Adding spins

S_1 and S_2

$S_1 = \frac{1}{2}$ $\quad |\vec{S}_1| = \sqrt{S_1(S_1+1)}\cdot\hbar = \frac{\sqrt{3}}{2}\hbar$

$m_{s_1} = -\frac{1}{2}\ ;\ +\frac{1}{2}$ $\quad S_{1z} = m_{s_1}\cdot\hbar$

S_2 : same

Question: $S_1 + S_2 = ?$

Answer:

$$S_1 + S_2 \begin{cases} \uparrow\downarrow \quad \left.\begin{matrix} S = S_1 + S_2 = 0 \\ m_s = 0 \end{matrix}\right\} \text{singlet} \\ \\ \begin{matrix}\uparrow \\ \uparrow\end{matrix} \quad \left.\begin{matrix} S = S_1 + S_2 = 1 \\ m_s = -1, 0, 1 \end{matrix}\right\} \text{triplet} \end{cases}$$

Multiplicity: $M = 2S + 1$

Momentum addition generally

$\vec{X}_1$: $|\vec{X}_1| = \sqrt{X_1(X_1+1)} \cdot \hbar$

$m_{X_1} = -X_1, \dots, 0, \dots, X_1 \rightarrow (\underbrace{2X_1+1}_{M_1})$

$\vec{X}_2$: $|\vec{X}_2| = \sqrt{X_2(X_2+1)} \cdot \hbar$

$m_{X_2} = -X_2, \dots, 0, \dots, X_2 \rightarrow (\underbrace{2X_2+1}_{M_2})$

$\vec{Y} = \vec{X}_1 + \vec{X}_2$: yes, but how?

$$\left.Y = \underbrace{|X_1 - X_2|}_{\text{magnitude of the difference}}, \dots, \underbrace{(X_1+X_2)}_{\text{sum}}\right\}$$ a set of possible quantum numbers

$|\vec{Y}_i| = \sqrt{Y_i(Y_i+1)} \cdot \hbar$

$m_{Y_i} = -Y_i, \dots, 0, \dots, Y_i$

$Y_{iz} = m_{Y_i} \cdot \hbar$

Momentum addition examples

X	m_X	Y	m_Y
$\frac{1}{2}$	$\pm\frac{1}{2}$	0	0
$\frac{1}{2}$	$\pm\frac{1}{2}$	1	$-1, 0, 1$

X	m_X	Y	m_Y
$\frac{1}{2}$	$\pm\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$
1	$-1, 0, 1$	$\frac{3}{2}$	$-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

X	m_X	Y	m_Y
1	$-1, 0, 1$	0	0
1	$-1, 0, 1$	1	$-1, 0, 1$
		2	$-2, -1, 0, 1, 2$

Single electron states

(n, ℓ, m_ℓ, m_s)

$L = |\vec{L}| = \sqrt{\ell(\ell+1)} \cdot \hbar \; ; \qquad L_z = m_\ell \cdot \hbar$

$S = |\vec{S}| = \sqrt{s(s+1)} \cdot \hbar \; ; \qquad S_z = m_s \cdot \hbar$

$$\vec{J} = \vec{L} + \vec{S}$$

$J = |\vec{J}| = \sqrt{j(j+1)} \cdot \hbar \; ; \qquad J_z = m_j \cdot \hbar$

(n, ℓ, m_ℓ, m_s) vs (n, ℓ, j, m_j)

(j, m_j) are "better" quantum numbers than (m_ℓ, m_s) because in magnetic spectroscopic experiments the measured or observed quantities are j and m_j.

Many electron atoms/states

$$(\vec{L}_1, \vec{S}_1), (\vec{L}_2, \vec{S}_2), \ldots, (\vec{L}_n, \vec{S}_n)$$

LS-coupling (Russel-Saunders):

$$\left.\begin{aligned} \vec{L} &= \vec{L}_1 + \vec{L}_2 + \ldots \vec{L}_n \\ \vec{S} &= \vec{S}_1 + \vec{S}_2 + \ldots \vec{S}_n \end{aligned}\right\} \vec{J} = \vec{L} + \vec{S}$$

LS-coupling works better for lighter atoms with 2-3 valence electrons: the spin-orbit interaction is weak, the spin-spin correlation exchange is strong.

jj-coupling:

$$\left.\begin{aligned} \vec{J}_1 &= \vec{L}_1 + \vec{S}_1 \\ \vec{J}_2 &= \vec{L}_2 + \vec{S}_2 \\ &\vdots \\ \vec{J}_n &= \vec{L}_n + \vec{S}_n \end{aligned}\right\} \vec{J} = \vec{J}_1 + \vec{J}_2 + \ldots + \vec{J}_n$$

The jj-coupling works better for heavier atoms, where the spin-orbit coupling is strong.

Spectroscopic symbols

$$n \; {}^{M}L_{J}$$

n : principal quantum number (often dropped)

L : orbital angular momentum (S, P, D, F, G, H)

M : multiplicity of the state

$M = 2S + 1$; S : spin q. n.

J : total angular momentum quantum number

Examples :

Hydrogen ground state :

$\underset{1s^1}{\boxed{\uparrow}}$: $1\,{}^2S_{1/2}$ or ${}^2S_{1/2}$

Helium ground state :

$\underset{1s^2}{\boxed{\uparrow\downarrow}}$: $1\,{}^1S_0$ or ${}^1S_0$