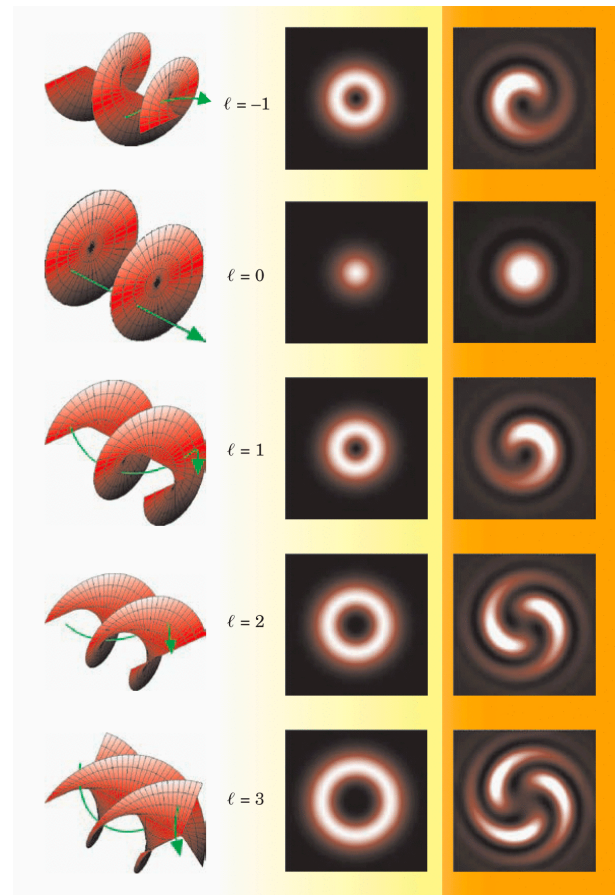
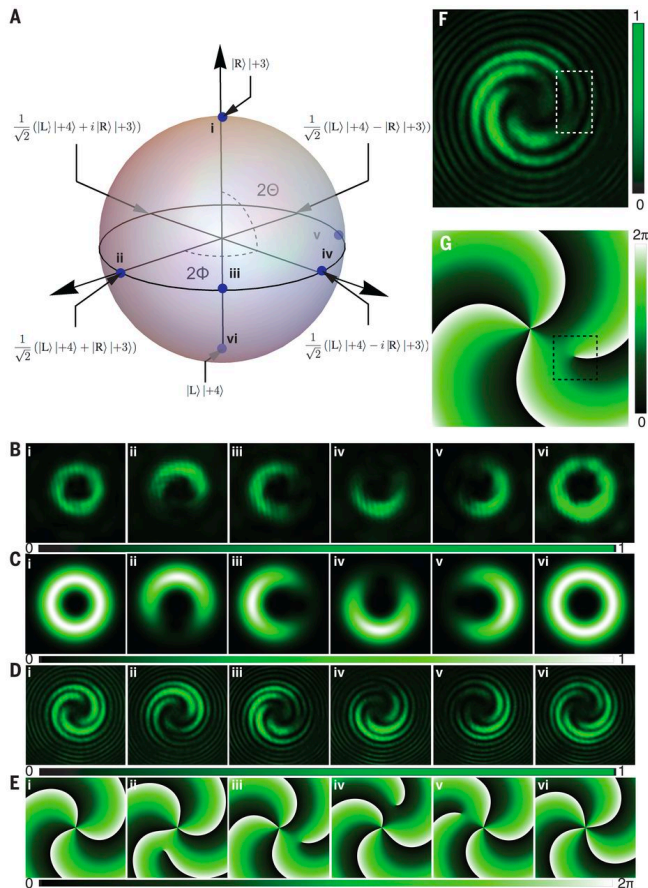




Quantum mechanics

Chapter IV Angular Momentum theory



The quantum mechanical operator for L , is obtained by replacing r and p , with their respective operators,

$$\hat{L} = \hat{r} \times \hat{p}.$$

The components of angular momentum operator can be expressed in Cartesian Coordinates

$$\hat{L}_x = y \hat{p}_z - z \hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right),$$

$$\hat{L}_y = z \hat{p}_x - x \hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right),$$

$$\hat{L}_z = x \hat{p}_y - y \hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right).$$

The operator corresponding to the square of the angular momentum is a scalar operator given by

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

The algebra of the angular momentum operators is given by their commutation relations. For instance,

$$[\hat{L}_x, \hat{L}_y] = [y \hat{p}_z - z \hat{p}_y, z \hat{p}_x - x \hat{p}_z] = [y \hat{p}_z, z \hat{p}_x] - [z \hat{p}_y, z \hat{p}_x] - [y \hat{p}_z, x \hat{p}_z] + [z \hat{p}_y, x \hat{p}_z].$$

Since

$$\begin{aligned} [y \hat{p}_z, z \hat{p}_x] &= y [\hat{p}_z, z \hat{p}_x] + [y, z \hat{p}_x] \hat{p}_z = yz [\hat{p}_z, \hat{p}_x] + y [\hat{p}_z, z] \hat{p}_x + z [y, \hat{p}_x] \hat{p}_z \\ &+ [y, z] \hat{p}_x \hat{p}_z = -i\hbar y \hat{p}_x, \end{aligned}$$

$$\begin{aligned} [z \hat{p}_y, z \hat{p}_x] &= z [\hat{p}_y, z \hat{p}_x] + [z, z \hat{p}_x] \hat{p}_y = z^2 [\hat{p}_y, \hat{p}_x] + z [\hat{p}_y, z] \hat{p}_x + z [z, \hat{p}_x] \hat{p}_y \\ &+ [z, z] \hat{p}_x \hat{p}_y = 0, \end{aligned}$$

$$\begin{aligned} [y \hat{p}_z, x \hat{p}_z] &= y [\hat{p}_z, x \hat{p}_z] + [y, x \hat{p}_z] \hat{p}_z = yx [\hat{p}_z, \hat{p}_z] + y [\hat{p}_z, x] \hat{p}_z + x [y, \hat{p}_z] \hat{p}_z \\ &+ [y, x] \hat{p}_z^2 = 0, \end{aligned}$$

$$\begin{aligned} [z \hat{p}_y, x \hat{p}_z] &= z [\hat{p}_y, x \hat{p}_z] + [z, x \hat{p}_z] \hat{p}_y = zx [\hat{p}_y, \hat{p}_z] + z [\hat{p}_y, x] \hat{p}_z + x [z, \hat{p}_z] \hat{p}_y \\ &+ [z, x] \hat{p}_z \hat{p}_y = i\hbar x \hat{p}_y. \end{aligned}$$

Therefore,

$$[\hat{L}_x, \hat{L}_y] = i\hbar (x \hat{p}_y - y \hat{p}_x) = i\hbar \hat{L}_z.$$

The other two commutators are calculated in a similar manner. The net result is

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

These commutation relations can be combined together into a single vector equation

$$i\hbar \hat{\mathbf{L}} = \hat{\mathbf{L}} \times \hat{\mathbf{L}}.$$

Equivalently, they can also be written as

$$[\hat{L}_j, \hat{L}_k] = i\hbar \varepsilon_{jkl} \hat{L}_l,$$

where summation over the repeated index l from 1 to 3 is understood. Here, the symbol ε_{ijk} is called the **Levi-Civita tensor density** and it is defined as

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{if } (ijk) \text{ is an even permutation of } (123) \\ -1 & \text{if } (ijk) \text{ is an odd permutation of } (123) \\ 0 & \text{otherwise.} \end{cases}$$

The uncertainty relations of orbital angular momentum

$$\Delta L_j \Delta L_k \geq \frac{1}{2} \sqrt{|\langle [\hat{L}_j, \hat{L}_k] \rangle|^2} = \frac{\hbar}{2} |\langle L_\ell \rangle|,$$

It then follows that no two components of the angular momentum can be measured simultaneously accurately.

We shall determine the possible eigenvalues of L^2 and L_z by algebraic means. In other words, we shall determine their eigenvalues without solving the differential equations representing the corresponding eigenvalue problems for these operators.

Since L^2 and L_z commute, they have a common set of eigenfunctions.

$$\hat{L}^2 \psi(\vec{r}) = \hbar^2 \lambda \psi_{\lambda \mu}(\vec{r}),$$

$$\hat{L}_z \psi(\vec{r}) = \hbar \mu \psi_{\lambda \mu}(\vec{r}).$$

λ and μ , respectively, are dimensionless.

Let us introduce the operators:

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y.$$

Using the commutation relations

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

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

Hence,

$$\begin{aligned} [\hat{L}^2, \hat{L}_{\pm}] &= [\hat{L}_x^2, \hat{L}_{\pm}] + [\hat{L}_y^2, \hat{L}_{\pm}] + [\hat{L}_z^2, \hat{L}_{\pm}] = [\hat{L}_x^2, \hat{L}_x \pm i\hat{L}_y] \\ &+ [\hat{L}_y^2, \hat{L}_x \pm i\hat{L}_y] + [\hat{L}_z^2, \hat{L}_x \pm i\hat{L}_y] = \pm i[\hat{L}_x^2, \hat{L}_y] + [\hat{L}_y^2, \hat{L}_x] \\ &+ [\hat{L}_z^2, \hat{L}_x] \pm i[\hat{L}_z^2, \hat{L}_y] = \mp\hbar(\hat{L}_x\hat{L}_z + \hat{L}_z\hat{L}_x) - i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y) \\ &+ i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y) \pm \hbar(\hat{L}_x\hat{L}_z + \hat{L}_z\hat{L}_x) = 0. \end{aligned}$$

We have the following results

$$\hat{L}_z (\hat{L}_+ \psi_{\lambda \mu}) = \hbar \hat{L}_+ \psi_{\lambda \mu} + \hat{L}_+ (\hat{L}_z \psi_{\lambda \mu}) = \hbar (\mu + 1) (\hat{L}_+ \psi_{\lambda \mu}),$$

$$\hat{L}_z (\hat{L}_- \psi_{\lambda \mu}) = -\hbar \hat{L}_- \psi_{\lambda \mu} + \hat{L}_- (\hat{L}_z \psi_{\lambda \mu}) = \hbar (\mu - 1) (\hat{L}_- \psi_{\lambda \mu}),$$

That is, the operator L_+ , by acting on the eigenfunction of L_z with a given eigenvalue, converts it into an eigenfunction of L_z with an eigenvalue raised by one unit of \hbar .

Therefore, the operators L_+ and L_- are called the raising (creation) and the lowering (annihilation) operators, respectively.

Therefore, we conclude that there must exist an **eigenstate**, $\psi_{\lambda \mu_{\max}}$, of L_z with the highest possible eigenvalue, $\hbar \mu_{\max}$, such that

$$\hat{L}^2 \psi_{\lambda \mu_{\max}} = \hbar^2 \lambda \psi_{\lambda \mu_{\max}}, \quad \hat{L}_z \psi_{\lambda \mu_{\max}} = \hbar \mu_{\max} \psi_{\lambda \mu_{\max}} \quad \text{and} \quad \hat{L}_+ \psi_{\lambda \mu_{\max}} = 0.$$

The next question is: How to find μ_{\max} ? To answer this question we notice that

$$\begin{aligned} \hat{L}_{\pm} \hat{L}_{\mp} &= (\hat{L}_x \pm i\hat{L}_y)(\hat{L}_x \mp i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 \mp i(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) \\ &= \hat{L}^2 - \hat{L}_z^2 \mp i(i\hbar \hat{L}_z) = \hat{L}^2 - \hat{L}_z^2 \pm \hbar \hat{L}_z, \end{aligned}$$

and hence

$$\hat{L}^2 = \hat{L}_{\pm} \hat{L}_{\mp} + \hat{L}_z^2 \mp (\hbar \hat{L}_z).$$

Therefore, using the lower sign in above equation, we obtain

$$\begin{aligned}\hat{L}^2 \psi_{\lambda \mu_{\max}} &= \hat{L}_- \hat{L}_+ \psi_{\lambda \mu_{\max}} + \hat{L}_z^2 \psi_{\lambda \mu_{\max}} + (\hbar \hat{L}_z) \psi_{\lambda \mu_{\max}} \\ &= 0 + \hbar^2 \mu_{\max}^2 \psi_{\lambda \mu_{\max}} + \hbar^2 \mu_{\max} \psi_{\lambda \mu_{\max}} = \hbar^2 \mu_{\max} (\mu_{\max} + 1) \psi_{\lambda \mu_{\max}},\end{aligned}$$

and hence

$$\lambda = \hbar^2 \mu_{\max} (\mu_{\max} + 1).$$

An argument similar to the one used in the case of L_+ , there must exist an eigenstate, $\psi_{\lambda \mu_{\min}}$, of L_z with the lowest possible eigenvalue, μ_{\min} , such that

$$\hat{L}^2 \psi_{\lambda \mu_{\min}} = \hbar^2 \lambda \psi_{\lambda \mu_{\min}}, \quad \hat{L}_z \psi_{\lambda \mu_{\min}} = \hbar \mu_{\min} \psi_{\lambda \mu_{\min}} \quad \text{and} \quad \hat{L}_- \psi_{\lambda \mu_{\min}} = 0.$$

Using the upper sign in the commutation relation, we have

$$\begin{aligned}\hat{L}^2 \psi_{\lambda \mu_{\min}} &= \hat{L}_+ \hat{L}_- \psi_{\lambda \mu_{\min}} + \hat{L}_z^2 \psi_{\lambda \mu_{\min}} - (\hbar \hat{L}_z) \psi_{\lambda \mu_{\min}} \\ &= (0 + \hbar^2 \mu_{\min}^2 - \hbar^2 \mu_{\min}) \psi_{\lambda \mu_{\min}} = \hbar^2 \mu_{\min} (\mu_{\min} - 1) \psi_{\lambda \mu_{\min}}.\end{aligned}$$

Therefore,

$$\lambda = \hbar^2 \mu_{\min} (\mu_{\min} - 1).$$

We conclude

$$\mu_{\max} (\mu_{\max} + 1) = \mu_{\min} (\mu_{\min} - 1).$$

We get from this equation that either

$$\mu_{\min} = \mu_{\max} + 1 \text{ or } \mu_{\min} = -\mu_{\max}.$$

The first solution is **unacceptable** since, if so, the eigenvalue of the lowest eigenstate of L_z will be greater than the eigenvalue of the highest eigenstate. Thus,

$$\mu_{\min} = -\mu_{\max}.$$

It is customary to denote μ_{\max} by l and μ by m (or, m_l). The numbers l and m are called the orbital quantum number and the magnetic quantum number, respectively.

The eigenvalues of L^2 and L_z can now be written as

$$\lambda_\ell = \hbar^2 \ell(\ell + 1), \quad \mu_m = \hbar m,$$

where, for a given l , m takes $(2l+1)$ values from $-l$ to l and l must be an integer

The eigenvalue equations for L^2 and L_z , respectively, are

$$\hat{L}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi),$$

$$\hat{L}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi).$$

where $l = 0, 1, 2, 3, \dots$ and $m = -l, -l+1, -l+2, -l+3, \dots, 0, 1, 2, 3, \dots, l-1, l$.

For the given purpose it is convenient to go over to the spherical system of coordinates. Using the chain rule for differentiation and the transformation equations, we obtain

$$\frac{\partial}{\partial \varphi} = \frac{\partial x}{\partial \varphi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \varphi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \varphi} \frac{\partial}{\partial z} \quad \frac{\partial}{\partial \theta} = \cot \theta \left(x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} \right) - \tan \theta z \frac{\partial}{\partial z}.$$

$$= -r \sin \theta \sin \varphi \frac{\partial}{\partial x} + r \sin \theta \cos \varphi \frac{\partial}{\partial y}$$

$$= x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x},$$

The expressions for the x , y and z components of the angular momentum operator in spherical coordinates can be written as

$$\hat{L}_x = i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right),$$

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

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

For the raised operator

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y = \hbar \left[iz \frac{\partial}{\partial y} + z \frac{\partial}{\partial x} - (x + iy) \frac{\partial}{\partial z} \right]$$

Taking into account that

$$z = r \cos \theta$$

$$x \pm iy = r \sin \theta (\cos \varphi \pm i \sin \varphi) = r e^{\pm i\varphi} \sin \theta,$$

we get

$$\begin{aligned}\hat{L}_+ &= \hbar e^{i\varphi} \left(i r e^{-i\varphi} \cos \theta \frac{\partial}{\partial y} + r e^{-i\varphi} \cos \theta \frac{\partial}{\partial x} - r \sin \theta \frac{\partial}{\partial z} \right) \\ &= \hbar e^{i\varphi} \left[i(x - iy) \cot \theta \frac{\partial}{\partial x} + (x - iy) \cot \theta \frac{\partial}{\partial x} - r \sin \theta \frac{\partial}{\partial z} \right] \\ &= \hbar e^{i\varphi} \left[\cot \theta \left(x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} \right) - \tan \theta z \frac{\partial}{\partial z} + i \cot \theta \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right].\end{aligned}$$

Finally

$$\hat{L}_+ = \hbar e^{i\varphi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right).$$

Using now

$$\hat{L}_+ \hat{L}_- = -\hbar^2 e^{i\varphi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \left\{ e^{-i\varphi} \left(\frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \varphi} \right) \right\}$$

and

$$= -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \varphi^2} + i \frac{\partial}{\partial \varphi} \right),$$

$$\hat{L}^2 = \hat{L}_+ \hat{L}_- + \hat{L}_z^2 - \hbar \hat{L}_z,$$

We finally obtain the formula for L^2 in spherical coordinates:

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

Since L_z depends only on φ , the eigenfunctions Y_{lm} are separable:

$$Y_{lm}(\theta, \varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi).$$

Therefore,

$$-i\hbar\Theta_{lm}(\theta)\frac{\partial\Phi_m(\varphi)}{\partial\varphi} = m\hbar\Theta_{lm}(\theta)\Phi_m(\varphi),$$

which reduces to,

$$-i\frac{\partial\Phi_m(\varphi)}{\partial\varphi} = m\Phi_m(\varphi).$$

The normalized solutions of this equation are given by

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi},$$

For Φ_m to be single-valued, it must be periodic in φ with period 2π , $\Phi_m(2\pi+\varphi)=\Phi_m(\varphi)$, hence

$$Y_{lm}(\theta, \varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi).$$

This relation shows that the expectation value of L_z , $l_z = \langle l m | L_z | l m \rangle$, is restricted to a *discrete set of values*

$$l_z = m\hbar, \quad m = 0, \pm 1, \pm 2, \pm 3, \dots$$

Thus, the values of m vary from $-l$ to l :

$$m = -l, -(l-1), -(l-2), \dots, 0, 1, 2, \dots, l-2, l-1, l.$$

Hence the quantum number l must also be an integer. This is expected since the orbital angular momentum must have integer values.

We begin by applying L^2 to the eigenfunctions

$$Y_{lm}(\theta, \varphi) = \frac{1}{\sqrt{2\pi}} \Theta_{lm}(\theta) e^{im\varphi}.$$

This gives

$$\begin{aligned} \hat{L}^2 Y_{lm}(\theta, \varphi) &= \frac{-\hbar^2}{\sqrt{2\pi}} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] \Theta_{lm}(\theta) e^{im\varphi} \\ &= \frac{\hbar^2 l(l+1)}{\sqrt{2\pi}} \Theta_{lm}(\theta) e^{im\varphi}, \end{aligned}$$

which, after eliminating the φ -dependence, reduces to

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta_{lm}(\theta)}{d\theta} \right) + \left[l(l+1) - \frac{m^2}{\sin^2\theta} \right] \Theta_{lm}(\theta) = 0.$$

This equation is known as the *Legendre differential equation*.

Its solutions can be expressed in terms of the associated

Legendre functions

$$\Theta_{lm}(\theta) = C_{lm} P_l^m(\cos \theta),$$

which are defined by

$$P_l^m(x) = (1 - x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x).$$

This shows that

$$P_l^{-m}(x) = P_l^m(x),$$

where $P_l(x)$ is the l th Legendre polynomial which is defined by the Rodrigues formula

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l.$$

and

$$\frac{1}{2} \sum_{l=0}^{\infty} (2l + 1) P_l(x') P_l(x) = \delta(x - x'). \quad P_l(-x) = (-1)^l P_l(x).$$

The full normalized eigenfunctions of L^2 and L_z are now given by

$$Y_{lm}(\theta, \varphi) = (-1)^m \sqrt{\left(\frac{2l+1}{4\pi}\right) \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\varphi} \quad (m \geq 0).$$

and

$$Y_{lm}(\theta, \varphi) = \sqrt{\left(\frac{2l+1}{4\pi}\right) \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\varphi} \quad m < 0.$$

P_l^m is the associated Legendre functions

Associated Legendre functions

$$P_1^1(\cos\theta) = \sin\theta$$

$$P_2^1(\cos\theta) = 3\cos\theta\sin\theta$$

$$P_2^2(\cos\theta) = 3\sin^2\theta$$

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

$$P_3^2(\cos\theta) = 15\sin^2\theta\cos\theta$$

$$P_3^3(\cos\theta) = 15\sin^3\theta$$

The completeness relation of Spherical Harmonics is

$$\sum_{m=-l}^l |l, m\rangle\langle l, m| = 1$$

or,

$$\begin{aligned}\sum_m \langle\theta\varphi | l, m\rangle\langle l, m | \theta'\varphi'\rangle &= \sum_m Y_{lm}^*(\theta', \varphi')Y_{lm}(\theta, \varphi) = \delta(\cos\theta - \cos\theta')\delta(\varphi - \varphi') \\ &= \frac{\delta(\theta - \theta')}{\sin\theta}\delta(\varphi - \varphi').\end{aligned}$$

The spherical harmonics are complex functions; their complex conjugate is given by

$$[Y_{lm}(\theta, \varphi)]^* = (-1)^m Y_{l,-m}(\theta, \varphi).$$

We can verify that Y_{lm} is an eigenstate of the parity operator P with an eigenvalue $(-1)^l$:

$$\hat{P}Y_{lm}(\theta, \varphi) = Y_{lm}(\pi - \theta, \varphi + \pi) = (-1)^l Y_{lm}(\theta, \varphi),$$

We can establish a connection between the spherical harmonics and the Legendre polynomials by simply taking $m=0$.

$$Y_{l0}(\theta, \varphi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{2l+1}{4\pi}} \frac{d^l}{d(\cos\theta)^l} (\sin\theta)^{2l} = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta),$$

with

$$P_l(\cos\theta) = \frac{1}{2^l l!} \frac{d^l}{d(\cos\theta)^l} (\cos^2\theta - 1)^l.$$

Note that Y_{lm} can also be expressed in terms of the Cartesian coordinates. For this, we need only to substitute

$$\sin \theta \cos \varphi = \frac{x}{r}, \quad \sin \theta \sin \varphi = \frac{y}{r}, \quad \cos \theta = \frac{z}{r}$$

 $Y_{lm}(\theta, \varphi)$ $Y_{lm}(x, y, z)$

$$Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{00}(x, y, z) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{10}(x, y, z) = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$

$$Y_{1,\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\varphi} \sin \theta$$

$$Y_{1,\pm 1}(x, y, z) = \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r}$$

$$Y_{20}(\theta, \varphi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{20}(x, y, z) = \sqrt{\frac{5}{16\pi}} \frac{3z^2 - r^2}{r^2}$$

$$Y_{2,\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\varphi} \sin \theta \cos \theta$$

$$Y_{2,\pm 1}(x, y, z) = \mp \sqrt{\frac{15}{8\pi}} \frac{(x \pm iy)z}{r^2}$$

$$Y_{2,\pm 2}(\theta, \varphi) = \sqrt{\frac{15}{32\pi}} e^{\pm 2i\varphi} \sin^2 \theta$$

$$Y_{2,\pm 2}(x, y, z) = \sqrt{\frac{15}{32\pi}} \frac{x^2 - y^2 \pm 2ixy}{r^2}$$

It is convenient to take the complete set of **spherical harmonics** $\{Y_{lm}(\theta, \varphi)\}$, which happens to be the common set of eigenfunctions of L^2 and L_z , as the basis set in the Hilbert space.

In this basis

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta Y_{\ell'}^{m'} \hat{L}^2 Y_\ell^m = \hbar^2 \ell(\ell+1) \delta_{\ell'\ell} \delta_{m'm},$$

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta Y_{\ell'}^{m'} \hat{L}_z Y_\ell^m = m\hbar \delta_{\ell'\ell} \delta_{m'm}.$$

The operators L_+ and L_- do not commute with L_z . Therefore, they are represented by non-diagonal matrices in this basis.

Using the relations

$$\hat{L}_{\mp} \hat{L}_{\pm} = \hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z,$$

$$\hat{L}^2 Y_{\ell}^m = \ell(\ell + 1) \hbar^2 Y_{\ell}^m,$$

$$\hat{L}_z Y_{\ell}^m = m \hbar Y_{\ell}^m,$$

we obtain

$$\begin{aligned} \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta Y_{\ell'}^{*m'} (\hat{L}_{\pm}^{\dagger} \hat{L}_{\pm}) Y_{\ell}^m &= \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta Y_{\ell'}^{*m'} (\hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z) Y_{\ell}^m \\ &= [\hbar^2 \ell(\ell + 1) - \hbar^2 m^2 \mp \hbar^2 m] \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta Y_{\ell'}^{*(m' \pm 1)} Y_{\ell}^{m \pm 1} \\ &= \hbar^2 (l \mp m)(l \pm m + 1), \end{aligned}$$

As a consequence, we have

$$\hat{L}_+ Y_\ell^m = \hbar \sqrt{(l-m)(l+m+1)} Y_\ell^{m+1},$$

$$\hat{L}_- Y_\ell^m = \hbar \sqrt{(l+m)(l-m+1)} Y_\ell^{m-1}.$$

Since

$$\hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2 \text{ and } \hat{L}_y = (\hat{L}_+ - \hat{L}_-)/2i,$$

we get

$$\begin{aligned} \hat{L}_x Y_\ell^m &= \frac{1}{2} [\hat{L}_+ + \hat{L}_-] Y_\ell^m \\ &= \frac{\hbar}{2} \left[\sqrt{(l-m)(l+m+1)} Y_\ell^{m+1} + \sqrt{(l+m)(l-m+1)} Y_\ell^{m-1} \right] \\ \hat{L}_y Y_\ell^m &= \frac{1}{2i} [\hat{L}_+ - \hat{L}_-] Y_\ell^m \\ &= \frac{\hbar}{2i} \left[\sqrt{(l-m)(l+m+1)} Y_\ell^{m+1} - \sqrt{(l+m)(l-m+1)} Y_\ell^{m-1} \right]. \end{aligned}$$

Finally,

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta Y_{\ell'}^{*m'} (\hat{L}_+ Y_\ell^m) = \hbar \sqrt{(l-m)(l+m+1)} \delta_{\ell'\ell} \delta_{m',m+1},$$

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta Y_{\ell'}^{*m'} (\hat{L}_- Y_\ell^m) = \hbar \sqrt{(l+m)(l-m+1)} \delta_{\ell'\ell} \delta_{m',m-1},$$

$$\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta Y_{\ell'}^{*m'} (\hat{L}_z Y_\ell^m) = m\hbar \delta_{\ell'\ell} \delta_{m'm}.$$

Consider the case in which $l = 1$. For $l = 1$, we have $m = -1, 0, 1$ and the joint eigenfunctions of L^2 and L_z are:

$$[Y_1^1, Y_1^0, Y_1^{-1}].$$

Therefore, the matrix representing L^2 is given by

$$L^2 = \begin{pmatrix} \langle Y_1^1, \hat{L}^2 Y_1^1 \rangle & \langle Y_1^1, \hat{L}^2 Y_1^0 \rangle & \langle Y_1^1, \hat{L}^2 Y_1^{-1} \rangle \\ \langle Y_1^0, \hat{L}^2 Y_1^1 \rangle & \langle Y_1^0, \hat{L}^2 Y_1^0 \rangle & \langle Y_1^0, \hat{L}^2 Y_1^{-1} \rangle \\ \langle Y_1^{-1}, \hat{L}^2 Y_1^1 \rangle & \langle Y_1^{-1}, \hat{L}^2 Y_1^0 \rangle & \langle Y_1^{-1}, \hat{L}^2 Y_1^{-1} \rangle \end{pmatrix} = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

We obtain the matrix representing L_z in this basis

$$L_z = \begin{pmatrix} \langle Y_1^1, \hat{L}_z Y_1^1 \rangle & \langle Y_1^1, \hat{L}_z Y_1^0 \rangle & \langle Y_1^1, \hat{L}_z Y_1^{-1} \rangle \\ \langle Y_1^0, \hat{L}_z Y_1^1 \rangle & \langle Y_1^0, \hat{L}_z Y_1^0 \rangle & \langle Y_1^0, \hat{L}_z Y_1^{-1} \rangle \\ \langle Y_1^{-1}, \hat{L}_z Y_1^1 \rangle & \langle Y_1^{-1}, \hat{L}_z Y_1^0 \rangle & \langle Y_1^{-1}, \hat{L}_z Y_1^{-1} \rangle \end{pmatrix} = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The matrices, corresponding to L_+ and L_- in this basis, are calculated to be

$$L_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad L_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

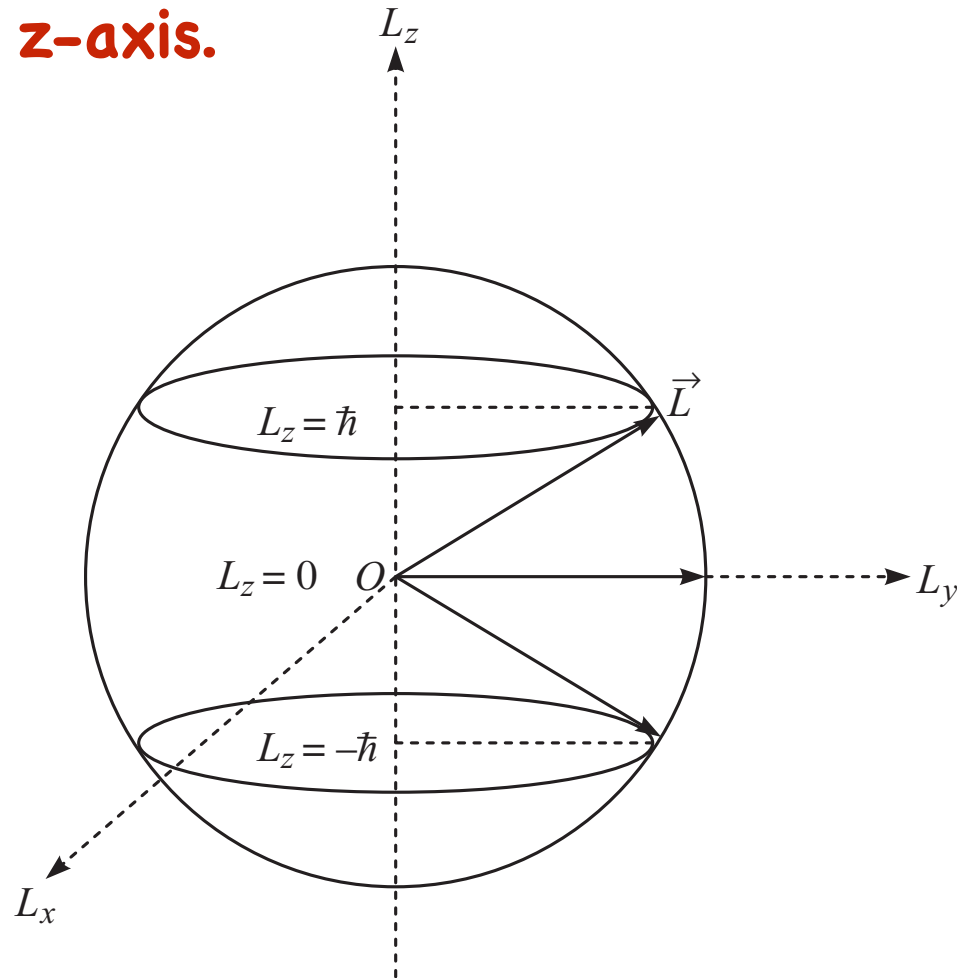
Taking into account that

$$\hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2 \text{ and } \hat{L}_y = (\hat{L}_+ - \hat{L}_-)/2i,$$

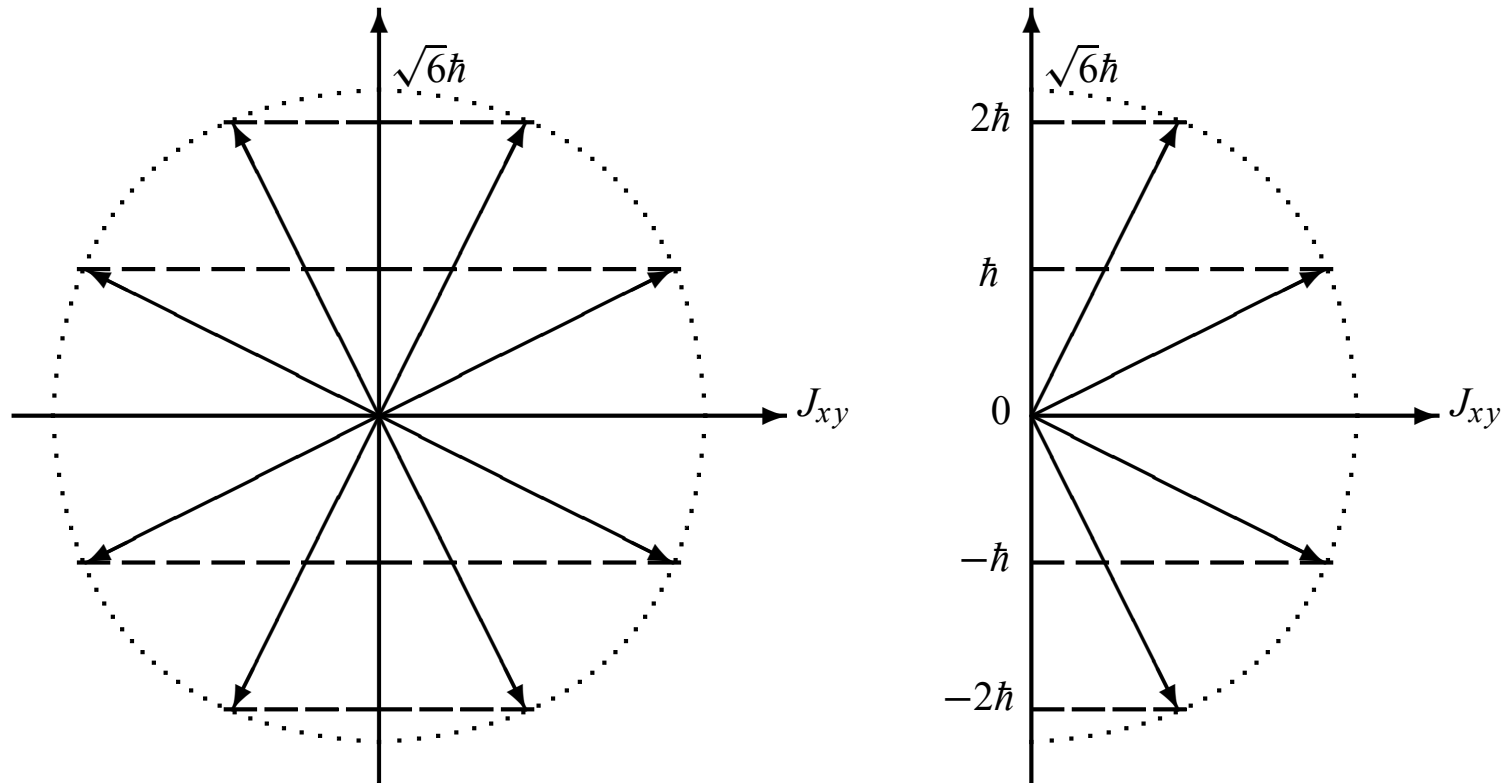
we get

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}.$$

Space quantization is essentially the quantization of the direction of the orbital angular momentum L in space with respect to the z -axis.



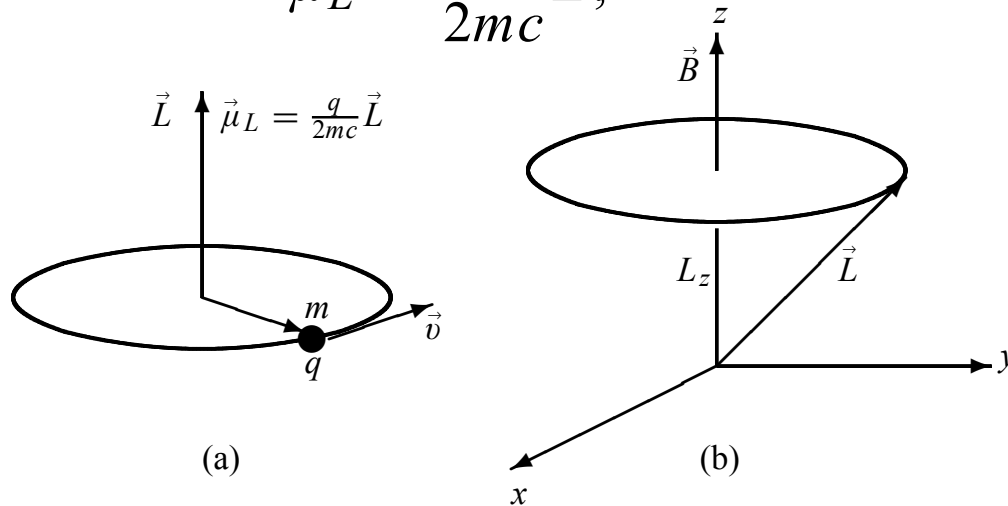
Graphical representation of the angular momentum $l=2$



$$\theta = \cos^{-1} \left(\frac{m}{\sqrt{l(l+1)}} \right)$$

From the classical theory of electromagnetism, an *orbital magnetic dipole moment* is generated with the orbital motion of a particle of charge q :

$$\vec{\mu}_L = \frac{q}{2mc} \vec{L},$$

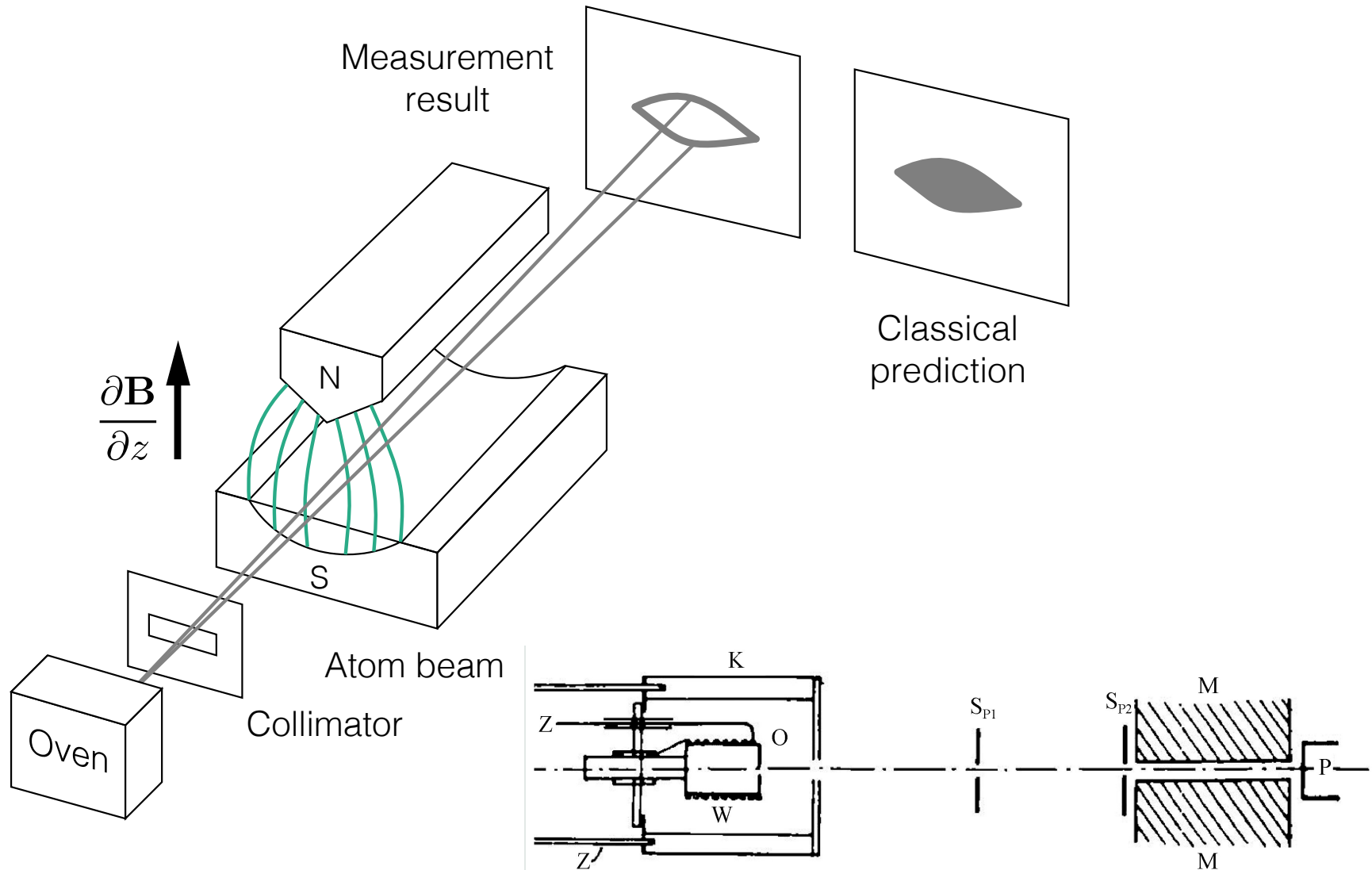


For electron

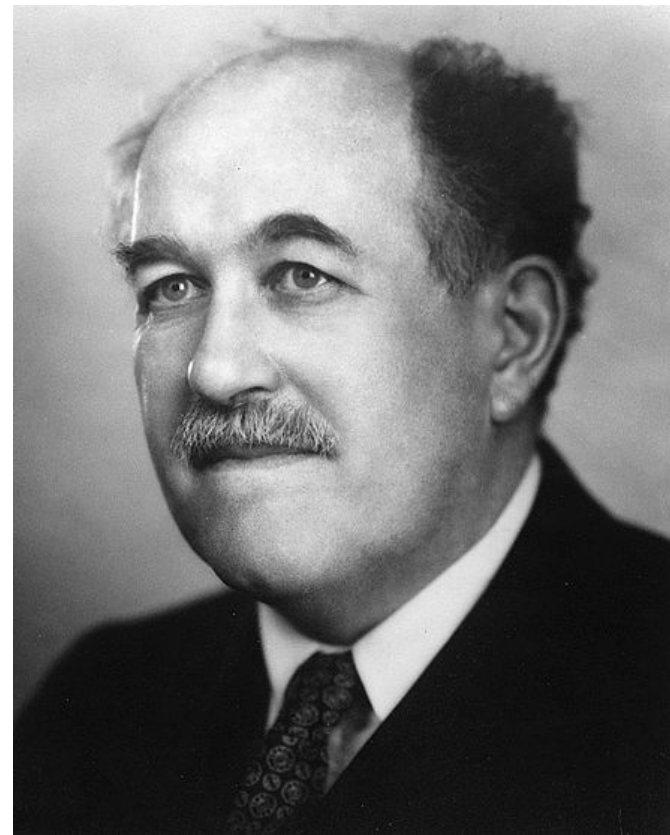
$$\vec{\mu}_L = -e\vec{L}/(2m_e c)$$



Stern-Gerlach experiment



Otto Stern was and Nobel laureate in physics. He was the second most nominated person for a Nobel Prize with 82 nominations in the years 1925–1945, ultimately winning in 1943. It was awarded to Stern alone, "for his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton" (not for the Stern–Gerlach experiment).



Walther Gerlach was a German physicist who co-discovered, through laboratory experiment, spin quantization in a magnetic field, the Stern-Gerlach effect. The experiment was conceived by Otto Stern in 1921 and first successfully conducted by Gerlach in early 1922.



Stern-Gerlach experiment



南開大學



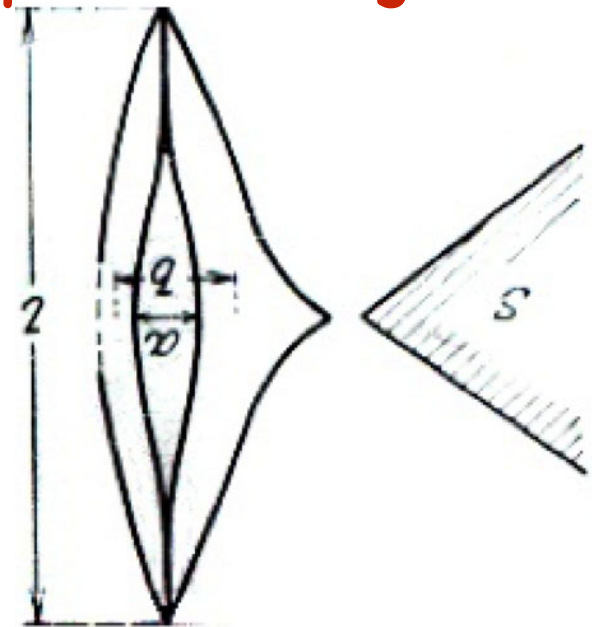
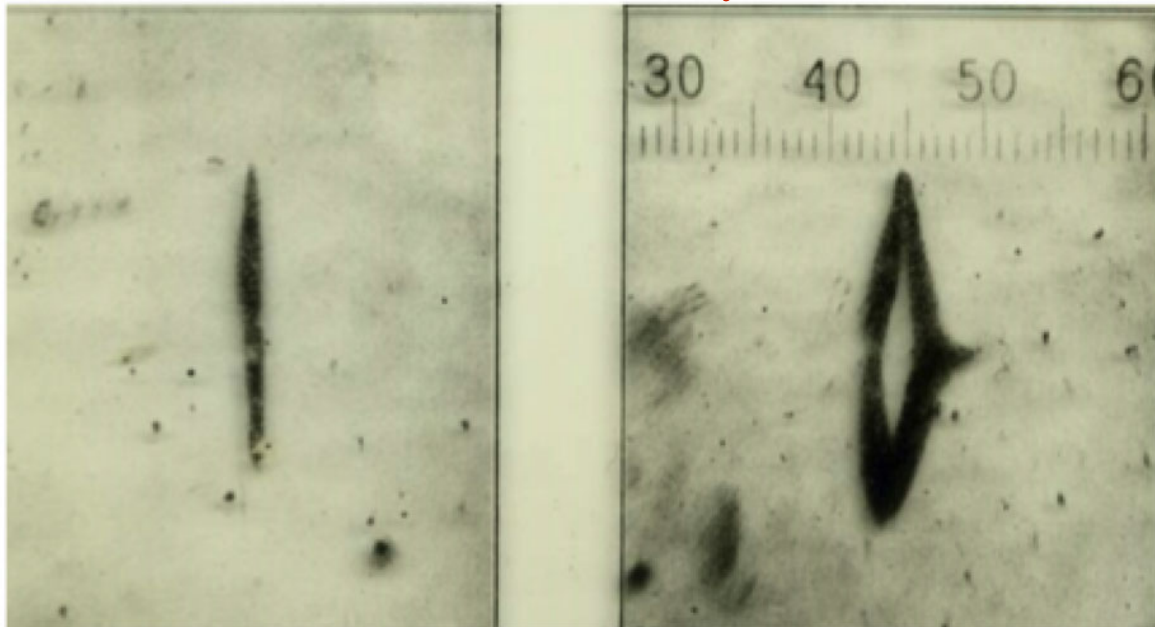
It is important to note that a silver atom has 47 electrons out of which 46 constitute the spherically symmetric charge distribution around the nucleus: they fill all the sub-shells for $n = 1$, $n = 2$, and $n = 3$, and the 4d sub-shell and contribute nothing to the orbital angular momentum of the atom.

The 47th electron is in the 5s state and it cannot have any orbital angular momentum too. Thus, a silver atom in its ground state does not have any orbital angular momentum and hence there is no magnetic moment associated with it.



Stern-Gerlach experiment

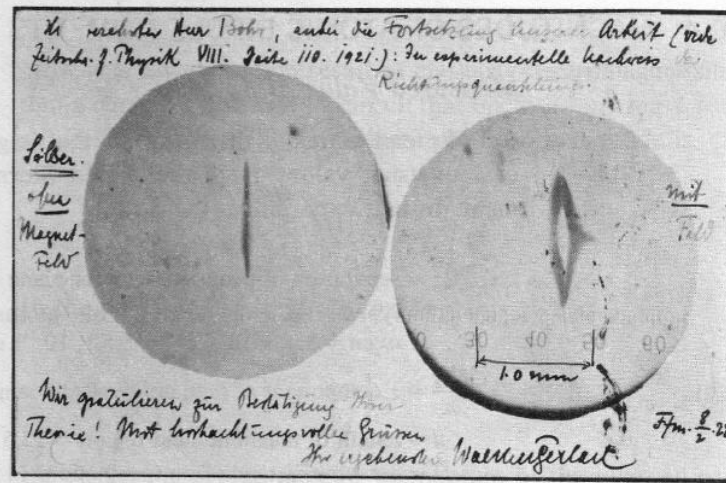
Observed pattern on the detector plate: left without magnetic field, middle with magnetic field and right beam spot geometry near the edge of the magnet. Since the magnetic field strength is fast decreasing with distance from the edge of the magnet (perpendicular to the direction of the B-Field) the beam components merge.





“Attached is the experimental proof of directional quantization. We congratulate you on the confirmation of your theory.”

— Postcard from Stern & Gerlach to Niels Bohr, February 8, 1922.



Through their clever experimental arrangement Stern and Gerlach not only demonstrated *ad oculos* [for the eyes] the space quantization of atoms in a magnetic field, but they also proved the quantum origin of electricity and its connection with atomic structure.

—**Arnold Sommerfeld (1868–1951)**

The most interesting achievement at this point is the experiment of Stern and Gerlach. The alignment of the atoms without collisions via radiative [exchange] is not comprehensible based on the current [theoretical] methods; it should take more than 100 years for the atoms to align. I have done a little calculation about this with [Paul] Ehrenfest. [Heinrich] Rubens considers the experimental result to be absolutely certain.

—**Albert Einstein (1879–1955)**

More important is whether this proves the existence of space quantization. Please add a few words of explanation to your puzzle, such as what's really going on.

—**James Franck (1882–1951)**

I would be very grateful if you or Stern could let me know, in a few lines, whether you interpret your experimental results in this way that the atoms are oriented only parallel or opposed, but not normal to the field, as one could provide theoretical reasons for the latter assertion.

—**Niels Bohr (1885–1962)**

This should convert even the nonbeliever Stern.

—**Wolfgang Pauli (1900–58)**

As a beginning graduate student back in 1923, I . . . hoped with ingenuity and inventiveness I could find ways to fit the atomic phenomena into some kind of mechanical system. . . . My hope to [do that] died when I read about the Stern–Gerlach experiment. . . . The results were astounding, although they were hinted at by quantum theory. . . . This convinced me once and for all that an ingenious classical mechanism was out and that we had to face the fact that the quantum phenomena required a completely new orientation.

—**Isidor I. Rabi (1898–1988)**

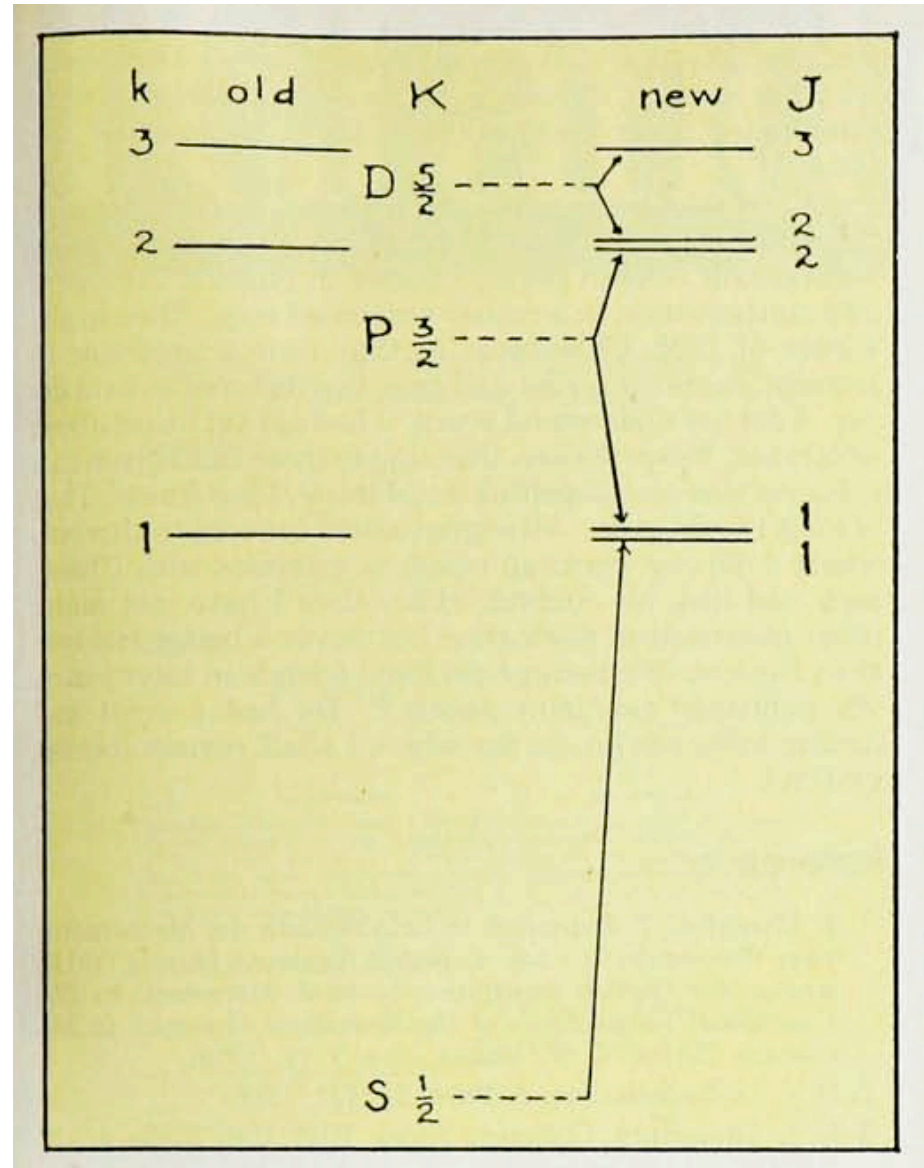
Spin angular momentum or simply spin is a fundamental property of all particles, irrespective of whether they are elementary or composite.

It belongs to an internal degree of freedom (completely independent of the spatial degrees of freedom) and manifests itself as some intrinsic angular momentum of the particle.

The spinning motion of an electron, proposed by Uhlenbeck and Goudsmit, was highly questionable in view of the fact that an electron was a point particle and the classical notion of angular momentum of a rigid body did not apply.

Now it is being told that Uhlenbeck got frightened, went to Ehrenfest and said: "Don't send it off, because it probably is wrong; it is impossible, one cannot have an electron that rotates at such high speed and has the right moment". And Ehrenfest replied: "It is too late, I have sent it off already". But I do not remember the event, I never had the idea that it was wrong because I did not know enough. The one thing I remember is that Ehrenfest said to me: "Well, that is a nice idea, though it may be wrong. But you don't yet have a reputation, so you have nothing to lose". That is the only thing I remember.





Since the beam split into two, it follows from the theory discussed in the previous section that

$$2s + 1 = 2 \quad \Rightarrow \quad s = \frac{1}{2}.$$

Since the state of an electron is characterized by two values of the projection of its spin on the z-axis, the wave function of the electron must consist of two components

$$\psi(\vec{r}, t) = \begin{pmatrix} \psi^+(\vec{r}, t) \\ \psi^-(\vec{r}, t) \end{pmatrix}.$$

Spin acts on vectors belonging to a two-dimensional Euclidean space, it must be represented by a 2×2 matrix.

Spin is denoted by a **vector S**. As required by the rules of quantum mechanics, it is represented by an operator \hat{S} with Cartesian components \hat{S}_x , \hat{S}_y and \hat{S}_z .

Same commutation relations that is satisfied by the Cartesian components of the orbital angular momentum.

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

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

$$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y.$$

\hat{S}^2 commutes with each of the operators \hat{S}_x , \hat{S}_y and \hat{S}_z , that is,

$$[\hat{S}^2, \hat{S}_x] = 0, \quad [\hat{S}^2, \hat{S}_y] = 0, \quad [\hat{S}^2, \hat{S}_z] = 0.$$

The operators S^2 and S_z can have a common set of eigenvectors, $|s, m_s\rangle$, characterized by two quantum numbers s and m_s .

The quantum number s is called the spin quantum number and takes integers as well as half-integer values.

On the other hand, the quantum number m_s is called the spin magnetic quantum number and takes $(2s + 1)$ values from $-s$ to s .

$$\hat{S}^2 |s, m_s\rangle = \hbar^2 s(s + 1) |s, m_s\rangle,$$

$$\hat{S}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle,$$

and

$$\hat{S}_{\pm} |s, m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} |s, m_s \pm 1\rangle$$

where

$$\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$$

Also, in a given state with quantum number s , the magnitude of spin is given by

$$S = \sqrt{s(s+1)}\hbar.$$

The z component of spin is quantized, $S_z = m_s\hbar$, and takes $(2s+1)$ different values.

Now, the magnetic dipole moment associated with spin is given by

$$\vec{\mu}_s = -\frac{e}{m_e} \vec{S},$$

where, e is the magnitude of the electronic charge and m_e is the mass of the electron. As a consequence, the Hamiltonian for an electron, with spin, in an external magnetic field B along the positive z direction, will have a potential energy term

$$\Delta W = -\vec{\mu}_s \cdot \vec{B} = \frac{eB}{m_e} S_z = \frac{e\hbar B}{m_e} m_s.$$

Since m_s takes $(2s + 1)$ values, the original degenerate energy level will split into $(2s + 1)$ distinct levels.

s can take both the integer and the half-integer values. Nature supports both kinds of particles: particles with integer spin, called bosons, and particles with half-integer spin, called fermions.

For instance, photons ($s = 1$), π -mesons ($s = 0$), gravitons ($s = 2$) and so on are bosons, while electrons ($s = 1/2$), protons ($s = 1/2$), neutrons ($s = 1/2$), delta particles ($s = 3/2$) and so on are fermions.

Let the axis for the projection of spin be the z-axis in an arbitrarily oriented Cartesian system of coordinates. The operator σ_z must be represented by a diagonal matrix with diagonal elements +1 and -1, that is,

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

This is usually called the S_z -representation for the sigma matrices. It then follows from the isotropy of space (equivalence of all the directions in space) that the matrices at x and y direction will also be 2×2 unit matrices with eigenvalues 1, that is

$$\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Hence,

$$\begin{aligned} \hat{\sigma}_y^2 \hat{\sigma}_z - \hat{\sigma}_z \hat{\sigma}_y^2 &= \hat{\sigma}_y \hat{\sigma}_y \hat{\sigma}_z - \hat{\sigma}_y \hat{\sigma}_z \hat{\sigma}_y + \hat{\sigma}_y \hat{\sigma}_z \hat{\sigma}_y - \hat{\sigma}_z \hat{\sigma}_y \hat{\sigma}_y \\ &= \hat{\sigma}_y (\hat{\sigma}_y \hat{\sigma}_z - \hat{\sigma}_z \hat{\sigma}_y) + (\hat{\sigma}_y \hat{\sigma}_z - \hat{\sigma}_z \hat{\sigma}_y) \hat{\sigma}_y = 0. \end{aligned}$$

Taking into account the commutation relations of σ -matrices, we obtain

$$2i(\hat{\sigma}_y \hat{\sigma}_x + \hat{\sigma}_x \hat{\sigma}_y) = 0. \quad \Rightarrow \quad \hat{\sigma}_x \hat{\sigma}_y + \hat{\sigma}_y \hat{\sigma}_x = 0.$$

This means that the matrices σ_x and σ_y anti-commute. Similarly, one can prove that all the σ -matrices anti-commute with each other.

This property along with the commutation relations leads to the following useful formulae

$$\hat{\sigma}_x \hat{\sigma}_y = -\hat{\sigma}_y \hat{\sigma}_x = i\hat{\sigma}_z,$$

$$\hat{\sigma}_y \hat{\sigma}_z = -\hat{\sigma}_z \hat{\sigma}_y = i\hat{\sigma}_x,$$

$$\hat{\sigma}_z \hat{\sigma}_x = -\hat{\sigma}_x \hat{\sigma}_z = i\hat{\sigma}_y.$$

If we multiply the first of the aforementioned relations by σ_z from the right, we arrive at the identity

$$\hat{\sigma}_x \hat{\sigma}_y \hat{\sigma}_z = iI$$

Let us determine the concrete expressions for the sigma matrices. The general form of σ_x can be written as

$$\hat{\sigma}_x = \begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix},$$

where the matrix elements a_1 , a_2 , a_3 and a_4 are, in general, complex and have to be determined using the basic properties of the sigma matrices.

Since σ_x and σ_z anti-commute, that is, $\sigma_x\sigma_z = -\sigma_z\sigma_x$, we have

$$\begin{pmatrix} a_1 & -a_2 \\ a_3 & -a_4 \end{pmatrix} = \begin{pmatrix} -a_1 & -a_2 \\ a_3 & a_4 \end{pmatrix}.$$

Therefore, $a_1=0$ and $a_4=0$. Using the property that $(\sigma_x)^2=I$, we get

$$\begin{pmatrix} a_2a_3 & 0 \\ 0 & a_3a_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \Rightarrow a_2a_3 = a_3a_2 = 1.$$

Therefore, $a_2 = e^{i\alpha}$ and $a_3 = e^{-i\alpha}$, where α is an arbitrary real constant. Since, without any loss of generality, we can put α equal to zero, we have

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Now using the relation $i\sigma_y = \sigma_z\sigma_x$, we obtain

$$\hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

The matrices

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

are called Pauli matrices in the S_z representation and along with the unit matrix

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

form the basis in the space of 2×2 matrices. Any 2×2 matrix can be expanded as a linear combination of these matrices.

In the state corresponding to the eigenvalue +1, the spin of the electron points along the +z-axis and we call it spin-up state. Similarly, in the state corresponding to the eigenvalue -1, the spin of the electron points along the -z direction and it is called the spin-down state.

The eigenfunctions of σ_z with eigenvalues $+1$ and -1 , respectively, are readily computed as

$$\chi_z^+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_z^- = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

Let us check whether these spin functions are eigenfunctions of σ_x and σ_y or not. We have

$$\hat{\sigma}_x \chi_z^+ = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \chi_z^-,$$

$$\hat{\sigma}_x \chi_z^- = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \chi_z^+,$$

$$\hat{\sigma}_y \chi_z^+ = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ i \end{pmatrix} = i\chi_z^-,$$

$$\hat{\sigma}_y \chi_z^- = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -i \\ 0 \end{pmatrix} = -i\chi_z^+$$

In many problems of interest it is necessary to add angular momenta. For instance, one is required to add the orbital angular momentum, L , and the spin angular momentum, S , while studying spin-orbit coupling in atoms.

Therefore, it is important to discuss the procedure of addition of angular momenta in quantum mechanics.

We shall write the eigenfunctions of L^2 in the bra-ket notation as: $|l,m\rangle$. Thus, $|l,m\rangle$ is an eigenvector (or eigenket) of L^2 with two quantum numbers l and m .

Let us, without specifying the nature, consider the addition of two angular momenta L_1 and L_2

$$\hat{J} = \hat{L}_1 + \hat{L}_2.$$

Individually, L_1 and L_2 satisfy the following quantum mechanical commutation relations

$$[\hat{L}_{1i}, \hat{L}_{1j}] = i\hbar \sum_k \varepsilon_{ijk} \hat{L}_{1k},$$

$$[\hat{L}_{2i}, \hat{L}_{2j}] = i\hbar \sum_k \varepsilon_{ijk} \hat{L}_{2k},$$

where the indices i, j and k take values from 1 to 3. Note that, it is assumed here that L_1 and L_2 either correspond to different degrees of freedom, or correspond to the same degree of freedom but belong to different particles.

In view of the preceding assumption, the operator L_1 and L_2 act in different vector spaces: L_1 acts in the $(2l_1 + 1)$ dimensional space spanned by the kets $\{|l_1, m_1\rangle\}$, while L_2 acts in the $(2l_2 + 1)$ dimensional space spanned by the kets $\{|l_2, m_2\rangle\}$,

Hence, they commute and can have a common set of eigenvectors. Let us write these common eigenvectors as

$$|l_1, m_1; l_2, m_2\rangle = |l_1, m_1\rangle \otimes |l_2, m_2\rangle,$$

where $l_i, i = 1, 2$ and $m_i, i = 1, 2$ are the individual quantum numbers and \otimes stands direct (tensorial) product. Then according to the earlier discussions

$$\hat{L}_1^2 |\ell_1, m_1; \ell_2, m_2\rangle = \hbar^2 \ell_1 (\ell_1 + 1) |\ell_1, m_1; \ell_2, m_2\rangle,$$

$$\hat{L}_{1z} |\ell_1, m_1; \ell_2, m_2\rangle = \hbar m_1 |\ell_1, m_1; \ell_2, m_2\rangle$$

$$\hat{L}_2^2 |\ell_1, m_1; \ell_2, m_2\rangle = \hbar^2 \ell_2 (\ell_2 + 1) |\ell_1, m_1; \ell_2, m_2\rangle,$$

$$\hat{L}_{2z} |\ell_1, m_1; \ell_2, m_2\rangle = \hbar m_2 |\ell_1, m_1; \ell_2, m_2\rangle$$

Let us show that the total angular momentum operators $\mathbf{J}_i = \mathbf{L}_{1i} + \mathbf{L}_{2i}$, ($i = 1, 2, 3$) also obey the usual angular momentum commutation relations, i.e.,

$$[\hat{J}_i, \hat{J}_j] = i\hbar \sum_k \varepsilon_{ijk} \hat{J}_k,$$

where, once again, each of the indices i , j and k takes three values 1, 2 and 3.

We have

$$\begin{aligned} [\hat{J}_i, \hat{J}_j] &= [\hat{L}_{1i} + \hat{L}_{2i}, \hat{L}_{1j} + \hat{L}_{2j}] = [\hat{L}_{1i}, \hat{L}_{1j}] + [\hat{L}_{1i}, \hat{L}_{2j}] + [\hat{L}_{2i}, \hat{L}_{1j}] + [\hat{L}_{2i}, \hat{L}_{2j}] \\ &= i\hbar \sum_k \varepsilon_{ijk} \hat{L}_{1k} + i\hbar \sum_r \varepsilon_{ijk} \hat{L}_{2k} \\ &= i\hbar \sum_k \varepsilon_{ijk} (\hat{L}_{1k} + \hat{L}_{2k}) \\ &= i\hbar \sum_k \varepsilon_{ijk} \hat{J}_k, \end{aligned}$$

where we have taken into account that

$$[\hat{L}_{1i}, \hat{L}_{2j}] = 0 \text{ and } [\hat{L}_{2i}, \hat{L}_{1j}] = 0.$$

Given the values of the individual angular momenta $|L_1|$ and $|L_2|$ (i.e., the quantum numbers l_1 and l_2), find the values that the total angular momentum $|J|$ (i.e., the quantum number j corresponding to it).

Since the total angular momentum operators J_i , ($i = 1, 2, 3$), satisfy the usual angular momentum commutation relations, we can easily show that

$$[\hat{J}^2, \hat{J}_z] = 0, \quad [\hat{J}^2, \hat{J}_\pm] = 0, \quad , [\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z, \quad , [\hat{J}_z, \hat{J}_\pm] = \pm\hbar\hat{J}_\pm,$$

where

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y, \quad \hat{J}_- = \hat{J}_x - i\hat{J}_y$$

are the total angular momentum raising and lowering operators, respectively. Further, the Hilbert space in which the total angular momentum operator J^2 acts is the product space spanned by the kets $|l_1, l_2, m_1, m_2\rangle = |l_1, m_1\rangle \otimes |l_2, m_2\rangle$.

The kets $\{|\ell_1, \ell_2, m_1, m_2\rangle\}$ also form a complete and orthonormal basis:

$$\begin{aligned}\langle \ell_1, \ell_2; m_1, m_2 | \ell'_1, \ell'_2, m'_1, m'_2 \rangle &= \langle \ell_1, m_1 | \ell'_1, m'_1 \rangle \langle \ell_2, m_2 | \ell'_2, m'_2 \rangle \\ &= \delta_{\ell_1 \ell'_1} \delta_{\ell_2 \ell'_2} \delta_{m_1 m'_1} \delta_{m_2 m'_2},\end{aligned}$$

$$\begin{aligned}\sum_{m_1 m_2} |\ell_1, \ell_2; m_1, m_2\rangle \langle \ell_1, \ell_2; m_1, m_2| \\ = \left(\sum_{m_1=-\ell_1}^{\ell_1} |\ell_1, m_1\rangle \langle \ell_1, m_1| \right) \left(\sum_{m_2=-\ell_2}^{\ell_2} |\ell_2, m_2\rangle \langle \ell_2, m_2| \right) = \hat{I}^2 = \hat{I}.\end{aligned}$$

It is straightforward to prove that

$$[\hat{J}^2, \hat{L}_1^2] = 0, [\hat{J}^2, \hat{L}_2^2] = 0, [\hat{J}_z, \hat{L}_1^2] = 0, [\hat{J}_z, \hat{L}_2^2] = 0,$$

but

$$[\hat{J}^2, \hat{L}_{1z}] \neq 0, \text{ and } [\hat{J}^2, \hat{L}_{2z}] \neq 0.$$

Therefore, the maximal set of commuting operators for the system is given by J^2 , J_z , L_1^2 and L_2^2 . They can be simultaneously diagonalized and their joint eigenfunctions are characterized by four quantum numbers j , m_j , l_1 and l_2 . Let $|l_1, l_2, j, m\rangle$ be the simultaneous eigenfunctions of J^2 and J_z . Since l_1 and l_2 are fixed, we shall write these vectors as $|j, m\rangle$.

The above completeness and orthonormality conditions can now be rewritten as

$$\sum_j \sum_{m=-j}^j |j, m\rangle \langle j, m| = \hat{I},$$

$$\langle j', m' | j, m \rangle = \delta_{jj'} \delta_{mm'}.$$

Also, it is not difficult to show that

$$\hat{J}^2 |j, m\rangle = j(j+1)\hbar^2 |j, m\rangle,$$

$$\hat{J}_z |j, m\rangle = m\hbar |j, m\rangle,$$

$$\hat{J}_+ |j, m\rangle = \sqrt{(j-m)(j+m+1)}\hbar |j, m+1\rangle,$$

$$\hat{J}_- |j, m\rangle = \sqrt{(j+m)(j-m+1)}\hbar |j, m-1\rangle,$$

$$\hat{J}_z |j, m\rangle = m\hbar |j, m\rangle,$$

$$\hat{J}_+ |j, m = j\rangle = 0, \quad \hat{J}_- |j, m = -j\rangle = 0.$$

let us expand the basis vector $|j, m\rangle$ in terms of the basis $\{|l_1, l_2; m_1, m_2\rangle\}$ as

$$|j, m\rangle = \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} C_{l_1 l_2 j}^{m_1 m_2 m} |\ell_1, \ell_2; m_1, m_2\rangle,$$

where the coefficients of expansion

$$C_{\ell_1 \ell_2 j}^{m_1 m_2 m} = \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle$$

are called the **Clebsch-Gordan (CG) coefficients**.

By convention, Clebsch-Gordan coefficients are taken to be real, i.e.,

$$\langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle = \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle^\dagger = \langle j, m | \ell_1, \ell_2; m_1, m_2 \rangle.$$

Also, using the complete and orthonormal relation, we get

$$\sum_{m_1 m_2} \langle j', m' | \ell_1, \ell_2; m_1, m_2 \rangle \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle = \delta_{j' j} \delta_{m' m}.$$

Since the Clebsch-Gordan coefficients are real, we can write this equation as

$$\sum_{m_1 m_2} \langle \ell_1, \ell_2; m_1, m_2 | j', m' \rangle \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle = \delta_{j' j} \delta_{m' m}.$$

The last equation leads to

$$\sum_{m_1 m_2} \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle^2 = 1.$$

Similarly, we can derive the following relation

$$\sum_j \sum_{m=-j}^j \langle \ell_1, \ell_2, m'_1, m'_2 | j, m \rangle \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle = \delta_{m'_1 m_1} \delta_{m'_2 m_2},$$

which yields

$$\sum_j \sum_{m=-j}^j \langle \ell_1, \ell_2, m_1, m_2 | j, m \rangle^2 = 1$$

Since

$$\hat{J}_z = \hat{L}_{1z} + \hat{L}_{2z},$$

We have

$$\langle \ell_1, \ell_2; m_1, m_2 | \hat{J}_z - \hat{L}_{1z} - \hat{L}_{2z} | j, m \rangle = 0.$$

Using the following relations

$$\hat{J}_z |j, m\rangle = m\hbar |j, m\rangle,$$

$$\langle \ell_1, \ell_2; m_1, m_2 | \hat{L}_{1z} = m_1 \hbar \langle \ell_1, \ell_2; m_1, m_2 |,$$

$$\langle \ell_1, \ell_2; m_1, m_2 | \hat{L}_{2z} = m_2 \hbar \langle \ell_1, \ell_2; m_1, m_2 |,$$

we obtain

$$(m - m_1 - m_2) \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle = 0.$$

Therefore, for $\langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle$ to be nonzero, we must have

$$m = m_1 + m_2.$$

This is the first constraint for the Clebsch-Gordan coefficients.

Since the dimension of the product space is $N = (2l_1 + 1) \times (2l_2 + 1)$, there are $(2l_1 + 1) \times (2l_2 + 1)$ number of basis vectors $|j, m\rangle$ in this space. On the other hand, for each value of j there are $(2j + 1)$ basis vectors $|j, m\rangle$, and hence

$$\sum_{j=j_{\min}}^{j_{\max}} (2j + 1) = (2l_1 + 1)(2l_2 + 1).$$

Finally, we can obtain

$$j_{\max} = l_1 + l_2. \quad j_{\min}^2 = (l_1 - l_2)^2.$$

We have the following range of variation of j :

$$|l_1 - l_2| \leq j \leq (l_1 + l_2).$$

For instance, it can be shown that the CG coefficients corresponding to **two limiting cases** $\{m_1 = l_1, m_2 = l_2, j = l_1 + l_2, m = (l_1 + l_2)\}$ and $\{m_1 = -l_1, m_2 = -l_2, j = l_1 + l_2, m = -(l_1 + l_2)\}$ are equal to 1. That is

$$\langle l_1, l_2, l_1, l_2 | (l_1 + l_2), (l_1 + l_2) \rangle = 1,$$

$$\langle l_1, l_2, -l_1, -l_2 | (l_1 + l_2), -(l_1 + l_2) \rangle = 1.$$

To calculate CG coefficients, other than the aforementioned simple cases, one uses either the **recursion relations** between the CG coefficients or the **ladder operator method**.

Finally, we can obtain

$$\begin{aligned} & \sqrt{(j \mp m)(j \pm m + 1)} \langle \ell_1, \ell_2; m_1, m_2 | j, m \pm 1 \rangle \\ = & \sqrt{(\ell_1 \pm m_1)(\ell_1 \mp m_1 + 1)} \langle \ell_1, \ell_2; m_1 \mp 1, m_2 | j, m \rangle \\ + & \sqrt{(\ell_2 \pm m_2)(\ell_2 \mp m_2 + 1)} \langle \ell_1, \ell_2; m_1, m_2 \mp 1 | j, m \rangle. \end{aligned}$$

and

$$\begin{aligned} & \sqrt{(j \pm m)(j \mp m + 1)} \langle \ell_1, \ell_2; m_1, m_2 | j, m \rangle \\ = & \sqrt{(\ell_1 \pm m_1)(\ell_1 \mp m_1 + 1)} \langle \ell_1, \ell_2; m_1 \mp 1, m_2 | j, m \mp 1 \rangle \\ + & \sqrt{(\ell_2 \pm m_2)(\ell_2 \mp m_2 + 1)} \langle \ell_1, \ell_2; m_1, m_2 \mp 1 | j, m \mp 1 \rangle. \end{aligned}$$

Let us consider the addition of the orbital angular momentum and the spin angular momentum, i.e.,

$$\hat{J} = \hat{L} + \hat{S},$$

of a spin half particle (say, of an electron). In the given case $l_1 = l$ (an integer) $m_1 = m_l$ (takes values from $-l$ to l), $l_2 = s = 1/2$, and $m_2 = m_s = \pm 1/2$.

The value of j in this case is restricted in the interval

$$\left| l - \frac{1}{2} \right| \leq j \leq \left| l + \frac{1}{2} \right|.$$

The maximal set of commuting observables in this case is given by:

$$\{\hat{J}^2, \hat{L}^2, \hat{S}^2, \hat{J}_z\}.$$

The joint eigenvectors of these operators are:

$$|\ell, s, m_\ell, m_s\rangle.$$

The eigenvectors of \mathbf{J}^2 are:

$$|\ell, s; j, m\rangle;$$

l and s being fixed. Obviously, the following hold:

$$\hat{S}^2 |j, m\rangle = \hbar^2 s(s+1) |j, m\rangle = \frac{3}{4} \hbar^2 |j, m\rangle,$$

$$\hat{J}_z |j, m\rangle = \hbar m |j, m\rangle.$$

The state with maximal total angular momentum $j = l+1/2$
and $m_{\max} = l+1/2$

$$|j_{\max}, m_{\max}\rangle = \left| l + \frac{1}{2}, l + \frac{1}{2} \right\rangle = |l, l\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle.$$

The corresponding CG coefficient

$$\left\langle l, \frac{1}{2}; l, \frac{1}{2} \left| l + \frac{1}{2}, l + \frac{1}{2} \right\rangle = 1,$$

in accordance with our earlier discussions. On one hand we have

$$\begin{aligned} \hat{J}_- \left| l + \frac{1}{2}, l + \frac{1}{2} \right\rangle &= \hbar \sqrt{\left[\left(l + \frac{1}{2} \right) + \left(l + \frac{1}{2} \right) \right] \left(l + \frac{1}{2} - l - \frac{1}{2} + 1 \right)} \left| l + \frac{1}{2}, l - \frac{1}{2} \right\rangle \\ &= \hbar \sqrt{2l + 1} \left| l + \frac{1}{2}, l - \frac{1}{2} \right\rangle, \end{aligned}$$

while on the other

$$\begin{aligned} (\hat{L}_- + \hat{S}_-) \left| l + \frac{1}{2}, l + \frac{1}{2} \right\rangle &= \hat{L}_- |l, l\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + |l, l\rangle \otimes \hat{S}_- \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\ &= \hbar \sqrt{2l} |l, l - 1\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \hbar |l, l\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle. \end{aligned}$$

Therefore, we get

$$\left| l + \frac{1}{2}, l - \frac{1}{2} \right\rangle = \frac{1}{\sqrt{2l+1}} \left[\sqrt{2l} |l, l-1\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + |l, l\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right].$$

Similarly, we have

$$\left| l + \frac{1}{2}, l - \frac{3}{2} \right\rangle = \sqrt{\frac{2l-1}{2l+1}} |l, l-2\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{2l+1}} |l, l-1\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle.$$

The other states are given by

$$\begin{aligned} \left| l + \frac{1}{2}, m \right\rangle &= \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} \left| l, m - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle & \left| l - \frac{1}{2}, m \right\rangle &= \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} \left| l, m + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\ &+ \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} \left| l, m + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle, & &- \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} \left| l, m - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle, \end{aligned}$$

where

$$m = l + \frac{1}{2}, l - \frac{1}{2}, l - \frac{3}{2}, \dots, -l + \frac{1}{2}, -\left(l + \frac{1}{2} \right).$$

1. Find the value of the commutators

(a) $[\hat{x}, \hat{L}_x]$, (b) $[\hat{x}, \hat{L}_y]$, and $[\hat{p}_x, \hat{L}_y]$.

Find the value of the commutators

(a) $[\hat{x}, \hat{L}_x]$, (b) $[\hat{x}, \hat{L}_y]$, and $[\hat{p}_x, \hat{L}_y]$.

Solution:

$$\begin{aligned} [\hat{x}, \hat{L}_x] &= [\hat{x}, (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y)] = [\hat{x}, \hat{y} \hat{p}_z] - [\hat{x}, \hat{z} \hat{p}_y] \\ &= [\hat{x}, \hat{y}] \hat{p}_z + \hat{y} [\hat{x}, \hat{p}_z] - [\hat{x}, \hat{z}] \hat{p}_y - \hat{z} [\hat{x}, \hat{p}_y] \\ &= 0. \end{aligned}$$

$$[\hat{x}, \hat{L}_y] = i\hbar \hat{z} = i\hbar z.$$

$$[\hat{p}_x, \hat{L}_y] = i\hbar \hat{z} = i\hbar z.$$

2. Consider a particle in a superposition state with the wave function

$$|\psi(\theta, \varphi)\rangle = \sqrt{\frac{1}{5}} Y_1^{-1}(\theta, \varphi) + A Y_1^0 + \sqrt{\frac{1}{5}} Y_1^1(\theta, \varphi),$$

where A is an arbitrary constant and Y_l^m are the spherical harmonics. (a) Find A so that ψ is normalized. (b) What is the probability that a measurement of L_z will yield a value $L_z = 0$? (c) Find the expectation values of L^2 and L_+ in this state.

Solution: (a) For the normalized wave function, we must have

$$\langle \psi | \psi \rangle = \frac{2}{5} + A^2 = 1, \Rightarrow A = \sqrt{\frac{3}{5}}.$$

(b) The normalized wave function is now given by

$$\psi(\theta, \varphi) = \sqrt{\frac{1}{5}} Y_1^{-1}(\theta, \varphi) + \sqrt{\frac{3}{5}} Y_1^0 + \sqrt{\frac{1}{5}} Y_1^1(\theta, \varphi),$$

and therefore the probability of finding the value $L_z = 0$ is

$$P = \frac{|\langle Y_1^0 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{3}{5}.$$

(c) We have

$$\hat{L}^2 |\psi(\theta, \varphi)\rangle = \hat{L}^2 \left[\sqrt{\frac{1}{5}} Y_1^{-1}(\theta, \varphi) + \sqrt{\frac{3}{5}} Y_1^0 + \sqrt{\frac{1}{5}} Y_1^1(\theta, \varphi) \right] = 2\hbar^2 |\psi(\theta, \varphi)\rangle.$$

The expectation value of L^2 will be

$$\langle \hat{L}^2 \rangle = \frac{\langle \psi | \hat{L}^2 | \psi \rangle}{\langle \psi | \psi \rangle} = 2\hbar^2 \frac{\langle \psi | \psi \rangle}{\langle \psi | \psi \rangle} = 2\hbar^2.$$

We get

$$\hat{L}_+ \psi(\theta, \varphi) = \sqrt{\frac{2}{5}} Y_1^0 + \sqrt{\frac{6}{5}} Y_1^1$$

Therefore, the expectation value of L_+ is given by

$$\langle \hat{L}_+ \rangle = \langle \psi | \hat{L}_+ | \psi \rangle = 2 \frac{\sqrt{6}}{5} \hbar$$

3. Find the eigenvalues and eigenstates of the spin operator S of an electron in the direction of a unit vector n that lies in the xy plane making an angle θ with the x -axis.

3. Find the eigenvalues and eigenstates of the spin operator S of an electron in the direction of a unit vector n that lies in the xy plane making an angle θ with the x -axis.

Solution: The projection of the spin operator S on n will be $S_n = \hbar/2\sigma_n$, where

$$\hat{\sigma}_n = \begin{pmatrix} 0 & \cos\theta \\ \cos\theta & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i\sin\theta \\ i\sin\theta & 0 \end{pmatrix} = \begin{pmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{pmatrix}.$$

The requirement of non-trivial solutions to the eigenvalue equation for σ_n yields

$$\begin{vmatrix} -\lambda & e^{-i\theta} \\ e^{i\theta} & -\lambda \end{vmatrix} = 0, \Rightarrow \lambda = \pm 1.$$

Hence, the eigenvalues of the operator S_n are $\pm\hbar/2$

For the eigenvectors of S_n , We have

$$\begin{pmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} be^{-i\theta} \\ ae^{i\theta} \end{pmatrix} = \pm \begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow a = e^{-i\theta/2}, b = \pm e^{i\theta/2},$$

The normalized eigenvectors of S_n , corresponding to the eigenvalues $\pm\hbar/2$, are

$$\chi_n^+ = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta/2} \\ e^{i\theta/2} \end{pmatrix}, \quad \chi_n^- = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta/2} \\ -e^{i\theta/2} \end{pmatrix}.$$

4. Consider the case of $l = 1$ and $s = 1/2$. Find all the states and the corresponding CG coefficients.

4. Consider the case of $l = 1$ and $s = 1/2$. Find all the states and the corresponding CG coefficients.

Solution:

$$\begin{aligned} \left| \frac{3}{2}, \frac{3}{2} \right\rangle &= \sqrt{\frac{1 + \frac{3}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{3}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1 - \frac{3}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{3}{2} + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\ &= |1, 1\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle \equiv \left| 1, \frac{1}{2}; 1, \frac{1}{2} \right\rangle, \end{aligned}$$

$$\begin{aligned} \left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{1 + \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{1}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1 - \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{1}{2} + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\ &= \sqrt{\frac{2}{3}} |1, 0\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |1, 1\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\ &\equiv \sqrt{\frac{2}{3}} \left| 1, \frac{1}{2}; 0, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| 1, \frac{1}{2}; 1, -\frac{1}{2} \right\rangle, \end{aligned}$$

$$\begin{aligned}
 \left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \sqrt{\frac{1 - \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, -\frac{1}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1 + \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{1}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
 &= \sqrt{\frac{1}{3}} |1, -1\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} |1, 0\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
 &\equiv \sqrt{\frac{1}{3}} \left| 1, \frac{1}{2}; -1, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| 1, \frac{1}{2}; 0, -\frac{1}{2} \right\rangle,
 \end{aligned}$$

$$\begin{aligned}
 \left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= \sqrt{\frac{1 - \frac{3}{2} + \frac{1}{2}}{2+1}} \left| 1, -\frac{3}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1 + \frac{3}{2} + \frac{1}{2}}{2+1}} \left| 1, -\frac{3}{2} + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
 &= |1, -1\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \equiv \left| 1, \frac{1}{2}; -1, -\frac{1}{2} \right\rangle.
 \end{aligned}$$

$$\begin{aligned}
 \left| \frac{1}{2}, \frac{1}{2} \right\rangle &= \sqrt{\frac{1 + \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{1}{2} + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{1 - \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, \frac{1}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\
 &= \sqrt{\frac{2}{3}} |1, 1\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} |1, 0\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\
 &\equiv \sqrt{\frac{2}{3}} \left| 1, \frac{1}{2}; 1, -\frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| 1, \frac{1}{2}; 0, \frac{1}{2} \right\rangle,
 \end{aligned}$$

$$\begin{aligned}
 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle &= \sqrt{\frac{1 - \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, -\frac{1}{2} + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{1 + \frac{1}{2} + \frac{1}{2}}{2+1}} \left| 1, -\frac{1}{2} - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\
 &= \sqrt{\frac{1}{3}} |1, 0\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} |1, -1\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\
 &\equiv \sqrt{\frac{1}{3}} \left| 1, \frac{1}{2}; 0, -\frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} \left| 1, \frac{1}{2}; -1, \frac{1}{2} \right\rangle.
 \end{aligned}$$