Spin ½ (Pages 1-12 are needed)

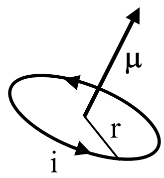
Recall that in the H-atom solution, we showed that the fact that the wavefunction $\psi(r)$ is single-valued requires that the angular momentum quantum number be integer: ℓ = 0, 1, 2.. However, operator algebra allowed solutions ℓ = 0, 1/2, 1, 3/2, 2…

Experiment shows that the electron possesses an intrinsic angular momentum called *spin* with ℓ = ½. By convention, we use the letter s instead of ℓ for the spin angular momentum quantum number : s = ½. The existence of spin is not derivable from non-relativistic QM. It is not a form of orbital angular momentum; it cannot be derived from $\vec{L} = \vec{r} \times \vec{p}$. (The electron is a point particle with radius r = 0.)

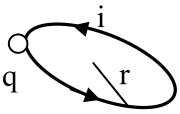
Electrons, protons, neutrons, and quarks all possess spin s = ½. Electrons and quarks are elementary point particles (as far as we can tell) and have no internal structure. However, protons and neutrons are made of 3 quarks each. The 3 half-spins of the quarks add to produce a total spin of ½ for the composite particle (in a sense, ↑↑↓ makes a single ↑). Photons have spin 1, mesons have spin 0, the delta-particle has spin 3/2. The graviton has spin 2. (Gravitons have not been detected experimentally, so this last statement is a theoretical prediction.)

Spin and Magnetic Moment

We can detect and measure spin experimentally because the spin of a charged particle is always associated with a magnetic moment. Classically, a magnetic moment is defined as a vector $\vec{\mu}$ associated with a loop of current. The direction of $\vec{\mu}$ is perpendicular to the plane of the current loop (right-hand-rule), and the magnitude is $\mu = iA = i\pi r^2$. The connection between orbital angular momentum (not spin) and magnetic moment can be seen in the following classical model: Consider a particle with mass m, charge q in circular orbit of radius r, speed v, period T.



$$i = \frac{q}{T}, \qquad v = \frac{2\pi r}{T} \qquad \Rightarrow \qquad i = \frac{q v}{2\pi r} \qquad \mu = i A = \left(\frac{q v}{2 \pi r}\right)\left(\pi r^2\right) = \frac{q v r}{2}$$



| angular momentum | = L = p r = m v r , so v r = L/m , and $\mu = \frac{q v r}{2} = \frac{q}{2m} L$.

So for a classical system, the magnetic moment is proportional to the orbital angular momentum:

$$\vec{\mu} = \frac{q}{2m}\vec{L} \quad \text{(orbital)}.$$

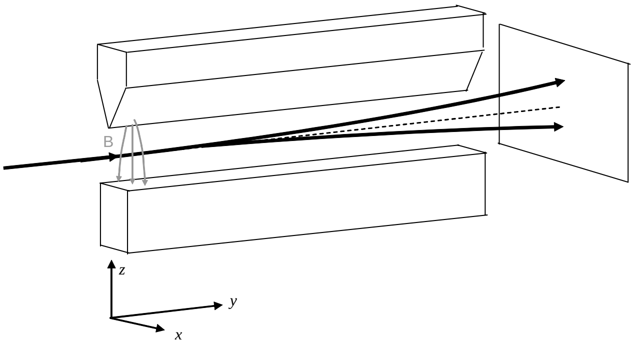
The same relation holds in a quantum system.

In a magnetic field B, the energy of a magnetic moment is given by $E = -\vec{\mu}\cdot\vec{B} = -\mu_z B$ (assuming $\vec{B} = B\hat{z}$). In QM, $L_z = \hbar m$. Writing electron mass as m_e (to avoid confusion with the magnetic quantum number m) and q = –e we have $\mu_z = -\frac{e\hbar}{2m_e} m$, where m = – ℓ .. + ℓ. The quantity $\mu_B \equiv \frac{e\hbar}{2m_e}$ is called the Bohr magneton. The possible energies of the magnetic moment in $\vec{B} = B\hat{z}$ is given by $E_{orb} = -\mu_z B = -\mu_B B m$.

For *spin* angular momentum, it is found experimentally that the associated magnetic moment is twice as big as for the orbital case: $\vec{\mu} = \frac{q}{m}\vec{S}$ (spin) (We use S instead of L when referring to spin angular momentum.) This can be written $\mu_z = -\frac{e\hbar}{m_e} m = -2\mu_B m$. The energy of a spin in a field is

$E_{spin} = -2\mu_B B m$ (m = ±1/2) a fact which has been verified experimentally. The existence of spin (s = ½) and the strange factor of 2 in the gyromagnetic ratio (ratio of $\vec{\mu}$ to $\vec{S}$) was first deduced from spectrographic evidence by Goudsmit and Uhlenbeck in 1925.

Another, even more direct way to experimentally determine spin is with a Stern-Gerlach device, (This page from QM notes of Prof. Roger Tobin, Physics Dept, Tufts U.)
Stern-Gerlach Experiment (W. Gerlach & O. Stern, Z. Physik **9**, 349-252 (1922).



$$\vec{F} = -\vec{\nabla}\left(\vec{\mu}\bullet\vec{B}\right) = -\vec{\mu}\bullet\vec{\nabla}\vec{B}$$

$$\vec{F} = \hat{z}\left(\mu_z \frac{\partial B_z}{\partial z}\right)$$

Deflection of atoms in z-direction is proportional to z-component of magnetic moment μ_z, which in turn is proportional to L_z. The fact that there are two beams is proof that ℓ = s = ½. The two beams correspond to m = +1/2 and m = –1/2. If ℓ = 1, then there would be three beams, corresponding to m = –1, 0, 1. The separation of the beams is a direct measure of μ_z, which provides proof that $\mu_z = -2\mu_B m$

The extra factor of 2 in the expression for the magnetic moment of the electron is often called the "g-factor" and the magnetic moment is often written as $\mu_z = -g\mu_B m$. As mentioned before, this cannot be deduced from non-relativistic QM; it is known from experiment and is inserted "by hand" into the theory. However, a relativistic version of QM due to Dirac (1928, the "Dirac Equation") predicts the existence of spin (s = ½) and furthermore the theory predicts the value g = 2. A later, better version of relativistic QM, called Quantum Electrodynamics (QED) predicts that g is a little larger than 2. The g-factor has been carefully measured with fantastic precision and the latest experiments give g = 2.0023193043718(±76 in the last two places). Computing g in QED requires computation of a infinite series of terms that involve progressively more messy integrals, that can only be solved with approximate numerical methods. The computed value of g is not known quite as precisely as experiment, nevertheless the agreement is good to about 12 places. QED is one of our most well-verified theories.

Spin Math

Recall that the angular momentum commutation relations

$$[\hat{L}^2, \hat{L}_z] = 0, \qquad [\hat{L}_i, \hat{L}_j] = i\hbar \hat{L}_k \quad \text{(i, j, and k cyclic)}$$

were derived from the definition of the orbital angular momentum operator: $\vec{L} = \vec{r} \times \vec{p}$.

The spin operator $\vec{S}$ does not exist in Euclidean space (it doesn't have a position or momentum vector associated with it), so we cannot derive its commutation relations in a similar way. Instead we boldly ***postulate*** that the same commutation relations hold for spin angular momentum:

$$[\hat{S}^2, \hat{S}_z] = 0, \qquad [\hat{S}_i, \hat{S}_j] = i\hbar \hat{S}_k .$$

From these, we derive, just a before, that

$$\hat{S}^2 |s\, m_s\rangle = \hbar^2 s(s+1) |s\, m_s\rangle = \frac{3}{4}\hbar^2 |s\, m_s\rangle \qquad \text{(since s = ½)}$$

$$\hat{S}_z |s\, m_s\rangle = \hbar m_s |s\, m_s\rangle = \pm\frac{1}{2}\hbar |s\, m_s\rangle \qquad \text{(since } m_s = -s, +s = -1/2, +1/2 \text{)}$$

Notation: since s = ½ always, we can drop this quantum number, and specify the eigenstates of $\hat{S}^2$, and $\hat{S}_z$ by giving only the m_s quantum number. There are various ways to write this:

$$\chi_\pm = |s, m_s> = |m_s> \equiv \begin{cases} \text{spin up } (\uparrow) \equiv \chi_+ \equiv |\alpha\rangle \equiv |\frac{1}{2}> \equiv |+> \equiv \begin{pmatrix}1\\0\end{pmatrix} \\ \text{spin down } (\downarrow) \equiv \chi_- \equiv |\beta\rangle \equiv |-\frac{1}{2}> \equiv |-> \equiv \begin{pmatrix}0\\1\end{pmatrix} \end{cases}$$

These states exist in a 2D subset of the full Hilbert Space called *spin space*. Since these two states are eigenstates of a Hermitian operator, they form a complete orthonormal set (within their part of Hilbert space) and any, arbitrary state in spin space can always be written as $|\chi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \begin{pmatrix}a\\b\end{pmatrix}$ and the normalization gives:

$$\langle\chi|\chi\rangle = 1 \quad \Rightarrow \quad |a|^2 + |b|^2 = 1.$$

.

Note that:

$$\langle\uparrow|\uparrow\rangle = \begin{pmatrix}1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = 1,$$

similarly:

$$\langle\downarrow|\downarrow\rangle = 1, \quad \langle\uparrow|\downarrow\rangle = \langle\downarrow|\uparrow\rangle = 0$$

If we were working in the full Hilbert Space of, say, the H-atom problem, then our basis states would be $|\ell\ m_\ell\ s\ m_s\rangle$. *n* is another degree of freedom, so that the full specification of a basis state requires 4 quantum numbers without *n*. (More on the connection between spin and space parts of the state later.)

[Note on language: throughout this section I will use the symbol $\hat{S}_z$ (and $\hat{S}_x$, etc) to refer to both the observable ("the measured value of $\hat{S}_z$ is $+\hbar/2$") and its associated operator ("the eigenvalue of $\hat{S}_z$ is $+\hbar/2$").

The matrix form of S^2 and S_z in the $|m^{(z)}\rangle$ basis can be worked out element by element. (Recall that for any operator $\hat{A}$, $A_{mn} = \langle m|\hat{A}|n\rangle$

$$\langle\uparrow|\hat{S}^2|\uparrow\rangle = +\frac{3}{4}\hbar^2\,\delta_{ss'}\delta_{m_s m_s'}, \quad \langle\downarrow|\hat{S}^2|\downarrow\rangle = +\frac{3}{4}\hbar^2\,\delta_{ss'}\delta_{m_s m_s'}, \quad \langle\uparrow|\hat{S}^2|\downarrow\rangle = 0, \text{ etc.}$$

$$\langle\uparrow|\hat{S}_z|\uparrow\rangle = +\frac{1}{2}\hbar\,\delta_{ss'}\delta_{m_s m_s'}, \quad \langle\downarrow|\hat{S}_z|\downarrow\rangle = -\frac{1}{2}\hbar\,\delta_{ss'}\delta_{m_s m_s'}, \quad \langle\uparrow|\hat{S}_z|\downarrow\rangle = 0, \text{ etc.}$$

Then in the matrix notation one finds:

$$\left(\hat{S}_z\right) = \begin{pmatrix}\langle\alpha|\hat{S}_z|\alpha\rangle & \langle\alpha|\hat{S}_z|\beta\rangle \\ \langle\beta|\hat{S}_z|\alpha\rangle & \langle\beta|\hat{S}_z|\beta\rangle\end{pmatrix} = \begin{pmatrix}\frac{\hbar}{2}\langle\alpha|\alpha\rangle & -\frac{\hbar}{2}\langle\alpha|\beta\rangle \\ \frac{\hbar}{2}\langle\beta|\alpha\rangle & -\frac{\hbar}{2}\langle\beta|\beta\rangle\end{pmatrix} = \begin{pmatrix}\frac{\hbar}{2}\times 1 & -\frac{\hbar}{2}\times 0 \\ \frac{\hbar}{2}\times 0 & -\frac{\hbar}{2}\times 1\end{pmatrix}$$

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

and

$$\left(\hat{S}^2\right) = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

Operator equations can be written in matrix form, for instance,

$$\hat{S}_z\left|\uparrow\right\rangle = +\frac{\hbar}{2}\left|\uparrow\right\rangle \quad \Rightarrow \quad \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = +\frac{\hbar}{2}\begin{pmatrix}1\\ 0\end{pmatrix}$$

We are going ask; what happens when we make measurements of S_z, as well as S_x and S_y ?, (using a Stern-Gerlach apparatus). Will need to know: What are the matrices for the operators S_x and S_y ? These are derived from the raising and lowering operators:

$$\begin{aligned}\hat{S}_+ &= \hat{S}_x + i\hat{S}_y\\ \hat{S}_- &= \hat{S}_x - i\hat{S}_y\end{aligned} \quad \Rightarrow \quad \begin{aligned}\hat{S}_x &= \tfrac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right)\\ \hat{S}_y &= \tfrac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right)\end{aligned}$$

To get the matrix forms of $\hat{S}_+$ and $\hat{S}_-$, we need a result:

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

For the case s = ½, the square root factors are always 1 or 0. For instance, s = ½, m = −1/2 gives $s(s+1) - m(m+1) = \tfrac{1}{2}\left(\tfrac{3}{2}\right) - \left(-\tfrac{1}{2}\right)\left(\tfrac{1}{2}\right) = 1$. Consequently,

$$\hat{S}_+\left|\downarrow\right\rangle = \hbar\left|\uparrow\right\rangle, \quad \hat{S}_+\left|\uparrow\right\rangle = 0 \text{ and } \hat{S}_-\left|\uparrow\right\rangle = \hbar\left|\downarrow\right\rangle, \quad \hat{S}_-\left|\downarrow\right\rangle = 0,$$

leading to

$$\left\langle\uparrow\right|S_+\left|\uparrow\right\rangle = 0, \quad \left\langle\uparrow\right|S_+\left|\downarrow\right\rangle = \hbar, \text{ etc.}$$

Then:

$$\left(\hat{S}_+\right) = \begin{pmatrix}\langle +|\hat{S}_+|+\rangle & \langle +|\hat{S}_+|-\rangle\\ \langle -|\hat{S}_+|+\rangle & \langle -|\hat{S}_+|-\rangle\end{pmatrix} = \begin{pmatrix}0 & \hbar\langle +|+\rangle\\ 0 & \hbar\langle -|+\rangle\end{pmatrix} = \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}$$

and

$$\left(\hat{S}_-\right) = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}$$

Notice that S_+, S_- are not Hermitian.

Using $\hat{S}_x = \tfrac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right)$ and $\hat{S}_y = \tfrac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right)$ yields

$$\left(\hat{S}_x\right) = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \left(\hat{S}_y\right) = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$$

These are Hermitian, of course.

H.W. Check the following table:

	$\vert\alpha\rangle$	$\vert\beta\rangle$		$\vert\alpha\rangle$	$\vert\beta\rangle$
$\hat{S}^2$	$\frac{3}{4}\vert\alpha\rangle$	$\frac{3}{4}\vert\beta\rangle$	$\hat{S}_y$	$\frac{i}{2}\vert\beta\rangle$	$-\frac{i}{2}\vert\alpha\rangle$
$\hat{S}_z$	$\frac{1}{2}\vert\alpha\rangle$	$-\frac{1}{2}\vert\beta\rangle$	$\hat{S}_+$	0	$\vert\alpha\rangle$
$\hat{S}_x$	$\frac{1}{2}\vert\beta\rangle$	$\frac{1}{2}\vert\alpha\rangle$	$\hat{S}_-$	$\vert\beta\rangle$	0

Example: Find the expectation value for the Hamiltonian $\hat{H} = a(\hat{S}_x^2 + \hat{S}_y^2 - 2\hat{S}_z^2) + b\hat{S}_z$ **, where a and b are constants.**

Answer: Use the expression; $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$

We can find:

$$\begin{aligned}\hat{H} &= a(\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 - 3\hat{S}_z^2) + b\hat{S}_z \\ &= a\hat{S}^2 - 3a\hat{S}_z^2 + b\hat{S}_z\end{aligned}$$

And

$$\begin{aligned}\hat{H}\left|s, m_s\right\rangle &= \left\{a\hat{S}^2 - 3a\hat{S}_z^2 + b\hat{S}_z\right\}\left|s, m_s\right\rangle \\ &= \left\{as(s+1) - 3am_s^2 + bm_s\right\}\left|s, m_s\right\rangle \\ &= \left\{\frac{3}{4}a - 3\frac{1}{4}a + bm_s\right\}\left|s, m_s\right\rangle = bm_s\left|s, m_s\right\rangle\end{aligned}$$

Then

$$\left\langle s, m_s\right|\hat{H}\left|s, m_s\right\rangle = bm_s\left\langle s, m_s \middle| s, m_s\right\rangle = bm_s$$

One-electron system

The Hamiltonian

$$H_o = \frac{p^2}{2m} - \frac{Z}{r}$$

has the uncoupled wave function $\left|\ell, m_\ell, s, m_s\right\rangle = \left|\ell, m_\ell\right\rangle\left|s, m_s\right\rangle$ which identify the angular and spin parts of the wave function. m_ℓ is the projection quantum number associated with ℓ and m_s is the projection quantum number associated with s satisfies the relations:

$$\left\langle \ell', m_\ell', s', m_s'\right|\hat{L}^2\left|\ell, m_\ell, s, m_s\right\rangle = \ell(\ell+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

$$\left\langle \ell', m_\ell', s', m_s'\right|\hat{L}_z\left|\ell, m_\ell, s, m_s\right\rangle = m_\ell\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

$$\left\langle \ell', m_\ell', s', m_s'\right|\hat{S}^2\left|\ell, m_\ell, s, m_s\right\rangle = s(s+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

$$\left\langle \ell', m_\ell', s', m_s'\right|\hat{S}_z\left|\ell, m_\ell, s, m_s\right\rangle = m_s\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

Aslo, the wave function $\left|\ell, s, j, m_j\right\rangle$ in LS-coupling has similar relations:

$$\left\langle \ell', s', j', m_j'\right|\hat{L}^2\left|\ell, s, j, m_j\right\rangle = \ell(\ell+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\left\langle \ell', s', j', m_j'\right|\hat{S}^2\left|\ell, s, j, m_j\right\rangle = s(s+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\left\langle \ell', s', j', m_j'\right|\hat{J}^2\left|\ell, s, j, m_j\right\rangle = j(j+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\left\langle \ell', s', j', m_j'\right|\hat{J}_z\left|\ell, s, j, m_j\right\rangle = m_j\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

In which $\vec{J} = \vec{L} + \vec{S}$, and

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}.\hat{S} = \hat{L}^2 + \hat{S}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+ ,$$

Note that $\left|\ell, s, j, m_j\right\rangle$ are not eigenfunctions of $\hat{L}_z$ or $\hat{S}_z$. $\left|\ell, s, j, m_j\right\rangle$ are said to be in the coupled representation.

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

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

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

$$\hat{L}_\pm\left|l, m\right\rangle = \hbar\sqrt{l(l+1) - m(m\pm 1)}\left|l, m\pm 1\right\rangle$$

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y = \pm\hbar e^{\pm i\varphi}\left[\frac{\partial}{\partial\theta} \pm i\,\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

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

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

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

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}.\hat{S} = \hat{L}^2 + \hat{S}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+$$

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z, \quad \left[\hat{J}_y, \hat{J}_z\right] = i\hbar\hat{J}_x, \quad \left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y \Rightarrow \vec{\hat{J}} \times \vec{\hat{J}} = i\hbar\vec{\hat{J}}$$

$$\hat{J}^2 \mid j, m_j > = \hbar^2 j(j+1) \mid j, m_j >$$

$$\hat{J}_z \mid j, m_j > = m_j\hbar \mid j, m_j >; \quad \hat{J}_z^2 \mid j, m_j > = m_j^2\hbar \mid j, m_j >$$

$$\hat{J}_\pm \mid j, m_j > = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)} \mid j, m_j \pm 1 >$$

$$\left[\hat{J}_+, \hat{J}_-\right] = 2\hbar\hat{J}_z, \quad \left[\hat{J}_z, \hat{J}_-\right] = -\hbar\hat{J}_-, \quad \left[\hat{J}_z, \hat{J}_+\right] = \hbar\hat{J}_+$$

$$\left[\hat{J}^2, \hat{J}_+\right] = \left[\hat{J}^2, \hat{J}_-\right] = \left[\hat{J}^2, \hat{J}_x\right] = \left[\hat{J}^2, \hat{J}_y\right] = \left[\hat{J}^2, \hat{J}_z\right] = 0,$$

Addition of Angular momentum

1- Two spin $\frac{1}{2}$ particles

Let $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ denote spin operators of two different electrons (or neutrons and protons). Then, there are 4 independent states.

$|s_{1z}, s_{2z}\rangle = |\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$

where $|\uparrow\rangle = |s=\frac{1}{2}, s_z=\frac{1}{2}\rangle$ and $|\downarrow\rangle = |s=\frac{1}{2}, s_z=-\frac{1}{2}\rangle \Rightarrow |\uparrow\uparrow\rangle = |s_1, s_2, s_{1z}, s_{2z}\rangle = |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle$

These eigenstates are direct product of $\chi^{\uparrow}(1)$, $\chi^{\downarrow}(1)$, $\chi^{\uparrow}(2)$, $\chi^{\downarrow}(2)$ which are eigenstates of $\hat{S}_1^2$, $\hat{S}_2^2$, $\hat{S}_{1z}$, and $\hat{S}_{2z}$.

Example) $|\uparrow\uparrow\rangle = \chi^{\uparrow}(1)\chi^{\uparrow}(2)$

$\Rightarrow \hat{S_{1z}}|\uparrow\uparrow\rangle = \frac{\hbar}{2}|\uparrow\uparrow\rangle$, $\hat{S_{2z}}|\uparrow\uparrow\rangle = \frac{\hbar}{2}|\uparrow\uparrow\rangle$, $\hat{S_1^2}|\uparrow\uparrow\rangle = \frac{3}{4}\hbar^2|\uparrow\uparrow\rangle$, $\hat{S_2^2}|\uparrow\uparrow\rangle = \frac{3}{4}\hbar^2|\uparrow\uparrow\rangle$

We can also consider the total spin $\hat{\mathbf{S}}$ of the two electron system. $\boxed{\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2}$

Since $[\hat{\mathbf{S}}_1, \hat{\mathbf{S}}_2] = 0$ (because they act on different particles), we see that $\hat{S}_i$, $\hat{S}_j$, and $\hat{S}_k$ satisfy the angular momentum commutator relation.

$[\hat{S}_i, \hat{S}_j] = [\hat{S}_{1i} + \hat{S}_{2i}, \hat{S}_{1j} + \hat{S}_{2j}] = [\hat{S}_{1i}, \hat{S}_{1j}] + [\hat{S}_{2i}, \hat{S}_{2j}] = i\hbar\varepsilon_{ijk}\hat{S}_{1k} + i\hbar\varepsilon_{ijk}\hat{S}_{2k}$

$\Rightarrow \boxed{[\hat{S}_i, \hat{S}_j] = i\hbar\varepsilon_{ijk}\hat{S}_k}$

Hence it follows that $[\hat{S}^2, \hat{S}_z] = 0$ and we can construct simultaneous eigenstates of $\hat{S}^2$ and $\hat{S}_z$ (total angular momentum magnitude and its z-component) $|s, s_z\rangle$ where $s_z = -s, -s+1, \cdots, s-1, s$

The problem is

(i) What are possible eigenstates of $\hat{S}^2$ and $\hat{S}_z$?

(ii) How can we construct the eigenstate $|s, s_z\rangle$ in terms of the 4 basis states $(|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle)$?

First, note that 4 basis states are eigenstates of $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$.

$$\begin{aligned}
\hat{S}_z|\uparrow\uparrow\rangle &= (\hat{S}_{1z} + \hat{S}_{2z})|\uparrow\uparrow\rangle = \frac{\hbar}{2}|\uparrow\uparrow\rangle + \frac{\hbar}{2}|\uparrow\uparrow\rangle = \hbar|\uparrow\uparrow\rangle \\
\hat{S}_z|\uparrow\downarrow\rangle &= (\hat{S}_{1z} + \hat{S}_{2z})|\uparrow\downarrow\rangle = \frac{\hbar}{2}|\uparrow\downarrow\rangle - \frac{\hbar}{2}|\uparrow\downarrow\rangle = 0|\uparrow\downarrow\rangle \\
\hat{S}_z|\downarrow\uparrow\rangle &= (\hat{S}_{1z} + \hat{S}_{2z})|\downarrow\uparrow\rangle = -\frac{\hbar}{2}|\downarrow\uparrow\rangle + \frac{\hbar}{2}|\downarrow\uparrow\rangle = 0|\downarrow\uparrow\rangle \\
\hat{S}_z|\downarrow\downarrow\rangle &= (\hat{S}_{1z} + \hat{S}_{2z})|\downarrow\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\downarrow\rangle - \frac{\hbar}{2}|\downarrow\downarrow\rangle = -\hbar|\downarrow\downarrow\rangle
\end{aligned}$$

Possible eigenvalues of $\hat{S}_z$ are $0, \hbar, 0, -\hbar$. But these direct product states are not eigenstates of $\hat{S}^2$ in general.

$$\hat{S}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z})$$

Alternative way to get eigenstates of $\hat{S}^2$ and $\hat{S}_z$

In order to obtain eigenstates of $\hat{S}^2$ and $\hat{S}_z$, using $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$ as basis state, you can construct and diagonalize the corresponding matrices of $\hat{S}^2$ and $\hat{S}_z$.

$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + (\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}) + 2\hat{S}_{1z}\hat{S}_{2z}$

$$\begin{aligned}
\hat{S}^2|\uparrow\uparrow\rangle &= (\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2)|\uparrow\uparrow\rangle + 0 + 0 + 2\frac{\hbar}{2}\frac{\hbar}{2}|\uparrow\uparrow\rangle = 2\hbar^2|\uparrow\uparrow\rangle \\
\hat{S}^2|\uparrow\downarrow\rangle &= (\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2)|\uparrow\downarrow\rangle + 0 + \hbar^2|\uparrow\downarrow\rangle + 2\frac{\hbar}{2}(-\frac{\hbar}{2})|\uparrow\downarrow\rangle = \hbar^2(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\
\hat{S}^2|\downarrow\uparrow\rangle &= (\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2)|\downarrow\uparrow\rangle + \hbar^2|\downarrow\uparrow\rangle + 0 + 2(-\frac{\hbar}{2})\frac{\hbar}{2}|\downarrow\uparrow\rangle = \hbar^2(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) \\
\hat{S}^2|\downarrow\downarrow\rangle &= \; = 2\hbar^2|\downarrow\downarrow\rangle
\end{aligned}$$

Then, matrix corresponding to $\hat{S}^2$

$$\hat{S}^2 = \begin{pmatrix} 2\hbar^2 & 0 & 0 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & \hbar^2 & \hbar^2 & 0 \\ 0 & 0 & 0 & 2\hbar^2 \end{pmatrix} \quad \Rightarrow \quad |\hat{S}^2 - \lambda\hat{1}| = 0$$

Diagonalization: eigenvalue and eigenvector

(i) eigenvalue: $2\hbar^2$, eigenvector: $\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$ (ii) eigenvalue: $2\hbar^2$, eigenvector: $\begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$

Diagonalize $\hbar^2 \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \Rightarrow \begin{vmatrix} 1-\lambda & 1 \\ 1 & 1-\lambda \end{vmatrix} = 0 \Rightarrow (1-\lambda)^2 = 1 \Rightarrow \lambda = 2, 0$

(iii) eigenvalue: $2\hbar^2$, eigenvector: $\frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix}$ (iv) eigenvalue: 0, eigenvector: $\frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}$

Therefore, we have two basis sets and the transformation between them are given as follows.

Uncoupled representation:

$|s_1^2, s_2^2, s_{1z}, s_{2z}\rangle = |\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$

Coupled representation:

$$|s^2, s_z, s_1^2, s_2^2\rangle = \left\{ \begin{array}{cc} \text{triplet states} & \text{singlet state} \\ |1,1\rangle = |\uparrow\uparrow\rangle & \\ |1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & |0,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ |1,-1\rangle = |\downarrow\downarrow\rangle & \end{array} \right.$$

$$\hat{s}_{iz}\left|s_i m_i\right\rangle = m_i\hbar\left|s_i m_i\right\rangle$$

$$\hat{s}_i^2\left|s_i m_i\right\rangle = s_i(s_i+1)\hbar^2\left|s_i m_i\right\rangle \quad , \quad i=1,2 \qquad \text{(I)}$$

$$\left|s_1 m_1 s_2 m_2\right\rangle \equiv \left|s_1 m_1\right\rangle\left|s_2 m_2\right\rangle \qquad \text{(II)}$$

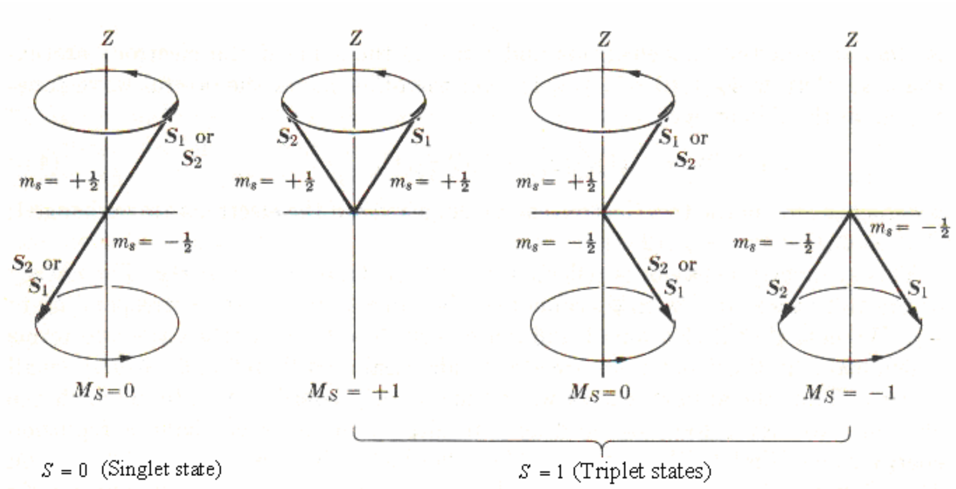
$s_1 = s_2 = \frac{1}{2}$

$$\begin{aligned}
\hat{s}_{1z}\left|s_1 m_1 s_2 m_2\right\rangle &= m_1\hbar\left|s_1 m_1 s_2 m_2\right\rangle \\
\hat{s}_1^2\left|s_1 m_1 s_2 m_2\right\rangle &= s_1(s_1+1)\hbar^2\left|s_1 m_1 s_2 m_2\right\rangle \\
\hat{s}_{2z}\left|s_1 m_1 s_2 m_2\right\rangle &= m_2\hbar\left|s_1 m_1 s_2 m_2\right\rangle \\
\hat{s}_2^2\left|s_1 m_1 s_2 m_2\right\rangle &= s_2(s_2+1)\hbar^2\left|s_1 m_1 s_2 m_2\right\rangle
\end{aligned} \qquad \text{(III)}$$

$$\begin{aligned}
\hat{s}_z\left|s_1 m_1 s_2 m_2\right\rangle &= \left(\hat{s}_{1z}+\hat{s}_{2z}\right)\left|s_1 m_1 s_2 m_2\right\rangle \\
&= \left(\hat{s}_{1z}\left|s_1 m_1\right\rangle\right)\left|s_2 m_2\right\rangle + \left(\hat{s}_{2z}\left|s_2 m_2\right\rangle\right)\left|s_1 m_1\right\rangle \\
&= \hbar\left[\left(m_1\left|s_1 m_1\right\rangle\right)\left|s_2 m_2\right\rangle + \left(m_2\left|s_2 m_2\right\rangle\right)\left|s_1 m_1\right\rangle\right] \\
&= \left(m_1+m_2\right)\hbar\left|s_1 m_1 s_2 m_2\right\rangle \\
&= m\hbar\left|s_1 m_1 s_2 m_2\right\rangle
\end{aligned} \qquad \text{(IV)}$$

$$m = m_1 + m_2 \qquad \text{(V)}$$

$$\hat{s}^2 = \left(\hat{s}_1+\hat{s}_2\right)^2 = \left(\hat{s}_{1x}+\hat{s}_{2x}\right)^2 + \left(\hat{s}_{1y}+\hat{s}_{2y}\right)^2 + \left(\hat{s}_{1z}+\hat{s}_{2z}\right)^2$$



$$\chi_S = \left\{\begin{array}{lll} |11\rangle & = & |\alpha\rangle_1|\alpha\rangle_2 \\ |10\rangle & = & \frac{1}{\sqrt{2}}\left[|\beta\rangle_1|\alpha\rangle_2 + |\alpha\rangle_1|\beta\rangle_2\right] \\ |1-1\rangle & = & |\beta\rangle_1|\beta\rangle_2 \end{array}\right\} \text{ triplet states (Symmetric, Ortho or Even)}$$

$$\chi_A = \quad |00\rangle = \frac{1}{\sqrt{2}}\left[|\beta\rangle_1|\alpha\rangle_2 - |\alpha\rangle_1|\beta\rangle_2\right] \quad \text{singlet states (Antisymmetric, Para or Odd)}$$

$$\hat{S}_z\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2-\beta_1\alpha_2\right)=\sqrt{\frac{1}{2}}\left(\hat{s}_{1z}+\hat{s}_{2z}\right)\left(\alpha_1\beta_2-\beta_1\alpha_2\right)$$
$$=\sqrt{\frac{1}{2}}\left[\beta_2\left(\hat{s}_{1z}\alpha_1\right)-\alpha_2\left(\hat{s}_{1z}\beta_1\right)+\alpha_1\left(\hat{s}_{2z}\beta_2\right)-\beta_1\left(\hat{s}_{2z}\alpha_2\right)\right]$$
$$=\hbar\sqrt{\frac{1}{2}}\left(\frac{1}{2}\beta_2\alpha_1+\frac{1}{2}\alpha_2\beta_1-\frac{1}{2}\alpha_1\beta_2-\frac{1}{2}\beta_1\alpha_2\right)=0$$

H.W.

$$\hat{S}^2=\left(\hat{s}_1+\hat{s}_2\right)^2=\hat{s}_1^2+\hat{s}_2^2+2\hat{s}_1\cdot\hat{s}_2=\hat{s}_1^2+\hat{s}_2^2+2\left[\hat{s}_{1z}\hat{s}_{2z}+\frac{1}{2}\left(\hat{s}_{+1}\hat{s}_{-2}+\hat{s}_{-1}\hat{s}_{+2}\right)\right]$$
$$=\hat{s}_1^2+\hat{s}_2^2+2\hat{s}_{1z}\hat{s}_{2z}+\left(\hat{s}_{+1}\hat{s}_{-2}+\hat{s}_{-1}\hat{s}_{+2}\right)$$

H.W. check the following

$$\hat{S}^2\psi=0\,\psi,\quad \psi=\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2-\beta_1\alpha_2\right)$$
$$\hat{s}_1^2\psi=\frac{3}{4}\psi,\quad \hat{s}_2^2\psi=\frac{3}{4}\psi,\quad 2\hat{s}_{1z}\hat{s}_{2z}\psi=2\left(-\frac{1}{4}\right)\psi$$
$$\hat{s}_{+1}\hat{s}_{-2}\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2-\beta_1\alpha_2\right)=\sqrt{\frac{1}{2}}\left(0-\alpha_1\beta_2\right)$$
$$\hat{s}_{-1}\hat{s}_{+2}\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2-\beta_1\alpha_2\right)=\sqrt{\frac{1}{2}}\left(\beta_1\alpha_2-0\right)$$

$$\hat{S}^2\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2+\beta_1\alpha_2\right)=1(1+1)\hbar^2\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2+\beta_1\alpha_2\right),$$
$$\hat{S}_z\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2+\beta_1\alpha_2\right)=0\hbar\sqrt{\frac{1}{2}}\left(\alpha_1\beta_2+\beta_1\alpha_2\right)$$

Q: What is the configuration for the p -orbital (ℓ=1) for the electron in the Hydrogen atom in LSJ-coupling scheme?

Answer: The wave function of the Hydrogen atom can be given by:

$$\Psi_{total} \equiv R_{n\ell}(r)Y_{\ell,m_\ell}(\theta,\varphi)\chi_{\pm} = \left|n,\ell,m_\ell\right\rangle\left|s,m_s\right\rangle = \left|n,\ell,m_\ell,s,m_s\right\rangle = \left|n,\ell,s,j,m_j\right\rangle$$

Where $\left|\ell=1, s=\frac{1}{2}, j=1\pm\frac{1}{2}, m_j = j, j-1,\cdots,-j\right\rangle$.

Here we have two cases;

First case at:

$$j_{\max} = \ell + s = 1+\frac{1}{2} = \frac{3}{2} \quad \Rightarrow \quad m_j = \frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2}$$

And it has **four** degenerate states.

Second case at:

$$j_{\min} = \ell - s = 1-\frac{1}{2} = \frac{1}{2} \quad \Rightarrow \quad m_j = \frac{1}{2},-\frac{1}{2}$$

And it has **two** degenerate states.

Start with the highest value $j_{\max} = \frac{3}{2}$, so

coupled		uncoupled
$\left\|j,m_j\right\rangle$		$\left\|m_\ell,m_s\right\rangle$
$\left\|\frac{3}{2}\frac{3}{2}\right\rangle' = Y_{1,1}\alpha$	=	$\left\|1,\frac{1}{2}\right\rangle$

Using the relation: $\hat{J}_{\pm}\left|j,m_j\right\rangle = \hbar\sqrt{j(j+1)-m_j(m_j\pm1)}\left|j,m_j\pm1\right\rangle$, one finds in the coupled representation:

$$\hat{J}_{-}\left|\frac{3}{2},\frac{3}{2}\right\rangle' = \left(\hat{L}_{-}+\hat{S}_{-}\right)\left|1,\frac{1}{2}\right\rangle \qquad (*)$$

LHS of (*) implies:

$$\hat{J}_{-}\left|\frac{3}{2},\frac{3}{2}\right\rangle' = \left[\frac{3}{2}(\frac{3}{2}+1)-\frac{3}{2}(\frac{3}{2}-1)\right]^{1/2}\left|\frac{3}{2},\frac{1}{2}\right\rangle' = \sqrt{3}\left|\frac{3}{2},\frac{1}{2}\right\rangle' \qquad (A)$$

And the RHS of (*) implies:

$$\left(\hat{L}_{-}+\hat{S}_{-}\right)\left|1,\frac{1}{2}\right\rangle = \hat{L}_{-}\left|1,\frac{1}{2}\right\rangle + \hat{S}_{-}\left|1,\frac{1}{2}\right\rangle$$

$$= \left[1(1+1)-1(1-1)\right]^{1/2}\left|0,\frac{1}{2}\right\rangle + \left[\frac{1}{2}(\frac{1}{2}+1)-\frac{1}{2}(\frac{1}{2}-1)\right]^{1/2}\left|1,-\frac{1}{2}\right\rangle = \sqrt{2}\left|0,\frac{1}{2}\right\rangle + 1\left|1,-\frac{1}{2}\right\rangle \qquad (B)$$

Equate the equations (A) and (B), we have:

$$\left|\frac{3}{2},\frac{1}{2}\right\rangle' = \sqrt{\frac{2}{3}}\left|0,\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|1,-\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}Y_{1,0}\alpha + \sqrt{\frac{1}{3}}Y_{1,1}\beta$$

What is the last equation mean? The last equation indicates that the eigen state $\left|j,m_j\right\rangle$ is a linear combination of the eigen states $\left|l,s\right\rangle\left|m_l,m_s\right\rangle$.

Check your expression: $\underbrace{\left|\frac{3}{2},\frac{1}{2}\right\rangle'}_{|j,m_j\rangle} = \underbrace{\sqrt{\frac{2}{3}}}_{c_1} \underbrace{\left|0,\frac{1}{2}\right\rangle}_{|m_l,m_S\rangle} + \underbrace{\sqrt{\frac{1}{3}}}_{c_2} \underbrace{\left|1,-\frac{1}{2}\right\rangle}_{|m_l,m_S\rangle} = \sqrt{\frac{2}{3}}Y_{1,0}\alpha + \sqrt{\frac{1}{3}}Y_{1,1}\beta$

Is $c_1^2 + c_2^2 = 1$? Is $J = L + s$? Is $m_j = m_l + m_s$?

H.W. Prove the following

$$\left|\frac{3}{2},-\frac{1}{2}\right\rangle' = \sqrt{\frac{1}{3}}\left|-1,\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|0,-\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}Y_{1,-1}\alpha + \sqrt{\frac{2}{3}}Y_{1,0}\beta$$

$$\left|\frac{3}{2},-\frac{3}{2}\right\rangle' = \left|-1,-\frac{1}{2}\right\rangle = Y_{1,-1}\beta$$

These are the last two states for the value $j_{\max} = \frac{3}{2}$. Note that the degeneracy is $d_{3/2} = 2\times\frac{3}{2} + 1 = 4$

For the second case, start with the maximum one, $\left|\frac{1}{2},\frac{1}{2}\right\rangle'$, with $j_{\min} = \frac{1}{2}$ and we will suppose that it take the linear combination form:

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle' = c_1\left|0,\frac{1}{2}\right\rangle + c_2\left|1,-\frac{1}{2}\right\rangle = c_1 Y_{1,0}\alpha + c_2 Y_{1,1}\beta$$

From the normalization we have

$$'\left\langle\frac{1}{2},\frac{1}{2}\middle|\frac{1}{2},\frac{1}{2}\right\rangle' = |c_1|^2 + |c_2|^2 = 1$$

And from the orthogonality with the state $\left|\frac{3}{2},\frac{1}{2}\right\rangle'$ we have

$$'\left\langle\frac{3}{2},\frac{1}{2}\middle|\frac{1}{2},\frac{1}{2}\right\rangle' = \sqrt{\frac{2}{3}}c_1 + \sqrt{\frac{1}{3}}c_2 = 0 \quad\Rightarrow\quad c_2 = -\sqrt{2}\,c_1$$

From both, we have

$$c_1 = \pm\sqrt{\frac{1}{3}}$$

Finally, we reach the relation:

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle' = -\sqrt{\frac{1}{3}}\left|0,\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|1,-\frac{1}{2}\right\rangle = -\sqrt{\frac{1}{3}}Y_{1,0}\alpha + \sqrt{\frac{2}{3}}Y_{1,1}\beta$$

Using the lowering operator, we can have:

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle' = \sqrt{\frac{1}{3}}\left|0,-\frac{1}{2}\right\rangle - \sqrt{\frac{2}{3}}\left|-1,\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}Y_{1,0}\beta - \sqrt{\frac{2}{3}}Y_{1,-1}\alpha$$

Suppose we measure S_z on a system in some state $|\chi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$. Postulate 2 says that the possible results of this measurement are one of the S_z eigenvalues: $+\hbar/2$ or $-\hbar/2$. Postulate 3 says the probability of finding, say $-\hbar/2$, is $\text{Prob(find } -\hbar/2) = \left|\langle\downarrow|\chi\rangle\right|^2 = \left|\begin{pmatrix} 0 & 1 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix}\right|^2 = |b|^2$. Postulate 4 says that, as a result of this measurement, which found $-\hbar/2$, the initial state $|\chi\rangle$ collapses to $|\downarrow\rangle$.

But suppose we measure S_x? (Which we can do by rotating the SG apparatus.) What will we find? Answer: one of the eigenvalues of S_x, which we show below are the same as the eigenvalues of S_z: $+\hbar/2$ or $-\hbar/2$. (Not surprising, since there is nothing special about the z-axis.) What is the probability that we find, say, $S_x = +\hbar/2$? To answer this we need to know the eigenstates of the S_x operator. Let's call these (so far unknown) eigenstates $|\uparrow^{(x)}\rangle$ and $|\downarrow^{(x)}\rangle$ (Griffiths calls them $|\chi_+^{(x)}\rangle$ and $|\chi_-^{(x)}\rangle$). How do we find these?

Answer: We must solve the eigenvalue equation:

$$S_x|\chi\rangle = \lambda|\chi\rangle,$$

where λ are the unknown eigenvalues. In matrix form $\left(\hat{S}_x\right) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ and

$$\left(\hat{S}_x\right)\begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda\begin{pmatrix} a \\ b \end{pmatrix}$$ which gives,

$$\begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda\begin{pmatrix} a \\ b \end{pmatrix}$$ which can be rewritten as $$\begin{pmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0.$$

In linear algebra, this last equation is called the characteristic equation.

This system of linear equations only has a solution if $\text{Det}\begin{pmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{pmatrix} = \begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0$. So

$$\lambda^2 - (\hbar/2)^2 = 0 \quad \Rightarrow \quad \lambda = \pm\hbar/2$$

As expected, the eigenvalues of S_x are the same as those of S_z (or S_y).

Now we can plug in each eigenvalue and solve for the eigenstates:

$$\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow a = b \; ; \quad \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow a = -b.$$

So we have $|\uparrow^{(x)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $|\downarrow^{(x)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

Now back to our question: Suppose the system in the state $|\uparrow^{(z)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, and we measure S_x. What is the probability that we find, say, $S_x = +\hbar/2$? Postulate 3 gives the recipe for the answer:

$$\text{Prob(find } S_x = +\hbar/2) = \left|\langle\uparrow^{(x)}|\uparrow^{(z)}\rangle\right|^2 = \left|\tfrac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\right|^2 = \left|\tfrac{1}{\sqrt{2}}\right|^2 = 1/2$$

Question for the student: Suppose the initial state is an arbitrary state $|\chi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$ and we measure S_x.

What are the probabilities that we find $S_x = +\hbar/2$ and $-\hbar/2$?

Let's review the strangeness of Quantum Mechanics.

Suppose an electron is in the $S_x = +\hbar/2$ eigenstate $|\uparrow^{(x)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$. If we ask: What is the value of S_x? Then there is a definite answer: $+\hbar/2$. But if we ask: What is the value of S_z, then this is no answer. The system *does not possess* a value of S_z. If we measure S_z, then the act of measurement will produce a definite result and will force the state of the system to collapse into an eigenstate of S_z, but that very act of measurement will destroy the definiteness of the value of S_x. The system can be in an eigenstate of either S_x or S_z, but not both.

HW Check the following:

$(\hat{S}_z) = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	**Eigen-values**	**symbol**	**Eigen states**
	$\frac{\hbar}{2}$	$\|+\rangle$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$
	$-\frac{\hbar}{2}$	$\|-\rangle$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$(\hat{S}_x) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	**Eigen-values**	**symbol**	**Eigen states**
	$\frac{\hbar}{2}$	$\|+_x\rangle$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\left\{\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix}\right\} = \frac{1}{\sqrt{2}}\{\alpha + \beta\}$
	$-\frac{\hbar}{2}$	$\|-_x\rangle$	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}\left\{\begin{pmatrix} 1 \\ 0 \end{pmatrix} - \begin{pmatrix} 0 \\ 1 \end{pmatrix}\right\} = \frac{1}{\sqrt{2}}\{\alpha - \beta\}$

$\left(\hat{S}_y\right)=\frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$	**Eigen-values**	**symbol**	**Eigen states**
	$\frac{\hbar}{2}$	$\left\|+_y\right\rangle$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\end{pmatrix}=\frac{1}{\sqrt{2}}\left\{\begin{pmatrix}1\\ 0\end{pmatrix}+i\begin{pmatrix}0\\ 1\end{pmatrix}\right\}=\frac{1}{\sqrt{2}}\{\alpha+i\,\beta\}$
	$-\frac{\hbar}{2}$	$\left\|-_y\right\rangle$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -i\end{pmatrix}=\frac{1}{\sqrt{2}}\left\{\begin{pmatrix}1\\ 0\end{pmatrix}-i\begin{pmatrix}0\\ 1\end{pmatrix}\right\}=\frac{1}{\sqrt{2}}\{\alpha-i\,\beta\}$

EXAMPLE 11.4 e.g.

A particle is in the state

$$|\psi\rangle = \frac{1}{\sqrt{5}}\begin{pmatrix}2\\ i\end{pmatrix}$$

Find the probabilities of

(a) Measuring spin-up or spin-down in the z direction.

(b) Measuring spin-up or spin-down in the y direction.

SOLUTION ✓

(a) First we expand the state in the standard basis $|\pm\rangle$:

$$|\psi\rangle = \frac{1}{\sqrt{5}}\begin{pmatrix}2\\ i\end{pmatrix} = \frac{1}{\sqrt{5}}\begin{pmatrix}2\\ 0\end{pmatrix}+\frac{1}{\sqrt{5}}\begin{pmatrix}0\\ i\end{pmatrix} = \frac{2}{\sqrt{5}}\begin{pmatrix}1\\ 0\end{pmatrix}+\frac{i}{\sqrt{5}}\begin{pmatrix}0\\ 1\end{pmatrix} = \frac{2}{\sqrt{5}}|+\rangle+\frac{i}{\sqrt{5}}|-\rangle$$

The Born rule determines the probability of measuring spin-up in the z-direction, which is found from computing $|\langle + | \psi\rangle|^2$. In this case we have

$$|\langle + | \psi\rangle|^2 = \left|\frac{2}{\sqrt{5}}\right|^2 = \frac{4}{5} = 0.8$$

Application of the Born rule allows us to find the probability of measuring spin-down

$$|\langle - | \psi\rangle|^2 = \left|\frac{i}{\sqrt{5}}\right|^2 = \left(\frac{-i}{\sqrt{5}}\right)\left(\frac{i}{\sqrt{5}}\right) = \frac{1}{5} = 0.2$$

Notice that the probabilities sum to one, as they should.

(b) To find the probabilities of finding spin-up/down along the y-axis, we can use the relationship we derived earlier that allows us to express a state written in the $|\pm\rangle$ in the S_y states. We restate this relationship here:

$$|\psi\rangle = \alpha\,|+\rangle + \beta\,|-\rangle = \alpha\left(\frac{|+_y\rangle + |-_y\rangle}{\sqrt{2}}\right) + \beta\left(\frac{-i\,|+_y\rangle + i\,|-_y\rangle}{\sqrt{2}}\right)$$

$$= \left(\frac{\alpha - i\beta}{\sqrt{2}}\right)|+_y\rangle + \left(\frac{\alpha + i\beta}{\sqrt{2}}\right)|-_y\rangle$$

For the state in this problem, we find

$$|\psi\rangle = \frac{2}{\sqrt{5}}|+\rangle + \frac{i}{\sqrt{5}}|-\rangle = \frac{1}{\sqrt{2}}\left(\frac{2}{\sqrt{5}} + \frac{1}{\sqrt{5}}\right)|+_y\rangle + \frac{1}{\sqrt{2}}\left(\frac{2}{\sqrt{5}} - \frac{1}{\sqrt{5}}\right)|-_y\rangle$$

$$= \frac{3}{\sqrt{10}}|+_y\rangle + \frac{1}{\sqrt{10}}|-_y\rangle$$

Therefore the probability of measuring spin-up along the y-direction is

$$|\langle +_y | \psi\rangle|^2 = \left(\frac{3}{\sqrt{10}}\right)^2 = \frac{9}{10} = 0.9$$

and the probability of finding spin-down is

$$|\langle -_y | \psi\rangle|^2 = \left(\frac{1}{\sqrt{10}}\right)^2 = \frac{1}{10} = 0.1$$

e.g. EXAMPLE 11.5

A spin-1/2 system is in the state

$$|\psi\rangle = \frac{1+i}{\sqrt{3}}|+\rangle + \frac{1}{\sqrt{3}}|-\rangle$$

(a) If spin is measured in the z-direction, what are the probabilities of fin $\pm\hbar/2$?

(b) If instead, spin is measured in the x-direction, what is the probability of fin spin-up?

(c) Calculate $\langle S_z\rangle$ and $\langle S_x\rangle$ for this state.

SOLUTION

(a) The probability of finding $+\hbar/2$ is found from the Born rule, and s calculate

$$|\langle + \mid \psi\rangle|^2 = \left|\frac{1+i}{\sqrt{3}}\right|^2 = \left(\frac{1+i}{\sqrt{3}}\right)\left(\frac{1-i}{\sqrt{3}}\right) = \frac{2}{3}$$

The probability of finding $-\hbar/2$ is given by

$$|\langle - \mid \psi\rangle|^2 = \left|\frac{1}{\sqrt{3}}\right|^2 = \frac{1}{3}$$

(b) In the chapter quiz, you will show that

$$|+_x\rangle = \frac{|+\rangle + |-\rangle}{\sqrt{2}}$$

From the Born rule, the probability of finding spin up in the x-direction is $|\langle +_x \mid \psi\rangle|^2$. Now

$$\begin{aligned}\langle +_x \mid \psi\rangle &= \left(\frac{\langle +| + \langle -|}{\sqrt{2}}\right)\left(\frac{1+i}{\sqrt{3}}|+\rangle + \frac{1}{\sqrt{3}}|-\rangle\right) \\ &= \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1+i}{\sqrt{3}}\right)\langle + \mid +\rangle + \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}}\right)\langle - \mid -\rangle \\ &= \frac{2+i}{6}\end{aligned}$$

Therefore the probability is

$$|\langle +_x \mid \psi\rangle|^2 = \left(\frac{2-i}{6}\right)\left(\frac{2+i}{6}\right) = \frac{5}{6}$$

(Exercise: Calculate $|\langle -_x \mid \psi\rangle|^2$ and verify the probabilities sum to one.)

(c) The expectation values are given by

$$S_z|\psi\rangle = \left(\frac{1+i}{\sqrt{3}}\right)S_z|+\rangle + \frac{1}{\sqrt{3}}S_z|-\rangle = \frac{\hbar}{2}\left[\left(\frac{1+i}{\sqrt{3}}\right)|+\rangle - \frac{1}{\sqrt{3}}|-\rangle\right]$$

$\Rightarrow$

$$\langle S_z\rangle = \langle\psi|S_z|\psi\rangle = \frac{\hbar}{2}\left[\left(\frac{1-i}{\sqrt{3}}\right)\langle +| + \frac{1}{\sqrt{3}}\langle -|\right]\left[\left(\frac{1+i}{\sqrt{3}}\right)|+\rangle - \frac{1}{\sqrt{3}}|-\rangle\right]$$

$$= \frac{\hbar}{2}\left[\left(\frac{1-i}{\sqrt{3}}\right)\left(\frac{1+i}{\sqrt{3}}\right)\langle +|+\rangle + \left(\frac{1}{\sqrt{3}}\right)\left(-\frac{1}{\sqrt{3}}\right)\langle -|-\rangle\right]$$

$$= \frac{\hbar}{2}\left(\frac{2}{3} - \frac{1}{3}\right) = \frac{\hbar}{6}$$

For S_x, recalling that it flips the states (i.e. $S_x|\pm\rangle = \hbar/2|\mp\rangle$), we have

$$S_x|\psi\rangle = \left(\frac{1+i}{\sqrt{3}}\right)S_x|+\rangle + \frac{1}{\sqrt{3}}S_x|-\rangle = \frac{\hbar}{2}\left[\left(\frac{1+i}{\sqrt{3}}\right)|-\rangle + \frac{1}{\sqrt{3}}|+\rangle\right]$$

and so the expectation value is

$$\langle S_x\rangle = \langle\psi|S_x|\psi\rangle = \frac{\hbar}{2}\left[\left(\frac{1-i}{\sqrt{3}}\right)\langle +| + \frac{1}{\sqrt{3}}\langle -|\right]\left[\left(\frac{1+i}{\sqrt{3}}\right)|-\rangle + \frac{1}{\sqrt{3}}|+\rangle\right]$$

$$= \frac{\hbar}{2}\left[\left(\frac{1-i}{\sqrt{3}}\right)\frac{1}{\sqrt{3}}\langle +|+\rangle + \left(\frac{1+i}{\sqrt{3}}\right)\frac{1}{\sqrt{3}}\langle -|-\rangle\right]$$

$$= \frac{\hbar}{2}\left[\frac{1}{3} + \frac{1}{3}\right] = \frac{\hbar}{3}$$

Pauli spin matrices

Often written: $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$, Where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

are called the ***Pauli spin matrices*** and they have the following properties:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \mathbf{1}, \quad Tr(\sigma_i) = 0, \quad \det|\sigma_i| = -1,$$

$$\{\sigma_i, \sigma_j\} = \sigma_i\sigma_j + \sigma_j\sigma_i = 2\delta_{ij}, \qquad (i, j) = (x, y, z)$$