the correct value of γ.

Convince yourself that you understood this method by finding the Euler angles for a $\pi/2$ rotation around the axis $\hat{\mathbf{n}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}}+\hat{\mathbf{y}})$. Try the rotation with the Python code for $Y_{l=2}^{m=1}(\theta,\phi)$. If you want a more challenging exercise try a $\pi/2$ rotation around $\hat{\mathbf{n}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{y}}+\hat{\mathbf{z}})$!

5.3 Constructing real-valued superpositions of spherical harmonics

For simplicity let us consider the case $l = 1$. The spherical harmonic $Y_{l=1}^{m=0}(\theta,\phi)$ is very simple: just two lobes aligned along the Z axis, the upper one has positive values and the lower one negative values. This spherical harmonic multiplied by $R_{n,l=1}(r)$ forms a p_z orbital. The other two, $Y_{l=1}^{m=1}(\theta,\phi)$ and $Y_{l=1}^{m=-1}(\theta,\phi)$, have a completely different shape as you probably confirmed in the activities suggested in Section 5.1, furthermore they are complex-valued functions. Can we construct two new real-valued functions similar to $Y_{l=1}^{m=0}(\theta,\phi)$, replacing $Y_{l=1}^{m=1}(\theta,\phi)$ and $Y_{l=1}^{m=-1}(\theta,\phi)$? This can be accomplished using the method described in Section 3. Find the new functions and plot them using the Python program. How do they look? You should get functions that look exactly as $Y_{l=1}^{m=0}(\theta,\phi)$ but oriented along the X and Y axes, respectively. Therefore, when we multiply the new functions by $R_{n,l=1}(r)$ we get p_x and p_y orbitals.

You can actually construct a $p_{\hat{n}}$ orbital aligned along an arbitrary direction $\hat{\mathbf{n}}$. Derive an expression for such orbital. Try plotting one for the direction $\hat{\mathbf{n}} = \frac{1}{\sqrt{3}}(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$.

For further reference check: Complement E_{VII} in C. Cohen-Tannoudji, et al., *Quantum Mechanics - Volume I*, Wiley-Interscience (1977).