Quantum Mechanics

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Lesson IX
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- Operators can be often constructed taking corresponding dynamical variable of classical mechanics expressed in terms of coordinates and momenta replacing $\left\{ \begin{array}{ccc} x & \rightarrow & \hat{x} \\ p & \rightarrow & \hat{p} \end{array} \right.$
- Apply this prescription to angular momentum
- In classical mechanics one defines angular momentum by

$$\vec{L} = \vec{r} \times \vec{p}$$

- We get angular momentum operator by replacing:
  - vector $\vec{r}$ ☞ vector operator $\hat{r} = (\hat{x}, \hat{y}, \hat{z})$
  - momentum vector $\vec{p}$ ☞ momentum vector operator $\hat{p} = -i\hbar\nabla$
  - $\nabla = (\partial_x, \partial_y, \partial_z)$ ☞ $\partial_i = \partial/\partial_i$

- Complete fundamental commutation relations of coordinate and momentum operators are:

$$[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$$

  and

$$[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = \cdots = [\hat{z}, \hat{p}_y] = 0$$

- It will be convenient to use following notation
  $\hat{x}_1 = \hat{x},\ \hat{x}_2 = \hat{y},\ \hat{x}_3 = \hat{z} \quad \text{and} \quad \hat{p}_1 = \hat{p}_x,\ \hat{p}_2 = \hat{p}_y,\ \hat{p}_3 = \hat{p}_z$
- Summary of fundamental commutation relations

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$$

- Kronecker symbol:

$$\delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases}$$

Commutation relations for components of angular momentum operator

- Convenient to get at first commutation relations with $\hat{x}_i$ and $\hat{p}_i$
- Using fundamental commutation relations
  - $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$ ☞ $[\hat{x}, \hat{L}_x] = 0$
  - $\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$ ☞ $[\hat{x}, \hat{L}_y] = [\hat{x}, \hat{z}\hat{p}_x] - [\hat{x}, \hat{x}\hat{p}_z] = i\hbar\hat{z}$
  - similarly ☞ $[\hat{x}, \hat{L}_z] = -i\hbar\hat{y}$
- We can ummarize the nine commutation relations

$$[\hat{x}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{x}_k$$

and summation over the repeated index k is implied

- Levi-Civita tensor

$$\epsilon_{ijk} = \begin{cases} 1 & \text{if} \quad (ijk) = (1,2,3) \text{ or } (2,3,1) \text{ or} (3,1,2) \\ -1 & \text{if} \quad (ijk) = (1,3,2) \text{ or } (3,2,1) \text{ or } (2,1,3) \\ 0 & \text{if} \quad i = j \text{ or } i = k \text{ or } j = k \end{cases}$$

- Similarly we can show

$$[\hat{p}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{p}_k$$

- Now ☞ it is straightforward to deduce:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$$

- Important conclusion from this result:
  components of $\hat{L}$ have no common eigenfunctions
- Must show that angular momentum operators are hermitian
- This is of course plausible (reasonable) since we know that angular momentum is dynamical variable in classical mechanics
- Proof is left as exercise

- Construct operator that commutes with all components of $\hat{L}$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- It follows that ☞ $[\hat{L}_x, \hat{L}^2] = [\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] = [\hat{L}_x, \hat{L}_y^2] + [\hat{L}_x, \hat{L}_z^2]$
- There is simple technique to evaluate commutator like $[\hat{L}_x, \hat{L}_y^2]$
  - write down explicitly known commutator

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z$$

  - multiply on left by $\hat{L}_y$

$$\hat{L}_y\hat{L}_x\hat{L}_y - \hat{L}_y^2\hat{L}_x = i\hbar\hat{L}_y\hat{L}_z$$

  - multiply on right by $\hat{L}_y$

$$\hat{L}_x\hat{L}_y^2 - \hat{L}_y\hat{L}_x\hat{L}_y = i\hbar\hat{L}_z\hat{L}_y$$

  - Add these commutation relations to get

$$\hat{L}_x\hat{L}_y^2 - \hat{L}_y^2\hat{L}_x = i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)$$

- Similarly ☞ $\hat{L}_x\hat{L}_z^2 - \hat{L}_z^2\hat{L}_x = -i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)$
- All in all ☞ $[\hat{L}_x, \hat{L}^2] = 0$ and likewise $[\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0$

Summary of angular momentum operator

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = -i\hbar\, \hat{\vec{r}} \times \hat{\vec{\nabla}} \tag{1}$$

in cartesian coordinates

$$\begin{aligned} \hat{L}_x &= \hat{y}\hat{p}_z - \hat{p}_y\hat{z} = -i\hbar\left(y\frac{\partial}{\partial z} - \frac{\partial}{\partial y}z\right) \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{p}_z\hat{x} = -i\hbar\left(z\frac{\partial}{\partial x} - \frac{\partial}{\partial z}x\right) \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{p}_x\hat{y} = -i\hbar\left(x\frac{\partial}{\partial y} - \frac{\partial}{\partial x}y\right) \end{aligned} \tag{2}$$

commutation relations

$$[\hat{L}_i, \hat{L}_j] = i\hbar\, \varepsilon_{ijk}\, \hat{L}_k \quad \text{and} \quad [\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \tag{3}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- Prescription to obtain 3D Schrödinger equation for free particle:
  - substitute into classical energy momentum relation

$$E = \frac{|\vec{p}\,|^2}{2m} \tag{4}$$

  - differential operators

$$E \to i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad \vec{p} \to -i\hbar\vec{\nabla} \tag{5}$$

  - resulting operator equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi = i\hbar\frac{\partial}{\partial t}\psi \tag{6}$$

    acts on complex wave function $\psi(\vec{x}, t)$

- Interpret $\rho = |\psi|^2$ as ☞ probability density
  $|\psi|^2 d^3x$ gives probability of finding particle in volume element d^3x

Continuity equation

- We are often concerned with moving particles
  e.g. collision of particles
- Must calculate density flux of particle beam $\vec{j}$
- From conservation of probability
  rate of decrease of number of particles in a given volume
  is equal to total flux of particles out of that volume

$$-\frac{\partial}{\partial t}\int_V \rho \, dV = \int_S \vec{j}\cdot\hat{n}\, dS = \int_V \vec{\nabla}\cdot\vec{j}\, dV \tag{7}$$

(last equality is Gauss' theorem)

- Probability and flux densities are related by continuity equation

$$\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot\vec{j} = 0 \tag{8}$$

Flux

To determine flux…

- First form $\partial\rho/\partial t$ by substracting wave equation multiplied by $-i\psi^*$ from the complex conjugate equation multiplied by $-i\psi$

$$\frac{\partial\rho}{\partial t} - \frac{\hbar}{2m}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*) = 0 \tag{9}$$

- Comparing this with continuity equation ☞ probability flux density

$$\vec{j} = -\frac{i\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*) \tag{10}$$

- Example ☞ free particle of energy E and momentum $\vec{p}$

$$\psi = Ne^{i\vec{p}\cdot\vec{x}-iEt} \tag{11}$$

has ☞ $\rho = |N|^2$ and $\vec{j} = |N^2|\,\vec{p}/m$

Time-independent Schrödinger equation for central potential

- Potential depends only on distance from origin

$$V(\vec{r}) = V(|\vec{r}\,|) = V(r) \tag{12}$$

hamiltonian is spherically symmetric

- Instead of using cartesian coordinates $\vec{x} = \{x, y, z\}$ use spherical coordinates $\vec{x} = \{r, \vartheta, \varphi\}$ defined by

$$\left\{ \begin{array}{l} x = r\sin\vartheta\cos\varphi \\ y = r\sin\vartheta\sin\varphi \\ z = r\cos\vartheta \end{array} \right\} \Leftrightarrow \left\{ \begin{array}{l} r = \sqrt{x^2+y^2+z^2} \\ \vartheta = \arctan\left(z/\sqrt{x^2+y^2}\right) \\ \varphi = \arctan(y/x) \end{array} \right\} \tag{13}$$

- Express the Laplacian ∇^2 in spherical coordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \tag{14}$$

To look for solutions...

- Use separation of variable methods ☞ $\psi(r,\vartheta,\varphi) = R(r)Y(\vartheta,\varphi)$

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{R}{r^2\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right]+V(r)RY = ERY$$

- Divide by RY/r^2 and rearrange terms

$$-\frac{\hbar^2}{2m}\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right]+r^2(V-E) = \frac{\hbar^2}{2mY}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right]$$

- Each side must be independently equal to a constant ☞ $\varkappa = -\frac{\hbar^2}{2m}l(l+1)$
- Obtain two equations

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V-E) = l(l+1) \qquad (15)$$

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2} = -l(l+1)Y \qquad (16)$$

- What is the meaning of operator in angular equation?

- Choose polar axis along cartesian z direction
- After some tedious calculation ☞ angular momentum components

$$\begin{aligned} \hat{L}_x &= i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\varphi\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ \hat{L}_y &= -i\hbar\left(\cos\varphi\frac{\partial}{\partial\vartheta} - \cot\vartheta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ \hat{L}_z &= -i\hbar\frac{\partial}{\partial\varphi} \end{aligned} \tag{17}$$

- Form of $\hat{L}^2$ should be familiar

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{18}$$

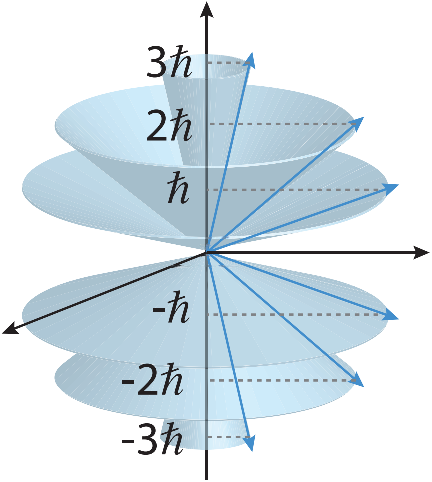
- Eigenvalue equations for $\hat{L}^2$ and $\hat{L}_z$ operators:

$$\hat{L}^2 Y(\vartheta,\varphi) = \hbar^2 l(l+1) Y(\vartheta,\varphi) \quad \text{and} \quad \hat{L}_z Y(\vartheta,\varphi) = \hbar m Y(\vartheta,\varphi)$$

We can always know:

length of angular momentum plus one of its components

E.g. ☞ choosing the z-component



Solution of angular equation

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y_l^m(\vartheta,\varphi)}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y_l^m(\vartheta,\varphi)}{\partial\varphi^2}=-l(l+1)Y_l^m(\vartheta,\varphi)$$

- Use separation of variables ☞ $Y(\vartheta,\varphi)=\Theta(\vartheta)\Phi(\varphi)$
- By multiplying both sides of the equation by $\sin^2\vartheta/Y(\vartheta,\varphi)$

$$\frac{1}{\Theta(\vartheta)}\left[\sin\vartheta\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)\right]+l(l+1)\sin^2\vartheta=-\frac{1}{\Phi(\varphi)}\frac{d^2\Phi}{d\varphi^2} \qquad (19)$$

- 2 equations in different variables ☞ introduce constant m^2:

$$\frac{d^2\Phi}{d\varphi^2}=-m^2\Phi(\varphi) \qquad (20)$$

$$\sin\vartheta\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)=[m^2-l(l+1)\sin^2\vartheta]\Theta(\vartheta) \qquad (21)$$

Solution of angular equation

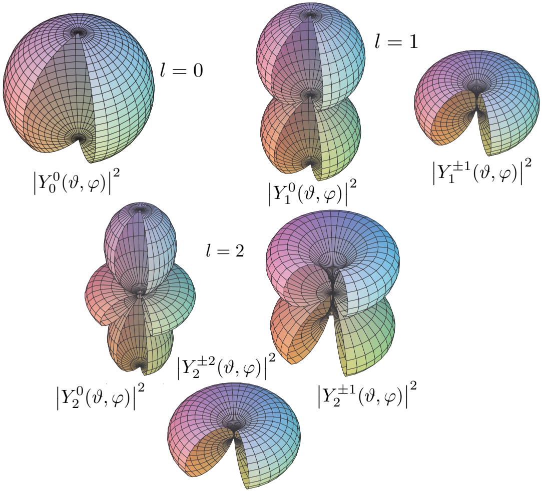
- First equation is easily solved to give ☞ $\Phi(\varphi) = e^{im\varphi}$
- Imposing periodicity $\Phi(\varphi + 2\pi) = \Phi(\varphi)$ ☞ $m = 0, \pm 1, \pm 2, \cdots$
- Solutions to the second equation ☞ $\Theta(\vartheta) = AP_l^m(\cos\vartheta)$
- P_l^m ☞ associated Legendre polynomials
- Normalized angular eigenfunctions

$$Y_l^m(\vartheta, \varphi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}\, P_l^m(\cos\vartheta) e^{im\varphi} \tag{22}$$

- Spherical harmonics are orthogonal:

$$\int_0^{\pi}\int_0^{2\pi} Y_l^{m*}(\vartheta, \varphi)\, Y_{l'}^{m'} \sin\vartheta d\vartheta d\varphi = \delta_{ll'}\delta_{mm'} \,, \tag{23}$$

m / l	0	1	2	3
0	$P_0^0 = 1$			
1	$P_1^0 = \cos\vartheta$	$P_1^1 \sin\vartheta$		
2	$P_2^0 = (3\cos^2\vartheta - 1)/2$	$P_2^1 = 3\cos\vartheta\sin\vartheta$	$P_2^2 = 3\sin^2\vartheta$	
3	$P_3^0(5\cos^3\vartheta - 3\cos\vartheta)/2$	$P_3^1 = 3(5\cos^2\vartheta - 1)/2\,\sin\vartheta$	$P_3^2 = 15\cos\vartheta\sin^2\vartheta$	$P_3^3 = 15\sin^3\vartheta$



Solution of radial equation

$$\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) - \frac{2mr^2}{\hbar^2}(V-E) = l(l+1)R(r) \tag{24}$$

- to simplify solution ☞ $u(r) = rR(r)$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar}{2m}\frac{l(l+1)}{r^2}\right]u(r) = Eu(r) \tag{25}$$

- define an effective potential

$$V'(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} \tag{26}$$

(25) is very similar to the one-dimensional Schrödinger equation

- Wave function ☞ need 3 quantum numbers (n, l, m)

$$\psi_{n,l,m}(r,\vartheta,\varphi) = R_{n,l}(r)Y_l^m(\vartheta,\varphi) \tag{27}$$

Internal states of the hydrogen atom

We start with the equation for

the relative motion of electron and proton

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}}+V(\mathbf{r})\right]U(\mathbf{r})=E_H U(\mathbf{r})$$

We use the spherical symmetry of this equation

and change to spherical polar coordinates

From now on, we drop the subscript $\mathbf{r}$ in the operator ∇^2

Internal states of the hydrogen atom

In spherical polar coordinates, we have

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

where the term in square brackets

is the operator $\nabla^2_{\theta,\phi} \equiv -\hat{L}^2/\hbar^2$ we introduced

in discussing angular momentum

Knowing the solutions to the angular momentum problem

we propose the separation

$$U(\mathbf{r}) = R(r)Y(\theta,\phi)$$

Internal states of the hydrogen atom

The mathematics is simpler using the form

$$U(\mathbf{r}) = \frac{1}{r}\chi(r)Y(\theta,\phi)$$

where, obviously

$$\chi(r) = rR(r)$$

This choice gives a convenient simplification of the radial derivatives

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\frac{\chi(r)}{r} = \frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}$$

Internal states of the hydrogen atom

Hence the Schrödinger equation becomes

$$-\frac{\hbar^2}{2\mu}Y(\theta,\phi)\frac{1}{r}\frac{\partial^2\chi(r)}{\partial r^2}+\frac{\chi(r)}{r^3}\frac{1}{2\mu}\hat{L}^2Y(\theta,\phi)+Y(\theta,\phi)V(r)\frac{\chi(r)}{r}$$

$$=E_H\frac{1}{r}\chi(r)Y(\theta,\phi)$$

Dividing by $-\hbar^2\chi(r)Y(\theta,\phi)/2\mu r^3$

and rearranging, we have

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)$$

Internal states of the hydrogen atom

In

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=\frac{1}{\hbar^2}\frac{1}{Y(\theta,\phi)}\hat{L}^2Y(\theta,\phi)=l(l+1)$$

- in the usual manner for a separation argument
  - the left hand side depends only on $\mathbf{r}$
  - and the right hand side depends only on θ and ϕ
    - so both sides must be equal to a constant

We already know what that constant is explicitly

- i.e., we already know that $\hat{L}^2Y_{lm}(\theta,\phi)=\hbar^2 l(l+1)Y_{lm}(\theta,\phi)$
  - so that the constant is $l(l+1)$

Internal states of the hydrogen atom

Hence, in addition to the $\hat{L}^2$ eigenequation

which we had already solved

from our separation above, we also have

$$\frac{r^2}{\chi(r)}\frac{\partial^2\chi(r)}{\partial r^2}+r^2\frac{2\mu}{\hbar^2}\left(E_H-V(r)\right)=l(l+1)$$

or, rearranging

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

which we can write as an ordinary differential equation

All the functions and derivatives are in one variable, r

Internal states of the hydrogen atom

Hence we have mathematical equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

for this radial part of the wavefunction

which looks like a Schrödinger wave equation

with an additional effective potential energy term of the form

$$\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$$

Central potentials

Note incidentally that

though here we have a specific form for $V(r)$

in our assumed Coulomb potential

$$V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right) = -\frac{e^2}{4\pi\varepsilon_o \left|\mathbf{r}_e - \mathbf{r}_p\right|}$$

the above separation works for any potential

that is only a function of r

sometimes known as a central potential

Central potentials

The precise form of the equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2}+\left(V(r)+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r)=E_H\chi(r)$$

will be different for different central potentials

- but the separation remains
  - We can still separate out the $\hat{L}^2$ angular momentum eigenequation
    - with the spherical harmonic solutions

Radial equation solutions

Using a separation of the hydrogen atom wavefunction solutions into radial and angular parts

$$U(\mathbf{r}) = R(r)Y(\theta,\phi)$$

and rewriting the radial part using

$$\chi(r) = rR(r)$$

we obtained the radial equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(r)}{dr^2} - \left(\frac{e^2}{4\pi\varepsilon_o r} - \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)\chi(r) = E_H\chi(r)$$

where we know l is 0 or any positive integer

Radial equation solutions

We now choose to write our energies in the form

$$E_H = -\frac{Ry}{n^2}$$

where n for now is just an arbitrary real number

We define a new distance unit

$$s = \alpha r$$

where the parameter α is

$$\alpha = \frac{2}{na_o} = 2\sqrt{-\frac{2\mu}{\hbar^2}E_H}$$

Radial equation solutions

We therefore obtain an equation

$$\frac{d^2\chi}{ds^2}-\left[\frac{l(l+1)}{s^2}-\frac{n}{s}+\frac{1}{4}\right]\chi=0$$

Then we write

$$\chi(s)=s^{l+1}L(s)\exp(-s/2)$$

so we get

$$s\frac{d^2L}{ds^2}-\left[s-2(l+1)\right]\frac{dL}{ds}+\left[n-(l+1)\right]L=0$$

Radial equation solutions

The technique to solve this equation

$$s\frac{d^2L}{ds^2}-\left[s-2\left(l+1\right)\right]\frac{dL}{ds}+\left[n-\left(l+1\right)\right]L=0$$

is to propose a power series in s

- The power series will go on forever
  - and hence the function will grow arbitrarily
    - unless it "terminates" at some finite power
      - which requires that
        - n is an integer, and
        - $n \geq l+1$

Radial equation solutions

The normalizable solutions of

$$s\frac{d^2L}{ds^2}-\left[s-2\left(l+1\right)\right]\frac{dL}{ds}+\left[n-\left(l+1\right)\right]L=0$$

then become the finite power series

known as the associated Laguerre polynomials

$$L_{n-l-1}^{2l+1}\left(s\right)=\sum_{q=0}^{n-l-1}\left(-1\right)^q\frac{\left(n+l\right)!}{\left(n-l-q-1\right)!\left(q+2l+1\right)!}s^q$$

or equivalently

$$L_p^j\left(s\right)=\sum_{q=0}^{p}\left(-1\right)^q\frac{\left(p+j\right)!}{\left(p-q\right)!\left(j+q\right)!q!}s^q$$

Radial equation solutions

Now we can work back to construct the whole solution

In our definition $\chi(s) = s^{l+1} L(s) \exp(-s/2)$

we now insert the associated Laguerre polynomials

$$\chi(s) = s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2)$$

where $s = (2/na_o)r$

Since our radial solution was $\chi(r) = rR(r)$

we now have

$$R(r = na_o s/2) \propto \frac{1}{r} s^{l+1} L_{n-l-1}^{2l+1}(s) \exp(-s/2)$$
$$\propto s^{l} L_{n-l-1}^{2l+1}(s) \exp(-s/2)$$

Radial equation solutions - normalization

We formally introduce a normalization coefficient A so

$$R\left(r = na_o s/2\right) = \frac{1}{A} s^l L_{n-l-1}^{2l+1}\left(s\right)\exp\left(-s/2\right)$$

The full normalization integral of the wavefunction

$$U\left(\mathbf{r}\right) = R\left(r\right)Y\left(\theta,\phi\right)$$

would be

$$1 = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|R\left(r\right)Y\left(\theta,\phi\right)\right|^2 r^2 \sin\theta d\theta d\phi dr$$

but we have already normalized the spherical harmonics

so we are left with the radial normalization

Radial equation solutions - normalization

Radial normalization would be $1 = \int_0^\infty R^2(r) r^2 dr$

We could show $\int_0^\infty s^{2l} \left[L_{n-l-1}^{2l+1}(s) \right]^2 \exp(-s) s^2 ds = \frac{2n(n+l)!}{(n-l-1)!}$

so the normalized radial wavefunction becomes

$$R(r) = \left[\frac{(n-l-1)!}{2n(n+l)!} \left(\frac{2}{na_o} \right)^3 \right]^{1/2} \left(\frac{2r}{na_o} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na_o} \right) \exp\left(-\frac{r}{na_o} \right)$$

Hydrogen atom radial wavefunctions

We write the wavefunctions

using the Bohr radius a_o as the unit of radial distance

so we have a dimensionless radial distance

$$\rho = r / a_o$$

and we introduce the subscripts

n - the principal quantum number, and

l - the angular momentum quantum number

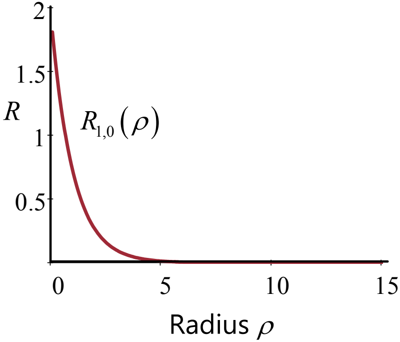
to index the various functions $R_{n,l}$

Radial wavefunctions - $n = 1$

Principal quantum number
$n = 1$

Angular momentum quantum number
$l = 0$

$$R_{1,0}(\rho) = 2\exp(-\rho)$$



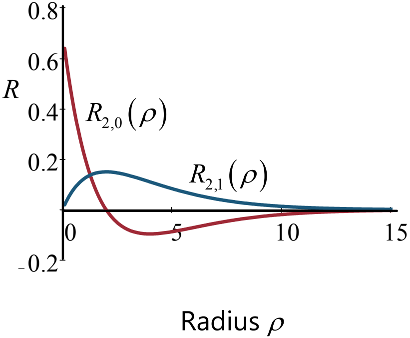
Radial wavefunctions - $n = 2$

$l = 0$

$$R_{2,0}(\rho) = \frac{\sqrt{2}}{4}(2-\rho)\exp(-\rho/2)$$

$l = 1$

$$R_{2,1}(\rho) = \frac{\sqrt{6}}{12}\rho\exp(-\rho/2)$$



Radial wavefunctions - $n = 3$

$l = 0$

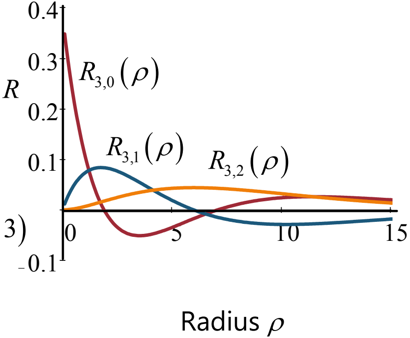
$$R_{3,0}(\rho) = \frac{2\sqrt{3}}{27}\left(3 - 2\rho + \frac{2}{9}\rho^2\right)\exp(-\rho/3)$$

$l = 1$

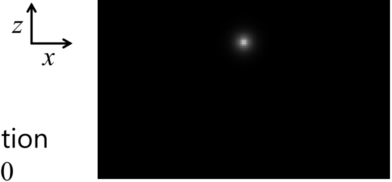
$$R_{3,1}(\rho) = \frac{\sqrt{6}}{81}\rho\left(4 - \frac{2}{3}\rho\right)\exp(-\rho/3)$$

$l = 2$

$$R_{3,2}(\rho) = \frac{2\sqrt{30}}{1215}\rho^2\exp(-\rho/3)$$



Hydrogen orbital probability density

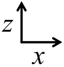


x - z
cross-section
at $y = 0$

1s

$n = 1$
$l = 0$
$m = 0$

Hydrogen orbital probability density

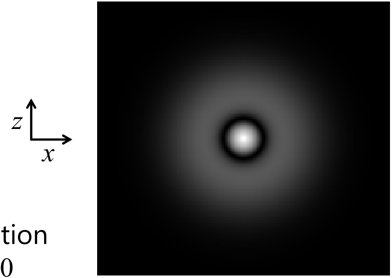


x - z
cross-section
at $y = 0$

2s

$n = 2$
$l = 0$
$m = 0$

Hydrogen orbital probability density



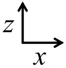
x - z
cross-section
at $y = 0$

logarithmic intensity scale

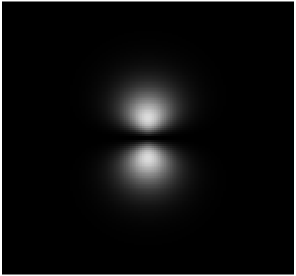
2s

$n = 2$
$l = 0$
$m = 0$

Hydrogen orbital probability density



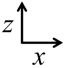
x - z
cross-section
at $y = 0$



2p

$n = 2$
$l = 1$
$m = 0$

Hydrogen orbital probability density

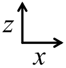


x - z
cross-section
at $y = 0$

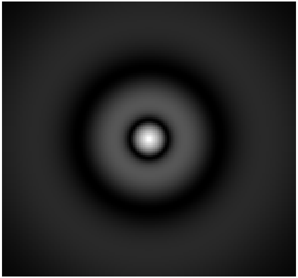
3s

$n = 3$
$l = 0$
$m = 0$

Hydrogen orbital probability density



x - z
cross-section
at $y = 0$

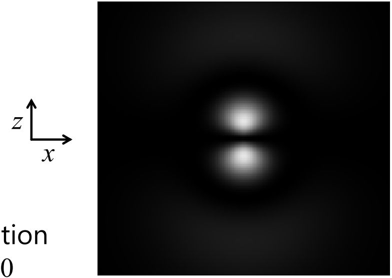


logarithmic intensity scale

3s

$n = 3$
$l = 0$
$m = 0$

Hydrogen orbital probability density

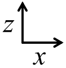


x - z
cross-section
at $y = 0$

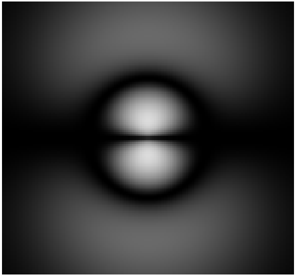
3p

$n = 3$
$l = 1$
$m = 0$

Hydrogen orbital probability density



x - z
cross-section
at $y = 0$

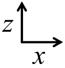


logarithmic intensity scale

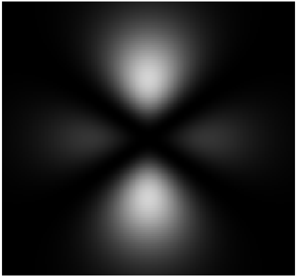
3p

$n = 3$
$l = 1$
$m = 0$

Hydrogen orbital probability density



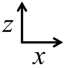
x - z
cross-section
at $y = 0$



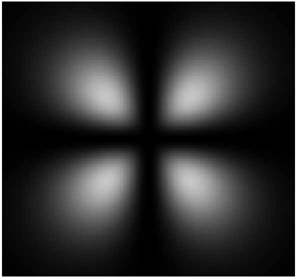
3d

$n = 3$
$l = 2$
$m = 0$

Hydrogen orbital probability density



x - z
cross-section
at $y = 0$



3d

$n = 3$
$l = 2$
$m = 1$

Behavior of the complete hydrogen solutions

(i) The overall "size" of the wavefunctions becomes larger with larger n

(ii) The number of zeros in the wavefunction is $n-1$

The radial wavefunctions have $n-l-1$ zeros

and the spherical harmonics have l nodal "circles"

The radial wavefunctions appear to have an additional zero at $r = 0$ for all $l \geq 1$, but this is already counted

because the spherical harmonics have at least one nodal "circle" for all $l \geq 1$

which already gives a zero as $r \to 0$ in these cases

Behavior of the complete hydrogen solutions

In summary of the quantum numbers

- for the so-called principal quantum number

$$n = 1, 2, 3, \dots$$

and $$l \leq n - 1$$

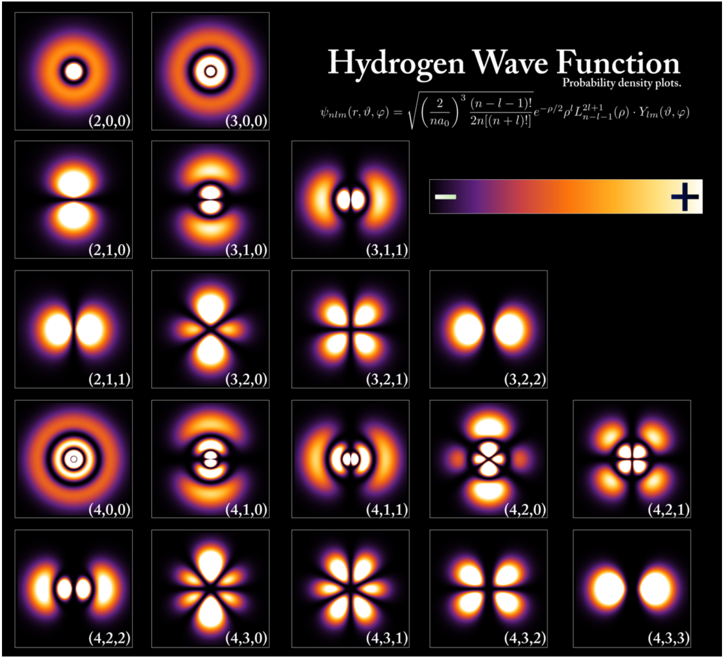
We already deduced that l is a positive or zero integer

We also now know the eigenenergies

- Given the possible values for n

$$E_H = -\frac{Ry}{n^2}$$

Note the energy does not depend on l (or m)


Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}}\, e^{-\rho/2}\rho^l L^{2l+1}_{n-l-1}(\rho)\cdot Y_{lm}(\vartheta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,0,0)
(4,1,0)
(4,1,1)
(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

TAKE HOME MESSAGE

- Angular momentum operators
  commute with Hamiltonian of particle in central field
- E.g. ☞ Coulomb field
- This implies that $\hat{L}^2$ and one of $\hat{L}$ components
  can be chosen to have common eigenfunctions with Hamiltonian

In this appendix, we will show how to derive the expressions of the gradient $\vec{\nabla}$, the Laplacian ∇^2, and the components of the orbital angular momentum in spherical coordinates.

B.1 Derivation of Some General Relations

The Cartesian coordinates (x, y, z) of a vector $\vec{r}$ are related to its spherical polar coordinates (r, θ, φ) by

$$x = r\sin\theta\cos\varphi, \qquad y = r\sin\theta\sin\varphi, \qquad z = r\cos\theta \tag{B.1}$$

The orthonormal Cartesian basis $(\hat{x}, \hat{y}, \hat{z})$ is related to its spherical counterpart $(\hat{r}, \hat{\theta}, \hat{\varphi})$ by

$$\begin{aligned} \hat{x} &= \hat{r}\sin\theta\cos\varphi + \hat{\theta}\cos\theta\cos\varphi - \hat{\varphi}\sin\varphi && \text{(B.2)}\\ \hat{y} &= \hat{r}\sin\theta\sin\varphi + \hat{\theta}\cos\theta\sin\varphi + \hat{\varphi}\cos\varphi, && \text{(B.3)}\\ \hat{z} &= \hat{r}\cos\theta - \hat{\theta}\sin\theta. && \text{(B.4)} \end{aligned}$$

Differentiating (B.1), we obtain

$$\begin{aligned} dx &= \sin\theta\cos\varphi\, dr + r\cos\theta\cos\varphi\, d\theta - r\sin\theta\sin\varphi\, d\varphi && \text{(B.5)}\\ dy &= \sin\theta\sin\varphi\, dr + r\cos\theta\sin\varphi\, d\theta + r\cos\varphi\, d\varphi, && \text{(B.6)}\\ dz &= \cos\theta\, dr - r\sin\theta\, d\theta. && \text{(B.7)} \end{aligned}$$

Solving these equations for dr, $d\theta$ and $d\varphi$, we obtain

$$\begin{aligned} dr &= \sin\theta\cos\varphi\, dx + \sin\theta\sin\varphi\, dy + \cos\theta\, dz && \text{(B.8)}\\ d\theta &= \frac{1}{r}\cos\theta\cos\varphi\, dx + \frac{1}{r}\cos\theta\sin\varphi\, dy - \frac{1}{r}\sin\theta\, dz, && \text{(B.9)}\\ d\varphi &= -\frac{\sin\varphi}{r\sin\theta}\, dx + \frac{\cos\varphi}{r\sin\theta}\, dy. && \text{(B.10)} \end{aligned}$$

We can verify that (B.5) to (B.10) lead to

$$\frac{\partial r}{\partial x} = \sin\theta\cos\varphi, \qquad \frac{\partial\theta}{\partial x} = \frac{1}{r}\cos\varphi\cos\theta, \qquad \frac{\partial\varphi}{\partial x} = -\frac{\sin\varphi}{r\sin\theta}, \tag{B.11}$$

$$\frac{\partial r}{\partial y} = \sin\theta\sin\varphi, \qquad \frac{\partial\theta}{\partial y} = \frac{1}{r}\sin\varphi\cos\theta, \qquad \frac{\partial\varphi}{\partial y} = \frac{\cos\varphi}{r\sin\theta}, \tag{B.12}$$

$$\frac{\partial r}{\partial z} = \cos\theta, \qquad \frac{\partial\theta}{\partial z} = -\frac{1}{r}\sin\theta, \qquad \frac{\partial\varphi}{\partial z} = 0, \tag{B.13}$$

which, in turn, yield

$$\begin{aligned}\frac{\partial}{\partial x} &= \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial\varphi}\frac{\partial\varphi}{\partial x}\\ &= \sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\theta},\end{aligned} \tag{B.14}$$

$$\begin{aligned}\frac{\partial}{\partial y} &= \frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial}{\partial\varphi}\frac{\partial\varphi}{\partial y}\\ &= \sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi},\end{aligned} \tag{B.15}$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial z} + \frac{\partial}{\partial\varphi}\frac{\partial\varphi}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{\partial r}\frac{\partial}{\partial\theta}. \tag{B.16}$$

B.2 Gradient and Laplacian in Spherical Coordinates

We can show that a combination of (B.14) to (B.16) allows us to express the operator $\vec{\nabla}$ in spherical coordinates:

$$\vec{\nabla} = \hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\varphi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}, \tag{B.17}$$

and also the Laplacian operator ∇^2

$$\nabla^2 = \vec{\nabla}.\vec{\nabla} = \left(\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\hat{\varphi}}{r\sin\varphi}\frac{\partial}{\partial\varphi}\right)\cdot\left(\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\hat{\varphi}}{r\sin\theta}\frac{\partial}{\partial\varphi}\right). \tag{B.18}$$

Now, using the relations

$$\frac{\partial\hat{r}}{\partial r} = 0, \qquad \frac{\partial\hat{\theta}}{\partial r} = 0, \qquad \frac{\partial\hat{\varphi}}{\partial r} = 0, \tag{B.19}$$

$$\frac{\partial\hat{r}}{\partial\theta} = \hat{\theta}, \qquad \frac{\partial\hat{\theta}}{\partial\theta} = -\hat{r}, \qquad \frac{\partial\hat{\varphi}}{\partial\theta} = 0, \tag{B.20}$$

$$\frac{\partial\hat{r}}{\partial\varphi} = \hat{\varphi}\sin\theta, \qquad \frac{\partial\hat{\theta}}{\partial\varphi} = \hat{\varphi}\cos\theta, \qquad \frac{\partial\hat{\varphi}}{\partial\varphi} = -\hat{r}\sin\theta - \hat{\theta}\cos\theta, \tag{B.21}$$

we can show that the Laplacian operator reduces to

$$\nabla^2 = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{B.22}$$

B.3 Angular Momentum in Spherical Coordinates

The orbital angular momentum operator $\vec{L}$ can be expressed in spherical coordinates as:

$$\hat{\vec{L}} = \hat{\vec{R}} \times \hat{\vec{P}} = (-i\hbar r)\hat{r} \times \vec{\nabla} = (-i\hbar r)\hat{r} \times \left[\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial \theta} + \frac{\hat{\varphi}}{r\sin\theta}\frac{\partial}{\partial\varphi}\right], \tag{B.23}$$

or as

$$\hat{\vec{L}} = -i\hbar\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right). \tag{B.24}$$

Using (B.24) along with (B.2) to (B.4), we express the components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ within the context of the spherical coordinates. For instance, the expression for $\hat{L}_x$ can be written as follows

$$\begin{aligned}\hat{L}_x &= \hat{x}.\vec{L} = -i\hbar\left(\hat{r}\sin\theta\cos\varphi + \hat{\theta}\cos\theta\cos\varphi - \hat{\varphi}\sin\varphi\right)\cdot\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right)\\ &= i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right).\end{aligned} \tag{B.25}$$

Similarly, we can easily obtain

$$\hat{L}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \tag{B.26}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}. \tag{B.27}$$

From the expressions (B.25) and (B.26) for $\hat{L}_x$ and $\hat{L}_y$, we infer that

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y = \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right), \tag{B.28}$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y = \hbar e^{-i\varphi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\varphi}\right). \tag{B.29}$$

The expression for $\vec{L}^2$ is

$$\vec{L}^2 = -\hbar^2 r^2(\hat{r}\times\vec{\nabla})\cdot(\hat{r}\times\vec{\nabla}) = -\hbar^2 r^2\left[\nabla^2 - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]; \tag{B.30}$$

it can be easily written in terms of the spherical coordinates as

$$\vec{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]; \tag{B.31}$$

this expression was derived by substituting (B.22) into (B.30).

Note that, using the expression (B.30) for $\vec{L}^{\,2}$, we can rewrite ∇^2 as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\vec{L}^{\,2} = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{\hbar^2 r^2}\vec{L}^{\,2}. \tag{B.32}$$