

## Chapter 2

# Atomic Orbital

**Abstract** In one-electron atom such as hydrogen atom and hydrogenic atom, the exact solution of Schrödinger equation can be obtained. The wave-function, which stands for atomic orbital, is separated into the two radial and angular wave-functions. Radial wave-function contains two quantum numbers such as principal quantum number and orbital angular momentum quantum number. The former and latter denote shell and subshell, respectively. Due to the relationship between two quantum numbers, 2p and 3d orbitals have the three and five orbitals. Angular wave-function expresses electron spread by using two angular parameters. The wave-function cannot be directly plotted into three-dimensional space. Instead, it is possible to visualize electron density, which is given by the square of wave-function. In many-electron atom, the effect of spin cannot be negligible. Spin has two quantum numbers of total spin angular momentum and spin angular momentum along the standard direction. When the latter quantum number is  $+1/2$  or  $-1/2$ , it is called  $\alpha$  or  $\beta$  spins, respectively. To incorporate electron spin in wave-function, spin function is introduced. Spin orbital is expressed by the product between spatial orbital and spin function. To satisfy inversion principle, the total wave-function is represented by Slater determinant. Finally, building-up principle is also explained.

**Keywords** Hydrogenic atom • Radial wave-function • Angular wave-function • Electron spin • Slater determinant

## 2.1 Hydrogenic Atom

### 2.1.1 Schrödinger Equation

As explained in Chap. 1, in quantum manner, electron is represented by wave-function. The wave-function standing for an electron is called orbital. In atom and molecule, it is called atomic orbital (AO) and molecular orbital (MO), respectively. Let us explain atomic orbitals of hydrogenic atom, where one electron

exists around atomic nucleus with nuclear charge  $Ze$ . Note that  $Z$  is positive integer. Coulomb potential energy ( $V$ ) between atomic nucleus and electron is expressed as

$$V = -\frac{Ze^2}{4\pi\epsilon_e r} \quad (2.1)$$

where  $e$ ,  $\epsilon_0$  and  $r$  denote charge, vacuum permittivity and electron-atom distance, respectively. The Hamiltonian of hydrogenic atom is given by

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{\hbar^2}{2m_N} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_e r} \quad (2.2)$$

where  $\hbar = h/2\pi$ ,  $m_e$  is the mass of electron, and  $m_N$  is the mass of nucleus. The first, second and third terms denote kinetic energy of electron, kinetic energy of atomic nucleus and Coulomb potential energy, respectively. The Schrödinger equation for hydrogenic atom is expressed as

$$\left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{\hbar^2}{2m_N} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_e r} \right) \Psi = E\Psi \quad (2.3)$$

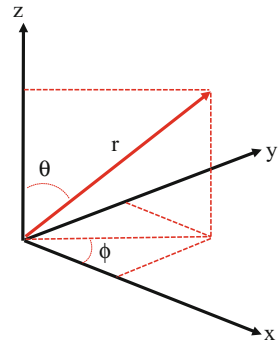
where  $\Psi$  and  $E$  denote the wave-function of an electron and the total energy, respectively. The wave-function can be separated into two parts by three variables such as radial ( $r$ ) and two angular ( $\theta$ ,  $\phi$ ) components (see Fig. 2.1).

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (2.4)$$

When the reduced mass ( $\mu$ ) is defined as

$$\mu = \frac{m_e m_N}{m_e + m_N} \quad (2.5)$$

**Fig. 2.1** Relationship between Cartesian coordinates and polar coordinates



the  $\mu$  value is approximately similar to the electron mass.

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N} \approx \frac{1}{m_e} \quad (2.6)$$

It is because the nucleus mass is much larger than electron mass. By the substitution of Eq. (2.6), Eq. (2.3) is written as

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_e r} \right) \Psi = E\Psi \quad (2.7)$$

In spherical polar coordinates,  $\nabla^2$  is defined as

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2 \quad (2.8)$$

where  $\Lambda^2$  is defined as

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \quad (2.9)$$

The Schrödinger equation is rewritten as

$$-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2 \right) RY - \frac{Ze^2}{4\pi\epsilon_e r} RY = ERY \quad (2.10)$$

Finally, it is rewritten as

$$-\frac{\hbar^2}{2\mu R} \left( r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} \right) + \frac{Ze^2}{4\pi\epsilon_e} r^2 - \frac{\hbar^2}{2\mu \Theta \Phi} \Lambda^2 Y = Er^2 \quad (2.11)$$

Equation (2.11) can be separated into two equations.

$$-\frac{\hbar^2}{2\mu \Theta \Phi} \Lambda^2 Y = \text{constant} \quad (2.12)$$

$$-\frac{\hbar^2}{2\mu R} \left( \frac{d^2 R}{dr^2} + \frac{2}{r^2} \frac{dR}{dr} \right) + \frac{Ze^2}{4\pi\epsilon_e} r^2 - Er^2 = -\text{constant} \quad (2.13)$$

The parameters of Eq. (2.12) are two angular components ( $\phi$  and  $\theta$ ). On the other hand,  $r$  is the sole parameter in Eq. (2.13).

**Table 2.1** Radial wave-functions of hydrogenic atom

$n$	$l$	$R(r)$
1	0	$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2	0	$R_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \rho)e^{-\rho/2}$
2	1	$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}$
3	0	$R_{3s} = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - 6\rho + \rho^2)e^{-\rho/2}$
3	1	$R_{3p} = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (4 - \rho)\rho e^{-\rho/2}$
3	2	$R_{3d} = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/2}$

### 2.1.2 Radial Wave-Function

We go through the detailed mathematical process to solve the radial equation. Table 2.1 shows the radial wave-functions of hydrogenic atom. The wave-functions are written in terms of dimensionless quantity ( $\rho$ ).

$$\rho = \frac{Zr}{a_0} \quad (2.14)$$

where  $a_0$  is Bohr radius.

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad (2.15)$$

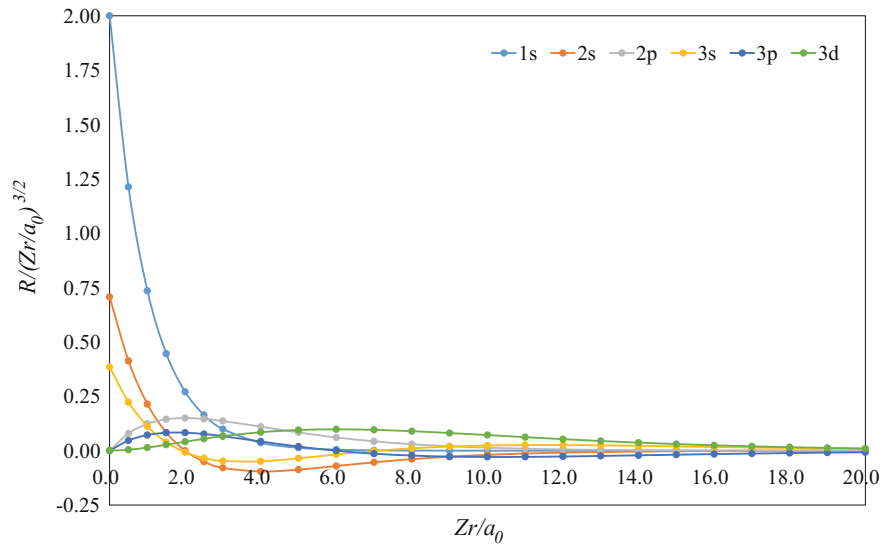
In radial wave-function, two quantum numbers are defined. One is the principal quantum number ( $n$ ), corresponding to a shell. For example, electrons with  $n = 2$  belong to the L shell. The other is orbital angular momentum quantum number ( $l$ ), corresponding to a subshell. Two quantum numbers satisfies the following condition.

$$l = 0, 1, 2, 3, \dots, (n - 1) \quad (2.16)$$

Table 2.2 shows the relationship between quantum numbers, shell and subshell in hydrogenic atom. When  $n = 1$ , there is only one  $s$ -type subshell ( $l = 0$ ). Quantum numbers of  $n = 1$  and  $l = 0$  stand for 1s atomic orbital. When  $n = 2$ , there are  $s$ -type ( $l = 0$ ) and  $p$ -type ( $l = 1$ ) subshells. Quantum numbers of  $n = 2$  and  $l = 0$  stand for 2s atomic orbital, and  $n = 2$  and  $l = 1$  stand for 2p atomic orbital. Figure 2.2 shows the variation of  $R/(Zr/a_0)^{3/2}$  value, changing  $Zr/a_0$  value. In 2s, 3s and 3p AOs, positive and negative  $R/(Zr/a_0)^{3/2}$  values are given. The total energy ( $E$ ) is given by

**Table 2.2** Relationship between quantum numbers, shell and subshell in hydrogenic atom

$n$	Shell	$l$	Subshell	Atomic orbital
1	K	0	s	1s
2	L	0	s	2s
2	L	1	p	2p
3	M	0	s	3s
3	M	1	p	3p
3	M	2	d	3d



**Fig. 2.2** Variation of  $R/(Zr/a_0)^{3/2}$  value, changing  $Zr/a_0$  value

$$E = -\frac{\hbar^2}{2m_e a_0^2} \frac{Z^2}{n^2} \tag{2.17}$$

$E$  depends only on principal quantum number. It is why 2s and 2p atomic orbitals of hydrogenic atom are degenerated.

**2.1.3 Angular Wave-Function**

The sign of the total wave-function is determined by the signs of the radial and angular wave-functions. The angular wave-functions are written in terms of angular components ( $\theta$  and  $\phi$ ). We go through the detailed mathematical process to solve the angular equation. Table 2.3 shows the angular wave-functions of hydrogenic atom.

**Table 2.3** Angular wave-functions of hydrogenic atom

$l$	$Y(\theta, \phi)$
0	$\frac{1}{2\sqrt{\pi}}$
1	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$
1	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$
2	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\sin\theta\cos\theta\cos\phi$
2	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\sin\theta\cos\theta\sin\phi$
2	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$
2	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$

In 1s, 2s and 3s AOs, one angular wave-function has no angular parameter. It implies that the AOs spread uniformly to all directions. The sign of wave-function is determined by the radial wave-function. In 1s AO, the sign of wave-function becomes positive. On the other hand, in 2s and 3s AOs, the sign of radial wave-functions is positive or negative, depending on a radius. It implies that the sign of wave-function is changeable.

In 2p and 3p AOs, three angular wave-functions are given. In  $n = 2$ , the AOs are called 2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub> AOs. Though the sign of radial wave-function ( $R_{2p}$ ) is positive, the signs of angular wave-functions are positive or negative, depending on angular parameters. Hence, the sign of wave-function is changeable in 2p AOs.

In 3d AOs, five angular wave-functions are given. The AOs are called 3d<sub>xy</sub>, 3d<sub>yz</sub>, 3d<sub>xz</sub>, 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, 3d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> AOs. Though the sign of radial wave-function ( $R_{3d}$ ) is positive, the signs of angular wave-functions are positive or negative, depending on angular parameters. Hence, the sign of wave-function is changeable in 3d AOs.

The positive and negative signs in the wave-function represent the qualitative difference of wave-function. In electron–electron interaction, the difference has an important role.

### 2.1.4 Visualization of Hydrogenic Atomic Orbital

In hydrogenic atom, one electron spreads as one wave-function. The wave-function of the ground state consists of  $R_{1s}$  and  $Y(= 1/2\sqrt{\pi})$ . It is because minimum total energy is given when  $n = 1$ . However, the wave-function ( $\Psi$ ) cannot be directly plotted into three-dimensional space. Instead, it is possible to visualize electron

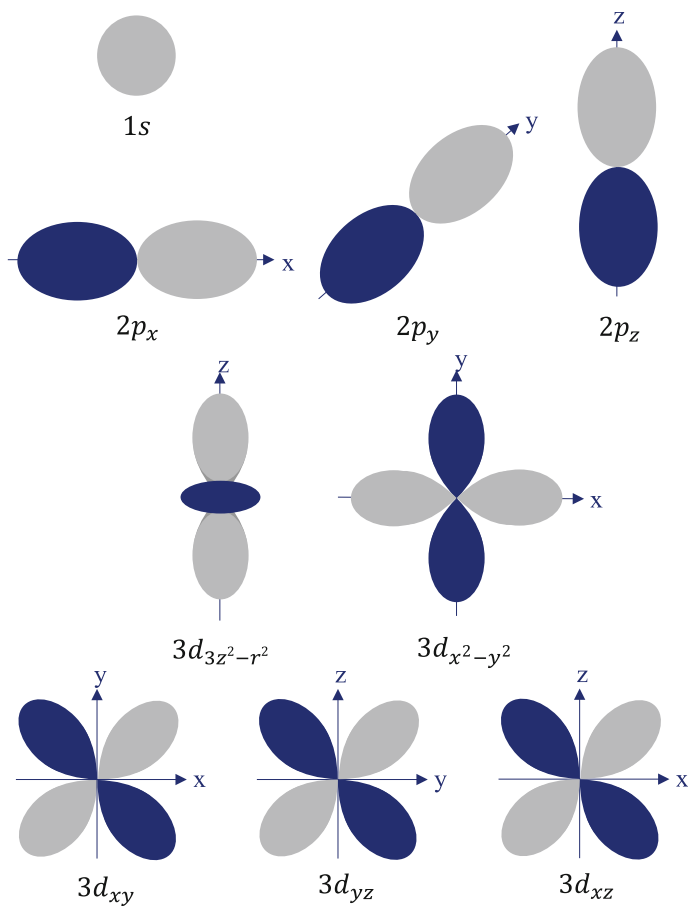
density, which is given by the square of wave-function ( $|\Psi^2|$ ). Electron density in an finite volume ( $d\tau$ ) is given by

$$|\Psi^2|d\tau \quad (2.18)$$

Electron density is normalized in three-dimensional space.

$$\int |\Psi^2|d\tau = 1.00 \quad (2.19)$$

In general, the atomic orbital envelope diagrams are drawn based on the contours, within which the values of electron density is 0.95. Figure 2.3 depicts the atomic orbital envelope diagram of hydrogenic atom. Note that electron density is



**Fig. 2.3** Atomic orbital envelope diagrams of hydrogenic atom

dense around the centre, though the radial wave-function spreads in a large distance. The positive and negative signs of wave-functions are discriminated by colour difference. In this book, grey- and blue-coloured lobes represent the positive and negative signs of wave-function, respectively.

## 2.2 Many-Electron Atom

### 2.2.1 Schrödinger Equation

First, we consider helium atom as the simple example of two-electron atom (see Fig. 2.4). Two electrons are labelled as electron 1 and electron 2. Each electron has both electron–atomic nucleus interaction and electron–electron interaction. The Hamiltonian of the Schrödinger equation is expressed by

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\hbar^2}{2m_N} \nabla^2 - \frac{2e^2}{4\pi\epsilon_e r_1} - \frac{2e^2}{4\pi\epsilon_e r_2} + \frac{e^2}{4\pi\epsilon_e r_{12}} \quad (2.20)$$

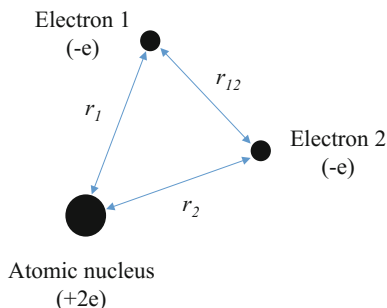
In many-electron atom ( $n$ -electron system), all electron–atomic nucleus and electron–electron interactions must be included in the Hamiltonian.

$$H = -\frac{\hbar^2}{2m_e} \sum_i^n \nabla_i^2 - \frac{\hbar^2}{2m_N} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_e} \sum_i^n \frac{1}{r_i} + \frac{e^2}{4\pi\epsilon_e} \sum_{i<j}^n \frac{1}{r_{ij}} \quad (2.21)$$

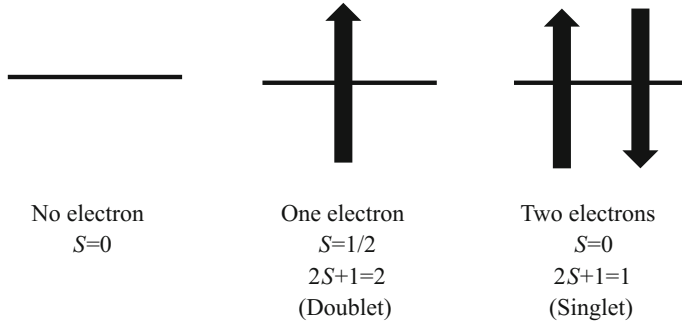
### 2.2.2 Electron Spin

In many-electron atom, which means that more than two electrons exist in one atom, the effect of spin cannot be negligible. In general, two quantum numbers related to spin are defined. One is quantum number of total spin angular momentum

**Fig. 2.4** Schematic drawing of helium atom







**Fig. 2.5** Electron allocation in one atomic orbital

( $S$ ). The other is quantum number of spin angular momentum along the standard direction ( $m_s$ ). When  $m_s = +1/2$ , electron has  $\alpha$  spin. On the other hand, when  $m_s = -1/2$ , electron has  $\beta$  spin. Figure 2.5 depicts the schematic drawing of electron allocation in one atomic orbital. In one electron case, one electron occupies one atomic orbital. The spin multiplicity, which is defined as  $(2S + 1)$ , becomes two. It is called doublet spin state. When two electrons occupy one atomic orbital, two spins are paired, due to Pauli exclusion principle. Two electrons with paired spins have zero resultant spin angular momentum. Hence, the spin multiplicity becomes one. It is called singlet spin state.

### 2.2.3 Spin Orbital

To incorporate electron spin in wave-function, two kinds of spin functions such as  $\alpha(\omega)$  and  $\beta(\omega)$  are introduced.  $\omega$  is a parameter of spin coordinates. Two spin functions are normalized.

$$\int \alpha^*(\omega)\alpha(\omega)d\omega = \int \beta^*(\omega)\beta(\omega)d\omega = 1 \quad (2.22)$$

Using the bra and ket symbols, they are rewritten:

$$\langle \alpha(\omega) | \alpha(\omega) \rangle = \langle \beta(\omega) | \beta(\omega) \rangle = 1 \quad (2.23)$$

Two spin functions satisfy an orthogonality.

$$\int \alpha^*(\omega)\beta(\omega)d\omega = \int \beta^*(\omega)\alpha(\omega)d\omega = 0 \quad (2.24)$$

Using the bra and ket symbols, they are rewritten:

$$\langle \alpha(\omega) | \beta(\omega) \rangle = \langle \beta(\omega) | \alpha(\omega) \rangle = 1 \quad (2.25)$$

The spin orbital ( $\chi$ ) is defined by the product between spatial orbital ( $\psi$ ) and spin function. When one electron has  $\alpha$  spin, it is expressed as

$$\chi(x) = \psi(r)\alpha(\omega) \quad (2.26)$$

where  $\chi$  denotes both space and spin coordinates. On the other hand, one electron has  $\beta$  spin, and it is expressed as

$$\chi(x) = \psi(r)\beta(\omega) \quad (2.27)$$

Note that it is assumed that  $\alpha$  and  $\beta$  spins are allowed in one spatial orbital. The different spatial orbitals are also orthonormal.

$$\int \psi_i^*(r)\psi_j(r)dr = \delta_{ij} \quad (2.28)$$

where  $\delta_{ij}$  is called Kronecker delta.

$$\delta_{ij} = \begin{cases} 1 (i=j) \\ 0 (i \neq j) \end{cases} \quad (2.29)$$

As the result, the different spin orbitals are orthonormal.

$$\int \chi_i^*(r)\chi_j(r)dr = \delta_{ij} \quad (2.30)$$

### 2.2.4 Total Wave-Function

By using Hartree product, the total wave-function ( $\Phi$ ) of  $n$ -electron system is expressed as the product of all spin orbitals.

$$\Phi^{\text{HP}}(x_1, x_2, \dots, x_n) = \chi_1(x_1) \cdot \chi_2(x_2) \dots \chi_n(x_n) \quad (2.31)$$

If there is no electron–electron interaction,  $\Phi^{\text{HP}}$  is the eigenfunction of the Schrödinger equation. However, if there is an electron–electron interaction, Hartree product is different from the exact total wave-function.

Electron belongs to fermion, which is a quantum particle with half-integer quantum number for spin angular momentum. Fermion must satisfy “inverse

principle” that the total wave-function changes the sign, when the labels of any two identical fermions are exchanged.

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_n) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_n) \quad (2.32)$$

In order to satisfy inverse principle, by using Slater determination, the total wave-function is expressed as

$$\Phi(\chi_1, \chi_2, \dots, \chi_n) = (n!)^{-\frac{1}{2}} \begin{bmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_n(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & & \chi_n(x_2) \\ & \vdots & \ddots & \vdots \\ \chi_1(x_n) & \chi_2(x_n) & \dots & \chi_n(x_n) \end{bmatrix} \quad (2.33)$$

The convenient representation of Slater determination is expressed as

$$|\chi_1(x_1)\chi_2(x_2)\dots\chi_n(x_n)\rangle \quad (2.34)$$

Let us consider the simple example of many-electron atom. Helium atom has two electrons with paired spins. They are allocated into the same atomic orbital. The spin orbitals are given by

$$\chi_1(x_1) = \psi_1(r_1)\alpha(\omega_1) \quad (2.35)$$

$$\chi_2(x_2) = \psi_1(r_2)\beta(\omega_2) \quad (2.36)$$

Slater determination is rewritten as

$$\Phi(\chi_1, \chi_2) = |\chi_1(x_1)\chi_2(x_2) = (2!)^{-\frac{1}{2}} \begin{bmatrix} \chi_1(x_1) & \chi_2(x_1) \\ \chi_1(x_2) & \chi_2(x_2) \end{bmatrix} \quad (2.37)$$

$$= (2!)^{-\frac{1}{2}} \begin{bmatrix} \psi_1(r_1)\alpha(\omega_1) & \psi_1(r_1)\beta(\omega_1) \\ \psi_1(r_2)\alpha(\omega_2) & \psi_1(r_2)\beta(\omega_2) \end{bmatrix} \quad (2.38)$$

$$= \frac{\psi_1(r_1)\psi_1(r_2)}{\sqrt{2}} \{\alpha(\omega_1) \cdot \beta(\omega_2) - \beta(\omega_1) \cdot \alpha(\omega_2)\} \quad (2.39)$$

However, the Schrödinger equation for many-electron atom cannot be analytically solved. Many calculation methods have been developed to solve it approximately with high precision.

### 2.2.5 Building-Up Rule

Building-up principle is the plausible and empirical rule to predict the ground-state electron configuration of a single atom. It is a starting point before actual calculation. It is based on two types of allocations for one AO: (1) one electron with  $\alpha$  spin and (2) two electrons with paired spins. The order of occupation is as follows.

$$(1)1s, (2)2s, (3)2p, (4)3s, (5)3p, (6)3d \dots \quad (2.40)$$

In hydrogen atom, which is one-electron system, one electron occupies 1s orbital with  $\alpha$  spin.

$$\text{H} : 1s^1 \quad (2.41)$$

In helium atom, which is two-electron system, two electrons occupy 1s orbital with paired spins.

$$\text{He} : 1s^2 \quad (2.42)$$

In lithium atom, which is three-electron system, two electrons occupy 1s orbital with paired spins, and one electron occupies 2s orbital with  $\alpha$  spin.

$$\text{Li} : 1s^2 2s^1 \quad (2.43)$$

Table 2.4 summarizes the number of electrons in atomic orbitals, based on building-up principle. Neutral carbon, oxygen and nitrogen have six, seven and eight electrons. Their electron configuration is expressed as follows.

$$\text{C} : 1s^2 2s^2 2p^2 \quad (2.44)$$

$$\text{O} : 1s^2 2s^2 2p^3 \quad (2.45)$$

$$\text{N} : 1s^2 2s^2 2p^4 \quad (2.46)$$

**Table 2.4** Number of electrons in atomic orbitals, based on building-up principle

$n$		$l$	Atomic orbital	Number of electrons	
1	K	0	1s	2	$(1\alpha, 1\beta)$
2	L	0	2s	2	$(1\alpha, 1\beta)$
		1	2p	6	$(3\alpha, 3\beta)$
3	M	0	3s	2	$(1\alpha, 1\beta)$
		1	3p	6	$(3\alpha, 3\beta)$
		2	3d	10	$(5\alpha, 5\beta)$

## Further Readings

1. Atkins P, de Paula J (2006) Physical chemistry 8th edn, Chapters 9 and 10 (in Japanese)
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