2.4   LS coupling

We explained Hund's rule through estimation of Coulomb mutual interaction. In addition to these two terms ($\mathcal{H}_0$, $\mathcal{H}_C$), the hamiltonian (2.1) for localized electron system in solids, has $\mathcal{H}_{\mathrm{SOI}}$ and $\mathcal{H}_{\mathrm{CF}}$. It is difficult to treat these simultaneously and we need to treat the term with higher priority and to treat the other as perturbation. First, let us examine the case the effect of $\mathcal{H}_{\mathrm{SOI}}$ is stronger than that of $\mathcal{H}_{\mathrm{CF}}$. Within this framework, there are several approaches: (i) first the ground state LS multiplex is picked and examine how that is split into sub-levels with $\mathcal{H}_{\mathrm{SOI}}$ (**LS coupling** approach); (ii) Single-electron state with spin-orbit interaction is prepared firstly, then the Coulomb effect is taken into account via Hund's rule to find the ground state (**j-j coupling**). This and the next sections are devoted to these two approaches illustrated in Fig. 2.2.

2.4.1   Effect of spin-orbit interaction on single-electron states

Here we revisit the single electron Hamiltonian for relativistic electron. The third term in eq. (1.72) is

$$-\frac{e\hbar\boldsymbol{\sigma}\cdot\boldsymbol{p}\times\boldsymbol{E}}{4m^2c^2} = -\frac{e^2\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\boldsymbol{p}\times\nabla V) = \frac{e^2\hbar}{2m^2c^2}\zeta(r)\boldsymbol{s}\cdot\boldsymbol{l} \equiv \xi(r)\boldsymbol{l}\cdot\boldsymbol{s},\tag{2.27}$$

where $V(\boldsymbol{r})$ is a potential with spherical symmetry. We first write it as $V(r)$ taking the origin at the center of the potential, then define $\zeta(r)$ as $\nabla V = (\boldsymbol{r}/r)(dV(r)/dr) \equiv \zeta(r)\boldsymbol{r}$, and apply $\boldsymbol{l} = \boldsymbol{r}\times\boldsymbol{p}$ for the above. Assuming it as the Coulomb potential $V(r) = -Ze^2/(4\pi\epsilon_0 r)$, ξ is given by

$$\xi(r) = \frac{Ze^2}{2m^2c^2}\frac{1}{(4\pi\epsilon_0)r^3},\tag{2.28}$$

which tells that the spin-orbit interaction is important for the atoms with large atomic number Z and for the atomic orbitals with smaller r, namely the orbitals closer to the atomic core. As examples of representative atoms, ions that have
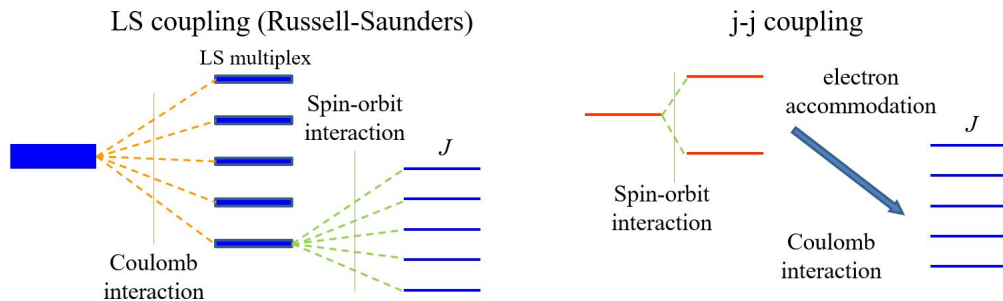

Fig. 2.2   Illustration of two representative approaches. In LS coupling (Russell-Saunders coupling) approach, the ground state LS multiplex split by the Coulomb interaction is further split into the levels with J as the quantum number by the spin-orbit interaction. In j-j coupling approach, spin-orbit interaction is considered at the single-electronic states, then the Coulomb interaction in multi-electron states is taken into account through Hund's rule.

open shells, we have listed $3d$ transition metals and Lanthanoid with $4f$ open shells. The above thought suggests that the approaches of "SOI-first" (both LS and j-j) are more appropriate for Lanthanoid than $3d$ transition metals.

The single-electron Hamiltonian with the SOI is then given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\mathrm{so}} = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}) + \xi(r)\boldsymbol{l} \cdot \boldsymbol{s}. \tag{2.29}$$

The Hamiltonian (2.27) does not commute with $\boldsymbol{l}$, $\boldsymbol{s}$, which are no longer constants of motion. This can easily be confirmed from (1.78) and (1.79). On the other hand, commutation relations, e.g,

$$[\boldsymbol{l} \cdot \boldsymbol{s}, \hat{l}_z] = i\hbar(-l_y s_x + l_x s_y), \quad [\boldsymbol{l} \cdot \boldsymbol{s}, \hat{s}_z] = i\hbar(-l_x s_y + l_y s_x) = -[\boldsymbol{l} \cdot \boldsymbol{s}, \hat{l}_z],$$

tell that the total angular momentum

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s} \tag{2.30}$$

commutes with Hamiltonian (2.27), and is a constant of motion. $\boldsymbol{j}$ satisfies the commutation relations in the same forms as (1.78) and (1.79). Hence it gets directional quantization, and the eigenfunction is indexed by (j, m) as $|j, m\rangle$ $(m = -j, -j+1, \cdots, j)$. $|j, m\rangle$ can be obtained, e.g., in the form of expansion with the eigenfunctions of $\mathcal{H}_0$.

Fig. 2.3 Illustrates precessions of $\boldsymbol{l}$ and $\boldsymbol{s}$ around $\boldsymbol{j}$.

On the other hand, $\boldsymbol{l}^2$, $\boldsymbol{s}^2$ commute with $\boldsymbol{l} \cdot \boldsymbol{s}$, thus with $\mathcal{H}$, making them as constants of motion. $\boldsymbol{l} \cdot \boldsymbol{s}$ is also written as

$$\boldsymbol{l} \cdot \boldsymbol{s} = (\boldsymbol{l} + \boldsymbol{s}) \cdot \boldsymbol{s} - \boldsymbol{s}^2 = \boldsymbol{j} \cdot \boldsymbol{s} - \boldsymbol{s}^2.$$

This form tells that $\boldsymbol{s}$ and $\boldsymbol{l}$ have the Zeeman-like term with $\boldsymbol{j}$ (a constant of motion) as magnetic field in eq. (2.9). In a classical picture, $\boldsymbol{l}$ and $\boldsymbol{s}$ precess around $\boldsymbol{j}$ satisfying eq. (2.30) as illustrated in Fig. 2.3. The angular velocity of the precession is proportional to the spin-orbit coupling strength ξ.

The eigenvalues of $\boldsymbol{l} \cdot \boldsymbol{s}$ are obtained from

$$2\boldsymbol{l} \cdot \boldsymbol{s} = (\boldsymbol{l} + \boldsymbol{s})^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2 = \boldsymbol{j}^2 - \boldsymbol{l}^2 - \boldsymbol{s}^2 \tag{2.31}$$

as

$$[j(j+1) - l(l+1) - s(s+1)]/2 = \frac{1}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]. \tag{2.32}$$

Then the energy eigenvalues are given by

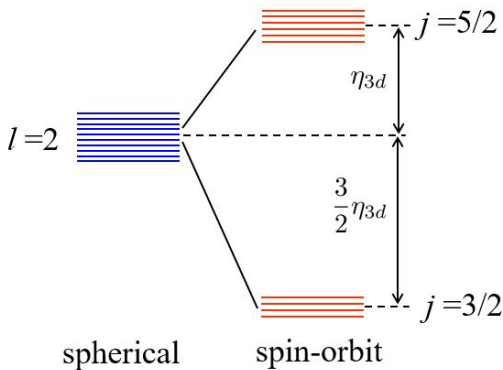$$\epsilon_{nlj} = \epsilon_{nl} + \frac{\eta_{nl}}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right], \tag{2.33}$$

Fig. 2.4 Schematic diagram for splitting of $l = 2$ (i.e. $3d$ orbital) multiplet state with $(2l+1)(2s+1) = 10$ fold degeneracy by the SOI. η_{3d} is the integrated value of eq. (2.34) for $3d$-orbital.
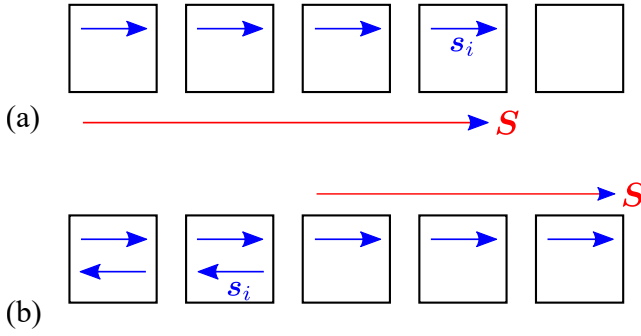
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Fig. 2.5 Schematic diagrams of how electrons are packed according to Hund's rules into a degenerate state with the same angular momentum quantum number. (a) The number of electrons is less than or the same as the number of orbitals. (b) The number of electrons is more than that of orbitals. The sum of the orbital contributions corresponding to the spins represented by the arrows in the upper column is zero.

where η_{nl} is the integral of the radial wavefunction and $\xi(r)$, namely

$$\eta_{nl} = \int_0^\infty \xi(r) R_{nl}(r)^2 r^2 dt. \tag{2.34}$$

j can take values $|l \pm 1/2|$, splitting the energy level indicated by (n, l) into two levels. Figure 2.4 shows the case of $3d$ orbital.

2.4.2 Spin-orbit interaction in multi-electron states

The SOI Hamiltonian for a multi-electron system, then can be written as

$$\mathcal{H}_{\mathrm{SOI}} = \sum_i \xi(r_i) \boldsymbol{l}_i \cdot \boldsymbol{s}_i \;\rightarrow\; \sum_i \xi_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \;\rightarrow\; \xi \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i. \tag{2.35}$$

In the above we first replace $\xi(r_i) \to \xi_i$ because the radial part will be integrated out as in eq. (2.34). Next ξ_i comes out from the summation on i because in an LS-multiplet, the orbitals should have the same radial part. The Coulomb repulsion splits the degenerated levels in the single-electron problem into LS-multiplets. In the previous section, Hund's rule has been derived as a way to find the state in which the effect of Coulomb repulsion is minimized. An LS-multiplet (L, S) still has $(2L + 1)(2S + 1)$-fold degeneracy due to the freedom of orbital and spin angular momenta.

In the presence of $\mathcal{H}_{\mathrm{SOI}}$, just as in the single-electron problem, neither the total orbital angular momentum $\boldsymbol{L}$ nor the total spin angular momentum $\boldsymbol{S}$ (defined in (2.15)) commutes with the Hamiltonian, that is, they are not constants of motion. The total angular momentum defined as

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \tag{2.36}$$

is a constant of motion.

The whole energy level structure is importtant in the discusstion of localized electron systems. For the magnetism, the ground state is particulary important. As noted, in the LS-coupling approach, we first consider the "ground state" LS-multiplet, and examine how this is split by $\mathcal{H}_{\mathrm{SOI}}$, find the ground state among them. When the number of electons n is smaller than that of degenerated orbitals $2l + 1$ for the orbital angular momentum l, in the ground state every orbital accomodates 0 or 1 electron. Then according to Hund's rule, in the ground state all electron spins are in parallel. Namely a spin dose not depend on orbital index i:

$$\boldsymbol{s}_i = \frac{1}{n} \boldsymbol{S} = \frac{1}{2S} \boldsymbol{S} \quad (n \leq 2l + 1). \tag{2.37}$$

Substituting the above into eq. (2.35), we can write

$$\mathcal{H}_{\mathrm{SOI}} = \xi \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i = \xi \left(\sum_i \boldsymbol{l}_i \right) \cdot \boldsymbol{s} = \frac{\xi}{2S} \boldsymbol{L} \cdot \boldsymbol{S} \equiv \lambda \boldsymbol{L} \cdot \boldsymbol{S}. \tag{2.38}$$

In the case of $n > 2l + 1$, as shown in Fig. 2.5(b), though the electron spins are still in parallel for $2l + 1$ electrons, the corresponding orbitals take all possible values of m_l, and the summation over $\boldsymbol{l}_i$ vanishes in (2.38). Hence the residual

Elements (Lanthanoid)	Electronic Configuration atom R	Electronic Configuration ion R^{3+}	L	S	J	Ground state multiplet	g_J
La	$5d6s^2$		0	0	0	$^1S_0$	0
Ce	$4f5d6s^2$	$4f^1$	3	1/2	5/2	$^2F_{5/2}$	6/7
Pr	$4f^36s^2$	$4f^2$	5	1	4	$^3H_4$	4/5
Nd	$4f^46s^2$	$4f^3$	6	3/2	9/2	$^4I_{9/2}$	8/11
Pm	$4f^56s^2$	$4f^4$	6	2	4	$^5I_4$	1/5
Sm	$4f^66s^2$	$4f^5$	5	5/2	5/2	$^6H_{5/2}$	2/7
Eu	$4f^76s^2$	$4f^6$	3	3	0	$^7F_0$	0
Gd	$4f^75d6s^2$	$4f^7$	0	7/2	7/2	$^8S_{7/2}$	2
Tb	$4f^96s^2$	$4f^8$	3	3	6	$^7F_6$	3/2
Dy	$4f^{10}6s^2$	$4f^9$	5	5/2	15/2	$^6H_{15/2}$	4/3
Ho	$4f^{11}6s^2$	$4f^{10}$	6	2	8	$^5I_8$	5/4
Er	$4f^{12}6s^2$	$4f^{11}$	6	3/2	15/2	$^4I_{15/2}$	6/5
Tm	$4f^{13}6s^2$	$4f^{12}$	5	1	6	$^3H_6$	7/6
Yb	$4f^{14}6s^2$	$4f^{13}$	3	1/2	7/2	$^2F_{7/2}$	8/7
Lu	$4f^{14}5d6s^2$	$4f^{14}$	0	0	0	$^1S_0$	0

Tab. 2.3 The electron configuration of the lanthanoid ion and the basis multiplex of the ion. Spectroscopic symbols are also listed for the ground state. A spectroscopic symbol $^{2S+1}L_J$ expresses a multielectron state indexed by $(L, S.J)$. $2S + 1$ and J are given in Arabic numbers, and L is given from the correspondence $0, 1, 2, 3, \cdots$ with symbols $S, P, D, F, \cdots$.

$n - (2l + 1)$ spins and orbitals actually contribute the SOI. Those effective spins are in anti-parallel states written as $-s$, where s is defined in eq. (2.37). The above discussion is summarized in the following form [*1].

$$\mathcal{H}_{\text{SOI}} = \xi \left[\left(\sum_{i=1}^{2l+1} l_i \right) \cdot s - \left(\sum_{i=2l+2}^{n} l_i \right) \cdot s \right] = -\frac{\xi}{2S} \boldsymbol{L} \cdot \boldsymbol{S} = -\lambda \boldsymbol{L} \cdot \boldsymbol{S}. \tag{2.39}$$

In the above we have found that the SOI on the ground state LS-multiplet found from Hund's rule can be expressed in the same form as that on a single-electron state by using $(\boldsymbol{L}, \boldsymbol{S}, \boldsymbol{J})$. Then as in the case of single electron problem, the split states of the ground LS-multiplet with $(2L + 1)(2S + 1)$-fold degeneracy can be indexed by J, the eigenvalue of $\boldsymbol{J}$. Possible value of J are from the definition,

$$J = |L - S|, |L - S| + 1, \cdots, L + S. \tag{2.40}$$

The expectation value of $\boldsymbol{L} \cdot \boldsymbol{S}$ is obtained just as in (2.31) and (2.32). The result is

$$\boldsymbol{L} \cdot \boldsymbol{S} = \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2) = \frac{1}{2}[J(J + 1) - L(L + 1) - S(S + 1)]. \tag{2.41}$$

Then from eq. (2.38) and eq. (2.39), the ground state is the state for $J = |L - S|$ in the case of $n \le 2l + 1$, and that is the state for $J = |L - S|$ in the case of $n > 2l + 1$.

The above is applied to obtain the multiplet ground states thus obtained for lanthanoid are listed in Tab. 2.3. These atoms often constitute (compound) ionic insulators. In many cases, $5d$, $6s$ electrons on the outer shells and also a $4f$ electron are emitted. In such ions, the outmost shell composed of $5s$, $5p$ electrons is closed just as Xe while $4f$ electrons on the open shell still exist *inside* the outmost shell. This situation is advantageous for localized electron system in

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[*1] Such simplification of operator form can be generalized into the method of "operator equivalent" by Stevens[1].

spherical potential because the effect of $\mathcal{H}_{\mathrm{CF}}$ is comparatively weak[2]. The SOI has strong effect and the LS-coupling approach is a good approximation in most cases with some exceptions[3].

The eigenstates with quantum numbers J and M, composed of (L, S)-multiplet is formally written as

$$|J, M\rangle = \sum_{M_l M_s} \langle L, M_l; S, M_s | J, M\rangle |L, M_l; S, M_s\rangle, \tag{2.42}$$

where $\langle L, M_l; S, M_s | J, M\rangle$ are **Clebsch-Gordan** or **Wigner** coefficients.

So far we have assumed the second quantization formalism and estimated the matrix elements on the assumption of "independent calculation of matrix elements and particle statistics." We can write, e.g., the second quantization representation of $\mathcal{H}_{\mathrm{SOI}}$ on the orbital (n, l), as

$$\mathcal{H}_{\mathrm{SOI}} = \sum_{mm'\sigma\sigma'} \lambda_{nl}(m\sigma, m'\sigma') a_{m\sigma}^{\dagger} a_{m'\sigma'}, \tag{2.43a}$$

$$\lambda_{nl}(m\sigma, m'\sigma') \equiv \frac{Z_{\mathrm{eff}} e^2 \hbar^2 \langle r^3 \rangle}{2m^2 c^2 (4\pi\epsilon_0)} \langle m|\boldsymbol{l}|m'\rangle_{nl} \cdot \left(\frac{\boldsymbol{\sigma}}{2}\right)_{\sigma\sigma'}. \tag{2.43b}$$

Here for the spherical potential, we take the effect of screening by core electrons into account by changing Z into an effective atomic number Z_{eff} to get $V(r) = -Z_{\mathrm{eff}} e^2 / (4\pi\epsilon_0 r)$.

2.5   j-j coupling

As mentioned in the beginning of the previous section, the j-j coupling approach starts from the single-electron states in which the SOI is already included as in Fig. 2.2. In the thought similar to the derivation of Hund's rule in Sec. 2.3.1, the ground state in which the effect of Coulomb interaction is taken into account, is obtained for the electron configuration that maximizes the quantum number J.

Let us see the case of Pr^{3+} $((4f)^2)$ as an example. f-electron has $l = 3$, then $j = 3 \pm 1/2 = 5/2, 7/2$. The single electron ground state is thus $j = 5/2$. The electron configuration with the maximum J is $j = 5/2, 3/2$ then $J_{\max} = 4$. This value of J agrees with that in the LS-coupling approach (Tab. 2.3). This state in number representation is obtained as

$$|J, M\rangle = |4, +4\rangle = a_{+5/2}^{\dagger} a_{+3/2}^{\dagger} |0\rangle. \tag{2.44}$$

From eq. (2.42), the creation operator of $j = 5/2$ and $j_z = m$ state, $a_{j_z}^{\dagger}$ can be represented by the creation operator $a_{ms}^{\dagger}$ of states $(l = 3, m, s)$ as

$$a_{j_z}^{\dagger} = \sum_{m,s} \langle 3, m; 1/2, s | 5/2, j_z\rangle a_{ms}^{\dagger} = \sqrt{\frac{7 + 2j_z}{14}} a_{j_z + 1/2\downarrow}^{\dagger} - \sqrt{\frac{7 - 2j_z}{14}} a_{j_z - \uparrow}^{\dagger}. \tag{2.45}$$

The way of approximation is different for j-j coupling and LS-coupling. Hence they give different ground states. Although according to the report ref. [4], they have large overlaps to each other. Care should be taken for the following. As will be seen in the next section, in LS-coupling paramagnetic moment expressed as $\boldsymbol{\mu} = \mu_{\mathrm{B}}(\boldsymbol{L} + g\boldsymbol{S})$ is not parallel to $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ due to the g-factor. Hence $\boldsymbol{\mu}$ precesses around $\boldsymbol{J}$ and the coefficient is given as the average. In j-j coupling $\boldsymbol{\mu}$ is given as the sum of electronic magnetic moments. Therefore the g-factor is the same as that of single electron. Namely l in the discussion of LS-coupling is replaced with j, thus $(2j + 1)/2(j + 1)$ for $n \leq 2j + 1$ and $(2j + 1)/2J$ for $n > 2j + 1$.

2.6 Paramagnetism generated by magnetic ions

As mentioned, $\mathcal{H}_{\mathrm{CF}}$ is important for magnetic ions with an open-shell structure of $3d$ electrons, but before proceeding to the theoretical examination, we will apply the LS-coupling approach to paramagnetism and examine to what extent it can explain the experiments.

2.6.1 Free local moment and Curie law

The LS-coupling approach is a tool to find the ground state of magnetic ions in crystals. Hence we examine the behavior of magnetization in a simple model of magnetic moments free to each other.

The Hamiltonian in the first order of mgnetic field is from eq. (1.75b)

$$\mathcal{H}_1 = \mu_{\mathrm{B}}(\boldsymbol{L} + g\boldsymbol{S}) \cdot \boldsymbol{B}. \tag{2.46}$$

On the other hand, in the ground multiplet state in the LS-coupling, $\boldsymbol{J}$ is the angular momentum quantum number. The main term thus should be in the form of

$$\mathcal{H}_1 = g_j \mu_{\mathrm{B}} \boldsymbol{J} \cdot \boldsymbol{B}, \tag{2.47}$$

where the coefficient g_J includes various effects. Comparison of these two, $g_J \boldsymbol{J} = \boldsymbol{L} + g\boldsymbol{S}$, $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, we reach

> **Landé g-factor**
> $$g_J = \frac{1+g}{2} - \frac{g-1}{2} \frac{L(L+1) - S(S+1)}{J(J+1)}. \tag{2.48}$$

i This g_J is called **Landé g-factor**. g_J is listed in Tab. 2.3 for lanthanoid. As already noted, this expression is obtained within the narrow space of ground state in LS-coupling.

The expectation value of magnetic moment $-g_j \mu_{\mathrm{B}} \boldsymbol{J}$ is

$$M = \langle -g_j \mu_{\mathrm{B}} J_z \rangle = -\frac{\mathbf{Tr}[g_j \mu_{\mathrm{B}} J_z \exp(-g_j \mu_{\mathrm{B}} J_z B / k_{\mathrm{B}} T)]}{\mathrm{Tr}[\exp(-g_j \mu_{\mathrm{B}} J_z B / k_{\mathrm{B}} T)]} = k_{\mathrm{B}} T \frac{\partial}{\partial B} \log \left[\mathrm{Tr} \left(\exp \frac{-g_j \mu_{\mathrm{B}} J_z B}{k_{\mathrm{B}} T} \right) \right], \tag{2.49}$$

with taking the field along z-axis. The partition function is calculated as

$$\mathrm{Tr} \left(\exp \frac{-g_j \mu_{\mathrm{B}} J_z B}{k_{\mathrm{B}} T} \right) = \frac{\sinh \left[\dfrac{1}{2k_{\mathrm{B}} T} g_J \mu_{\mathrm{B}} \left(J + \dfrac{1}{2} \right) B \right]}{\sinh(g_J \mu_{\mathrm{B}} B / 2k_{\mathrm{B}} T)}. \tag{2.50}$$

From the above, the magnetization per a single ion M is obtained as

$$M = g_J \mu_{\mathrm{B}} J B_J \left(\frac{g_J \mu_{\mathrm{B}} J B}{k_{\mathrm{B}} T} \right), \tag{2.51}$$

where $B_J(x)$ is called **Brillouin function** given by

> **Brillouin function**
> $$B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J}. \tag{2.52}$$

The functional behavior is drawn in Fig. 2.6.

In the case of $x \ll 1$ (weak field, high temperature), the Brillouin function can be approximated as $B_J(x) \sim (J+1)x/3J$, then we reach the **Curie law**:

$$\chi = \frac{dM}{dB} = (g_J \mu_{\mathrm{B}})^2 \frac{J(J+1)}{3k_{\mathrm{B}} T}, \tag{2.53}$$
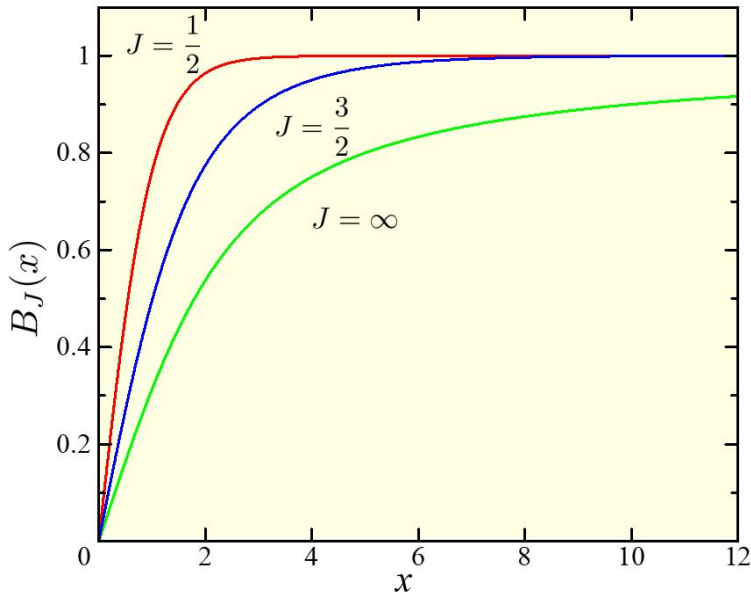
which is also obtained in the classical theory.

Fig. 2.6 Brillouin function(2.52) for $J = 1/2, 3/2, \infty$.

2.6.2 Comparison with experiments: magnetization curve

Figure 2.7 shows well-known experimental results, in which the magnetizations of alums (sulfate) with various magnetic ions are successfully fit to the Brillouin function. A systematic response to expected values of J is observed.
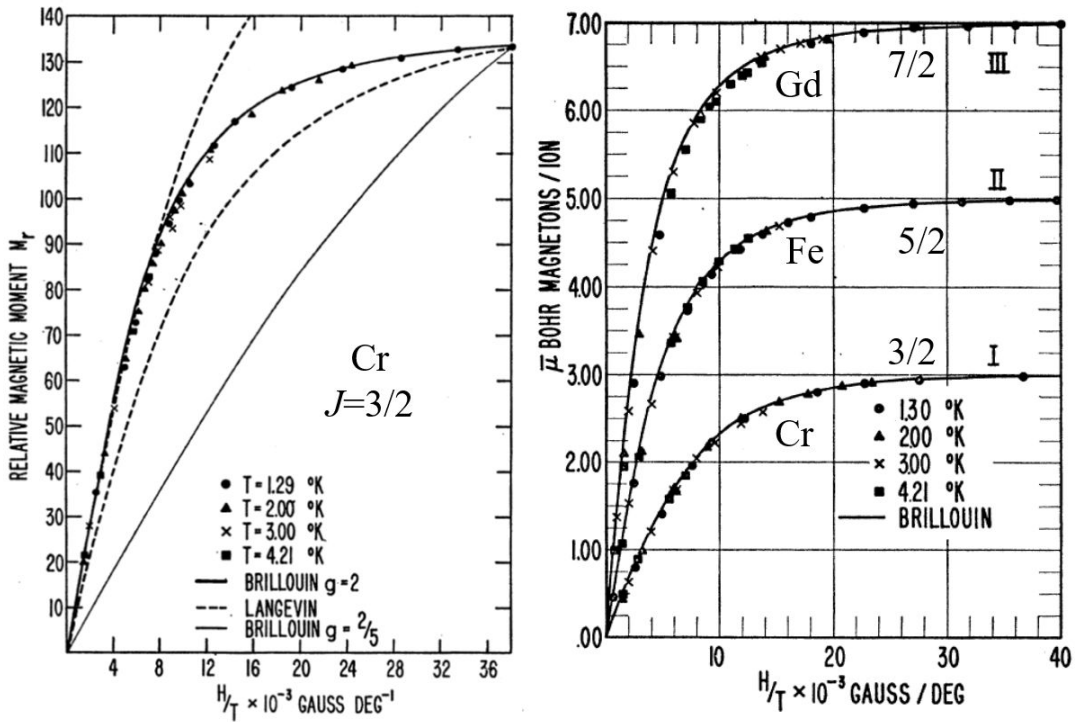

Fig. 2.7 Fittings of the Brillouin function to the magnetic field and temperature dependencies of magnetization of various paramagnetic salt (sulfates (alum) with various magnetic ions). Left: Cr ($J = 3/2$). Annotation of "Langevin" means the Langevin function corresponding to $J = \infty$ in the Brillouin function. Right: The same experiments for Cr ($J = 3/2$), Fe ($J = 5/2$), Gd ($J = 7/2$). From [5].

Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$3d^1$	$^2D_{3/2}$	V^{4+}	1.8	1.55	1.73
$3d^2$	$^3F_2$	V^{3+}	2.8	1.63	2.83
$3d^3$	$^4F_{3/2}$	V^{2+}	3.8	0.77	3.87
		Cr^{3+}	3.7	0.77	3.87
		Mn^{4+}	4.0	0.77	3.87
$3d^4$	$^5D_0$	Cr^{2+}	4.8	0	4.90
		Mn^{3+}	5.0	0	4.90
$3d^5$	$^6S_{5/2}$	Mn^{2+}	5.9	5.92	5.92
		Fe^{3+}	5.9	5.92	5.92
$3d^6$	$^5D_4$	Fe^{2+}	5.4	6.7	4.90
$3d^7$	$^4F_{9/2}$	Co^{2+}	4.8	6.63	3.87
$3d^8$	$^3F_4$	Ni^{2+}	3.2	5.59	2.83
$3d^9$	$^2D_{5/2}$	Cu^{2+}	1.9	3.55	1.73

Tab. 2.4 Comparison of effective Bohr magneton number p (eq. (2.55)) obtained in experiments, that given by the LS-coupling approach (2.54), and that by "spin-only" model for $3d$ transition metal ions. The data are taken from [6], [7].

Configuration		ion	p (exp.)	$g_J[J(J+1)]^{1/2}$	$2[S(S+1)]^{1/2}$
$4f^1$	$^2F_{5/2}$	Ce^{3+}	2.5	2.54	2.56
$4f^2$	$^3H_4$	Pr^{3+}	3.6	3.58	3.62
$4f^3$	$^4I_{9/2}$	Nd^{3+}	3.8	3.62	3.68
$4f^5$	$^6H_{5/2}$	Sm^{3+}	1.5	0.84	1.53
$4f^6$	$^7F_0$	Eu^{3+}	3.6	0.00	3.40
$4f^7$	$^8S_{7/2}$	Gd^{3+}	7.9	7.94	7.94
$4f^8$	$^7F_0$	Tb^{3+}	9.7	9.72	9.7
$4f^9$	$^6H_{15/2}$	Dy^{3+}	10.5	10.65	10.6
$4f^{10}$	$^5I_8$	Ho^{3+}	10.5	10.61	10.6
$4f^{11}$	$^4I_{15/2}$	Er^{3+}	9.4	9.58	9.6
$4f^{12}$	$^3H_6$	Tm^{3+}	7.2	7.56	7.6
$4f^{13}$	$^2F_{7/2}$	Yb^{3+}	4.5	4.54	4.5

Tab. 2.5 Comparison of effective Bohr magneton number p (eq. (2.55)) obtained in experiments, that given by the LS-coupling approach (2.54), and that by "spin-only" model for $4f$ lanthanoid. The data are taken from [6], [7].

2.6.3 Effective Bohr magneton number

Another check of the theory is the effective Bohr magneton number p defined from the inverse proportionality constant C to temperature from the Curie law. In eq. (2.53) we write

$$p = g_j\sqrt{J(J+1)}, \tag{2.54}$$

then p in the theory is

$$p = \sqrt{3k_{\mathrm{B}}C}/\mu_{\mathrm{B}}. \tag{2.55}$$

In Tab. 2.4 and in Tab. 2.5, we compare effective Bohr magneton number p (eq. (2.55)) obtained in experiments, that given by the LS-coupling approach (2.54), and that by "spin-only" model for $3d$ transition metal ions and $4f$ lanthanoid respectively.

In the case of lanthanoid in Tab. 2.5, the experimental values of p is well explained by $g_J\sqrt{J(J+1)}$ obtained from the LS-coupling other than Eu^{3+}, Sm^{3+}. On the other hand, in the case of $3d$ transition metals, the experiments differ so much from $g_J\sqrt{J(J+1)}$, rather they are close to "spin-only" $2\sqrt{S(S+1)}$. That looks as if $L=0$ and the phenomenon
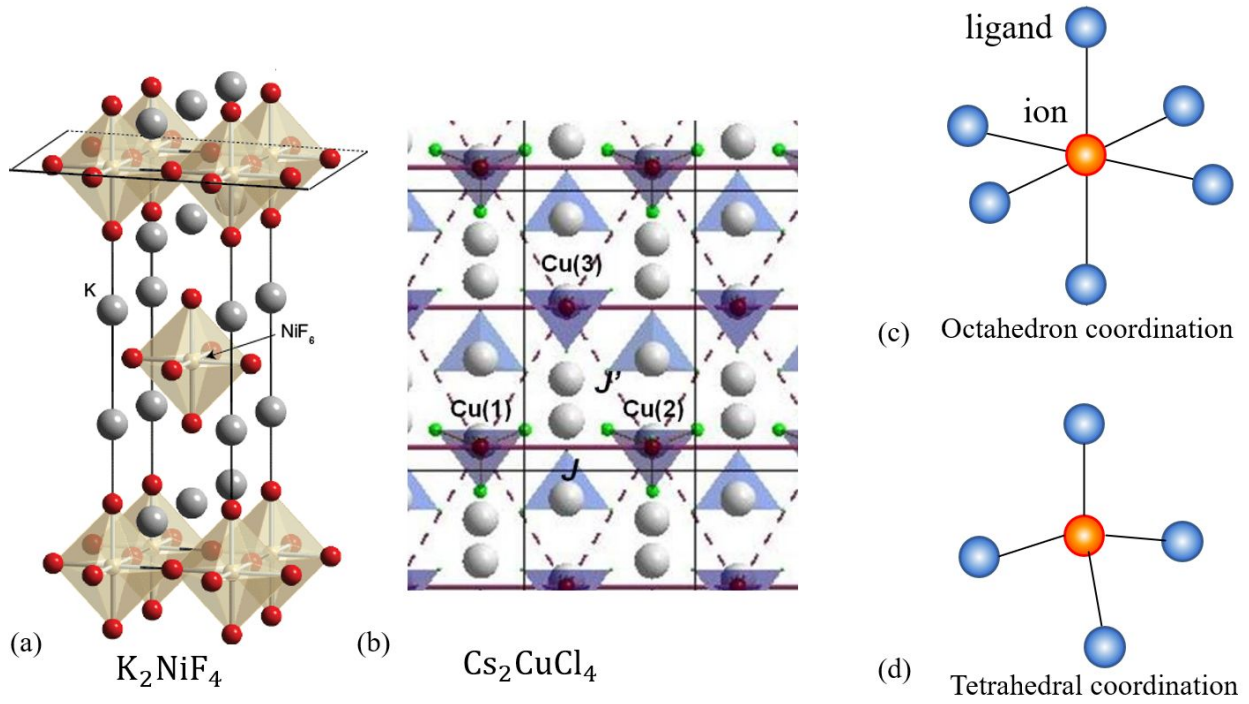
Fig. 2.8 (a) Crystal structure of K_2NiF_4, in which Ni ion has an octahedron coordination. (b) Crystal structure of Cs_2CuCl_4, in which Cu ion has a tetrahedron coordination. (c) Schematic view of octahedron coordination. (d) Schematic view of tetrahedron coordination.

is called "quenching of orbital angular moment." In $3d$ electron systems, the difference from the LS-coupling is so large that it is also difficult to explain with j-j coupling.

As mentioned above, the $4f$ electron system is relatively inside the atomic structure even though the shell is open, the influence of the surroundings is small, and the approximation of the lone electron system is relatively small. Accordingly, it is indicated that the breakdown of LS-coupling approach in $3d$ electron systems is considered to be due to the effect of $\mathcal{H}_{CF}$. Therefore, next, let us consider incorporating the influence of the crystal field from the beginning.

2.7 Magnetic ions in crystal fields

Magnetic atoms (atoms of open electron shells) exist as positive ions in many insulators with strong paramagnetism. Such ions are surrounded by negative ions. An example in Fig. 2.8(a) is K_2NiF_4, in which structure Ni ion is surrounded by F ions in octahedron coordination. Figure 2.8(c) shows a schematic view. As annotated, the surrounding ions or molecules are called **ligand**. Another example in (b) is Cs_2CuCl_4, in which structure Cu ion is surrounded in tetrahedron coordination. These two are the representative coordination.

2.7.1 Level splitting by octahedron coordination

Let us consider the octahedron coordination in Fig. 2.8(c) in a simplest way. We take the coordinate origin at the ion, and ligand ions are at $(\pm R, 0, 0)$, $(0, \pm R, 0)$, $(0, 0, \pm R)$. The vectors pointing them are written as $\boldsymbol{R}_i = (R, \theta_i, \varphi_i)$ and the potential generated by the ligands is written as

$$v_c(\boldsymbol{r}) = \sum_i \frac{Z_i e^2}{|\boldsymbol{r} - \boldsymbol{R}_i|} = \sum_i \frac{Z e^2}{\sqrt{r^2 + R^2 - 2Rr\cos\omega_i}}. \tag{2.56}$$

Here we take CGSesu for the simpler form of Coulomb potential. In the polar coordinate, (θ_i, φ_i) are

$$(\pi/2, 0),\ (\pi/2, \pi/2),\ (0, 0),\ (\pi/2, \pi),\ (\pi/2, 3\pi/2),\ (\pi, 0) \tag{2.57}$$

for $i = 1 \sim 6$.

We assume that the averaged distance of $3d$ electrons from the nucleus is sufficiently shorter than R. Then v_c can be expanded with r/R as

$$v_c(\boldsymbol{r}) = \sum_i \frac{Ze^2}{R} \sum_{k=0}^{\infty} \left(\frac{r}{R}\right)^k P_k(\cos \omega_i), \tag{2.58}$$

where $P_k(\cos \omega_i)$ are Legendre functions defined as

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n}[(x^2 - 1)]. \tag{2.59}$$

Apparently these are the expansion coefficients of

$$\frac{1}{\sqrt{1 - 2xt + t^2}} = \sum_{n=0}^{\infty} P_n(x)t^n. \tag{2.60}$$

From an identity of spherical harmonic function $Y_{km}(\theta, \varphi)$,

$$P_k(\cos \omega_i) = \frac{4\pi}{2k + 1} \sum_{m=-k}^{k} Y_{km}(\theta, \varphi) Y_{km}^*(\theta_i, \varphi_i). \tag{2.61}$$

Note ω_i is a function of $\boldsymbol{r}$. This results in dropping of i from the argument in the first Y_{km}. Here we define two functions:

$$T_{km} \equiv \sqrt{\frac{4\pi}{2k + 1}} \frac{Ze^2}{R^{k+1}} \sum_i Y_{km}(\theta_i, \varphi_i), \quad C_{km} \equiv \sqrt{\frac{4\pi}{2k + 1}} Y_{km}(\theta, \varphi), \tag{2.62}$$

with which $v_c(\boldsymbol{r})$ is written as

$$v_c(\boldsymbol{r}) \sum_{k=0}^{\infty} \sum_{m=-k}^{k} r^k T_{km} C_{km}(\theta, \varphi). \tag{2.63}$$

From the symmetry of positions (2.57), $T_{km} = 0$ for odd m. Others are

$$T_{k0} = \sqrt{\frac{2}{2k + 1}} \frac{Ze^2}{R^{k+1}} \left[\Theta_{k0}(0) + 4\Theta_{k0}\left(\frac{\pi}{2}\right) + \Theta_{k0}(\pi)\right], \tag{2.64a}$$

$$T_{km} = \sqrt{\frac{8}{2k + 1}} \frac{Ze^2}{R^{k+1}} \Theta_{km}\left(\frac{\pi}{2}\right) \left(1 + \cos \frac{m\pi}{2}\right) \quad (m: \text{even}), \tag{2.64b}$$

where $\Theta(\theta)_{km}$ are defined as

$$Y_{km}(\theta, \varphi) = \Theta_{km}(\theta)e^{im\varphi}. \tag{2.65}$$

From the form of $\Theta(\theta)_{km}$, T_{km}'s are also zero for odd k.

From above, we reach the expression to the fourth order of k:

$$v_c(\boldsymbol{r}) = \frac{6Ze^2}{R} + \frac{2}{5} Der^4 \left[C_{40}(\theta, \varphi) + \sqrt{\frac{5}{14}} (C_{44}(\theta, \varphi) + C_{4-4}(\theta, \varphi))\right], \tag{2.66}$$

where

$$D = \frac{35Ze}{4R^5}. \tag{2.67}$$

Let $v_c b(\boldsymbol{r})$ be the potential without the energy shift term (the first term in eq. (2.66)). We also restore $v_c b(\boldsymbol{r})$ into the expression in cartesian coordinate, then obtain

$$v_{cb}(\boldsymbol{r}) = eD \left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right). \tag{2.68}$$

Appendix 3A: Isolated electron systems and point group

3A.1 Definition of group

When the operation $*$ is defined between any elements of a set A and the following conditions are satisfied, we call A a "group" with respect to $*$.

1. $\forall a_1,\, a_2 \in A\ \{a_1 * a_2 \in A\}$ (closed for the operation *)
2. $\forall a_1.\ a_2,\, a_3 \in A\ \{(a_1 * a_2) * a_3 = a_1 * (a_2 * a_3)\}$ (associative law).
3. $\exists E \in A\ \{\forall a_1 \in A\ \{a_1 E = E a_1 = a_1\}\}$ (existence of unit element).
4. $\exists a_1^{-1} \in A\ \{\forall a_1 \in A\ \{a_1 a_1^{-1} = a_1^{-1} a_1 = E\}\}$ (existence of the inverse element).

When elements a_i, a_j of a group A are written as $a_i = a a_j a^{-1}$, where a is also an element of A, we say a_i and a_j are conjugate to each other. Generally a group is classified into classes, which are sets of conjugate elements.

An element of a group a_i has a corresponding square matrix $D(a_i)$ and the operation $a * b = c$ is projected to $D(a)D(b) = D(c)$. We call $D(a_i)$ as a representation of group A. There are infinite number of representations. When a square matrix S transfers as $D'(a_i) = S^{-1} D(a_i) S$, we call $D'(a_i)$ an equivalent representation to $D(a_i)$. The direct sum of $D^{(1)}$ and $D^{(2)}$ is defined as

$$\forall a_i:\ D(a_i) = \begin{pmatrix} D^{(1)}(a_i) & 0 \\ 0 & D^{(2)}(a_i) \end{pmatrix},$$

which is expressed as $D = D^{(1)} \oplus D^{(2)}$. The above is summarized as "D is reduced to $D^{(1)}$ and $D^{(2)}$ by equivalent conversion with S." Expressions that cannot be further reduced are called irreducible expressions. Expression of an element a can be written as $D_{ij}(a) = \langle \chi_i | a | \chi_j \rangle$ by using a basis $|\chi_i\rangle$ of expression. Equivalent conversion matrix S is a basis transformation matrix. When a is an operator, the matrix representation with basis $|\chi_i\rangle$ is χ-expression of a.

3A.2 Symmetry operations of point group

A set of symmetry operations around a point in space is called a point group.

E	:	Identical operation
C_n	:	Rotation of $2\pi/n$
C_2'	:	π rotation around two-fold axis perpendicular to the principal axis. Written as C_2' or U_2 and called Umklappung.
I	:	Space inversion ($\boldsymbol{r} \to -\boldsymbol{r}$)
σ	:	Mirroring
IC_n	:	Circumference. Space inversion after rotation of $2\pi/n$.
S_n	:	Improper rotation. Mirroring after rotation of $2\pi/n$.

(Continue to next time)

Appendix 3B: Clebsch-Gordan coefficient

Students must have learned about coupling of angular momentum in elementary quantum mechanics. But here we have a short review. Even in classical mechanics, additive quantities should be summed up in the coupled system. In the case of angular momentum, they should be summed up as vectors. In quantum mechanics, the operator of total angular

momentum is written as the sum of angular momentum operators. However in quantum mechanics, due to the directional quantization, eigenfunctions and eigenvalues are not the sums of each eigenfunction and eigenvalue.

3B.1 General treatment

Let $\hat{\boldsymbol{j}}_1$, $\hat{\boldsymbol{j}}_2$ be independent angular momentums, and consider simultaneous eigenstates $|j_i^2, m_i\rangle$ of operators $\hat{\boldsymbol{j}}_1^2$, $\hat{j}_{iz}$ ($i = 1, 2$). We write a wavefunction of the coupled system as

$$\psi = |j_1^2, m_1\rangle|j_2^2, m_2\rangle. \tag{3B.1}$$

The total angular momentum $\hat{\boldsymbol{J}}$ of the coupled system is

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{j}}_1 + \hat{\boldsymbol{j}}_2. \tag{3B.2}$$

However, ψ in eq. (3B.1) is not an eigenstate of, e.g., $\hat{\boldsymbol{J}}^2$ apparently. From the independence of $\hat{\boldsymbol{j}}_1$, $\hat{\boldsymbol{j}}_2$ (thus they commute each other), and from the general properties of angular momentum, $[\hat{\boldsymbol{J}}^2, \hat{J}_z]$, $[\hat{\boldsymbol{j}}_1^2, \hat{\boldsymbol{j}}_2^2]$ are apparently zero, and the following commutation relation can be proven.

$$[\hat{\boldsymbol{J}}^2, \hat{\boldsymbol{j}}_\alpha^2] = [\hat{J}_z, \hat{\boldsymbol{j}}_\alpha^2] = 0. \tag{3B.3}$$

Simultaneous eigenstates of $\hat{\boldsymbol{J}}^2$, $\hat{J}_z$, $\hat{\boldsymbol{j}}_1^2$, $\hat{\boldsymbol{j}}_2^2$ can be obtained from basis transformation from eq. (3B.1) as

$$|J^2, M, j_1^2, j_2^2\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C_{j_1 m_1 j_2 m_2}^{JM} |j_1^2, m_1\rangle|j_2^2, m_2\rangle, \tag{3B.4}$$

where $C_{j_1 m_1 j_2 m_2}^{JM}$ are called **Clebsch–Gordan coefficients**.

3B.2 Coupling of two spins

For general way to find $C_{j_1 m_1 j_2 m_2}^{JM}$, refer to textbooks. Instead we obtain them for the simplest case of $j_1 = j_2 = 1/2$, namely two spins. We take $\hat{s}_i$ ($i = 1, 2$) for the two spin operators and write the total spin operator as

$$\hat{\boldsymbol{S}} = \hat{s}_1 + \hat{s}_2. \tag{3B.5}$$

Because $\hat{s}_1$ commutes with $\hat{s}_2$,

$$\hat{\boldsymbol{S}}^2 = \hat{s}_1^2 + 2\hat{s}_1 \cdot \hat{s}_2 + \hat{s}_2^2, \qquad \hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}. \tag{3B.6}$$

First, for $\hat{S}_z$ we see

$$\hat{S}_z \begin{pmatrix} |\uparrow_1\rangle|\uparrow_2\rangle & |\uparrow_1\rangle|\downarrow_2\rangle \\ |\downarrow_2\rangle|\uparrow_2\rangle & |\downarrow_1\rangle|\downarrow_2\rangle \end{pmatrix} = \begin{pmatrix} |\uparrow_1\rangle|\uparrow_2\rangle & 0 \\ 0 & -|\downarrow_1\rangle|\downarrow_2\rangle \end{pmatrix}. \tag{3B.7}$$

Therefore the eigenvalues of $\hat{S}_z$ are ± 1, 0 with two-fold degeneracy. The "size" of $\boldsymbol{S}$, S is then 0 or 1. Next, generally for the operator $\hat{s}$ of spin 1/2

$$\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_0^2 = \frac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{3B.8}$$

holds. In $\hat{\boldsymbol{S}}^2$ $\hat{s}_1^2 + \hat{s}_2^2$ are 3/2

$\hat{s}_1 \cdot \hat{s}_2 \hat{s}_1 \cdot \hat{s}_2 \hat{s}_1 \cdot \hat{s}_2 \hat{s}_1 \cdot \hat{s}_2 \hat{s}_1 \cdot \hat{s}_2$, Residual $\hat{s}_1 \cdot \hat{s}_2$ are calculated as follows. For simplicity we use expression $|\uparrow_1\rangle|\downarrow_2\rangle = |\uparrow\downarrow\rangle$.

$$\hat{s}_1 \cdot \hat{s}_2 \begin{pmatrix} |\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \end{pmatrix} = \frac{1}{4} \begin{pmatrix} \cdot|\uparrow\uparrow\rangle & -|\uparrow\downarrow\rangle + 2|\downarrow\uparrow\rangle \\ 2|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle & |\downarrow\downarrow\rangle \end{pmatrix}.$$

Because neither $|\uparrow\downarrow\rangle$ nor $|\downarrow\rangle|\uparrow\rangle$ is not eigenstates, this part should be diagonalized by transformation. The results are simply

$$\chi_{\pm} \equiv |\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle. \tag{3B.9}$$

This is easily confirmed as

$$\hat{\boldsymbol{s}}_1 \cdot \hat{\boldsymbol{s}}_2 \chi_+ = (1/4)\chi_+, \qquad \hat{\boldsymbol{s}}_1 \cdot \hat{\boldsymbol{s}}_2 \chi_- = (3/4)\chi_-. \tag{3B.10}$$

From the above, the eigenvalues of $\hat{\boldsymbol{S}}^2$ are 0, 2, the eigenfunctions are

$$\begin{aligned} |1,-1\rangle &= |\downarrow\downarrow\rangle, \quad |1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad |1,1\rangle = |\uparrow\uparrow\rangle, \\ |0,0\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \end{aligned} \tag{3B.11}$$

Here we use S as index, not $S(S+1)$. The state of $S=1$ is called spin triplet state, $S=0$ is called spin singlet state. Then we obtain follows as Clebsch-Gordan coefficient in eq. (3B.4),

$$\begin{aligned} C^{11}_{1/2,1/2,1/2,1/2} &= C^{1-1}_{1/2,-1/2,1/2,-1/2} = 1, \\ C^{10}_{1/2,1/2,1/2,-1/2} &= C^{10}_{1/2,-1/2,1/2,1/2} = C^{00}_{1/2,1/2,1/2,-1/2} = 1/\sqrt{2}, \\ C^{00}_{1/2,-1/2,1/2,1/2} &= -1/\sqrt{2}. \end{aligned}$$

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