Quantum Chemistry

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Chapter 2

Atom

Chemical elements, which are chemical varieties of atoms, are classified by atomic numbers. Atoms of the same element are called isotopes, when total numbers of protons and neutrons in the nuclei (mass numbers) are different. Although phenomena concerning with masses depnend on isotopes and their abundance, chemcical properties are usually irrespective of the isotopes. This is due to decisive roles of electrons which are small and mobile. Probabilities of electron transfer are governed by numbers of electrons around nuclei. Electronic motion depends on the attractive force caused by the nucleus charges. Since the number of electrons and the nucleus charge are chararacteristic to each atomic number, chemical properties of atoms are closely related to the atomic numbers.

In this chapter, we will study how characteristic properties of atoms appear dependning on the atomic number. In the last section of this chapter, we will aslo study excited states and spectra of atoms.

2.1 The hydrogenic atom

Let us first consider a hydrogenic atom, in which an electron is moving around a nucleus as shown in fig.2.1. Based on such a simple system, we will study the fundamental characteristics of energy levels and wavefunctions.

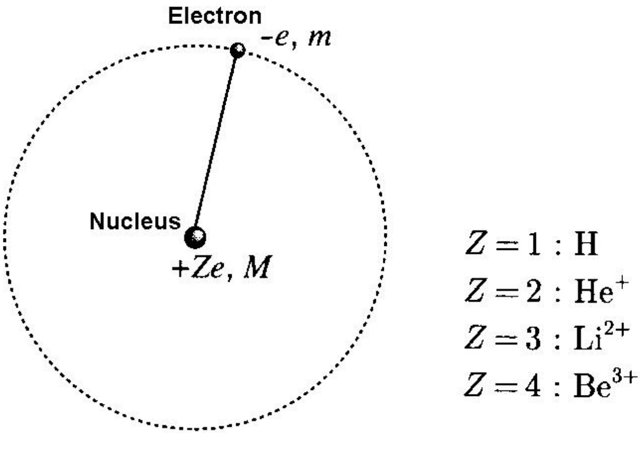


Figure 2.1: A hydrogenic atom. Z: atomic number, M: mass of the nucleus, m: mass of the electron

The electric charge of the nucleus is represented by the product of the atomic number Z and the elementary charge e. The potential energy U is given by $U = -Ze^2/4\pi\varepsilon_0 r$. Using the formula (1.73) for a two-particle system introduced in section 1.12, the Hamiltonian operator $\hat{H}$ of this system is expressed by the following equation.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{2.1}$$

Here, μ is the reduced mass, which is given for the mass of the nucleus M and the mass of the electron m by the following equation.

$$\mu = \frac{1}{1/M + 1/m} \tag{2.2}$$

When $1/M$ in the denominator of this equation for μ is neglected by noting $M \gg m$, the equation reduces to $\mu = m$, and the system becomes a simple model that an electron moves around the resting nucleus. Errors due to this approximation are not very large, as can be seen below from the Example 2.1. It follows that solutions of the wave equation of the Hamiltonian in eq.(1.73), which are rigorously for the relative motion, can be understood to represent motions of the electron in the atom.

A comparison with the case of a hydrogen atom ($Z = 1$) indicates that e^2 is simply replaced by Ze^2 in the expression for the potential energy. Therefore, from eqs.(1.79) and (1.80), the energy levels are given by the following equations.

$$E_n = -\frac{W(Z)}{n^2} \qquad (n = 1, 2, 3, \cdots) \tag{2.3}$$

$$W(Z) = \frac{\mu Z^2 e^4}{8{\varepsilon_0}^2 h^2} \tag{2.4}$$

Here, n is the principal quantum number that determines the energy level. $W(Z)$ is the energy required for removing one electron from the hydrogenic atom. This quantity for $Z = 1$ corresponds to the ionization energy of hydrogen atom W_{H}.

Example 2.1 How many times the energy is required for producing a di-positive ion of helium (He^{2+}) by removing an electron from a helium ion (He^{+}) in comparison with the ionization energy of hydrogen atom ?

(Solution) Ionization energy of an atom depends on the reduced mass μ and the atomic number Z. Approximating the mass ratio of a proton and an electron as 1836 : 1 and also approximating the mass ratio of a hydrogen nucleus and a helium nucleus as 1 : 4, we obtain the ratio of the reduced masses as

$$\frac{\mu(\mathrm{He})}{\mu(\mathrm{H})} = \frac{1/1836 + 1}{1/(1836 \times 4) + 1} = \frac{4 \times (1 + 1836)}{1 + 1836 \times 4} = 1.00041$$

For the difference of the atomic numbers, $Z(\mathrm{He})^2/Z(\mathrm{H})^2 = 2^2/1^2 = 4$. It follows that the ratio obtained becomes 4.0016.

$$W(2) = 4 \times 1.00041 \times W_{\mathrm{H}} = 4.00164$$

If the difference of the reduced masses is neglected as $\mu(\mathrm{He}) = \mu(\mathrm{H}) = m$, then $W(2) = 4W_{\mathrm{H}}$, which leads to an answer of 4 as the ratio to be obtained.

Using the Hamiltonian operator in eq.(1.77), the wave equation can be expressed in terms of polar coordinates as follows.

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \Lambda\right)\Psi = (E - U)\Psi \tag{2.5}$$

As studied for the angular momentum, Legendrian Λ only includes angular coordinates (θ, ϕ), and it satisfies the following equation with the spherical harmonic functions $Y_{l,m}$.

$$\Lambda Y_{l,m} = -l(l+1)Y_{l,m} \tag{2.6}$$

Noting this equation, let us take the wave function in the following form.

$$\Psi = R(r) \cdot Y_{l,m}(\theta, \phi) \tag{2.7}$$

From eqs.(2.5)-(2.7) we obtain

$$\left[-\frac{\hbar^2}{2\mu r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - l(l+1) \right) R(r) + (U - E)R(r) \right] Y_{l,m} = 0 \tag{2.8}$$

The Ψ introduced in eq.(2.7) is able to become the solution of the wave equation of the hydrogenic atom, provided that the function $R(r)$ is determined to satisfy $[\quad] = 0$. In this way, the wave function of the hydrogenic atom is given in a form of a product of the radial part $R(r)$ and the angular part $Y_{l,m}(\theta, \phi)$.

The equation determining $R(r)$ is given by as follows.

$$-\frac{\hbar^2}{2\mu r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - l(l+1) \right) R(r) = (E - U)R(r) \tag{2.9}$$

By solving this differential equation to obtain continuous and finite functions, energy eigen values E agree with eqs.(1.79) and (1.80), and the following restrictions to n and l are derived.

$$n = l+1, l+2, l+3, \cdots \qquad (n = 1, 2, 3, \cdots) \tag{2.10}$$

Functions $R(r)$ for the radial part are expressed in terms of mathematically well known Laguerre polynomials L_α and a function of r given below as ρ.

$$\rho = \frac{2Zr}{na_0} \tag{2.11}$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi \mu e^2} \tag{2.12}$$

$$R_{n,l}(\rho) = -\sqrt{\frac{4(n-l-1)!}{n^4[(n+l)!]^3}} \left(\frac{Z}{a_0} \right)^{3/2} \rho^l \mathrm{e}^{-\rho/2} L_{n+l}{}^{2l+1}(\rho) \tag{2.13}$$

$$L_\alpha{}^\beta(\rho) = \frac{\mathrm{d}^\beta}{\mathrm{d}\rho^\beta} L_\alpha(\rho) \qquad (\beta = 0, 1, 2, \cdots, \ \beta \leq \alpha) \tag{2.14}$$

$$L_\alpha(\rho) = \mathrm{e}^\rho \frac{\mathrm{d}^\alpha}{\mathrm{d}\rho^\alpha} (\rho^\alpha \mathrm{e}^{-\rho}) \qquad (\alpha = 0, 1, 2, \cdots) \tag{2.15}$$

Table 2.1: The radial part of the wave functions $R_{n,l}(r)$

$$R_{1,0} = 2 \left(\frac{Z}{a_0} \right)^{3/2} \mathrm{e}^{-(Z/a_0)r}$$

$$R_{2,0} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) \mathrm{e}^{-(Z/2a_0)r}$$

$$R_{2,1} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} \mathrm{e}^{-(Z/2a_0)r}$$

$$R_{3,0} = \frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} \left(27 - \frac{18Zr}{a_0} + \frac{2Z^2r^2}{{a_0}^2} \right) \mathrm{e}^{-(Z/3a_0)r}$$

$$R_{3,1} = \frac{4}{81\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{6Zr}{a_0} - \frac{Z^2r^2}{a_0} \right) \mathrm{e}^{-(Z/3a_0)r}$$

$$R_{3,2} = \frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Z^2r^2}{{a_0}^2} \mathrm{e}^{-(Z/3a_0)r}$$

Here, ${L_\alpha}^\beta$ are associated Laguerre polynomials. a_0 is a constant, which is equal to the Bohr radius a_{B}, when $\mu = m$. As can be seen from Example 2.1, errors due to the approximation of $\mu = m$ are as small as less than 0.1%. Thus, a_0 may be considered to be equal to the Bohr radius a_{B}. Table 2.1 shows the radial part of the wave functions $R_{n,l}$ which can be obtained from eqs.(2.11)-(2.15). Graphs of $R_{n,l}$ for hydrogen are shown in fig.2.2.

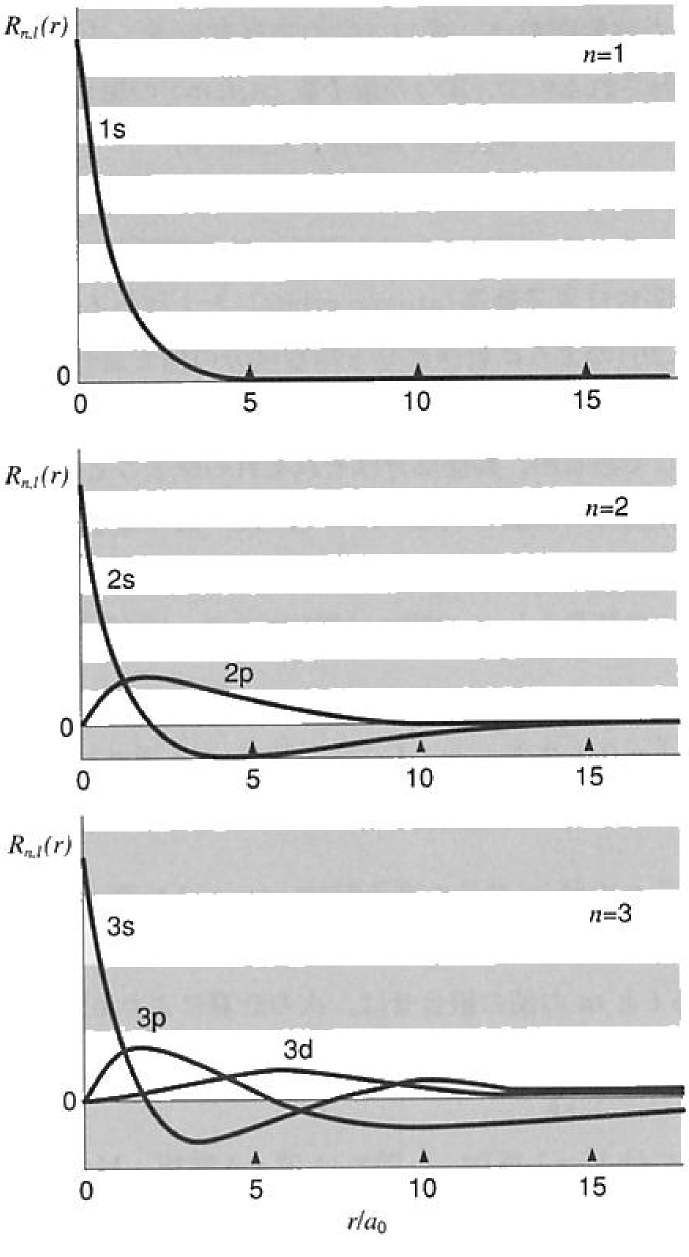


Figure 2.2: Radial part $R_{n,l}(r)$ of hydrogenic wave functions.

Since the square of the absolute value of the wave function is proportional to the probability finding a particle, the form of $R_{n,l}(r)$ determines the behavior of an electron in the atom with respect to the distance r from the nucleus. This has a great significance in various chemical phenomena in connection with the behavior of electrons in a general atom. As can be seen from Table 2.1 and fig.2.2, the radial part of the wave functions $R_{n,l}$ have mathematical properties listed below. In connection with these properties, characteristic remarks on the r-dependence of the probability finding an electron in the atom are shown in [ ]. As will be seen in Section 2.2, the r-dependence of the probability of finding an electron is proportional to $r^2 {R_{n,l}}^2$.

[Mathematical properties of the radial part of the wave functions and the r-dependence of the probability of finding an electron]

(1) Because of an exponential factor, the functional value approaches 0 asymptotically associated with the increase of r [moving outward from the nucleus, the probability of finding an electron becomes to be vanishing].

(2) The coefficient of r in the exponent becomes smaller for the larger principal quantum number n, and it follows that the functional value approaches 0 more slowly for the larger n [The probability of finding an electron extends into the more outer regions on going from $n = 1$, $n = 2$, and $n = 3$].

(3) The functional value at $r = 0$ is 0 except for $l = 0$ [There is no possibility of finding an electron at the nuclear position except for $l = 0$].

(4) There are $n - l - 1$ distances (spheres) where no electron can be found with the functional value being vanishing [In cases of $n - l > 1$, the probability of finding an electron decreases to the outer regions with an oscillating behavior].

The principal quantum number n has an important significance that classifies the energy levels, and it also characterizes the spatial behavior of the probability of finding an electron. It follows that electrons in an atom extend outwards in forming electron shells of the K shell ($n = 1$), the L shell ($n = 2$), the M shell ($n = 3$), the N shell ($n = 4$), the O shell ($n = 5$), the P shell ($n = 6$) and so on. This propensity corresponds to the orbital radius in the Bohr model becoming larger, associated with the increase of n.

In the Bohr model, the motion of an electron belonging to each electron shell is limited to a simple circular orbit. In quantum mechanics, electronic motion becomes more complex because forms of the wave functions depend not only on n but also on l and m. l and m are also quantum numbers that specify atomic states and wave functions. l is called the azimuthal quantum number, and m is called the magnetic quantum number. l is related to the directions and forms of wave functions, and m is concerned with the phenomena that energy levels may vary with the applied magnetic field.

The wave functions $\{\Psi\}$ of a hydrogenic atom are expressed as a product of the radial part $R_{n,l}(r)$ in eq.(2.13) and the spherical harmonics functions $Y_{l,m}$, and thus $\{\Psi\}$ are specified by a combination of three quantum numbers (n, l, m).

$$\Psi_{n,l,m} = R_{n,l}(r) \cdot Y_{l,m}(\theta, \phi) \tag{2.16}$$

(r, θ, ϕ) are electron coordinates with respect to the nuclear position, and $\Psi_{n,l,m}$ represents the electronic motion in the atom. According to the correspondence with the orbital motion of the electron in the Bohr model, wave functions for an electron in an atom are called atomic orbitals. Atomic orbitals for general atoms are also expressed as a product of the radial part and the angular part(spherical harmonics) as eq.(2.16) and are specified by three quantum numbers (n, l, m). Although the angular part of atomic orbitals is the same for both hydrogenic atoms and general atoms, the radial part is different for each atom. The characteristic properties of the radial part (1)-(4) given above are common for all atoms.

As mentioned for the angular momentum, there are some restrictions for the two integers l and m associated with the spherical harmonics functions $Y_{l,m}$. Taking into account the relation between l and n in eq.(2.10), we obtain the following equations.

$$l = 0, 1, 2, 3, \cdots, n-1 \qquad (n\,\text{cases}) \tag{2.17}$$

$$m = -l, -l+1, \cdots, 0, \cdots, l-1, l \qquad (2l+1\,\text{cases}) \tag{2.18}$$

There are n cases of l values for the same n (the n-th electron shell), and there are $2l + 1$ cases of m values for the same l. It follows that the acceptable combinations of l and m for a particular electron shell such as the n-th shell are determined to be n^2 by the following calculation.

$$\sum_{l=0}^{n-1} (2l+1) = \frac{2 \times n(n-1)}{2} + n = n^2 \tag{2.19}$$

Thus, there are $1^2 = 1$ wave functions for the K shell, $2^2 = 4$ for the L shell, and $3^2 = 9$ for the M shell. These numbers are related to the upper limits of numbers of electrons that can be incorporated in a particular electron shell, as will be seen below in Section 2.5.

Although energy levels of hydrogenic atoms depend only on the principal quantum number n as can be seen from eq.(2.3), wave functions representing the statistical nature of particles depend on l and m as well as on n to have varieties of functional forms; there are one type for $n = 1$, four types for $n = 2$, and nine types for $n = 3$, respectively. In other words, there are n^2 different types of wave functions with the same energy eigen value of E_n for all excited states ($n > 1$) except for the ground state ($n = 1$). Wave functions have a four fold degeneracy for $n = 2$ and a nine fold degeneracy for $n = 3$.

2.2 Forms of atomic orbitals

The creation and destruction of chemical bonds occurs under the action of interference among electron waves. Their mechanisms are related to the forms of atom orbital functions. In this section, classification and characteristics of orbital forms are discussed for atomic orbitals of hydrogenic atoms as typical examples.

2.2.1 Classification of atomic orbitals

Atomic orbitals are wave functions representing electronic motion in an atom, and atomic orbitals are classified into several types with the principal quantum number n and the azimuthal quantum number l, as listed in Table 2.2.

Table 2.2: Classification of atomic orbitals

electron shell	principal quantum number n	azimuthal quantum number l					
		0 s	1 p	2 d	3 f	4 g	5 h
K	1	1s					
L	2	2s	2p				
M	3	3s	3p	3d			
N	4	4s	4p	4d	4f		
O	5	5s	5p	5d	5f	5g	
P	6	6s	6p	6d	6f	6g	6h

The azimuthal quantum number is related to the characteristic features of spectral series in atomic spectra. It follows that the first letters of the names for spectral series, such as sharp, principal, diffuse, and fundamental, have been used as s for $l = 0$, p for $l = 1$, d for $l = 2$, and f for $l = 3$.

2.2.2 s,p,d functions for the angular part

The names s, p, d for atomic orbitals are used for classification of the angular part. Although prototypes of the angular part functions are spherical harmonic functions $Y_{l,m}(\theta, \phi)$, in actual calculations and considerations conventional functions shown in Table 2.3 are used instead for some reasons described below. The angular part such as s, p, and d are related to mechanisms and directional characteristics in the formation of chemical bonds, and it follows that directions and signs of the angular part should be studied carefully.

The s function of the angular part is only one kind, the spherical harmonic function of $Y_{0,0}$, as shown in Table 2.3, which has a constant value, irrespective of the angles θ and ϕ. Namely, s-orbital functions are spherical, and values of s-orbital functions are the same for a constant value of the distance r, irrespective of the directions.

Three types of spherical harmonics $Y_{1,-1}, Y_{1,0}, Y_{1,1}$ correspond to p functions. As shown in Table 1.3 in Section 1.13, $Y_{1,-1}$, and $Y_{1,1}$ are functions of complex numbers, and $Y_{1,0}$ is a real

Table 2.3: s, p, d functions for the angular part

	l	m	definition	functional form
s	0	0	$Y_{0,0}$	$\frac{1}{\sqrt{4\pi}}$
p_x	1	±1	${Y_{1,1}}^+$	$\sqrt{\frac{3}{4\pi}}\frac{x}{r}$
p_y	1	±1	${Y_{1,1}}^-$	$\sqrt{\frac{3}{4\pi}}\frac{y}{r}$
p_z	1	0	$Y_{1,0}$	$\sqrt{\frac{3}{4\pi}}\frac{z}{r}$
d_{xy}	2	±2	${Y_{2,2}}^-$	$\sqrt{\frac{15}{4\pi}}\frac{xy}{r^2}$
d_{yz}	2	±1	${Y_{2,1}}^-$	$\sqrt{\frac{15}{4\pi}}\frac{yz}{r^2}$
d_{zx}	2	±1	${Y_{2,1}}^+$	$\sqrt{\frac{15}{4\pi}}\frac{zx}{r^2}$
$\mathrm{d}_{x^2\text{-}y^2}$	2	±2	${Y_{2,2}}^+$	$\sqrt{\frac{15}{16\pi}}\frac{1}{r^2}(x^2-y^2)$
d_{z^2}	2	0	$Y_{2,0}$	$\sqrt{\frac{5}{16\pi}}\frac{1}{r^2}(3z^2-r^2)$

function expressed as follows.

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \tag{2.20}$$

Here, the relation of $z = r\cos\theta$ from the definition of polar coordinates is used. $Y_{1,0}$ depends on the polar angle θ indicating the angle deflected from the z-axis, and the absolute value of $Y_{1,0}$ is at a maximum for the direction of the z-axis. Therefore, the $Y_{1,0}$ function is called p_z function.

$$\mathrm{p}_z = Y_{1,0} = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \tag{2.21}$$

Similar functions depending on the angles deflected from the x-axis and the y-axis can also be defined by the following equations, and they are called the p_x function and the p_y function.

$$\mathrm{p}_x = \frac{Y_{1,1} + Y_{1,-1}}{\sqrt{2}} = \sqrt{\frac{3}{4\pi}}\frac{x}{r} \tag{2.22}$$

$$\mathrm{p}_y = \frac{Y_{1,1} - Y_{1,-1}}{\sqrt{2}i} = \sqrt{\frac{3}{4\pi}}\frac{y}{r} \tag{2.23}$$

Except for some special cases such as under a magnetic field, the three functions of $\mathrm{p}_x, \mathrm{p}_y, \mathrm{p}_z$ are conventionally used as the angular part of p functions. These p functions all satisfy the eigen equation of (2.6) with an azimuthal quantum number of $l = 1$.

In the cases of $m \neq 0$ the spherical harmonics in Table 1.3 are functions of complex numbers in general, and their mathematical treatments are cumbersome. It is convenient to use the following functions with real values, which are denoted as ${Y_{l,m}}^+$ and ${Y_{l,m}}^-$ and are equivalent to $Y_{l,m}, Y_{l,-m}$ to satisfy eq.(2.6).

$${Y_{l,m}}^+ = \frac{Y_{l,m} + Y_{l,-m}}{\sqrt{2}} \tag{2.24}$$

$${Y_{l,m}}^- = \frac{Y_{l,m} - Y_{l,-m}}{\sqrt{2}i} \tag{2.25}$$

These functions are used in Table 2.3 for p and d functions.

The five types of d function shown in Table 2.3 correspond to the angular part for $l = 2$ and their directional characteristics are more complex than p orbitals. The three dimensional characteristics of orbital functions are not easily seen from their mathematical expressions, and it follows that we will introduce several types of typical expression showing their forms.

2.2.3 Angular dependence and figures of polar coordinates

The angular part $Y(\theta, \phi)$ determines the angular dependence of the probability of finding an electron. Taking $|Y|$ in each direction as the length of a vector with the respective direction from the origin, a contour produced with the top point of the vector gives a figure of polar coordinates as the three dimensional surfaces shown in Fig. 2.3. These figures represent the angular dependence of atomic orbitals. Symbols of + and − in Fig. 2.3 indicate the signs for $Y(\theta, \phi)$.

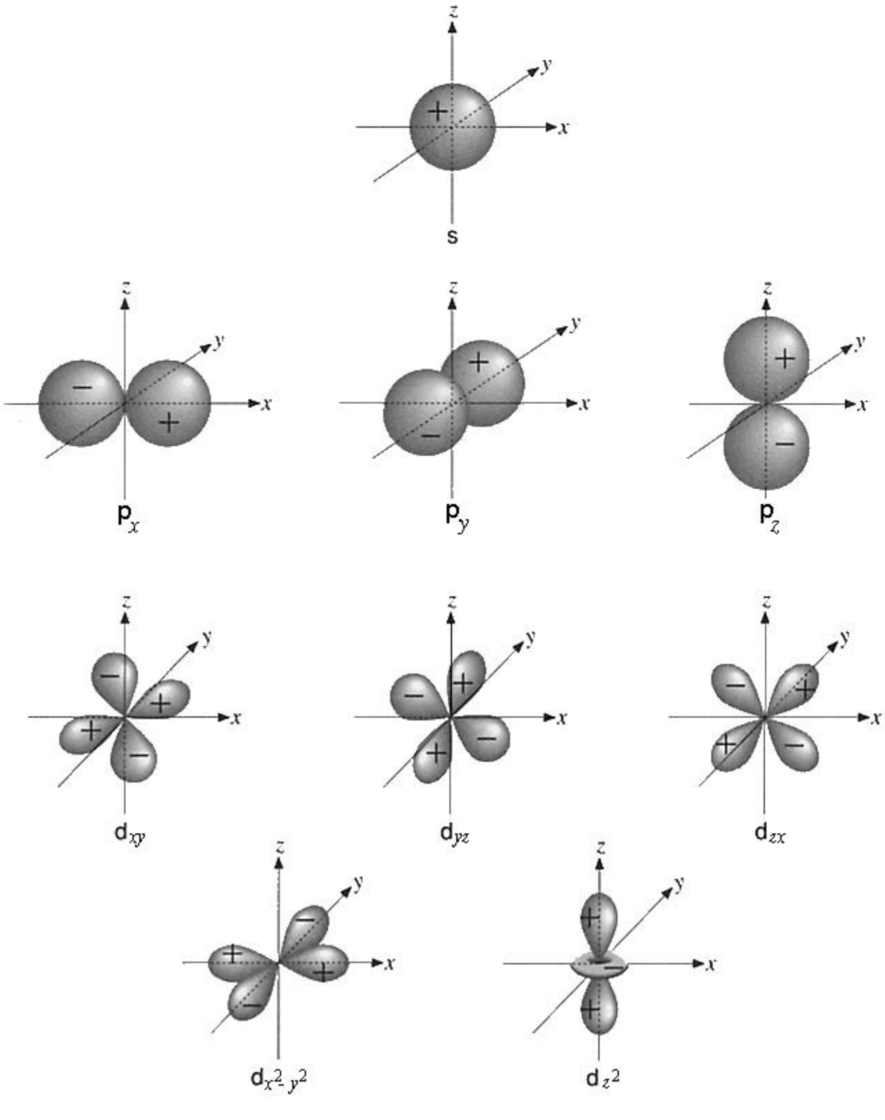


Figure 2.3: Angular dependence of s, p, d orbitals

Example 2.2 Draw the figure of polar coordinates for p_z function $Y_{1,0}$ in the x-z plane.

(Solution) Since $\phi = 0$, $y = 0$ in the x–z plane, x and z coordinates of the top point of the vector $P(x, 0, z)$ showing the magnitude as its length from the origin are given as follows.

$$x = |Y| \sin\theta$$
$$z = |Y| \cos\theta$$

Here, Y is

$$Y(\theta, 0) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

Noting $|\cos\theta| = \cos\theta$ for $0 \le \theta \le \pi/2$ and using a constant a,

$$a = \sqrt{\frac{3}{4\pi}}$$

x and z are expressed as

$$x = a \cos\theta \sin\theta$$
$$z = a \cos\theta \cos\theta = a \cdot \cos^2\theta$$

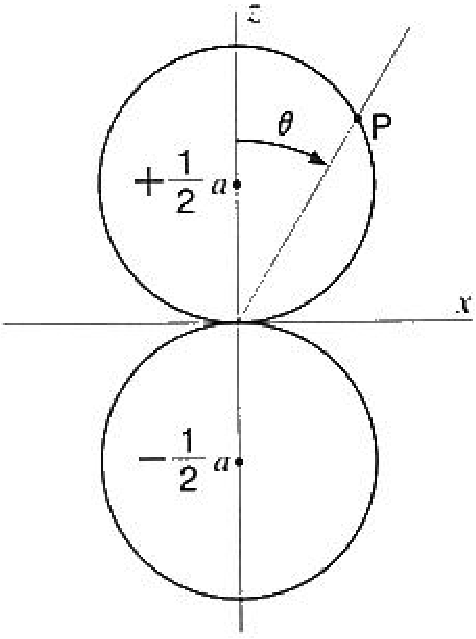
Therefore,

$$\begin{aligned} x^2 &= a^2 \cos^2\theta \sin^2\theta = a^2 \cos^2\theta (1 - \cos^2\theta) = a \cdot z - z^2 \\ &= -\left(z - \frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 \end{aligned}$$

Thus, we obtain

$$x^2 + \left(z - \frac{a}{2}\right)^2 = \left(\frac{a}{2}\right)^2$$

This is a circle with a radius of $a/2$ located at $(x, z) = (0, a/2)$. Another circle with a radius of $a/2$ located at $(x, z) = (0, -a/2)$ also satisfies the required condition, since $|\cos\theta| = -\cos\theta$ for $\pi/2 \le \theta \le \pi$. Thus, we obtain two circles of the same radius with centers on the z axis, which make contact with each other at the origin, as shown in the next figure.



As for $\phi \ne 0$, the above figure should be rotated at an angle ϕ around the z axis leading to a three dimensional figure composed of a pair of spheres as shown in Fig. 2.3.

2.2.4 The radial dependence and the radial distribution

The radial dependence of atomic orbitals on the distance r from the nucleus is determined by the radial part $R_{n,l}(r)$. The probability of finding an electron in a region between a pair of spheres with radii r and $r + dr$ is introduced as $D(r)dr$, and this $D(r)$ is defined as the radial distribution function, which is used to understand the radial dependence of the wave function. Fig. 2.4 shows some examples of $D(r)$ for a hydrogen atom. Derivation of the radial distribution function $D(r)$ will be made below. Since $D(r)$ becomes 0 where the radial part R has a node, there are $(n - l)$ maxima which is one more than the number of nodes for R. The largest value of $D(r)$ is located at the outermost maximum. The distance of the largest value $r_{\max}$ increases with the increase of n. $r_{\max}$ indicates the place where the probability of finding an electron is large, and this distance gives a measure for the size of electron shells as well as for the size of the atom and the bond length.

Let us derive a formula for $D(r)$. Integration of $D(r)$ from 0 to ∞ should be equal to the probability of finding an electron in the total space, which is the integrated value of the square of the wave function Ψ over the whole range of the three dimensional space. This value should be unity because of the normalization condition. Thus,

$$\int_0^{\infty} D(r)\mathrm{d}r = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi|^2 \mathrm{d}x\mathrm{d}y\mathrm{d}z = 1 \tag{2.26}$$

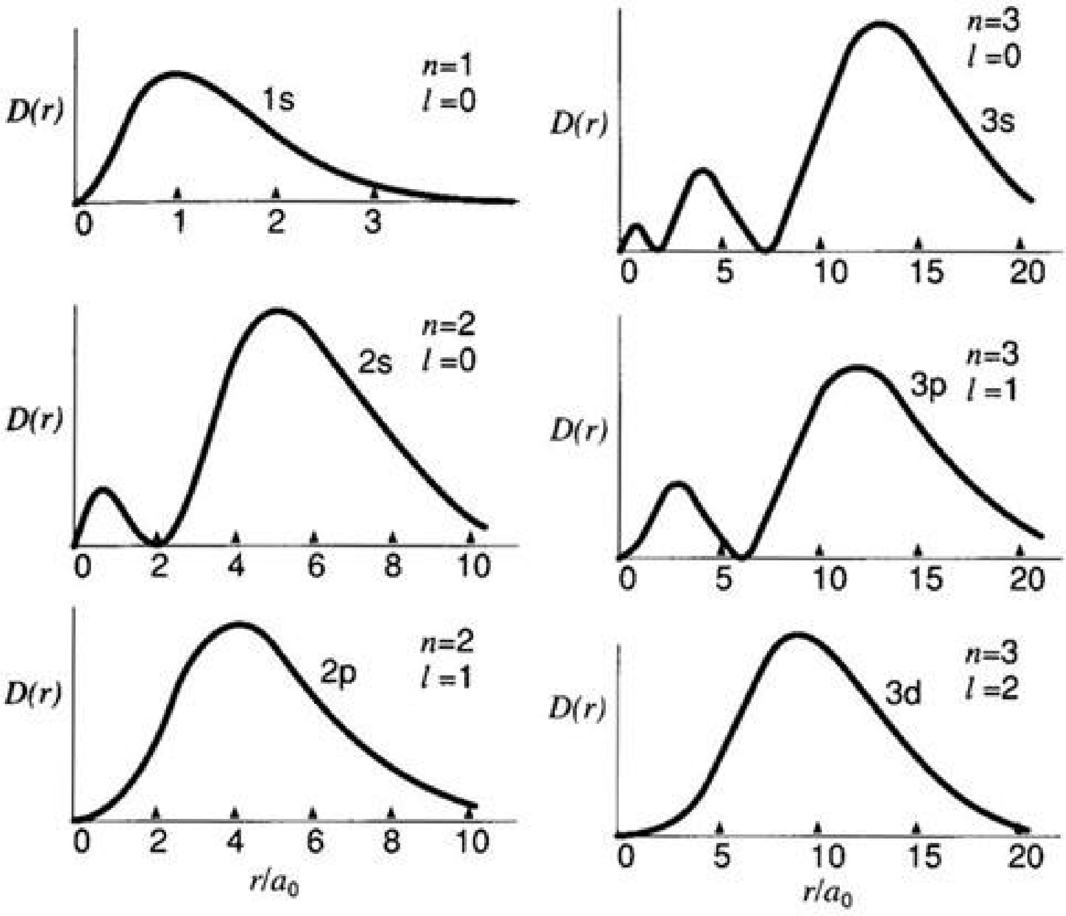


Figure 2.4: The radial distribution function $D(r) = r^2 R_{n,l}^2$

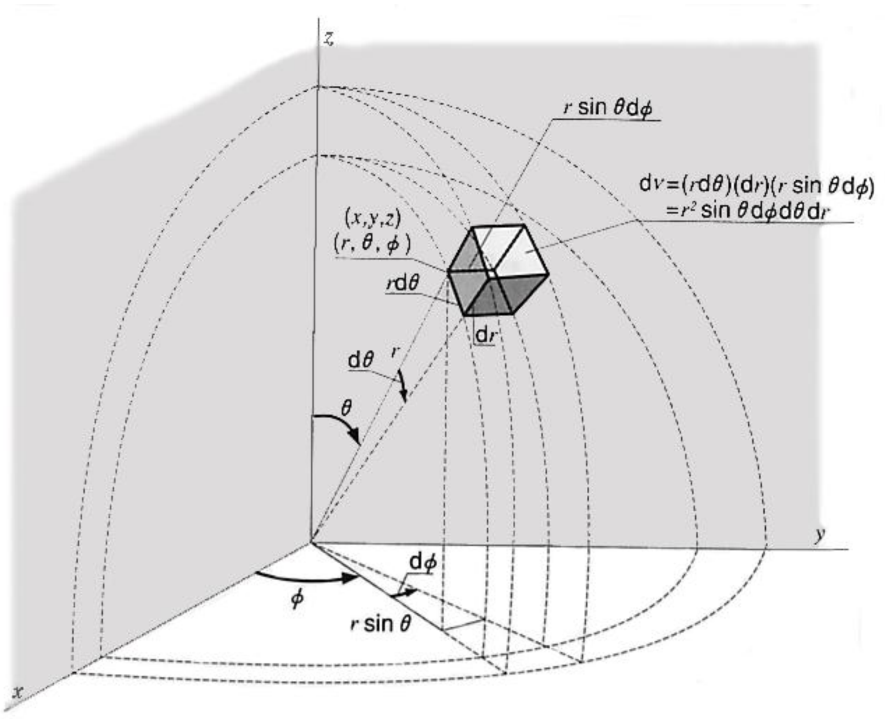


Figure 2.5: The volume element $\mathrm{d}v = r^2\sin\theta\mathrm{d}\phi\mathrm{d}\theta\mathrm{d}r$ for polar coordinates

As can be seen in Fig. 2.5, for polar coordinates (r, θ, ϕ), the volume element $\mathrm{d}v = \mathrm{d}x\mathrm{d}y\mathrm{d}z$ can be replaced by the following equation.

$$\mathrm{d}v = \mathrm{d}x\mathrm{d}y\mathrm{d}z = r^2 \sin\theta\mathrm{d}\phi\mathrm{d}\theta\mathrm{d}r \tag{2.27}$$

It should be noted that the ranges of the integration are from 0 to 2π for ϕ, from 0 to π for θ, and from 0 to ∞ for r. Substituting this replacement into the right side of eq.(2.26) and comparing it with the left side, we obtain the formula for $D(r)$ as the following integrations.

$$D(r) = \int_{0(\theta)}^{\pi} \int_{0(\phi)}^{2\pi} |\Psi|^2 r^2 \sin\theta\mathrm{d}\phi\mathrm{d}\theta \tag{2.28}$$

Next, replacement of Ψ by a product of the radial part R leads to an integration of the angular part Y with respect to the angles θ and ϕ, which is the same as the normalization condition of spherical harmonic functions Y.

$$\int\int |Y|^2 \sin\theta\mathrm{d}\phi\mathrm{d}\theta = 1 \tag{2.29}$$

Thus, we obtain a formula for $D(r)$ as follows.

$$D(r) = r^2 R_{n,l}(r)^2 \tag{2.30}$$

Example 2.3 Obtain $D(r)$ for 1s wave function for a hydrogenic atom.

(Solution) The 1s wave function for a hydrogenic atom is given as

$$\Psi_{1\mathrm{s}} = \Psi_{1,0,0} = R_{1,0}Y_{0,0}$$

Using the radial part of this wave function and eq.(2.30), the radial distribution function $D(r)$ is expressed as

$$D_{1\mathrm{s}}(r) = r^2 {R_{1,0}}^2$$

Here,

$$R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2} \mathrm{e}^{-(Z/a_0)r}$$

and we obtain

$$D_{1\mathrm{s}}(r) = 4\left(\frac{Z}{a_0}\right)^{3} r^2 \mathrm{e}^{-(2Z/a_0)r}$$

It is clear from the differentiation of this equation that the maximum of $D(r)$ is located at $r = a_0/Z$. In the case of a hydrogen atom ($Z = 1$), the distance for the maximum equals a_0, and this is nearly the same as the Bohr radius a_{B}.

2.2.5 Contour lines

Some devices are required to represent atomic wavefunctions, since they are functions of three-dimensional coordinates. For example, contour lines may be drawn on a certain plane for Ψ or $|\Psi|^2$ with the same value (Fig.2.6).

Since s orbitals have spherical symmetry, concentric circular lines will be drawn for any plane. On the other hand, $\mathrm{p}_x, \mathrm{p}_y$, and p_z orbitals have axial symmetries of the corresponding Cartesian axes, and thus the largest values appear as a pair of points on the axes at symmetric positions. The signs of the p functions for these pairs of points are opposite to each other. Since each p function changes its sign on reflection in the plane including the origin and being vertical to the axis, $\Psi = 0$ in the plane. In other words, each p function has a nodal plane vertical to the axis.

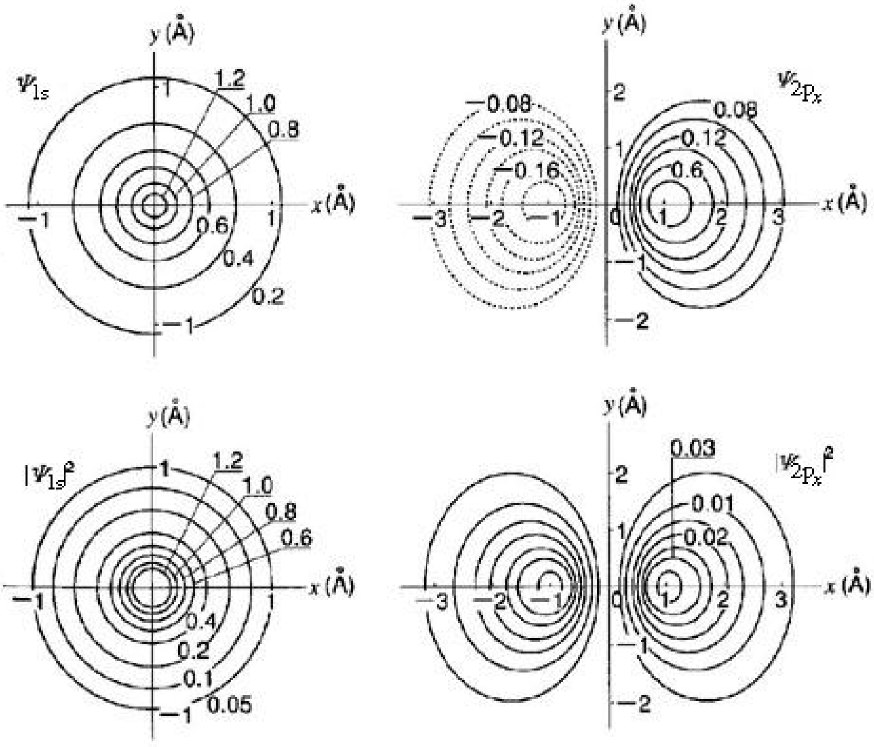


Figure 2.6: Contour lines for Ψ and $|\Psi|^2$

2.3 Many electron atoms

The problem to determining the motion of electrons in general atoms having many electrons is not so easy as the problem of hydrogenic atoms. This is largely due to the following two reasons. One reason is because interactions between electrons do not allow a treatment of independent motion of individual electrons. Another reason is due to the presence of angular momenta of electrons called electron spins which cannot easily be handled. Even for two electron systems such as a helium atom, the wave equation cannot be solved rigorously. Hence, approximate treatments are required. At the birth of the quantum theory, there was no modern computer so that problems of two or more electron systems (many electron systems) were handled with approximation methods such as perturbation or variation methods described in Chapter 3. In these days, variational treatments suitable to modern computers have been developed to enable us to perform calculations rather easily with some conventional program packages. In this section, characteristics of wavefunctions and energy levels for many electron atoms will be compared with those for hydrogenic atoms.

We may conclude here that the motion of individual electrons can be treated similarly to $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x$,
$2\mathrm{p}_y, 2\mathrm{p}_z$ atomic orbitals in hydrogenic atoms. Although energy levels of hydrogenic atoms depend only on the principal quantum number n, energy levels of many electron atoms with the same principal quantum number n may become different as the lower values of the azimuthal quantum number lead to the lower (more stable) energy levels. In the next section, consideration of electron spins will make it possible to understand electron configurations in atomic orbitals and their energy levels, which will be helpful to discuss individual properties of chemical elements.

2.3.1 Independent electron model

As mentioned for hydrogenic atoms, the motion of nucleus can be neglected with respect to the motion of electrons. Thus, nuclei are fixed at the equilibrium positions in dealing with many electron systems. Under this approximation, the Hamiltonian operator $\hat{H}$ for an N electron system is given by the following equation.

$$\hat{H} = \sum_{i=1}^{N} \left[-\left(\frac{\hbar^2}{2m}\right) \Delta_i - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{2.31}$$

Here, the inside of the parenthesis [ ] of the first term can be denoted as $\hat{h}_i$, which is an operator concerned with the coordinates of the i-th electron. r_{ij} in the right side denotes the distance between the i-th and the j-th electrons, and the terms including r_{ij} represent interactions between electrons. As an exchange of i and j in interactions between electrons also leads to the same pair of electrons, $i > j$ attached to the summation symbol Σ indicates to sum up only once for a pair of i and j. $\hat{h}_i$ is the same as the Hamiltonian operator $\hat{H}$ of a hydrogenic atom with $(\mu = m)$ except for the suffix i attached to Δ and r, and its characteristic equation and solutions are as follows.

$$\hat{h}_i \phi_{nlm} = \varepsilon_n \phi_{nlm} \tag{2.32}$$

$$\varepsilon_n = -\frac{mZ^2e^4}{8{\varepsilon_0}^2 h^2 n^2} \tag{2.33}$$

$$\phi_{n,l,m}(r_i, \theta_i, \phi_i) = R_{n,l}(r_i) \cdot Y_{l,m}(\theta_i, \phi_i) \tag{2.34}$$

$\phi_{n,l,m}$ is an atomic orbital representing the motion of an individual electron, as in the case of hydrogenic atoms. In general, the orbital function representing motion of an electron is called an orbital. The corresponding energy eigen value ε_0 is called an orbital energy.

The omission of interactions between electrons in the second terms of eq.(2.31) yields a Hamiltonian $\hat{H}_0$ of the following form.

$$\hat{H}_0 = \sum_{i=1}^{N} \hat{h}_i \tag{2.35}$$

The eigen equation of this $\hat{H}_0$ is $\hat{H}_0\Phi = E\Phi$, and it can be solved easily from eqs.(2.32)-(2.34) to give the following solutions.

$$\hat{H}_0\Phi_{n_1\cdots n_N} = E_{n_1\cdots n_N}\Phi_{n_1\cdots n_N} \tag{2.36}$$

$$\Phi_{n_1\cdots n_N} = \phi_{n_1}\phi_{n_2}\cdots\phi_{n_N} \tag{2.37}$$

$$E_{n_1\cdots n_N} = \varepsilon_{n_1} + \varepsilon_{n_2} + \cdots + \varepsilon_{n_N} \tag{2.38}$$

Here, the atomic orbital and the orbital energy for the first electron are shown as ϕ_{n_1} and ε_{n_1} rather than written as ϕ_{n_1,l_1,m_1} and $\varepsilon_{n_1,l_1,m_1}$ with three quantum numbers explicitly. This abbreviation is applied to the last ones of $\phi_{n_N}, \varepsilon_{n_N}$.

In hypothetical cases without interactions between electrons, the wave function and the energy for collective motion of electrons can be expressed in terms of orbitals and their energies for independent motion of individual electrons. Characteristic features for the independent electron model are as follows.

[**Characteristic features of the independent electron model**]

(1) The wave function for a many electron system is expressed as a product of wavefunctions for one-electron systems (orbitals).

(2) The energy for a many electron system is given as a simple summation of energies for one-electron systems (orbital energies).

The feature (1) indicates that the probability of finding an electron at a certain position is given as a product of the probabilities of finding individual electrons. The feature (2) suggests that the lowest energy state, the ground state, of a many electron system is realized when individual electrons are in their lowest energy states. Although occupation of all electrons in the 1s orbital is possible for H and He atoms, this is not allowed for all other atoms with the larger atomic numbers $Z \geq 3$. The reason will be given in Section 2.4 in connection with the electron spin.

2.3.2 Screening effect and effective nucleus charge model

Interactions between electrons are omitted in the independent electron model. However, such an approximate treatment is not appropriate for real systems, where interactions between electrons are significant. Let us consider effects of interactions between electrons by using a simple model.

Now, let us estimate the effect of repulsive forces caused by other electrons on an electron moving at a distance of r_0 from the nucleus. The electrostatics gives the following two features for the effects of repulsive interactions between electrons in an atom depending on the regions whether other electrons are located at $r > r_0$ or $r < r_0$, provided that the electron distribution is assumed to be spherical.

(1) There are no forces on average from the outer electrons ($r > r_0$).

(2) Forces to the outward direction are caused on average by the inner electrons, and this effect is equivalent to reducing the attractive force due to the nuclear charge, as if an electron is fixed on the nucleus to decrease the nuclear charge by one.

The effect of the inner electrons reducing the electric attractive forces by the nucleus is called the screening effect. The magnitude of the screening effect is larger for the outer electrons than for the inner electrons. The screening effect is considered to be equivalent to replacing the atomic number Z of the nucleus by the smaller number. The extent of the reduction s is introduced as the screening constant, and the effective nucleus charge $\overline{Z}$ is defined as $\overline{Z} = Z - s$. The screening constant s approximately represents the number of the inner electrons. If an electron is located in the outer most region, the screening constant for this electron will become $s = Z - 1$, and then the corresponding effective nucleus charge becomes $\overline{Z} = Z - (Z - 1) = 1$. This is important when we will discuss the periodicity of ionization energies.

If we replace Z in the first terms in eq.(2.31) by $\overline{Z}$ together with omission of the interactions between electrons, a Hamiltonian $\hat{H}$ of a model in which interactions between electrons are effectively included in the effective nucleus charge defined as $\overline{Z}$, given by

$$\hat{H} = \sum_{i=1}^{N} \left[-\left(\frac{\hbar^2}{2m} \right) \Delta_i - \frac{\overline{Z} e^2}{4\pi\varepsilon_0 r_i} \right] \tag{2.39}$$

This model is called the effective nuclear charge model. Rewriting the inside of [ ] in eq.(2.39) by $\hat{h}_i$, we obtain the same results as eqs.(2.36)-(2.38). It follows that the characteristic features mentioned for the independent electron model may also hold for the effective nuclear charge model. It should be noted that the orbital energies in eq.(2.33) are modified by the replacement of Z by $\overline{Z}$, which depends on the orbital type and especially on the relative order of the inner or the outer location with respect to other electrons. The effective nuclear charge model is useful to discuss electronic configurations of atoms and their periodicity.

2.3.3 Atomic orbitals and energy levels for many electron atoms

Based on the variation method, a theoretical treatment, which is much more rigorous and rational than the effective nuclear charge model, can be established to obtain orbital functions and energies for many electron systems. Characteristic features of such results by the variation method are described below.

The atomic orbital function ϕ is given as a product of the radial part $R'(r)$ and the angular part $Y(\theta, \phi)$ as in the case of the hydrogenic atoms, and these atomic orbitals are classified with a set of three quantum numbers, n, l, and m.

$$\phi_{n,l,m} = R_{n,l}{}'(r) \cdot Y_{l,m}(\theta, \phi) \tag{2.40}$$

$Y_{l,m}$ is the spherical harmonic, and $R'(r)$, which is different from $R(r)$ for hydrogenic atoms, is a function of r, qualitatively very similar to the hydrogenic function $R(r)$ in the aforementioned four respects concerning the asymptotic behavior and the nodes.

It follows that atomic orbitals are classified into 1s, 2s, $2\mathrm{p}_x$, $2\mathrm{p}_y$, $2\mathrm{p}_z$, 3s, $3\mathrm{p}_x$, $3\mathrm{p}_y$, $3\mathrm{p}_z$, $3\mathrm{d}_{xy}$, $3\mathrm{d}_{yz}$, $3\mathrm{d}_{zx}$, $3\mathrm{d}_{x^2-y^2}$, $3\mathrm{d}_{z^2}$, $\cdots$, as in the case of hydrogenic orbitals.

Energy levels with the same principal quantum number n are degenerate for hydrogenic atoms, while for more general many electron atoms, energies for orbitals with the same n may differ when the l values are different; the smaller l leads to the lower energy. For example, the order of 3s, 3p, and 3d orbital energies for many electron atoms are as follows.

$$3\mathrm{s}\,(l=0) < 3\mathrm{p}\,(l=1) < 3\mathrm{d}\,(l=2) \tag{2.41}$$

The reason for this is related to the magnitude of the screening effects. The smaller l becomes, the larger the probability of finding electrons in proximity to the nucleus, where the screening effects are not effective. Hence, the lower l leads to the stronger attractive force from the nucleus on average resulting in the lower energy and becoming more stable. If l is the same, the smaller n gives the lower energy, as in the case of hydrogenic atoms.

2.4 Electron spin

Electron orbitals and energy levels of many electron systems are classified into 1s, 2s, 2p, 3s, 3p, 3d, and so on as in the case of hydrogenic atoms. The problem is how the electrons are distributed into electron orbitals. Are all electrons incorporated into the most stable 1s orbital with the lowest energy ? The conclusion of the quantum theory is such that only two electrons can occupy the same orbital. This rule is related to the special angular momentum of the electron spin.

2.4.1 Experimental grounds for the electron spin

The existence of the electron spin was verified by some experiments.

(1) Atomic beam experiments by Stern and Gerlach

A stream of atoms can be produced in a vacuum through a nozzle after evaporation of silver or alkali metal by heating. Such a stream of atoms in vacuum is called an atomic beam. O. Stern and W. Gerlach discovered in 1922 that atomic beams of silver or sodium atoms, which have one electron in the outermost electron shell, split into two lines in an inhomogeneous magnetic field (Fig.2.7). This experiments suggested that an electron has a magnetic moment, which is a magnetic property associated with a circular electric current.

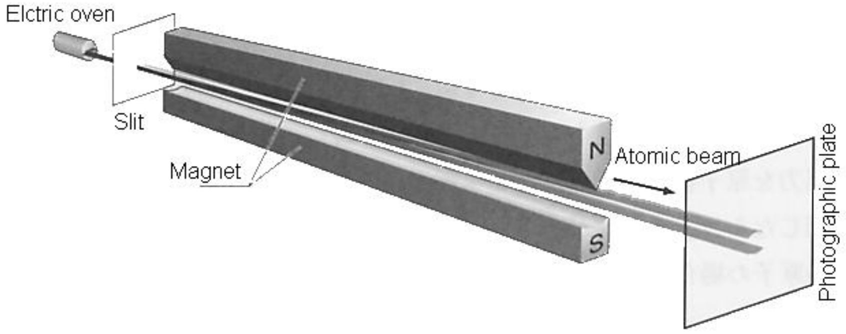


Figure 2.7: Atomic beam experiments by Stern and Gerlach

(2) Double lines (doublets) in the spectrum of an alkali metal atom

An orange light from the flame reaction of sodium is also emitted from a discharge lamp including sodium vapor. The dark lines (Fraunhofer lines) found in the spectrum of the sun light contain the same wavelength lines as the sodium flame spectrum, called D lines. The D lines of sodium originate from transitions between 3s and 3p levels, and they are observed as two adjacent lines (doublets) of 5895.93 Å and 5889.97 Å. Such doublets were also found for other alkali atoms, and intervals of the splitting were found to increase in the order of Li < Na < K < Rb < Cs. S.A.Goudsmit and G.E.Uhlenbeck proposed that the splitting of the spectral lines is due to the magnetic moment of an electron associated with its circular motion. Since an angular momentum is associated with circular motion of an electric charge, this angular momentum is the origin of the magnetic moment of an electron. The angular momentum associated with the circular motion of an electron is called electron spin.

2.4.2 Operators, eigen functions, and quantum numbers for electron spin

In order to consider electron spins in quantum mechanics, operators should be introduced similarly to the orbital angular momentum. Let us denote the spin angular momentum as $\hat{s}$ and its z-component as $\hat{s}_z$. By analogy with the orbital angular momentum, a common eigen function Γ for both $\hat{s}$ and $\hat{s}_z$ is expected to exist and to have the following relations.

$$\hat{s}^2\Gamma = s(s+1)\hbar^2\Gamma \tag{2.42}$$

$$\hat{s}_z\Gamma = m_s\hbar\Gamma \tag{2.43}$$

s is the quantum number for the square of the spin and is called the spin quantum number. m_s is the quantum number for the component and is called the spin magnetic quantum number. General rules for the angular momentum suggest that m_s should have $2s+1$ possible values of $s, s-1, \cdots, -s+1, -s$. By experiments, atomic beams are split into two components in a magnetic field, and spectra of alkali atoms are split into two lines. Based on these findings, m_s is concluded to have only two possible values. It follows that $2s+1 = 2$, and thus we obtain $s = 1/2$, $m_s = \pm 1/2$. It should be noted that the spin quantum number is a half integer with only one value of $s = 1/2$. Allowed values for m_s are limited to be $\pm 1/2$. The spin is a very special angular momentum in comparison with the orbital angular momentum.

Although such special properties of the spin angular momentum are difficult to be understood conceptually, their mathematical treatments are much more simplified. Because of only two allowed states, there are only two eigen functions. Usually, the spin function corresponding to $m_s = 1/2$ is denoted as α, and the other spin function for $m_s = -1/2$ is denoted as β.

$$\hat{s}_z\alpha = \frac{1}{2}\hbar\alpha \tag{2.44}$$

$$\hat{s}_z\beta = -\frac{1}{2}\hbar\beta \tag{2.45}$$

In connection with the orientation of the magnetic moment associated with the spinning motion, the upward one is called the α spin, and the downward one is called the β spin, respectively. The variable σ for spin functions $\alpha(\sigma), \beta(\sigma)$ is called the spin coordinate.

Although the significance of the spin coordinate σ is not clear, we need not to consider what it represents. The spin coordinate is the fourth coordinate following the other three coordinates for the position in the three dimensional space. Formally, allowed values for the spin coordinates are only two cases, the upward orientation of $\sigma = \uparrow$ and the downward orientation of $\sigma = \downarrow$.

$$\begin{array}{ll} \alpha(\uparrow) = 1, & \alpha(\downarrow) = 0 \\ \beta(\uparrow) = 0, & \beta(\downarrow) = 1 \end{array} \tag{2.46}$$

The probability of finding an electron at $\sigma = \uparrow$ is 1 in the upward spin state of α and 0 in the downward spin state β. On the other hand, the probability of finding an electron at $\sigma = \downarrow$ is 0 in the upward spin state of α and 1 in the downward spin state β.

In quantum mechanics, integrals are need to be calculated in connection with probabilities and normalization. As for the spin, a simple summation for the two coordinates $\uparrow$ and $\downarrow$ is only required. For example, eq.(2.46) leads to

$$\begin{aligned} \int |\alpha|^2 \mathrm{d}\sigma &= |\alpha(\uparrow)|^2 + |\alpha(\downarrow)|^2 \\ &= 1 + 0 = 1 \end{aligned} \tag{2.47}$$

and similarly

$$\begin{aligned} \int |\beta|^2 \mathrm{d}\sigma &= |\beta(\uparrow)|^2 + |\beta(\downarrow)|^2 \\ &= 0 + 1 = 1 \end{aligned} \tag{2.48}$$

In addition,

$$\begin{aligned} \int \alpha^* \beta \mathrm{d}\sigma &= \alpha^*(\uparrow)\beta(\uparrow) + \alpha^*(\downarrow)\beta(\downarrow) \\ &= 1 \cdot 0 + 0 \cdot 1 = 0 \end{aligned} \tag{2.49}$$

As can be seen from these calculations, the spin functions α, β in eq.(2.46) satisfy the orthonormality.

For a wave function Ψ of an electron considering the electron spin, the variables are the spatial coordinates x, y, z and the spin coordinate σ. If the component of the electron spin s_z has a certain value, the spin function is either α or β. It follows that the spatial orbital functions for Cartesian coordinates $\phi(x, y, z)$ lead to the following pair of wavefunctions for electrons accommodated in this spatial orbital.

$$\Psi(x, y, z, \sigma) = \phi(x, y, z) \cdot \alpha(\sigma) \tag{2.50}$$

$$\Psi(x, y, z, \sigma) = \phi(x, y, z) \cdot \beta(\sigma) \tag{2.51}$$

These equations are related with a rule that the number of electrons in each spatial orbital (in the case of an atom, $1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}_x, 2\mathrm{p}_y, 3\mathrm{d}_{xy}$ orbitals, etc.) should not exceed two.

2.4.3 Restriction to many-electron wavefunctions and the Pauli principle

The question of how many electrons can occupy an atomic orbital such as the 1s orbital is an important problem in connection with atomic spectra and atomic properties. The solution of this problem was given by Pauli in 1924, and it is a rule called the Pauli principle or The Pauli exclusion principle.

[**The Pauli principle (The exclusion principle)**]

Each orbital can be occupied by an electron with α spin or β spin, but it cannot be occupied by two or more electrons with the same spin.

This rule is established by Pauli, based on experimental results such as atomic spectra. It is very important that electrons obey this rule, in connection with the construction of many-electron wavefunctions.

Let us consider two electrons. One is located at a coordinate q_1 and the other at q_2. This state is represented by a wave function written as $\Psi(q_1, q_2)$. Similarly, a state of two electrons with their coordinates interchanged may be written as $\Psi(q_2, q_1)$. Although $\Psi(q_1, q_2)$ and $\Psi(q_2, q_1)$ are mathematically different expressions specifying the numbering of the electrons as 1 and 2, we cannot recognize any difference of the numbering when we observe the electrons. It follows that the probability of finding the number 1 electron at q_1 and the number 2 electron at q_2 should be exactly the same as the probability finding the number 1 electron at q_2 and the number 2 electron at q_1. This condition is expressed by the following equation.

$$|\Psi(q_1, q_2)|^2 = |\Psi(q_2, q_1)|^2 \tag{2.52}$$

Noting that wavefunctions are complex numbers in general, we obtain

$$\Psi(q_1, q_2) = \exp(i\theta) \cdot \Psi(q_2, q_1) \tag{2.53}$$

The initial choice of the two electrons as well as their geometries is arbitrary. Thus, it is not reasonable to assume that the constant θ in eq.(2.53) is different depending on the choice of electrons and their geometries. Therefore, the same relationship should hold for an interchange of q_1 and q_2.

$$\Psi(q_2, q_1) = \exp(i\theta) \cdot \Psi(q_1, q_2) \tag{2.54}$$

These two equations lead to

$$\Psi(q_1, q_2) = \exp(i\theta)^2 \cdot \Psi(q_1, q_2) \tag{2.55}$$

Thus,

$$\exp(i\theta)^2 = \exp(2i\theta) = 1 \tag{2.56}$$

This leads to

$$\exp(i\theta) = \pm 1 \tag{2.57}$$

It follows that

$$\Psi(q_2, q_1) = \pm\Psi(q_1, q_2) \tag{2.58}$$

Namely, the sign of a wave function is either unchanged or changed when a pair of identical particles are interchanged with their geometrical coordinates.

The nature of the particles determines which of the two possibilities is the case.

(1) For the sign unchanged with a multiplication of $+1$, wavefunctions are symmetric with respect to the interchange of coordinates, and this type of particle is called a Bose particle or Boson.

(2) For the sign changed with a multiplication of -1, wavefunctions are antisymmetric with respect to the interchange of coordinates, and this type of particle is called a Fermi particle or Fermion.

The Pauli principle shows that electrons are Fermions and that the wave function changes its sign on the interchange of the coordinates.

If a symmetric wave function were allowed for electrons, it would contradict the Pauli principle. For example, let us assume that there are two electrons occupying the 1s orbital with α spin. The corresponding wave function Ψ for this assumption is expressed with the orbital function ϕ_{1s} as follows.

$$\begin{aligned}&\Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)\\&= \phi_{1s}(x_1, y_1, z_1)\alpha(\sigma_1)\phi_{1s}(x_2, y_2, z_2)\alpha(\sigma_2)\end{aligned} \tag{2.59}$$

Now, let us interchange the coordinates of number 1 and number 2, and then we obtain

$$\begin{aligned}
&\Psi(x_2, y_2, z_2, \sigma_2, x_1, y_1, z_1, \sigma_1) \\
&= \phi_{1s}(x_2, y_2, z_2)\alpha(\sigma_2)\phi_{1s}(x_1, y_1, z_1)\alpha(\sigma_1) \\
&= \phi_{1s}(x_1, y_1, z_1)\alpha(\sigma_1)\phi_{1s}(x_2, y_2, z_2)\alpha(\sigma_2) \\
&= \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)
\end{aligned} \tag{2.60}$$

This clearly shows the symmetry of wavefunctions for a Boson. In other words, if electrons are Bosons, there would be two or more electrons occupying the same $1s\alpha$ state in an atom. However, this situation contradicts the Pauli principle.

On the other hand for an antisymmetric wave function, no state that contradicts the Pauli principle is acceptable. This feature can be seen easily when a determinant wave function, which is proposed by J. C. Slater and is called a Slater determinant, is used.

Let us introduce two orbital functions ψ_1, and ψ_2 which include spin coordinates in addition to spatial coordinates. We write the wave function Ψ for the system of 2 electrons as the following determinant.

$$\Psi(q_1, q_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(q_1) & \psi_2(q_1) \\ \psi_1(q_2) & \psi_2(q_2) \end{vmatrix} \tag{2.61}$$

After expansion, we obtain the following equations showing the antisymmetric character.

$$\begin{aligned}
\Psi(q_1, q_2) &= \frac{1}{\sqrt{2}}\{\psi_1(q_1)\psi_2(q_2) - \psi_1(q_2)\psi_2(q_1)\} \\
&= -\frac{1}{\sqrt{2}}\{\psi_1(q_2)\psi_2(q_1) - \psi_1(q_1)\psi_2(q_2)\} \\
&= -\Psi(q_2, q_1)
\end{aligned} \tag{2.62}$$

It should be noted here that the Hamiltonian $\hat{H}$ is invariant on the interchange of coordinates of identical particles, and that if $\Psi = \psi_1(q_1)\psi_2(q_2)$ is a solution of $\hat{H}\Psi = E\Psi$, then $\Psi = \psi_1(q_2)\psi_2(q_1)$ is also a solution of $\hat{H}\Psi = E\Psi$. It follows that the above determinant satisfies $\hat{H}\Psi = E\Psi$. Using a determinant as proposed by Slater, we can construct an antisymmetric wave function composed of orbital functions.

Now, let us assume again that there are two electrons occupying the 1s orbital with the same α spin. In this case, $\psi_1 = \phi_{1s} \cdot \alpha$, $\psi_2 = \phi_{1s} \cdot \alpha$, that is $\psi_1 = \psi_2$. Thus, we may omit the suffixes as $\psi_1 = \psi_2 = \psi$. The determinant wave function for this system becomes

$$\begin{aligned}
\Psi(q_1, q_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(q_1) & \psi_2(q_1) \\ \psi_1(q_2) & \psi_2(q_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi(q_1) & \psi(q_1) \\ \psi(q_2) & \psi(q_2) \end{vmatrix} \\
&= \frac{1}{\sqrt{2}}\{\psi(q_1)\psi(q_2) - \psi(q_2)\psi(q_1)\} = 0
\end{aligned} \tag{2.63}$$

The vanishing value of this determinant is a necessary result of a general rule for determinants that a determinant with a pair of the same rows or the same columns becomes vanishing. If this rule is used, the determinant in eq.(2.63) is easily found to be vanishing without expansion. Based on this result, it is easily seen that a configuration of electrons occupying orbitals in contradiction with the Pauli principle leads to a physically unacceptable wave function with a vanishing value indicating no particles at all. Careful and detailed inspections have shown that antisymmetric wavefunctions are compatible with the Pauli principle. It follows that electrons are Fermions with the antisymmetric character.

Hence, it is convenient to express a many-electron wave function as a determinant of a matrix in which orbital functions are arrayed. A determinant wave function composed of normalized orbital functions is also normalized as a many electron function, provided that a factor of $1/\sqrt{N!}$ is attached. In order to express a determinant wave function in a short form, we may write it as $|\psi_1\psi_2 \cdots \psi_N|$ by an array of orbital functions $\{\psi_i\}$ between a pair of vertical bars.

An array of orbital functions in a matrix form is equivalent to making an electron configuration corresponding to occupation of the electrons in respective orbitals. This in other words implies that electrons occupy the respective electron energy levels. Thus, the situation of electrons occupying certain orbitals or levels is called electron configuration or electronic configuration. Determinant wavefunctions are used as the mathematical expressions of electron configuration. The conceptual treatment of making an electron configuration can be understood as the occupation of orbitals by electrons.

The construction of determinant wavefunctions has no physical significance if its value is vanishing in contradiction with the existence of electrons. In order to avoid such a nonsensical situation, care should be taken so that no identical orbital functions may be included in the array of orbitals in the determinant. In other words, we should not use the same combination of a function of spatial coordinates and a spin function more than once in the determinant. The use of determinant wave functions guarantees the satisfaction of the antisymmetric properties of electrons, and hence electron configurations contradicting Pauli principle are automatically avoided, since values of such determinants are vanishing.

2.5 Electron configuration in atoms

Based on spectroscopic experiments and quantum theoretical studies, the electron configurations in the ground states of atoms were determined as shown in Table 2.4.

[Construction principle of electron configurations in atoms]

Electron configurations in the ground states of atoms can be constructed by the following rules.

(1) Electrons occupy preferentially the lower energy orbitals according to the order of the orbital energies.

(2) The order of the orbital energies are as follows.

$$\begin{aligned} &1\mathrm{s} < 2\mathrm{s} < 2\mathrm{p} < 3\mathrm{s} < 3\mathrm{p} < (4\mathrm{s}, 3\mathrm{d}) < 4\mathrm{p} < (5\mathrm{s}, 4\mathrm{d}) \\ &< 5\mathrm{p} < (6\mathrm{s}, 4\mathrm{f}, 5\mathrm{d}) < 6\mathrm{p} < (7\mathrm{s}, 5\mathrm{f}, 6\mathrm{d}) \end{aligned} \tag{2.64}$$

The items on the left are more stable with lower energy than the items on the right. Among orbitals in the same parentheses, the left ones are preferred to be occupied, though the order may be reversed sometimes.

(3) The Pauli principle should be satisfied. Namely, the allowed occupancy of orbitals is one of the following four cases.

(4) ns orbitals are occupied by 0∼2 electrons.
np orbitals is classified into three types, $n\mathrm{p}_x, n\mathrm{p}_y, n\mathrm{p}_z$, and each orbital is occupied by 0∼2 electrons. Altogether, np orbitals can be occupied by 0∼6 electrons.
There are five types for nd orbitals. Each one is occupied by 0∼2 electrons. Altogether, nd orbitals can be occupied by 0∼10 electrons.
There are seven types for nd orbitals. Each one is occupied by 0∼2 electrons. Altogether, nf orbitals can be occupied by 0∼14 electrons.

(5) Configurations in which two or more electrons occupy orbitals with the same energy should follow Hund's rule.
Hund's rule (1) Electrons are separated in different orbitals as far as possible.
Hund's rule (2) Spins are aligned to be parallel as far as possible.

Hund's rule (1) is a rule to reduce the increase of the interaction energy due to repulsion between electrons, for which separation of electrons in different orbitals is effective. Hund's rule 2 is a propensity that spins with the same directions tend to be more stabilized. Consideration of these rules leads to the following order of the total energies for electronic configurations of two-electron systems in a pair of equivalent orbitals.

(2.65)

As an example, let us construct the electron configuration of a Ga atom with the atomic number 31. $1s, 2s, 2p, 3s, 3p, 4s$, and 3d orbitals are occupied by $2+2+6+2+6+2+10=30$ electrons. The remaining $31-30=1$ electron occupies a 4p orbital. Thus, the electron configuration of a Ga atom, [Ga], is expressed as follows.

$$[\mathrm{Ga}] = (1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^6(3\mathrm{s})^2(3\mathrm{p})^6(4\mathrm{s})^2(3\mathrm{d})^{10}(4\mathrm{p})^1$$

The insides of ( ) represent orbitals with the same principal quantum number n and the same azimuthal quantum number l, a part of the electron shells, and thus they are called subshells. The right-hand superscript attached to ( ) denotes the total number of electrons occupying the subshell. When the number of electrons is 1, the figure 1 of the right-hand superscript may be omitted. Among electron shells having electrons, the electron shell of the largest n is called the outermost shell. In the case of Ga, $n \leq 4$, and thus the N shell is the outermost shell.

Typical examples of electron configurations are shown for some atoms.

Examples of electron configurations of atoms

$[\mathrm{He}] = (1\mathrm{s})^2$

$[\mathrm{Li}] = (1\mathrm{s})^2(2\mathrm{s})^1 = [\mathrm{He}](2\mathrm{s})^1$

$[\mathrm{Ne}] = [\mathrm{He}](2\mathrm{s})^2(2\mathrm{p})^6$

$[\mathrm{Ar}] = [\mathrm{Ne}](3\mathrm{s})^2(3\mathrm{p})^6$

$[\mathrm{Cr}] = [\mathrm{Ar}](4\mathrm{s})^1(3\mathrm{d})^5$

$[\mathrm{Fe}] = [\mathrm{Ar}](4\mathrm{s})^2(3\mathrm{d})^6$

$[\mathrm{Cu}] = [\mathrm{Ar}](4\mathrm{s})^1(3\mathrm{d})^{10}$

$[\mathrm{Ge}] = [\mathrm{Ar}](4\mathrm{s})^2(3\mathrm{d})^{10}(4\mathrm{p})^2$

Here, it should be noted that electron configurations for Cr and Cu are exceptions of the order among the inside of ( ) for the rule (2) in the construction principle; the configuration of the (4s) subshell is $(4s)^1$ rather than $(4s)^2$, and one electron occupies a 3d orbital so that the (3d) subshell becomes a half-occupied configuration of $(3d)^5$ or a fully occupied configuration of $(3d)^{10}$.

Exercise 2.4 Show the electron configuration of a carbon atom using electron energy levels.

(Solution) The electron configuration of a C atom is

$[\mathrm{C}] = (1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^2$

Since atomic orbitals up to 2p are occupied by electrons, electron energy levels from 1s to 2p should be shown, and the higher levels may be omitted. According to Hund's rules (1) and (2), the electron configuration for (2p) subshell becomes the following spin parallel configuration.

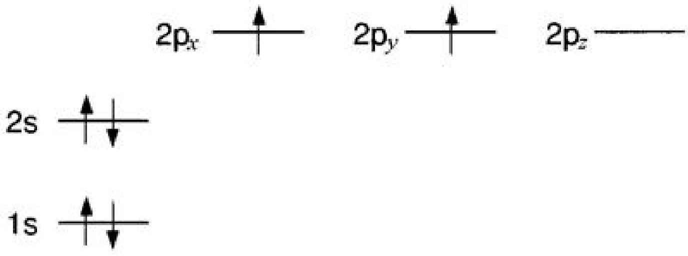


Table 2.4: Electron configurations of atomic ground-states and spectral terms

period	shell	K	L		M			N				O				term
	orbital	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	
1	1 H	1														$^2S_{1/2}$
	2 He	2														$^1S_0$
2	3 Li	2	1													$^2S_{1/2}$
	4 Be	2	2													$^1S_0$
	5 B	2	2	1												$^2P_{1/2}$
	6 C	2	2	2												$^3P_0$
	7 N	2	2	3												$^4S_{3/2}$
	8 O	2	2	4												$^3P_2$
	9 F	2	2	5												$^2P_{3/2}$
	10 Ne	2	2	6												$^1S_0$
3	11 Na	2	2	6	1											$^2S_{1/2}$
	12 Mg	2	2	6	2											$^1S_0$
	13 Al	2	2	6	2	1										$^2P_{1/2}$
	14 Si	2	2	6	2	2										$^3P_0$
	15 P	2	2	6	2	3										$^4S_{3/2}$
	16 S	2	2	6	2	4										$^3P_2$
	17 Cl	2	2	6	2	5										$^2P_{3/2}$
	18 Ar	2	2	6	2	6										$^1S_0$
4	19 K	2	2	6	2	6		1								$^2S_{1/2}$
	20 Ca	2	2	6	2	6		2								$^1S_0$
	21 Sc	2	2	6	2	6	1	2								$^2D_{3/2}$
	22 Ti	2	2	6	2	6	2	2								$^3F_2$
	23 V	2	2	6	2	6	3	2								$^4F_{3/2}$
	24 Cr	2	2	6	2	6	5	1								$^7S_3$
	25 Mn	2	2	6	2	6	5	2								$^6S_{5/2}$
	26 Fe	2	2	6	2	6	6	2								$^5D_4$
	27 Co	2	2	6	2	6	7	2								$^4F_{9/2}$
	28 Ni	2	2	6	2	6	8	2								$^3F_4$
	29 Cu	2	2	6	2	6	10	1								$^2S_{1/2}$
	30 Zn	2	2	6	2	6	10	2								$^1S_0$
	31 Ga	2	2	6	2	6	10	2	1							$^2P_{1/2}$
	32 Ge	2	2	6	2	6	10	2	2							$^3P_0$
	33 As	2	2	6	2	6	10	2	3							$^4S_{3/2}$
	34 Se	2	2	6	2	6	10	2	4							$^3P_2$
	35 Br	2	2	6	2	6	10	2	5							$^2P_{3/2}$
	36 Kr	2	2	6	2	6	10	2	6							$^1S_0$
5	37 Rb	2	2	6	2	6	10	2	6			1				$^2S_{1/2}$
	38 Sr	2	2	6	2	6	10	2	6			2				$^1S_0$
	39 Y	2	2	6	2	6	10	2	6	1		2				$^2D_{3/2}$
	40 Zr	2	2	6	2	6	10	2	6	2		2				$^3F_2$
	41 Nb	2	2	6	2	6	10	2	6	4		1				$^6D_{1/2}$
	42 Mo	2	2	6	2	6	10	2	6	5		1				$^7S_3$
	43 Tc	2	2	6	2	6	10	2	6	5		2				$^6S_{5/2}$
	44 Ru	2	2	6	2	6	10	2	6	7		1				$^5F_5$
	45 Rh	2	2	6	2	6	10	2	6	8		1				$^4F_{9/2}$
	46 Pd	2	2	6	2	6	10	2	6	10						$^1S_0$
	47 Ag	2	2	6	2	6	10	2	6	10		1				$^2S_{1/2}$
	48 Cd	2	2	6	2	6	10	2	6	10		2				$^1S_0$
	49 In	2	2	6	2	6	10	2	6	10		2	1			$^2P_{1/2}$
	50 Sn	2	2	6	2	6	10	2	6	10		2	2			$^3P_0$
	51 Sb	2	2	6	2	6	10	2	6	10		2	3			$^4S_{3/2}$
	52 Te	2	2	6	2	6	10	2	6	10		2	4			$^3P_2$
	53 I	2	2	6	2	6	10	2	6	10		2	5			$^2P_{3/2}$
	54 Xe	2	2	6	2	6	10	2	6	10		2	6			$^1S_0$

period	shell	K	L	M	N				O					P						Q	term
	orbital				4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s···	
6	55 Cs	2	8	18	2	6	10		2	6				1							$^2S_{1/2}$
	56 Ba	2	8	18	2	6	10		2	6				2							$^1S_0$
	57 La	2	8	18	2	6	10		2	6	1			2							$^2D_{3/2}$
	58 Ce	2	8	18	2	6	10	1	2	6	1			2							$^3H_4$
	59 Pr	2	8	18	2	6	10	3	2	6				2							^4I
	60 Nd	2	8	18	2	6	10	4	2	6				2							$^5I_4$
	61 Pm	2	8	18	2	6	10	5	2	6				2							^6H
	62 Sm	2	8	18	2	6	10	6	2	6				2							$^7F_0$
	63 Eu	2	8	18	2	6	10	7	2	6				2							$^8S_{7/2}$
	64 Gd	2	8	18	2	6	10	7	2	6	1			2							$^9D_2$
	65 Tb	2	8	18	2	6	10	9	2	6				2							$^6H_{17/2}$
	66 Dy	2	8	18	2	6	10	10	2	6				2							^5I
	67 Ho	2	8	18	2	6	10	11	2	6				2							^4I
	68 Er	2	8	18	2	6	10	12	2	6				2							^3H
	69 Tm	2	8	18	2	6	10	13	2	6				2							$^2F_{7/2}$
	70 Yb	2	8	18	2	6	10	14	2	6				2							$^1S_0$
	71 Lu	2	8	18	2	6	10	14	2	6	1			2							$^2D_{3/2}$
	72 Hf	2	8	18	2	6	10	14	2	6	2			2							$^3F_2$
	73 Ta	2	8	18	2	6	10	14	2	6	3			2							$^4F_{3/2}$
	74 W	2	8	18	2	6	10	14	2	6	4			2							$^5D_0$
	75 Re	2	8	18	2	6	10	14	2	6	5			2							$^6S_{5/2}$
	76 Os	2	8	18	2	6	10	14	2	6	6			2							$^5D_4$
	77 Ir	2	8	18	2	6	10	14	2	6	7			2							$^4F_{9/2}$
	78 Pt	2	8	18	2	6	10	14	2	6	9			1							$^3D_3$
	79 Au	2	8	18	2	6	10	14	2	6	10			1							$^2S_{1/2}$
	80 Hg	2	8	18	2	6	10	14	2	6	10			2							$^1S_0$
	81 Tl	2	8	18	2	6	10	14	2	6	10			2	1						$^2P_{1/2}$
	82 Pb	2	8	18	2	6	10	14	2	6	10			2	2						$^3P_0$
	83 Bi	2	8	18	2	6	10	14	2	6	10			2	3						$^4S_{3/2}$
	84 Po	2	8	18	2	6	10	14	2	6	10			2	4						$^3P_2$
	85 At	2	8	18	2	6	10	14	2	6	10			2	5						$^2P_{3/2}$
	86 Rn	2	8	18	2	6	10	14	2	6	10			2	6						$^1S_0$
7	87 Fr	2	8	18	2	6	10	14	2	6	10			2	6					1	$^2S_{1/2}$
	88 Ra	2	8	18	2	6	10	14	2	6	10			2	6					2	$^1S_0$
	89 Ac	2	8	18	2	6	10	14	2	6	10			2	6	1				2	$^2D_{3/2}$
	90 Th	2	8	18	2	6	10	14	2	6	10			2	6	2				2	$^3F_2$
	91 Pa	2	8	18	2	6	10	14	2	6	10	2		2	6	1				2	
	92 U	2	8	18	2	6	10	14	2	6	10	3		2	6	1				2	$^5L_4$
	93 Np	2	8	18	2	6	10	14	2	6	10	4		2	6	1				2	
	94 Pu	2	8	18	2	6	10	14	2	6	10	6		2	6					2	
	95 Am	2	8	18	2	6	10	14	2	6	10	7		2	6					2	$^8S_{7/2}$
	96 Cm	2	8	18	2	6	10	14	2	6	10	7		2	6	1				2	
	97 Bk	2	8	18	2	6	10	14	2	6	10	(8)		2	6	(1)				2	
	98 Cf	2	8	18	2	6	10	14	2	6	10	(9)		2	6	(1)				2	

(Note) In the 6-th or 7-th period, the total number of electrons is only shown for K, L, and M shells since they are fully occupied.

2.6 The periodicity

The properties of the elements exhibit a periodicity, which originates from the periodicity in electron configurations. In this section, ionization energies and electron affinities are studied in connection with the periodicity. First, experimental results are surveyed, and then relations with electron configurations are discussed.

2.6.1 Ionization energy and electron affinity

The energy required to make the $n + 1$ valent ionic state by removing an electron from the n valent ionic state of a matter is called the $n + 1$-th ionization energy. This definition may be applied to $n \geq 0$. In the case of $n = 0$, namely the energy required to remove an electron from neutral matter is called the first ionization energy. Usually, the ionization energy denotes the first ionization energy. Figure 2.8. and Table 2.5. show the periodicity of the first ionization energies for atoms, and their main features are as follows.

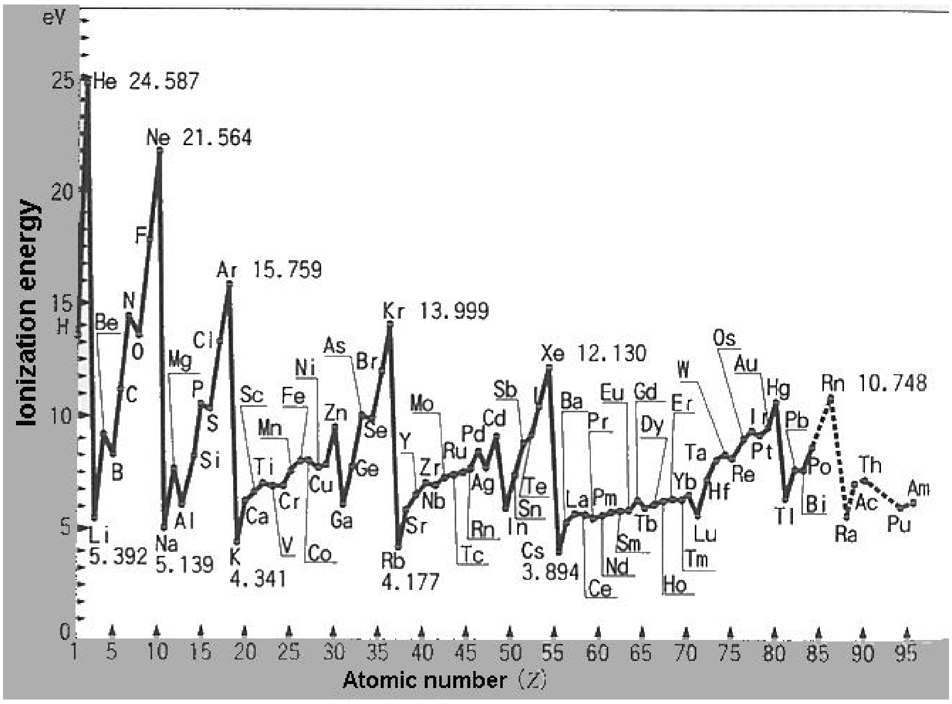


Figure 2.8: The periodicity of ionization energy

Feature (1) Associated with the increase of the atomic number, maxima are found at the rare gas atoms.

Feature (2) Associated with the increase of the atomic number, minima together with sudden drops from rare gas atoms are found at the alkali metal atoms.

Feature (3) Along the same row of the periodic Table, an increasing propensity is found as a whole on going from alkali metal atoms to rare gas atoms.

Feature (4) Fine features along the same row of the periodic Table include small maxima at the second or the fifteenth group together with minima at the next group.

Feature (5) In the same group, a decreasing propensity is found on going downward in the periodic Table.

Table 2.5: Ionization energies of atoms(eV)

H																	He
13.6																	24.6
Li	Be											B	C	N	O	F	Ne
5.4	9.3											8.3	11.3	14.5	13.6	17.4	21.6
Na	Mg											Al	Si	P	S	Cl	Ar
5.1	7.6											6.0	8.1	11.0	10.4	13.0	15.8
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	8.1	10.0	9.8	11.8	14.0

The energy emitted on attachment of an electron to electrically neutral matter is called the electron affinity, which is equivalent to the energy required to remove an electron from a monovalent negative ion. Electron affinities for atoms also exhibit a periodicity variation as shown in Table 2.6. Although their propensities for variations along vertical and horizontal arrays in the periodic Table are largely similar to those for ionization energies, locations of the outstanding maxima are displaced to halogen atoms from rare gas atoms, and minima are shifted to rare gas atoms.

Table 2.6: Electron affinities of atoms(eV)

H																	He
0.75																	< 0
Li	Be											B	C	N	O	F	Ne
0.62	< 0											0.28	1.27	-0.1	1.46	3.40	< 0
Na	Mg											Al	Si	P	S	Cl	Ar
0.55	< 0											0.46	1.39	0.74	2.08	3.62	< 0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.50	< 0	< 0	0.2	0.5	0.66	< 0	0.25	0.7	1.15	1.23	~ 0	0.30	1.2	0.80	2.02	3.36	< 0

Various methods were devised for measuring the energy W required to remove one electron. For example, based on a method similar to the study of the photoelectric effect, the kinetic energy $\frac{1}{2}mv^2$ of electrons ejected from matter irradiated with a photon of $h\nu$ can be determined, and then W is obtained from the following formula.

$$W = h\nu - \frac{1}{2}mv^2 \tag{2.66}$$

This method is often used for the measurement of ionization energies and electron affinities.

2.6.2 Effective nuclear charge and rules to calculate screening constants

On account of the periodicity in electron configurations, effective nuclear charges of atoms are closely related to the periodicity in ionization energies and electron affinities. Let us study how effective nuclear charges depend on the screening effects mentioned in section 2.3.

In order to obtain the effective nuclear charge $\bar{Z}$, the screening constant s should be determined in addition to the atomic number Z. The screening constant s can be estimated easily based on the following rules.

[Rules to calculate screening constants]

(1) Since screening effects are caused by the repulsive forces of the other electrons against the electron concerned, the screening constant is estimated as a sum of contributions due to individual electrons.

(2) Since screening effects depend crucially on the location of the electrons, whether inside or outside of the electron concerned, as mentioned in section 2.3, relative positions of electron orbitals in atoms are classified into the following groups divided with slashes.

/1s/2s, 2p/3s, 3p/3d/4s, 4p/4d/4f/5s, 5p/5d/5f/

From the left to the right, the orbitals expand from the most inward to the most outward. *ns* and *np* belong to the same group considering the similar location of these orbitals.

(3) Contributions due to electrons of the outer groups are 0, since they do not cause screening effects.

(4) Contributions due to electrons of the same group are considered to be 1/3, because of incomplete screening effects associated with the relative probability of residing in the inward region.

(5) Contributions due to electrons of the inner groups are set equal to 1, since the inner electrons give complete screening effects.

The above rules are simplified versions of Slater's rules in 1930, from which the essential parts are only retained. The rules (1)-(3) are the same. As for (4), Slater introduced a subtle difference between 1s and other orbitals, 0.30 for 1s and 0.35 for others. Though (5) is the same except for electrons in ns or np, Slater considered that electrons in $(n-1)$s or $(n-1)$p have contributions of 0.85 for the screening with respect to the selected electron in the n-th shell, since the screening effects may be incomplete for the nearly overlapping electron shells. Slater's rules have been used to construct atomic orbital functions by simple treatments for various atoms, and they played important roles especially in early days of quantum chemistry. Atomic orbital functions with a form proposed by J. C. Slater are called Slater type orbital(STO), and they have been used even in recent program packages for quantum chemistry.

2.6.3 Effective nuclear charge and ionization energies

Loosely bound electrons in the outermost electron shell are the most important to be considered for ionization energies of atoms. Now, let us estimate the effective nuclear charge for an electron in the outermost electron shell, using the above rules for screening constants. For example, we consider a 2p electron of a fluorine atom F (Z=9). The electron configuration of a F atom is as follows.

$$(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^5$$

On the inner side of the noted 2p electron, there are two 1s electrons, which yield a contribution of 1×2 from the rule (5). In the same region as 2p, there are six electrons altogether, two 2s electrons and 5-1=4 electrons in 2p, which give a contribution of $\frac{1}{3} \times 6$ from the rule (4). Thus, $s = 1 \times 2 + \frac{1}{6} = 4$, and it follows that the effective nucleus charge $\bar{Z}$ becomes $\bar{Z} = Z - s = 9 - 4 = 5$.

Table 2.7 lists the effective nuclear charges for an electron in the outermost shell of atoms from hydrogen H to argon Ar, which are estimated on the basis of the above rules for screening constants. Features (1) $\sim$ (5) found for the periodicity in ionization energies can now be discussed in terms of the effective nuclear charges listed in the Table. Since ionization energies increase, associated with the increase of the attractive force by the nucleus, there should be the following two tendencies.

(Tendency 1): Ionization energies increase with the increase of the effective nuclear charge, because of the dependence of the Coulomb force on the electric charge.

(Tendency 2): Ionization energies decrease with the electron shell becoming more outer, because of the dependence of the Coulomb force on the distance.

Within a row in the periodic Table, valence electrons belong to the same electron shell, and effective nucleus charges increase on going from the left to the right. It follows that Tendency 1 explains the Feature 3 that along the same row ionization energies increase from the left to the right. On going from the right end to the top of the next row, the electron shell changes to the outer one(Tendency 2) associated with the sudden drop of the effective nuclear charge(Tendency 1), and therefore these tendencies explain the maximum at the right end(Feature 1) and the minimum at the left end(Feature 2). Among the same group effective nuclear charges are the same except for a change between He and Ne in the rare gas atoms, and the outer electron shell contributes to the lower elements. It follows that the lower rows give the lower ionization energies(Feature 5). In the change between He and Ne, it is difficult to guess the relative order since Tendency 1 and Tendency 2 work oppositely. Experimental values show a distinct decrease from He to Ne, and this indicates that Tendency 2, the effect of the distances from K shell to L shell, is much more important to the magnitude of the ionization energies. This effect can also be understood for a large drop of the ionization energies from 13.6 eV (H) to 5.4 eV (Li) in spite of the same effective nuclear charge of the unity.

Feature 4 for experimental values of ionization energies includes rather fine changes, and it cannot be explained only from Tendency 1 and Tendency 2. The change from the group 2 to the group 13 is due to the change of electron subshells from ns to np. An electron in an s orbital has the higher probability of approaching to the nucleus than an electron in a p orbital. Since the potential energy of Coulombic interactions is proportional to the inverse of the distance, behavior around the nucleus is most effective. Thus, the screening effects of s electrons are much smaller than those of p electrons. It follows that the effective nuclear charge for s electrons become larger than those for p electrons. This effect explains the difference of the ionization energies on going from the

Table 2.7: Effective nuclear charges for an electron in the outermost electron shell

H 1.00							He 1.67
Li 1.00	Be 1.67	B 2.33	C 3.00	N 3.67	O 4.33	F 5.00	Ne 5.67
Na 1.00	Mg 1.67	Al 2.33	Si 3.00	P 3.67	S 4.33	Cl 5.00	Ar 5.67

group 2 to the group 13. The change from the group 15 to the group 16 can be understood clearly when electron configurations of N and O atoms are compared in detail. N has a configuration of $[\mathrm{He}](2\mathrm{s})^2(2\mathrm{p}_x)^1(2\mathrm{p}_y)^1(2\mathrm{p}_z)^1$, while O has a configuration of $[\mathrm{He}](2\mathrm{s})^2(2\mathrm{p}_x)^2(2\mathrm{p}_y)^1(2\mathrm{p}_z)^1$. In an O atom, an electron is added to the same 2p orbital, which causes the larger electron repulsion to increase the energy of the electron in the outermost electron shell, and hence the ionization energy decreases.

2.6.4 Effective nuclear charge and electron affinity

Let us study the periodicity in electron affinities of atoms on the basis of the effective nuclear charges. Since the electron affinity equals the energy to remove an additional electron, we consider the effective nuclear charge for an electron in the outermost electron shell in the mononegative ion. For a 2p electron of the F^- ion ($Z = 9$) as an example, the electron configuration of the F^- ion is given by

$$(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^6$$

There are two 1s electrons in the inner side of the selected 2p electron, and thus their screening effects amount to 1×2 from the rule (5). Electrons in the same group of the selected 2p electron are seven altogether, two 2s electrons and 6-1=5 2p electrons, which leads to a contribution of $\frac{1}{3} \times 7$ as a whole from the rule (4). It follows that the screening constant s becomes $s = 1 \times 2 + \frac{1}{3} \times 7 = \frac{13}{3} = 4.33$. Thus, the effective nucleus charge $\overline{Z}$ is estimated as $\overline{Z} = Z - s = 9 - \frac{13}{3} = \frac{14}{3} = 4.67$. If a negative ion is formed for a Ne atom with an atomic number of $Z = 10$, the outermost electron of Ne^- is in a 3s orbital. The screening constant for this 3s electron becomes $s = 10$, since the number of the inner electrons are ten. Therefore, the effective nuclear charge becomes $\overline{Z} = 10 - 10 = 0$.

Table 2.8 lists effective nuclear charges for an electron in the outermost shell of mononegative ion from hydrogen H to argon Ar.

Table 2.8: Effective nuclear charges for an electron in the outermost electron shell in the mononegative ion

H 0.67							He 0.00
Li 0.67	Be 1.33	B 2.00	C 2.67	N 3.33	O 4.00	F 4.67	Ne 0.00
Na 0.67	Mg 1.33	Al 2.00	Si 2.67	P 3.33	S 4.00	Cl 4.67	Ar 0.00

Although the periodicity of the effective nuclear charges for mononegative ions are similar to those for neutral atoms, positions of the minima and maxima are displaced to the lower atomic numbers by one, respectively. It follows that electron affinities give their maxima at halogen atoms and their minima at rare gas atoms. Small maxima and minima as Feature 4 in ionization energies are also found at displaced positions to the left by one; at the groups 2 and 15, the values become smaller with respect to the atoms on their left.

2.7 Excited atoms and spectral terms

In a hydrogenic atom, states of $n \geq 2$ are called excited states. Atoms in excited states with excess energies larger than the energy of the ground state($n = 1$) are called excited atoms. Excited atoms may be formed by excess energies of chemical reactions in a flame or discharge. Contrary to hydrogenic atoms, electron configurations of excited atoms are complicated in general, since there are two or more electrons. Now, let us study the excited-state wavefunctions of a helium atom as a typical example for systems with many electrons. Then, we will also study spectral terms which are very important in spectroscopic classification of energy levels as well as their relationship with various angular momenta.

2.7.1 The ground state of a helium atom

As has been already studied, the electron configuration of the ground-state helium atom is $(1\mathrm{s})^2$. The corresponding determinant wave function of this configuration is given by

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) \\ \psi_1(2) & \psi_2(2) \end{vmatrix} \tag{2.67}$$

Here, electron coordinates are denoted simply by their number 1 or 2 in place of writing q_1 or q_2. ψ_1 and ψ_2 are orbital functions of electrons including their spins, and they are constructed from a combination of orbital functions of spatial coordinates $\phi_{1\mathrm{s}}$ and spin functions α or β.

$$\psi_1 = \phi_{1\mathrm{s}} \cdot \alpha \tag{2.68}$$

$$\psi_2 = \phi_{1\mathrm{s}} \cdot \beta \tag{2.69}$$

Using these equations and expanding the above determinant, we obtain the following formula.

$$\Psi(1,2) = \phi_{1\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)\frac{\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}}{\sqrt{2}} \tag{2.70}$$

$\phi_{1\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)$ in this formula is symmetric with respect to the permutation of the electrons, while the inside of { } depending on the spins is antisymmetric with respect to the permutation of the electrons. It follows that as a whole this formula is symmetric($+1$) × antisymmetric(-1) = antisymmetric(-1).

2.7.2 Excited states of a helium atom

Now let us consider an electron configuration $(1\mathrm{s})^1(2\mathrm{s})^1$, in which an electron is excited to the 2s orbital from the 1s orbital. Including electron spins, we obtain the following four configurations of (a)-(d) as shown in Fig.2.9.

Using spatial orbital functions $\phi_{1\mathrm{s}}$ and $\phi_{2\mathrm{s}}$ together with spin functions α, β, let us construct the functions for two-electron systems. We obtain symmetric and antisymmetric functions as follows.

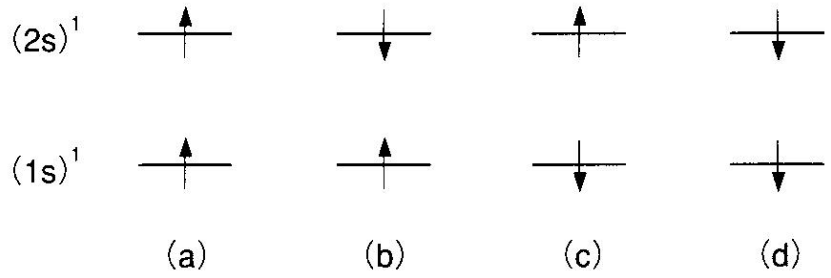


Figure 2.9: Electron configurations for $(1\mathrm{s})^1(2\mathrm{s})^1$

The symmetric function for the spatial part is given by

$$\Phi^{+} = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) + \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \tag{2.71}$$

and the antisymmetric function for the spatial part is given by

$$\Phi^{-} = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \tag{2.72}$$

There are three symmetric functions for the spin part as follows,

$$\Gamma_1 = \alpha(1)\alpha(2) \tag{2.73}$$

$$\Gamma_2 = \beta(1)\beta(2) \tag{2.74}$$

$$\Gamma_3 = \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.75}$$

and the antisymmetric spin function is given by

$$\Gamma_4 = \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.76}$$

Combinations of these functions lead to the following antisymmetric functions.

For the symmetric spatial function, there is only one antisymmetric spin function, ant thus we obtain

$$\Phi_1 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) + \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.77}$$

The excited state represented by this equation is called a singlet state.

For the antisymmetric spatial function, there are three symmetric spin functions to yield the following three combinations of antisymmetric functions.

$$\Phi_2 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \alpha(1)\alpha(2) \tag{2.78}$$

$$\Phi_3 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \beta(1)\beta(2) \tag{2.79}$$

$$\Phi_4 = \frac{\phi_{1\mathrm{s}}(1)\phi_{2\mathrm{s}}(2) - \phi_{2\mathrm{s}}(1)\phi_{1\mathrm{s}}(2)}{\sqrt{2}} \cdot \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.80}$$

Excited states represented by these functions are called triplet states. Experiments show that the triplet sates are more stable with the lower energies than the singlet state. This can be confirmed by theoretical calculations of expectation values. Energies for Φ_2, Φ_3, Φ_4 are the same, and they are triply degenerate states.

2.7.3 Angular momenta and spectral terms for many electron systems

In order to understand the excited states of atoms, angular momenta need to be studied in detail. As studied in section 1.13, the angular momentum is a vector with a magnitude and direction. The angular momentum of a many-electron system is given as a vector summation of individual angular momenta of the electrons and called the resultant angular momentum. Construction of such summations can be made for the orbital angular momentum $\hat{l}_i$, the spin angular momentum $\hat{s}_i$, and the total angular momentum of their sum $\hat{j}_i = \hat{l}_i + \hat{s}_i$. Thus, the resultant orbital angular momentum $\hat{L}$, the resultant spin angular momentum $\hat{S}$, and the resultant total angular momentum $\hat{J}$ are defined by the following equations.

$$\hat{L} = \sum_i \hat{l}_i \tag{2.81}$$

$$\hat{S} = \sum_i \hat{s}_i \tag{2.82}$$

$$\hat{J} = \sum_i \hat{j}_i \tag{2.83}$$

Since $\hat{j}_i = \hat{l}_i + \hat{s}_i$, we obtain $\hat{J} = \hat{L} + \hat{S}$.

The three types of angular momenta for an electron satisfy the respective eigen equations as follows.

$$\hat{l}^2\Gamma = l(l+1)\hbar^2\Gamma \tag{2.84}$$

$$\hat{l}_z\Gamma = m_l\hbar\Gamma \tag{2.85}$$

$$\hat{s}^2\Gamma = s(s+1)\hbar^2\Gamma \tag{2.86}$$

$$\hat{s}_z\Gamma = m_s\hbar\Gamma \tag{2.87}$$

$$\hat{j}^2\Gamma = j(j+1)\hbar^2\Gamma \tag{2.88}$$

$$\hat{j}_z\Gamma = m_j\hbar\Gamma \tag{2.89}$$

The subscript i should be attached to both of the operators and the quantum numbers in order to denote the i-th electron. The quantum number m for the component should have respective subscripts specifying l, s, j.

The resultant angular momenta introduced above should also satisfy similar eigen equations as follows.

$$\hat{L}^2\Gamma = L(L+1)\hbar^2\Gamma \tag{2.90}$$

$$\hat{L}_z\Gamma = M_L\hbar\Gamma \tag{2.91}$$

$$\hat{S}^2\Gamma = S(S+1)\hbar^2\Gamma \tag{2.92}$$

$$\hat{S}_z\Gamma = M_S\hbar\Gamma \tag{2.93}$$

$$\hat{J}^2\Gamma = J(J+1)\hbar^2\Gamma \tag{2.94}$$

$$\hat{J}_z\Gamma = M_J\hbar\Gamma \tag{2.95}$$

L, S, J are quantum numbers corresponding to the operators of the squares, and M_L, M_S, M_J are quantum numbers corresponding to their components. M_L, M_S, M_J are equal to summations of the contributions due to individual electrons.

$$M_L = \sum_i (m_l)_i \tag{2.96}$$

$$M_S = \sum_i (m_s)_i \tag{2.97}$$

$$M_J = \sum_i (m_j)_i \tag{2.98}$$

Using quantum numbers for the resultant angular momenta L, S, J and the principal quantum number n, atomic energy levels are represented by the following symbol.

$$n^{2S+1}\{L\}_J \tag{2.99}$$

This symbol is useful and important, especially in atomic spectroscopy, and is called a spectral term. n is the maximum value among the principal quantum numbers of the electrons, and this value is placed on the top. For the symbol $\{L\}$, capital letters of S,P,D,F,G,H are assigned with respect to the value of L=0,1,2,3,4,5, respectively. $2S+1$ is called the spin multiplicity, and its value calculated from the value of S is attached to the left shoulder of a letter such as S and P corresponding to the symbol $\{L\}$; the superscript for the letter of $\{L\}$ becomes 3 for triplet and 1 for singlet. The value of J is attached as a subscript to the right side of the letter of $\{L\}$. n and J are often omitted for abbreviation unless they are necessary.

L	0	1	2	3	4	5
$\{L\}$	S	P	D	F	G	H

$\hat{L}$ and $\hat{S}$ are commutable with $\hat{H}$, the Hamiltonian operator for a many electron atom given by eq.(2.31). Therefore, energy levels corresponding to spectral terms with the same combinations of L and S and the same electron configurations, which are called LS terms, are identical and degenerate. For such degenerate cases, the right subscript J may be omitted, since they are not important. However, experiments sometimes shows plitting of LS terms. One of the causes is spin-orbit interactions, which yield splitting proportional to the fourth power of the atomic number Z. Thus, the effect becomes significant for heavy atoms. On the other hand, splitting due to external magnetic fields is called the Zeeman effect.

In the case of hydrogenic atoms, it is easy to obtain spectral terms, since the system has only one electron. For example, let us consider a state of one 2p electron. Because of a 2p electron, $n = 2$, and $s = \frac{1}{2}$ with $m_s = \pm\frac{1}{2}$. For a single electron system, $M_s = m_s$, and thus $S = \frac{1}{2}$ leading to the spin multiplicity $2S + 1 = 2 \times (1/2) + 1 = 2$, which is called a doublet. Similarly, $M_l = m_l$, and thus $L = 1$ corresponding to the letter P for the symbol $\{L\}$. In order to determine the quantity of J, we need to know the rule for the permitted values of coupled angular momenta.

[The rule for permitted values of coupled angular momenta]

We introduce a coupled angular momentum of $\hat{J} = \hat{J}_1 + \hat{J}_2$, where $\hat{J}_1$ and $\hat{J}_2$ are both angular momenta commutable with each other. Using quantum numbers J_1 and J_2 for $\hat{J}_1$ and $\hat{J}_2$, permitted values of the quantum number J for the square of $\hat{J}$ are as follows.

$$J = J_1 + J_2,\ J_1 + J_2 - 1,\ \cdots,\ |J_1 - J_2| \tag{2.100}$$

Since $\hat{J}$ is a coupled vector of $\hat{L}$ and $\hat{S}$, the magnitude of the coupled angular momentum $\hat{J}$ has a value between the maximum of $L+S$ and the minimum of $|L-S|$. In the case of one 2p electron, $L = 1$ and $S = \frac{1}{2}$, and thus the possible cases are $J = 1 + 1/2 = 3/2$ or $J = 1 - 1/2 = 1/2$. It follows that the spectral term for $(2p)^1$ are given by

$$2^2\mathrm{P}_{3/2} \text{ and } 2^2\mathrm{P}_{1/2}$$

These two terms have the same combination of L and S, and they are degenerate, if the spin orbit interactions are negligible. In the case of a hydrogen atom, the splitting due to the spin orbit interactions are very small, and $^2\mathrm{P}_{1/2}$ is only 0.365 cm^{-1} lower than the other term.

Example 2.5 Verify that spin functions $\Gamma_1 \sim \Gamma_4$ for a two-electron system(equations(2.73)-(2.76)) are eigen functions of the z-component operator of the resultant spin angular momentum $\hat{S}_z$, and obtain individual values of M_s.

(Solution) First derive equations in the form of $\hat{S}_z\Gamma = M_S\hbar\Gamma$, and second obtain values of M_s.

(1) $\Gamma_1 = \alpha(1)\alpha(2)$

$$\begin{aligned}\hat{S}_z\Gamma_1 &= (\hat{s}_{z_1} + \hat{s}_{z_2})\alpha(1)\alpha(2) = \hat{s}_{z_1}\alpha(1)\alpha(2) + \hat{s}_{z_2}\alpha(1)\alpha(2) \\ &= \{\hat{s}_{z_1}\alpha(1)\}\alpha(2) + \alpha(1)\{\hat{s}_{z_2}\alpha(2)\} = \frac{1}{2}\hbar\alpha(1)\alpha(2) + \alpha(1)\frac{1}{2}\hbar\alpha(2) \\ &= \left(\frac{1}{2} + \frac{1}{2}\right)\hbar\alpha(1)\alpha(2) = \hbar\Gamma_1\end{aligned}$$

Thus, Γ_1 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = 1$.

(2) $\Gamma_2 = \beta(1)\beta(2)$

$$\begin{aligned}\hat{S}_z\Gamma_2 &= (\hat{s}_{z_1} + \hat{s}_{z_2})\beta(1)\beta(2) = \{\hat{s}_{z_1}\beta(1)\}\beta(2) + \beta(1)\{\hat{s}_{z_2}\beta(2)\} \\ &= -\frac{1}{2}\hbar\beta(1)\beta(2) + \beta(1)\left(-\frac{1}{2}\right)\hbar\beta(2) = \left(-\frac{1}{2} - \frac{1}{2}\right)\hbar\beta(1)\beta(2) = -\hbar\Gamma_2\end{aligned}$$

Thus, Γ_2 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = -1$.

(3) $\Gamma_3 = \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/\sqrt{2}$

$$\hat{S}_z\Gamma_3 = \left(\frac{1}{2} - \frac{1}{2}\right)\hbar\Gamma_3 = 0\hbar\Gamma_3$$

Thus, Γ_3 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = 0$.

(4) $\Gamma_4 = \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2}$

$$\hat{S}_z\Gamma_4 = \left(\frac{1}{2} - \frac{1}{2}\right)\hbar\Gamma_4 = 0\hbar\Gamma_4$$

Thus, Γ_4 is an eigenfunction of $\hat{S}_z$, and the quantum number $M_S = 0$.

Next, let us study the spectral terms of excited states $(1s)^1(2s)^1$ for a He atom. The largest principal quantum number is for a 2s electron, and thus $n = 2$.Since all electrons are in s orbitals with $m_l = 0$, then $L = 0 + 0 = 0$. The value of S depends on the spin multiplicity, singlet or triplet. From Example 2.5, the only possible value for M_S is 0, and this leads to $S = 0$ and $2S + 1 = 0 + 1 = 1$. From $S = 0$ and $L = 0$, $J = 0 + 0 = 0$. It follows that the spectral term for the singlet excited-state is given by $2^1\mathrm{S}_0$.

For triplet excited-states, there are three values of M_S, 1 for Γ_1, 0 for Γ_3, and -1 for Γ_2, and thus $S = 1$. Noting $L = 0$, we find $J = 1 + 0 = 1 - 0 = 1$. It follows that the spectral term of the triplet excited states is given by $2^3\mathrm{S}_1$.

The following rules are very useful for obtaining spectral terms.

[How to obtain spectral terms]

(1) When a subshell is fully occupied by electrons, those electrons in the subshell may be disregarded, since contributions of the subshell to M_S and M_L are vanishing. For example, in order to obtain the spectral term for the ground-state of Li $(1s)^2(2s)^1$, we may only deal with $(2s)^1$ neglecting $(1s)^2$.

(2) When a subshell with an azimuthal quantum number of l is fully occupied by electrons, the configuration can be expressed as $(n\{l\})^{(4l+2)}$, where $l = 0, 1, 2$ correspond to $\mathrm{s}, \mathrm{p}, \mathrm{d}$, respectively. A pair of incompletely occupied subshells, $(n\{l\})^{(4l+2-k)}$ and $(n\{l\})^{(k)}$, give the same spectral terms. For example, $(2p)^5$ and $(2p)^1$ give the same set of spectral terms, $2^2\mathrm{P}_{3/2}$ and $2^2\mathrm{P}_{1/2}$.

Exercises

2.1 Calculate the energy of a photon emitted in a transition of an electron in the monopositive helium ion from an excited state of principal quantum number $n = 2$ to the ground state $n = 1$.

2.2 Show that an anticlockwise rotation of the $\mathrm{d}_{x^2-y^2}$ orbital by 45 degrees in the x–y plane leads to a d_{xy} orbital. Verify that the d_{z^2} orbital is made of a linear combination of $\mathrm{d}_{y^2-z^2}$ and $\mathrm{d}_{z^2-x^2}$ orbitals, which are equivalent to $\mathrm{d}_{x^2-y^2}$ orbital.

2.3 Calculate the distances where the radial distribution functions for the 1s and 2p orbitals of a hydrogen atom are maxima, and compare the results with the Bohr radius.

2.4 Construct the wave function with a Slater determinant for an electron configuration of He in which one electron occupies the 1s orbital with α spin and the other electron occupies the 2s orbital with α spin. Show that for this wave function the probability of finding two electrons at identical spatial coordinates is vanishing (the probability of finding electrons occupying different spatial orbitals with the same spin at the same place is vanishing).

2.5 Construct the electron configuration of an iodide ion (I^-).

2.6 Which group in the periodic table gives the maximum for the energies (the second ionization energy) required for producing a dipositive ion from a monopositive ion, when the energies are compared as functions of the atomic numbers? Which group gives the minimum? Answer these questions by considering the effective nuclear charges in the range of atomic numbers from 2 to 18.

2.7 Determine all wavefunctions for excited states of He in which one of 1s electrons is excited to a 2p orbital. Determine their spectral terms.