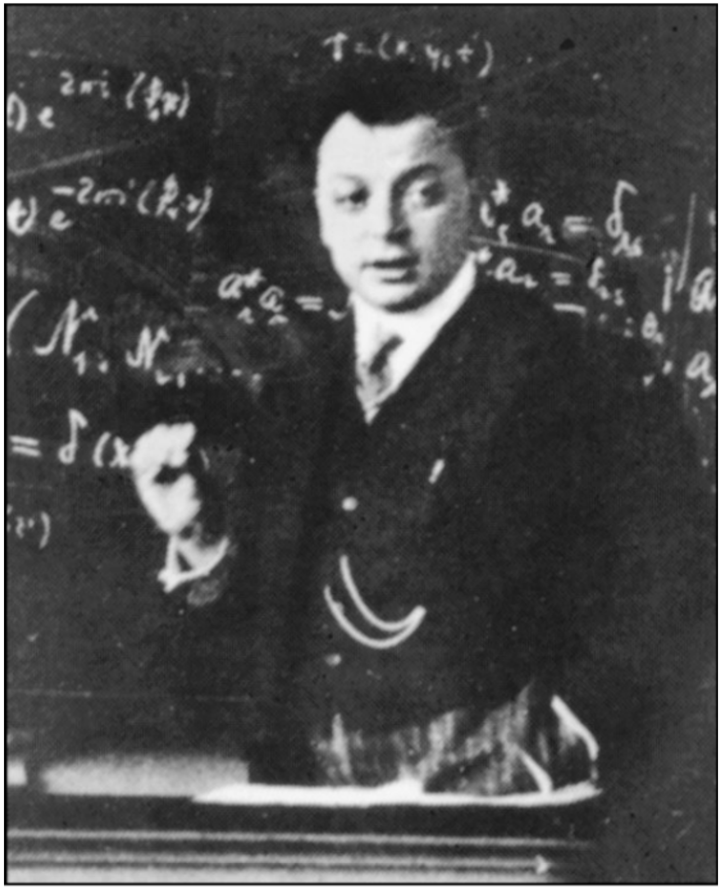
Ch. 7. Many-Electron Atoms



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Wolfgang Pauli
(1900-1958)

Normal and Anomalous Zeeman Effects

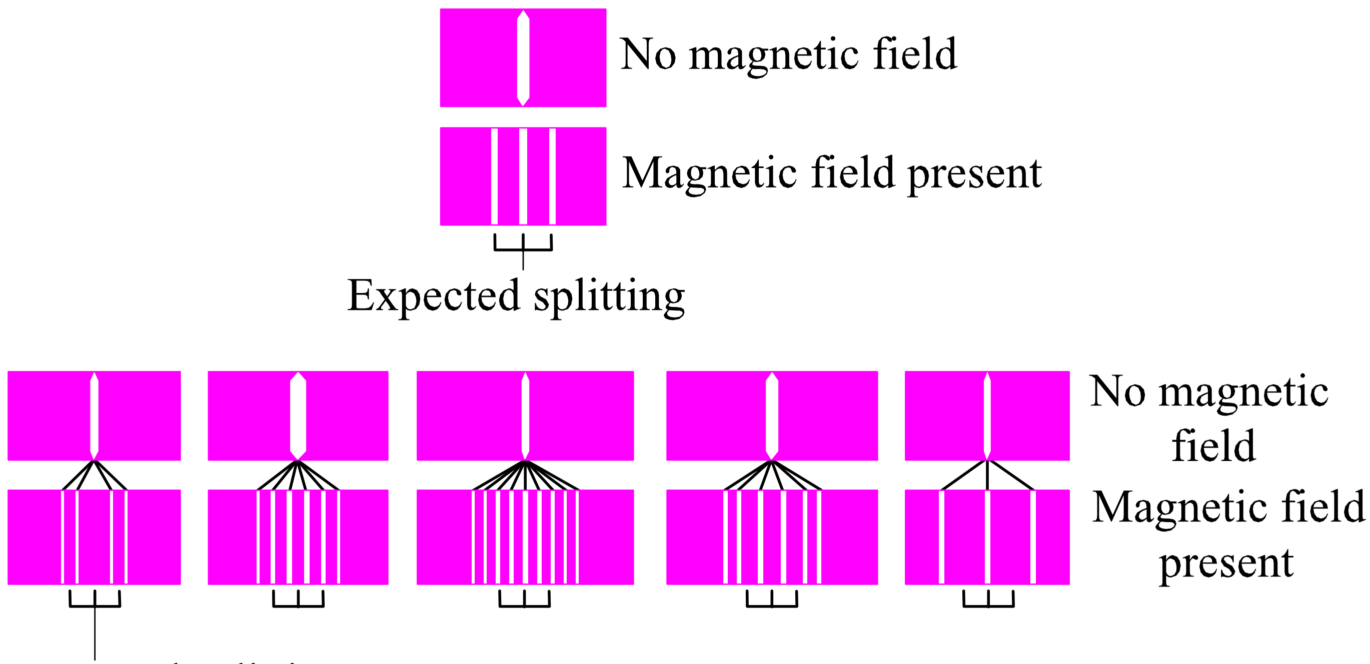
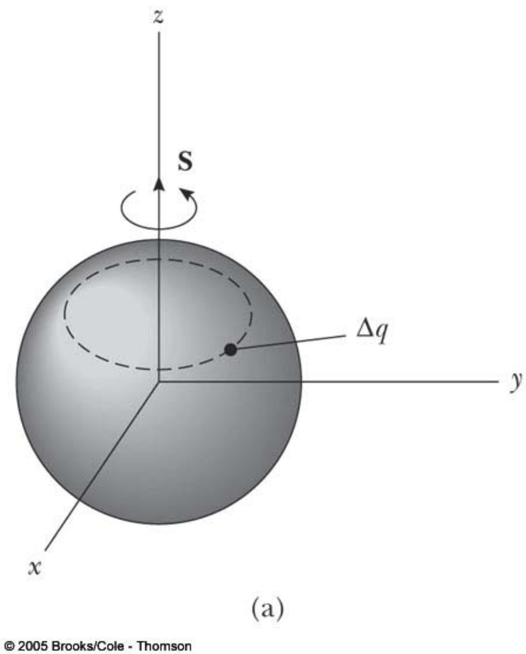
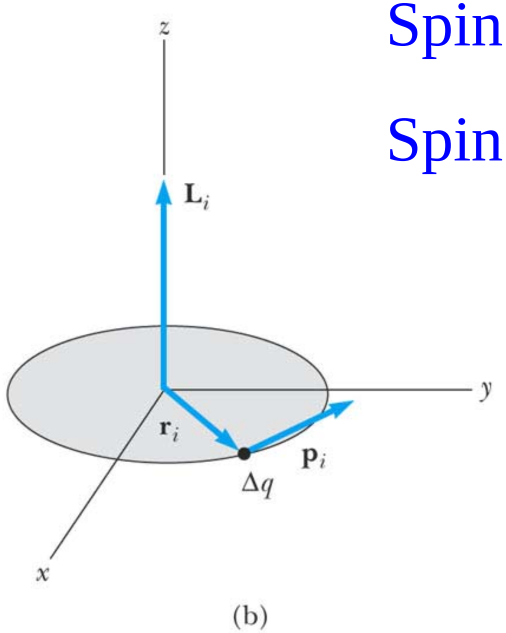


그림 7.1 여러 스펙트럼 선에서의 정상 Zeeman 효과와 비정상적 Zeeman 효과.

Spin – Classical Analogy





Spin magnetic moment $\boldsymbol{\mu}_s$

Spin angular momentum $\mathbf{S}$

$$\boldsymbol{\mu}_s = \frac{q}{2m_e}\sum \mathbf{L}_i = \frac{q}{2m_e}\mathbf{S}$$

$$\boldsymbol{\mu}_s = \frac{-e}{2m_e} g\mathbf{S}$$

$$g = 2$$

Stern-Gerlach Experiment

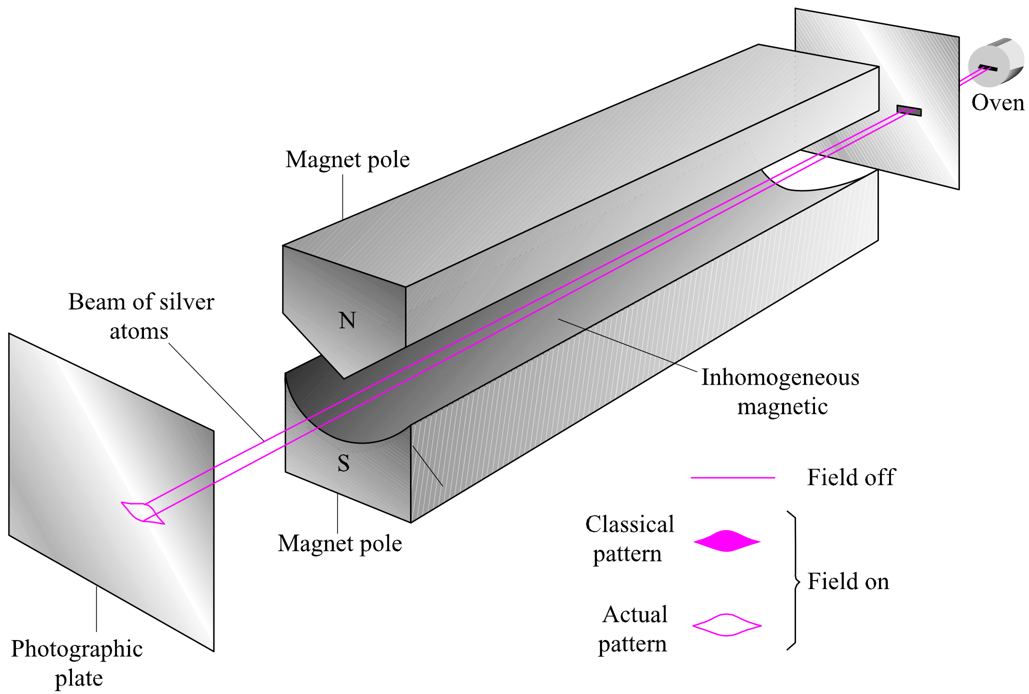
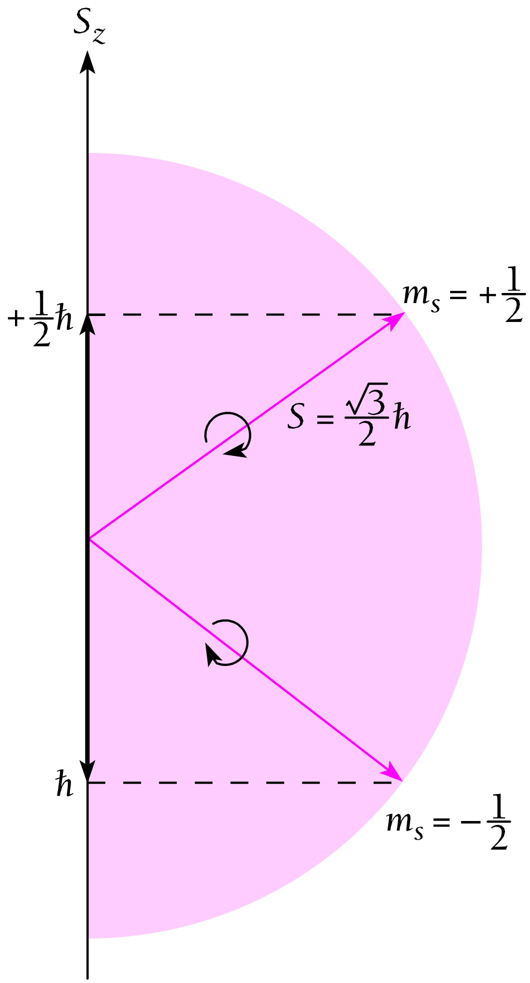


그림 7.3 슈테런-게를라흐(Stern-Gerlach)실험.

Spin



$$s = \frac{1}{2}$$

$$m_s = -\frac{1}{2},\ \frac{1}{2}$$

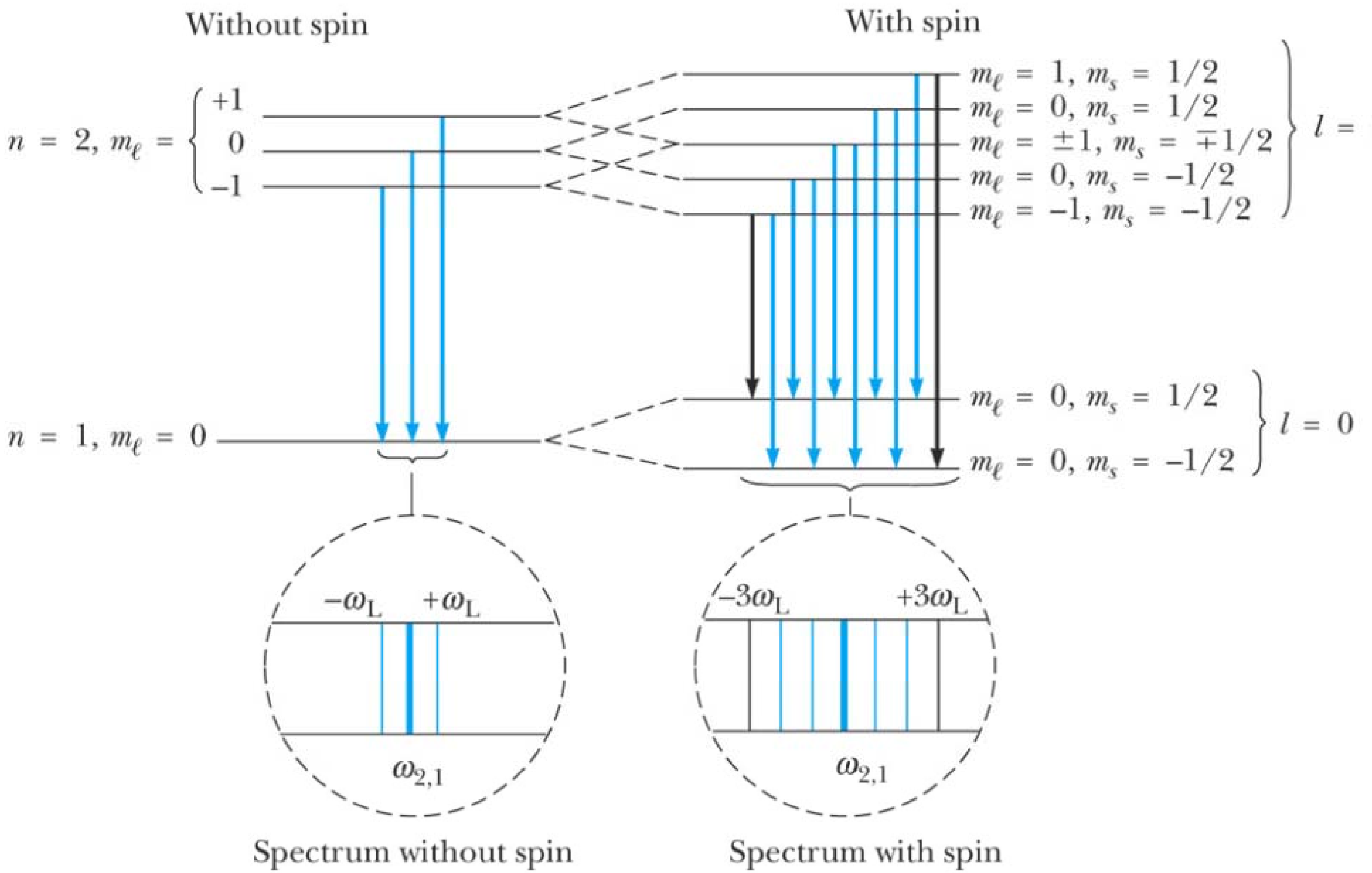
$$S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

$$S_z = m_s\hbar = -\frac{\hbar}{2},\ \frac{\hbar}{2}$$

표 7.1 원자 전자의 양자수

이름	기호	가능한 값	결정하는 물리량
주	n	$1, 2, 3, \ldots$	Electron energy
궤도	l	$0, 1, 2, \ldots, n-1$	Orbital angular-momentum magnitude
자기	m_l	$-l, \ldots, 0, \ldots, +l$	Orbital angular-momentum direction
스핀 자기	m_s	$-\frac{1}{2}, +\frac{1}{2}$	Electron spin direction

$$\boldsymbol{\mu} = \boldsymbol{\mu}_o + \boldsymbol{\mu}_s = \frac{-e}{2m_e}\left(\mathbf{L} + g\mathbf{S}\right) \qquad U = -\boldsymbol{\mu} \cdot \mathbf{B}$$



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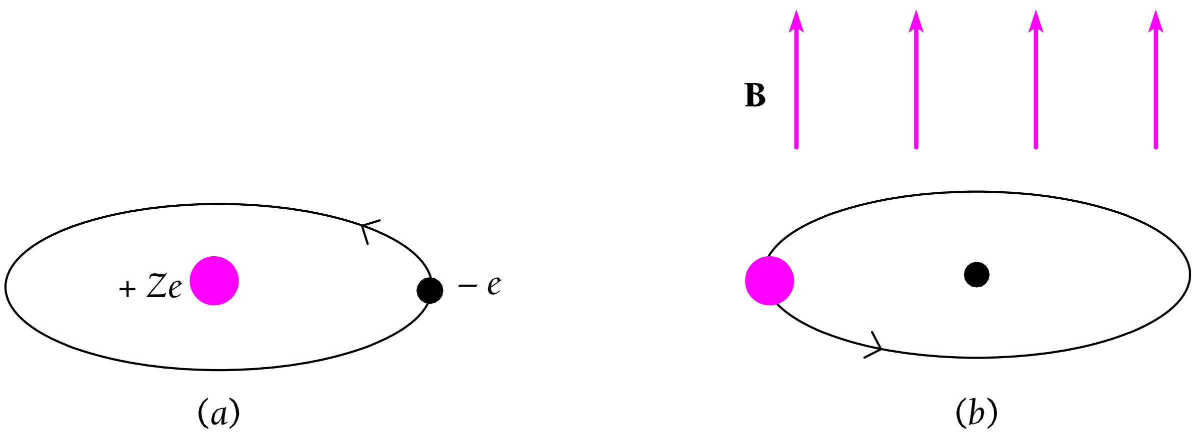
Spin-Orbit Coupling



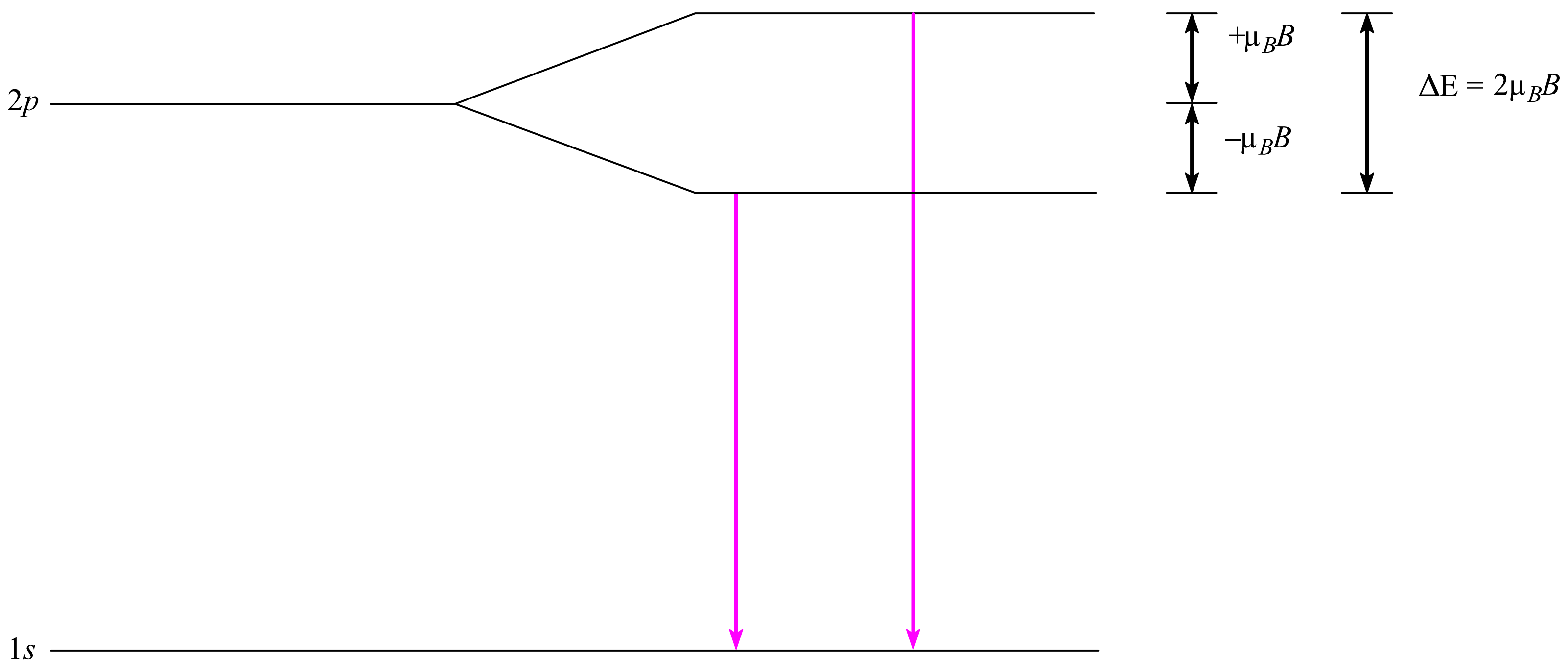
$$U_m = -\mu B \cos\theta$$

$$\mu \cos\theta = \pm \mu_B$$

$$U_m = \pm \mu_B B$$

그림 7.13 (a) 핵이 정지하고 있는 좌표계에서 바라볼 때 전자가 핵 주위를 돌고 있다. (b) 전자가 정지하고 있는 좌표계에서 바라볼 때 핵이 전자 주위를 돌고 있다. 그 결과 전자가 느끼는 핵에 의한 자기장은 궤도면 위로 수직인 방향이다. 이 자기장 과 전자 스핀과의 상호작용에 의해 스핀-궤도 결합 현상이 일어난다.

Spin-Orbit Coupling



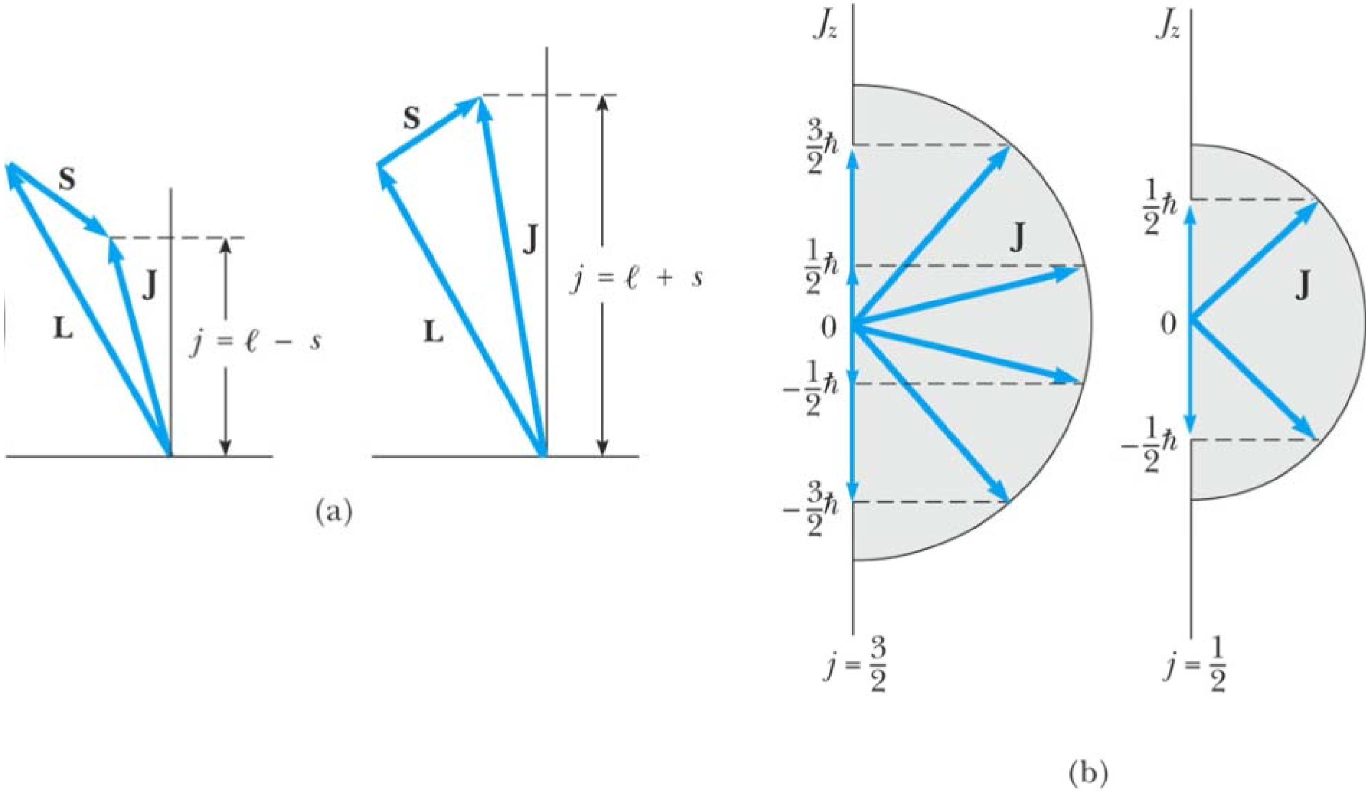
Total Angular Momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

$$J = \sqrt{j(j+1)}\hbar$$

$$J_z = m_j\hbar \qquad \text{with } m_j = j,\ j-1,\ \cdots,\ -j$$

$$j = l+s,\ l+s-1,\ \cdots,\ |l-s|$$



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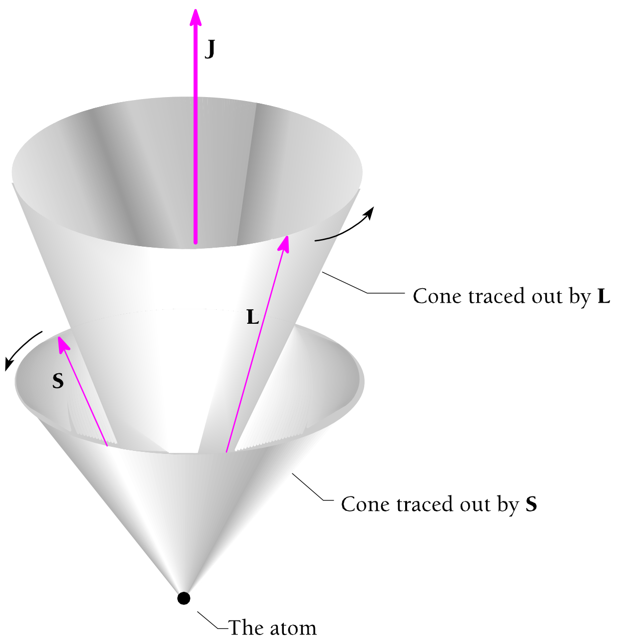


그림 7.17 궤도 각운동량 L과 스핀 각운동량 S는 J에 대해 세차 운동을 한다.

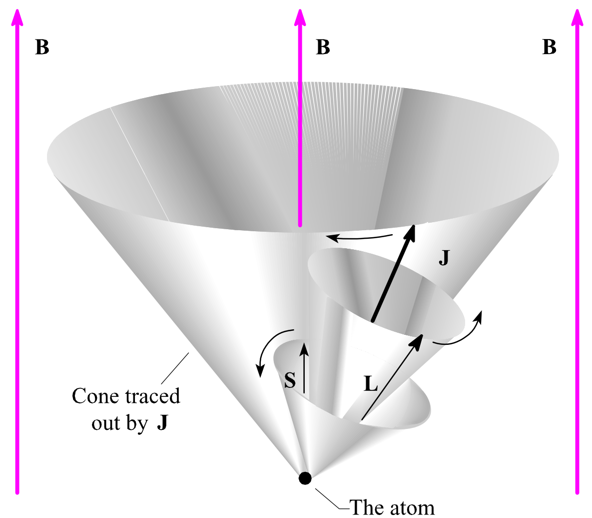


그림 7.18 외부 자기장 B가 존재할 경우 총 각운동량 J가 B에 대해 세차 운동을 한다.

Pauli and Einstein

“I will never forget the speech about me, and for me, that he gave at Princeton in 1945 after I got the Nobel Prize. It was like the abdication of a king, installing me as a kind of elected son, as his successor," Wolfgang Pauli reminisced in a 1955 letter to Max Born.

The "king" was, of course, the 66-year-old Einstein. His realm was physics and Pauli was his appointed heir. The occasion was a banquet in Princeton honoring Pauli, who had been awarded the prize for his discovery of the exclusion principle.

In 1969, eleven years after Pauli's death, Born commented, "Since the time when he was my assistant in Göttingen, I knew he was a genius, comparable only to Einstein himself. As a scientist he was, perhaps, even greater than Einstein. But he was a completely different type of man, who, in my eyes, did not attain Einstein's greatness."

http://www.aip.org/pt/vol-54/iss-2/p43.html

What would Pauli say?

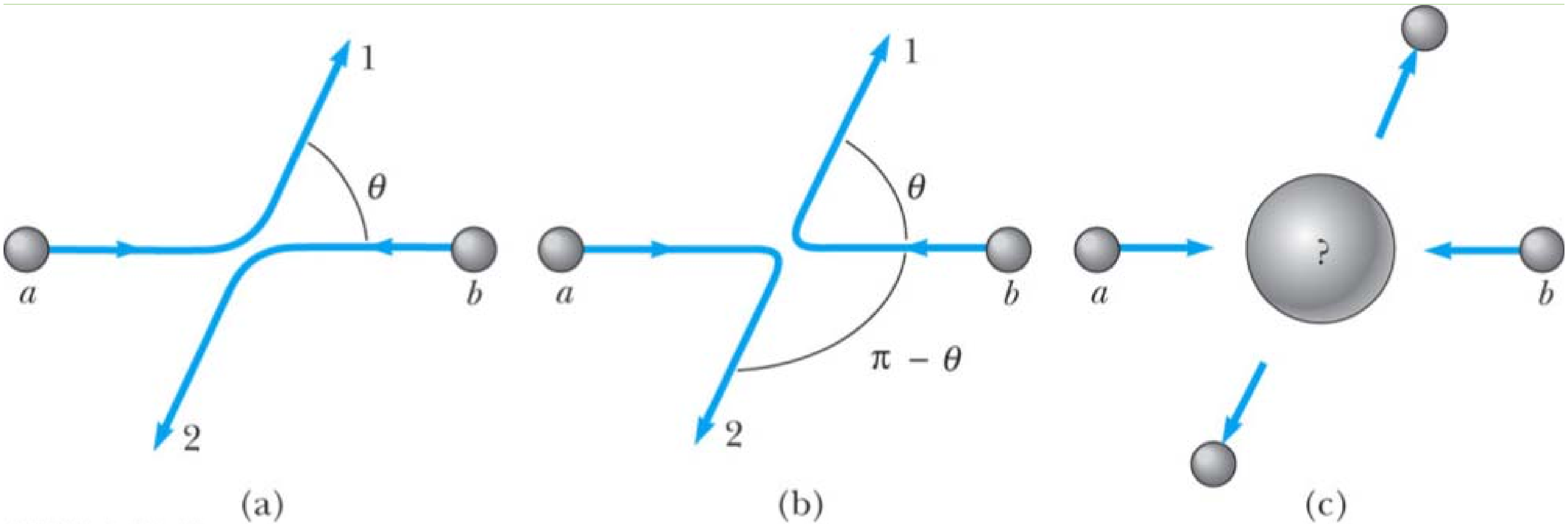
“It is not even wrong.”

“I do not mind if you think slowly, but I do object when you publish more quickly than you think.”

“Oh, no. Far from it. What you said was so confused that one could not tell whether it was nonsense or not.”

“You know, what Mr. Einstein said is not so stupid.”

Distinguishable and Indistinguishable Particles



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Exchange Symmetry

$$\left|\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)\right|^2=\left|\psi\left(\mathbf{r}_2,\mathbf{r}_1\right)\right|^2$$

$$\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)=\psi\left(\mathbf{r}_2,\mathbf{r}_1\right)$$

bosons (예: photons)

$$\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)=-\psi\left(\mathbf{r}_2,\mathbf{r}_1\right)$$

fermions (예: electrons)

Example: He Atom

$$-\frac{\hbar^2}{2m_e}\nabla_1^2\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)+k\frac{(2e)(-e)}{r_1}\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)-\frac{\hbar^2}{2m_e}\nabla_2^2\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)+k\frac{(2e)(-e)}{r_2}\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)=E\psi\left(\mathbf{r}_2,\mathbf{r}_1\right)$$

$$H(1)\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)+H(2)\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)=E\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)$$

$$H(1)\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)=E_a\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)$$

$$H(2)\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)=E_b\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)$$

$$\left[H(1)+H(2)\right]\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)=\left(E_a+E_b\right)\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)$$

$$\psi_{ab}\left(\mathbf{r}_1,\mathbf{r}_2\right)=\frac{1}{\sqrt{2}}\left[\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)-\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)\right]$$

$$\psi_{ab}\left(\mathbf{r}_2,\mathbf{r}_1\right)=\frac{1}{\sqrt{2}}\left[\psi_a\left(\mathbf{r}_2\right)\psi_b\left(\mathbf{r}_1\right)-\psi_a\left(\mathbf{r}_1\right)\psi_b\left(\mathbf{r}_2\right)\right]=-\psi_{ab}\left(\mathbf{r}_1,\mathbf{r}_2\right)$$

$$\psi_{aa}\left(\mathbf{r}_1,\mathbf{r}_2\right)=0$$

Pauli's exclusion principle

(No two electrons in an atom can have the same set of quantum numbers.)

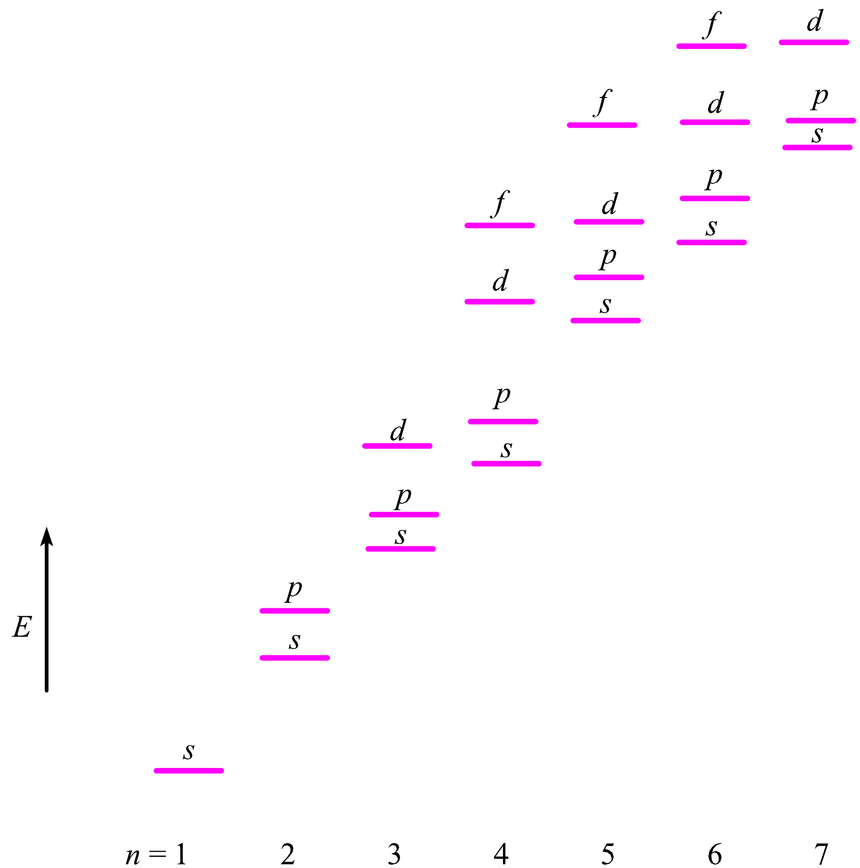

그림 7.12 원자의 양자상태 순서, 실제 크기가 아님.

Pauli's Exclusion Principle and Hund's Rule

Atom	1s	2s	2p			Electron configuration
Li	↑↓	↑				$1s^2 2s^1$
Be	↑↓	↑↓				$1s^2 2s^2$
B	↑↓	↑↓	↑			$1s^2 2s^2 2p^1$
C	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$
N	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$

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Dimitri Ivanovitch Mendeleev (1834-1907)

Table 7.2

The Periodic Table of the Elements

The number above the symbol of each element is its atomic number, and the number below its name is its average atomic mass. The elements whose atomic masses are given in parentheses do not occur in nature but have been created in nuclear reactions. The atomic mass in such a case is the mass number of the most long-lived radioisotope of the element.

Elements with atomic numbers 110, 111, 112, 114, and 116 have also been created but not yet named.

Group	1	2											3	4	5	6	7	8
Period 1	1 H Hydrogen 1.008																	2 He Helium 4.003
2	3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
3	11 Na Sodium 22.99	12 Mg Magnesium 24.31	Transition metals										13 Al Aluminium 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
4	19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.8	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
5	37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.1	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.9	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.8
6	55 Cs Cesium 132.9	56 Ba Barium 137.3		72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium 226.0		104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Ns Nielsbohrium (262)	108 Hs Hassium (264)	109 Mt Meitnerium (266)								Halogens	Inert gases
	Alkali metals																	

Lanthanides (rare earths)

57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 184.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
89 Ac Actinium (227)	90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (260)	102 No Nobelium (259)	103 Lw Lawrencium (262)

Actinides

Table 7.4 Electron Configurations of the Elements

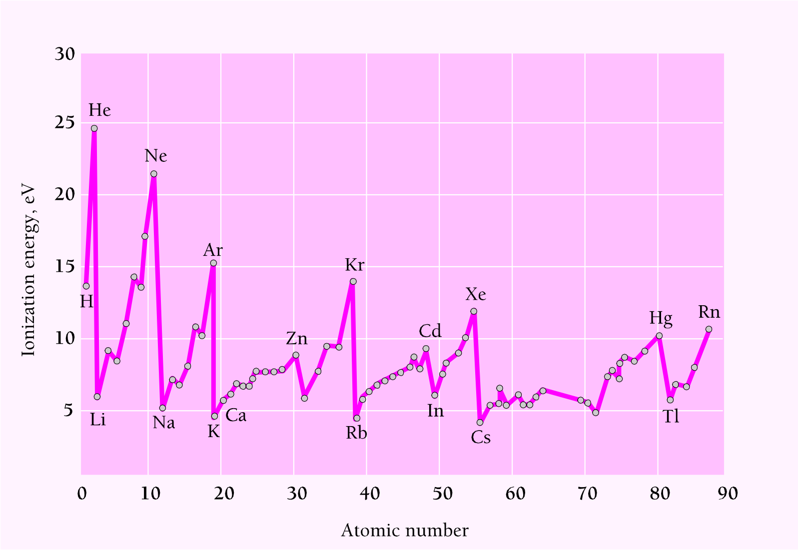
	K	L		M			N				O				P			Q	
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s	
1 H	1																		
2 He	2																		← Inert gas
3 Li	2	1																	← Alkali metal
4 Be	2	2																	
5 B	2	2	1																
6 C	2	2	2																
7 N	2	2	3																
8 O	2	2	4																
9 F	2	2	5																← Halogen
10 Ne	2	2	6																← Inert gas
11 Na	2	2	6	1															← Alkali metal
12 Mg	2	2	6	2															
13 Al	2	2	6	2	1														
14 Si	2	2	6	2	2														
15 P	2	2	6	2	3														
16 S	2	2	6	2	4														
17 Cl	2	2	6	2	5														← Halogen
18 Ar	2	2	6	2	6														← Inert gas
19 K	2	2	6	2	6		1												← Alkali metal
20 Ca	2	2	6	2	6		2												
21 Sc	2	2	6	2	6	1	2												Transition elements (21–30)
22 Ti	2	2	6	2	6	2	2												
23 V	2	2	6	2	6	3	2												
24 Cr	2	2	6	2	6	5	1												
25 Mn	2	2	6	2	6	5	2												
26 Fe	2	2	6	2	6	6	2												
27 Co	2	2	6	2	6	7	2												
28 Ni	2	2	6	2	6	8	2												
29 Cu	2	2	6	2	6	10	1												
30 Zn	2	2	6	2	6	10	2												
31 Ga	2	2	6	2	6	10	2	1											
32 Ge	2	2	6	2	6	10	2	2											
33 As	2	2	6	2	6	10	2	3											
34 Se	2	2	6	2	6	10	2	4											
35 Br	2	2	6	2	6	10	2	5											← Halogen
36 Kr	2	2	6	2	6	10	2	6											← Inert gas
37 Rb	2	2	6	2	6	10	2	6			1								← Alkali metal
38 Sr	2	2	6	2	6	10	2	6			2								
39 Y	2	2	6	2	6	10	2	6	1		2								Transition elements (39–48)
40 Zr	2	2	6	2	6	10	2	6	2		2								
41 Nb	2	2	6	2	6	10	2	6	4		1								
42 Mo	2	2	6	2	6	10	2	6	5		1								
43 Tc	2	2	6	2	6	10	2	6	5		2								
44 Ru	2	2	6	2	6	10	2	6	7		1								
45 Rh	2	2	6	2	6	10	2	6	8		1								
46 Pd	2	2	6	2	6	10	2	6	10										
47 Ag	2	2	6	2	6	10	2	6	10		1								
48 Cd	2	2	6	2	6	10	2	6	10		2								
49 In	2	2	6	2	6	10	2	6	10		2	1							
50 Sn	2	2	6	2	6	10	2	6	10		2	2							
51 Sb	2	2	6	2	6	10	2	6	10		2	3							
52 Te	2	2	6	2	6	10	2	6	10		2	4							

Table 7.4 (*Cont.*)

	K	L		M			N				O				P			Q	
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s	
53 I	2	2	6	2	6	10	2	6	10		2	5 ← Halogen							
54 Xe	2	2	6	2	6	10	2	6	10		2	6 ← Inert gas							
55 Cs	2	2	6	2	6	10	2	6	10		2	6			1 ← Alkali metal				
56 Ba	2	2	6	2	6	10	2	6	10		2	6			2				
57 La	2	2	6	2	6	10	2	6	10		2	6	1		2				Lanthanides; Transition elements
58 Ce	2	2	6	2	6	10	2	6	10	2	2	6			2				Lanthanides; Transition elements
59 Pr	2	2	6	2	6	10	2	6	10	3	2	6			2				Lanthanides; Transition elements
60 Nd	2	2	6	2	6	10	2	6	10	4	2	6			2				Lanthanides; Transition elements
61 Pm	2	2	6	2	6	10	2	6	10	5	2	6			2				Lanthanides; Transition elements
62 Sm	2	2	6	2	6	10	2	6	10	6	2	6			2				Lanthanides; Transition elements
63 Eu	2	2	6	2	6	10	2	6	10	7	2	6			2				Lanthanides; Transition elements
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2				Lanthanides; Transition elements
65 Tb	2	2	6	2	6	10	2	6	10	9	2	6			2				Lanthanides; Transition elements
66 Dy	2	2	6	2	6	10	2	6	10	10	2	6			2				Lanthanides; Transition elements
67 Ho	2	2	6	2	6	10	2	6	10	11	2	6			2				Lanthanides; Transition elements
68 Er	2	2	6	2	6	10	2	6	10	12	2	6			2				Lanthanides; Transition elements
69 Tm	2	2	6	2	6	10	2	6	10	13	2	6			2				Lanthanides; Transition elements
70 Yb	2	2	6	2	6	10	2	6	10	14	2	6			2				Lanthanides; Transition elements
71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2				Lanthanides; Transition elements
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2				Transition elements
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2				Transition elements
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4		2				Transition elements
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2				Transition elements
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2				Transition elements
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2				Transition elements
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1				Transition elements
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1				Transition elements
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2				Transition elements
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3			
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4			
85 At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5 ← Halogen			
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6 ← Inert gas			
87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1 ← Alkali metal	
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2	
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2	
90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2	Actinides
91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2	Actinides
92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2	Actinides
93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2	Actinides
94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2	Actinides
95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2	Actinides
96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2	Actinides
97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2	Actinides
98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2	Actinides
99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2	Actinides
100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2	Actinides
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2	Actinides
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2	Actinides
103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2	Actinides

표 7.5 원자번호 Z=5부터 Z=10까지 원소의 전자배열. p전자들은 훈트 규칙에 의해 가능한 한 나란한 스핀들을 가진다.

Element	Atomic Number	Configuration	Spins of p Electrons		
Boron	5	$1s^2 2s^2 2p^1$	↑		
Carbon	6	$1s^2 2s^2 2p^2$	↑	↑	
Nitrogen	7	$1s^2 2s^2 2p^3$	↑	↑	↑
Oxygen	8	$1s^2 2s^2 2p^4$	↑↓	↑	↑
Fluorine	9	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑
Neon	10	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓



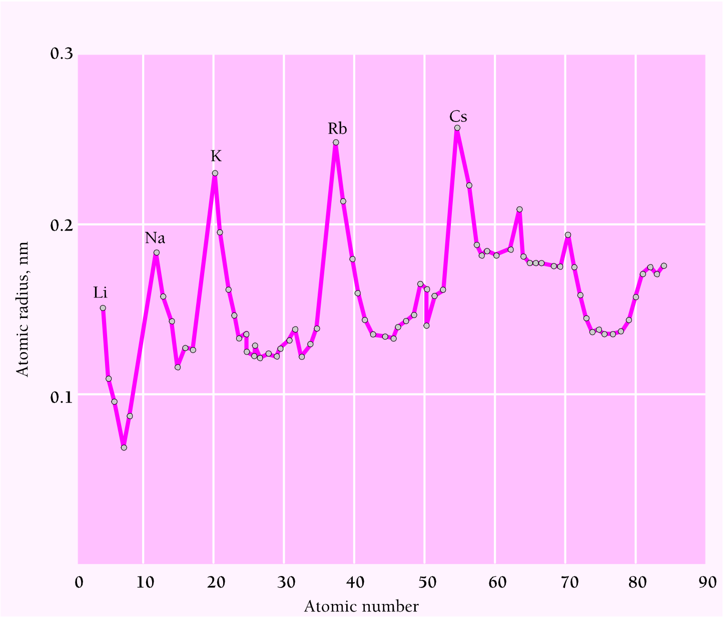


그림 7.10 원자번호에 따르는 이온화 에너지의 변화.

그림 7.11 원소들의 원자 반지름.

표 7.3 M(n=3) 껍질의 버금껍질 용량

	$m_l = 0$	$m_l = -1$	$m_l = +1$	$m_l = -2$	$m_l = +2$	
$l = 0$:	⇃↾					↾$m_s = +\frac{1}{2}$
$l = 1$:	⇃↾	⇃↾	⇃↾			⇃$m_s = -\frac{1}{2}$
$l = 2$:	⇃↾	⇃↾	⇃↾	⇃↾	⇃↾	

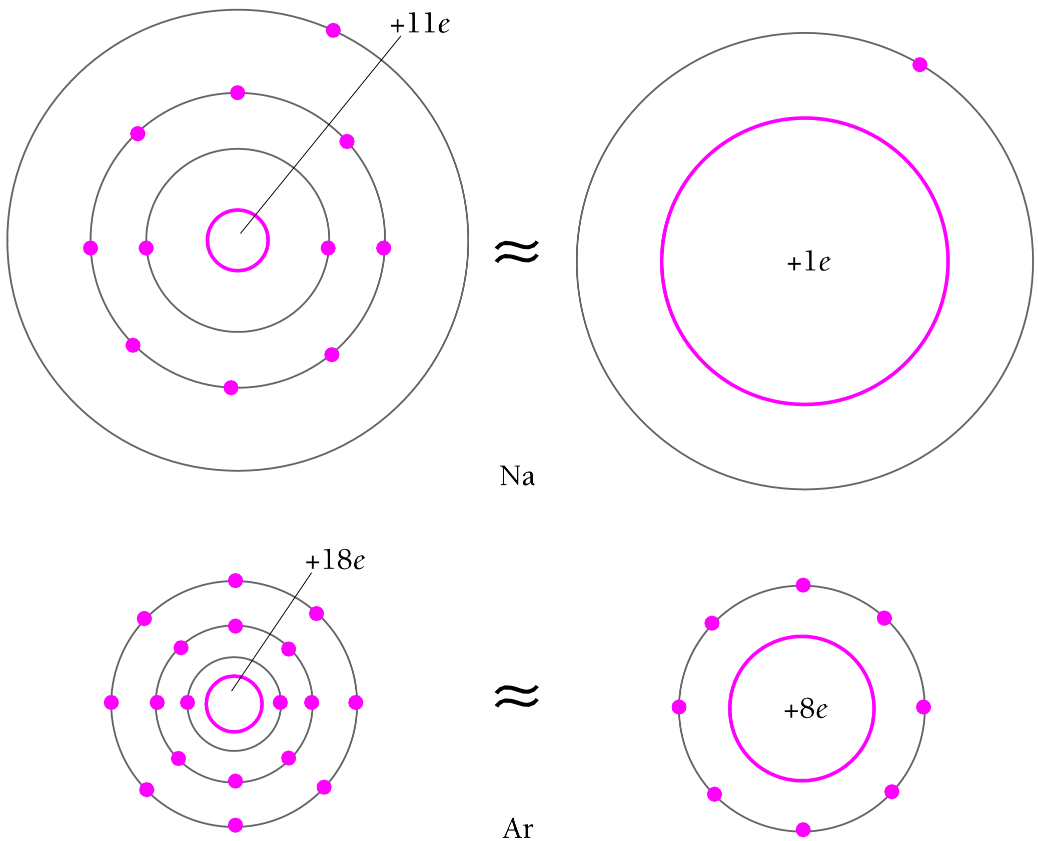


그림 7.9 나트륨과 아르곤 원자에서 전자 가려짐(혹은 차폐)의 도식적 설명. 이 투박한 모델에서의 Ar 원자 외각전자는 Na 원자의 외각전자 보다 8배나 더 큰 핵의 유효 전하 영향을 받는다. 따라서, Ar 원자의 크기는 Na보다 작고 이온화 에너지는 더 크다. 실제 원자에서는 각 전자의 확률 밀도 분포가 복잡한 형태로 겹쳐지므로 차폐되는 전하량은 다를 수 있지만, 그 기본 효과는 이 모델에서와 같다.