Note that $\Psi_{n l m} = R_{n l} Y_l^m$

and that l is a positive integer and $m = -l, -l+1, \ldots 0, \ldots l-1, l$. Thus there are $(2l+1)$ values of m.

For the H-atom $n > l$. 1

Spin

Postulate V of QM :→ This postulate has no classical analog. All elementary particles have an immutable intrinsic property called spin. The spin can take any positive $\frac{1}{2}$ integer or integer value. The values of spin are

$$S = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots\ldots$$

Each type of fundamental particle has a fixed value of spin. E.g. proton has spin $S = 1/2$

Electron has $S = 1/2$

Neutron " $S = 1/2$

Photons " $S = 1$

Δ " $S = 3/2$

Gravitons " $S = 2$

π mesons " $S = 0$.

The components of the spin operator obey the following commutation relations

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

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

Eigenvectors of $\hat{S}_z$ and $\hat{S}^2$ satisfy

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

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

Kets of spin s are denoted by columns of dimension $2s+1$. Example

$$|s=1\rangle = \begin{bmatrix} a \\ b \\ c \end{bmatrix}_{3\times 1} , \quad |s=3/2\rangle = \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix}_{4\times 1}$$

The total wave-function $\Psi_s(\bar{r})$ is given by

$$\Psi_s(\bar{r}) = \Psi(\bar{r})\, \chi_s \quad \text{where}$$

χ_s is a column matrix of dimension $(2s+1)$. If

$$\Psi_s(\bar{r}) = \begin{bmatrix} \Psi_1(\bar{r}) \\ \Psi_2(\bar{r}) \\ \vdots \\ \Psi_{2s+1}(\bar{r}) \end{bmatrix} \quad \text{then}$$

normalization of $\Psi_s(\bar{r}) \Rightarrow$

$$\int \Psi_s^\dagger(\bar{r})\, \Psi_s(\bar{r})\, d^3\bar{r} = 1$$

$$\Rightarrow \int \left[|\Psi_1|^2 + |\Psi_2|^2 + \cdots + |\Psi_{2s+1}|^2 \right] d^3\vec{r} = 1.$$

We can define $\hat{S}_\pm \equiv \hat{S}_x \pm i \hat{S}_y$.

Then $\hat{S}_\pm |s, m\rangle = \hbar \left[s(s+1) - m_s(m_s \pm 1) \right]^{1/2} |s, m_s \pm 1\rangle$

$m_s = -s, -s+1, \ldots, s-1, s$, m_s takes $2s+1$ values.

Now consider $s = 1/2 \Rightarrow |s = 1/2, m_s = 1/2\rangle \equiv |\tfrac{1}{2}, \tfrac{1}{2}\rangle$

$$= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad |\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$\hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\hat{S}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \frac{\hbar}{2}, \quad \hat{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

These are related to the Pauli spin matrices as

$$\hat{\vec{S}} \equiv \frac{\hbar}{2} \hat{\vec{\sigma}} \quad \text{where}$$

$$\hat{\vec{\sigma}} = \hat{i}\, \hat{\sigma}_x + \hat{j}\, \hat{\sigma}_y + \hat{k}\, \hat{\sigma}_z$$

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

Addition of Angular Momentum (AM)

Angular Momentum, denoted by the operator $\hat{\vec{J}}$ can be of 2 forms

orbital $\Rightarrow$ $\hat{\vec{J}} \equiv \hat{\vec{L}}$ or spin $\Rightarrow \hat{\vec{J}} \equiv \hat{\vec{S}}$

In general $\hat{\vec{J}} = a\hat{\vec{L}} + b\hat{\vec{S}}$ where a and b are scalars.

Now we consider two types of AM $\hat{\vec{J}}_1$ and $\hat{\vec{J}}_2$ of different particles or they may be orbital and spin AM respectively. For each of these we have

$$\left[\hat{\vec{J}}_i^{\,2}, \hat{J}_{iz}\right] = 0 \ , \quad i = 1, 2$$

Also since they are of different types

$$\left[\hat{\vec{J}}_i, \hat{\vec{J}}_j\right] = 0 \ , \quad \forall i, j = 1, 2 .$$

With these relationships of the commutators we can form a basis of product states

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle \equiv |j_1, m_1; j_2, m_2\rangle$$

$$\ni \quad \hat{\vec{J}}_i^{\,2} |j_1, m_1; j_2, m_2\rangle = \hbar^2 j_i(j_i+1) |j_1, m_1; j_2, m_2\rangle$$

and $$\hat{J}_{iz} |j_1, m_1; j_2, m_2\rangle = \hbar m_i |j_1, m_1; j_2, m_2\rangle$$

where $i = 1, 2$

This basis thus maybe called a product basis. Allowed values of m_i are

$$|m_i| \leq j_i \quad , \forall i = 1, 2.$$
$$j_i = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \tfrac{5}{2}, \ldots$$

$\therefore$ total # of states in the basis are $(2j_1+1)(2j_2+1)$. Also this basis is orthonormal.

$$\langle j_1' m_1' ; j_2', m_2' | j_1, m_1 ; j_2, m_2 \rangle = \delta_{j_1' j_1} \delta_{j_2' j_2} \delta_{m_1' m_1} \delta_{m_2' m_2}.$$

This basis may be called a basis of product states.

There also exists an alternative basis for two angular momentum states. This is in general made of sums of product states.

Define $\hat{\vec{J}} \equiv \hat{\vec{J}}_1 + \hat{\vec{J}}_2$

$$\Rightarrow \hat{J}_z \equiv \hat{J}_{1z} + \hat{J}_{2z}$$

Then $\left[\hat{\vec{J}}^2, \hat{J}_z\right] = 0$

Also $\left[\hat{J}^2, \hat{\vec{J}}_1\right] = \left[\hat{J}^2, \hat{\vec{J}}_2\right] = 0$ and

$$\left[\hat{\vec{J}}_1^2, \hat{J}_z\right] = \left[\hat{\vec{J}}_2^2, \hat{J}_z\right] = 0.$$

So we can contruct a basis which is a simultaneous eigenfunction of $\hat{\vec{J}}^2, \hat{J}_z, \hat{\vec{J}}_1^2, \hat{\vec{J}}_2^2$

This basis follows the following four ~~equa~~ eigenvalue equations.

$$\hat{\vec{J}}_i^2 |j, m, j_1, j_2\rangle = \hbar^2 j_i(j_i+1) |j, m, j_1, j_2\rangle$$

$\forall i = 1, 2.$

$$\hat{\vec{J}}^2 |j, m, j_1, j_2\rangle = \hbar^2 j(j+1) |j, m, j_1, j_2\rangle$$

$$\hat{J}_z |j, m, j_1, j_2\rangle = \hbar m |j, m, j_1, j_2\rangle$$

The allowed values of j are
$|j_1 - j_2|, |j_1 - j_2| + 1, \ldots\ldots j_1 + j_2$.

Allowed value of m is $m = m_1 + m_2$

Total # of states is still $(2j_1+1)(2j_2+1)$.

Also in general for any state of the form $|j, m\rangle$ we have

$$\hat{\vec{J}}_\pm |j, m\rangle = \hbar \left[j(j+1) - m(m\pm1) \right]^{1/2} |j, m\rangle$$

$$\Rightarrow \quad \hat{J}_\pm |j, \pm j\rangle = 0$$

$\hat{\vec{J}}_\pm$ are defined by $\hat{J}_\pm = \hat{J}_x \pm i \hat{J}_y$.