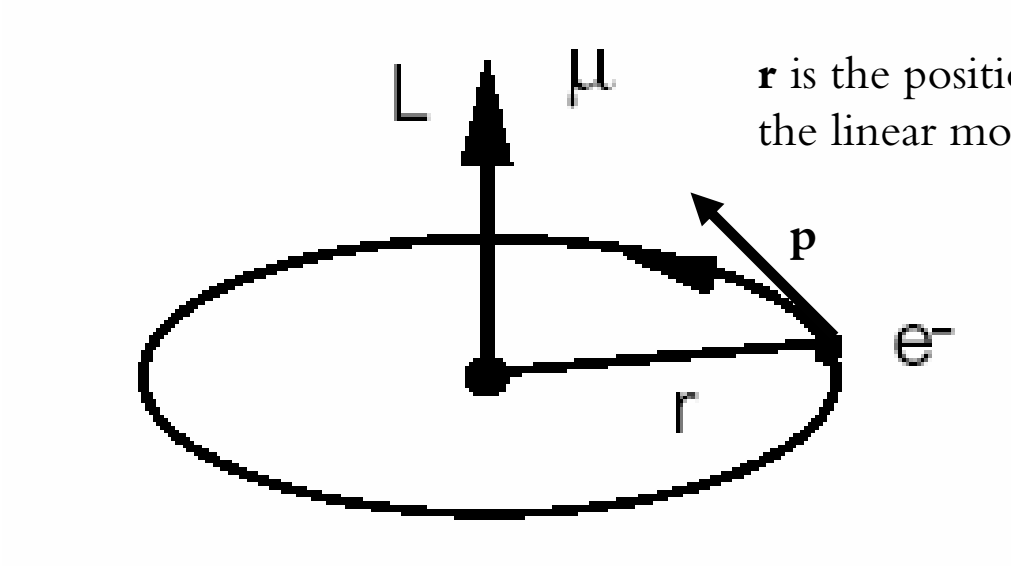
Physical origin for orbital angular momentum

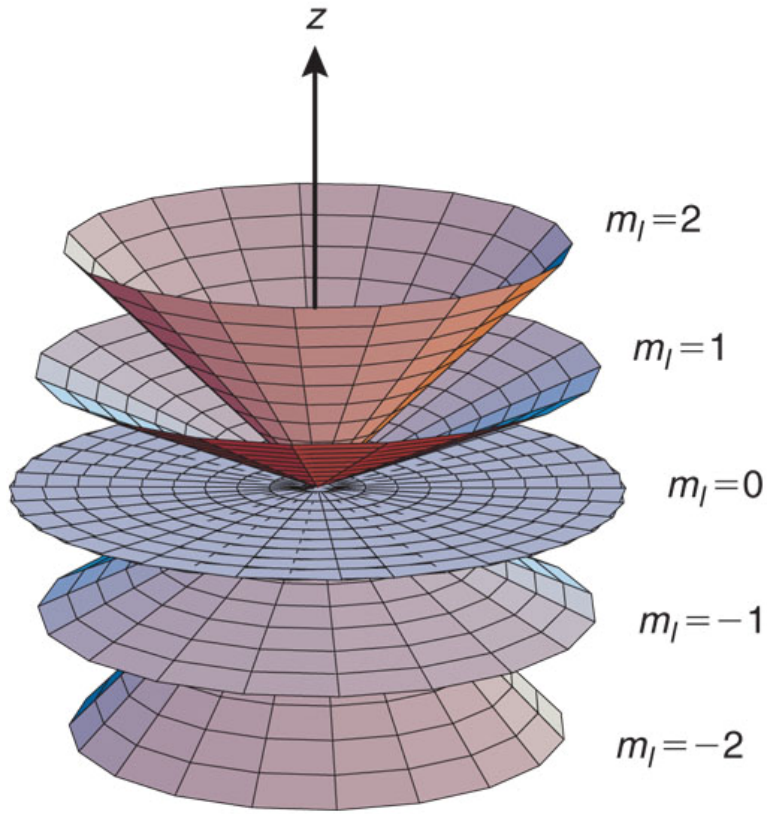


r is the position vector and **p** is the linear momentum vector.

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

$$\vec{\mathbf{L}} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

Since the operators, $\hat{\ell}^2, \hat{\ell}_z$ do not commute with $\hat{\ell}_x, \hat{\ell}_y$,we can only measure their averages. This leads to these sort of pictures:



We can express the eigenfunctions in terms of x, y, and z, although not all are eigenfunctions of $\mathbf{L_z}$

Despite this, it is useful to think about the quantum number, m, as defining the orientation of the orbital.

4.2: Spin Angular Momentum

There exists an angular momentum **S** which is associated with the spin of the electron

It obeys all the same properties of **M** and **L** except it is half integer; that is, s = ½ for every electron, and $m_s = \pm \frac{1}{2}$

$$\therefore \hat{S}^2 \psi_{s,m_s} = s(s+1)\hbar^2 \psi_{s,m_s} = \frac{3}{4}\hbar^2 \psi_{s,m_s}$$

$$\hat{S}_z \psi_{s,m_s} = m_s \hbar \psi_{s,m_s} = \pm \frac{1}{2}\hbar \psi_{s,m_s}$$

Normally spin is introduced in an ad hoc manner in normal QM. Not to worry. Spin does fall out naturally from more sophisticated quantum mechanic treatments (relativistic QM due to Dirac) where it does not have to be introduced artificially. We won't go there!

Similar to orbital angular momentum, for the spin angular momentum, the quantum picture is:

It is customary to write the wave functions of the electron which are eigenfunctions of $\mathbf{S}^2$ and $\mathbf{S}_z$ as α and β so that:

$$\hat{S}_z\alpha = m_s\hbar\alpha = +\frac{1}{2}\hbar\alpha$$

$$\hat{S}_z\beta = m_s\hbar\beta = -\frac{1}{2}\hbar\beta$$

Common thought is that the spin of the electron can be understood by think of the electron as a spinning sphere.

This is **wrong**. Spin does **not** depend on spatial coordinates. It is an intrinsic quantum property which has no classical analogue.

Electron spin is a bit weird!

Let $\alpha = |\uparrow\rangle$ and $\beta = |\downarrow\rangle$ = basis set functions of "spin space".

Can construct the matrix operator for $\mathbf{S}_z$ as:

$$\begin{pmatrix} \langle\uparrow|\hat{S}_z|\uparrow\rangle & \langle\uparrow|\hat{S}_z|\downarrow\rangle \\ \langle\downarrow|\hat{S}_z|\uparrow\rangle & \langle\downarrow|\hat{S}_z|\downarrow\rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2}\langle\uparrow|\uparrow\rangle & -\frac{\hbar}{2}\langle\uparrow|\downarrow\rangle \\ \frac{\hbar}{2}\langle\downarrow|\uparrow\rangle & -\frac{\hbar}{2}\langle\downarrow|\downarrow\rangle \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\hat{\sigma}_3$$

$\boldsymbol{\sigma}_3$ = one of three Pauli matrices = $\boldsymbol{\sigma}_z$

Eigenfunctions are $|+\rangle$ and $|-\rangle$

In the basis set of $|\uparrow>$ and $|\downarrow>$ matrices for $\mathbf{S}_x$ and $\mathbf{S}_y$ can also be derived;

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \text{ and } \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

This leads to the two other Pauli matrices:

$$\hat{\sigma}_x = \hat{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \text{ and } \hat{\sigma}_y = \hat{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Note: There is nothing special about the z-direction. The eigenvalues for electron spin along the x- or y-directions are also ±½; that is, the electron has spin one-half no matter which way you look at it.

Let the eigenfunctions of $\mathbf{S}_x$ = $|\rightarrow>$ and $|\leftarrow>$

Let the eigenfunctions of $\mathbf{S}_y$ = $|\otimes>$ and $|\bullet>$

Can show using the Pauli matrices that these eigenfunctions can be expressed as:

$$|\rightarrow\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle$$

$$|\leftarrow\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\rangle$$

$$|\otimes\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle + \frac{i}{\sqrt{2}}|\downarrow\rangle$$

$$|\bullet\rangle = \frac{1}{\sqrt{2}}|\uparrow\rangle - \frac{i}{\sqrt{2}}|\downarrow\rangle$$

This implies some remarkable information regarding spin.

For example: the spin-up state $|\uparrow\rangle$ and the spin-right state $|\rightarrow\rangle$ are **not** orthogonal.

$$\langle\uparrow|\rightarrow\rangle = \frac{1}{\sqrt{2}}\langle\uparrow|\uparrow\rangle + \frac{1}{\sqrt{2}}\langle\downarrow|\downarrow\rangle = \frac{1}{\sqrt{2}}$$

This is counter-intuitive. Your might expect spins in the **x** and **z** directions to be orthogonal.

One the other hand, you might not expect spins along the +**z** and –**z** directions to be orthogonal but they are! Spin is not spatial!

An electron whose spin is exactly along **x** is in a mixed state with respect to **z**: it is "half-up" and "half-down".

The expectation value of such a measurement can be found:

$$< \hat{S}_z >=<\rightarrow| \hat{S}_z |\rightarrow>= 0$$

This is consistent with a classical intuition. But be aware of what it really means quantum mechanically.

The probability of finding a component along **z** (up in the $|\uparrow>$ state or down in the $|\downarrow>$ state) is"

$$P(\uparrow)=\left|<\uparrow|\rightarrow>\right|^2=\frac{1}{2} \text{ and } P(\downarrow)=\left|<\downarrow|\rightarrow>\right|^2=\frac{1}{2}$$

The expectation value of $\mathbf{S}_z$ combines both values (up and down)

$$< \hat{S}_z >= \left(+\frac{\hbar}{2} \right) P(\uparrow) + \left(-\frac{\hbar}{2} \right) P(\downarrow) = 0$$

One will get zero only through doing many measurement. A single measurement won't work because $m_s = 0$ is not an eigenvalue of S_z. One can only measure **±½.**

Other particles have intrinsic spin:

Protons	$s = ½$	$m_s = \pm ½$
Neutrons	$s = ½$	$m_s = \pm ½$
Photons	$s = 1$	$m_s = \pm 1^{\star}$
Deuterons	$s = 1$	$m_s = o, \pm 1$

$\star$: light is a special case; no $m_s = 0$. $m_s = \pm 1$ refers to left-hand and right-hand circularly polarized light.

We know many atomic nuclei are NMR active which implies an intrinsic nuclear spin. Phenomenon is common.

Since electron spin is a separate independent variable we can write:

$$\left[\hat{H},\hat{S}_2\right]=\left[\hat{H},\hat{S}_{x,y,z}\right]$$
$$=\left[\hat{L}^2,\hat{S}^2\right]=\left[\hat{L}^2,\hat{S}_{x,y,z}\right]$$
$$=\left[\hat{L}_z,\hat{S}^2\right]=\left[\hat{L}_z,\hat{S}_{x,y,z}\right]$$
$$=\left[\hat{\Pi},\hat{S}^2\right]=\left[\hat{\Pi},\hat{S}_{x,y,z}\right]$$

Here **Π** is the parity operator which take **r** → -**r.**

If we call the spin eigenfunctions **χ**(m_s) the complete H-atom wave functions for example would be written:

$$\psi_{n,\ell,m_\ell,m_s}\left(\vec{r},m_s\right)=\psi_{n,\ell,m_\ell}\left(\vec{r}\right)\chi\left(m_s\right)$$ and

$$\left\langle\psi_{n,\ell,m_\ell}\chi(m_s)\middle|\psi_{n',\ell',m_\ell'}\chi(m_s')\right\rangle=\left\langle\psi_{n,\ell,m_\ell}\middle|\psi_{n',\ell',m_\ell'}\right\rangle\left\langle\chi(m_s)\middle|\chi(m_s')\right\rangle=\delta_{n,n'}\delta_{\ell,\ell'}\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'}$$

Summary of the H-atom eigenvalue problem with spin.

$$\hat{H}\psi_{n,\ell,m_\ell,m_s} = E_n\psi_{n,\ell,m_\ell,m_s}$$

$$\hat{L}^2\psi_{n,\ell,m_\ell,m_s} = \ell(\ell+1)\hbar^2\psi_{n,\ell,m_\ell,m_s}$$

$$\hat{S}^2\psi_{n,\ell,m_\ell,m_s} = s(s+1)\hbar^2\psi_{n,\ell,m_\ell,m_s}$$

$$\hat{L}_z\psi_{n,\ell,m_\ell,m_s} = m_\ell\hbar\,\psi_{n,\ell,m_\ell,m_s}$$

$$\hat{S}_z\psi_{n,\ell,m_\ell,m_s} = m_s\hbar\,\psi_{n,\ell,m_\ell,m_s}$$

$$\hat{\Pi}\,\psi_{n,\ell,m_\ell,m_s} = (-1)^\ell\psi_{n,\ell,m_\ell,m_s}$$

Parity (even/oddness of state not affected by spin)