

## Chapter 2

# Magnetism of Atoms

The magnetic moments of magnetic materials originate from magnetic moments of the atoms. The hyperfine interactions have important applications in magnetism. This chapter introduces the basic theories relating to atomic magnetism and hyperfine interactions in atom. It contains the sections of Electron configuration of atom; Term and multiplet; Intrinsic magnetic moment and gyromagnetic ratio of atom; Paramagnetism and diamagnetism of atom; Exchange interaction in He atom; Exchange interaction in H<sub>2</sub> molecule; and Hyperfine interactions in atom; and Appendices 4 to 6. The eigenfunctions are assumed orthonormalized.

### 2.1 Electron Configuration of Atom

Intrinsic atomic magnetic moment is decided by the state of the electrons. Consider an atom or an ion of atomic number  $Z$  which has  $N$  electrons.

#### 2.1.1 Electron Spin

An electron has an intrinsic angular momentum called spin angular momentum, or tersely spin. The operators of its projections on the  $x$ ,  $y$  and  $z$  axes ( $z$  axis = quantum axis) are

$$\hat{s}_\alpha \equiv \frac{\hbar}{2} \hat{\sigma}_\alpha, \quad (\alpha = x, y, z), \quad (2.1)$$

where  $\hat{\sigma}_\alpha$  is the Pauli spin matrices,

$$\hat{\sigma}_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{\sigma}_\alpha^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.2)$$

Let  $|s, m_s\rangle$  denote the simultaneous eigenfunction (eigenstate) of  $\hat{s}^2$  and  $\hat{s}_z$ :

$$\hat{s}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle, \quad (s = 1/2: \text{spin quantum number}) \quad (2.3)$$

$$\hat{s}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle, \quad (m_s = \pm s: \text{spin projection quantum number}) \quad (2.4)$$

$$|s, s\rangle \equiv \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (2.5)$$

$$|s, -s\rangle \equiv \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (2.6)$$

$$\langle \chi_\sigma | \chi_{\sigma'} \rangle \equiv \chi_\sigma^+ \chi_{\sigma'} = \delta(\sigma, \sigma'). \quad (\sigma, \sigma' = \pm) \quad (2.7)$$

Here  $\chi_\sigma^+$  is the conjugate transpose of  $\chi_\sigma$  such as  $\chi_+^+ = (1, 0)$ , and  $\delta(\alpha, \beta)$  is the Kronecker delta which is equal to 1 if  $\sigma = \sigma'$  and 0 if  $\sigma \neq \sigma'$ .

### 2.1.2 Hartree–Fock Equations

By taking into account only the Coulomb interactions, the Hamiltonian of the electron system of an atom is the sum of one-particle Hamiltonian  $\hat{H}_1$  and two-particle Hamiltonian  $\hat{H}_2$ :

$$\hat{H}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \hat{H}_1 + \hat{H}_2, \quad (\vec{r}_i: \text{position of } i^{\text{th}} \text{ electron relative to the nucleus}) \quad (2.8)$$

$$\hat{H}_1(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i^{1, \dots, N} \hat{h}(\vec{r}_i). \quad (2.9)$$

$$\hat{h}(\vec{r}) = \frac{\hat{p}^2(\vec{r})}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}, \quad (m: \text{electron rest mass}) \quad (2.10)$$

$$\hat{H}_2(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i,j}^{1, \dots, N; i \neq j} g(\vec{r}_i, \vec{r}_j). \quad (2.11)$$

$$g(\vec{r}_1, \vec{r}_2) = \frac{e^2}{4\pi\epsilon_0 r_{12}}. \quad (e: \text{electron charge}, r_{ij} \equiv |\vec{r}_i - \vec{r}_j|) \quad (2.12)$$

By solving the Schrödinger equation (1926)

$$\hat{H}\Psi(\vec{r}_1, \sigma(1), \vec{r}_2, \sigma(2), \dots, r_N, \sigma(N)) = E\Psi(\vec{r}_1, \sigma(1), \vec{r}_2, \sigma(2), \dots, r_N, \sigma(N)) \quad (2.13)$$

the eigenfunctions  $\{\Psi\}$  and eigenvalues  $\{E\}$  of the system can be obtained. Here  $\sigma$  is the variable of spin which takes  $+(m_s = s)$  or  $-(m_s = -s)$ . Equation (2.13) for multi-electron system is very difficult to solve. The method which has long been used to approximately solve is to approximate  $\Psi$  by a Slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{r}_1)\chi_{\sigma_1}(1) & \varphi_2(\vec{r}_1)\chi_{\sigma_2}(1) & \dots & \varphi_N(\vec{r}_1)\chi_{\sigma_N}(1) \\ \varphi_1(\vec{r}_2)\chi_{\sigma_1}(2) & \varphi_2(\vec{r}_2)\chi_{\sigma_2}(2) & \dots & \varphi_N(\vec{r}_2)\chi_{\sigma_N}(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(\vec{r}_N)\chi_{\sigma_1}(N) & \varphi_2(\vec{r}_N)\chi_{\sigma_2}(N) & \dots & \varphi_N(\vec{r}_N)\chi_{\sigma_N}(N) \end{vmatrix}. \quad (2.14)$$

Here  $\varphi_\alpha(\vec{r}_i)$  and  $\chi_{\sigma_\alpha}(i)$  are the orbital and spin state of the  $i^{\text{th}}$  electron occupying the orbit  $\alpha$ .  $\psi_{\alpha, \sigma_\alpha}(i) = \varphi_\alpha(\vec{r}_i)\chi_{\sigma_\alpha}(i)$  is called spin orbital. The best set of  $\{\varphi_\alpha(\vec{r})\}$  could be obtained by invoking the variational principle  $\delta\langle\Psi|\hat{H}|\Psi\rangle = 0$  under the condition of orthonormality of  $\{\varphi_\alpha(\vec{r})\}$ . The  $\{\varphi_\alpha(\vec{r})\}$  satisfies the  $N$ -coupled Hartree–Fock equations (1930–1935)

$$\left[ \hat{h}(\vec{r}) + \sum_{\beta}^{1, \dots, N} \int |\varphi_{\beta}(\vec{r}')|^2 g(\vec{r}, \vec{r}') d\mathbf{v}' - \sum_{\beta}^{1, \dots, N} \delta(\sigma_{\alpha}, \sigma_{\beta}) \int \varphi_{\beta}^*(\vec{r}') g(\vec{r}, \vec{r}') \varphi_{\alpha}(\vec{r}') \frac{\varphi_{\beta}(\vec{r})}{\varphi_{\alpha}(\vec{r})} d\mathbf{v}' \right] \varphi_{\alpha}(\vec{r}) = \varepsilon_{\alpha} \varphi_{\alpha}(\vec{r}). \quad (2.15)$$

( $\alpha = 1, 2, \dots, N$ . Note 1 of this section)

Thus, the many-body problem transforms to the problem to solve  $N$ -coupled one-electron equations. The above method is called Hartree–Fock approximation. More widely, such kind of approach to solve a many-body problem by use of one-electron equations is called one-electron method. In the left of (2.15), the first term in the bracket is the sum of the kinetic energy and Coulomb potential in the electric field produced by the nucleus (2.10); the second term is the Coulomb potential in the average electric field produced by all the electrons; and the third term the average exchange potential. Those of  $\beta = \alpha$  in the second and third terms cancel each other. Equation (2.15) shows that an electron moves around in the potential consisted of the Coulomb potential of the nucleus, average Coulomb potential, and average exchange field produced by the electrons. Therefore, Hartree–Fock approximation is a mean field approximation. Here the space distribution of  $\varphi_{\beta}(\vec{r}')$  is not affected by the variation of position  $\vec{r}$  of the  $\alpha$  electron.

### 2.1.3 Central Field Approximation

The total potential in the bracket of the left of (2.15) is spherically asymmetric and is slightly different for different  $\varphi_\alpha(\vec{r})$ . By averaging the potentials for all  $\varphi_\alpha(\vec{r})$  and approximating it by its spherically symmetrical part  $u(r)$ , the  $N$ -coupled Hartree–Fock equations simplify to a single equation of

$$\left[ \frac{\hat{p}^2(\vec{r})}{2m} + u(r) \right] \varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r}), \quad (2.16)$$

where  $u(r)$  is common for all  $\varphi_\alpha(\vec{r})$ . Such approximation is called central field approximation.

The solution of (2.16) is

$$\begin{aligned} \varphi_\alpha(\vec{r}) &= \varphi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) Y_{lm_l}(\theta, \phi), \\ (n &= 1, 2, \dots; l = 0, 1, \dots, n-1; m_l = -l, -l+1, \dots, l) \end{aligned} \quad (2.17)$$

where  $\theta$  and  $\phi$  is the zenith angle of  $\vec{r}$  from the positive  $z$  axis direction and azimuth angle from the positive  $x$  axis direction, respectively, and  $n$ ,  $l$ , and  $m_l$  are the principal quantum number, orbital angular quantum number (or azimuthal quantum number), and magnetic quantum number.  $Y_{lm_l}(\theta, \phi)$  is the spherical harmonics,

$$\begin{aligned} Y_{lm_l}(\theta, \phi) &= (-1)^{\frac{m_l+|m_l|}{2}} \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-|m_l|)!}{(l+|m_l|)!}} \\ &\times P_l^{|m_l|}(\cos \theta) \exp(im_l \phi), \text{ (Table 2.1)} \end{aligned} \quad (2.18)$$

$$P_l^{|m_l|}(\xi) = (1 - \xi^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|}}{d\xi^{|m_l|}} P_l(\xi), \quad (2.19)$$

where  $P_l^{|m_l|}(\xi)$  is the associated Legendre function and  $P_l(\xi)$  is the Legendre polynomial (1.63). The orbital angular momentum operator of an electron is

$$\hat{\vec{l}} = \vec{r} \times \hat{\vec{p}} = -i\hbar \vec{r} \times \nabla, \quad (1.116) \quad (2.20)$$

and  $Y_{lm_l}(\theta, \phi)$  is the simultaneous eigenfunction of  $\hat{l}^2$  and  $\hat{l}_z$ :

$$\hat{l}^2 Y_{lm_l}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm_l}(\theta, \phi), \quad (2.21)$$

$$\hat{l}_z Y_{lm_l}(\theta, \phi) = \hbar m_l Y_{lm_l}(\theta, \phi). \quad (2.22)$$

**Table 2.1** Expressions of spherical harmonics  $Y_{lm_l}(\theta, \phi)$  and  $Y_{lm_l}(x/r, y/r, z/r)$ 

$l$	$m_l$	$Y_{lm_l}(\theta, \phi)$	$Y_{lm_l}(x/r, y/r, z/r)$
0	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{1}{2}}$
1	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{2}} \cos \theta$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{2}} \frac{z}{r}$
	$\pm 1$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{4}} \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{4}} \frac{x \pm iy}{r}$
2	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{5}{8}} (3 \cos^2 \theta - 1)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{5}{8}} \frac{3z^2 - r^2}{r^2}$
	$\pm 1$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{4}} \cos \theta \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{4}} \frac{z(x \pm iy)}{r^2}$
	$\pm 2$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{16}} \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{16}} \frac{(x \pm iy)^2}{r^2}$
3	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{7}{8}} \cos \theta (5 \cos^2 \theta - 3)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{7}{8}} \frac{z(5z^2 - 3r^2)}{r^2}$
	$\pm 1$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{21}{32}} (5 \cos^2 \theta - 1) \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{21}{32}} \frac{(5z^2 - r^2)(x \pm iy)}{r^3}$
	$\pm 2$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{105}{16}} \cos \theta \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{105}{16}} \frac{z(x \pm iy)^2}{r^3}$
	$\pm 3$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{35}{32}} \sin^3 \theta \exp(\pm i3\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{35}{32}} \frac{(x \pm iy)^3}{r^3}$

The spherical harmonic addition theorem

$$Y_{l0}(\theta_{12}, 0) = \sqrt{\frac{4\pi}{2l+1}} \sum_m^{-l, -l+1, \dots, l} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta_{12}) \quad (2.23)$$

holds, where  $\theta_{12}$  is the angle between  $\vec{r}(\theta_1, \phi_1)$  and  $\vec{r}(\theta_2, \phi_2)$  directions. The function

$$U_{m_l}^l \equiv \sqrt{\frac{4\pi}{2l+1}} Y_{lm_l} \quad (2.24)$$

is used instead of  $Y_{lm_l}$  in some cases for convenience.

The radial function  $R_{nl}(r)$  (2.17) satisfies the radial equation

$$\left\{ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2} [\varepsilon_\alpha - u(r)] \right\} R_{nl}(r) = 0. \quad (2.25)$$

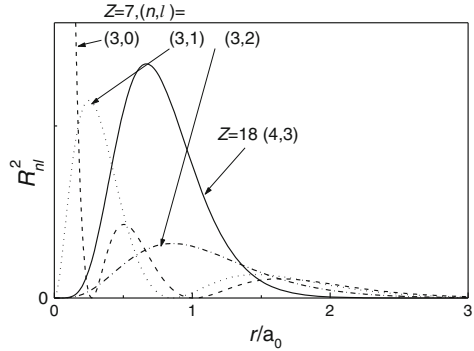
A general characteristics of  $R_{nl}(r)$  can be seen from the analytical solutions for the simple case of nuclear Coulomb potential  $u(r) = -Ze^2/4\pi\varepsilon_0 r$  (Table 2.2, Fig. 2.1). It has  $n - l - 1$  spherical surfaces of  $R_{nl}(r) = 0$ , and

$$R_{n0}(0) \neq 0, \quad R_{n,l \neq 0}(0) = 0. \quad (2.26)$$

**Table 2.2** Expressions of  $R_{nl}(r)$  for  $u(r) = -Ze^2/4\pi\epsilon_0 r$

$n$	$l$	$R_{nl}(r) (a_0 \equiv 4\pi\epsilon_0\hbar^2/me^2: \text{Bohr radius})$
1	0	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2 \exp\left(-\frac{Zr}{a_0}\right)$
2	0	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{\sqrt{2}} \left(1 - \frac{Zr}{2a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$
	1	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{2\sqrt{6}} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right)$
3	0	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{2}{3\sqrt{3}} \left[1 - \frac{2Zr}{3a_0} + \frac{2}{27} \left(\frac{Zr}{a_0}\right)^2\right] \exp\left(-\frac{Zr}{3a_0}\right)$
	1	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{8}{27\sqrt{6}} \frac{Zr}{a_0} \left(1 - \frac{Zr}{6a_0}\right) \exp\left(-\frac{Zr}{3a_0}\right)$
	2	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{4}{81\sqrt{30}} \left(\frac{Zr}{a_0}\right)^2 \exp\left(-\frac{Zr}{3a_0}\right)$
4	3	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{768\sqrt{35}} \left(\frac{Zr}{a_0}\right)^3 \exp\left(-\frac{Zr}{4a_0}\right)$

**Fig. 2.1**  $r/a_0$  dependences of some  $R_{nl}^2$  of  $R_{nl}$  given in Table 2.2



The eigenvalue  $\varepsilon_\alpha = \varepsilon_{nl}$  of (2.25) is related with  $n$  and  $l$  but not with  $m_l$ .

To get the solution of  $R_{nl}(r)$ ,  $u(r)$  should be known in advance, but  $u(r)$  is a function of the set of  $\{R_{nl}(r)\}$  including  $R_{nl}(r)$  itself. Therefore, it should be solved by means of an iterative method called self-consistent field method. First assume a set of  $\{R_{nl}(r)\}$  with which  $u(r)$  is calculated. A set of solutions  $\{R_{nl}(r)\}$  is solved using this  $u(r)$ . Calculate  $u(r)$  by using the new set of  $\{R_{nl}(r)\}$ . Repeat this process until the set of  $\{R_{nl}(r)\}$  for the calculation of  $u(r)$  becomes essentially the same with those solutions solved using the  $u(r)$ . In this way, we get the eigenstates  $\{\varphi_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta, \phi)\}$  and the eigenvalues  $\{\varepsilon_{nl}\}$ .

### 2.1.4 Electron Configuration of Atom

The energy degeneracy of the energy level  $\varepsilon_{nl}$  is  $2(2l + 1)$ . According to the Pauli's exclusion principle, the  $N$  electrons have different spin-orbitals. The arrangement of the electrons in the electronic orbital subshells  $\{(n, l)\}$  is called atomic orbital electron configuration or tersely electron configuration, and the total energy is called the energy of the configuration. If the electrons fill the lowest energy levels, we get the ground state electron configuration, otherwise an excited state configuration. The energy gaps between the excited state energy levels and ground state energy level are so large that the probability of occupation of excited states is extremely small under usual magnetic experimental conditions, and the effect of them on the magnetic properties can be neglected. Thus, the magnetic properties of an atom are related only to the ground state configuration. At the ground configuration, the inner electron subshells are fully filled and only the outermost subshell may be filled partially for the atoms of  $Z \leq 18$  ( $Z = 18$  for Ar atom). For example, the electron configuration of oxygen atom ( $Z = 8$ ) is  $1s^2 2s^2 2p^4$  which is often tersely denoted by  $2p^4$  by omitting the fully filled subshell symbols. Here s, p, d, f, ... stands for  $l = 0, 1, 2, 3, \dots$ , and  $2p^4$  refers to that the electron subshell of  $n = 2$  and  $l = 1$  is filled by four electrons.

Most important magnetic atoms and ions for magnetic materials are  $\text{Fe}(3d^6)$ ,  $\text{Co}(3d^7)$ , and  $\text{Ni}(3d^8)$  of 3d transition elements ( $3d^k 4s^2$ ) and  $\text{Pr}^{+3}(4f^2 5s^2 5p^6)$ ,  $\text{Nd}^{+3}(4f^3 5s^2 5p^6)$ ,  $\text{Sm}^{+3}(4f^5 5s^2 5p^6)$ ,  $\text{Tb}^{+3}(4f^8 5s^2 5p^6)$ , and  $\text{Dy}^{+3}(4f^9 5s^2 5p^6)$  of 4f transition (rare-earth) ions ( $4f^k 5s^2 5p^6$ ). Their atomic magnetic moments originate from the partially filled 3d subshell enclosed by the fully filled outer subshell  $4s^2$  for the 3d atoms, and partially filled 4f subshell enclosed by the fully filled outer subshells of  $5s^2 5p^6$  for the 4f transition ions.

### 2.1.5 Angular Momentum Operators

For succinctness of expressions hereafter all angular momentum operators will be formulated in  $\hbar$  unit. Thus, (2.1), (2.3), (2.4), and (2.20)–(2.22) become

$$\hat{s}_\alpha \equiv \frac{1}{2} \hat{\sigma}_\alpha, \quad (2.27)$$

$$\hat{s}^2 |s, m_s\rangle = s(s + 1) |s, m_s\rangle, \quad (2.28)$$

$$\hat{s}_z |s, m_s\rangle = m_s |s, m_s\rangle, \quad (2.29)$$

$$\hat{l} = -i\vec{r} \times \nabla, \quad (2.30)$$

$$\hat{l}^2 Y_{lm_l}(\theta, \phi) = l(l+1)Y_{lm_l}(\theta, \phi), \quad (2.31)$$

$$\hat{l}_z Y_{lm_l}(\theta, \phi) = m_l Y_{lm_l}(\theta, \phi). \quad (2.32)$$

Any angular momentum operator  $\hat{J}$  satisfies the following relations.

$$\hat{J}_{\pm} \equiv \hat{J}_x \pm i\hat{J}_y, \quad (\text{called raising and lowering operators}) \quad (2.33)$$

$$\hat{J} \times \hat{J} = i\hat{J}, \quad (2.34)$$

$$\hat{J}^2 |J, M_J\rangle = J(J+1)|J, M_J\rangle, \quad (J: \text{angular momentum quantum number}) \quad (2.35)$$

$$\hat{J}_z |J, M_J\rangle = M_J |J, M_J\rangle, \quad (M_J: \text{magnetic quantum number}) \quad (2.36)$$

$$\begin{aligned} \hat{J}_{\pm} |J, M_J\rangle &= \sqrt{J(J+1) - M_J(M_J \pm 1)} |J, M_J \pm 1\rangle. \\ (M_J &= -J, -J+1, \dots, J) \end{aligned} \quad (2.37)$$

Here  $|J, M_J\rangle$  is the simultaneous eigenfunction of  $\hat{J}^2$  and  $\hat{J}_z$ . If

$$\hat{J} = \hat{J}_1 + \hat{J}_2, \quad (2.38)$$

$$J = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2. \quad (2.39)$$

### Note 1

Define the Coulomb, exchange, and Fock operators  $\hat{K}_{\alpha}(\vec{r})$ ,  $\hat{A}_{\alpha}(\vec{r})$ , and  $\hat{F}(\vec{r})$  by the relations of

$$\hat{K}_{\alpha}(\vec{r})\varphi_{\beta}(\vec{r}) \equiv \int \varphi_{\alpha}^*(\vec{r}') g(\vec{r}, \vec{r}') \varphi_{\alpha}(\vec{r}') d\vec{r}' \varphi_{\beta}(\vec{r}), \quad (2.40)$$

$$\hat{A}_{\alpha}(\vec{r})\varphi_{\beta}(\vec{r}) \equiv \int \varphi_{\alpha}^*(\vec{r}') g(\vec{r}, \vec{r}') \varphi_{\beta}(\vec{r}') d\vec{r}' \varphi_{\alpha}(\vec{r}), \quad (2.41)$$

$$\hat{F}(\vec{r})\varphi_{\alpha}(\vec{r}) \equiv \left[ \hat{h}(\vec{r}) + \sum_{\beta}^{1, \dots, N} [\hat{K}_{\beta}(\vec{r}) - \delta(\sigma_{\alpha}, \sigma_{\beta}) \hat{A}_{\beta}(\vec{r})] \right] \varphi_{\alpha}(\vec{r}). \quad (2.42)$$

Equation (2.42) is the left of the Hartree–Fock equation (2.15).



$$\begin{aligned}
E &= \langle \Psi | \hat{H} | \Psi \rangle = \langle N, \dots, 2, 1 | \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu} \\
&\quad + \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\gamma\delta} \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu}^{\dagger} \hat{a}_{\gamma} \hat{a}_{\delta} | 1, 2, \dots, N \rangle \\
&= \sum_{\alpha}^{1, \dots, N} h_{\alpha\alpha} + \frac{1}{2} \sum_{\alpha, \beta}^{1, \dots, N} [g_{\alpha\beta\beta\alpha} - \delta(\sigma_{\alpha}, \sigma_{\beta}) g_{\alpha\beta\alpha\beta}], \quad (\text{Appendix 5}) \quad (2.43)
\end{aligned}$$

$$h_{\alpha\beta} \equiv \int \varphi_{\alpha}^* \hat{h} \varphi_{\beta} dv = \int \varphi_{\beta} \hat{h} \varphi_{\alpha}^* dv, \quad (\text{a4.8}) \quad (2.44)$$

$$g_{\alpha\beta\gamma\delta} \equiv \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\gamma}(\vec{r}_2) \varphi_{\delta}(\vec{r}_1) dv_1 dv_2, \quad (2.45)$$

$$\delta h_{\alpha\alpha} = \int \delta \varphi_{\alpha}^* \hat{h} \varphi_{\alpha} dv + \int \varphi_{\alpha}^* \hat{h} \delta \varphi_{\alpha} dv = \int \delta \varphi_{\alpha}^* \hat{h} \varphi_{\alpha} dv + \int \delta \varphi_{\alpha} \hat{h} \varphi_{\alpha}^* dv, \quad (2.46)$$

$$\begin{aligned}
\delta g_{\alpha\beta\beta\alpha} &= \int \delta \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\beta}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \delta \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\beta}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \delta \varphi_{\beta}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\beta}(\vec{r}_2) \delta \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&= \int \delta \varphi_{\alpha}^* \hat{K}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{K}_{\alpha} \varphi_{\beta} dv + \int \delta \varphi_{\beta} \hat{K}_{\alpha}^* \varphi_{\beta}^* dv + \int \delta \varphi_{\alpha} \hat{K}_{\beta}^* \varphi_{\alpha}^* dv, \quad (2.47)
\end{aligned}$$

$$\begin{aligned}
\delta g_{\alpha\beta\alpha\beta} &= \int \delta \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \delta \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \delta \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \delta \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&= \int \delta \varphi_{\alpha}^* \hat{A}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{A}_{\alpha} \varphi_{\beta} dv + \int \delta \varphi_{\alpha} \hat{A}_{\beta}^* \varphi_{\alpha}^* dv + \int \delta \varphi_{\beta} \hat{A}_{\alpha}^* \varphi_{\beta}^* dv, \quad (2.48)
\end{aligned}$$

$$\begin{aligned}
\delta E &= \sum_{\alpha}^{1,\dots,N} \delta h_{\alpha\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^{1,\dots,N} [\delta g_{\alpha\beta\beta\alpha} - \delta(\sigma_{\alpha}, \sigma_{\beta}) \delta g_{\alpha\beta\alpha\beta}] \\
&= \sum_{\alpha}^{1,\dots,N} \left( \int \delta \varphi_{\alpha}^* \hat{h} \varphi_{\alpha} dv + \int \delta \varphi_{\alpha} \hat{h} \varphi_{\alpha}^* dv \right) \\
&\quad + \frac{1}{2} \sum_{\alpha,\beta}^{1,\dots,N} \left\{ \int \delta \varphi_{\alpha}^* \hat{K}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{K}_{\alpha} \varphi_{\beta} dv \right. \\
&\quad + \int \delta \varphi_{\beta} \hat{K}_{\alpha}^* \varphi_{\beta}^* dv + \int \delta \varphi_{\alpha} \hat{K}_{\beta}^* \varphi_{\alpha}^* dv \\
&\quad - \delta(\sigma_{\alpha}, \sigma_{\beta}) \left[ \int \delta \varphi_{\alpha}^* \hat{A}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{A}_{\alpha} \varphi_{\beta} dv \right. \\
&\quad \left. \left. + \int \delta \varphi_{\alpha} \hat{A}_{\beta}^* \varphi_{\alpha}^* dv + \int \delta \varphi_{\beta} \hat{A}_{\alpha}^* \varphi_{\beta}^* dv \right] \right\} \\
&= \sum_{\alpha}^{1,\dots,N} \left[ \int \delta \varphi_{\alpha}^* \hat{F} \varphi_{\alpha} dv + \int \delta \varphi_{\alpha} \hat{F}^* \varphi_{\alpha}^* dv \right]. \tag{2.49}
\end{aligned}$$

Suppose  $\{\varphi_{\alpha}\}$  is orthonormal. Let  $\{\lambda_{\alpha\beta}\}$  denote the Lagrange multipliers.

$$S_{\alpha\beta} \equiv \int \varphi_{\alpha}^* \varphi_{\beta} dv = \delta(\alpha, \beta), \tag{2.50}$$

$$\sum_{\alpha,\beta}^{1,\dots,N} \lambda_{\alpha\beta} \delta S_{\alpha\beta} = \sum_{\alpha,\beta}^{1,\dots,N} \lambda_{\alpha\beta} \left( \int \delta \varphi_{\alpha}^* \varphi_{\beta} dv + \int \varphi_{\alpha}^* \delta \varphi_{\beta} dv \right) = 0, \tag{2.51}$$

$$\begin{aligned}
\delta E - \sum_{\alpha,\beta}^{1,\dots,N} \lambda_{\alpha\beta} \delta S_{\alpha\beta} &= \sum_{\alpha}^{1,\dots,N} \left[ \int \delta \varphi_{\alpha}^* (\hat{F} \varphi_{\alpha} - \sum_{\beta}^{1,\dots,N} \lambda_{\alpha\beta} \varphi_{\beta}) dv \right. \\
&\quad \left. + \int \delta \varphi_{\alpha} (\hat{F}^* \varphi_{\alpha}^* - \sum_{\beta}^{1,\dots,N} \lambda_{\beta\alpha} \varphi_{\beta}^*) dv \right] = 0. \tag{2.52}
\end{aligned}$$

$\delta \varphi_{\alpha}^*$  and  $\delta \varphi_{\alpha}$  ( $\alpha = 1, 2, \dots, N$ ) being independent, (2.52) means

$$\hat{F} \varphi_{\alpha} = \sum_{\beta}^{1,\dots,N} \lambda_{\alpha\beta} \varphi_{\beta}, \quad (\alpha, \beta = 1, 2, \dots, N) \tag{2.53}$$

$$\hat{F}^* \varphi_\alpha^* = \sum_{\beta}^{1, \dots, N} \lambda_{\beta\alpha} \varphi_\beta^*, \quad \hat{F} \varphi_\alpha = \sum_{\beta}^{1, \dots, N} \lambda_{\beta\alpha}^* \varphi_\beta. \quad (2.54)$$

From (2.53) and the second relation of (2.54) we get

$$\sum_{\beta}^{1, \dots, N} (\lambda_{\alpha\beta} - \lambda_{\beta\alpha}^*) \varphi_\beta = 0, \quad (2.55)$$

$$\lambda_{\alpha\beta} = \lambda_{\beta\alpha}^*, \quad (2.56)$$

that is,  $(\lambda)$  is a Hermitian matrix which can be diagonalized by an appropriate unitary matrix (A4.2.4) and the diagonal elements  $\lambda_{\alpha\alpha} = \varepsilon_\alpha$  are real numbers. Equation (2.15) is (2.53) of diagonalized  $(\lambda)$ .

## 2.2 Term and Multiplet

### 2.2.1 Residual Coulomb Interaction and Term

If electron subshells  $\{(n, l)\}$  are fully filled, the wave function of the atom  $\Psi$  is solely determined, and the configuration energy is nondegenerate. Take atom Ca( $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ ) as an example. All of the subshell 1s, 2s, 2p, 3s, 3p, and 4s are fully filled and the spin-orbitals for each subshells are unique such as they are  $\{R_{21} Y_{1m_1} \chi_\sigma\} (m_1 = 0, \pm 1; \sigma = \pm)$  for the 2p subshell. The situation is different if one of the subshell is partly filled. Take atom Ti( $3d^2 4s^2$ ) of two more electrons as an example. The situation of the full subshells is the same with that of atom Ca. Another two electrons are in the 3d subshell which has ten different spin-orbital states  $\{R_{32} Y_{2m_2} \chi_\sigma\} (m_2 = 0, \pm 1, \pm 2; \sigma = \pm)$ . Therefore, there are  $10 \times (10 - 1)/2! = 45$  different spin-orbitals for the two 3d electrons. The radial wave function  $R_{32}$  of them being the same, they have the same energy, that is, the configuration energy level is 45-fold degenerate.

The above results are obtained under the central field approximation which approximates the potential  $\frac{1}{2} \sum_{i,j}^{1, \dots, N; i \neq j} \frac{e^2}{4\pi \varepsilon_0 r_{ij}} - \sum_i^{1, 2, \dots, N} \frac{Ze^2}{4\pi \varepsilon_0 r_i}$  (2.8)–(2.12) by  $\sum_i^{1, 2, \dots, N} u(r_i)$  (2.16). Take the neglected residual Coulomb interaction

$$\hat{H}'_2 = \frac{1}{2} \sum_{i,j}^{1, \dots, N; i \neq j} \frac{e^2}{4\pi \varepsilon_0 r_{ij}} - \sum_i^{1, 2, \dots, N} \frac{Ze^2}{4\pi \varepsilon_0 r_i} - \sum_i^{1, 2, \dots, N} u(r_i) \quad (2.57)$$

as perturbation and solve the perturbation secular equation

$$|\langle \Psi_\beta | \hat{H}'_2 | \Psi_\gamma \rangle - \varepsilon \delta(\beta, \gamma)| = 0, \quad (\beta, \gamma = 1, 2, \dots, d. \text{ Appendix 6}) \quad (2.58)$$

where  $\{\Psi_\beta\}$  is the configuration wave functions,  $d$  the degeneracy of the configuration energy level, and  $\varepsilon$  the perturbation energy. Let  $n$  denote the number of the electrons partially filling the subshell. Each sum of the orbital angular momenta and spin angular momenta of full electron subshells being zero, the orbital and spin angular momenta of the atom are

$$\hat{L} = \sum_i^{1, \dots, n} \hat{l}_i, \quad (2.59)$$

$$\hat{S} = \sum_i^{1, \dots, n} \hat{s}_i. \quad (2.60)$$

$\hat{H}'_2$  being irrelevant to spins,  $\Psi_\beta$  is a product of the functions of positions and spins  $\Phi_\beta(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) |S, M_S\rangle$ .

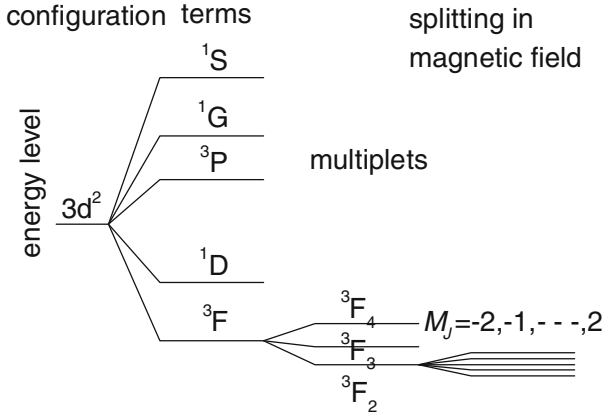
$\hat{H}'_2$  is invariant under the rotation–reflection operations (Note 1 of this section) and  $\{|L, M_L\rangle\}$  is the basis vectors of irreducible representation of rotation–reflection group (A4.4.2). Therefore, under the  $|\alpha, L, M_L\rangle$  representation of  $\{\Phi_\beta\}$  the perturbation secular equation

$$|\langle \alpha, L, M_L | \hat{H}'_2 | \alpha, L', M_{L'} \rangle - \varepsilon \delta(L, L') \delta(M_L, M_{L'})| = 0$$

( $\alpha$ : quantum numbers other than  $L$  and  $M_L$ ) (2.61)

is diagonalized (A4.7), and the eigenstates are  $\{|\alpha, L, M_L, S, M_S\rangle = |\alpha, L, M_L\rangle |S, M_S\rangle\}$  which have definite values of  $L$  and  $S$ . The energy being irrelevant to  $M_S$  and  $M_L$  the degeneracy of each eigenenergy is  $(2L + 1) \times (2S + 1)$ .

Take atom Ti( $3d^2 4s^2$ ) as an example. Under the residual Coulomb interaction the 45-fold degenerate configuration energy level splits to five energy levels of  $^3F$ ,  $^1D$ ,  $^3P$ ,  $^1G$ , and  $^1S$  (Fig. 2.2, Note 2 of this section). Here S, P, D, F, and G represent the orbital state of  $L = 0, 1, 2, 3$ , and 4, respectively, and the superscript on the left is the multiplicity  $2S + 1$  of total spin.  $^{2S+1}L$  represents a set of degenerate states called a term.  $^3F$  and  $^3P$  have the largest value of  $S$ , among which  $^3F$  has the largest value of  $L$ . So according to the Hund's first and second rules (Note 3 of this section)  $^3F$  is the ground term. In general, the energy gaps of excited term energy levels with the ground state term energy level are very large so that the excited terms affect magnetic properties of atom little. Hereafter, the excited terms will be neglected unless otherwise mentioned.



**Fig. 2.2** Energy levels of the ground configuration, terms, multiplets, and the split of the ground multiplet energy level in a magnetic field for atom Ti

### 2.2.2 Spin-Orbit Interaction and Multiplet

An electron in an atom circumrotates around the nucleus, thus the nucleus circumrotates relatively around the electron and produces a magnetic field. This magnetic field interacts with the electron spin magnetic moment. This interaction belongs to a relativity effect and is called spin-orbit interaction. The spin-orbit interaction operator could be obtained from the relativistic Dirac equation (1928) [1]. The Hamiltonian of the electron in a single-electron atom in this equation is

$$\hat{H}_D = \frac{(\hat{\vec{p}} - e\vec{A})^2}{2m + (E' - eV)/c^2} + eV - \frac{e\hbar\hat{\vec{\sigma}} \cdot \vec{B}}{2m + (E' - eV)/c^2} + \frac{ie\hbar}{[2m + (E' - eV)/c^2]^2 c^2} \vec{E} \cdot [(\hat{\vec{p}} - e\vec{A}) + i(\hat{\vec{p}} - e\vec{A}) \times \hat{\vec{\sigma}}], \quad (2.62)$$

$$eV = u(r), \quad (2.63)$$

$$\vec{E} = \frac{E_r \vec{r}}{r} = -\frac{1}{e} \frac{du(r)}{dr} \frac{\vec{r}}{r}, \quad (2.64)$$

where  $c$  is the speed of light in vacuum,  $m$  the electron rest mass,  $E' = E - mc^2$  the eigenenergy not including the rest-mass energy  $mc^2$ ,  $\vec{A}$ ,  $\vec{B}$ ,  $V$ , and  $\vec{E}$  the magnetic vector potential, magnetic induction, electric potential, and electric field produced by the nucleus. The spin-orbit interaction is the term in the right of (2.62) which includes the product of  $\hat{\vec{\sigma}}$  and  $\hat{\vec{p}}$ , that is,

$$\hat{H}_{LS} = \frac{ie\hbar}{[2m + (E' - eV)/c^2]^2 c^2} \vec{E} \cdot (i\hat{\vec{p}} \times \hat{\vec{\sigma}})$$

$$= \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{du(r)}{dr} \hat{l} \cdot \hat{s} \equiv \xi(r) \hat{l} \cdot \hat{s}. \quad ((E' - eV)/c^2 \ll 2m, \quad (\text{a3.3})) \quad (2.65)$$

The spin-orbit interactions in a multiple electron atom is

$$\hat{H}_{LS} = \sum_i^{1, \dots, n} \xi(r_i) \hat{l}_i \cdot \hat{s}_i, \quad (2.66)$$

where  $\xi(r_i)$  is given by the last relation of (2.65) but with the central field  $u(r_i)$  produced by both of the nucleus and the other electrons.  $\hat{H}_{LS}$  for a term can be formulated simply as

$$\hat{H}_{LS} = \lambda \hat{L} \cdot \hat{S}. \quad (\text{Note 4 of this section}) \quad (2.67)$$

$\lambda$  is called spin-orbit coupling constant.

The non-relativistic Hamiltonian for an atom including the spin-orbit interaction is  $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{LS}$ .  $\hat{H}$  is invariant under the rotation-reflection operations (Note 1 of this section).  $\hat{J} = \hat{L} + \hat{S}$  is the total angular momentum of the atom. The simultaneous eigenfunction  $|J, M_J\rangle$  of  $\hat{J}^2$  and  $\hat{J}_z$  is a basis vector of the irreducible representation of rotation-reflection group (A4.4.2). Therefore, under the representation of  $|\alpha, L, S, J, M_J\rangle$  the secular equation

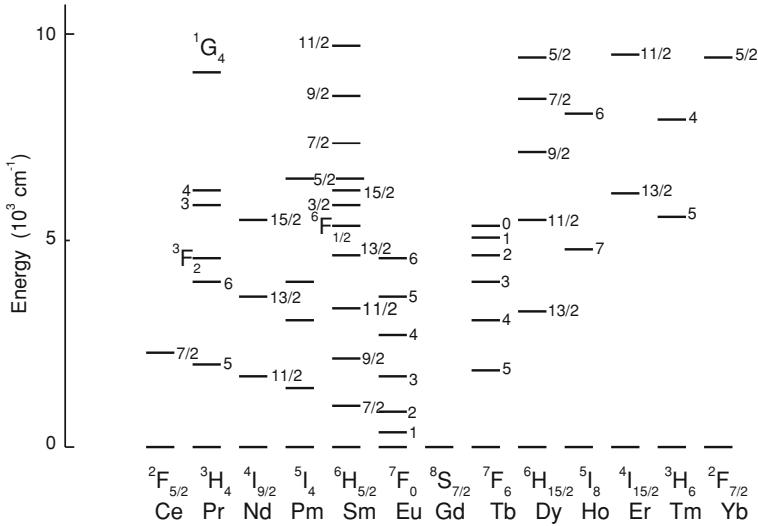
$$|\langle \alpha, L, S, J, M_J | \hat{H} | \alpha, L, S, J', M_{J'} \rangle - \varepsilon \delta(J, J') \delta(M_J, M_{J'})| = 0 \quad (2.68)$$

is diagonalized (A4.7) and the eigenstate is  $|\alpha, L, S, J, M_J\rangle$  ( $J = |L - S|, |L - S| + 1, \dots, L + S$ ). The perturbation energy of  $\hat{H}_{LS}$  is

$$\begin{aligned} \varepsilon_{LS} &= \lambda \langle \alpha, L, S, J, M_J | \hat{L} \cdot \hat{S} | \alpha, L, S, J, M_J \rangle \\ &= \frac{1}{2} \lambda [J(J+1) - L(L+1) - S(S+1)], \end{aligned} \quad (2.69)$$

which is independent of  $M_J$  and is  $2J + 1$  fold degenerate. Under the spin-orbit interaction the energy level of the term  $^{2S+1}L$  splits into energy levels of  $\{^{2S+1}L_J\}$  ( $J = |L - S|, |L - S| + 1, \dots, L + S$ ). Here  $^{2S+1}L_J$  represents the set of the eigenstates  $\{|\alpha, L, S, J, M_J\rangle\}$  ( $M_J = -J, -J + 1, \dots, J$ ) which is called multiplet. If the partially filled subshell is filled less than half or more than half,  $\lambda$  is positive or negative (Note 5 of this section), and  $J$  of the ground multiplet is  $|L - S|$  or  $L + S$ . The last result is just the Hund's third rule (Note 3 of this section). The energy gap between the neighboring multiplets is

$$\varepsilon_{LS}(\alpha, L, S, J) - \varepsilon_{LS}(\alpha, L, S, J - 1) = \lambda J. \quad (2.70)$$



**Fig. 2.3** The observed multiplet energy levels of the R (rare-earth) ions in RCl<sub>2</sub>

Take atom Ti(3d<sup>2</sup>4s<sup>2</sup>) as an example. Under the spin-orbit interaction, the energy level of the ground term <sup>3</sup>F splits into the energy levels of <sup>3</sup>F<sub>2</sub>, <sup>3</sup>F<sub>3</sub>, and <sup>3</sup>F<sub>4</sub> multiplets. The 3d subshell is filled less than a half and hence <sup>3</sup>F<sub>2</sub> is the ground state (Fig. 2.2).

In most cases, the energy gaps between excited multiplet energy levels and the ground multiplet energy level are still very large. Figure 2.3 demonstrates the multiplet energy levels of the rare-earth ions R observed in RCl<sub>2</sub> [2]. Take ion Nd<sup>+3</sup>(4f<sup>3</sup>) as an example. The energy gap between the first excited multiplet <sup>4</sup>I<sub>11/2</sub> energy level and the ground state <sup>4</sup>I<sub>9/2</sub> energy level is about 2,100 cm<sup>-1</sup> = 3,000 K which is about 10-folds of thermal energy at R. T.. Except for the ions of small value of *J* for ground multiplet, such as Eu (*J* = 0) and Sm (*J* = 5/2), the neglect of the excited multiplets does not affect the quality of the analysis of magnetic properties very much. In the following, the excited multiplets will be neglected unless otherwise mentioned.

### Note 1

$r_i$  and  $|\vec{r}_i - \vec{r}_j|$  are the lengths and  $\hat{L} \cdot \hat{S}$  is a scalar product. Apparently all of them are invariant under rotation-reflection operations.

Below it will be proven that  $\sum_{\alpha}^{x,y,z} \partial^2 / \partial \alpha^2$  also remains unchanged under the rotation-reflection operations. Let the coordinate of a fixed in the space position be  $\vec{r}(x, y, z)$  before a rotation-reflection operation. After the coordinate system is rotation-reflection operated the position vector in the new coordinate system becomes  $\vec{r}'(x', y', z')$ .  $(x', y', z')$  and  $(x, y, z)$  are linearly related and  $|\vec{r}'| = |\vec{r}|$ , that is

$$(r') = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = (T) (r) = \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial x'}{\partial y} & \frac{\partial x'}{\partial z} \\ \frac{\partial y'}{\partial x} & \frac{\partial y'}{\partial y} & \frac{\partial y'}{\partial z} \\ \frac{\partial z'}{\partial x} & \frac{\partial z'}{\partial y} & \frac{\partial z'}{\partial z} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (2.71)$$

$$(r')^T = (x' \ y' \ z') = (r)^T (T)^T = (x \ y \ z) \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} & \frac{\partial z'}{\partial x} \\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} & \frac{\partial z'}{\partial y} \\ \frac{\partial x'}{\partial z} & \frac{\partial y'}{\partial z} & \frac{\partial z'}{\partial z} \end{pmatrix}, \quad ((r')^T : \text{transpose of } (r)) \quad (2.72)$$

$$r'^2 = (r')^T (r') = (r)^T (T)^T (T) (r) = (r)^T (r) = r^2. \quad (2.73)$$

From above equation we get

$$(T)^T (T) = 1 = (T) (T)^T, \quad (2.74)$$

that is,

$$\sum_{\alpha}^{x,y,z} \frac{\partial \beta'}{\partial \alpha} \frac{\partial \gamma'}{\partial \alpha} = \delta(\beta', \gamma'), \quad (\beta', \gamma' = x', y', z') \quad (2.75)$$

$$\begin{aligned} \sum_{\alpha}^{x,y,z} \frac{\partial^2}{\partial \alpha^2} &= \sum_{\alpha}^{x,y,z} \sum_{\gamma}^{x',y',z'} \frac{\partial \gamma}{\partial \alpha} \frac{\partial}{\partial \gamma} \sum_{\beta}^{x',y',z'} \frac{\partial \beta}{\partial \alpha} \frac{\partial}{\partial \beta} = \sum_{\beta,\gamma}^{x',y',z'} \frac{\partial^2}{\partial \beta \partial \gamma} \sum_{\alpha}^{x,y,z} \frac{\partial \gamma}{\partial \alpha} \frac{\partial \beta}{\partial \alpha} \\ &= \sum_{\beta}^{x',y',z'} \frac{\partial^2}{\partial \beta^2}. \end{aligned} \quad (2.76)$$

## Note 2

$l_1 = l_2 = l = 2$ ;  $L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, l_1 + l_2 = 0, 1, 2, 3, 4$ ;  $s_1 = s_2 = s = 1/2$ ; and  $S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, s_1 + s_2 = 0, 1$ . The atomic orbitals  $\Phi_{LM_L}(1, 2)$  and  $\Phi_{LM_L}(2, 1)$  are

$$\Phi_{LM_L}(1, 2) = \sum_{m_l, m'_l} C(l l L; m_l m'_l M_L) \varphi_{lm_l}(1) \varphi_{lm'_l}(2), \quad (\varphi_{lm_l}(i) \equiv \varphi_{3lm_l}(\vec{r}_i)) \quad (2.77)$$



$$\begin{aligned}
\Phi_{LM_L}(2, 1) &= \sum_{m_l, m'_l} C(1L; m_l m'_l M_L) \phi_{lm_l}(2) \phi_{lm'_l}(1) \\
&= (-1)^{2l-L} \sum_{m_l, m'_l} C(1L; m'_l m_l M_L) \phi_{lm'_l}(1) \phi_{lm_l}(2) \\
&= (-1)^{2l-L} \Phi_{LM_L}(1, 2), \quad (\text{a4.27})
\end{aligned} \tag{2.78}$$

where  $C(1L; m_l m'_l M_L)$  is the Clebsch–Gordan coefficient (A4.8.1). In the same way

$$X_{SM_S}(2, 1) = (-1)^{1-S} X_{SM_S}(1, 2). \tag{2.79}$$

Since the wave function of the atom is antisymmetric, it holds

$$\begin{aligned}
\Phi_{LM_L}(1, 2) X_{SM_S}(1, 2) &= -\Phi_{LM_L}(2, 1) X_{SM_S}(2, 1) \\
&= (-1)^{2l-L+1-S} \Phi_{LM_L}(2, 1) X_{SM_S}(2, 1), \quad (\text{2.80})
\end{aligned}$$

thus  $L + S$  should be even integer. In brief summary, the possible values of the set  $(L, S)$  are (0,0), (2,0), (4,0), (1,1), and (3,1). Therefore, the 45 degenerate configuration energy level of Ti atom splits into five energy levels of  $^1S$ ,  $^1D$ ,  $^1G$ ,  $^3P$ , and  $^3F$  terms.

### Note 3

The Hund's rules ( $\sim 1927$ ) are

- ① The lowest energy term is that which has the largest  $S$ .
- ② For terms that have the same  $S$ , the term with the largest  $L$  lies lowest in energy.
- ③ If the partly filled subshell is exactly or more than half full, the level with the largest  $J$  value has the lowest energy. If the partly filled subshell is less than half full, the level with the smallest  $J$  value has the lowest energy.

### Note 4

$$\begin{aligned}
&\sum_i^{1,2,\dots,n} \langle L, M'_L, S, M'_S | \hat{l}_i \cdot \hat{s}_i | L, M_L, S, M_S \rangle \\
&= n \sum_{\alpha}^{\pm 1,0} (-1)^{\alpha} \langle L, M'_L | \hat{l}_{\alpha 1} | L, M_L \rangle \langle S, M'_S | \hat{s}_{-\alpha 1} | S, M_S \rangle \quad (\text{A4.6, A4.8.3}) \\
&= n \langle l, \dots, l, L | \hat{l} | l, \dots, l, L \rangle \langle s, \dots, s, S | \hat{s} | s, \dots, s, S \rangle \\
&\quad \times \sum_{\alpha}^{\pm 1,0} (-1)^{\alpha} C(L1L; M_L \alpha M'_L) C(S1S; M_S, -\alpha, M'_S), \quad (\text{a4.35})
\end{aligned} \tag{2.81}$$

$$\begin{aligned}
& \langle L, M'_L, S, M'_S | \hat{\vec{L}} \cdot \hat{\vec{S}} | L, M_L, S, M_S \rangle \\
&= \sum_{\alpha}^{\pm 1, 0} (-1)^{\alpha} \langle L, M'_L | \hat{L}_{\alpha} | L, M_L \rangle \langle S, M'_S | \hat{S}_{-\alpha} | S, M_S \rangle \\
&= \langle L \| \hat{L} \| L \rangle \langle S \| \hat{S} \| S \rangle \sum_{\alpha}^{\pm 1, 0} (-1)^{\alpha} C(L 1 L; M_L \alpha M'_L) C(S 1 S; M_S, -\alpha, M'_S).
\end{aligned} \tag{2.82}$$

Equations (2.81) and (2.82) have the same relations with respect to  $M_L, M'_L, M_S$  and  $M'_S$  and hence (2.66) can be expressed as (2.67).

### Note 5

$$\begin{aligned}
\varepsilon_{LS} &= \lambda \langle \alpha, L, S, J, M_J | \hat{\vec{L}} \cdot \hat{\vec{S}} | \alpha, L, S, J, M_J \rangle = \lambda M_L M_S \\
&= \left\langle \alpha, L, S, J, M_J \left| \sum_i^{1, 2, \dots, n} \xi(r_i) \hat{l}_{zi} \hat{s}_{zi} \right| \alpha, L, S, J, M_J \right\rangle = \langle \xi \rangle \sum_i^{1, 2, \dots, n} m_{li} m_{si},
\end{aligned} \tag{2.83}$$

$$M_L = \sum_i m_{li}, \quad M_S = \sum_i m_{si}, \tag{2.84}$$

where  $\langle \xi \rangle$  is the average of  $\xi(r_i)$ . From (2.83) we get

$$\lambda = \langle \xi \rangle \frac{\sum_i^{1, 2, \dots, n} m_{li} m_{si}}{M_L M_S}. \quad (M_L M_S \neq 0) \tag{2.85}$$

The electron spins are strongly exchange coupled to align parallel (Sect. 2.5.2). Therefore, if the subshell is filled less than half,  $m_{si} = 1/2$ ,  $M_S = n/2 = S$ , or  $m_{si} = -1/2$ ,  $M_S = -n/2 = -S$  and  $M_L = \sum_i^{1, 2, \dots, n} m_{li}$ , thus

$$\lambda = \langle \xi \rangle \frac{\frac{1}{2} \sum_i^{1, 2, \dots, n} m_{li}}{M_L \frac{n}{2}} = \frac{\langle \xi \rangle}{n} = \frac{\langle \xi \rangle}{2S} > 0. \tag{2.86}$$

If the subshell is filled more than half,

$$\begin{aligned}
M_S &= \frac{1}{2} \{ (2l+1) - [n - (2l+1)] \} = \frac{1}{2} [2(2l+1) - n] = S \quad (\text{or } M_S = -S), \\
\sum_i^{1, 2, \dots, n} m_{li} m_{si} &= \frac{1}{2} \left[ \sum_i^{1, 2, \dots, 2l+1} m_{li} - \sum_i^{(2l+1)+1, 2l+1)+2, \dots, n} m_{li} \right]
\end{aligned}$$

$$= -\frac{1}{2} \sum_i^{(2l+1)+1, 2l+1)+2, \dots, n} m_{li} = -\frac{1}{2} M_L$$

$$\left( \text{or } \sum_i^{1, 2, \dots, n} m_{li} m_{si} = \frac{1}{2} M_L \right), \quad (2.87)$$

thus

$$\lambda = \langle \xi \rangle \frac{(-1/2)M_L}{M_L(2l+1-n/2)} = \frac{-\langle \xi \rangle}{2(2l+1)-n} = \frac{-\langle \xi \rangle}{2S} < 0. \quad (2.88)$$

## 2.3 Intrinsic Magnetic Moment and Gyromagnetic Ratio of Atom

### 2.3.1 Magnetic Moment and Gyromagnetic Ratio of an Electron Orbit

The orbital of an electron in an atom is  $\varphi_{nlm_l}(\vec{r}) = |n, l, m_l\rangle$  (2.17). The  $z$  component of the orbital magnetic polarization moment is (Note 1 of this section)

$$p_J(m_l) = -m_l \mu_B = -\langle n, l, m_l | \hbar \hat{L}_z | n, l, m_l \rangle \gamma_l, \quad (2.89)$$

where

$$\mu_B = \frac{\mu_0 |e| \hbar}{2m} \quad (\text{J} \cdot \text{m/A}) \quad (2.90)$$

is the Bohr magneton ( $\mu_B$  is often defined by  $|e| \hbar / (2m)$  (J/T) such that all the magnetic polarization moments in this section are replaced by corresponding magnetic moments such as (2.89) by  $p_M(m_l) = -m_l \mu_B$ . This book adopts the  $\mu_B$  of (2.90)), and

$$\gamma_l \equiv \left| \frac{p_J(m_l)}{\hbar m_l} \right| = \frac{\mu_B}{\hbar} \quad (2.91)$$

is the absolute value of the ratio of the orbital magnetic polarization moment to the orbital angular momentum, which is called the gyromagnetic ratio of the electron orbit.

### 2.3.2 Magnetic Moment and Gyromagnetic Ratio of an Electron Spin

The  $z$  component of an electron spin magnetic polarization moment is

$$p_J(m_s) = -g_e m_s \mu_B = -\langle s, m_s | \hbar \hat{S}_z | s, m_s \rangle \gamma_s, \quad (g_e = 2.00232 \approx 2) \quad (2.92)$$

where

$$\gamma_s \equiv \left| \frac{p_J(m_s)}{\hbar m_s} \right| = 2 \frac{\mu_B}{\hbar} = 2\gamma_l \quad (2.93)$$

is the absolute value of the ratio of the spin magnetic polarization moment to the spin angular momentum, which is called the gyromagnetic ratio of an electron spin.

### 2.3.3 Intrinsic Magnetic Moment, $g$ Factor, and Effective Magnetic Moment of an Atom

The  $z$  component of the orbital magnetic polarization moment of an atom is

$$p_J(M_L) = -M_L \mu_B = -\langle L, M_L | \hbar \hat{L}_z | L, M_L \rangle \gamma_l. \quad (2.94)$$

The largest value of  $p_J(M_L)$   $p_J(-L) = L \mu_B$  is called the intrinsic orbital magnetic polarization moment or tersely orbital magnetic polarization moment of an atom.

$$\sqrt{\langle L, M_L | \hbar^2 \hat{L}^2 | L, M_L \rangle} \gamma_l = \sqrt{L(L+1)} \mu_B \quad (2.95)$$

is called the effective orbital magnetic polarization moment of an atom.

The  $z$  component of the spin magnetic polarization moment of an atom is

$$p_J(M_S) = -2M_S \mu_B = -\langle S, M_S | \hbar \hat{S}_z | S, M_S \rangle \gamma_s. \quad (2.96)$$

The largest value of  $p_J(M_S)$   $p_J(-S) = 2S \mu_B$  is called the intrinsic spin magnetic polarization moment or tersely spin magnetic polarization moment of an atom.

$$\sqrt{\langle S, M_S | \hbar^2 \hat{S}^2 | S, M_S \rangle} \gamma_s = 2\sqrt{S(S+1)} \mu_B \quad (2.97)$$

is called the effective spin magnetic polarization moment of an atom.

The  $z$  component of the magnetic polarization moment of an atom is

$$\begin{aligned} p_J(M_J) &= -\langle L, S, J, M_J | \hbar(\hat{L}_z + 2\hat{S}_z) | L, S, J, M_J \rangle \gamma_l \\ &= -g_J M_J \mu_B = -\langle L, S, J, M_J | \hbar \hat{J}_z | L, S, J, M_J \rangle \gamma_J, \end{aligned} \quad (2.98)$$

where

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{Note 2 of this section}) \quad (2.99)$$

is called the Landé  $g$  factor (or tersely  $g$  factor), and

**Table 2.3** Ground electron configurations, ground multiplets, and the values of  $S$ ,  $L$ ,  $J$ ,  $g_J$ ,  $g_J J$ , and  $g_J \sqrt{J(J+1)}$  for three-valence rare-earth ions

Ion	Configuration	Multiplet	$S$	$L$	$J$	$g_J$	$g_J J$	$g_J \sqrt{J(J+1)}$
La	4f <sup>0</sup>	<sup>1</sup> S <sub>0</sub>	0	0	0	0	0	0
Ce	4f <sup>1</sup>	<sup>2</sup> F <sub>5/2</sub>	1/2	3	5/2	6/7	2.14	2.54
Pr	4f <sup>2</sup>	<sup>3</sup> H <sub>4</sub>	1	5	4	4/5	3.20	3.58
Nd	4f <sup>3</sup>	<sup>4</sup> I <sub>9/2</sub>	3/2	6	9/2	8/1	3.27	3.62
Pm	4f <sup>4</sup>	<sup>5</sup> I <sub>4</sub>	2	6	4	3/5	2.40	2.68
Sm	4f <sup>5</sup>	<sup>6</sup> H <sub>5/2</sub>	5/2	5	5/2	2/7	0.71	0.85
Eu	4f <sup>6</sup>	<sup>7</sup> F <sub>0</sub>	3	3	0	0	0	0
Gd	4f <sup>7</sup>	<sup>8</sup> S <sub>7/2</sub>	7/2	0	7/2	2	7	7.94
Tb	4f <sup>8</sup>	<sup>7</sup> F <sub>6</sub>	3	3	6	3/2	9	9.72
Dy	4f <sup>9</sup>	<sup>6</sup> H <sub>15/2</sub>	5/2	5	15/2	4/3	10	10.65
Ho	4f <sup>10</sup>	<sup>5</sup> I <sub>8</sub>	2	6	8	5/4	10	10.61
Er	4f <sup>11</sup>	<sup>4</sup> I <sub>15/2</sub>	3/2	6	15/2	6/5	9	9.58
Tm	4f <sup>12</sup>	<sup>3</sup> H <sub>6</sub>	1	5	6	7/6	7	7.56
Yb	4f <sup>13</sup>	<sup>2</sup> F <sub>7/2</sub>	1/2	3	7/2	8/7	4	4.54
Lu	4f <sup>14</sup>	<sup>1</sup> S <sub>0</sub>	0	0	0	0	0	0

$$\gamma_J = \left| \frac{p_J(M_J)}{\hbar M_J} \right| = g_J \frac{\mu_B}{\hbar} \quad (2.100)$$

is the absolute value of the ratio of the atomic magnetic polarization moment to the angular momentum, which is called the gyromagnetic ratio of an atom.

The largest value of  $p_J(M_J)$   $p_J(-J) = g_J J \mu_B$  is called the intrinsic atomic magnetic polarization moment or tersely atomic magnetic polarization moment.

$$p_{J\text{eff}} \equiv g_J \sqrt{\langle J, M_J | \hat{J}^2 | J, M_J \rangle} \mu_B = g_J \sqrt{J(J+1)} \mu_B \quad (2.101)$$

is called effective magnetic polarization moment of an atom.

Table 2.3 lists the ground electron configurations, ground multiplets, and the values of  $S$ ,  $L$ ,  $J$ ,  $g_J$  ( $g$  factor),  $g_J J$  (magnetic polarization moment in  $\mu_B$  unit), and  $g_J \sqrt{J(J+1)}$  (effective magnetic polarization moment in  $\mu_B$  unit) for three-valence rare-earth ions.

### Note 1

First consider a general case in which an electron is moving in an arbitrary potential  $u$ . The orbital  $\varphi$  satisfies the Schrödinger equation

$$i\hbar \frac{\partial \varphi}{\partial t} = \left( -\frac{\hbar^2}{2m} \nabla^2 + u \right) \varphi. \quad (2.102)$$

The conjugate complex of the equation is

$$-i\hbar \frac{\partial \varphi^*}{\partial t} = \left( -\frac{\hbar^2}{2m} \nabla^2 + u \right) \varphi^*. \quad (2.103)$$

By subtracting the product of (2.102) and  $e\varphi^*$  by the product of (2.103) and  $e\varphi$ , we get the law of conservation of electric charge

$$-e \frac{\partial}{\partial t} (\varphi^* \varphi) = \frac{ie\hbar}{2m} \nabla \cdot (\varphi \nabla \varphi^* - \varphi^* \nabla \varphi), \quad (2.104)$$

in which the left is the diverging rate of the electric charge density and the right the divergence of the electric current density  $\vec{j} = (ie\hbar/2m)(\varphi \nabla \varphi^* - \varphi^* \nabla \varphi)$ .

In this section  $\varphi = \varphi_{nlm_l}(\vec{r})$  and

$$\vec{j} = \frac{ie\hbar}{2m} [\varphi_{nlm_l}(\vec{r}) \nabla \varphi_{nlm_l}^*(\vec{r}) - \varphi_{nlm_l}^*(\vec{r}) \nabla \varphi_{nlm_l}(\vec{r})]. \quad (2.105)$$

The  $r$  and  $\theta$  components of  $\vec{j}$  are zero. The  $\phi$  component is

$$\begin{aligned} j_\phi &= \frac{ie\hbar}{2m} \frac{1}{r \sin \theta} \left[ \varphi_{nlm_l}(\vec{r}) \frac{\partial \varphi_{nlm_l}^*(\vec{r})}{\partial \phi} - \varphi_{nlm_l}^*(\vec{r}) \frac{\partial \varphi_{nlm_l}(\vec{r})}{\partial \phi} \right] \quad (\text{a3.20}) \\ &= \frac{e\hbar m_l}{m} \frac{1}{r \sin \theta} |\varphi_{nlm_l}(\vec{r})|^2. \quad (2.17)-(2.18) \end{aligned} \quad (2.106)$$

$$p_J(m_l) = \mu_0 \int_0^\infty \int_0^\pi \pi (r \sin \theta)^2 j_\phi r d\theta dr = -m_l \mu_B. \quad ((1.21), (2.90)) \quad (2.107)$$

## Note 2

$\{\hat{L}_{\pm 1}, \hat{L}_0\}$  and  $\{\hat{J}_{\pm 1}, \hat{J}_0\}$  are the first-rank irreducible tensors (A4.6), thereby

$$\langle J, M_J | \hat{J}_\alpha | J, M'_J \rangle = C(J1J; M'_J \alpha M_J) \langle J \| \hat{J} \| J \rangle, \quad (\alpha = \pm 1, 0) \quad (2.108)$$

$$\langle L, S, J, M_J | \hat{L}_\alpha | L, S, J, M'_J \rangle = C(J1J; M'_J \alpha M_J) \langle J \| \hat{L} \| J \rangle, \quad (\text{a4.35}) \quad (2.109)$$

$$\begin{aligned} &\langle L, S, J, M_J | \hat{L}_\alpha + 2\hat{S}_\alpha | L, S, J, M'_J \rangle \\ &= \langle J, M_J | \hat{J}_\alpha | J, M'_J \rangle + \langle L, S, J, M_J | \hat{L}_\alpha | L, S, J, M'_J \rangle \\ &= \langle J, M_J | g_J \hat{J}_\alpha | J, M'_J \rangle, \end{aligned} \quad (2.110)$$

where the proportional coefficient  $g_J$  is irrelevant to  $M_J$  and  $M'_J$ . Equation (2.110) shows that

$$\hat{\vec{L}} + 2\hat{\vec{S}} = \hat{\vec{J}} + \hat{\vec{S}} = g_J \hat{\vec{J}}, \quad (2.111)$$

$$\hat{\vec{J}} \cdot \hat{\vec{S}} = (g_J - 1) \hat{\vec{J}}^2, \quad (2.112)$$

$$\begin{aligned} \hat{\vec{L}}^2 &= (\hat{\vec{J}} - \hat{\vec{S}})^2 = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2\hat{\vec{J}} \cdot \hat{\vec{S}} = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2(g_J - 1) \hat{\vec{J}}^2, \\ g_J \hat{\vec{J}}^2 &= \hat{\vec{J}}^2 + \frac{1}{2}(\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2), \end{aligned} \quad (2.113)$$

$$\begin{aligned} g_J &= 1 + \frac{\langle L, S, J, M_J | \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2 | L, S, J, M_J \rangle}{2\langle L, S, J, M_J | \hat{\vec{J}}^2 | L, S, J, M_J \rangle} \\ &= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \end{aligned} \quad (2.114)$$

## 2.4 Paramagnetism and Diamagnetism of Atom

### 2.4.1 Magnetic Moment Operator of an Atom in a Magnetic Field

In the magnetic field  $\vec{B} = B\vec{e}_z$  the Hamiltonian of an atom is

$$\begin{aligned} \hat{H} &= \sum_i^{1,\dots,Z} \left\{ \frac{1}{2m} [\hat{p}_i - e\vec{A}(\vec{r}_i)]^2 + 2\mu_B \hat{s}_{zi} H \right\} + \text{intra-atomic interactions}, \\ &\quad (\text{Sect. 1.5, (2.92), (1.75)}) \end{aligned} \quad (2.115)$$

$$\vec{A}(\vec{r}) = \frac{1}{2} \vec{B} \times \vec{r} = -\frac{1}{2} B y \vec{e}_x + \frac{1}{2} B x \vec{e}_y. \quad (\text{Note 1 of this section}) \quad (2.116)$$

The terms including the magnetic field in the Hamiltonian is

$$\sum_i^{1,\dots,Z} \left[ \mu_B (\hat{l}_{zi} + 2\hat{s}_{zi}) H + \frac{(e\mu_0 H)^2}{8m} (x_i^2 + y_i^2) \right], \quad (\text{Note 2 of this section}) \quad (2.117)$$

and the projection of atomic magnetic polarization moment operator in the  $\vec{H}$  direction and its eigenvalue are

$$\hat{p}_J = -\frac{\partial \hat{H}}{\partial H} = -\mu_B(\hat{L}_z + 2\hat{S}_z) - \frac{e^2\mu_0^2}{4m}H \sum_i^{1,\dots,Z} (x_i^2 + y_i^2), \quad (2.118)$$

$$\begin{aligned} & \langle \alpha, L, S, J, M_J | \hat{p}_J | \alpha, L, S, J, M_J \rangle \\ &= -g_J M_J \mu_B - \frac{e^2\mu_0^2}{4m} \frac{2Z \langle r^2 \rangle}{3} H. \quad (\langle r^2 \rangle = 3\langle x^2 \rangle = 3\langle y^2 \rangle: \text{average of } r_i^2) \end{aligned} \quad (2.119)$$

Suppose there are  $N$  atoms in a unit volume.

### 2.4.2 Paramagnetism of Atom

The first term in the last expression of (2.119) is the eigenvalue of the  $z$  component of the magnetic polarization moment operator of the atom. The magnetization is

$$M = \frac{N \sum_{M_J}^{-J, -J+1, \dots, J} -g_J M_J \mu_B \exp\left(-\frac{g_J M_J \mu_B H}{k_B T}\right)}{\mu_0 \sum_{M_J}^{-J, -J+1, \dots, J} \exp\left(-\frac{g_J M_J \mu_B H}{k_B T}\right)} = \frac{N g_J J \mu_B}{\mu_0} B_J(x), \quad (2.120)$$

$$x \equiv \frac{g_J J \mu_B H}{k_B T}, \quad (2.121)$$

$$B_J(x) \equiv \frac{2J+1}{2J} \text{cth}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \text{cth}\frac{x}{2J}. \quad (2.122)$$

$B_J(x)$  is called Brillouin function. Such magnetic property of  $M > 0$  is called paramagnetism.

If  $x \ll 1$ ,

$$B_J(x) = \frac{x}{3} \frac{J+1}{J}, \quad (2.123)$$

$$M = \frac{N g_J^2 J(J+1) \mu_B^2}{3\mu_0 k_B T} H, \quad (2.124)$$

and hence

$$\chi = \frac{C}{T}, \quad (2.125)$$

$$C = \frac{N g_J^2 J(J+1) \mu_B^2}{3\mu_0 k_B}. \quad (2.126)$$



Equation (2.125) is called the Curie law and  $C$  the Curie constant. The value of  $C$  can be obtained from the slope of the straightline  $1/\chi(T)$  of experiment, and the effective magnetic polarization moment of the atom  $g_J\sqrt{J(J+1)}\mu_B$  can be obtained from (2.126) by using the experimental value of  $C$ .

### 2.4.3 Diamagnetism of Atom

The last terms in the last expressions of (2.118) and (2.119) are negative, that is, the magnetization of negative susceptibility is oriented opposite to the magnetic field direction. Such magnetic property is called diamagnetism.

The term of (2.118) can also be deduced by using the following semiclassical model. An electron circumrotating with velocity  $\vec{v}$  on a circular orbit of radius  $r$  has an orbital angular momentum  $\hbar\vec{l} = m\vec{r} \times \vec{v}$  and orbital magnetic polarization moment

$$\vec{p}_J = \mu_0 I \vec{S} = \mu_0 \frac{ve}{2\pi r} \pi r^2 \frac{\vec{r} \times \vec{v}}{rv} = \frac{\mu_0 e}{2m} \hbar \vec{l}. \quad (1.21) \quad (2.127)$$

The absolute value of the ratio of  $\vec{p}_J$  to  $\hbar\vec{l}$  is  $|\mu_0 e/2m| = \gamma_l$  in coincidence with (2.91). According to the equation of motion for an angular momentum, the derivative of the angular momentum  $\hbar\vec{l}$  with respect to time equals to the torque exerted on the magnetic moment by the applied magnetic field  $\vec{p}_J \times \vec{H} = -\gamma_l \hbar\vec{l} \times \vec{H}$ , that is,

$$\frac{d\vec{l}}{dt} = -\gamma_l \vec{l} \times \vec{H}. \quad (2.128)$$

Let  $\vec{l} = \vec{l}_0 \exp(i\omega t)$ . The  $x$  and  $y$  components of (2.128) are

$$i\omega l_x + \gamma_l H l_y = 0, \quad (2.129)$$

$$-\gamma_l H l_x + i\omega l_y = 0. \quad (2.130)$$

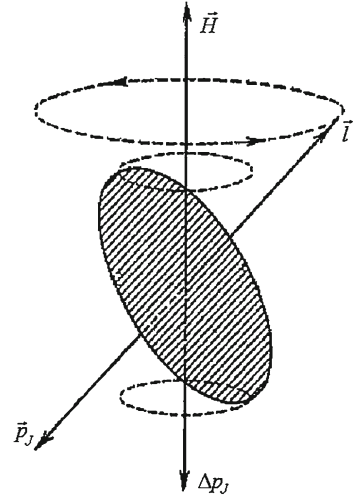
The solution of (2.129) and (2.130) are (Sect. 3.6.7.3)

$$\omega = \gamma_l H, \quad (2.131)$$

$$l_y = -il_x, \quad (2.132)$$

that is,  $\vec{l}$  makes a precession about the  $\vec{H}$  direction along the right-hand direction with angular speed  $\gamma_l H$  (Fig. 2.4). Such precession is called Larmor precession. The precession increases the angular momentum and magnetic polarization moment in the field direction by

$$\Delta l = m\omega r_{\perp}^2 = m\gamma_l (x^2 + y^2) H, \quad (2.133)$$

**Fig. 2.4** Larmor precession

and

$$\Delta p_J = -\gamma_l \Delta l = -\frac{\mu_0^2 e^2 (x^2 + y^2)}{4m} H. \quad ((2.90)-(2.91)) \quad (2.134)$$

The sum of  $\Delta \vec{p}_J$  over the electrons of an atom is just the last term in the right of (2.118).

The diamagnetic susceptibility is

$$\chi = -N \frac{\mu_0 e^2}{4m} \sum_i^{1, \dots, Z} (x_i^2 + y_i^2) = -N \frac{\mu_0 Z e^2 \langle r^2 \rangle}{6m}. \quad (2.135)$$

$\langle r^2 \rangle$  being little affected by temperature,  $\chi$  is essentially independent of temperature.

### Note 1

$A_\alpha$  ( $\alpha = x, y, z$ ) satisfying the relations of

$$\begin{aligned} B_x &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} = 0, & B_y &= \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} = 0, \\ B_z &= \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} = B, \end{aligned} \quad (1.11) \quad (2.136)$$

$$\nabla \cdot \vec{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} = 0 \quad (1.14) \quad (2.137)$$

can be expressed as

$$A_\alpha = \sum_{\beta}^{x,y,z} C_{\alpha\beta} \beta, \quad (2.138)$$

in which  $C_{\alpha\beta}$  satisfies the conditions

$$C_{zy} = C_{yz}, \quad C_{xz} = C_{zx}, \quad C_{yx} - C_{xy} = B, \quad (2.136) \quad (2.139)$$

$$C_{xx} + C_{yy} + C_{zz} = 0. \quad (2.137)$$

There are many ways to select the values of  $C_{\alpha\beta}$ . This section takes  $C_{yx} = -C_{xy} = B/2$ , and the others zero.

### Note 2

Let  $\varphi$  be an arbitrary function of  $\vec{r}$ .

$$\nabla \cdot (\vec{A}\varphi) = \vec{A} \cdot \nabla\varphi + (\nabla \cdot \vec{A})\varphi = \vec{A} \cdot \nabla\varphi, \quad ((a3.16), (1.14)) \quad (2.140)$$

$$\hat{\vec{p}} \cdot \vec{A}\varphi = -i\hbar \nabla \cdot (\vec{A}\varphi) = -i\hbar \vec{A} \cdot \nabla\varphi = \vec{A} \cdot \hat{\vec{p}}\varphi, \quad (2.141)$$

thus

$$\hat{\vec{p}} \cdot \vec{A} = \vec{A} \cdot \hat{\vec{p}}, \quad (2.142)$$

$$-\frac{e}{2m}(\hat{\vec{p}} \cdot \vec{A} + \vec{A} \cdot \hat{\vec{p}}) = -\frac{e}{m}\vec{A} \cdot \hat{\vec{p}} = -\frac{e\mu_0 H}{2m}(-y\hat{p}_x + x\hat{p}_y) = \mu_B \hat{l}_z H. \quad ((2.116), (2.90)) \quad (2.143)$$

## 2.5 Exchange Interaction in He Atom

### 2.5.1 Exchange Hamiltonian

By taking into account only the Coulomb interactions, the Hamiltonian of the two electron system of He atom is

$$\hat{H}(\vec{r}_1, \vec{r}_2) = \hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2) + g(\vec{r}_1, \vec{r}_2), \quad (2.144)$$

$$\hat{h}(\vec{r}) = \frac{\hat{p}^2(\vec{r})}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}, \quad (Z = 2) \quad (2.10)$$

$$g(\vec{r}_1, \vec{r}_2) = \frac{e^2}{4\pi\epsilon_0 r_{12}}. \quad (2.12)$$

Since the Hamiltonian is irrelevant to spin, the eigenstate of the system  $\Psi$  is the product of the functions of the position vectors and that of spins, which is exchange antisymmetric:

$$\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = \Phi(\vec{r}_1, \vec{r}_2)X(\sigma_1, \sigma_2) = -\Psi(\vec{r}_2, \sigma_2, \vec{r}_1, \sigma_1). \quad (2.145)$$

Thereby

$$\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = \begin{cases} \Phi_s(\vec{r}_1, \vec{r}_2)X_a(\sigma_1, \sigma_2), \\ \text{or} \\ \Phi_a(\vec{r}_1, \vec{r}_2)X_s(\sigma_1, \sigma_2). \end{cases} \quad (2.146)$$

The subscripts a and s denote that the function is exchange symmetric and antisymmetric, respectively.  $X_a$  and  $X_s$  are the spin eigenstates of total spin quantum number  $S = 0$  and  $=1$  for the two electron system, and are

$$\begin{aligned} X_a &= X_a(S = 0, M_S = 0) = \frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)] \\ &= |S = 0, M_S = 0\rangle, \end{aligned} \quad (2.147)$$

$$X_s(1, 1) = \chi_+(1)\chi_+(2) = |1, 1\rangle, \quad (2.148)$$

$$X_s(1, 0) = \frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)] = |1, 0\rangle, \quad (2.149)$$

$$X_s(1, -1) = \chi_-(1)\chi_-(2) = |1, -1\rangle. \quad (2.150)$$

Let  $\varphi_\alpha(\vec{r})$  and  $\varepsilon_\alpha$  denote the orbital eigenfunction and eigenenergy of  $\text{He}^{+1}$  ion, then

$$\begin{aligned} [\hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2)]\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) &= (\varepsilon_\alpha + \varepsilon_\beta)\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) \\ &= [\hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2)]\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1) \\ &= (\varepsilon_\alpha + \varepsilon_\beta)\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1). \end{aligned} \quad (2.151)$$

Take  $g(\vec{r}_1, \vec{r}_2)$  perturbation. By approximating the total orbital state of He by the linear combination of  $\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2)$  and  $\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1)$  ( $\alpha \neq \beta$ ), we get the orbital states and eigennergies

$$\Phi_s(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) + \varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1)], \quad (2.152)$$

$$E(S=0) = \varepsilon_\alpha + \varepsilon_\beta + K + J_A, \quad (2.153)$$

$$\Phi_a(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) - \varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1)], \quad (2.154)$$

$$E(S=1) = \varepsilon_\alpha + \varepsilon_\beta + K - J_A, \quad (2.155)$$

$$K \equiv \int \frac{e^2}{4\pi\epsilon_0 r_{12}} |\varphi_\alpha(\vec{r}_1)|^2 |\varphi_\beta(\vec{r}_2)|^2 d\mathbf{v}_1 d\mathbf{v}_2, \quad (2.156)$$

$$J_A \equiv \int \frac{e^2}{4\pi\epsilon_0 r_{12}} \varphi_\alpha^*(\vec{r}_1)\varphi_\beta^*(\vec{r}_2)\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1) d\mathbf{v}_1 d\mathbf{v}_2. \quad (2.157)$$

Here  $K$  and  $J_A$  are the Coulomb interaction energy and exchange integral between the two electrons. The eigenenergy is related with  $S$  but not with  $M_S$ . Since

$$\begin{aligned} & \langle s, s, S, M_S | (\hat{s}_1 + \hat{s}_2)^2 | s, s, S, M_S \rangle \\ &= \langle s, s, S, M_S | \hat{S}^2 | s, s, S, M_S \rangle \\ &= 2s(s+1) + \langle s, s, S, M_S | 2\hat{s}_1 \cdot \hat{s}_2 | s, s, S, M_S \rangle = S(S+1), \end{aligned} \quad (2.158)$$

$$\begin{aligned} & \langle s, s, S, M_S | 2\hat{s}_1 \cdot \hat{s}_2 | s, s, S, M_S \rangle = S(S+1) - 2s(s+1) \\ &= \begin{cases} -\frac{3}{2}, & (S=1) \\ \frac{1}{2}, & (S=0) \end{cases} \end{aligned} \quad (2.159)$$

equations (2.153) and (2.155) can be expressed in a unified form of

$$E = \varepsilon_\alpha + \varepsilon_\beta + K - \frac{1}{2}J_A - \langle s, s, S, M_S | 2J_A \hat{s}_1 \cdot \hat{s}_2 | s, s, S, M_S \rangle. \quad (2.160)$$

From the above equation we get the expression of the exchange Hamiltonian (also called Heisenberg Hamiltonian) as

$$\hat{H}_{\text{ex}} = -2J_A \hat{s}_1 \cdot \hat{s}_2. \quad (2.161)$$

By extending this result to the atom in which  $n$  electrons partially fill an electron subshell, the exchange Hamiltonian in general case is expressed as

$$\hat{H}_{\text{ex}} = -\frac{1}{2} \sum_{i,j}^{1,\dots,n; i \neq j} 2J_A \hat{s}_i \cdot \hat{s}_j. \quad (2.162)$$

### 2.5.2 Positiveness of Exchange Integral of Form (2.157)

Assume that the electric charge of density

$$\rho^*(\vec{r}) \equiv e\varphi_\alpha^*(\vec{r})\varphi_\beta(\vec{r}) \quad (2.163)$$

is distributed in the space.  $\varphi_\alpha(\vec{r})$  and  $\varphi_\beta(\vec{r})$  are arbitrary functions localized within a limited space. The relations between  $\rho^*(\vec{r})$  and the electric potential  $V(\vec{r})$  produced by the former are

$$\frac{\rho^*(\vec{r})}{\varepsilon_0} = -\nabla^2 V(\vec{r}), \quad ((1.33), (1.35)) \quad (2.164)$$

$$V(\vec{r}) = \int \frac{\rho^*(\vec{r}')}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|} dv'. \quad (1.37) \quad (2.165)$$

Inserting (2.163)–(2.165) into (2.157) we get

$$\begin{aligned} J_A &\equiv \int \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|} \varphi_\alpha^*(\vec{r})\varphi_\beta^*(\vec{r}')\varphi_\alpha(\vec{r}')\varphi_\beta(\vec{r}) dv dv' \\ &= \int \frac{\rho^*(\vec{r})\rho(\vec{r}')}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|} dv dv' = -\varepsilon_0 \int_{\infty} V^*(\vec{r})\nabla^2 V(\vec{r}) dv \\ &= -\varepsilon_0 \oint_{\infty} V^*(\vec{r})\nabla V(\vec{r}) \cdot d\vec{S} + \varepsilon_0 \int_{\infty} |\nabla V(\vec{r})|^2 dv \quad (\text{a3.28}) \\ &= \varepsilon_0 \int_{\infty} |\nabla V(\vec{r})|^2 dv > 0, \end{aligned} \quad (2.166)$$

that is the exchange integral of the form of (2.157) is permanently positive regardless of that the electrons belong to the same atom or different atoms.  $J_A$  of (2.157) belonging to this kind of integral, the exchange interactions within an atom align the electron spins as parallel as possible. This result can explain the Hund's first rule that the ground term of an atom has the largest value of spin quantum number  $S$ . Thus, the 3d transition atom of  $\text{Mn}(3d^5 4s^2)$ ,  $\text{Fe}(3d^6 4s^2)$ ,  $\text{Co}(3d^7 4s^2)$ , and  $\text{Ni}(3d^8 4s^2)$ , for instance, has the spin magnetic moments of  $5\mu_B$ ,  $4\mu_B$ ,  $3\mu_B$ , and  $2\mu_B$ , respectively.

## 2.6 Exchange Interaction in H<sub>2</sub> Molecule

### 2.6.1 Eigenstates and Eigenenergies of the Two Electron System of H<sub>2</sub>

By taking into account only the Coulomb interactions, the Hamiltonian of the two electron system is

$$\begin{aligned}\hat{H}(\vec{r}_1, \vec{r}_2) &= \frac{\hat{p}_1^2 + \hat{p}_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right) \\ &= \hat{h}_a(\vec{r}_1) + \hat{h}_b(\vec{r}_2) + \hat{g}(\vec{r}_1, \vec{r}_2) = \hat{h}_a(\vec{r}_2) + \hat{h}_b(\vec{r}_1) + \hat{g}(\vec{r}_2, \vec{r}_1),\end{aligned}\quad (2.167)$$

$$\hat{h}_\alpha(\vec{r}_i) \equiv \frac{\hat{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_{i\alpha}}, \quad (i = 1, 2; \alpha = a, b) \quad (2.168)$$

$$\hat{g}(\vec{r}_i, \vec{r}_j) \equiv \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{ij}} - \frac{1}{r_{ib}} - \frac{1}{r_{ja}} \right), \quad ((i, j) = (1, 2), (2, 1)) \quad (2.169)$$

where the subscripts  $a$  and  $b$  denote the nuclei and  $r_{i\alpha}$  the distance of the  $i^{\text{th}}$  electron from the nucleus  $\alpha$ . Let  $\varphi_\alpha$  and  $\varepsilon$  represent the ground orbital and eigenenergy of the electron in the isolated H atom of nucleus  $\alpha$ , then

$$\hat{h}_\alpha(\vec{r})\varphi_\alpha(\vec{r}) = \varepsilon\varphi_\alpha(\vec{r}). \quad (2.170)$$

When the two H atoms are distant apart, there are two ground orbital states of the two electron system:

$$\Phi(\vec{r}_1, \vec{r}_2) \equiv \varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2), \quad (2.171)$$

$$\Phi(\vec{r}_2, \vec{r}_1) \equiv \varphi_a(\vec{r}_2)\varphi_b(\vec{r}_1), \quad (2.172)$$

which satisfy the Schrödinger equations

$$[\hat{h}_a(\vec{r}_1) + \hat{h}_b(\vec{r}_2)]\Phi(\vec{r}_1, \vec{r}_2) = 2\varepsilon\Phi(\vec{r}_1, \vec{r}_2), \quad (2.173)$$

$$[\hat{h}_a(\vec{r}_2) + \hat{h}_b(\vec{r}_1)]\Phi(\vec{r}_2, \vec{r}_1) = 2\varepsilon\Phi(\vec{r}_2, \vec{r}_1). \quad (2.174)$$

Take  $\hat{g}(\vec{r}_i, \vec{r}_j)$  or  $\hat{g}(\vec{r}_j, \vec{r}_i)$  as perturbation when the two H atoms approach, and solve the orbital eigenfunction

$$C_1\Phi(\vec{r}_1, \vec{r}_2) + C_2\Phi(\vec{r}_2, \vec{r}_1) \quad (2.175)$$

and eigenenergy  $2\varepsilon + \Delta$  from the Schrödinger equation

$$\begin{aligned}
& C_1[\hat{H} - (2\varepsilon + \Delta)]\Phi(\vec{r}_1, \vec{r}_2) + C_2[\hat{H} - (2\varepsilon + \Delta)]\Phi(\vec{r}_2, \vec{r}_1) \\
& = C_1[\hat{g}(\vec{r}_1, \vec{r}_2) - \Delta]\Phi(\vec{r}_1, \vec{r}_2) + C_2[\hat{g}(\vec{r}_2, \vec{r}_1) - \Delta]\Phi(\vec{r}_2, \vec{r}_1) = 0. \quad (2.176)
\end{aligned}$$

Let

$$\begin{aligned}
K & \equiv \langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle = \langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle \\
& = \int \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{r_{12}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} \right) |\varphi_a(\vec{r}_1)|^2 |\varphi_b(\vec{r}_2)|^2 dv_1 dv_2, \quad (2.177)
\end{aligned}$$

$$\begin{aligned}
J_A & \equiv \langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle = \langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle \\
& = \int \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{2b}} \right) \varphi_a^*(\vec{r}_1) \varphi_b^*(\vec{r}_2) \varphi_a(\vec{r}_2) \varphi_b(\vec{r}_1) dv_1 dv_2, \quad (2.178)
\end{aligned}$$

$$S_{ab} \equiv \int \varphi_a^*(\vec{r}) \varphi_b(\vec{r}) dv, \quad (2.179)$$

and suppose  $|S_{ab}|^2 \ll 1$ .

Left multiplying  $\Phi^*(\vec{r}_1, \vec{r}_2)$  and  $\Phi^*(\vec{r}_2, \vec{r}_1)$ , respectively, on the last relation of (2.176) and then integrating them we get

$$\begin{aligned}
& C_1[\langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle - \Delta] \\
& + C_2[\langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle - \Delta \langle \Phi(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_2, \vec{r}_1) \rangle] \\
& = C_1(K - \Delta) + C_2(J_A - \Delta|S_{ab}|^2) = C_1(K - \Delta) + C_2J_A = 0, \quad (2.180)
\end{aligned}$$

$$\begin{aligned}
& C_1[\langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle - \Delta \langle \Phi(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_1, \vec{r}_2) \rangle] \\
& + C_2[\langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle - \Delta] \\
& = C_1(J_A - \Delta|S_{ab}|^2) + C_2(K - \Delta) = C_1J_A + C_2(K - \Delta) = 0. \quad (2.181)
\end{aligned}$$

The two solutions of simultaneous (2.180) and (2.181) are

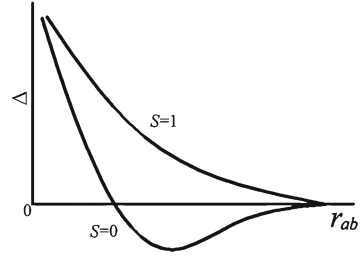
$$\Delta(S = 0) = K + J_A, \quad (2.182)$$

$$\Phi_s(\vec{r}_1, \vec{r}_2) \approx \frac{1}{\sqrt{2}}[\Phi(\vec{r}_1, \vec{r}_2) + \Phi(\vec{r}_2, \vec{r}_1)], \quad (2.183)$$

$$\Delta(S = 1) = K - J_A, \quad (2.184)$$

$$\Phi_a(\vec{r}_1, \vec{r}_2) \approx \frac{1}{\sqrt{2}}[\Phi(\vec{r}_1, \vec{r}_2) - \Phi(\vec{r}_2, \vec{r}_1)]. \quad (2.185)$$



**Fig. 2.5**  $\Delta$  versus  $r_{ab}$ 

$\Phi_s$  is exchange symmetric and  $\Phi_a$  is antisymmetric. Since the Hamiltonian (2.167) is irrelevant to spin, the spin-orbit eigenfunctions are the products of the above orbital functions and the spin functions, and are antisymmetric, that is

$$\Psi_1 = \Phi_s(\vec{r}_1, \vec{r}_2)X_a(\sigma_1, \sigma_2), \quad (2.186)$$

$$\Psi_2 = \Phi_a(\vec{r}_1, \vec{r}_2)X_s(\sigma_1, \sigma_2). \quad ((2.147)-(2.150)) \quad (2.187)$$

### 2.6.2 Exchange Interaction in H<sub>2</sub>

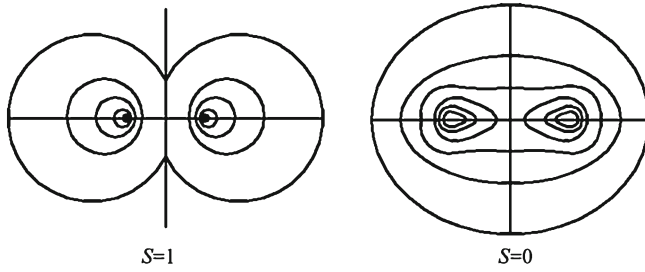
The relations between the perturbation energy and the total spin quantum number in (2.182) and (2.184) are completely the same with those in (2.153 and (2.155). Therefore, the perturbation energies  $\Delta(S = 0)$  and  $\Delta(S = 1)$  can be expressed in the unified form of

$$\Delta = K - \frac{1}{2}J_A - \langle S, M_S | 2J_A \hat{s}_1 \cdot \hat{s}_2 | S, M_S \rangle \quad (2.188)$$

as that in (2.160). The exchange Hamiltonian is

$$\hat{H}_{ex} = -2J_A \hat{s}_1 \cdot \hat{s}_2 \quad (2.189)$$

as (2.161) for He atom. The difference is that there are two extra two terms in the  $J_A$  of (2.178) for H<sub>2</sub> molecule then that of (2.157) for He atom. If  $J_A > 0$  the energy of the  $S = 1$  state is smaller than that of  $S = 0$  state and hence the parallel coupled spin state is stable. If  $J_A < 0$ , the  $S = 0$  state is stable. H<sub>2</sub> molecule belongs to the latter case. Figure 2.5 demonstrates  $\Delta$  as a function of  $r_{ab}$ . It shows that when  $S = 0$  there appears a minimum of  $\Delta < 0$  at a certain value of  $r_{ab}$ , thus forming a stable H<sub>2</sub> molecule. Figure 2.6 demonstrates the electron density distribution on a section plane passing through the two nuclei. The electrons itinerate in the whole molecule. When  $S = 1$  the two electrons of same spin repulse each other caused by the Pauli's



**Fig. 2.6** Electron density distribution for state  $S = 1$  and  $0$

exclusion principle and have a tendency to localize in each atom H. When  $S = 0$ , there is no such repulsion and the degree of itineration is higher.

## 2.7 Hyperfine Interactions in Atom

### 2.7.1 Spin, Magnetic Moment, and Quadrupole of Nucleus

A nucleus mainly constitutes of positrons and neutrons. The masses of positron and neutron are  $m_p = 1836.153 m$  and  $m_n = 1838.684 m$ , where  $m$  is the electron rest mass. A nucleus is denoted by the nuclear symbol  ${}^A_Z X$  or  ${}^A X$ , where  $Z$  is the atomic number which is the number of the positrons,  $X$  is the element symbol such as Fe, and  $A$  the mass number which is the sum of the number of positrons and neutrons. The spin quantum number, magnetic polarization moment, and electric charge of a positron, neutron, and nucleus are

$$I_p = \frac{1}{2}, \quad p_{Jp} = 2.79284734 \mu_N, \quad |e|, \quad (2.190)$$

$$I_n = \frac{1}{2}, \quad p_{Jn} = -1.9128 \mu_N, \quad 0, \quad (2.191)$$

$$I, \quad p_{JN} = g_N I \mu_N, \quad Z|e|, \quad (2.192)$$

respectively, where

$$\mu_N \equiv \frac{\mu_0 |e| \hbar}{2m_p} = \frac{1}{1836.153} \mu_B \quad (2.193)$$

is the nuclear magneton.  $I$  is zero if both of  $Z$  and number of the neutrons  $A-Z$  are even, a half-integer if  $Z$  is even and  $A-Z$  is odd, and an integer if both of  $Z$  and  $A-Z$  are odd. The values of  $p_{JN}$  are three orders smaller than that of electron and can be neglected compared to the latter, but the magnetic moment plays a very important

**Table 2.4** Values of  $I$ ,  $g_N$ ,  $g_N I$ , and  $Q_I$  for  $^1\text{H}$ ,  $^{57}\text{Fe}$ , and  $^{143}\text{Nd}$  [3]

Nucleus	$I$	$g_N$	$g_N I$	$Q_I/(10^{-28}\text{m}^2)$	State
$^1\text{H}$	1/2	5.585,691,2	2.792,847,34	0	Ground
$^{57}\text{Fe}$	1/2	0.188,8	0.090,44	0	Ground
	3/2	-0.103,3	-0.154,9	0.21	First excited
$^{143}\text{Nd}$	7/2	-0.304	-1.063	-0.48	Ground

role as a detector of the hyperfine magnetic field which is proportional to the magnetic moment of the atom in solids (Sect. 3.9).

If the weak interaction is neglected, the nuclear wavefunction  $\psi_{\alpha I M_I}(\vec{r}) = |\alpha, I, M_I\rangle$  ( $\vec{r}$ : logogram of all position vectors of positrons;  $M_I$ : the magnetic quantum number;  $\alpha$ : the quantum numbers other than  $I$  and  $M_I$ ) has a definite parity:

$$\psi_{\alpha I M_I}(\vec{r}) = \pm \psi_{\alpha I M_I}(-\vec{r}), \quad (2.194)$$

and hence the dipole moment of the positrons  $\langle \alpha, I, M_I | \sum_p^{1,\dots,Z} \vec{r}_p | \alpha, I, M_I \rangle$  is zero. Here  $\vec{r}_p$  is the position vector of the  $p^{\text{th}}$  positron.

For most of nuclei, the space distribution of the positrons has the symmetry of rotational ellipsoid. The quadrupole  $Q_I$  characterizing the extent of deviation of the positron distribution from spherical symmetry is defined and is

$$\begin{aligned}
 Q_I &\equiv \left\langle \alpha, I, I \left| \sum_p^{1,\dots,Z} (3z_p^2 - r_p^2) \right| \alpha, I, I \right\rangle \quad (z_p: z \text{ component of } \vec{r}_p) \\
 &= \left\langle \alpha, I, I \left| 2 \sum_p^{1,\dots,Z} r_p^2 U_0^2(\vec{r}_p/r_p) \right| \alpha, I, I \right\rangle \quad (2.24, \text{Table 2.1}) \\
 &= \langle I, I | 3\hat{I}_z^2 - \hat{I}^2 | I, I \rangle \left\langle \sum_p^{1,\dots,Z} r_p^2 \right\rangle \langle I || U^2 || I \rangle \quad (\text{A4.9.2}) \\
 &= I(2I-1) \left\langle \sum_p^{1,\dots,Z} r_p^2 \right\rangle \langle I || U^2 || I \rangle, \quad (2.195)
 \end{aligned}$$

where  $\langle \sum_p^{1,\dots,Z} r_p^2 \rangle$  is the average of  $\sum_p^{1,\dots,Z} r_p^2$ .  $|e|Q_I$  is called electric-quadrupole.

Table 2.4 demonstrates the values of  $I$ ,  $g_N$ ,  $g_N I$ , and  $Q_I$  for some nuclei.

### 2.7.2 Hyperfine Interactions

So far a nucleus has been considered to interact with the electrons as a point electric charge (2.10). The interaction of the finite volume nucleus which has a magnetic moment is a bit different from the above interaction, but the difference is far smaller than the latter and spin-orbit interaction and is called hyperfine interaction. Some of the interaction belong to the relativity effects and the hyperfine interactions will be discussed on the basis of the Hamiltonian of Dirac equation [1]

$$\hat{H}_D = \frac{(\hat{\vec{p}} - e\vec{A})^2}{2m + (E' - eV)/c^2} + eV - \frac{e\hbar\hat{\vec{\sigma}}\cdot\vec{B}}{2m + (E' - eV)/c^2} + \frac{ie\hbar}{[2m + (E' - eV)/c^2]^2 c^2} \vec{E} \cdot [\hat{\vec{p}} - e\vec{A} + i(\hat{\vec{p}} - e\vec{A}) \times \hat{\vec{\sigma}}], \quad (2.62)$$

$$eV = u(r), \quad (2.63)$$

$$\vec{E} = \frac{E_r \vec{r}}{r} = -\frac{1}{e} \frac{du(r)}{dr} \frac{\vec{r}}{r}, \quad (2.64)$$

$$\vec{A} = \frac{\hat{\vec{p}}_{JN} \times \vec{r}}{4\pi r^3}, \quad (1.49) \quad (2.196)$$

$$\vec{H} = \frac{\vec{B}}{\mu_0} = \frac{1}{4\pi\mu_0} \left[ \frac{3(\hat{\vec{p}}_{JN} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{\vec{p}}_{JN}}{r^3} \right]. \quad (1.46) \quad (2.197)$$

### 2.7.3 Hyperfine Magnetic Interaction

Hyperfine magnetic interaction  $\hat{H}_{hm}$  includes the terms in the right of (2.62) proportional to  $\hat{\vec{p}}_{JN}$  of the nucleus and also to  $\hat{\vec{p}}$  and  $\hat{\vec{s}} = \hat{\vec{\sigma}}/2$  of the electron, that is

$$\hat{H}_{hm} = -\frac{e}{m} \hat{\vec{p}} \cdot \vec{A} + 2\mu_B \hat{\vec{s}} \cdot \vec{H} + \frac{2e^2 \hbar E_r}{[2m + (E' - u(r))/c^2]^2 c^2 r} \vec{r} \cdot \vec{A} \times \hat{\vec{s}}. \quad (2.198)$$

The first and second terms in the right of above equation are the same with corresponding terms of the non-relativistic Hamiltonian Equation (2.115). The third term is of relativistic effect called Fermi contact term or tersely called contact term.

$\hat{H}_{hm}$  being proportional to  $\hat{\vec{p}}_{JN}$ , it can be expressed as a potential energy of  $\hat{\vec{p}}_{JN}$  in the hyperfine magnetic field  $\hat{\vec{H}}_{hm}$  produced by the electron:

$$\hat{H}_{hm} = -\hat{\vec{p}}_{JN} \cdot \hat{\vec{H}}_{hm}. \quad (2.199)$$

First consider the hyperfine magnetic field of the first and second terms in the right of Equation (2.198). They can be reformulated as

$$-\frac{e}{m} \hat{p} \cdot \vec{A} = -\frac{e}{m} \hat{p} \cdot \frac{\hat{p}_{JN} \times \vec{r}}{4\pi r^3} = -\hat{p}_{JN} \cdot \frac{-\mu_B \hat{l}}{2\pi \mu_0 r^3}, \quad (2.200)$$

$$2\mu_B \hat{s} \cdot \vec{H} = -\hat{p}_{JN} \cdot \frac{-\mu_B}{2\pi \mu_0} \left[ \frac{3(\hat{s} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{s}}{r^3} \right], \quad (2.201)$$

so their hyperfine magnetic fields are

$$\hat{H}_l = \frac{-\mu_B}{2\pi \mu_0} \frac{\hat{l}}{r^3}, \quad (2.202)$$

$$\hat{H}_s = \frac{-\mu_B}{2\pi \mu_0} \left[ \frac{3(\hat{s} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{s}}{r^3} \right]. \quad (2.203)$$

These fields are produced by non-s electrons. For an s electron  $l$  is zero and hence the average of  $\hat{H}_l$  is zero. The space distribution of the s electron cloud being spherically symmetric, the average of  $\hat{H}_s$  is also zero (Note 1 of this section).

Now analyze the last term in the right of (2.198). By exploiting the relation of

$$\begin{aligned} \vec{r} \cdot \vec{A} \times \hat{s} &= \hat{s} \cdot \vec{r} \times \frac{\hat{p}_{JN} \times \vec{r}}{4\pi r^3} = \hat{s} \cdot \frac{\hat{p}_{JN} r^2 - \vec{r}(\hat{p}_{JN} \cdot \vec{r})}{4\pi r^3} \quad ((2.196), (a3.3)-(a3.4)) \\ &= \frac{1}{4\pi} \hat{p}_{JN} \cdot \left[ \frac{\hat{s}}{r} - \frac{(\hat{s} \cdot \vec{r})\vec{r}}{r^3} \right] \end{aligned} \quad (2.204)$$

we get the contact term  $\hat{H}_F$  and its hyperfine magnetic field  $\hat{H}_F$  as

$$\begin{aligned} \hat{H}_F &= \frac{2e^2 \hbar E_r}{[2m + (E' - u(r))/c^2]^2 c^2 r} \vec{r} \cdot \vec{A} \times \hat{s} \\ &= \frac{-e\mu_B}{4\pi m \mu_0} \frac{E_r}{[1 + (E' - eV)/2mc^2]^2 c^2} \hat{p}_{JN} \cdot \left[ \frac{\hat{s}}{r^2} - \frac{(\hat{s} \cdot \vec{r})\vec{r}}{r^4} \right] = -\hat{p}_{JN} \cdot \hat{H}_F, \end{aligned} \quad (2.205)$$

$$\hat{H}_F = \frac{1}{4\pi} \frac{e\mu_B}{mc^2 \mu_0} \frac{E_r}{[1 + (E' - u(r))/2mc^2]^2} \left[ \frac{\hat{s}}{r^2} - \frac{(\hat{s} \cdot \vec{r})\vec{r}}{r^4} \right]. \quad (2.206)$$

Since

$$\frac{\hat{s}}{r^2} - \frac{(\hat{s} \cdot \vec{r})\vec{r}}{r^4} = \frac{2\hat{s}}{3r^2}, \quad (\text{Note 2 of this section}) \quad (2.207)$$

and

$$\frac{-e}{2mc^2} \frac{E_r}{[1 + (E' - u(r))/2mc^2]^2} = \frac{d}{dr} \frac{1}{1 + (E' - u(r))/2mc^2} \equiv f(r) \quad (2.208)$$

has the characteristics of Dirac  $\delta$  (Note 3 of this section), (2.206) simplifies to

$$\hat{H}_F = -\frac{\mu_B}{2\pi\mu_0} \delta(r) \frac{2\hat{s}}{3r^2}. \quad (2.209)$$

The hyperfine magnetic field of the contact term produced by the electron of orbital state  $|n, l, m_l\rangle$  is

$$\begin{aligned} \int \hat{H}_F |\varphi_{nlm_l}(\vec{r})|^2 r^2 \sin\theta dr d\theta d\phi &= - \int \frac{\mu_B}{2\pi\mu_0} \frac{2}{3} \delta(r) R_{nl}^2(r) \hat{s} dr \\ &= -\frac{\mu_B}{2\pi\mu_0} \frac{2}{3} |\varphi_{nlm_l}(0)|^2 \hat{s}. \quad (R_{nl}^2(0) = |\varphi_{nlm_l}(0)|^2) \end{aligned} \quad (2.210)$$

Since  $R_{nl}(0)$  is nonzero only for  $l = 0$  (2.26), only s electrons contribute to the contact term.

The total hyperfine magnetic field is the sum of (2.202), (2.203), and (2.209):

$$\hat{H}_{\text{hm}} = -\frac{\mu_B}{2\pi\mu_0} \left[ \frac{\hat{l}}{r^3} + \frac{3(\hat{s} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{s}}{r^3} + \frac{2}{3r^2} \delta(r) \hat{s} \right]. \quad (2.211)$$

### 2.7.4 Electric-Quadrupole Interaction

Let  $V(\vec{r}_p)$  denote the Coulomb potential produced by the electrons outside the nucleus. The Coulomb interactions of the nucleus with the electrons are

$$\begin{aligned} \hat{H}_e &= \sum_p^{1, \dots, Z} |e| V(\vec{r}_p) = |e| \sum_p^{1, \dots, Z} \left[ V(0) + \sum_{\alpha}^{x, y, z} \frac{\partial V}{\partial \alpha} \Big|_0 \alpha_p \right. \\ &\quad \left. + \frac{1}{2} \sum_{\alpha, \beta}^{x, y, z} \frac{\partial^2 V}{\partial \alpha \partial \beta} \Big|_0 \alpha_p \beta_p + \dots \right]. \end{aligned} \quad (2.212)$$

The first term in the last expression is the Coulomb potential of the point charge nucleus which does not belong to the hyperfine interaction. The electric moment of the nucleus being zero, the second term is zero. The third term

$$\hat{H}_q = \frac{|e|}{2} \sum_p \sum_{\alpha, \beta}^{1, \dots, Z} V_{\alpha\beta} \alpha_p \beta_p \quad \left( V_{\alpha\beta} \equiv \frac{\partial^2 V}{\partial \alpha \partial \beta} \Big|_0 \right) \quad (2.213)$$

is called the electric-quadrupole interaction.

### 2.7.5 Hyperfine Coulomb Interaction of the Nucleus with an Overlapping Electron Cloud

Consider the nucleus to be approximately a sphere of radius  $r_N$ , and the orbital of the electron within the nucleus  $\varphi_{nlm_l}(0)$ . The Coulomb interaction energy with respect to that of the electric point charged nucleus is

$$\hat{H}_{e0} = e \int_0^{r_N} \frac{-Ze}{4\pi\epsilon_0 r} \left( \frac{r^3}{r_N^3} - 1 \right) 4\pi r^2 |\varphi_{nlm_l}(0)|^2 dr = \frac{3Ze^2}{10\epsilon_0} |\varphi_{nlm_l}(0)|^2 r_N^2. \quad (2.214)$$

$\varphi_{nlm_l}(0)$  being nonzero only for s electrons, this interaction is produced by an s electron.

### 2.7.6 Total Hyperfine Interaction

Total hyperfine interaction of an atom is

$$\hat{H}_{\text{hf}} = \sum_i^{1, \dots, Z} [\hat{H}_{\text{hm}}(i) + \hat{H}_q(i) + \hat{H}_{e0}(i)]. \quad (2.215)$$

#### Note 1

Let  $\vec{e}_z$  and  $\vec{e}_\perp$  denote the unit vectors in the  $\hat{s}$  direction and normal to  $\hat{s}$  in the plane formed by  $\vec{r}$  and  $\hat{s}$  and  $\theta$  the angle between  $\vec{r}$  and  $\hat{s}$ .  $\vec{r} = r(\vec{e}_z \cos \theta + \vec{e}_\perp \sin \theta)$ .

$$\int_0^\pi \left[ \frac{3(\hat{s} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{s}}{r^3} \right] r^2 \sin \theta d\theta$$

$$\begin{aligned}
&= \frac{\hat{s}_z}{r} \int_0^\pi [3 \cos \theta (\vec{e}_z \cos \theta + \vec{e}_\perp \sin \theta) - \vec{e}_z] \sin \theta d\theta \\
&= \frac{\hat{s}_z}{r} \left\{ [-\cos^3 \theta + \cos \theta]_0^\pi \vec{e}_z + \left[ \frac{1}{3} \sin^3 \theta \right]_0^\pi \vec{e}_\perp \right\} = 0.
\end{aligned} \tag{2.216}$$

### Note 2

By exploiting the relations of

$$\begin{aligned}
\hat{\sigma}_x \hat{\sigma}_y &= -\hat{\sigma}_y \hat{\sigma}_x = i\hat{\sigma}_z, & \hat{\sigma}_y \hat{\sigma}_z &= -\hat{\sigma}_z \hat{\sigma}_y = i\hat{\sigma}_x, \\
\hat{\sigma}_z \hat{\sigma}_x &= -\hat{\sigma}_x \hat{\sigma}_z = i\hat{\sigma}_y, & (2.2)
\end{aligned} \tag{2.217}$$

we get

$$(\hat{s} \cdot \vec{r})^2 = \frac{1}{4} \left[ \sum_{\beta}^{x,y,z} \sigma_{\beta}^2 \beta^2 + \sum_{\beta\gamma}^{xy,yz,zx} (\sigma_{\beta} \sigma_{\gamma} + \sigma_{\gamma} \sigma_{\beta}) \beta\gamma \right] = \frac{r^2}{4}, \tag{2.27}$$

$$\tag{2.218}$$

$$\begin{aligned}
&\left\langle s, m'_s \left| \frac{\hat{s}}{r^2} - \frac{(\hat{s} \cdot \vec{r}) \vec{r}}{r^4} \right| s, m_s \right\rangle \\
&= \left\langle s, m'_s \left| \frac{\hat{s}}{r^2} - \frac{\hat{s}(\hat{s} \cdot \vec{r})^2}{s(s+1)r^4} \right| s, m_s \right\rangle \tag{a4.36} \\
&= \left\langle s, m'_s \left| \frac{2\hat{s}}{3r^2} \right| s, m_s \right\rangle \cdot \left( s = \frac{1}{2}, m'_s, m_s = \pm s \right) \tag{2.219}
\end{aligned}$$

### Note 3

Dirac delta  $\delta(x)$  is a function which satisfies the relations of  $\delta(x \neq 0) = 0$ ,  $\delta(0) = \infty$ , and  $\int \delta(x) dv = 1$ .

When  $r$  is not very small ( $> 10^{-3}$  nm),  $(E' - u(r))/2mc^2$  in the denominator of the first expression can be neglected.  $eE_r$  in the numerator is the finite force acting on the electron and its integral is the energy of the electron of  $10 \sim 10^3$  eV order which can be neglected compared with  $2mc^2 \sim 10^6$  eV of the denominator,

$$\int_{r>10^{-3}\text{nm}}^{\infty} f(r) dr \approx \frac{u(r)}{2mc^2} \ll 1,$$



and hence  $f(r)$  can be considered zero. When  $r$  approaches zero,  $E_r \propto 1/r^2$ ,  $u(r) \propto 1/r$ , and  $f(r) \rightarrow \infty$ .

$$\int_0^{\infty} f(r) dr = \left[ \frac{1}{1 + (E' - u(r))/2mc^2} \right]_0^{\infty} = 1. \quad (2.220)$$

## Appendix 4: Selections from Group Theory

### A4.1 Group

#### A4.1.1 Group

If a set of  $n$  elements  $\{A, B, C, \dots\}$   $G$  satisfies following four conditions,  $G$  is called group of order  $n$ .

- ①  $G$  is closed under a binary operation, that is, the combination of any two elements  $AB$  is also an element in  $G$ ;
- ② There exists an identity element  $E$  such that  $EA = AE$  for all  $A$ ;
- ③

$$A(BC) = (AB)C; \quad (\text{a4.1})$$

- ④ For each element  $A$  there is an invert element  $A^{-1}$  such that  $AA^{-1} = A^{-1}A = E$ .

An example: A series of integer  $\{n\}$  with plus-minus operations is a group of infinite order.

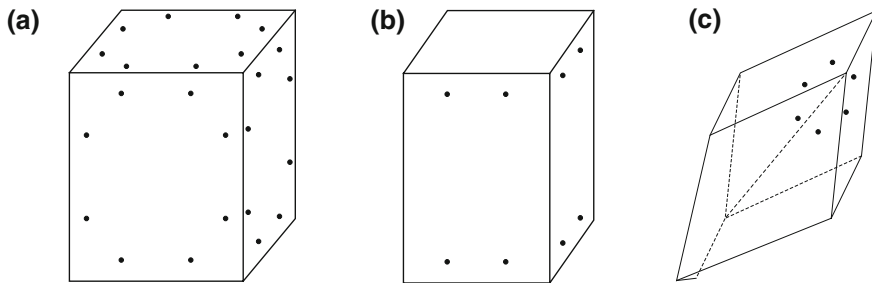
#### A4.1.2 Symmetry Group

A symmetry operation is an operation which transforms the system into a state indistinguishable from the starting state.

The group consisted of symmetry operation elements is called symmetry group.

#### A4.1.3 Rotation-Reflection Group

If a system is spherically symmetric, the operations of any angle rotation about any axis passing through the center of symmetry, reflection over any plane passing through the center, and combination of above operations do not change the system. The group consisting of these operations is called rotation-reflection group.



**Fig. a4.1** Symmetrical points of  $O_h$  (a),  $D_{4h}$  (b) and  $D_{3d}$  (c)

#### A4.1.4 Point Group

If a system is a crystal, the operations of rotation about some major crystal axes by certain angles, reflections over certain crystal planes, inversion with respect to the center, and the combinations of the above operations do not change the system. The group consisting of these operations is called point group.

Examples:

- ① A crystal of cubic symmetry does not change under the operations of rotation about any fourfold rotation axis  $\langle 100 \rangle$  by integral multiple of  $2\pi/4$ , rotation about any threefold rotation axis  $\langle 111 \rangle$  by integral multiple of  $2\pi/3$ , inversion with respect to the center, reflection on  $\{110\}$  plane, and the combinations of above operations. There are 48 such symmetry operations which constitute  $O_h$  group (sometimes tersely called  $O_h$ ).
- ② If a  $O_h$  symmetrical cubic crystal is elongated or compressed along the  $[001]$  axis, only 16 operations among the 48 operations of  $O_h$  satisfy the new symmetry which has only one fourfold rotation symmetry axis  $[001]$  ( $O_h$  has three axes of  $[100]$ ,  $[010]$ , and  $[001]$ ). The 16 operations constitute  $D_{4h}$  group.
- ③ If an  $O_h$  symmetrical cubic crystal is elongated or contracted along the  $[111]$  axis, only 12 symmetrical operations among the 48 operations of  $O_h$  satisfy the new symmetry which has only one threefold rotation symmetry axis  $[111]$  ( $O_h$  has four axes of  $[111]$ ,  $[1\bar{1}1]$ ,  $[\bar{1}11]$  and  $[\bar{1}\bar{1}1]$ ). These 12 operations constitute  $D_{3d}$  group.

Figure a4.1 demonstrates the symmetrical points of  $O_h$ ,  $D_{4h}$ , and  $D_{3d}$  obtained through symmetrical operations on a point of general position.

#### A4.1.5 Subgroup

If a part of the elements of group  $G$  constitute another group  $Q$  under the same binary operation,  $Q$  is called subgroup of group  $G$ .

Examples: Any point group is a subgroup of rotation-reflection group.  $D_{4h}$  and  $D_{3d}$  are subgroups of  $O_h$ .

## A4.2 Vector Space and Operators (Matrices)

### A4.2.1 Vector Space

A set of linearly independent  $n$  functions  $\{\psi_i\}$  ( $i = 1, 2, \dots, n$ ) constitutes  $n$ -dimensional vector (function) space  $L_n$ . Any vector  $|\alpha\rangle$  in this space is a linear combination of  $\{\psi_i\}$  which can be considered a column vector. The row vector  $\langle\alpha|$  in the dual space is the conjugate transpose (adjoint) of  $|\alpha\rangle$ . Inner product  $\langle\alpha|\beta\rangle$  satisfies the relation

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*. \quad (\text{a4.2})$$

### A4.2.2 Hermitian Adjoint

Hermitian adjoint  $\hat{\Omega}^+$  of operator  $\hat{\Omega}$  is defined by the relation

$$\langle\hat{\Omega}^+\alpha|\beta\rangle = \langle\alpha|\hat{\Omega}\beta\rangle \equiv \Omega_{\alpha\beta}. \quad (\text{a4.3})$$

It holds

$$\Omega_{\beta\alpha}^+ = \Omega_{\alpha\beta}^*, \quad \hat{\Omega}^{++} = \hat{\Omega}. \quad (\text{a4.4})$$

The matrix of operator  $\hat{\Omega}$  in the vector space  $L_n$  is

$$(\Omega) \equiv \begin{pmatrix} \Omega_{11} & \Omega_{12} & \cdots & \cdots \\ \Omega_{21} & \Omega_{22} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \Omega_{nn} \end{pmatrix},$$

$\Omega_{ij} = \langle\psi_i|\hat{\Omega}|\psi_j\rangle$ .  $(\Omega)$  is often represented by  $\hat{\Omega}$ . Equation (a4.4) shows that Hermitian adjoint matrix  $(\Omega^+)$  is the conjugate transpose of  $(\Omega)$ .

### A4.2.3 Unitary Operator (Matrix)

The operator (matrix) which satisfies the relation

$$\hat{\Omega}^+ = \hat{\Omega}^{-1} \quad (\text{a4.5})$$

is called unitary operator (matrix). It satisfies the relation

$$\langle \hat{\Omega}\alpha | \hat{\Omega}\beta \rangle = \langle \alpha | \beta \rangle. \quad (\text{a4.6})$$

Any operator (matrix) of rotation–reflection group and point group is unitary.

#### A4.2.4 Hermitian Operator (Matrix)

The operator (matrix) which satisfies the relation

$$\hat{\Omega}^+ = \hat{\Omega} \quad (\text{a4.7})$$

is called Hermitian operator (matrix). It satisfies the relation

$$\Omega_{\alpha\beta} = \Omega_{\beta\alpha}^*. \quad (\text{a4.8})$$

Arbitrary operator representing physical property is Hermitian.

The operation

$$\hat{A}^{-1} \hat{B} \hat{A} = \hat{C} \quad (\text{a4.9})$$

is called similarity transformation of  $\hat{B}$  by  $\hat{A}$ .

An Hermitian matrix  $\hat{\Omega}$  can be diagonalized by an appropriate unitary matrix  $\hat{U}$  through similarity transformation  $\hat{U}^{-1} \hat{\Omega} \hat{U}$ .

A necessary and enough condition for that two Hermitian matrices  $\hat{\Omega}_1$  and  $\hat{\Omega}_2$  can be diagonalized by a unitary matrix is they are commutable:

$$\hat{\Omega}_1 \hat{\Omega}_2 = \hat{\Omega}_2 \hat{\Omega}_1. \quad (\text{a4.10})$$

### A4.3 Representation of Group

#### A4.3.1 Representation of Group

Consider a vector space  $L_n$  constituted of functions  $\{\psi_i\}$  ( $i = 1, 2, \dots, n$ ). If the function  $\psi'_i(R)$  obtained through operation  $\hat{P}(R)$  of arbitrary element  $R$  of group  $G$  on any  $\psi_i$  is a linear combination of  $\{\psi_j\}$ , that is

$$\hat{P}(R)\psi_i = \psi'_i(R) = \sum_j^{1,2,\dots,n} \psi_j D(R)_{ji}, \quad (\text{a4.11})$$

$L_n$  is called closed under group  $G$ .

The  $n$  order matrices  $\{(D(A)), (D(B)), \dots\}$ , noted by  $(D)$ , are called representation of group  $G$  in the vector space  $L_n$ . In many cases  $(D(R))$  is also tersely denoted by  $(D)$ .  $\psi_i$  is called a basis vector (or basis function) of representation  $(D)$ .

### A4.3.2 Unitary Representation

If  $\hat{P}$  in (a4.11) is a unitary operator,  $(D)$  is unitary and is called unitary representation. The transformation of (a4.11) is called unitary transformation of the basis vector.

### A4.3.3 Equivalent and Inequivalent Representations

If a representation  $(D)$  of group  $G$  is similarity transformed by a non-singular matrix (determinant  $\neq 0$ )  $(S)$ :

$$(D') = (S)^{-1} (D) (S), \quad (\text{a4.12})$$

$(D')$  is also a representation of  $G$ .  $(D')$  and  $(D)$  are called equivalent representations. If two representations cannot be transformed each other by a similarity transformation, the two are called inequivalent representations.

## A4.4 Reduction of Representation

### A4.4.1 Reduction of Representation

Suppose there are two vector spaces  $L_m$  and  $L_n$  which are closed under group  $G$ . The dimension  $m$  of  $L_m$  is smaller than the dimension  $n$  of  $L_n$ , and all vectors in  $L_m$  are included in  $L_n$ . Then  $L_n$  is called reducible under  $G$ , and  $L_m$  is called invariant subspace of  $L_n$ . The unitary representation  $(D)$  of  $G$  in  $L_n$  can be similarity transformed to a new representation consisting of the super matrices

$$(D) = \begin{pmatrix} (D_1) & 0 \\ 0 & (D_2) \end{pmatrix}, \quad (\text{a4.13})$$

where  $(D_1)$  and  $(D_2)$  are matrices of order  $m$  and  $n - m$ . The set of the basis vectors of  $(D_1)$  and  $(D_2)$  constitutes invariant subspace  $L_m$  and  $L_{n-m}$ , respectively. Each of  $(D_1)$  and  $(D_2)$  is a unitary representation of group  $G$ . The transformation is called the reduction of  $(D)$  into direct sum of  $(D_1)$  and  $(D_2)$  which is expressed as

$$(D) = (D_1) \oplus (D_2). \quad (\text{a4.14})$$

### A4.4.2 Irreducible Representation

If after reduction we get  $(D) = (D_1) \oplus (D_2) \cdots \oplus (D_k)$  where  $k$  is the largest value of possible reduction, that is,  $(D_i)$  ( $i = 1, 2, \dots, k$ ) cannot be reduced further any

**Table a4.1** Reduction of  $D^l$  for  $O_h$ , reduction of the irreducible representations of  $O_h$  for  $D_{3d}$  and  $D_{4h}$ , and basis vectors of irreducible representations of  $O_h$  produced by  $\{Y_{lm_l}\}$  of  $D^l$ 

$D^l$	Reduction of $D^l$ for $O_h$ , and basis vectors of irreducible representations of $O_h$	Reduction of irreducible representations of $O_h$ for $D_{3d}$	Reduction of irreducible representations of $O_h$ for $D_{4h}$
$D^1$	$T_{1u}$ $Y_{11},$ $Y_{10},$ $Y_{1-1}$	$A_{2u} + E_u$	$A_{2u} + E_u$
$D^2$	$E_g$ $Y_{20},$ $(1/2)^{1/2}(Y_{22} + Y_{2-2})$	$E_g$	$A_{1g} + B_{1g}$
	$T_{2g}$ $Y_{2-1},$ $-Y_{21},$ $(1/2)^{1/2}(Y_{22} - Y_{2-2})$	$A_{1g} + E_g$	$B_{2g} + E_g$
$D^3$	$A_{2u}$ $(1/2)^{1/2}(Y_{32} - Y_{3-2})$	$A_{2u}$	$B_{1u}$
	$T_{1u}$ $-(1/8)^{1/2}(\sqrt{5}Y_{3-3} + \sqrt{3}Y_{31}),$ $Y_{30},$ $-(1/8)^{1/2}(\sqrt{5}Y_{33} + \sqrt{3}Y_{3-1})$	$A_{2u} + E_u$	$A_{2u} + E_u$
	$T_{2u}$ $-(1/8)^{1/2}(\sqrt{3}Y_{33} + \sqrt{5}Y_{3-1}),$ $-(1/8)^{1/2}(\sqrt{5}Y_{32} + \sqrt{3}Y_{3-2}),$ $-(1/8)^{1/2}(\sqrt{3}Y_{3-3} - \sqrt{5}Y_{31})$	$A_{1u} + E_u$	$B_{2u} + E_u$

more,  $(D_i)$  is called an irreducible representation. The vector space of  $(D)$  completely reduces to  $k$  invariant subspaces.

The simultaneous eigenstate of angular momentum operators  $\hat{j}^2$  and  $\hat{j}_z$   $|j, m_j\rangle$  of definite  $j$  is a basis vector of  $2j + 1$ -dimensional irreducible representation  $D^l$  of rotation-reflection group.

#### A4.4.3 Reduction of Irreducible Representation of Group for Subgroup

Among the irreducible representations  $\{(D(R))\}$  of a group, the representations for a subgroup  $(D(R_s))$  ( $\{R_s\}$ : set of elements of the subgroup) may be reducible:

$$(D(R_s)) = n_1 (D_1(R_s)) \oplus n_2 (D_2(R_s)) \oplus \dots \quad (n_i: \text{integer}) \quad (\text{a4.15})$$

Table a4.1 demonstrates reduction of the irreducible representation  $D^l$  of rotation-reflection group for its subgroup  $O_h$ , the reduction of the irreducible representations of  $O_h$  group for its subgroup  $D_{3d}$  and  $D_{4h}$ , respectively, and the basis vectors of the irreducible representation of subgroup  $O_h$  produced by the basis vectors  $\{Y_{lm_l}\}$  of  $D^l$ .

Irreducible representations  $A$ ,  $E$ , and  $T$  are one-, two-, and three-dimensional. The subscript  $g$  and  $u$  represent that the basis vector is symmetrical and antisymmetrical with respect to the inversion operation.

## A4.5 Direct Product of Two Representations

### A4.5.1 Representation of Direct Product of Two Representations

Take two-dimensional representation  $(D) = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix}$  and three-dimensional representation  $(W) = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix}$  as an example. Define the direct product of them by

$$\begin{aligned} (D) \otimes (W) &\equiv \begin{pmatrix} D_{11}(W) & D_{12}(W) \\ D_{21}(W) & D_{22}(W) \end{pmatrix} \\ &= \begin{pmatrix} D_{11}W_{11} & D_{11}W_{12} & D_{11}W_{13} & D_{12}W_{11} & D_{12}W_{12} & D_{12}W_{13} \\ D_{11}W_{21} & D_{11}W_{22} & D_{11}W_{23} & D_{12}W_{21} & D_{12}W_{22} & D_{12}W_{23} \\ D_{11}W_{31} & D_{11}W_{32} & D_{11}W_{33} & D_{12}W_{31} & D_{12}W_{32} & D_{12}W_{33} \\ D_{21}W_{11} & D_{21}W_{12} & D_{21}W_{13} & D_{22}W_{11} & D_{22}W_{12} & D_{22}W_{13} \\ D_{21}W_{21} & D_{21}W_{22} & D_{21}W_{23} & D_{22}W_{21} & D_{22}W_{22} & D_{22}W_{23} \\ D_{21}W_{31} & D_{21}W_{32} & D_{21}W_{33} & D_{22}W_{31} & D_{22}W_{32} & D_{22}W_{33} \end{pmatrix}. \end{aligned} \quad (\text{a4.16})$$

Suppose  $\{\psi_i^i\}$  and  $\{\psi_k^j\}$  are the set of basis vectors of irreducible representations  $(D^i)$  and  $(D^j)$ , respectively.  $\psi_i^i \psi_k^j$  is a basis vector of the direct product representation  $(D^i) \otimes (D^j)$  and transforms under the  $(D) = (D^i) \otimes (D^j)$  representation (a4.11).

### A4.5.2 Reduction of Representation of Direct Product of Irreducible Representations of Rotation–Reflect Group

The representation of direct product of irreducible representations  $D^L$  and  $D^S$  of rotation–reflect group completely reduces by

$$D^L \otimes D^S = D^{|L-S|} \oplus D^{|L-S|+1} \dots \oplus D^{L+S}. \quad (\text{a4.17})$$

## A4.6 Irreducible Tensor

If a set of functions or operators  $\{\hat{Q}_\kappa^\mu\}$  ( $\kappa = -\mu, -\mu + 1, \dots, \mu$ ) transforms under the  $2\mu + 1$ -dimensional irreducible representation  $D^\mu$  of rotation–reflection group by

$$\hat{P}^{-1} \hat{Q}_\kappa^\mu \hat{P} = \sum_\tau \hat{Q}_\tau^\mu D_{\tau\kappa}^\mu, \quad (\hat{P}: \text{rotation-reflection operator}) \quad (\text{a4.18})$$

the set of  $\{\hat{Q}_\kappa^\mu\}$  ( $\kappa = -\mu, -\mu + 1, \dots, \mu$ ) is called irreducible tensor of rank  $\mu$ , and  $\hat{Q}_\kappa^\mu$  is called a component of the tensor.

The set of the spherical harmonics  $\{Y_{lm_l}\}$  (and  $\{U_{m_l}^l\}$  (2.24) of definite  $l$  is an irreducible tensor of rank  $l$ . The set of the three angular momentum operators

$$\hat{j}_{\pm 1} \equiv \mp \frac{1}{\sqrt{2}} \hat{j}_\pm, \quad \hat{j}_0 \equiv \hat{j}_z \quad (\text{2.33}) \quad (\text{a4.19})$$

which has the same form with the set of  $\{U_{\pm 1}^1, U_0^1\}$  is a first-rank irreducible tensor.

#### ***A4.7 Orthogonal Theorem of the Basis Vectors of Irreducible Unitary Representation and Corresponding Matrix Element Theorems***

Assume that  $(D^{l_i})$  is a  $l_i$ -dimensional irreducible unitary representation of group  $G$  and  $\psi_m^i$  is an orthonormalized  $m^{\text{th}}$  row basis vectors of  $(D^{l_i})$ . Define that  $(D^{l_i})$  and  $(D^{l_j})$  are inequivalent if  $i \neq j$ . It holds

①

$$\langle \psi_m^i | \psi_n^j \rangle = \delta(i, j) \delta(m, n) \frac{1}{l_i} \sum_{\alpha}^{1, \dots, l_i} \langle \psi_\alpha^i | \psi_\alpha^i \rangle. \quad (\text{a4.20})$$

② If operator  $\hat{S}$  is invariant under the operation of group  $G$ ,  $\hat{S} \psi_n^i$  is also the  $n^{\text{th}}$  row basis vector of  $(D^{l_i})$ , and hence

$$\langle \psi_m^i | \hat{S} | \psi_n^j \rangle = \delta(i, j) \delta(m, n) \frac{1}{l_i} \sum_{\alpha}^{1, \dots, l_i} \langle \psi_\alpha^i | \hat{S} | \psi_\alpha^i \rangle. \quad (\text{a4.21})$$

③ If  $\hat{Q}_\kappa^\mu$  is a component of an irreducible tensor of rank  $\mu$ ,  $\hat{Q}_\kappa^\mu \psi_m^j$  is a basis vector of representation  $(D^\mu) \otimes (D^{l_j})$ . If  $(D^\mu) \otimes (D^{l_j})$  does not include  $(D^{l_i})$ ,

$$\langle \psi_m^i | \hat{Q}_\kappa^\mu | \psi_n^j \rangle = 0. \quad (\text{a4.20}) \quad (\text{a4.22})$$



## A4.8 Clebsch-Gordan and Racah Coefficients and Coupling of Irreducible Tensors

### A4.8.1 Clebsch-Gordan Coefficient

If  $\hat{j} = \hat{j}_1 + \hat{j}_2$ , the simultaneous eigenfunction  $|j, m\rangle$  of  $\hat{j}^2$  and  $\hat{j}_z$  has the following relations with the products of simultaneous eigenfunctions  $|j_1, m_1\rangle$  of  $\hat{j}_1^2$  and  $\hat{j}_{1z}$  and  $|j_2, m_2\rangle$  of  $\hat{j}_2^2$  and  $\hat{j}_{2z}$ :

$$|j, m\rangle = |j_1, j_2, j, m\rangle = \sum_{m_1, m_2} C(j_1 j_2 j; m_1 m_2 m) |j_1, m_1\rangle |j_2, m_2\rangle, \quad (\text{a4.23})$$

$$|j_1, m_1\rangle |j_2, m_2\rangle = \sum_j C(j_1 j_2 j; m_1 m_2 m) |j_1, j_2, j, m\rangle. \quad (\text{a4.24})$$

$C(j_1 j_2 j; m_1 m_2 m)$  is called Clebsch-Gordan coefficient. It is a real function of the quantum numbers in the parenthesis. If  $m_1 + m_2 \neq m$ ,  $C(j_1 j_2 j; m_1 m_2 m) = 0$ , so  $C(j_1 j_2 j; m_1 m_2 m)$  in many cases are also formulated as  $C(j_1 j_2 j; m_1, m - m_1)$  by omitting  $m$ . They are orthonormal:

$$\sum_{m_1, m_2} C(j_1 j_2 j; m_1 m_2 m) C(j_1 j_2 j'; m_1 m_2 m') = \delta(j, j') \delta(m, m'), \quad (\text{a4.25})$$

$$\sum_j C(j_1 j_2 j; m_1, m - m_1) C(j_1 j_2 j; m'_1, m - m'_1) = \delta(m_1, m'_1), \quad (\text{a4.26})$$

and has some symmetrical relations such as

$$C(j_1 j_2 j; m_1 m_2 m) = (-1)^{j_1 + j_2 - j} C(j_2 j_1 j; m_2 m_1 m). \quad (\text{a4.27})$$

### A4.8.2 Construction of an Irreducible Tensor from Two Irreducible Tensors

A linear combination of the product  $\hat{T}_{M_1}^{L_1}(A_1) \hat{T}_{M_2}^{L_2}(A_2)$  of the components of irreducible tensors  $\{\hat{T}_{M_1}^{L_1}(A_1)\}$  and  $\{\hat{T}_{M_2}^{L_2}(A_2)\}$  generates irreducible tensor  $\{\hat{T}_M^L(A_1, A_2)\}$  ( $A_i$  represents the space of the variable (A4.8.3)) as below:

$$\begin{aligned} \hat{T}_M^L(A_1, A_2) &= \sum_{M_1, M_2} C(L_1 L_2 L; M_1, M_2, M) \hat{T}_{M_1}^{L_1}(A_1) \hat{T}_{M_2}^{L_2}(A_2) \\ &= \sum_{M_1} C(L_1 L_2 L; M_1, M - M_1) \hat{T}_{M_1}^{L_1}(A_1) \hat{T}_{M - M_1}^{L_2}(A_2). \end{aligned} \quad (\text{a4.28})$$

### A4.8.3 Scalar Product of Two Irreducible Tensors

The scalar product of irreducible tensors  $\hat{T}^{L_1}(A_1) (\equiv \{\hat{T}_{M_1}^{L_1}(A_1)\})$  and  $\hat{T}^{L_1}(A_2)$  is defined by and equals to

$$\begin{aligned}\hat{T}^{L_1}(A_1) \cdot \hat{T}^{L_1}(A_2) &\equiv \sum_M (-1)^M \hat{T}_M^{L_1}(A_1) \hat{T}_{-M}^{L_1}(A_2) \\ &= (-1)^{L_1} \sqrt{2L_1 + 1} \hat{T}_0^{L_1}(A_1, A_2).\end{aligned}\quad (\text{a4.29})$$

If  $L_1 = 1$ , it equals to the scalar product of two vectors. Examples: If  $\{\hat{T}_M^1(A_1)\} = (\hat{L}_0, \hat{L}_{\pm 1})$  and  $\{\hat{T}_M^1(A_2)\} = (\hat{S}_0, \hat{S}_{\pm 1})$ ,  $\hat{T}^1(A_1) \cdot \hat{T}^1(A_2) = \hat{L} \cdot \hat{S}$ . If  $\{\hat{T}_M^1(A_1)\} = \{\hat{T}_M^1(A_2)\} = (rU_0^1 = z, rU_{\pm 1}^1 = \mp(x \pm iy)/\sqrt{2}), \hat{T}^1(A_1) \cdot \hat{T}^1(A_2) = \vec{r} \cdot \vec{r} = r^2$ .

### A4.8.4 Racah Coefficient

Consider the addition of three angular momenta

$$\hat{j} = \hat{j}_1 + \hat{j}_2 + \hat{j}_3. \quad (\text{a4.30})$$

One kind of representation in which  $\hat{j}^2$  and  $\hat{j}_z$  are diagonal can be obtained by first coupling  $\hat{j}_1$  and  $\hat{j}_2$  into intermediate angular momentum  $\hat{j}_{12} = \hat{j}_1 + \hat{j}_2$  and then coupling it with  $\hat{j}_3$  into  $\hat{j}$ . In this case the six operators  $\hat{j}_1^2, \hat{j}_2^2, \hat{j}_3^2, \hat{j}_{12}^2, \hat{j}^2$ , and  $\hat{j}_z$  can be diagonalized simultaneously. Another kind of representation is first couple  $\hat{j}_2$  and  $\hat{j}_3$  into  $\hat{j}_{23} = \hat{j}_2 + \hat{j}_3$  and then couple  $\hat{j}_{23}$  with  $\hat{j}_1$  into  $\hat{j}$ . In this case  $\hat{j}_1^2, \hat{j}_2^2, \hat{j}_3^2, \hat{j}_{23}^2, \hat{j}^2$ , and  $\hat{j}_z$  can be diagonalized simultaneously. The simultaneous eigenfunction of  $\hat{j}^2$  and  $\hat{j}_z$  obtained by the above two couplings are

$$|j_3, j_{12}, j, m\rangle = \sum_{m_3, m_{12}} C(j_3 j_{12} j; m_3 m_{12} m) |j_3, m_3\rangle |j_1, j_2, j_{12}, m_{12}\rangle, \quad (\text{a4.31})$$

$$|j_1, j_{23}, j, m\rangle = \sum_{m_1, m_{23}} C(j_1 j_{23} j; m_1 m_{23} m) |j_1, m_1\rangle |j_2, j_3, j_{23}, m_{23}\rangle. \quad (\text{a4.32})$$

The states  $|j_3, j_{12}, j, m\rangle$  and  $|j_1, j_{23}, j, m\rangle$  are related with each other through the unitary transformation

$$|j_3, j_{12}, j, m\rangle = \sum_{j_{23}} R_{j_{23} j_{12}} |j_1, j_{23}, j, m\rangle. \quad (\text{a4.33})$$

$$W(j_1 j_2 j j_3; j_{12} j_{23}) \equiv \frac{R_{j_{23} j_{12}}}{\sqrt{(2j_{12} + 1)(2j_{23} + 1)}} \quad (\text{a4.34})$$

is called Racah coefficient. It is a function of the six quantum numbers of the angular momenta in the parenthesis of the left of above equation.

## A4.9 Matrix Element Theorems of Irreducible Tensor

### A4.9.1 Matrix Element Theorems of Irreducible Tensor

Suppose  $\hat{T}_M^L$  is a component of an irreducible tensor.

$$\textcircled{1} \quad \langle j', m' | \hat{T}_M^L | j, m \rangle = C(j L j'; m M m') \langle j' | \hat{T}^L | j \rangle. \quad (\text{a4.35})$$

$\langle j' | \hat{T}^L | j \rangle$  is a function of  $j'$ ,  $L$ , and  $j$  and does not depend on the magnetic quantum numbers  $m$ ,  $M$ , and  $m'$ . Such kind of function characterized by the pair of symbol  $\|$  is called reduced matrix element.

$$\textcircled{2} \quad \langle j, m' | \hat{T}_M^1 | j, m \rangle = \frac{\langle j, m' | \hat{j}_M (\hat{j} \cdot \hat{T}^1) | j, m \rangle}{j(j+1)}. \quad (\text{a4.36})$$

$$\textcircled{3} \quad \langle j', m' | \hat{j}_M (\hat{j} \cdot \hat{T}^1) | j, m \rangle = \langle j', m' | \hat{j}_M | j, m \rangle \langle j | \hat{j} \cdot \hat{T}^1 | j \rangle \delta(j', j). \quad (\text{a4.37})$$

$$\begin{aligned} \textcircled{4} \quad & \langle j'_1, j'_2, j', m' | \hat{T}^L(1) \cdot \hat{T}^L(2) | j_1, j_2, j, m \rangle \\ &= C(j 0 j'; m 0 m') \langle j'_1 j'_2 j' | \hat{T}^L(1) \cdot \hat{T}^L(2) | j_1 j_2 j \rangle \\ &= \delta(m', m) \delta(j', j) \langle j'_1 j'_2 j' | \hat{T}^L(1) \cdot \hat{T}^L(2) | j_1 j_2 j \rangle \\ &= \delta(m', m) \delta(j', j) (-1)^{j'_1 + j_2 - j} W(j_1 j_2 j'_1 j'_2; j L) \\ &\quad \times \sqrt{(2j'_1 + 1)(2j'_2 + 1)} \langle j'_1 | \hat{T}^L(1) | j_1 \rangle \langle j'_2 | \hat{T}^L(2) | j_2 \rangle, \end{aligned} \quad (\text{a4.38})$$

where  $\hat{j} = \hat{j}_1 + \hat{j}_2$ ,  $\hat{j}' = \hat{j}'_1 + \hat{j}'_2$ ;  $\hat{T}^L(1)$ ,  $\hat{j}_1$ , and  $\hat{j}'_1$  belong to the same space (such as position space), and  $\hat{T}^L(2)$ ,  $\hat{j}_2$ , and  $\hat{j}'_2$  to the same space (such as spin space).

$$\begin{aligned} \textcircled{5} \quad & \langle j'_1, j'_2, j', m' | T_M^L(1) | j_1, j_2, j, m \rangle \\ &= C(j L j'; m M m') \langle j'_1 j'_2 j' | T_M^L(1) | j_1 j_2 j \rangle \end{aligned}$$

**Table a4.2**  $U_{m_l}^l$  and  $\tilde{O}_{lm_l}$  for  $l = 1, 2, 3$  [4]

$l, m_l$	$U_{m_l}^l$	$\tilde{O}_{lm_l}(X = J(J+1))$
1, 0	$\cos \theta$	$\hat{J}_z$
1, $\pm 1$	$\mp \sqrt{\frac{1}{2}} \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2}} \hat{J}_{\pm}$
2, 0	$\frac{1}{2}(3 \cos^2 \theta - 1)$	$\frac{1}{2}(3\hat{J}_z^2 - X)$
2, $\pm 1$	$\mp \sqrt{\frac{3}{2}} \cos \theta \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{3}{2}} \frac{1}{2}(\hat{J}_z \hat{J}_{\pm} + \hat{J}_{\pm} \hat{J}_z)$
2, $\pm 2$	$\sqrt{\frac{3}{8}} \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{3}{8}} \hat{J}_{\pm}^2$
3, 0	$\frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta)$	$\frac{1}{2}[5\hat{J}_z^3 - 3(X - 1)\hat{J}_z]$
3, $\pm 1$	$\mp \sqrt{\frac{3}{16}}(5 \cos^2 \theta - 1) \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{3}{16}} \frac{1}{2} \left[ (5\hat{J}_z^2 - X - \frac{1}{2}) \hat{J}_{\pm} + \hat{J}_{\pm} (5\hat{J}_z^2 - X - \frac{1}{2}) \right]$
3, $\pm 2$	$\sqrt{\frac{15}{8}} \cos \theta \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{15}{8}} \frac{1}{2} (\hat{J}_z \hat{J}_{\pm}^2 + \hat{J}_{\pm}^2 \hat{J}_z)$
3, $\pm 3$	$\mp \sqrt{\frac{5}{16}} \sin^3 \theta \exp(\pm i3\phi)$	$\mp \sqrt{\frac{15}{8}} \hat{J}_{\pm}^3$

$$\begin{aligned}
&= C(jLj'; m M m')(-1)^{j_2+L-j_1-j'} \\
&\quad \times \delta(j'_2, j_2) \sqrt{(2j'_1+1)(2j+1)} W(j_1 j j'_1 j'; j_2 L) \langle j'_1 \| \hat{T}^L \| j_1 \rangle. \quad (\text{a4.39})
\end{aligned}$$

#### A4.9.2 Racah Operator Equivalent and Stevens Coefficient

$$\langle J, M_{J'} | U_{m_l}^l(i) | J, M_J \rangle = \langle J, M'_J | \tilde{O}_{lm_l} | J, M_J \rangle \langle J \| U^l \| J \rangle, \quad (2.24) \quad (\text{a4.40})$$

where  $\tilde{O}_{lm_l}$  is the operator consisting of the angular momentum operators  $\hat{J}_{\alpha}$  ( $\alpha = z, \pm$ , (2.33)), which is called Racah operator equivalent. The relations of  $\tilde{O}_{lm_l}$  with  $\hat{J}_{\alpha}$  are listed in Table a4.2.

For the case of  $|J, M_J\rangle$  is a state of the ground term  $|3d^n, L, M_L\rangle$  for a 3d ion or the state of the ground multiplet  $|4d^n, L, S, J, M_J\rangle$  for a 4f ion,

$$\theta_l = n \langle J \| U^l \| J \rangle \quad (\text{a4.41})$$

is called  $l^{\text{th}}$  order Stevens coefficient. The values of  $\alpha_J \equiv \theta_2$  for trivalent 4f ions are listed in Table 5.2.

## Appendix 5: Second Quantized Representation of Operators

### A5.1 Occupation Number Representation and Creation, Annihilation, and Number Operators

Let  $\{\psi_a = |a\rangle\}$  ( $a = \alpha_1, \alpha_2, \dots, \alpha, \dots, \beta_1, \beta_2, \dots, \beta, \dots, \gamma_1, \gamma_2, \dots, \gamma, \dots$ ) represent a complete orthonormal set of single-electron functions. The wave function of  $N$  electrons occupying the states of  $\alpha, \beta, \dots, \gamma, \dots$  is formulated by the Slater determinant

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \dots & \psi_\gamma(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(i) & \psi_\beta(i) & \dots & \psi_\gamma(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(N) & \psi_\beta(N) & \dots & \psi_\gamma(N) & \dots \end{vmatrix}. \quad (\text{a5.1})$$

The state can also be formulated by the following occupation number representation

$$\begin{aligned} \Psi &= |\alpha, \beta, \dots, \gamma, \dots\rangle \\ &\equiv \begin{array}{cccccccccccccccc} 0, & 0, & \bullet\bullet\bullet\bullet, & 1, & 0, & 0, & \bullet\bullet\bullet, & 1, & 0, & 0, & \bullet\bullet\bullet, & 1, & \bullet\bullet\bullet \end{array} \\ &\quad \begin{array}{cccccccccccccccc} \uparrow & \uparrow & & \uparrow\downarrow & \uparrow & & \uparrow\downarrow & \uparrow\downarrow & \uparrow & & \uparrow\downarrow & \uparrow & & \uparrow \end{array} \\ &\quad |\alpha_1, \alpha_2, \bullet\bullet\bullet\bullet, \alpha, \beta_1, \beta_2, \bullet\bullet\bullet, \beta, \gamma_1, \gamma_1, \bullet\bullet\bullet, \gamma, \bullet\bullet\bullet \rangle \end{aligned} \quad (\text{a5.2})$$

Here the ket vector  $|\alpha, \beta, \dots, \gamma, \dots\rangle$  is the state that the  $\alpha, \beta, \dots, \gamma, \dots$  single-electron states which appear within the  $|\rangle$  are occupied while the other states that do not appear are void as shown explicitly by the arrows in the last expression. Let

$$|\alpha, \beta, \gamma, \dots\rangle \equiv \hat{a}_\alpha^+ \hat{a}_\beta^+ \hat{a}_\gamma^+ \dots |\rangle \quad (\text{a5.3})$$

where

$$|\rangle \equiv |0, 0, \dots\rangle \quad (\text{a5.4})$$

represents the state in which all  $\{\psi_a = |a\rangle\}$  states are void. Equation (a5.3) shows that  $\hat{a}_\alpha^+$  is the operator which creates an electron in the  $\alpha$  state, so it is called creation operator.  $\Psi$  being antisymmetrical it holds

$$|\alpha, \beta, \dots, \gamma, \dots\rangle = -|\beta, \alpha, \dots, \gamma, \dots\rangle, \quad (\text{a5.5})$$

i.e.,

$$\hat{a}_\alpha^+ \hat{a}_\beta^+ |\dots, \gamma, \dots\rangle + \hat{a}_\beta^+ \hat{a}_\alpha^+ |\dots, \gamma, \dots\rangle = 0. \quad (\text{a5.6})$$

thus,

$$\hat{a}_\alpha^+ \hat{a}_\beta^+ + \hat{a}_\beta^+ \hat{a}_\alpha^+ = 0, \quad (\text{a5.7})$$

$$\hat{a}_\alpha^+ \hat{a}_\alpha^+ = 0. \quad (\text{a5.8})$$

$$\hat{a}_\alpha^+ \hat{a}_\alpha^+ |\gamma, \dots\rangle = |\alpha, \alpha, \gamma, \dots\rangle = 0 \quad (\text{a5.9})$$

expresses the Pauli exclusion principle.

The bra vector and counterparts of the creation operators in (a5.3) are

$$\langle \dots, \gamma, \beta, \alpha | = \langle \dots | \hat{a}_\gamma \hat{a}_\beta \hat{a}_\alpha. \quad (\text{a5.10})$$

From the analyses similar to (a5.5)–(a5.8) we get

$$\hat{a}_\alpha \hat{a}_\beta + \hat{a}_\beta \hat{a}_\alpha = 0, \quad (\text{a5.11})$$

$$\hat{a}_\alpha \hat{a}_\alpha = 0. \quad (\text{a5.12})$$

From the normal condition of

$$\langle \dots, \beta, \alpha | \alpha, \beta, \dots \rangle = \langle \dots, \beta | \hat{a}_\alpha \hat{a}_\alpha^+ | \beta, \dots \rangle = \langle \dots, \beta | \beta, \dots \rangle \quad (\text{a5.13})$$

we get

$$\hat{a}_\alpha \hat{a}_\alpha^+ | \beta, \dots \rangle = \hat{a}_\alpha | \alpha, \beta, \dots \rangle = | \beta, \dots \rangle. \quad (\text{a5.14})$$

Equation (a5.14) shows that the action of  $\hat{a}_\alpha$  on a ket vector is to eliminate an electron in the  $\alpha$  state, so it is called annihilation operator. The actions of  $\hat{a}_\alpha^+$  and  $\hat{a}_\alpha$  on arbitrary state are

$$\begin{aligned} & \hat{a}_\alpha^+ | 1, 2, \dots, \alpha - 1, n_\alpha, \alpha + 1, \dots \rangle \\ & (n_\alpha = 1 \text{ or } 0 \text{ represents } \alpha \text{ state is occupied or void}) \\ & = | \alpha, 1, 2, \dots, \alpha - 1, n_\alpha, \alpha + 1, \dots \rangle \\ & = (-1)^{\alpha-1} | 1, 2, \dots, \alpha - 1, \alpha, \alpha + 1, \dots \rangle \delta(n_\alpha, 0), \end{aligned} \quad (\text{a5.15})$$

$$\begin{aligned} & \hat{a}_\alpha | 1, 2, \dots, \alpha - 1, n_\alpha, \alpha + 1, \dots \rangle \\ & = (-1)^{\alpha-1} \hat{a}_\alpha | n_\alpha, 1, 2, \dots, \alpha - 1, \alpha + 1, \dots \rangle \\ & = (-1)^{\alpha-1} | 1, 2, \dots, \alpha - 1, \alpha + 1, \dots \rangle \delta(n_\alpha, 1). \end{aligned} \quad (\text{a5.16})$$

It is easily deduced from the above relations that

$$\hat{a}_\alpha^+ \hat{a}_\beta + \hat{a}_\beta \hat{a}_\alpha^+ = \delta(\alpha, \beta), \quad (\text{Sect. 2.1.1}) \quad (\text{a5.17})$$

$$\hat{a}_\alpha^+ \hat{a}_\alpha = \hat{n}_\alpha. \quad (\text{a5.18})$$

$\hat{n}_\alpha$  is the number operator of the  $\alpha$  state eigenvalue of which is  $n_\alpha$ .

### A5.2 Second Quantized Representation of One-Particle Hamiltonian

The values of matrix elements  $\langle \Psi' | \hat{H}_1 | \Psi \rangle$  of one-particle Hamiltonian

$$\hat{H}_1(1, 2, \dots, N) = \sum_i^{1, \dots, N} \hat{h}(i) \quad (\text{a5.19})$$

calculated by using ordinary representation are as follows.

① If  $\Psi' = \Psi$ ,

$$\begin{aligned} \langle \Psi | \hat{H}_1 | \Psi \rangle &= \sum_i^{1, \dots, N} \langle \dots, \gamma, \dots, \beta, \alpha | \hat{h}(i) | \alpha, \beta, \dots, \gamma, \dots \rangle \\ &= \frac{1}{N!} N \int \begin{vmatrix} \psi_\alpha^+(1) & \psi_\beta^+(1) & \dots & \psi_\gamma^+(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(i) & \psi_\beta^+(i) & \dots & \psi_\gamma^+(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(N) & \psi_\beta^+(N) & \dots & \psi_\gamma^+(N) & \dots \end{vmatrix} \hat{h}(1) \\ &\quad \times \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \dots & \psi_\gamma(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(i) & \psi_\beta(i) & \dots & \psi_\gamma(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(N) & \psi_\beta(N) & \dots & \psi_\gamma(N) & \dots \end{vmatrix} dv_1 dv_2 \dots dv_i \dots dv_N \\ &= \sum_{\mu}^{\alpha, \beta, \dots, \gamma, \dots} h_{\mu\mu}, \end{aligned} \quad (\text{a5.20})$$

$$h_{\mu\nu} \equiv \int \psi_\mu^+(i) \hat{h}(i) \psi_\nu(i) dv_i \equiv \langle \mu | \hat{h} | \nu \rangle. \quad (\text{a5.21})$$

② If one-electron state of  $\Psi'$  is different from that of  $\Psi$ ,

$$\begin{aligned} \langle \Psi' | \hat{H}_1 | \Psi \rangle &= \sum_i^{1, \dots, N} \langle \dots, \gamma', \dots, \beta, \alpha | \hat{h}(i) | \alpha, \beta, \dots, \gamma, \dots \rangle \quad (\gamma' \neq \gamma) \\ &= \frac{N}{N!} \int \begin{vmatrix} \psi_\alpha^+(1) & \psi_\beta^+(1) & \dots & \psi_{\gamma'}^+(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(i) & \psi_\beta^+(i) & \dots & \psi_{\gamma'}^+(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(N) & \psi_\beta^+(N) & \dots & \psi_{\gamma'}^+(N) & \dots \end{vmatrix} \hat{h}(1) \end{aligned}$$

$$\times \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \cdots & \psi_\gamma(1) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_\alpha(i) & \psi_\beta(i) & \cdots & \psi_\gamma(i) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_\alpha(N) & \psi_\beta(N) & \cdots & \psi_\gamma(N) & \cdots \end{vmatrix} dv_1 dv_2 \cdots dv_i \cdots dv_N = h_{\gamma'\gamma}. \quad (\text{a5.22})$$

③ If two or more electron states of  $\Psi'$  are different from those of  $\Psi$ ,

$$\langle \Psi' | \hat{H}_1 | \Psi \rangle = 0. \quad (\text{a5.23})$$

The operator in second quantization form is given by

$$\hat{H}_1 = \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu. \quad (\mu, \nu = \alpha_1, \alpha_2, \dots, \alpha, \dots, \beta_1, \beta_2, \dots, \beta, \dots, \gamma_1, \gamma_2, \dots, \gamma, \dots) \quad (\text{a5.24})$$

By substituting this operator for operator of (a5.19) and the occupation representations for the Slater determinants  $\Psi'$  and  $\Psi$ , the same values of the matrix elements of (a5.20), (a5.22), and (a5.23) can be obtained much easily as below.

①

$$\begin{aligned} & \left\langle \dots, \gamma, \dots, \beta, \alpha \left| \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle \\ &= \left\langle \dots, \gamma, \dots, \beta, \alpha \left| \sum_{\mu} h_{\mu\mu} \hat{a}_\mu^+ \hat{a}_\mu \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle = \sum_{\mu}^{\alpha, \beta, \dots, \gamma, \dots} h_{\mu\mu}, \end{aligned} \quad (\text{a5.25})$$

②

$$\left\langle \dots, \gamma', \dots, \beta, \alpha \left| \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle = h_{\gamma'\gamma}, \quad (\gamma' \neq \gamma) \quad (\text{a5.26})$$

③

$$\begin{aligned} & \left\langle \dots, \delta', \dots, \gamma', \dots, \beta, \alpha \left| \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle = 0. \\ & (\gamma' \neq \gamma \neq \delta \neq \delta') \end{aligned} \quad (\text{a5.27})$$



### A5.3 Second Quantized Representation of Two-Particle Hamiltonian

The values of matrix elements  $\langle \Psi' | \hat{H}_2 | \Psi \rangle$  of two-particle Hamiltonian

$$\hat{H}_2 = \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \hat{g}(i, j) \quad (\text{a5.28})$$

calculated by using ordinary representation are as follows.

① If  $\Psi' = \Psi$ ,

$$\begin{aligned} \langle \Psi | \hat{H}_2 | \Psi \rangle &= \left\langle \dots, \delta, \dots, \gamma, \dots, \beta, \alpha \left| \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \hat{g}(i, j) \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\ &= \frac{1}{2N!} N(N-1) \int \begin{vmatrix} \psi_\alpha^+(1) & \psi_\beta^+(1) & \dots & \psi_\gamma^+(1) & \dots & \psi_\delta^+(1) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(i) & \psi_\beta^+(i) & \dots & \psi_\gamma^+(i) & \dots & \psi_\delta^+(i) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(N) & \psi_\beta^+(N) & \dots & \psi_\gamma^+(N) & \dots & \psi_\delta^+(N) & \dots \end{vmatrix} \\ &\quad \times \hat{g}(1, 2) \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \dots & \psi_\gamma(1) & \dots & \psi_\delta(1) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(i) & \psi_\beta(i) & \dots & \psi_\gamma(i) & \dots & \psi_\delta(i) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(N) & \psi_\beta(N) & \dots & \psi_\gamma(N) & \dots & \psi_\delta(N) & \dots \end{vmatrix} dv_1 dv_2 \dots dv_i \dots dv_N \\ &= \frac{1}{2} \sum_v^{>\mu} \sum_\mu^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots} \int \begin{vmatrix} \psi_\mu^+(1) & \psi_v^+(1) \\ \psi_\mu^+(2) & \psi_v^+(2) \end{vmatrix} \hat{g}(1, 2) \begin{vmatrix} \psi_\mu(1) & \psi_v(1) \\ \psi_\mu(2) & \psi_v(2) \end{vmatrix} dv_1 dv_2 \\ &= \frac{1}{2} \sum_v^{>\mu} \sum_\mu^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots} (g_{\mu v v \mu} - g_{\mu v \mu v} + g_{v \mu \mu v} - g_{v \mu v \mu}) \\ &= \frac{1}{2} \sum_{\mu, v}^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots; \mu \neq v} (g_{\mu v v \mu} - g_{\mu v \mu v}), \quad (\text{a5.29}) \end{aligned}$$

$$g_{\mu v \gamma \delta} \equiv \int \psi_\mu^+(1) \psi_v^+(2) \hat{g}(1, 2) \psi_\gamma(2) \psi_\delta(1) dv_1 dv_2. \quad (\text{a5.30})$$

② If one-electron state of  $\Psi'$  is different from that of  $\Psi$ ,

$$\left\langle \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \hat{g}(i, j) \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle \quad (\gamma' \neq \gamma)$$

$$\begin{aligned}
&= \frac{1}{2} \sum_{\mu}^{1, \dots, N; \neq (\gamma', \gamma)} \int \left| \begin{array}{cc} \psi_{\gamma'}^+(1) & \psi_{\mu}^+(1) \\ \psi_{\gamma'}^+(2) & \psi_{\mu}^+(2) \end{array} \right| \hat{g}(1, 2) \left| \begin{array}{cc} \psi_{\gamma}(1) & \psi_{\mu}(1) \\ \psi_{\gamma}(2) & \psi_{\mu}(2) \end{array} \right| dv_1 dv_2 \\
&= \frac{1}{2} \sum_{\mu}^{\alpha, \beta, \dots, \delta, \dots; \neq (\gamma', \gamma)} (g_{\gamma' \mu \mu \gamma} - g_{\gamma' \mu \gamma \mu} + g_{\mu \gamma' \gamma \mu} - g_{\mu \gamma' \mu \gamma}). \quad (\text{a5.31})
\end{aligned}$$

③ If two electron states of  $\Psi'$  are different from those of  $\Psi$ ,

$$\begin{aligned}
&\left\langle \dots, \delta', \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{i, j}^{1, \dots, N; j \neq i} \hat{g}(i, j) \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
&\quad (\gamma' \neq \gamma \neq \delta \neq \delta') \\
&= \frac{1}{2} \int \left| \begin{array}{cc} \psi_{\gamma'}^+(1) & \psi_{\delta'}^+(1) \\ \psi_{\gamma'}^+(2) & \psi_{\delta'}^+(2) \end{array} \right| \hat{g}(1, 2) \left| \begin{array}{cc} \psi_{\gamma}(1) & \psi_{\delta}(1) \\ \psi_{\gamma}(2) & \psi_{\delta}(2) \end{array} \right| dv_1 dv_2 \\
&= \frac{1}{2} (g_{\gamma' \delta' \delta \gamma} - g_{\gamma' \delta' \gamma \delta} + g_{\delta' \gamma' \gamma \delta} - g_{\delta' \gamma' \delta \gamma}). \quad (\text{a5.32})
\end{aligned}$$

④ If more than two electron states of  $\Psi'$  are different from those of  $\Psi$ ,

$$\langle \Psi' | \hat{H}_2 | \Psi \rangle = 0. \quad (\text{a5.33})$$

The operator in second quantization form is given by

$$\begin{aligned}
\hat{H}_2 &= \frac{1}{2} \sum_{\mu, v, \gamma, \delta} g_{\mu v \gamma \delta} \hat{a}_{\mu}^+ \hat{a}_v^+ \hat{a}_{\gamma} \hat{a}_{\delta}. \\
&(\mu, v, \gamma, \delta = \alpha_1, \alpha_2, \dots, \alpha, \beta_1, \beta_2, \dots, \beta, \dots, \gamma_1, \gamma_2, \dots, \gamma, \dots) \quad (\text{a5.34})
\end{aligned}$$

The same results of the last formulations in (a5.29), (a5.31)–(a5.33) can be obtained much easily by use of this operator as below.

①

$$\begin{aligned}
&\left\langle \dots, \delta, \dots, \gamma, \dots, \beta, \alpha \left| \frac{1}{2} \sum_{\mu, v, \gamma, \delta} g_{\mu v \gamma \delta} \hat{a}_{\mu}^+ \hat{a}_v^+ \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
&= \frac{1}{2} \sum_v^{> \mu} \sum_{\mu}^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots} (g_{\mu v v \mu} - g_{\mu v \mu v} + g_{v \mu \mu v} - g_{v \mu v \mu}) \\
&= \frac{1}{2} \sum_{\mu, v}^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots; \mu \neq v} (g_{\mu v v \mu} - g_{\mu v \mu v}), \quad (\text{a5.35})
\end{aligned}$$

②

$$\begin{aligned}
& \left\langle \dots, \delta, \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\lambda\delta} \hat{a}_{\mu}^{+} \hat{a}_{\nu}^{+} \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
& \quad (\gamma' \neq \gamma) \\
& = \frac{1}{2} \sum_{\mu}^{\alpha, \beta, \dots, \delta, \dots; \neq (\gamma', \gamma)} (g_{\gamma'\mu\mu\gamma} - g_{\gamma'\mu\gamma\mu} + g_{\mu\gamma'\gamma\mu} - g_{\mu\gamma'\mu\gamma}), \quad (\text{a5.36})
\end{aligned}$$

③

$$\begin{aligned}
& \left\langle \dots, \delta', \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\lambda\delta} \hat{a}_{\mu}^{+} \hat{a}_{\nu}^{+} \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
& \quad (\gamma' \neq \gamma \neq \delta \neq \delta') \\
& = \frac{1}{2} (g_{\gamma'\delta'\delta\gamma} - g_{\gamma'\delta'\gamma\delta} + g_{\delta'\gamma'\gamma\delta} - g_{\delta'\gamma'\delta\gamma}), \quad (\text{a5.37})
\end{aligned}$$

④

$$\begin{aligned}
& \left\langle \dots, \delta', \dots, \gamma', \dots, \beta', \alpha \left| \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\lambda\delta} \hat{a}_{\mu}^{+} \hat{a}_{\nu}^{+} \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle = 0. \\
& \quad (\beta \neq \beta' \neq \gamma' \neq \gamma \neq \delta \neq \delta') \quad (\text{a5.38})
\end{aligned}$$

#### A5.4 Relations Between Creation and Annihilation Operators of Spin-Down and Spin-Up Electrons with Spin Operators

The following equivalent relations hold between the creation and annihilation operators of spin-up and down  $\{\hat{a}_{\pm}^{+}, \hat{a}_{\pm}\}$  and the spin operators  $\{\hat{s}_{\pm}, \hat{s}_z\}$ .

$$\hat{a}_{+}^{+} \hat{a}_{-} = \hat{s}_{+}, \quad (\hat{s}_{\pm} \equiv \hat{s}_x \pm i\hat{s}_y) \quad (\text{2.33}) \quad (\text{a5.39})$$

$$\hat{a}_{-}^{+} \hat{a}_{+} = \hat{s}_{-}, \quad (\text{a5.40})$$

$$\hat{a}_{+}^{+} \hat{a}_{+} - \hat{a}_{-}^{+} \hat{a}_{-} = \hat{n}_{+} - \hat{n}_{-} = 2\hat{s}_z. \quad (\text{a5.41})$$

In fact, representing  $\chi_{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ ,  $\chi_{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$  ((2.5) and (2.6)) and  $\begin{pmatrix} 0 \\ 0 \end{pmatrix}$  by  $|1, 0\rangle$ ,  $|0, 1\rangle$  and  $|0, 0\rangle = 0$ , respectively, and by using the relations of  $\hat{s}_{+} = \hat{s}_x + i\hat{s}_y =$

$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ ,  $\hat{s}_- = \hat{s}_x - i\hat{s}_y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$ , and  $\hat{s}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$  ((2.27), (2.2)) we get

$$\hat{s}_+|1, 0\rangle = |0, 0\rangle, \quad \hat{a}_+^+ \hat{a}_-|1, 0\rangle = |0, 0\rangle; \quad (\text{a5.42})$$

$$\hat{s}_+|0, 1\rangle = |1, 0\rangle, \quad \hat{a}_+^+ \hat{a}_-|0, 1\rangle = |1, 0\rangle; \quad (\text{a5.43})$$

$$\hat{s}_-|1, 0\rangle = |0, 1\rangle, \quad \hat{a}_-^+ \hat{a}_+|1, 0\rangle = |0, 1\rangle; \quad (\text{a5.44})$$

$$\hat{s}_-|0, 1\rangle = |0, 0\rangle, \quad \hat{a}_-^+ \hat{a}_+|0, 1\rangle = |0, 0\rangle; \quad (\text{a5.45})$$

$$2\hat{s}_z|1, 0\rangle = |1, 0\rangle, \quad (\hat{a}_+^+ \hat{a}_+ - \hat{a}_-^+ \hat{a}_-)|1, 0\rangle = |1, 0\rangle; \quad (\text{a5.46})$$

$$2\hat{s}_z|0, 1\rangle = -|0, 1\rangle, \quad (\hat{a}_+^+ \hat{a}_+ - \hat{a}_-^+ \hat{a}_-)|0, 1\rangle = -|0, 1\rangle. \quad (\text{a5.47})$$

## Appendix 6: Perturbation Theory

Suppose the solution of the Schrödinger equation

$$\hat{H}_0|\psi\rangle = \varepsilon|\psi\rangle \quad (\text{a6.1})$$

is known.  $\{|j\rangle\}$  ( $j$ : Arabic,  $= 1, 2, \dots, n$ ) and  $\varepsilon_0$  are the ground eigenstates and eigenenergy, and  $\{|\mu\rangle\}$ , ( $\mu$ : Greek) and  $\{\varepsilon_\mu\}$  are the excited eigenstates and eigenenergies.

$\hat{H}'(\ll \hat{H}_0)$  is the perturbation. The Schrödinger equation

$$(\hat{H}_0 + \hat{H}')|\psi'\rangle = \varepsilon|\psi'\rangle \quad (\text{a6.2})$$

will be solved approximately as below. Inserting

$$|\psi'\rangle = \sum_j a_j |j\rangle + \sum_\mu a_\mu |\mu\rangle \quad (\text{a6.3})$$

into (a6.2) we get

$$(\hat{H}_0 - \varepsilon) \sum_j a_j |j\rangle + (\hat{H}_0 - \varepsilon) \sum_\mu a_\mu |\mu\rangle = -\hat{H}'|\psi'\rangle. \quad (\text{a6.4})$$

Left multiplying  $\langle v|$  on (a6.4) we get

$$a_v = \frac{\langle v|\hat{H}'|\psi'\rangle}{\varepsilon - \varepsilon_v}$$

$$\begin{aligned}
&= \sum_j \frac{\langle v|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_v} a_j + \sum_\rho \frac{\langle v|\hat{H}'|\rho\rangle}{\varepsilon - \varepsilon_v} a_\rho \\
&= \sum_j \left[ \frac{\langle v|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_v} + \sum_\rho \frac{\langle v|\hat{H}'|\rho\rangle \langle \rho|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_v)(\varepsilon - \varepsilon_\rho)} \right. \\
&\quad \left. + \sum_{\mu,v} \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|v\rangle \langle v|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_v)} + \dots \right] a_j. \tag{a6.5}
\end{aligned}$$

Left multiplying  $\langle l|$  on (a6.4) we get

$$\begin{aligned}
\sum_j (\varepsilon_0 - \varepsilon) \delta(l, j) a_j &= - \sum_j \langle l|\hat{H}'|j\rangle a_j - \sum_\mu \langle l|\hat{H}'|\mu\rangle a_\mu \\
&= - \sum_j [\langle l|\hat{H}'|j\rangle + \sum_\mu \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_\mu} \\
&\quad + \sum_{\mu,v} \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|v\rangle \langle v|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_v)} + \dots] a_j, \tag{a6.6}
\end{aligned}$$

that is

$$\sum_j [\langle l|\hat{H}_{\text{eff}}|j\rangle - \varepsilon \delta(l, j)] a_j = 0, \tag{a6.7}$$

$$\begin{aligned}
\langle l|\hat{H}_{\text{eff}}|j\rangle &\equiv \varepsilon_0 \delta(l, j) + \langle l|\hat{H}'|j\rangle + \sum_\mu \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_\mu} \\
&\quad + \sum_{\mu,v} \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|v\rangle \langle v|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_v)} + \dots. \tag{a6.8}
\end{aligned}$$

The solution of (a6.2) can be obtained by solving the perturbation secular equation

$$\begin{aligned}
&|\langle l|\hat{H}_{\text{eff}}|j\rangle - \varepsilon \delta(l, j)| \quad (l, j = 1, 2, \dots, n) \\
&\equiv \begin{vmatrix} \langle 1|\hat{H}_{\text{eff}}|1\rangle - \varepsilon & \langle 1|\hat{H}_{\text{eff}}|2\rangle & \cdots & \langle 1|\hat{H}_{\text{eff}}|n\rangle \\ \langle 2|\hat{H}_{\text{eff}}|1\rangle & \langle 2|\hat{H}_{\text{eff}}|2\rangle - \varepsilon & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \langle n|\hat{H}_{\text{eff}}|1\rangle & \cdots & \cdots & \langle n|\hat{H}_{\text{eff}}|n\rangle - \varepsilon \end{vmatrix} = 0. \tag{a6.9}
\end{aligned}$$

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