1-1-2. Electron distribution in atom

When we substitute the total energy E and potential energy Ep into the eq. (1-34), we solve the wave equation.

If we express the potential energy in the rectangular coordinate system,

$$E_p = -\frac{Ze^2}{4\pi\varepsilon_o r} = -\frac{Ze^2}{4\pi\varepsilon_o\sqrt{x^2+y^2+z^2}} \qquad (1\text{-}34)$$

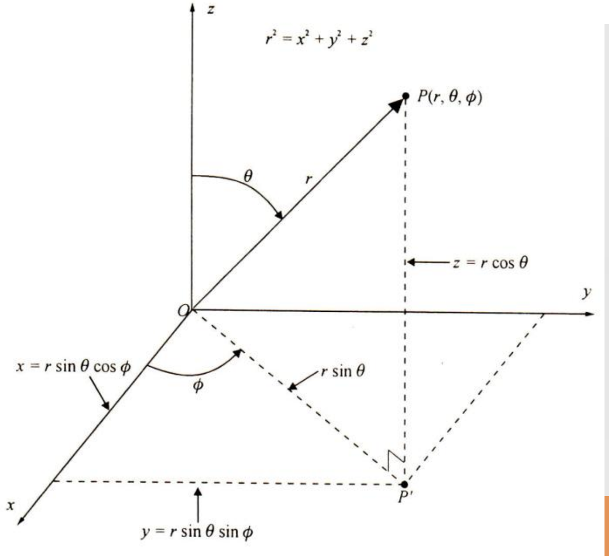


Fig. 1-3. Spherical polar coordinate

The relationship between rectangular and spherical coordinate.

$$x = r\sin\theta\cos\theta\,,\quad y = \sin\theta\sin\phi\,,\quad z = r\cos\theta$$

The wavefunction $\psi(x, y, z) = \psi(r, \theta, \phi)$

And using seperation of variable, the wavefunction will be

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Then, we can derive 3-dim. Wave equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial\psi}{\partial\phi} + \frac{8\pi^2 m_e}{h^2}(E - E_p)\psi = 0. \tag{1-35}$$

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

The wavefunction can be expressed by three quantum numbers, n, l, m

n : principle quantum number, shell number

n=1, 2, 3, 4……..

l : angular momentum quantum number,

l=0, 1, 2……..n-1

m : magnetic quantum number

The combination of (n, l, m) is called by 'atomic orbital'

The energy of electron in Hydrogen atom is given by

$$E_n = -\frac{13.6}{n^2}\ \text{eV} \qquad (1\text{-}14)$$

Quantum Numbers

- The wave functions for an atom with a single electron have three index numbers called quantum numbers. These indices allow a set of solutions to share the same form and yet allow each solution to be unique. A set of quantum numbers is sort of like a finger print: even though you have the same basic form as other human beings, you are unique and you have a unique finger print. Your finger print isn’t what makes you an individual, but it is a way to differentiate you from others. A set of quantum numbers doesn’t make an orbital, but it allows us to distinguish among them. But a set of quantum numbers is more than just an identifier. Their values give us information about the shape and orientation of the probability density.

- The principle quantum number, *n*, indicates the energy of the electron in that orbital. The higher the value of *n* is, the greater the energy the electron has. The principle quantum number has values that range from 1 to infinity, theoretically, but the principle quantum number also indicates the distance to the nucleus. High energy electrons far from the nucleus tend to get lost. Which brings us to an important digression: if an atom has got only one electron, doesn't it only have one orbital? NO! Every atom has an infinite number of orbitals because every wave equation has an infinite number of solutions. At any given instant an electron is occupying only one of these orbitals, but all the other possible energy states still exist.
- n : principle quantum number, shell number

n=1, 2, 3, 4……..

- The azimuthal quantum number, *l*, indicates the shape of the probability density that the electron occupies (or the shape of the orbital, if you prefer). The possible values for *l* depend on the value for *n* of that orbital, and *l* has values from zero up to *n* – 1. For example, if *n* = 3, *l* = 0, 1, 2. Many students balk at this point and demand to know which value is the right one. They are all equally right. Remember that we are building a large set of orbitals.

l : angular momentum quantum number,
  l=0,: s-orbital
  l=1 : p-orbital
  l=2 : d-orbital
  l=3 : f-orbital

- The magnetic quantum number, m_l, indicates the orientation of the probability density, or the direction the orbital is pointing. The value the magnetic quantum number can have depends on the value of the azimuthal quantum number with values ranging from negative l up to positive l.
- m : magnetic quantum number
- -l, -l+1,…, -1, 0, 1, …., l-1, l

- For example, if $l = 2$, $m_l = -2, -1, 0, 1, 2$.

- ms : spin quantum number

  ms=1/2, -1/2

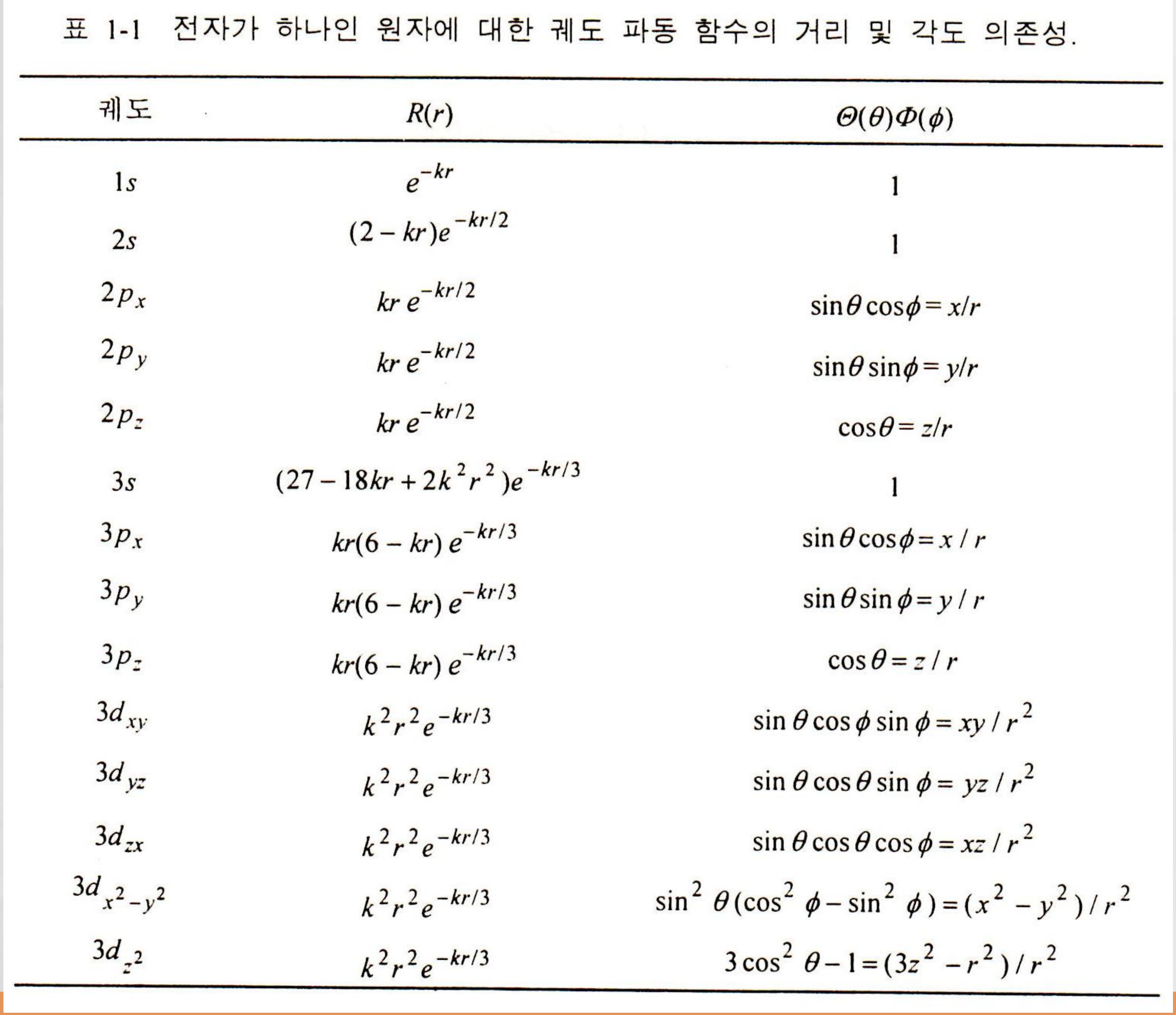
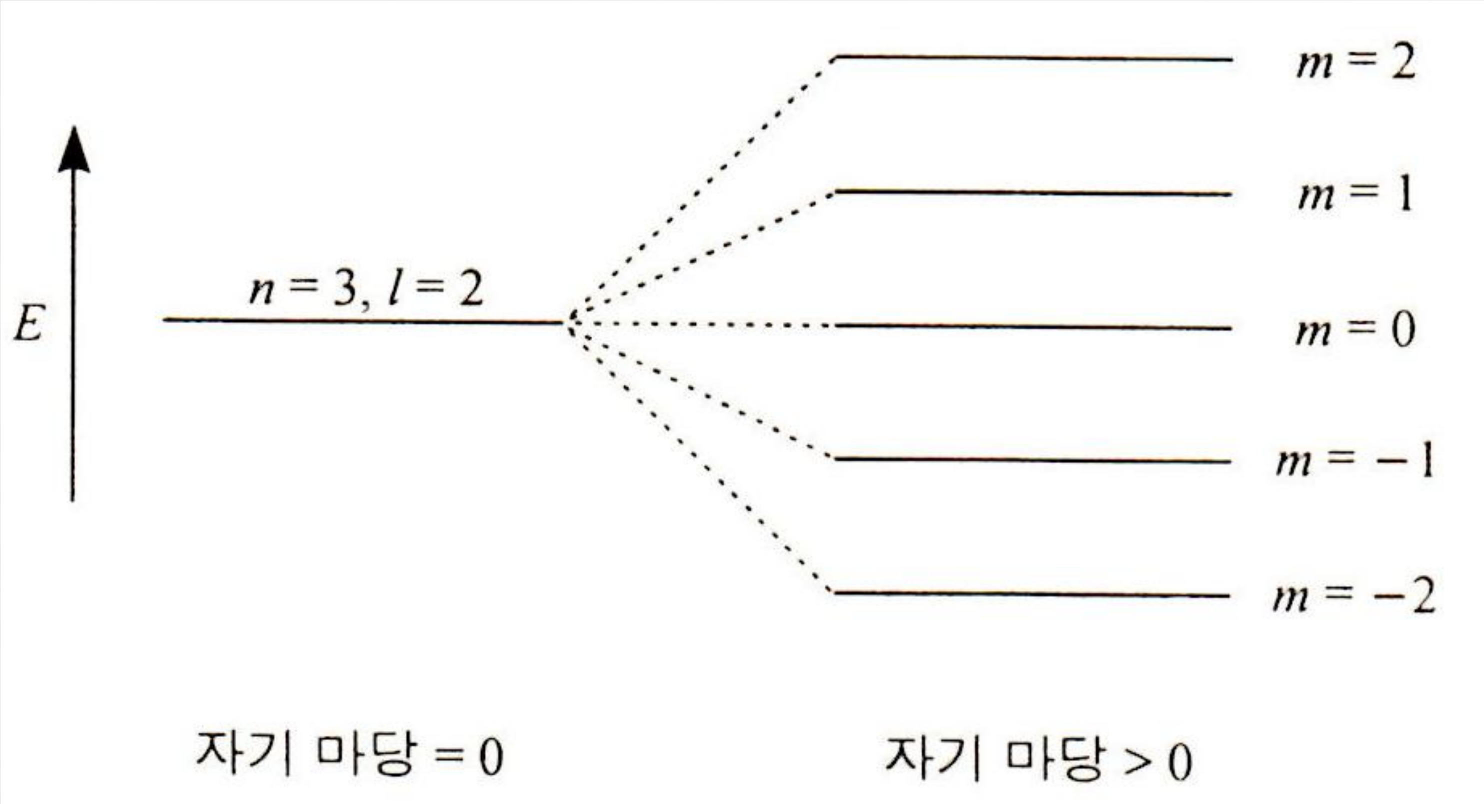


표 1-1 전자가 하나인 원자에 대한 궤도 파동 함수의 거리 및 각도 의존성.

궤도	$R(r)$	$\Theta(\theta)\Phi(\phi)$
$1s$	e^{-kr}	1
$2s$	$(2-kr)e^{-kr/2}$	1
$2p_x$	$kr\,e^{-kr/2}$	$\sin\theta\cos\phi = x/r$
$2p_y$	$kr\,e^{-kr/2}$	$\sin\theta\sin\phi = y/r$
$2p_z$	$kr\,e^{-kr/2}$	$\cos\theta = z/r$
$3s$	$(27-18kr+2k^2r^2)e^{-kr/3}$	1
$3p_x$	$kr(6-kr)\,e^{-kr/3}$	$\sin\theta\cos\phi = x/r$
$3p_y$	$kr(6-kr)\,e^{-kr/3}$	$\sin\theta\sin\phi = y/r$
$3p_z$	$kr(6-kr)\,e^{-kr/3}$	$\cos\theta = z/r$
$3d_{xy}$	$k^2r^2e^{-kr/3}$	$\sin\theta\cos\phi\sin\phi = xy/r^2$
$3d_{yz}$	$k^2r^2e^{-kr/3}$	$\sin\theta\cos\theta\sin\phi = yz/r^2$
$3d_{zx}$	$k^2r^2e^{-kr/3}$	$\sin\theta\cos\theta\cos\phi = xz/r^2$
$3d_{x^2-y^2}$	$k^2r^2e^{-kr/3}$	$\sin^2\theta(\cos^2\phi-\sin^2\phi) = (x^2-y^2)/r^2$
$3d_{z^2}$	$k^2r^2e^{-kr/3}$	$3\cos^2\theta-1 = (3z^2-r^2)/r^2$

Magnetic quantum number is necessary to explain the atomic state when the magnetic field is applied



When the magnetic field is zero, all the five states have same energy, the energy states will be seperated to five states when the magnetic field is applied.

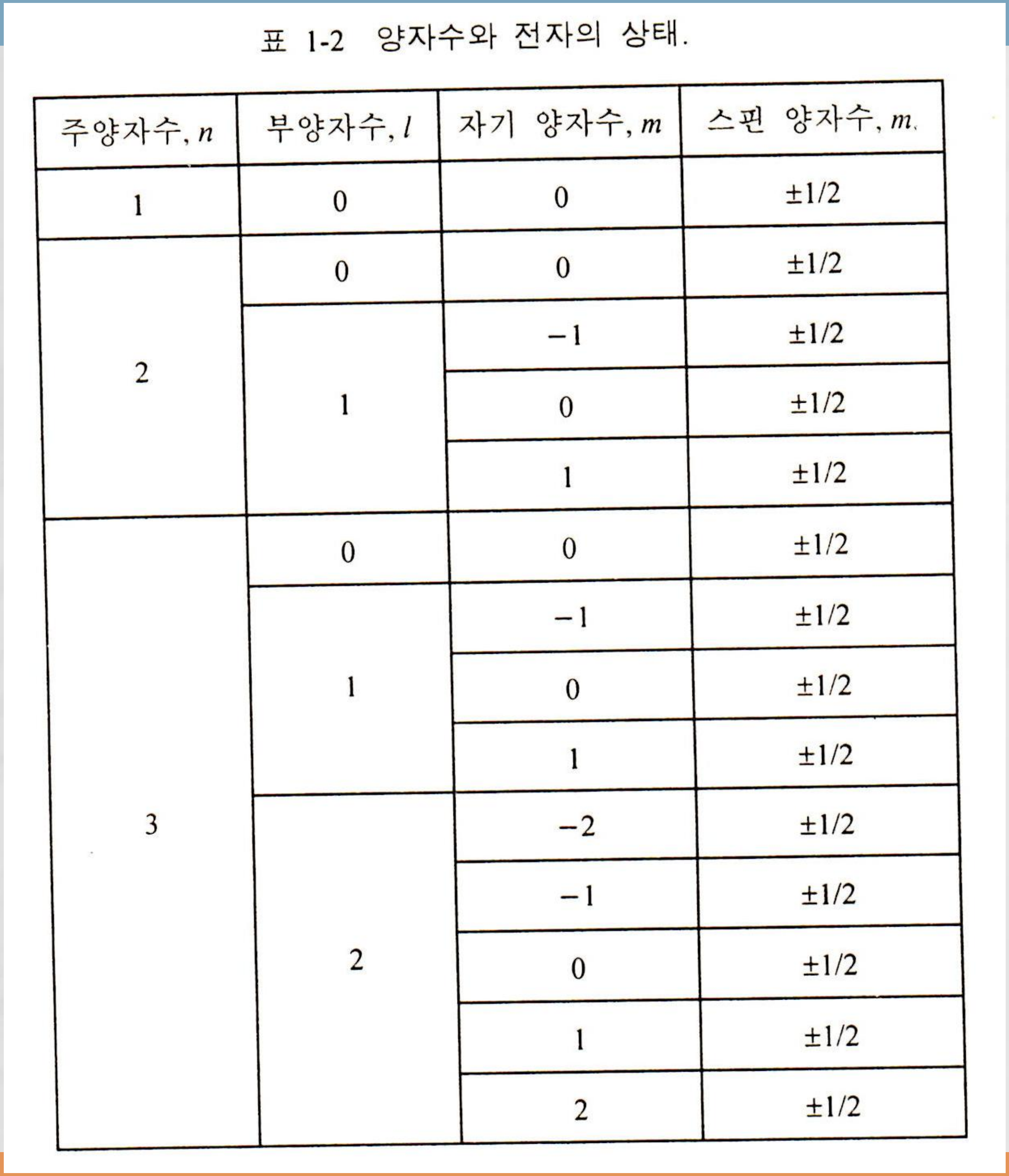


표 1-2 양자수와 전자의 상태.

주양자수, n	부양자수, l	자기 양자수, m	스핀 양자수, m_s
1	0	0	±1/2
2	0	0	±1/2
	1	−1	±1/2
		0	±1/2
		1	±1/2
3	0	0	±1/2
	1	−1	±1/2
		0	±1/2
		1	±1/2
	2	−2	±1/2
		−1	±1/2
		0	±1/2
		1	±1/2
		2	±1/2

The probability that the electron can be found between r and r+dr

$$\psi^2 dV = 4\pi r^2 \psi^2 dr \qquad (1\text{-}36)$$

If the wavefunction is $\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$

Then, the probability will be $4\pi r^2\, R^2(r)\,\Theta^2(\theta)\,\Phi^2(\phi)\,dr$

$R^2(r)$ the radial probability factor

$\Theta^2(\theta)\,\Phi^2(\phi)$ the angular dependent probability factor

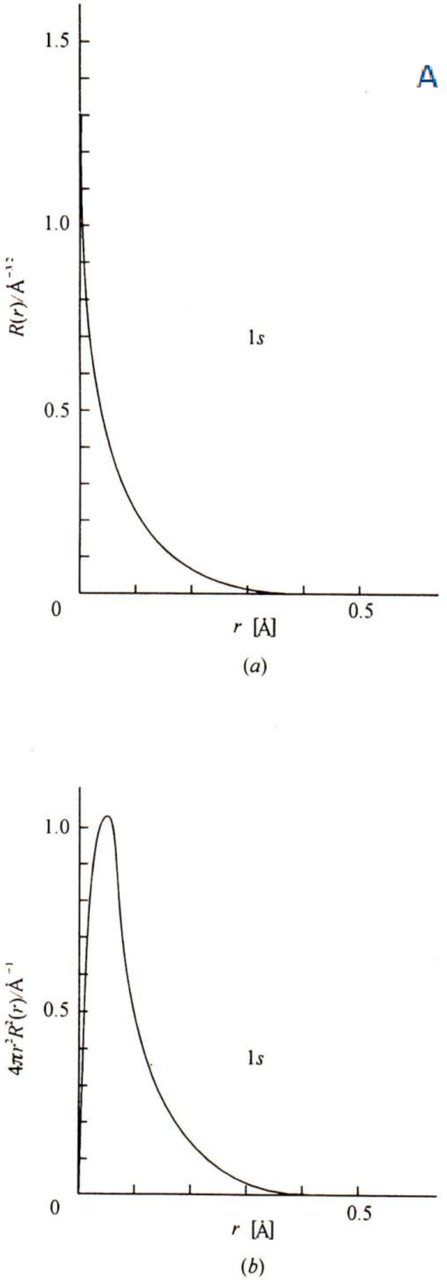
For the 1S state (from table 1-1), the wavefunction

$$R(r) = e^{-kr}, \quad \Theta(\theta)\Phi(\phi) = 1 \qquad (1\text{-}37)$$

For the 2S state (from table 1-1), the wavefunction

$$R(r) = (2 - kr)e^{-kr/2}, \quad \Theta(\theta)\Phi(\phi) = 1 \qquad (1\text{-}38)$$

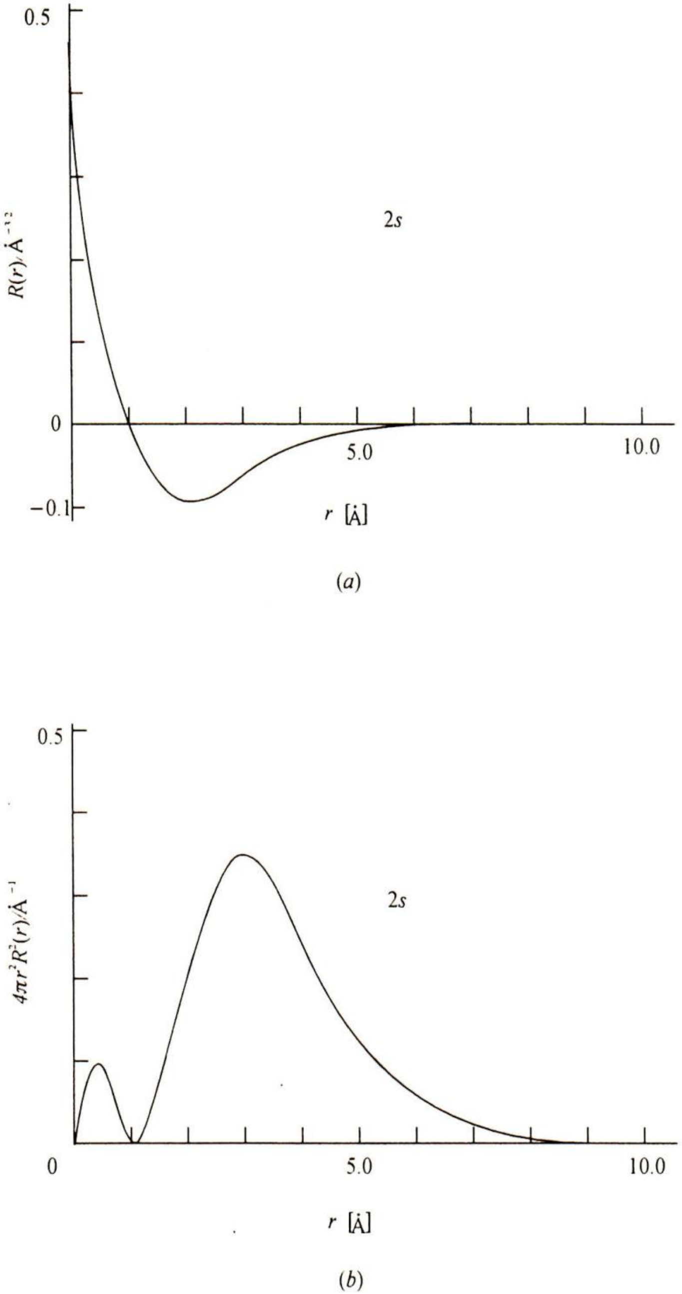
A 1s Orbital:



(a)

(b)

그림 1-5 (*a*) 1s 궤도에서 지름 부분 $R(r)$, (*b*) 1s 궤도에서 지름 부분의 확률 분포 $R^2(r)$.



(a)

(b)

그림 1-6 (*a*) 2s 궤도에서 지름 부분 $R(r)$, (*b*) 2s 궤도에서 지름 부분의 확률 분포 $R^2(r)$.

For the 2p state, the radial part of wavefunction

$$R(r) = kr\,e^{-kr/2} \tag{1-40}$$

For the 3p state, the radial part of wavefunction

$$R(r) = kr(6 - kr)e^{-kr/3} \tag{1-41}$$

And for the 3d state, the radial part of wavefunction

$$R(r) = k^2 r^2\, e^{-kr/3} \tag{1-42}$$

The function $\Theta(\theta)\Phi(\phi)$ will be for the 2px state

$$\cos\phi \sin\theta = \frac{x}{r} \tag{1-43}$$

$$\sin\phi \sin\theta = \frac{y}{r} \tag{1-44}$$

$$\cos\theta = \frac{z}{r} \tag{1-45}$$

R(r) function for 2p orbital state

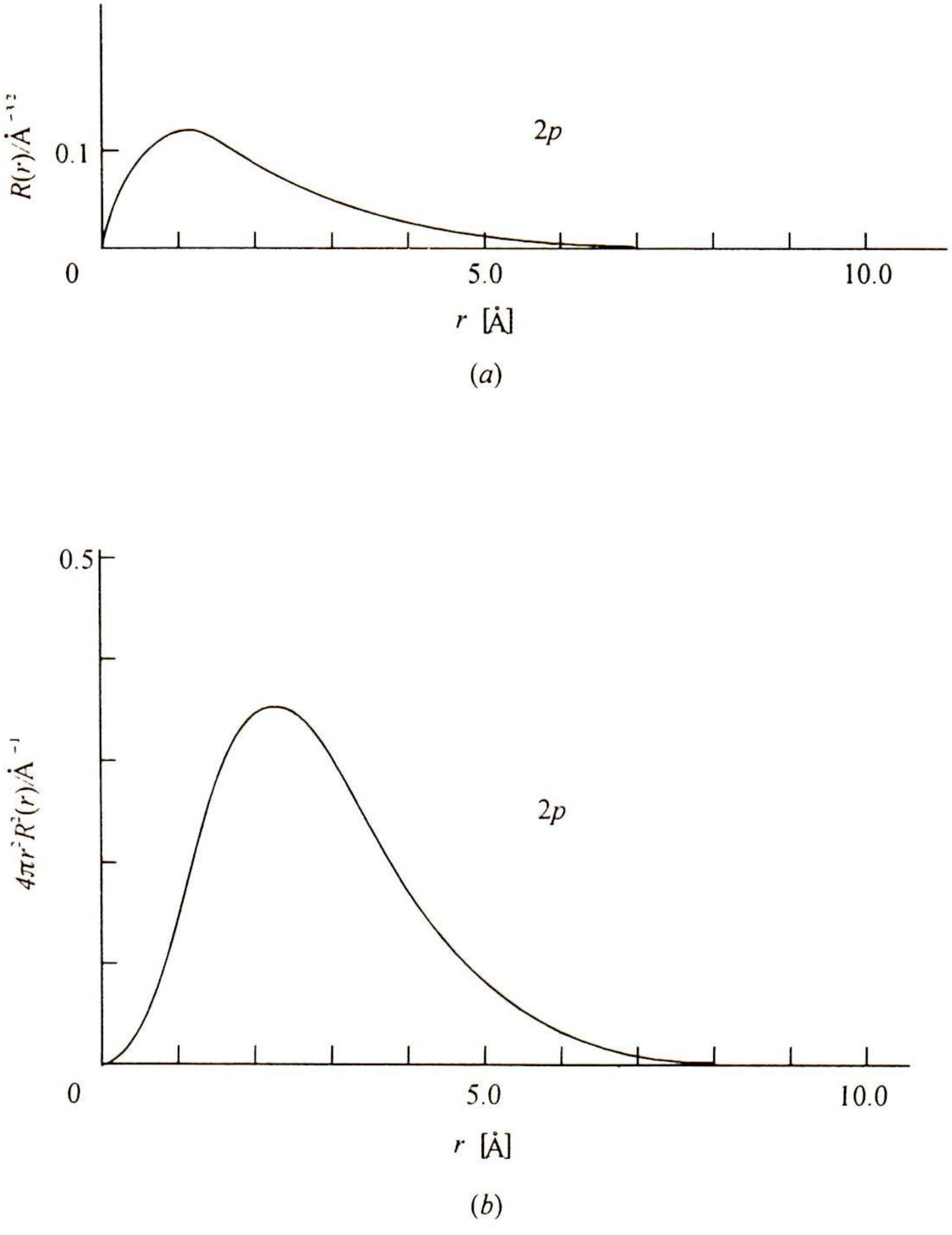


그림 1-8 (*a*) 2*p* 궤도에서 지름 부분 $R(r)$, (*b*) 2*p* 궤도에서 지름 부분의 확률 분포 $R^2(r)$.

R(r) function for 3p orbital state

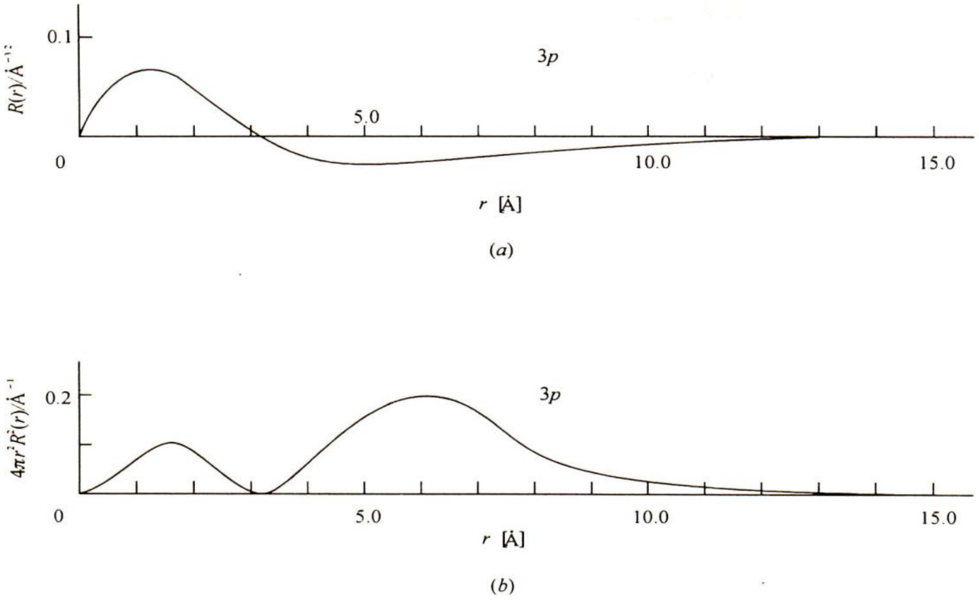


그림 1-9 (*a*) 3*p* 궤도에서 지름 부분 $R(r)$, (*b*) 3*p* 궤도에서 지름 부분의 확률 분포 $R^2(r)$.

R(r) function for 3d orbital state

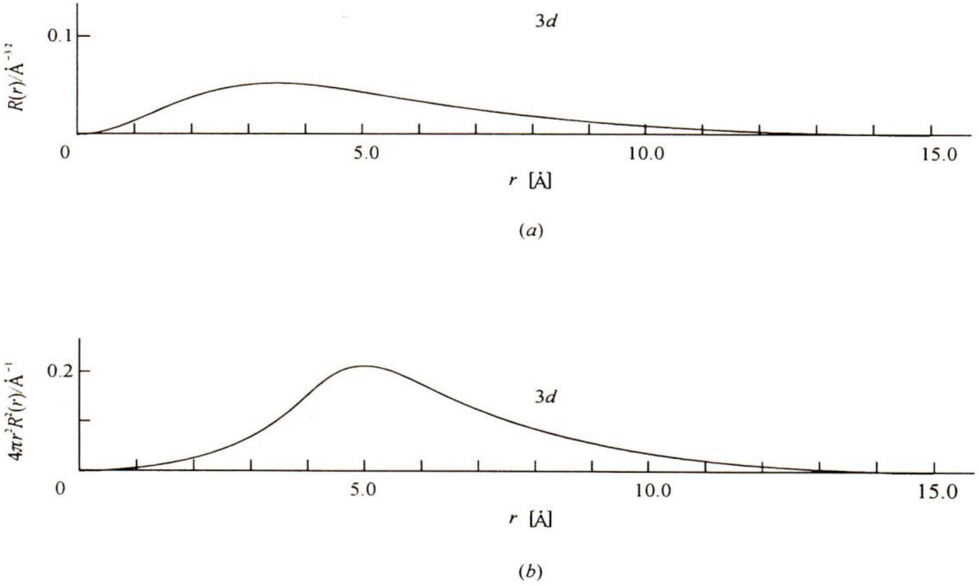
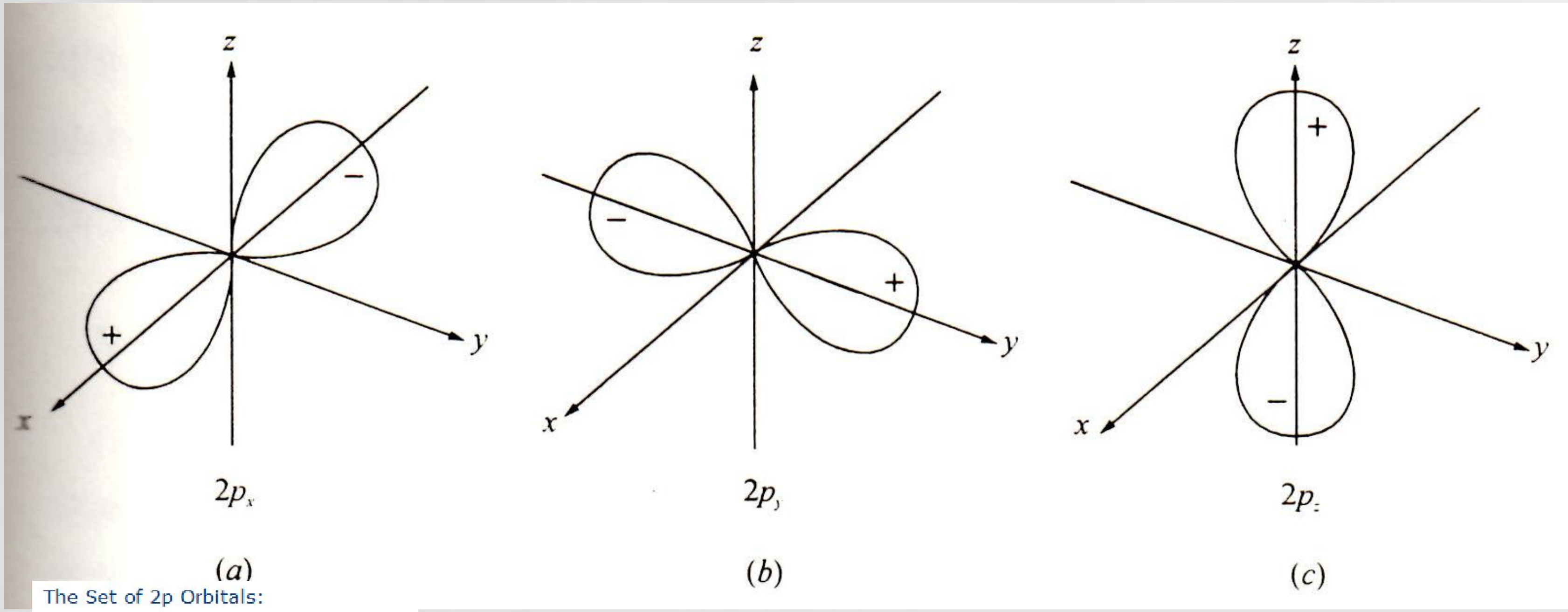
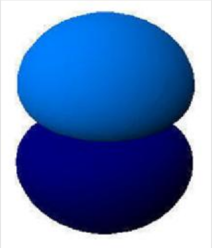


그림 1-10 (*a*) 3*d* 궤도에서 지름 부분 $R(r)$, (*b*) 3*d* 궤도에서 지름 부분의 확률 분포 $R^2(r)$.

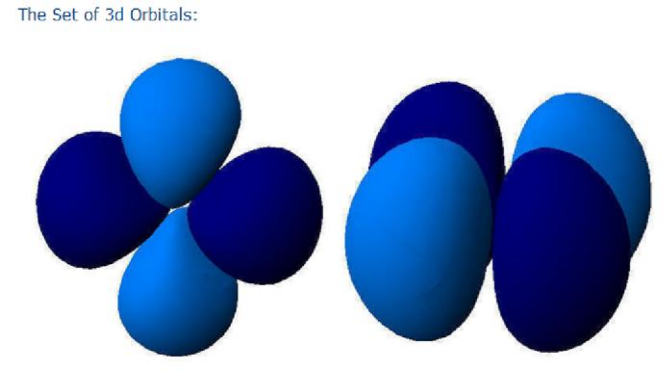
2Px, 2Py and 2Pz orbitals

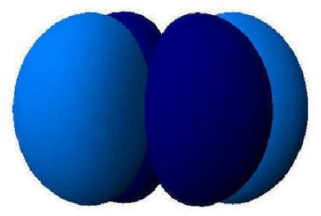


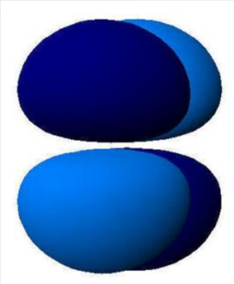

The Set of 2p Orbitals:

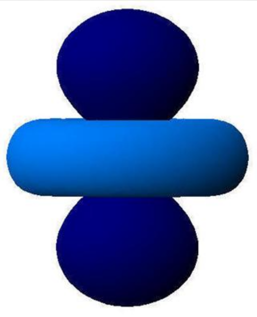


3dxy, 3dyz, 3dzx, 3dx2-y2, 3dz2 orbitals









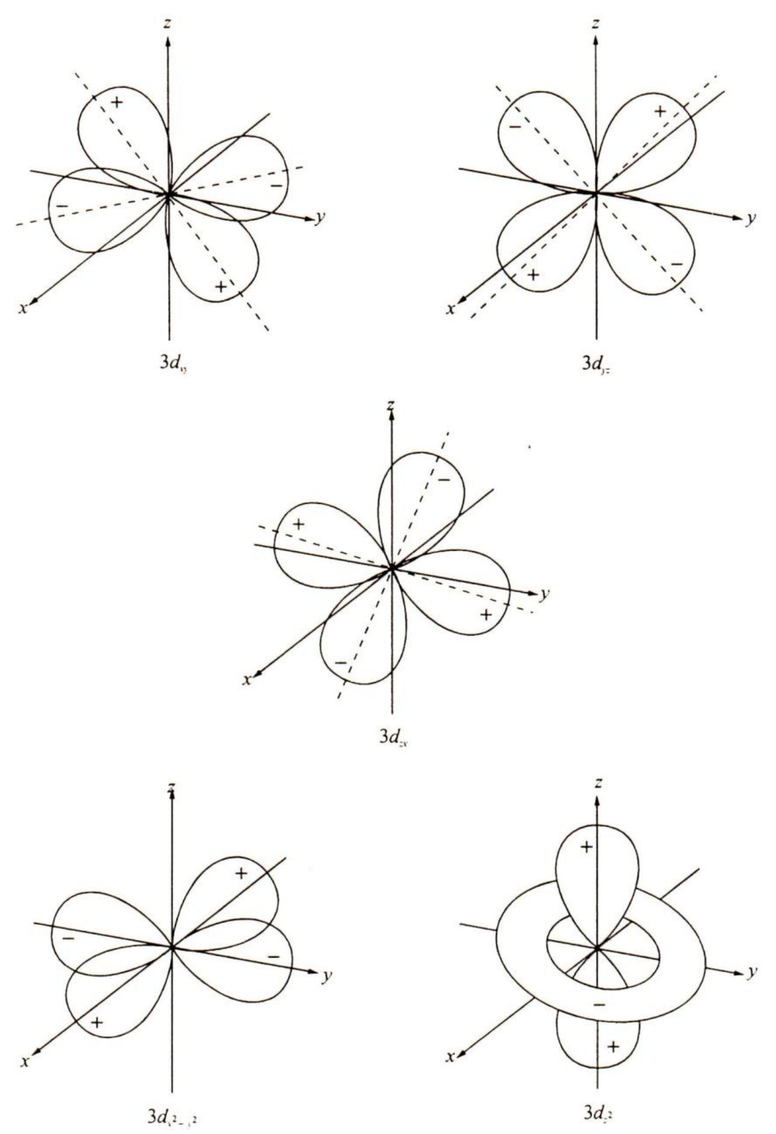


그림 1-12 궤도 $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$, $3d_{z^2}$.

1-1-3. Electron configuration in atoms

- For the ground state of hydrogen atom

is given by the n=1, l=0, m=0, ms=1/2.

For the excited state, the energy will be

$$E_n = -13.6\frac{Z^2}{n^2}\ \text{eV} \qquad (1\text{-}13)$$

For Z=1 case, the energy will be

$$E_n = -\frac{13.6}{n^2}\ \text{eV} \qquad (1\text{-}14)$$

Spectroscopic designation of electron

Fig. 1-14(a) Energy level of Hydrogen atom

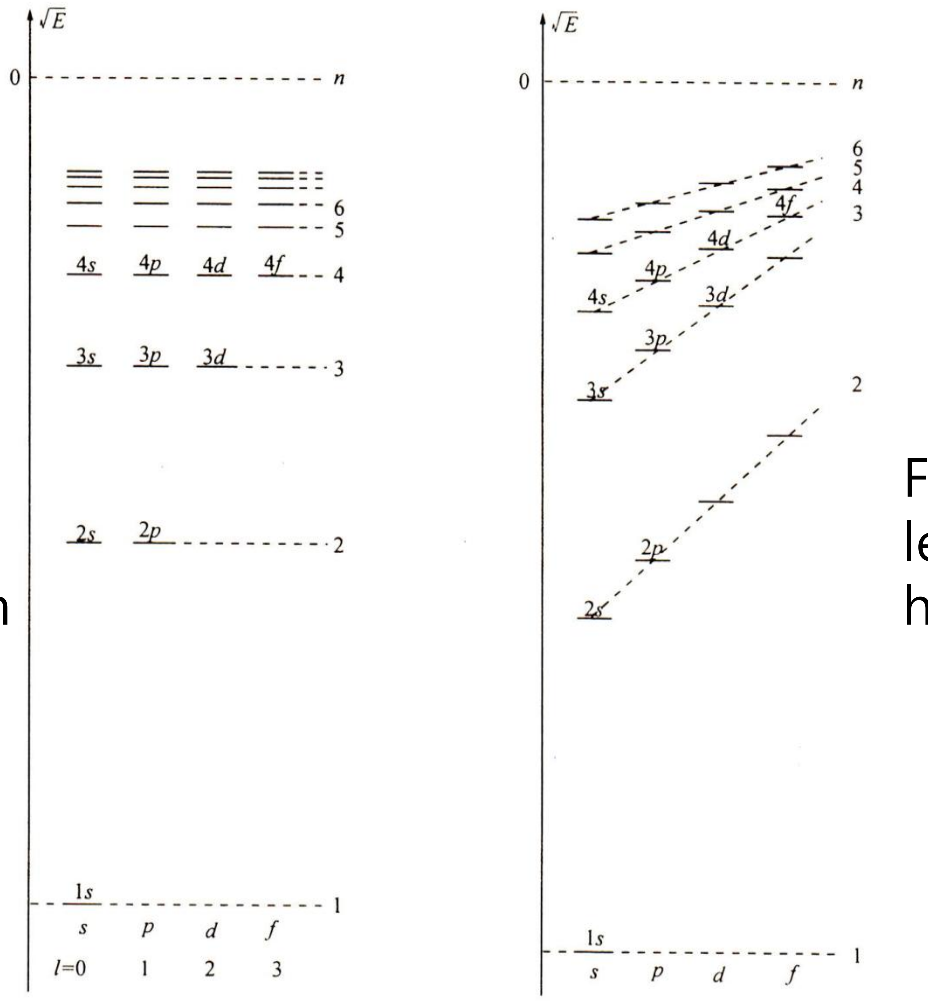


그림 1-14 (*a*) 수소의 에너지 준위, (*b*) 2 개 이상의 전자를 가진 원자의 에너지 준위.

Fig. 1-14(b) Energy level of atom that has 2 electrons

Electron Configuration

- An atom has an infinite number of orbitals, though many of them are so high in energy and so far from the nucleus that an electron would get lost out there. When all of the electrons are in the lowest energy orbitals the atom is said to be in its **ground state**. The most valuable quantum mechanics skill for a freshman chemistry student is being able to determine how many electrons occupy which orbitals in any given atom's ground state. When an atom gains energy one of its electrons moves to a higher energy state. The energy is given off when the electron moves to a lower energy state. The amount of energy needed to move electrons to higher and lower energy levels is a unique characteristic for each element and each molecule. Many important instruments use this aspect of quantum mechanics to identify elements and compounds in a field known as spectroscopy.

- In an atom with more than one electron, the orbitals within a subshell have the same energy, but the orbitals in different subshells have slightly different energies, even if they are in the same shell. The s orbitals are lower in energy than the p which are lower than the d and so on. Life would be nice if the energy ranking was the same as the order in the table above, but it isn't. The d and f orbitals are so much higher in energy that they are higher than the s and p orbitals of the next higher shell. The **Pauli Aufbau filling order** is a ranking of the orbitals from lowest energy to higher energies:
- 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p7s 5f 6d 7p

- We can use the filling order to determine how many electrons are in which orbitals for the ground state of an atom. The **electron configuration** is a list of the subshells that are occupied in the ground state with a superscript by each subshell name to indicate the number of electrons in that subshell. For example, phosphorus has 15 electrons.

P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

The order to fill the electron at the atomic energy level.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ \cdots$

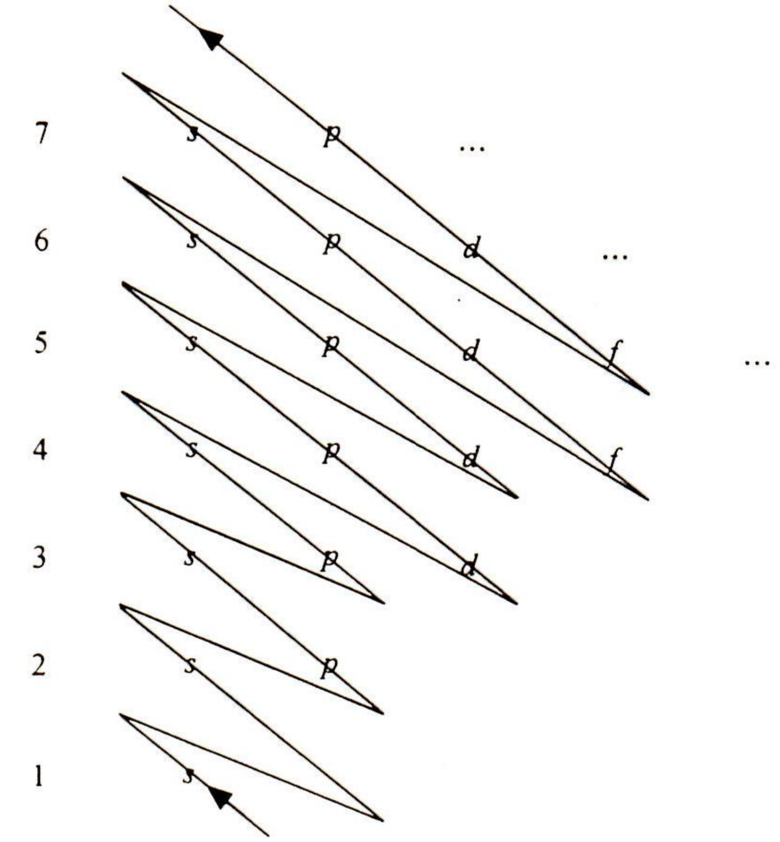


그림 1-15 전자가 2 개 이상인 원자에서 전자가 채워지는 순서.

표 1-3 주기율표의 처음 30가지 원소에 대한 전자 배치.

		1s	2s	2p	3s	3p	4s	3d
H	$1s$	↑		○ ○ ○				
He	$1s^2$	↑↓		○ ○ ○				
Li	$1s^2 2s$	↑↓	↑	○ ○ ○				
Be	$1s^2 2s^2$	↑↓	↑↓	○ ○ ○				
S	$1s^2 2s^2 2p$	↑↓	↑↓	↑ ○ ○				
C	$1s^2 2s^2 2p^2$	↑↓	↑↓	↑ ↑ ○				
N	$1s^2 2s^2 2p^3$	↑↓	↑↓	↑ ↑ ↑				
O	$1s^2 2s^2 2p^4$	↑↓	↑↓	↑↓ ↑ ↑				
F	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑↓ ↑↓ ↑				
Ne	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓				
Na	$3s$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	○ ○ ○		
Mg	$3s^2$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	○ ○ ○		
Al	$3s^2 3p$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ○ ○		
Si	$3s^2 3p^2$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ○		
P	$3s^2 3p^3$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑		
S	$3s^2 3p^4$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑		
Cl	$3s^2 3p^5$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑		
Ar	$3s^2 3p^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓		
K	$4s$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	○ ○ ○ ○ ○
Ca	$4s^2$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	○ ○ ○ ○ ○
Sc	$4s^2 3d$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ○ ○ ○ ○
Ti	$4s^2 3d^2$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ○ ○ ○
V	$4s^2 3d^3$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑ ○ ○
Cr	$4s^1 3d^5$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑ ↑ ↑ ↑ ↑
Mn	$4s^2 3d^5$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑ ↑ ↑
Fe	$4s^2 3d^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑ ↑ ↑
Co	$4s^2 3d^7$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑ ↑ ↑
Ni	$4s^2 3d^8$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑
Cu	$4s^1 3d^{10}$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Zn	$4s^2 3d^{10}$	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓