Basics of Angular momentum and Spin

Naoya Kawakami

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1 Angular momentum

In the classical pjysics, the angular momentum ($\boldsymbol{l}$) of a particle with the momentum $\boldsymbol{p}$ and radius $\boldsymbol{r}$ is defined by

$$\begin{aligned} \boldsymbol{l} &= \boldsymbol{r} \times \boldsymbol{p} \\ &= (yp_z - zp_y, zp_x - xp_z, xp_y - yp_x) \\ &= (l_x, l_y, l_z). \end{aligned} \tag{1}$$

The operator for angular momentum in quantum mechanics can be obtained by replacing $\hat{x} \to x$ and $\hat{p_x} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ as follows:

$$\begin{aligned} \hat{l_z} &= \hat{x}\hat{p_x} - \hat{y}\hat{p_x} \\ &= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \end{aligned} \tag{2}$$

By introducing a polar coodinates ($x = r\cos\phi$, $y = r\sin\phi$), the operator is expressed by

$$\hat{l_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}. \tag{3}$$

Let us assume that $\Phi(\phi)$ is the eigenfunction of eq. 3 with the eigenvalue of α, indicating that

$$\frac{\hbar}{i}\frac{\partial \Phi(\phi)}{\partial \phi} = \alpha\Phi(\phi). \tag{4}$$

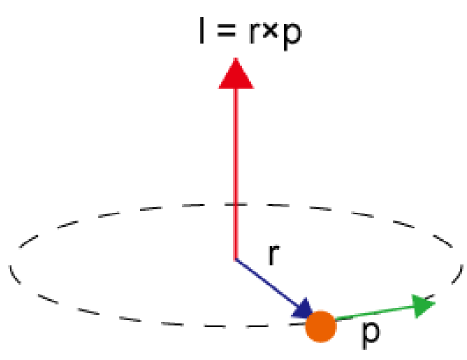

Figure 1: Classical defenition of angular momentum.

The general solution of eq. 4 is expressed by

$$\Phi(\phi) = N \exp\left(i\frac{\alpha\phi}{\hbar}\right). \tag{5}$$

Considering the periodisity of the wave function ($\Phi(\phi) = \Phi(\phi + 2\pi)$), the eigen value is limited to

$$\begin{aligned} e^{i2\pi\alpha/\hbar} &= 1 && (6)\\ \therefore \alpha &= m\hbar \ (m = 0, \pm 1, \pm 2, \dots) && (7) \end{aligned}$$

The eigenvalues of the angular momentum operator take the discrete value in the unit of $\hbar$.

2 Angular momentum operators in three dimensions

Equations 8 to 10 are the operators for angular momentums:

$$\begin{aligned} \hat{l_x} &= \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \hat{l_y} = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \hat{l_z} = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) && (8)\\ \hat{\boldsymbol{l}} &= (\hat{l_x}, \hat{l_y}, \hat{l_z}) && (9)\\ \hat{\boldsymbol{l}}^2 &= \hat{l_x}^2 + \hat{l}_y^2 + \hat{l}_z^2 && (10) \end{aligned}$$

The exchange relations of these operators are as follows:

$$\left[\hat{l_x}, \hat{l_y}\right] = i\hbar\hat{l_z}, \left[\hat{l_y}, \hat{l_z}\right] = i\hbar\hat{l_x}, \left[\hat{l_z}, \hat{l_x}\right] = i\hbar\hat{l_y} \tag{11}$$

$$\left[\hat{\boldsymbol{l}}^2, \hat{l_x}\right] = \left[\hat{\boldsymbol{l}}^2, \hat{l_y}\right], \left[\hat{\boldsymbol{l}}^2, \hat{l_z}\right] = 0. \tag{12}$$

$\hat{l_x}$, $\hat{l_y}$, and $\hat{l_x}$ can not be exchanged, indicating that there are no simultaneous eigenfunctions. Besides, only one of $\hat{l_x}$, $\hat{l_y}$, and $\hat{l_x}$ has the simultanious eigenfunctions with $\hat{\boldsymbol{l}}^2$. Therefore, we often take the z-axis along the magnetic field and consider the eigenstates of $\hat{\boldsymbol{l}}^2$ and $\hat{l_z}$.

The simultaneous eigenfunction is expressed by a spherical harmonics as follows:

$$Y_{lm}(\theta, \phi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{l+|m|)!}} P_l^{|m|} \cos\theta e^{im\phi}. \tag{13}$$

$P_l^{|m|}$ is called associated Legendle function. Two labels, l and m, are called azimuthal and magnetic quantum numbers. l takes positive integers, and m takes $-l, -l+1, \dots, l$ for each l. The wavefunction corresponding to each l is called $s, p, d, \dots$ orbital. $2l+1$ states are degenerate for each l. The eigenvalues of eq. 13 for $\hat{\boldsymbol{l}}^2$ and $\hat{l}_z$ is calculated as follows:

$$\begin{aligned} \hat{\boldsymbol{l}}^2 Y_{lm}(\theta, \phi) &= \hbar^2 l(l+1) Y_{lm}(\theta, \phi), && (14)\\ \hat{l}_z Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi). && (15) \end{aligned}$$

3 Ladder operators

We define the following operators, called ladder operators:

$$\hat{l}_\pm = \hat{l}_x \pm i\hat{l}_y. \tag{16}$$

The exchange relation with the $\hat{l}_z$ and $\hat{\boldsymbol{l}}^2$ are as follows:

$$\begin{aligned}
\left[\hat{l}_z, \hat{l}_\pm\right] &= \pm\hbar\hat{l}_\pm, &(17)\\
\left[\hat{l}_+, \hat{l}_-\right] &= 2\hbar\hat{l}_z, &(18)\\
\left[\hat{\boldsymbol{l}}^2, \hat{l}_\pm\right] &= 0. &(19)
\end{aligned}$$

For clarifying the function of ladder operators, we will apply $\hat{\boldsymbol{l}}^2$ and $\hat{l}_z$ on $\hat{l}_\pm |l,m\rangle$:[1]

$$\begin{aligned}
\hat{\boldsymbol{l}}^2\hat{l}_\pm |l,m\rangle &= \hat{l}_\pm\hat{\boldsymbol{l}}^2 |l,m\rangle \\
&= l(l+1)\hbar^2\hat{l}_\pm |l,m\rangle\,, &(20)\\
\hat{l}_z\hat{l}_\pm |l,m\rangle &= \left(\hat{l}_\pm\hat{l}_z \pm \hbar\hat{l}_\pm\right)|l,m\rangle \\
&= m\hbar\hat{l}_\pm |lm\rangle \pm \hbar\hat{l}_\pm |l,m\rangle \\
&= \hbar(m\pm 1)\hat{l}_\pm |l,m\rangle\,. &(21)
\end{aligned}$$

Equation 20 indicates that the ladder operators do not affect the eigenvalue of $\hat{\boldsymbol{l}}^2$ (in other words, $\hat{l}_\pm |lm\rangle$ and $|lm\rangle$ produce the same l). On the other hand, the eigenvalues for $\hat{l}_z$ for $\hat{l}_\pm |l,m\rangle$ is $m\pm1$, indicating that the magnetic number of $\hat{l}_\pm |l,m\rangle$ increases (decreses). These relations can be expressed as follows:

$$\begin{aligned}
\hat{l}_\pm |l,m\rangle &= C_\pm(l,m)\,|l,m\pm 1\rangle\,, &(22)\\
C_+(l,m) &= \hbar\sqrt{(l-m)(l+m+1)}, &(23)\\
C_-(l,m) &= \hbar\sqrt{(l+m)(l-m+1)}. &(24)
\end{aligned}$$

The ladder operators change the m one by one. Therefore, these will be used in the following sections to calculate the terms related to $\hat{l}_x$ and $\hat{l}_y$, which are not the eigenoperators, using the following relations:

$$\hat{l}_x = \frac{\hat{l}_+ + \hat{l}_-}{2}, \hat{l}_y = \frac{\hat{l}_+ - \hat{l}_-}{2i}. \tag{25}$$

4 Angular momentum and magnetics

We introduced that $\hat{z}$ and $\hat{\boldsymbol{l}}^2$ take the simultaneous eigenfunctions, indicating that the magnitude of angular momentum and its z component can be determined simultaneously, while x and y components can not. This relation is schematically shown in Fig. 2, for the case of $l=2$. The eigenvalue of $\hat{\boldsymbol{l}}^2$ is $\hbar^2 l(l+1)$, so the amplitude of the angular momentum is $\sqrt{l(l+1)}\hbar$. The angular momentum vector should be located on the sphere with the radius of $\sqrt{l(l+1)}\hbar$. In addition, there are $(2l+1)$ possible z componets, expressed by $m\hbar$ ($m = -l, -l+1, \ldots, l$). For the case of $l=2$, there are five $m\hbar$, corresponding to $m = -2,-1,0,1,2$. Therefore, the angular momentum vector is further limited to a point on the disks made by cutting the sphere at corresponding z. The x and y components can not be determined, indicating that the vector is located somewhere on the disks. When the electron has the angular momentum, the classical dynamics predicts the appearance of magnetics because of the circular current. Correspondingly, in quantum mechanics, the states with different m show different magnetic responses because of the different static z components of angular momentum.

5 Spin in electrons

A Stern-Gerlach experiment revealed that the magnetic moment of an electron is classified into two states, indicating the electrons have two possible magnetic numbers m. The electrons have the intrinsic magnetic

[1] Later, we will not express the specific formula of the wave functions. Instead, each state is expressed by its quantum numbers, such as $|l,m\rangle$, indicating the states with azimuth and magnetic quantum numbers of l and m.

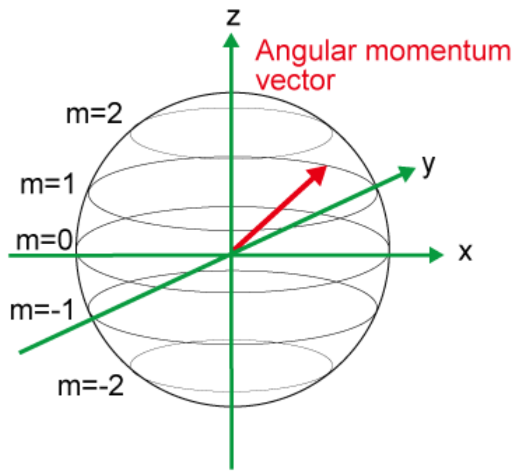

Figure 2: Quantized angular momentum for the case of $l = 2$.

moment, called spin. Remind that the magnetic numbers take $2l+1$ possible states with $(m = -l, -l+1, \ldots, l)$. Since there are only two possible m for an electron, electrons may have the angular number of $s = \frac{1}{2}$, where s is the angular number for spin corresponding to l for the normal angular momentum. To summarize, for electrons

$$s = \frac{1}{2}, m = \pm\frac{1}{2}. \tag{26}$$

The same mathematical expression with the angular momentum can be used by treating the spin as the angular momentum. We can express the relationships between spin operators as follows:

$$\hat{\boldsymbol{s}}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2, \tag{27}$$

$$\hat{s}_\pm = \hat{s}_x \pm i\hat{s}_y. \tag{28}$$

For the states with the number of s and m, the eigenvalues for $\hat{\boldsymbol{s}}^2$ and $\hat{s}_z$ are expressed as

$$\hat{\boldsymbol{s}}^2 \left|s, m\right\rangle = \hbar^2 s(s+1) \left|s, m\right\rangle, \tag{29}$$

$$\hat{s}_z \left|s, m\right\rangle = \hbar m \left|s, m\right\rangle, \tag{30}$$

$$\hat{s}_\pm \left|s, m\right\rangle = \hbar\sqrt{(s \mp m)(s \pm m + 1)} \left|s, m \pm 1\right\rangle. \tag{31}$$

6 Matrix expression

We will express the two spin states as follows:

$$|s = \frac{1}{2}, m = \frac{1}{2}\rangle = |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{32}$$

$$|s = \frac{1}{2}, m = -\frac{1}{2}\rangle = |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{33}$$

The eigenvalue for $\hat{s}_z$ should be $\hat{s}_z |s, m = \pm 1\rangle = \pm\frac{\hbar}{2} |s, m = \pm 1\rangle$. Therefore, the marix elements of $\hat{s}_z$ is expressed by

$$\langle\alpha| \hat{s}_z |\alpha\rangle = \frac{\hbar}{2}, \langle\beta| \hat{s}_z |\alpha\rangle = 0, \tag{34}$$

$$\langle\beta| \hat{s}_z |\alpha\rangle = 0, \langle\beta| \hat{s}_z |\beta\rangle = -\frac{\hbar}{2}, \tag{35}$$

$$\therefore \hat{s}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\sigma_z. \tag{36}$$

Because $\hat{s}_x$ and $\hat{s}_y$ are not the eigenstate of $|s, m\rangle$, the matrix expression can not be obtained in the same way. Instead, we use the ladder operators to get the matrix expression of $\hat{s}_x$ and $\hat{s}_y$. The matrix expression of the ladder operators is as follows:[2]

$$\langle\alpha| \hat{s}_+ |\alpha\rangle = 0, \langle\alpha| \hat{s}_+ |\beta\rangle = \hbar \langle\alpha|\alpha\rangle = \hbar, \tag{37}$$

$$\langle\beta| \hat{s}_+ |\alpha\rangle = 0, \langle\beta| \hat{s}_+ |\beta\rangle = \langle\beta|\alpha\rangle = 0 \tag{38}$$

$$\therefore \hat{s}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{39}$$

$$\langle\alpha| \hat{s}_- |\alpha\rangle = \langle\alpha|\beta\rangle = 0, \langle\alpha| \hat{s}_- |\beta\rangle = 0, \tag{40}$$

$$\langle\beta| \hat{s}_- |\alpha\rangle = \hbar \langle\beta|\beta\rangle = \hbar, \langle\beta| \hat{s}_- |\beta\rangle = 0 \tag{41}$$

$$\therefore \hat{s}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{42}$$

The matrix expression of $\hat{s}_x$ and $\hat{s}_y$ are obtained as follows using the definition of the ladder operators:

$$\hat{s}_x = \frac{\hat{s}_+ + \hat{s}_-}{2} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_x \tag{43}$$

$$\hat{s}_y = \frac{\hat{s}_+ - \hat{s}_-}{2i} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_y \tag{44}$$

The matrixes σ_x, σ_y, and σ_z are called Pauri's matrixes. The intrinsic nature of spin is obtained through solving the Schrödinger equation considering the relativity theory, called Dirac equations. The Pauri matrixes are also used in the Dirac equation, justifying the treatment of spin as the angular momentum.

7 Coupling of angular momentums

Let us consider the two independent angular momentums ($\boldsymbol{j_1}$ and $\boldsymbol{j}_2$). We will express the angular and magnetic number of these states as j_1, j_2 and m_1, m_2, respectively. If we define the combination of these two angular momentums as

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{j}}_1 + \hat{\boldsymbol{j}}_2 = (\hat{j}_{1x} + \hat{j}_{2x}, \hat{j}_{1y} + \hat{j}_{2y}, \hat{j}_{1z} + \hat{j}_{2z}), \tag{45}$$

the possible angular (J) and magnetic (M) number for the $\hat{\boldsymbol{J}}$ are as follows:

$$J = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|, \tag{46}$$

$$M = J, J - 1, \ldots, -J. \tag{47}$$

The fundamental relations for angular momentum can also be applied for combined angular momentum $\hat{\boldsymbol{J}}$.

[2] Note that $\hat{s}_+ |\alpha\rangle = \hat{s}_- |\beta\rangle = 0$ because the state with $m = \pm\frac{3}{2}$ does not exist for electron spin. This relation is included in the matrix expression.

8 Coupling of two spins

Let us consider the coupling of two spins. We will express the operators for the spins as follows:

$$\hat{\boldsymbol{s}}_1 = (\hat{s}_{1x}, \hat{s}_{1y}, \hat{s}_{1z}), \tag{48}$$
$$\hat{\boldsymbol{s}}_2 = (\hat{s}_{2x}, \hat{s}_{2y}, \hat{s}_{2z}). \tag{49}$$

The related operators are expressed as

$$\hat{s}_{1+} = \hat{s}_{1x} + i\hat{s}_{1y}, \tag{50}$$
$$\hat{s}_{1-} = \hat{s}_{1x} - i\hat{s}_{1y}, \tag{51}$$
$$\hat{s}_{2+} = \hat{s}_{2x} + i\hat{s}_{2y}, \tag{52}$$
$$\hat{s}_{2-} = \hat{s}_{2x} - i\hat{s}_{2y}. \tag{53}$$

The operators for the combined state can be defined as follows:

$$\hat{\boldsymbol{S}} = \hat{\boldsymbol{s}}_1 + \hat{\boldsymbol{s}}_2, \tag{54}$$
$$\begin{aligned} \hat{\boldsymbol{S}}^2 &= \hat{\boldsymbol{s}}_1^2 + 2\hat{\boldsymbol{s}}_1 \cdot \hat{\boldsymbol{s}}_2 + \hat{\boldsymbol{s}}_2^2 \\ &= \hat{\boldsymbol{s}}_1^2 + \hat{\boldsymbol{s}}_2^2 + \hat{s}_{1+}\hat{s}_{2-} + \hat{s}_{1-}\hat{s}_{2+} + 2\hat{s}_{1z}\hat{s}_{2z} \end{aligned} \tag{55}$$

We will express the angular and magnetic numbers of the combined state as S and M. In other words, for the combined state, the eigenvalues for $\hat{\boldsymbol{S}}^2$ and $\hat{S}_z$ are expressed as follows:

$$\hat{\boldsymbol{S}}^2 \rightarrow S(S+1)\hbar^2, \tag{56}$$
$$\hat{S}_z \rightarrow M\hbar. \tag{57}$$

Considering the rule of combined angular momentum in eq. 46, the two spin states should have two possible S, $S = 1, 0$.

Let us consider four combined states of two spins,

$$|\alpha\rangle_1 |\alpha\rangle_2 = |\uparrow\uparrow\rangle, \tag{58}$$
$$|\alpha\rangle_1 |\beta\rangle_2 = |\uparrow\downarrow\rangle, \tag{59}$$
$$|\beta\rangle_1 |\alpha\rangle_2 = |\downarrow\uparrow\rangle, \tag{60}$$
$$|\beta\rangle_1 |\beta\rangle_2 = |\downarrow\downarrow\rangle. \tag{61}$$

Here, we should note that the eq. 60 and 61 does not stisfy the exchnage relation of electrons.[3] Therefore, we should find the mixture state that satisfies the exchange relation. Firstly, we start from eq. 59, which satisfies the exchange relation. The eigenvalue of the state eq. $|\beta\rangle$ for $\hat{\boldsymbol{S}}^2$ is calculated as follows:

$$\begin{aligned} \hat{\boldsymbol{S}}^2 |\uparrow\uparrow\rangle &= (\hat{s}_1^2 + \hat{s}_2^2 + 2\hat{s}_{1z}\hat{s}_{2z}) |\uparrow\uparrow\rangle + \hat{s}_{1+}\hat{s}_{2-} |\uparrow\uparrow\rangle + \hat{s}_{1-}\hat{s}_{2+} |\uparrow\uparrow\rangle \\ &= (\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + \frac{1}{2}\hbar^2) |\uparrow\uparrow\rangle + 0 + 0 \\ &= 2\hbar^2 |\uparrow\uparrow\rangle . \end{aligned} \tag{62}$$

Therefore, considering the relation in eq. 56, the angular number of $|\uparrow\uparrow\rangle$ is $S = 1$. The eigenvalue for $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$ is calculated to be

$$\hat{S}_z |\uparrow\uparrow\rangle = \hbar |\uparrow\uparrow\rangle . \tag{63}$$

Therefore, the magnetic number of $|\uparrow\uparrow\rangle$ is $M = 1$. In the same way, we can obtain $S = 1$ and $M = -1$ for $|\downarrow\downarrow\rangle$.

[3] Because electrons are indistinguishable, the expected value of the wave function should not change by exchanging the two electrons. Therefore, $\phi(a,b) = \pm\phi(b,a)$. For example, if we exchange the spin state of in eq.60, $|\beta\rangle |\alpha\rangle \neq \pm |\alpha\rangle |\beta\rangle$.

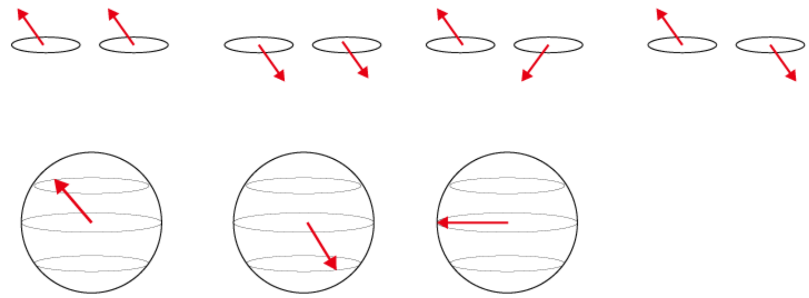

Figure 3: Schematic representation of triplet and singlet state.

Then we will consider the state with $M = 0$ by applying the ladder operator $\hat{S}_- = \hat{s}_{1-} + \hat{s}_{2-}$ to $|\uparrow\uparrow\rangle$ as follows:

$$\begin{aligned} \hat{S}_- |\uparrow\uparrow\rangle &= (\hat{s}_{1-} + \hat{s}_{2-}) |\uparrow\uparrow\rangle && (64)\\ &= |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle . && (65) \end{aligned}$$

By applying $\hat{\boldsymbol{S}}^2$ and $\hat{S}_z$, we can confirm the state in eq. 65 has $S = 1$ and $M = 0$.[4] The remainng state is $S = 0, M = 0$. The state should be orthogonal with the $S = 1, M = 0$ state, so we consider the following state:

$$|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle . \tag{66}$$

By applying $\hat{\boldsymbol{S}}^2$, we get $S = 0$ as follows:

$$\begin{aligned} \hat{\boldsymbol{S}}^2(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) &= (\hat{\boldsymbol{s}}_1^2 + \hat{\boldsymbol{s}}_2^2 + 2\hat{s}_{1z}\hat{s}_{2z} + \hat{s}_{1+}\hat{s}_{2-} + \hat{s}_{1-}\hat{s}_{2+})(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) \\ &= \hbar^2 \left(\frac{3}{4} |\downarrow\uparrow\rangle + \frac{3}{4} |\downarrow\uparrow\rangle + 2(-\frac{1}{2})(\frac{1}{2}) |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle + 0 \right) \\ &\quad -\hbar^2 \left(\frac{3}{4} |\uparrow\downarrow\rangle + \frac{3}{4} |\uparrow\downarrow\rangle + 2(\frac{1}{2})(-\frac{1}{2}) |\uparrow\downarrow\rangle + 0 + |\downarrow\uparrow\rangle \right) \\ &= 0 && (67)\\ \therefore S &= 0. && (68) \end{aligned}$$

We can also calculate that $M = 0$.

We got four states with different angular and magnetic numbers, as summarized below:

$$\begin{aligned} |\uparrow\uparrow\rangle &\qquad (S = 1, M = 1) && (69)\\ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle &\qquad (S = 1, M = 0) && (70)\\ |\downarrow\downarrow\rangle &\qquad (S = 1, M = -1) && (71)\\ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle &\qquad (S = 0, M = 0) && (72) \end{aligned}$$

The three states with $S = 1$ are called triplets, while those with $S = 0$ are called singlets. The schematic representation of the triplets and singlet is shown in Fig. 3. In the $S = 1, M = 0$ state, although the net spin in the z direction cancels out, the xy component remains, resulting in $S = 1$. On the other hand, in $S = 0, M = 0$ state, all the spin is canceled out, resulting in no net angular momentum.[5]

[4] Note that eq. 65 is not normarized.

[5] In this explanation, the spin phase in xy plane seems to be important. However, I still don't fully understand the phase of spin, and I also don't understand how the relation of Fig. 3 and the expression in eq. 65 and 66.

9 related topics for singlet and triplet

This section introduces several topics related to the singlet and triplet states.

9.1 Exchange relation

The particles should be symmetric or antisymmetric against the exchange. As we have already introduced in eq. 65, the spin component of the wave function for $S = 1, M = 0$ state is expressed by

$$\phi_T(s_1, s_2) = |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle \,. \tag{73}$$

By exchanging s_1 and s_2, we get

$$\begin{aligned} \phi_T(s_2, s_1) &= |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ &= \phi_T(s_1, s_2). \end{aligned} \tag{74}$$

Therefore, $S = 1, M = 0$ is symmetric against the exchange. In the same way, we can prove that all the triplets are symmetric against the exchange. In contrast, for the singlet state ($S = 0, M = 0$),

$$\phi_S(s_1, s_2) = |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \tag{75}$$

$$\begin{aligned} \phi_S(s_2, s_1) &= |\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle \\ &= -\phi(s_1, s_2), \end{aligned} \tag{76}$$

indicating that the singlet is antisymmetric against the exchange. An electron should be antisymmetric against exchange because it is a Fermion. Therefore, the whole wave function, including the orbital part, should be antisymmetric against exchange. Considering that the triplet (single) is symmetric (antisymmetric) for the exchange, the orbital part of the wave function for the triplet (singlet) should be antisymmetric (symmetric). In other words, if we express the orbital part of two electrons as $\psi_1(r)$ and $\psi_2(r)$, the orbital wave function can be expressed as

$$\Psi_+(r_1, r_2) = \frac{1}{\sqrt{2}}(\psi_1(r_1)\psi_2(r_2) + \psi_1(r_2)\psi_2(r_1)) \tag{77}$$

$$\Psi_-(r_1, r_2) = \frac{1}{\sqrt{2}}(\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)). \tag{78}$$

Here, Ψ_+ is symmetric against exchange, while Ψ_- is antisymmetric. Combining with the spin part, the possible states for an electron is

$$\Psi_+\phi_S, \Psi_-\phi_T, \tag{79}$$

both are antisymmetric against exchange.

9.2 Exchange interaction

In the previous part, we saw that the symmetry of the orbital wavefunction is different for the singlet and triplet states. It induces a difference in energy. Here, we will consider the Coulomb interaction in the two-electron systems. The Hamiltonian for the Coulomb interaction and its expected value for the state $\Psi(r_1, r_2)$ is expressed as follows:

$$H_{Coulomb} = \frac{e^2}{r_{12}}, \tag{80}$$

$$E_{Coulomb} = \int dr_1 dr_2 \Psi^*(r_1, r_2)\frac{e^2}{r_{12}}\Psi(r_1, r_2). \tag{81}$$

For the two possible states in eq. 77 and 78, the Coulomb energy is calculated to be

$$
\begin{aligned}
E^{\pm}_{Coulmb} &= \frac{1}{2}\int dr_1 dr_2 \left(\psi_1^*(r_1)\psi_2^*(r_2) \pm \psi_1^*(r_2)\psi_2^*(r_1)\right)\frac{e^2}{r_{12}}\left(\psi_1(r_1)\psi_2(r_2) \pm \psi_1(r_2)\psi_2(r_1)\right) \\
2E^{\pm}_{Coulmb} &= \int dr_1 dr_2 |\psi_1(r_1)|^2 \frac{e^2}{r_{ab}}|\psi_2(r_2)|^2 \\
&\pm \int dr_1 dr_2 \psi_1^*(r_1)\psi_2^*(r_2)\frac{e^2}{r_{ab}}\psi_1(r_2)\psi_2(r_1) \\
&\pm \int dr_1 dr_2 \psi_1^*(r_2)\psi_2^*(r_1)\frac{e^2}{r_{ab}}\psi_1(r_1)\psi_2(r_2) \\
&+ \int dr_1 dr_2 |\psi_1(r_2)|^2 \frac{e^2}{r_{ab}}|\psi_2(r_1)|^2 \\
&= 2K \pm 2J \qquad (82) \\
\therefore E &= K \pm J. \qquad (83)
\end{aligned}
$$

Here, we defined K and J as follows:

$$
\begin{aligned}
K &= \int dr_1 dr_2 |\psi_1(r_1)|^2 \frac{e^2}{r_{ab}}|\psi_2(r_2)|^2 = \int dr_1 dr_2 |\psi_1(r_2)|^2 \frac{e^2}{r_{ab}}|\psi_2(r_1)|^2 \qquad (84) \\
J &= \int dr_1 dr_2 \psi_1^*(r_1)\psi_2^*(r_2)\frac{e^2}{r_{ab}}\psi_1(r_2)\psi_2(r_1) = \int dr_1 dr_2 \psi_1^*(r_2)\psi_2^*(r_1)\frac{e^2}{r_{ab}}\psi_1(r_1)\psi_2(r_2) \qquad (85)
\end{aligned}
$$

K and J are called Coulomb and exchange integration, respectively. As Ψ_+ and Ψ_- corresponds to singlet and triplet, eq. 83 indicates that the triplet and singlet have the energy difference of $2J$, originating from the exchange interaction.

Let us consider the eigenvalues of $\hat{s}_1 \cdot \hat{s}_2$ on the triplet and singlet.

$$
\begin{aligned}
\hat{s}_1 \cdot \hat{s}_2 \left|S=1, M=0,\pm 1\right\rangle &= (\hat{\boldsymbol{S}}^2 - \hat{s}_1^2 - \hat{s}_2^2)\left|S=1, M=0,\pm 1\right\rangle \\
&= (2 - \frac{3}{4} - \frac{3}{4})\hbar^2 \left|S=1, M=0,\pm 1\right\rangle \\
&= \frac{1}{4}\hbar^2 \left|S=1, M=0,\pm 1\right\rangle \qquad (86) \\
\hat{s}_1 \cdot \hat{s}_2 \left|S=0, M=0\right\rangle &= -\frac{3}{4}\hbar^2 \left|S=0, M=0\right\rangle. \qquad (87)
\end{aligned}
$$

These equations indicate that the eigenvalue of $\hat{s}_1 \cdot \hat{s}_2$ on the singlet and triplet has the $\hbar^2$ difference. Therefore, the energy difference of $2J$ can be taken into account by introducing a Hamiltonian

$$
\hat{H}_{ex} = -\frac{2J}{\hbar^2}\hat{s}_1 \cdot \hat{s}_2. \qquad (88)
$$

This Hamiltonian expresses the exchange interaction originating from the exchange relation of the spin components.

10 Stern-Gerlach experiment

Figure 4 represents the subsequent measurement of the spin of an electron, showing an interesting aspect of quantum mechanics. Firstly, the state of the electron is unknown ($|\psi\rangle$). By measuring the z component of the spin, the electrons are divided into two states with $\pm\hbar/2$. This result indicates that the electron has two possible magnetic states, which is the main discovery of the Stern-Gerlach experiment. Then, we measure the x component of the electrons that showed $-\hbar/2$ in z compoenent, $|\downarrow\rangle$. The x component is also divided into two states with $\pm\hbar/2$. Furthermore, we measure the z component again for the $-\hbar/2$ state in x measurement,

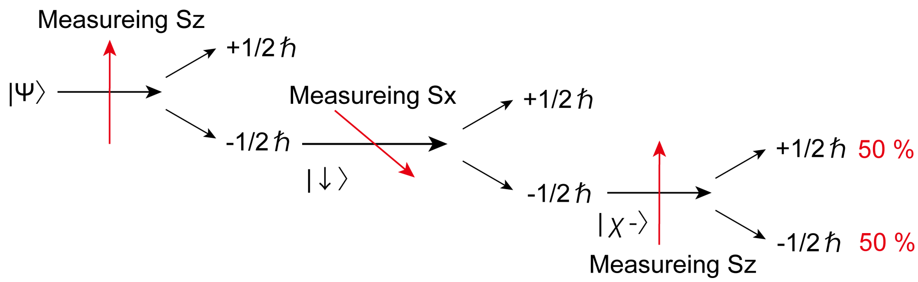

Figure 4: Subsequent Stern-Gerlach experiment.

$|\chi^-\rangle$. The z component is divided into two, although we have already picked the electrons with a down state in the first step. How can we understand this result in quantum mechanics?

As we have already discussed, $\hat{s}_z, \hat{s}_y$, and $\hat{s}_z$ do not have the simultaneous eigenvalues. Thus, we often express the spin state in $\hat{s}_z$ basis, as

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{89}$$

Let us try expressing the eigenstate for $\hat{s}_x$ on this basis. If we express the eigenvector and eigenvalue as $(x, y)^T$ and λ, the eigenequation is

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \lambda \begin{pmatrix} x \\ y \end{pmatrix} \tag{90}$$

The eigenvalues and eigenvectors are calculated to be

$$|\chi_+^x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \left(\lambda = \frac{\hbar}{2}\right) \tag{91}$$

$$|\chi_-^x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \left(\lambda = -\frac{\hbar}{2}\right) \tag{92}$$

$$\tag{93}$$

Let us go back to the Stern-Gerlach experiment. The state $|\downarrow\rangle$ is picked up in the first step. The $|\downarrow\rangle$ state can be expressed using the eigenfunctions for $\hat{s}_x$ as follows:

$$|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} |\chi_+^x\rangle - \frac{1}{\sqrt{2}} |\chi_-^x\rangle \tag{94}$$

Therefore, by measureing the s_x component of $|\downarrow\rangle$, two stats corresponding to $|\chi_+^x\rangle$ and $|\chi_-^x\rangle$ are obtained in the equal possibility. Then, for the s_z component measurement for $|\chi_-^x\rangle$, we will express it using $|\uparrow\rangle$ and $|\downarrow\rangle$:

$$|\chi_-^x\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle - |\downarrow\rangle) \tag{95}$$

The most important thing here is that by confirming the state for x, the information for the original state is collapsed. Therefore, the other component of the spin becomes uncertain. Following the eq. 95, the z component of the state $|\chi_-^x\rangle$ is devided into two with the equal possibility.

11 Spin in magnetic field

Let us assume an electron circularly moves around the z-axis, as shown in Fig. 5. The magnetic moment of the small circular current is expressed by

$$M_z = I\pi r^2. \tag{96}$$

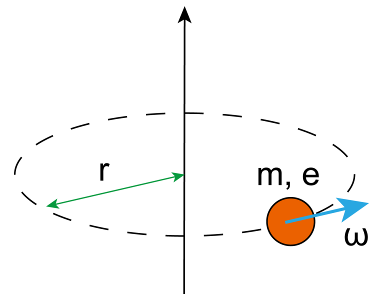

Figure 5: chematic of the circular motion of an electron.

The angular momentum and current are expressed by $L_z = mr^2\omega$ and $I = e\omega/2\pi$. Therefore,

$$\begin{aligned} M_z &= \pi r^2 \frac{e\omega}{2\pi} \\ &= \frac{e}{2m} L_z. \end{aligned} \tag{97}$$

As the angular momentum is quantized by the unit of $\hbar$ in quantum mechanics, we get

$$\begin{aligned} M_z &= \frac{e\hbar}{2m} n \\ &= \mu_B n. \end{aligned} \tag{98}$$

In quantum mechanics, the magnetic moment is quantized by μ_B, called Bour magnetic moment. The operator to get the magnetic moment is expressed as follows:

$$\hat{M}_z = \mu_B \frac{\hat{L}_z}{\hbar}. \tag{99}$$

For spins, the eigenvalues for the angular momentum is $\pm\hbar/2$. Therefore, the spin seems to show the magnetic moment of $\mu_B/2$, but the spin also shows the same magnetic moment as the μ_B. For compensate this difference, the magnetic moment of spin is expressed as

$$\mu_s = g\mu_B \frac{S_z}{\hbar}, \tag{100}$$

where g is called Lande's g-factor. For a free electron, it is known that $g \sim 2$.

The energy induced by the interaction between the magnetic moment and magnetic field is expressed by $-\vec{\mu} \cdot \vec{B}$. The energy operator for the spin under the magnetic field along z direction is thus expressed by

$$\hat{H} = -\gamma B_z \hat{s}_z. \tag{101}$$

The energy for $|\uparrow\rangle$ and $|\downarrow\rangle$ are

$$E_{\uparrow\downarrow} = \mp \frac{\gamma B_0 \hbar}{2}. \tag{102}$$

We will consider the evolution of the system over time. Let us consider the initial state is expressed by the combination of $|\uparrow\rangle$ and $|\downarrow\rangle$ as follows:

$$|\psi\rangle = a\,|\uparrow\rangle + b\,|\downarrow\rangle\,, \tag{103}$$

$$a = \cos(\frac{\alpha}{2}), b = \sin(\frac{\alpha}{2}). \tag{104}$$

a and b represent the normalized population of each state. Following the time-dependent Schrödinger equation , the time evolution of the system is expressed by

$$
\begin{aligned}
|\psi(t)\rangle &= a\,|\uparrow\rangle \exp\left(-\frac{iE_\uparrow t}{\hbar}\right) + b\,|\downarrow\rangle \exp\left(-\frac{iE_\downarrow t}{\hbar}\right) \\
&= \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right)\exp\left(\frac{i\gamma B_z t}{2}\right) \\ \sin\left(\frac{\alpha}{2}\right)\exp\left(-\frac{i\gamma B_z t}{2}\right) \end{pmatrix}. \qquad (105)
\end{aligned}
$$

Consider the expected value of $\hat{S}_x$.

$$
\begin{aligned}
< S_x > &= \langle\psi(t)|\hat{S}_x|\psi(t)\rangle \\
&= \left(\cos\left(\frac{\alpha}{2}\right)\exp\left(-\frac{i\gamma B_z t}{2}\right), \sin\left(\frac{\alpha}{2}\right)\exp\left(\frac{i\gamma B_z t}{2}\right)\right) \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right)\exp\left(\frac{i\gamma B_z t}{2}\right) \\ \sin\left(\frac{\alpha}{2}\right)\exp\left(-\frac{i\gamma B_z t}{2}\right) \end{pmatrix} \\
&= \frac{\hbar}{2}\cos\left(\frac{\alpha}{2}\right)\sin\left(\frac{\alpha}{2}\right)\left(\exp(-i\gamma B_0 t) + \exp(i\gamma B_0 t)\right) \\
&= \frac{\hbar}{2}\sin(\alpha)\cos(\gamma B_z t). \qquad (106)
\end{aligned}
$$

Equation 106 indicates that the expected value of the x component oscillates with the frequency of $\omega = \gamma B_0$. It means that under the magnetic field in the z direction, the magnetic moment of spin is rotating around the z axis. This motion is called Lamor precession.

12 Spin-orbital coupling (SOC)

The angular momentum and spin both show the magnetic property. Therefore, these magnetic moments interact, resulting in slightly different energy depending on the spin state. As discussed, the magnetic moment μ in magnetic field B has the energy of $E = -\mu \cdot B$. Considering that the field is proportional to the angular momentum L, the energy difference by the SOC should be proportional to $\hat{L} \cdot \hat{s}$. Considering the operator for the combined angular momentum, the $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{s}}$ can be expressed as follows:

$$
\begin{aligned}
\hat{\boldsymbol{J}}^2 &= (\hat{\boldsymbol{L}} + \hat{\boldsymbol{s}})^2 = \hat{\boldsymbol{L}}^2 + \hat{\boldsymbol{s}}^2 + 2\hat{\boldsymbol{s}} \cdot \boldsymbol{L} \qquad (107) \\
\therefore \hat{\boldsymbol{s}} \cdot \boldsymbol{L} &= \frac{1}{2}\hbar^2(j(j+1) - l(l+1) - s(s+1)) \qquad (108)
\end{aligned}
$$

Because of this SOC, the energy level of each state slightly differs depending on the total angular momentum j. This difference appears as a fine structure in the absorption spectrum.

The SOC Hamiltonian is not exchangeable with $\hat{s}$ and $\hat{l}$, while the total angular momentum $\hat{j} = \hat{l} + \hat{s}$ can be exchanged. It indicates that the $\hat{s}$ and $\hat{l}$ are not conserved under the SOC. Instead, the total angular momentum is conserved.