e. Spin

Before discussing spin angular momentum we discuss orbital magnetic dipole moments. A classical picture of an orbiting electron permits calculation of the magnetic moment resulting from this motion of a circulating charge, i.e. an electric current as depicted below.

The circulating electron causes the system to mimic a bar magnet, the magnetic moment, $\mu_\ell$, of which is

$$\mu_\ell = \text{orbital magnetic moment} = iA$$

where

$$i = \text{current of circulating electron} = \left(\frac{ev}{2\pi r}\right)$$

and

$$A = \text{area of the current loop} = \pi r^2$$

Then
The orbital angular momentum is $L = mvr$ so that

$$\mu_\ell = \left(\frac{eV}{2\pi r}\right)(\pi r^2) = \frac{eVr}{2}$$

But, the orbital angular momentum is $L = mvr$ so that

$$\mu_\ell = \frac{e}{2m} \cdot L$$

which shows that the angular momentum is directly related to the magnetic moment. If we choose $L$ to be one unit of angular momentum, i.e. $L = \hbar$, then

$$\mu_B = \text{Bohr magneton} = \frac{e\hbar}{2m}$$

This is the orbital magnetic dipole moment of an electron in the first Bohr orbit. More generally we may write

$$\text{Orbital magnetic moment} = \mu_\ell = -\frac{g_\ell \mu_B}{\hbar} L$$

where $g_\ell$ is the orbital g-factor which is equal to one. The minus sign arises because of the negative charge on the electron, that is, the magnetic dipole moment and the angular momentum point in opposite directions.

The term "spin" represents the magnetic moment associated with a "spinning" sphere of charge, the electron. Note that the electron is still regarded as a point particle. A point particle cannot spin, but the concept is carried over from classical notions. Because the magnetic moment is associated with the electron itself, and has nothing to do with its orbital motion, the magnetic dipole moment associated with the spin is an *intrinsic* magnetic moment. It is built in to the electron, even if the electron is isolated in space.
But, in general $\mu$ is proportional to the angular momentum. Therefore, we may write

$$\text{Spin magnetic moment} = \mu_S = -g_S \frac{\mu_B}{\hbar} \mathbf{S}$$

where $g_S$ is the spin g-factor, which is equal to $(2 + \epsilon$ where $\epsilon$ is a small number).

For an electron it is found that the quantum number $j \rightarrow s = 1/2$. The quantum number $s$ is always equal to one-half. Further, the spin is not included in the Schrödinger equation so an arbitrary state is represented by a superposition of orbital states, $\psi$, and spin states, $\chi$.

$$|\psi> = \sum \psi(r) \cdot \chi(\text{spin})$$

We must now distinguish between values of $m$, the quantum number associated with the z-component of angular momentum, for orbital motion and spin. The conventional designations are:

<table>
<thead>
<tr>
<th>Angular momentum quantum number</th>
<th>z-component quantum number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j$</td>
<td>$m_j$</td>
</tr>
<tr>
<td>$\ell$</td>
<td>$m_\ell$</td>
</tr>
<tr>
<td>$s$</td>
<td>$m_s$</td>
</tr>
</tbody>
</table>

For an electron $s = 1/2$. Therefore $m_s = \pm 1/2$. These are the only possibilities!

Let $\chi_{s,m_s}$ be the simultaneous eigenfunctions of $S^2$ and $S_z$. Then
\[ S^2 \chi_{s,m_s} = s(s + 1) \hbar^2 \chi_{s,m_s} \quad \text{and} \quad S \chi_{s,m_s} = m_s \hbar \chi_{s,m_s} \]

There are a number of ways of condensing the notation for \( \chi \), depending upon the author. In one notation

\[ |\alpha\rangle = \alpha = \chi_{1/2,1/2} = "\text{spin up}" \quad \text{and} \quad |\beta\rangle = \beta = \chi_{1/2,-1/2} = "\text{spin down}" \]

Another notation

\[ |+\rangle = |\alpha\rangle \quad \text{and} \quad |--\rangle = |\beta\rangle \]

Since the total spin operator \( S \) is hermetian, \( |+\rangle \) and \|--\rangle \) are orthogonal so that

\[ \langle + | + \rangle = \langle -- | -- \rangle = 1 \quad \text{and} \quad \langle + | -- \rangle = 0 \]

The basis set may be represented by the kets \( |q, \pm\rangle \) where \( q \) represents all orbital quantum numbers, e.g. \( n \ell \), \( \ell \) \( m_\ell \) if we are considering an atom and the \( \pm \) represent spin up or down. An arbitrary wavefunction may be expanded on this basis set

\[ |\psi\rangle = \sum_q C_q^+ |q, +\rangle + \sum_q C_q^- |q, --\rangle \]

This \( |\psi\rangle \) contains both spin and orbital coordinates. Let \( |r, \pm\rangle \) represent the state in which the electron is localized at \( r \) and has spin up/down. We can form two wavefunctions in position representation

\[ <r,+|\psi\rangle = \sum_q C_q^+ <r,+|q, +\rangle = \text{probability amplitude for finding the electron at } r \text{ with spin up.} \]

with an analogous expression for \( |\psi_-(r)\rangle \).

We can combine these two amplitudes into a single two-component object called a spinor

\[ \begin{pmatrix} \psi_+(r) \\ \psi_-(r) \end{pmatrix} = |\psi_+(r)\rangle \begin{pmatrix} 1 \\ 0 \end{pmatrix} + |\psi_-(r)\rangle \begin{pmatrix} 0 \\ 1 \end{pmatrix} \]
The unit "vectors" \( \begin{pmatrix} 1 \\ 0 \end{pmatrix} \) & \( \begin{pmatrix} 0 \\ 1 \end{pmatrix} \) may be regarded as representations of \(|+\rangle\) and \(|\rightarrow\rangle\) respectively. If we use this representation, then operators such as \( S \) will have to be represented by \( 2 \times 2 \) matrices. We have

\[
S_z = \begin{pmatrix}
(S_z)_{11} & (S_z)_{12} \\
(S_z)_{21} & (S_z)_{22}
\end{pmatrix}
\]

so that the equation \( S_z |\alpha\rangle = (1/2)\hbar |\alpha\rangle \) becomes

\[
\begin{pmatrix}
(S_z)_{11} & (S_z)_{12} \\
(S_z)_{21} & (S_z)_{22}
\end{pmatrix}
\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} (1/2)\hbar \\ 0 \end{pmatrix}
\]

or

\[
\begin{pmatrix}
(S_z)_{11} \\
(S_z)_{21}
\end{pmatrix} = \begin{pmatrix} (1/2)\hbar \\ 0 \end{pmatrix}
\]

Therefore,

\[
(S_z)_{11} = \frac{\hbar}{2} \quad \& \quad (S_z)_{21} = 0
\]

and

\[
(S_z)_{12} = 0 \quad \& \quad (S_z)_{22} = -\left(\frac{1}{2}\right)\hbar
\]

Thus, on the basis set of the eigenfunctions of \( S_z \) we have

\[
S_z = \begin{pmatrix} (1/2)\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{pmatrix}
\]

Now we may use \( S_+ \) and \( S_- \) to find \( S_x \) and \( S_y \). Obviously

\[
S_+ |\alpha\rangle = 0 \quad \text{and} \quad S_- |\beta\rangle = 0
\]

Also
Similarly, \( S_x|\alpha> = \hbar|\beta> \). Combining the two expressions with \(|\alpha>\) on the left side we get

\[
S_x|\alpha> + S_x|\alpha> = 2S_x|\alpha> = 0 + \hbar|\beta> \quad \Rightarrow \quad S_x|\alpha> = \frac{1}{2}\hbar|\beta>
\]

The same procedure for the two expressions with \(|\beta>\) on the left gives

\[
S_x|\beta> + S_x|\beta> = 2S_x|\beta> = \hbar|\alpha> + 0 \quad \Rightarrow \quad S_x|\beta> = \frac{1}{2}\hbar|\alpha>
\]

Then, using \( S_x|\alpha> = (1/2)\hbar|\beta> \) we have

\[
\begin{pmatrix}
(S_x)_{11} & (S_x)_{12} \\
(S_x)_{21} & (S_x)_{22}
\end{pmatrix}
\begin{pmatrix}
1 \\
0
\end{pmatrix}
= \left(\frac{1}{2}\right)\hbar\begin{pmatrix}
0 \\
1
\end{pmatrix}
\]

or

\[
\begin{pmatrix}
(S_x)_{11} \\
(S_x)_{21}
\end{pmatrix}
= \left(\frac{1}{2}\right)\hbar\begin{pmatrix}
0 \\
1
\end{pmatrix}
\]

so that

\[
(S_x)_{11} = 0 \quad \text{and} \quad (S_x)_{21} = \frac{1}{2}\hbar
\]
Using \( S_x |\beta> = (1/2)\hbar |\alpha> \) we have

\[
\begin{pmatrix}
(S_x)_{11} & (S_x)_{12} \\
(S_x)_{21} & (S_x)_{22}
\end{pmatrix}
\begin{pmatrix}
0 \\
1
\end{pmatrix} = \left( \frac{1}{2} \right) \hbar \begin{pmatrix}
1 \\
0
\end{pmatrix}
\]

or

\[
\begin{pmatrix}
(S_x)_{12} \\
(S_x)_{22}
\end{pmatrix} = \left( \frac{1}{2} \right) \hbar \begin{pmatrix}
0 \\
1
\end{pmatrix}
\]

from which

\[
(S_x)_{12} = \frac{1}{2} \hbar \quad \& \quad (S_x)_{22} = 0
\]

so that

\[
S_x = \frac{1}{2} \hbar \begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}
\]

Applying the same technique to \( S_y \) we obtain

\[
S_y = \frac{1}{2} \hbar \begin{pmatrix}
0 & -i \\
i & 0
\end{pmatrix}
\]

For convenience the Pauli spin matrices are frequently used. These are defined as

\[
\begin{array}{ccc}
\sigma_x = \begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}; & \sigma_y = \begin{pmatrix}
0 & -i \\
i & 0
\end{pmatrix}; & \sigma_z = \begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\end{array}
\]

so that

\[
S = \frac{1}{2} \hbar \sigma \quad \text{where} \quad \sigma = \sigma_x i + \sigma_y j + \sigma_z k
\]

**EXERCISE**

1. Prove that the Pauli spin matrices are hermetian.

2. Show that the Pauli spin matrices obey the usual angular momentum commutation rules.
We now find the eigenstates of $S_x$ and $S_y$. To do this we use the matrix representation to determine the eigenstates of the operator

$$S_n = S \cdot n \quad \text{where} \quad n = \cos \phi i + \sin \phi j$$

This means that $n$ lies in the xy-plane as shown in the figure below.

![Diagram showing n in the xy-plane](image)

The choice $\phi = 0$ ($\phi = \pi/2$) will yield the eigenstates of $S_x$ ($S_y$). The eigenvalue equation is then

$$S_n |\mu> = \mu \left( \frac{\hbar}{2} \right) |\mu>$$

where the factor $\hbar/2$ has been inserted for convenience. Note that we know that putting the $(\hbar/2)$ factor in the eigenvalue equation will be convenient because the eigenvalues of $S_z$ are $\pm(\hbar/2)$. Since our choice of z-axis is arbitrary, $\pm(\hbar/2)$ must also be the eigenvalues of $S_n$.

In matrix form

$$S_n = S \cdot n$$

$$= \left( \frac{\hbar}{2} \right) \begin{pmatrix} \cos \phi & 0 \\ 0 & \sin \phi \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & i \end{pmatrix}$$

We wish to write the eigenvector as a linear combination of $S_z$ eigenkets,

$$|\mu> = a|\alpha> + b|\beta> \quad \text{where} \quad a = <\alpha|\mu> \quad \text{and} \quad b = <\beta|\mu>$$

In matrix form we have
\[
\left(\frac{\hbar}{2}\right)\begin{pmatrix} \cos \phi & 0 \\ 0 & \sin \phi \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \mu \left(\frac{\hbar}{2}\right)\begin{pmatrix} a \\ b \end{pmatrix}
\]

Collecting, we have

\[
\begin{pmatrix} -\mu & e^{-i\phi} \\ e^{i\phi} & -\mu \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0 \cdot \begin{pmatrix} a \\ b \end{pmatrix}
\]

This is a homogeneous equation in \(a\) and \(b\). A non-trivial solution exists only if the determinant of the coefficients vanishes,

\[
\begin{vmatrix} -\mu & e^{-i\phi} \\ e^{i\phi} & -\mu \end{vmatrix} = 0
\]

or

\[
\mu^2 - 1 = 0 \quad \Rightarrow \quad \mu = \pm 1
\]

Thus, the eigenvalues are \(\pm (\hbar/2)\), which, of course, we already knew.

We require the eigenkets that correspond to each of these eigenvalues. For \(\mu = +1\) call the eigenket \(\mid \mu_+ \rangle\). We have

\[
\begin{pmatrix} 1 & e^{-i\phi} \\ e^{i\phi} & 1 \end{pmatrix}\begin{pmatrix} a_+ \\ b_+ \end{pmatrix} = 0\]

from which

\[-a_+ + b_+ e^{-i\phi} = 0 \quad \text{or} \quad a_+ e^{i\phi} - b_+ = 0\]

which are the same equation.

From this equation we have

\[b_+ = e^{i\phi}a_+\]
But, we also have the normalization condition

\[ |a_+|^2 + |b_+|^2 = 1 \]

These two equations lead to

\[ |a_+|^2 = |b_+|^2 = \frac{1}{2} \]

so that we arrive at one eigenket of \( S_n \)

\[ |\mu_+> = \frac{1}{\sqrt{2}} |\alpha> + \frac{e^{i\phi}}{\sqrt{2}} |\beta> \]

Similarly

\[ |\mu_-> = \frac{1}{\sqrt{2}} |\alpha> - \frac{e^{i\phi}}{\sqrt{2}} |\beta> \]

Now, we may choose \( \phi = 0 \) to obtain the eigenkets of \( S_x \) which we denote by \( |\alpha>_x \) and \( |\beta>_x \)

\[ |\pm>_x = \frac{1}{\sqrt{2}} |\alpha> \pm \frac{1}{\sqrt{2}} |\beta> \]

To obtain the eigenkets of \( S_y \) we choose \( \phi = \pi/2 \)

\[ |\pm>_y = \frac{1}{\sqrt{2}} |\alpha> \pm \frac{i}{\sqrt{2}} |\beta> \]