A New Degree of Freedom in Quantum Mechanics: Spin

The origin of the spin angular momentum was explained at first by a fact that an electron possesses a finite momentum associated with rotation that arises magnetic dipole excitation in the center of an electron. However, as we already know, we can explain the origin of the spin only by Dirac equations, which an electron obeys. Although Schrodinger's equations do not satisfy the invariance of Lorenz transformation in the "relativity" requires, Dirac equations was introduced as the first equation invariable to Lorenz transformation. This is a good example to realize how important the symmetry is for the new discovery.

Multiplet-term of Spectrum

Sodium is placed in a furnace, and heated to the point of evaporation then be passed through a small slit to produce atomic beam. Then let it pass through in between the magnets to leave a coating by evaporation on glass plate. Sodium atom on the glass plate is observed in two separate groups with a distance of the two proportional to the magnitude of the magnetic field. We can attribute the separation of the sodium beam to the following fact; in proportional to the magnetic field, the force perpendicular to the traveling direction of the atomic beam was acted in positive direction, while the other force was acted in negative. Apparently, magnetic field in between the magnets is not homogenious. The field ceates a negative and a positive force proportional to the rate of change $(\partial B/\partial z)$. The peripheral electron in sodium atom possesses a $3\mathrm{s}$ electron (closed with $(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^6$; identical to the inert gas Ne) so, the electron does not possess the orbital angular momentum and therefore, does not interact with the magnetic field.

Since we have magnetic flux density in z direction, $(0,0,B)$ can be given with $\boldsymbol{A}=(1/2)\boldsymbol{B}\times\boldsymbol{r}$ then Hailtonian may be:

$$\begin{aligned} H &= \frac{1}{2m}(\boldsymbol{p}-(-e)\boldsymbol{A})^2+V(\boldsymbol{r}) \\ &= \frac{1}{2m}\boldsymbol{p}^2+V(\boldsymbol{r})-\frac{(-e)}{2m}(-yp_x+xp_y)B+\frac{e^2}{2m}\frac{B^2}{4}(x^2+y^2) \end{aligned} \tag{1a}$$

The orbital angular momentum $\ell_z = xp_y - yp_x$ is expressed in the first term of B. With $\boldsymbol{A}=(B/2)(-y,x,0)$, we have established $\boldsymbol{p}\cdot\boldsymbol{A}=\boldsymbol{A}\cdot\boldsymbol{p}$. Accordingly, the Hamiltonian can be expressed as:

$$H=\frac{1}{2m}\boldsymbol{p}^2+V(\boldsymbol{r})-\frac{(-e)}{2m}\ell_z B+\frac{e^2B^2}{8m}(x^2+y^2) \tag{1b}$$

The third term in (1b) is called Zeeman term, and the fourth term is called diamagnetism. Zeeman term represents the interaction with an orbital angular momentum in uniform magnetic field, therefore splits the energy level at the magnetic field, and this is called Zeeman effect.

The orbital momentum of electrons interact with external magnetic field, yet sodium atom possesses one peripheral electron in $3s$ orbital with the orbital angular momentum $\ell = 0$, the third term in (1) becomes zero, and there is no contribution. We do not make two distinct orbital momentum groups for $\ell = 0$ but indeed, sodium atom is observed to split in two at the magnetic field with its magnetic dipole moment $\pm\mu_0(-e)\hbar/2m$. The split of the level at magnetic field that cannot be explained with normal Zeeman effect is called the anomalous Zeeman effect. The Stern-Gerlach experiment was performed by the silver beam, and the experiment attributed the cause for this split to be the spin. A dual structure of the spectrum (multiplet) is commonly known including the case in which the magnetic field is not being charged for the presence of the interaction for the spin angular momentum and the orbital angular momentum. We call it the spin-orbit interaction.

Spin Angular Momentum

The spin angular momentum is considered to have similar characteristics of orbital angular momentum, and the momentum is considered to take two values. This momentum can be added to the orbital angular momentum, and which is observed experimentally in composite angular momenta, also. In the case where orbital angular momentum is $\hbar\ell$, the momentum is split in two levels $2\ell + 1$. Now, let us express the spin angular momentum operator as $\boldsymbol{s}$. $\boldsymbol{s}$ represents the vector operator, and its components must satisfy the same commutation relation for the orbital angular momentum.

$$[s_x, s_y] = i\hbar s_z, \quad [s_y, s_z] = i\hbar s_x, \quad [s_z, s_x] = i\hbar s_y, \tag{2}$$

$$[s_x, s_x] = [s_y, s_y] = [s_z, s_z] = 0 \tag{3}$$

Moreover, the eigenfunction of the spin angular momentum operator $\boldsymbol{s}^2$ can be chosen simultaneously to take the eigenfunction of s_z. The spin is consisted of two eigenstates in corresponding to the eigenvalue $\pm\hbar/2$ of s_z. ($s = \hbar/2$)

Therefore, the electrons wavefunciton is considered as the functions of spin variable σ with spatial coordinates x, y, z. The spin variable σ (spin coordinates) can be understood by the case s_z, for example, when the eigenvalue m_s is $+\hbar/2$ to have $\sigma = 1$, when m_s is $-\hbar/2$ then to have $\sigma = -1$. The spin coordinates take no continuous value but take only the two distinct values. The spin wavefunction should be the following:

$$\alpha(\sigma) = \begin{cases} 1: & \sigma = 1 \\ 0: & \sigma = -1 \end{cases}, \quad \beta(\sigma) = \begin{cases} 0: & \sigma = 1 \\ 1: & \sigma = -1 \end{cases} \tag{4}$$

From (4), we understand the orthonormal relation is satisfied.

$$\sum_{\sigma=\pm1} |\alpha(\sigma)|^2 = \sum_{\sigma=\pm1} |\beta(\sigma)|^2 = 1, \quad \sum_{\sigma=\pm1} \alpha(\sigma)\beta(\sigma) = 0 \tag{5}$$

The following equations should be established by operating s_z to the spin wavefunction $\alpha(\sigma), \beta(\sigma)$:

$$s_z\alpha(\sigma) = \frac{\hbar}{2}\alpha(\sigma), \quad s_z\beta(\sigma) = -\frac{\hbar}{2}\beta(\sigma) \tag{6}$$

Since there are only two spin states of electrons existed, we can express them as the vector of two components (two-dimansional complex vector), and we call the two-dimensional complex vector a spinor. Now, we actually construct a matrix representation of spin operator. The spin wavefunction $\alpha(\sigma)$ that corresponds to the eigenvalue $m_s = \hbar/2$ of s_z may be written as:

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{7a}$$

Spin wavefunction $\beta(\sigma)$ for $m_s = -\hbar/2$ as:

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{7b}$$

Then the definition (6) should be:

$$s_z \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad s_z \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{8}$$

Thus, s_z can be written as 2x2 matrix:

$$s_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{9}$$

We try to write out in the 2x2 matrix for s_x, s_y, and define the spin angular momentum of step-up as well as step-down operators :

$$s_+ = s_x + \imath s_y, \quad s_- = s_x - \imath s_y \tag{10}$$

Then:

$$\begin{aligned} s_+\alpha(\sigma) = 0, \quad s_+\beta(\sigma) = \hbar\sqrt{(\frac{1}{2}+\frac{1}{2})(\frac{1}{2}-\frac{1}{2}+1)}\alpha(\sigma) = \hbar\alpha(\sigma), \\ s_-\beta(\sigma) = 0, \quad s_-\alpha(\sigma) = \hbar\sqrt{(\frac{1}{2}+\frac{1}{2})(\frac{1}{2}-\frac{1}{2}+1)}\beta(\sigma) = \hbar\beta(\sigma) \end{aligned} \tag{11}$$

Or, we can write with (7),

$$s_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0, \quad s_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix},$$
$$s_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0, \quad s_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{12}$$

The matrix for s_+, s_- may be written as:

$$s_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad s_- = \hbar \begin{pmatrix} 0 & 0 \\ 1^* & 0 \end{pmatrix} \tag{13}$$

Here putting them (13) back to the matrix of s_x, s_y:

$$s_x = \frac{1}{2}(s_+ + s_-)$$
$$s_y = \frac{1}{2i}(s_+ - s_-) \tag{14}$$

Accordingly, the matrix representation of the spin angular momentum is defined as:

$$s_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad s_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{15}$$

From (15) above, we can directly obtain the matrix of spin angular momentum $\boldsymbol{s}$:

$$\boldsymbol{s}^2 = s_x^2 + s_x^2 + s_x^2 = \frac{\hbar^2}{4}\{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\}$$
$$= \frac{1}{2}(\frac{1}{2} + 1)\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{16a}$$

Along with the commutation relation:

$$[s_x, \boldsymbol{s}^2] = [s_y, \boldsymbol{s}^2] = [s_z, \boldsymbol{s}^2] = 0 \tag{16b}$$

Pauli matrices are often used instead of the matrices s_x, s_y, s_z:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{17}$$

Spin-orbit Interactions

We stated earlier that there exist interactions between the spin angular momentum and the orbital angular momentum. By admitting the fact of the spin angular momentum and the magnetic dipole excitation, the interactions may be verified by taking following steps. Consider $\boldsymbol{r}$ and $\boldsymbol{v}$ as the coordinates and velocity of the electron having its atomic nucleus as its origin. Take a close look at the coordinates system fixed by the electron, atomic nucleus is moving with the velocity $-\boldsymbol{v}$ at $-\boldsymbol{r}$. The atomic nucleus in motion possesses the electric charge of Ze, thus there is the electric current $(-\boldsymbol{v})Ze$ around the electron. The effective magnetic field $\boldsymbol{H}$ caused by the electric current is,

$$\boldsymbol{H} = \frac{1}{4\pi}\cdot\frac{Ze(-\boldsymbol{v})\times(+\boldsymbol{r})}{r^3} = \frac{1}{4\pi}\frac{Ze(\boldsymbol{r}\times\boldsymbol{v})}{r^3} = \frac{1}{4\pi m}\cdot\frac{Ze}{r^3}\hat{\ell} \tag{18}$$

at the position of the electron (from Biot-Savart law). The magnetic dipole excitation occurred in association with the electric spin $\boldsymbol{s}$ may become:

$$\boldsymbol{m}_s = -\mu_0\frac{e}{m}\boldsymbol{s} \tag{19}$$

In the case of the orbital angular momentum $\hat{\ell}$,

$$\boldsymbol{m} = -\frac{1}{2}\mu_0\frac{e}{m}\hat{\ell}$$

Through the experiment in the magnetic field, the proportionality constant 1 for the spin magnetic moment is determined. In the case of the electron, the magnetic dipole moments $\boldsymbol{m}$ and $\boldsymbol{m}_s$ have opposite directions to the respective angular momentum because the electron is charged negative. The interaction energy of spin magnetic moment of the electrons (19) and the magnetic field (18) becomes

$$H_{so} = -\boldsymbol{m}_s\cdot\boldsymbol{H} = \frac{Ze^2\mu_0}{4\pi m^2}\frac{1}{r^3}\hat{\ell}\cdot\boldsymbol{s}$$

However, we need to conduct a complex correction to the rotational coordinates system due to the theory of the relativity, for the perspective atomic nucleus centered by the electrons. Which results in a necessary factor 1/2 (called Thomas factor) and the correct result is

$$H_{so} = \frac{\mu_0}{4\pi}\frac{Ze^2}{2m^2}\frac{1}{r^3}\hat{\ell}\cdot\boldsymbol{s} \tag{20a}$$

More generally, when electrons are in motion at the central force potential $V(r)$, we can write as:

$$H_{so} = \varepsilon_0\mu_0\frac{1}{2m^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\hat{\ell}\cdot\boldsymbol{s} = \frac{1}{2m^2c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\hat{\ell}\cdot\boldsymbol{s} \tag{20b}$$

(Be careful with $\varepsilon_0\mu_0c^2 = 1$). This is the spin-orbit interaction.

The Hamiltonian that describes the movement of electrons may be written with the spin-orbit interaction H_{so},

$$H = -\frac{1}{2m}\boldsymbol{p}^2 + V(r) + H_{so} \tag{21}$$

For now, we consider only for the situations of a single electron, and we study the kind of quantity that is conserved in this system. As we stated so many times before, $\hat{\ell}^2$ and $\hat{\ell}_z$ are commutative with the total Hamiltonian in the absence of the spin-orbit interactions and, thus in that case, it is possible to assign the electrons state to be the eigenvalues of $\hat{\ell}^2$ and $\hat{\ell}_z$.

The following can be established:

$$[\hat{\ell}_x, \hat{\ell}^2] = 0, \quad [\hat{s}_x, \boldsymbol{s}^2] = 0$$

Therefore, the Hamiltonian H with the spin-orbit interaction and $\hat{\ell}^2, \boldsymbol{s}^2$ are commutative. Since ($[\hat{\ell}_x \hat{s}_x, A] = \hat{\ell}_x [\hat{s}_x, A] + [\hat{\ell}_x, A]\hat{s}_x$), the following relations are established:

$$[H, \hat{\ell}^2] = 0, \quad [H, \boldsymbol{s}^2] = 0. \tag{22}$$

Subsequently, the orbital angular momentum $\hbar\ell$ and the spin angular momentum $\hbar/2$ are being conserved, the eigenstate then be assigned by these quantities. The z components $\hat{\ell}_z, \hat{s}_z$ of the orbital and the spin angular momentums are not commutative with H_{so}. Apparently, we have,

$$\begin{aligned}[H_{so}, \hat{\ell}_z] &= \frac{1}{2m^2c^2}(\frac{1}{r}\frac{dV}{dr})[\hat{\ell}\cdot \boldsymbol{s}, \hat{\ell}_z] = \frac{1}{2m^2c^2}(\frac{1}{r}\frac{dV}{dr})[\hat{\ell}, \hat{\ell}_z] \cdot \boldsymbol{s} \\ &= \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}(-i\hbar\hat{\ell}_y\hat{s}_x + i\hbar\hat{\ell}_x\hat{s}_y)\end{aligned} \tag{23a}$$

In the same way,

$$[H_{so}, \hat{s}_z] = \frac{1^2}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}(-i\hbar\hat{\ell}_x\hat{s}_y + i\hbar\hat{\ell}_y\hat{s}_x) \tag{23b}$$

Then (23) in above implies that the presence of the spin-orbit interaction made the state to be no longer assigned by the eigenvalues of $\hat{\ell}_z, \hat{s}_z$. Then, is there any other conserved quantity, which assigns the eigenstate?

The spin-orbit interactions appear to be the scalar product of the orbital angular momentum $\hat{\ell}$ and the spin angular momentum $\boldsymbol{s}$. The sum of the two angular momenta as:

$$\boldsymbol{j} = \hat{\ell} + \boldsymbol{s} \tag{24}$$

Each element $\hat{j}_x, \hat{j}_y, \hat{j}_z$ of this composite angular momentum $\boldsymbol{j}$ is defined as:

$$\hat{j}_x = \hat{\ell}_x + \hat{s}_x, \quad \hat{j}_y = \hat{\ell}_y + \hat{s}_y, \quad \hat{j}_z = \hat{\ell}_z + \hat{s}_z \tag{25}$$

We can show that composite angular momentum satisfies the same commutation relations for the general angular momentum in the following:

$$\begin{aligned}[\hat{j}_x, \hat{j}_y] &= [\hat{\ell}_x + \hat{s}_x, \hat{\ell}_y + \hat{s}_y] = [\hat{\ell}_x, \hat{\ell}_y] + [\hat{s}_x, \hat{s}_y] \\ &= i\hbar(\hat{\ell}_z + \hat{s}_z) = i\hbar\hat{j}_z,\end{aligned} \tag{26a}$$

$$\begin{aligned}&[\hat{j}_y, \hat{j}_z] = i\hbar\hat{j}_x, \quad [\hat{j}_z, \hat{j}_x] = i\hbar\hat{j}_y,\\ &\qquad [\hat{j}_x, \hat{j}_x] = [\hat{\ell}_x, \hat{\ell}_x] + [\hat{s}_x, \hat{s}_x] = 0,\\ &\qquad [\hat{j}_y, \hat{j}_y] = [\hat{j}_z, \hat{j}_z] = 0,\end{aligned} \tag{26b}$$

$$\begin{aligned}[\hat{j}_x, \boldsymbol{j}^2] &= [\hat{j}_x, \hat{j}_x^2] + [\hat{j}_x, \hat{j}_y^2] + [\hat{j}_x, \hat{j}_z^2]\\ &= 0 + \{[\hat{j}_x, \hat{j}_y]\hat{j}_y + \hat{j}_y[\hat{j}_x, \hat{j}_y]\} + \{[\hat{j}_x, \hat{j}_z]\hat{j}_z + \hat{j}_z[\hat{j}_x, \hat{j}_z]\}\\ &= i\hbar\{\hat{j}_z\hat{j}_y + \hat{j}_y\hat{j}_z - \hat{j}_y\hat{j}_z - \hat{j}_z\hat{j}_y\} = 0,\\ [\hat{j}_y, \boldsymbol{j}^2] &= [\hat{j}_z, \boldsymbol{j}^2] = 0.\end{aligned} \tag{26c}$$

Now, express $\boldsymbol{j}^2$,

$$\boldsymbol{j}^2 = \hat{\ell}^2 + \boldsymbol{s}^2 + 2\hat{\ell}\cdot \boldsymbol{s} \tag{27}$$

Inversely,

$$\hat{\ell}\cdot \boldsymbol{s} = \frac{1}{2}(\boldsymbol{j}^2 - \hat{\ell}^2 - \boldsymbol{s}^2) \tag{28}$$

Then the spin-orbit interaction is reformed as:

$$H_{so} = \frac{1}{2m^2c^2}(\frac{1}{r}\frac{dV}{dr})\frac{1}{2}(\boldsymbol{j}^2 - \hat{\ell}^2 - \boldsymbol{s}^2) \tag{29}$$

Since $\hat{\ell}^2, \boldsymbol{s}^2, \hat{\ell}_x, \hat{\ell}_y, \hat{\ell}_z, \hat{s}_x, \hat{s}_y, \hat{s}_z$ are commutative with $H - H_{so}$, in the same way, $\boldsymbol{j}^2, \hat{j}_x, \hat{j}_y, \hat{j}_z$ are commutative with $H - H_{so}$. Let us study the commutation relation between $\boldsymbol{j}^2, \hat{j}_z$ and H_{so}. From (22), (27) and $[\hat{j}\cdot \boldsymbol{s}\ ,\ \hat{j}\cdot \boldsymbol{s}] = 0$ we understand the following:

$$[H_{so}, \boldsymbol{j}^2] = 0 \tag{30}$$

In addition to (23a~b),

$$[H_{so}, \hat{j}_z] = [H_{so}, \hat{\ell}_z] + [H_{so}, s_z] = 0 \tag{31}$$

Equations (22)(30)(31) show that the Hamiltonian (21), in which the system added by the spin-orbit interaction, is commutative with $\hat{\ell}^2, \boldsymbol{s}^2, \boldsymbol{j}^2, \hat{j}_z$, therefore the eigenstate of a system that includes the spin-orbit interaction in the central force potential, can be assigned by the eigenstate of operators

$$\hat{\ell}^2, \boldsymbol{s}^2, \hat{\boldsymbol{j}}^2, \hat{j}_z. \tag{32}$$

We will look more specifically on the expectation value for the spin-orbit interaction in the above eigenstates. For the simplification, the Hamiltonian of the spin-orbit interaction can be written as:

$$H_{so} = \zeta(r)\hat{\ell}\boldsymbol{\cdot}\, \boldsymbol{s} = \frac{\zeta(r)}{2}(\hat{\boldsymbol{j}}^2 - \hat{\ell}^2 - \boldsymbol{s}^2)\ ,\ \zeta(r) = \frac{1}{2m^2c^2}(\frac{1}{r}\frac{dV}{dr}) \tag{33}$$

We need to pay a close attention to the fact that $\zeta(r)$ is a function exclusively consisted of the radal vector r. The electron takes the energy E, the orbital angular momentum $\hbar\ell$, the spin angular momentum $\hbar s = \hbar/2$, and the composite angular momentum $\hbar j$ with its z component $\hbar m_j$ then written as:

$$|E; \ell, s = \frac{1}{2}; j, m_j\rangle \tag{34}$$

Now,

$$\begin{aligned}
\hat{\boldsymbol{j}}^2|E; \ell, s = \frac{1}{2}; j, m_j\rangle &= \hbar^2 j(j+1)|E; \ell, s = \frac{1}{2}; j, m_j\rangle \\
\hat{j}_z|E; \ell, s = \frac{1}{2}; j, m_j\rangle &= \hbar m_j|E; \ell, s = \frac{1}{2}; j, m_j\rangle \\
\hat{\ell}^2|E; \ell, s = \frac{1}{2}; j, m_j\rangle &= \hbar\ell(\ell+1)|E; \ell, s = \frac{1}{2}; j, m_j\rangle \\
\mathbf{s}^2|E; \ell, s = \frac{1}{2}; j, m_j\rangle &= \hbar\frac{1}{2}(\frac{1}{2}+1)|E; \ell, s = \frac{1}{2}; j, m_j\rangle
\end{aligned} \tag{35}$$

The off-diagonal element of H_{so} turns zero hence the diagonal element may be calculated as:

$$\begin{aligned}
&\langle E; \ell, s = \frac{1}{2}, j, m_j|H_{so}|E; \ell, s = \frac{1}{2}, j, m_j\rangle \\
&\qquad\qquad = \zeta_\ell\frac{1}{2}\hbar^2\{j(j+1) - \ell(\ell+1) - \frac{3}{4}\}
\end{aligned} \tag{36}$$

Here we have ζ_ℓ,

$$\zeta_\ell = \langle E; \ell, s = \frac{1}{2}, j, m_j|\zeta(r)|E; \ell, s = \frac{1}{2}, j, m_j\rangle \tag{37}$$

(37) represents the magnitude of the spin-orbit interaction for single electron. $\zeta(r)$ is proportional to the atomic number, and it is natural that the heavier the atom the greater the magnitude of the spin-orbit interaction ζ_ℓ becomes. To make a rough

estimate for this magnitude, we take r_ℓ as the orbital radius,

$$\zeta_\ell \simeq \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{2m^2c^2}\frac{1}{{r_\ell}^3}$$

We understand from the above that magnitude of the energy is far smaller than the coulomb interaction energy between the electron and the atomic nucleus.

Eigenfunction of Composite Angular Momentum (j, m_j)

In the central force field, the single electron eigenstate can be assigned as (34) when the spin-orbit interaction is present. Now, write out this eigenstate by $\hat{\ell}^2, \hat{\ell}_z, \boldsymbol{s}^2, \hat{s}_z$.

The eigenvalue $\hbar m_j$ for j_z, the upper limit of m_j is $+j$ and the lower limit $-j$. Thus, m_j takes the values in $2j+1$ ways. The value j is the maximum value of m_j. Classically, this implies that $\hat{\ell}$ and $\boldsymbol{s}$ are combined in parallel, and facing in the same direction. The minimum value of j becomes $|\ell - 1/2|$ corresponding for the two angular momentums $\hat{\ell}$ and $\boldsymbol{s}$ combined in opposite direction. So, we understand that,

j takes the following two values $j = \ell + 1/2, \quad j = |\ell - 1/2|$ (39)

Apparently, we have the states with the orbital angular momentum $\hbar\ell$ and the spin angular momentum $\hbar/2$ as many as,

$$2(2\ell+1)$$

While the states consisted of $j = \ell \pm 1/2$, there exist as many as:

$$\begin{cases} 2\times\frac{1}{2}+1 = 2(2\ell+1) & : \quad \ell = 0 \\ \{2(\ell+\frac{1}{2})+1\}+\{2(\ell-\frac{1}{2})+1\} = 2(2\ell+1) & : \quad \ell \neq 0 \end{cases}$$

The above agrees with the total number of states. To define the step-up and step-down operator of composite angular momentum, we can write the following:

$$\begin{aligned} \hat{j}_\pm = \hat{j}_x \pm i\hat{j}_y &= (\hat{\ell}_x + \hat{s}_x) \pm i(\hat{\ell}_y + \hat{s}_y) \\ &= (\hat{\ell}_x \pm i\hat{\ell}_y) + (\hat{s}_x \pm i\hat{s}_y) = \hat{\ell}_\pm + \hat{s}_\pm \end{aligned} \tag{40}$$

From the commutation relations (26a~c),

$$\hat{j}_\pm|\ell, s; j, m_j\rangle = \hbar\sqrt{(j \mp m_j)(j \pm m_j + 1)}|\ell, s; j\ m_j \pm 1\rangle \tag{41}$$

In expressing the eigenstates for $\hat{j}^2$ and $\hat{j}_z$ in considering a simple case, we choose $\ell = 1$, $s = 1/2$ (p-electron orbit). The eigenstates with the basis $\hat{\ell}^2$, $\hat{\ell}_z$, $\boldsymbol{s}^2$, $\hat{s}_z$ may be selected as following:

$$|\ell = 1, m_\ell = 1; s = \frac{1}{2}, m_s = \frac{1}{2}\rangle \equiv |1; \frac{1}{2}\} \ ,$$

$$|\ell = 1, m_\ell = 1; s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle \equiv |1; -\frac{1}{2}\} \ ,$$

$$\begin{aligned}
&|\ell = 1, m_\ell = 0; s = \frac{1}{2}, m_s = \frac{1}{2}\rangle \equiv |0; \frac{1}{2}\} \ , \\
&|\ell = 1, m_\ell = 0; s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle \equiv |0; -\frac{1}{2}\} \ , \\
&|\ell = 1, m_\ell = -1; s = \frac{1}{2}, m_s = \frac{1}{2}\rangle \equiv |-1; \frac{1}{2}\} \ , \\
&|\ell = 1, m_\ell = -1; s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle \equiv |-1; -\frac{1}{2}\}
\end{aligned} \qquad (42)$$

Here the values ℓ and s are defined so, we write $|m_\ell; m_s\}$ with the values m_ℓ and m_s only. There are total of $2 \times (2 \times 1 + 1) = 6$ states existed, and the each state in above corresponds to $m_j = m_\ell + m_s$ $=3/2,\ 1/2,\ 1/2,\ -1/2,\ -1/2,\ -3/2$. These are the eigenstates of $\hat{j}_z$ and not of $\hat{\boldsymbol{j}}^2$. The state $m_j = \pm 3/2$ equals to the state $j = 1 + 1/2 = 3/2$, while the state $m_j = \pm 1/2$ may take either $j = 1 + 1/2 = 3/2$ or $j = 1/2$.

$$\begin{aligned}
&|\ell = 1, s = \frac{1}{2}; j = \frac{3}{2}, m_j = \frac{3}{2}\rangle = \\
&|\ell = 1, m_\ell = 1; s = \frac{1}{2}, m_s = \frac{1}{2}\rangle = |1; \frac{1}{2}\}
\end{aligned} \qquad (43a)$$

When we operate the states above to $\hat{j}_-$:

$$\begin{aligned}
&\hat{j}_-|\ell = 1, s = \frac{1}{2}; j = \frac{3}{2}, m_j = \frac{3}{2}\rangle = (\hat{\ell}_- + \hat{s}_-)|1; \frac{1}{2}\} \\
&= \hbar\sqrt{3}|\ell = 1, s = \frac{1}{2}; j = \frac{3}{2}, m_j = \frac{1}{2}\rangle = \hbar\sqrt{2}|0, \frac{1}{2}\} + \hbar\sqrt{1}|1; -\frac{1}{2}\}
\end{aligned}$$

To put in order,

$$|\ell = 1, s = \frac{1}{2}; j = \frac{3}{2}, m_j = \frac{1}{2}\rangle = \sqrt{\frac{2}{3}}|0; \frac{1}{2}\} + \sqrt{\frac{1}{3}}|1; -\frac{1}{2}\} \qquad (43b)$$

By operating to $\hat{j}_-$:

$$|\ell = 1, s = \frac{1}{2}; j = \frac{3}{2}, m_j = -\frac{1}{2}\rangle = \sqrt{\frac{1}{3}}|-1; \frac{1}{2}\} + \sqrt{\frac{2}{3}}|0; -\frac{1}{2}\} \qquad (43c)$$

$$|\ell = 1, s = \frac{1}{2}; j = \frac{3}{2}, m_j = -\frac{3}{2}\rangle = |-1; -\frac{1}{2}\} \qquad (43d)$$

According to (43a~d), all $2j + 1 = 4$ states for $j = 3/2$ are obtained.
For $2 \times (1/2) + 1 = 2$ states of $j = 1/2$, $m_j = 1/2$ has the following two:

$$|1; -\frac{1}{2}\} \quad , \quad |0; \frac{1}{2}\}$$

Since one of the two makes linear combination (43b) with $j = 3/2,\ m_j = 1/2$, we can easily understand that the other state $j = 1/2,\ m_j = 1/2$ is orthogonal to (43b):

$$|\ell = 1, s = \frac{1}{2}; j = \frac{1}{2}, m_j = \frac{1}{2}\rangle = -\sqrt{\frac{1}{3}}|0; \frac{1}{2}\} + \sqrt{\frac{2}{3}}|1; -\frac{1}{2}\} \qquad (44a)$$

However, we may obtain only the ratio of coefficient by the orthogonal condition, the absolute value can be defined by the orthonormal condition. To operate $\hat{j}_-$, we obtain the following:

$$\begin{aligned}
&\hat{j}_-|\ell = 1, s = \frac{1}{2}; j = \frac{1}{2}, m_j = \frac{1}{2}\rangle \\
&= \hbar\sqrt{1}|\ell = 1, s = \frac{1}{2}; j = \frac{1}{2}, m_j = -\frac{1}{2}\rangle \\
&= (\hat{\ell}_- + \hat{s}_-)[-\sqrt{\frac{1}{3}}|0; \frac{1}{2}\} + \sqrt{\frac{2}{3}}|1; -\frac{1}{2}\}] \\
&= -\sqrt{\frac{1}{3}}[\hbar\sqrt{1 \times 2}|-1; \frac{1}{2}\} + \hbar\sqrt{1 \times 1}|0; -\frac{1}{2}\}] + \sqrt{\frac{2}{3}}\hbar\sqrt{2 \times 1}|0; -\frac{1}{2}\} \\
&= -\hbar\sqrt{\frac{2}{3}}|-1; \frac{1}{2}\} + \hbar\sqrt{\frac{1}{3}}|0; -\frac{1}{2}\}
\end{aligned}$$

To have them in order, we can write as:

$$|\ell = 1, s = \frac{1}{2}; j = \frac{1}{2}, m_j = -\frac{1}{2}\rangle = -\sqrt{\frac{2}{3}}|-1; \frac{1}{2}\} + \sqrt{\frac{1}{3}}|0; -\frac{1}{2}\} \quad (44b)$$

The coefficients appearing in (43a=d)(44a~b):

$$\langle \ell = 1, m_\ell; s = \frac{1}{2}, m_s | \ell = 1, s = \frac{1}{2}; j, m_j\rangle \qquad (45)$$

(45) are commonly written as:

$$\langle \ell, m_\ell; s, m_s | j, m_j\rangle \qquad (46)$$

The above is often called Wigner coefficient or Clebsch-Gordan coefficient.

The rules for the composition $\boldsymbol{j} = \hat{\ell} + \boldsymbol{s}$ of orbital angular momentum and the spin angular momentum can be shared with the composition of general angular momentum $\boldsymbol{j}_1$ and $\boldsymbol{j}_2$, which may be expressed as:

$$|j_1 j_2; jm\rangle = \sum_{m_2} |j_1 m - m_2; j_2 m_2\rangle \langle j_1, m - m_2; j_2 m_2 | jm\rangle \qquad (47)$$

Here, in deed,

$$j = j_1 + j_2,\ j_1 + j_2 - 1,\ \cdots\cdots,\ |j_1 - j_2| \qquad (48)$$

$$m = j,\ j - 1,\ \cdots\cdots,\ -j \qquad (49)$$

Such compositions of angular momentum are useful in calculating coulomb interaction of many-electron systems.

Level Split By Spin-orbit Interaction

As we already seen, we know the composite angular momentum j takes the values $\ell \pm 1/2$, and the energy levels given in (36) may split in the following:

$$\langle H_{so}\rangle = \begin{cases} \hbar^2 \zeta_\ell \cdot \dfrac{\ell}{2}: & j = \ell + \dfrac{1}{2} \\ -\hbar^2 \zeta_\ell \cdot \dfrac{\ell + 1}{2}: & j = \ell - \dfrac{1}{2} \end{cases} \qquad (50)$$

Here, $j = \ell + 1/2$ has its level in $2j + 1 = 2(\ell + 1)$ folds, and $j = \ell - 1/2$ has the level in 2ℓ degeneracy.

Anomalous Zeeman Effect

The interaction energy between the spin magnetic dipole excitation (18) and the magnetic flux density is written as:

$$H_{sZ} = -\boldsymbol{m}_s \cdot \boldsymbol{H} = \frac{e}{m}\boldsymbol{s} \cdot \boldsymbol{B} \qquad (51)$$

(51) is called anomalous Zeeman effect correspond to the normal Zeeman effect that stems from orbital angular momentum. By adding the terms the normal Zeeman effect and the anomalous Zeeman effect, we can write the following

$$+\frac{e\boldsymbol{B}}{2m} \cdot (\hat{\ell} + 2\boldsymbol{s}) \qquad (52)$$

The total energy turns more complex when the energy level was split at the magnetic field. (52) clearly states that this term is not commutative with $\hat{\boldsymbol{j}}^2 = (\hat{\ell} + \boldsymbol{s})^2,\ \hat{j}_z$.

If the magnitude of the magnetic field is strong enough that we can ignore the magnitude of the spin-orbit interaction, it is more useful to assign the states by eigenfunctions of $\hat{\ell}^2,\ \hat{\ell}_z,\ \boldsymbol{s}^2,\ \hat{s}_z$. In the figure below shows the behaviors of energy levels shifting from $B = 0, j,\ m_j$ to $B = \infty,\ m_\ell,\ m_s$. Where B is in the finite region, $\hat{\ell}^2,\ \boldsymbol{s}^2$ are the only quantity to assign the states therefore, the electrons states possess the same ℓ、s may be mixed.

------Fig.-----