Lecture # 2

Orbital Angular momentum. Spherical harmonics

Last time we arrived at two separate equations for a radial part $R(r)$ and an angular part $Y(\theta,\varphi)$ of the wave function $\Psi(r,\theta,\varphi)$:

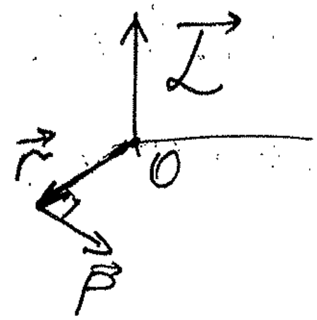
$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu r^2}{\hbar^2}\left(E-U(r)\right)-\lambda\right]R=0 \quad (2.1)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}+\lambda Y=0 \quad (2.2)$$

Since (2.2) does not contain any potential $\Rightarrow$ the solution of this equation must be universal for any spherically-symmetric potential $U(r)$ $\Rightarrow$ let's first concentrate on solving (2.2) and discussing its physical meaning.

Eq. (2.2) contains only angles θ, φ as variables related to rotations $\Rightarrow$ physical quantity related to rotations is orbital angular momentum $\Rightarrow$ recall classical mechanics $\Rightarrow$

The angular momentum $\mathcal{L}$ of the particle with respect to some point O is defined as



$$\vec{\mathcal{L}} = \underbrace{\vec{r}}_{\text{position vector with respect to } O} \times \underbrace{\vec{p}}_{\text{momentum}}$$

Components of $\vec{\mathcal{L}}$ (in Cartesian coordinates) $\Rightarrow$

$$\vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \vec{i}\,(y p_z - z p_y) + \vec{j}\,(z p_x - x p_z) + \vec{k}\,(x p_y - y p_x)$$

$$\Downarrow$$

$$\vec{\mathcal{L}} = (y p_z - z p_y,\ z p_x - x p_z,\ x p_y - y p_x) = (\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z)$$

In QM, $\vec{\mathcal{L}} \Rightarrow$ observable $\vec{L} = (L_x, L_y, L_z)$

$$\vec{L} = \vec{r} \times \vec{\underline{P}}$$

operators of position & momentum

Now, what are L_x, L_y and L_z?

Since $[\underbrace{r_i}_{(x,y,z)}, \underbrace{P_j}_{(P_x, P_y, P_z)}] = 0 \quad (i \neq j) \Rightarrow$

$$\boxed{\begin{aligned} L_x &= y P_z - z P_y \\ L_y &= z P_x - x P_z \\ L_z &= x P_y - y P_x \end{aligned}} \quad (2.3)$$

Note: what would happen if we had to make a transition from xp_x in classical mechanics to XP_x in QM? Classically, $xp_x = p_x x$, but since $[X, P_x] \neq 0$, in QM $XP_x \neq P_x X$. So, is xp_x transformed to XP_x or $P_x X$? $\Rightarrow$ In this case use symmetrization $xp_x \to \frac{XP_x + P_x X}{2}$

Can the components of $\vec{L}$ be measured simultaneously? What about $\vec{L}^2$? $\Rightarrow$ need to evaluate the commutators $[L_i, L_j]$, $[L_i, \vec{L}^2]$

It can be straightforwardly shown (HW!) that using (2.3) and $[r_i, P_j] = i\hbar\,\delta_{ij}$ we get $[L_i, L_j] = i\hbar L_k$ $(i \neq j)$ where ijk is a cyclic permutation $(xyz), (yzx), (zxy)$

$\Downarrow$

two components of the angular momentum cannot be measured simultaneously

$[\vec{L}^2, L_i] = 0 \Rightarrow$ can measure simultaneously L^2 and one of the components

How is this useful? $\Rightarrow$ we'll see shortly

$\Downarrow$

Let's go back to Eqs. (2.3) and write out these expressions: $L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$, $L_y = \ldots$ $L_z = \ldots$

Now change variables $x, y, z \Rightarrow r, \theta, \varphi$ $\Rightarrow$ morning coffee exercise

$$L_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}\right)$$

$$L_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\varphi}$$

Then, $\vec{L}^2 = L_x^2 + L_y^2 + L_z^2 =$

$$= -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

compare!

Let's go back to Eq. (2.2):

$$\underbrace{\frac{1}{\sin\theta}\left(\cos\theta\frac{\partial Y}{\partial\theta}\right)}_{= \frac{1}{\tan\theta}\frac{\partial Y}{\partial\theta}} + \frac{\partial^2 Y}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} + \lambda Y = 0$$

$\Updownarrow$

$$\vec{L}^2\, Y(\theta,\varphi) = \hbar^2\lambda\, Y(\theta,\varphi) \qquad (2.4)$$

$\Downarrow$

It turns out that our universal equation for an angular part of the wave function is directly related to the total angular momentum of the system!

orbital

Can we simplify a problem even more? $\Rightarrow$
use $[\vec{L}^2, L_z] = 0$ (why L_z? $\Rightarrow$ because it's the simplest operator out of L_x, L_y, L_z) or smth else? $\Rightarrow$ brain hase.

Since $[\vec{L}^2, L_z] = 0 \Rightarrow \vec{L}^2$ and L_z share the same eigenfunctions $\Rightarrow$

$$L_z Y(\theta, \varphi) = \hbar \underbrace{m}_{} Y(\theta, \varphi) \quad (2.5)$$

m – for now an arbitrary constant to be determined

So, we have Eqs. (2.4) and (2.5) to solve.

Let's define $\lambda = l(l+1)$ $\Leftarrow$ we'll show later where this form comes from
$\Downarrow$
(2.4) transforms into

$$\underline{\vec{L}^2 Y(\theta, \varphi) = \hbar^2 l(l+1) Y(\theta, \varphi)}$$

What do we know about l and m? $\Rightarrow$

1) Since the eigenvalues of physical observables are real $\Rightarrow$ l and m must be real

2) Consider $\langle \Psi | \vec{L}^2 | \Psi \rangle = \langle \Psi | L_x^2 | \Psi \rangle + \langle \Psi | L_y^2 | \Psi \rangle + \langle \Psi | L_z^2 | \Psi \rangle = \langle L_x \Psi | L_x \Psi \rangle + \langle L_y \Psi | L_y \Psi \rangle + \langle L_z \Psi | L_z \Psi \rangle = \| | L_x \Psi \rangle \|^2 + \| | L_y \Psi \rangle \|^2 + \| | L_z \Psi \rangle \|^2 \geq 0 \Rightarrow \underline{l(l+1) \geq 0}$

norm

$\Rightarrow \ell \geq 0$ or $\ell \leq -1$ $\Rightarrow$ conventionally it's chosen that $\ell \geq 0$

3) Consider Eq. (2.5) $\Rightarrow$

$$\underbrace{L_z}_{-i\hbar\frac{\partial}{\partial\varphi}} Y = \hbar m Y \; ; \quad -i\hbar \frac{\partial Y(\theta,\varphi)}{\partial\varphi} = \hbar m Y(\theta,\varphi)$$

present $Y(\theta,\varphi) = f_1(\theta) f_2(\varphi)$

can't determine $f_1(\theta)$ since it factors out, but from this equation

for $f_2(\varphi)$:

$$-i\hbar \frac{d f_2(\varphi)}{d\varphi} = \hbar m f_2(\varphi) \Rightarrow f_2(\varphi) = C e^{im\varphi}$$

Recall that $\varphi \in [0, 2\pi]$ $\Rightarrow$ $f_2(0) = f_2(2\pi)$ $\Rightarrow$

periodicity

$$e^{im \cdot 2\pi} = e^{im \cdot 0} = 1 \Rightarrow \text{m is integer}$$

$(m = 0, \pm 1, \pm 2, \ldots)$

called "magnetic quantum number" – we'll see why later...

Next step:

1) is there any restriction on ℓ (besides $\ell \geq 0$)?

2) is there a connection between ℓ and m?

So far we have been dealing with wavefunctions $\Psi(r, \theta, \varphi) = \underbrace{R_{nl}(r)}_{\text{as we show later}} \underbrace{Y_l^m(\theta, \varphi)}_{\text{spherical harmonics}}$,

spherical harmonics $\Leftarrow$ solutions of

$$\vec{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi)$$

and

$$L_z Y_l^m(\theta, \varphi) = \hbar m \, Y_l^m(\theta, \varphi)$$

$$\underline{\Psi(r, \theta, \varphi)} = \langle \vec{r} \, | \, n, l, m \rangle$$

$\uparrow$ projection of a state vector $|n, l, m\rangle$ on the coordinate space

Since the angular part of Ψ (for spherically symmetric potentials) is the same for all problems with spherical symmetry $\Rightarrow$ isolate $\underbrace{\langle \vec{n} | l, m \rangle}_{= Y_l^m(\theta, \varphi)}$, where $|\vec{n}\rangle$ is a <u>direction eigenket</u>.

So, eqs. (2.4) and (2.5) can be presented as

$$\vec{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle$$

$$L_z |l, m\rangle = \hbar m |l, m\rangle$$

Properties:

- orthogonality: $\langle l', m' | l, m \rangle = \delta_{ll'}\delta_{mm'}$

<u>or</u>

$$\int Y_l^{m*} Y_{l'}^{m'} d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \, Y_l^{m*}(\theta,\varphi).$$

$d\Omega$ ↑ solid angle

- $Y_{l'}^{m'}(\theta,\varphi) = \delta_{ll'}\delta_{mm'}$

- closure $\Rightarrow \sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_l^{m*}(\theta,\varphi) Y_l^{m}(\theta',\varphi') =$

$$= \frac{\delta(\theta-\theta')\delta(\varphi-\varphi')}{\sin\theta} = \delta(\Omega-\Omega')$$

The Y_l^m-set is a complete orthonormal set of square-integrable functions on the unit sphere

- recursion relations

$$L_\pm Y_l^m = \sqrt{l(l+1)-m(m\pm1)}\; Y_l^{m\pm1}$$

where $L_\pm = L_x \pm i L_y$