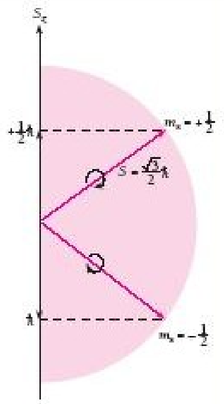
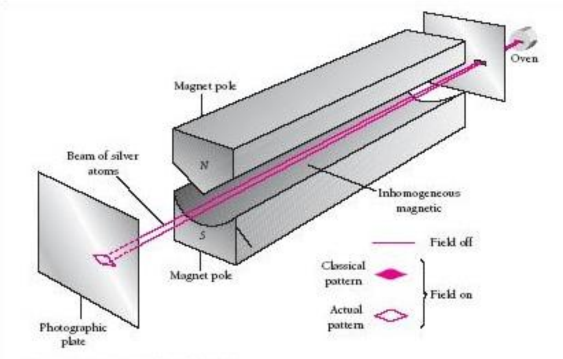
Chapter 5 Many-Electron Atoms

5-1 Total Angular Momentum





The Stern-Gerlach experiment.

Spin magnetic quantum number: $m_s=\pm\frac{1}{2}$ because electrons have two spin types.

Quantum number of spin angular momentum: $s=\frac{1}{2}$

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

Spin magnetic moment: $\mu_s=-eS/m$

The *z*-component of spin angular momentum: $S_z=m_s\hbar=\pm\frac{1}{2}\hbar$

$L=\sqrt{l(l+1)}\hbar$ and $S=\sqrt{s(s+1)}\hbar$ are both quantum vectors. They can be coupled to together: $J=L+S$.

The *z*-component of spin angular moment: $\mu_{sz}=\pm\frac{e\hbar}{2m}$

Total angular momentum *J*: $J=\sqrt{J(J+1)}\hbar$

The *z*-component of total angular momentum: $J_z=m_J\hbar$

For only one electron outside the inner shell: $J=\sqrt{j(j+1)}\hbar$ and $J_z=m_j\hbar=L_z+S_z$, $L_z=m_l\hbar$, $S_z=m_s\hbar \Rightarrow m_j=m_s\pm m_l$, $j=l\pm s=l\pm\frac{1}{2}$.

***LS* coupling:** $L=\sum L_i$, $S=\sum S_i$, and $J=L+S$. The scheme holds for most atoms and these atoms in a weak magnetic field. And the quantum numbers in *LS* coupling are

$L=\sqrt{L(L+1)}\hbar$, $L_z=m_L\hbar$, $S=\sqrt{S(S+1)}\hbar$, $S_z=m_S\hbar$, $J=\sqrt{J(J+1)}\hbar$, $J_z=m_J\hbar$

Rules of *LS* coupling:

$L=l_1+l_2,\ l_1+l_2-1,\ l_1+l_2-2,\ \ldots,\ |l_1-l_2|$

$S=s_1+s_2,\ s_1+s_2-1,\ s_1+s_2-2,\ \ldots,\ |s_1-s_2|$

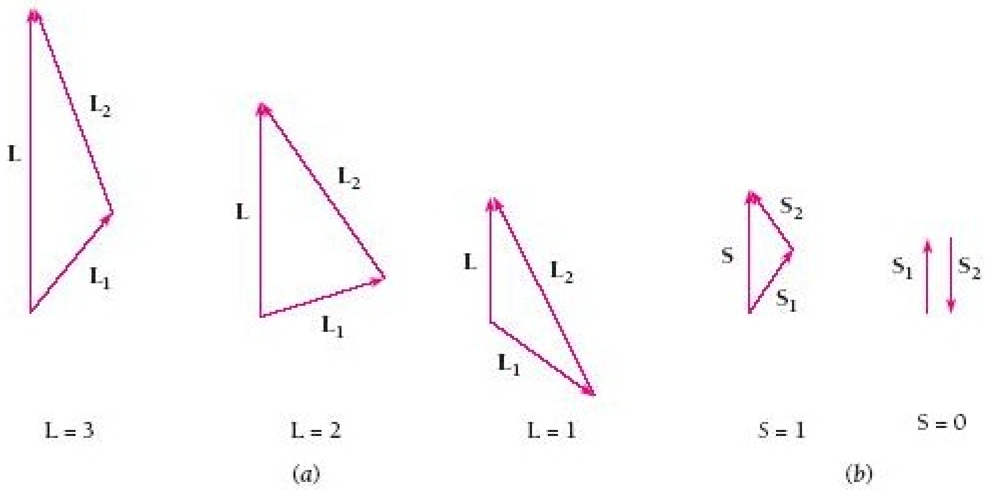
$J=L+S,\ L+S-1,\ L+S-2,\ \ldots,\ |L-S|$

Eg. Find the possible values of the total angular-momentum quantum number *J* under *LS* coupling of two atomic electrons whose orbital numbers are l_1=1 and l_2=2.

(Sol.) L=1+2, 1+2-1, 1+2-2(=|2-1|)=3, 2, 1

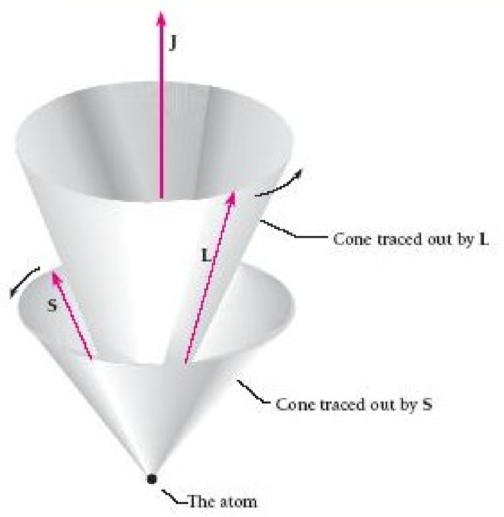
$S=\frac{1}{2}+\frac{1}{2},\ \frac{1}{2}+\frac{1}{2}-1(=|\frac{1}{2}-\frac{1}{2}|)=1, 0$

J=3+1, 3+1-1=3+0=2+1, 3+1-2=2+0=1+1, …, |1-1|=4, 3, 2, 1, 0

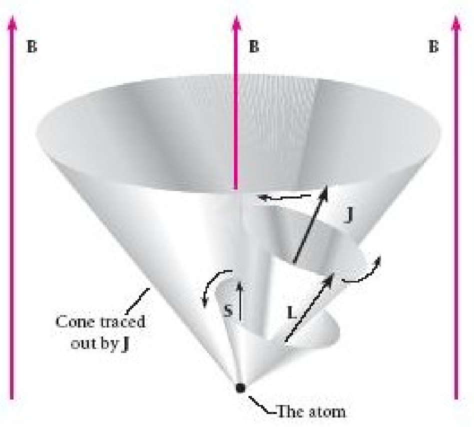


When $l_1 = 1$, $s_1 = \frac{1}{2}$, and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which L_1 and L_2 can combine to form L and two ways in which S_1 and S_2 can combine to form S.

Effect of magnetic filed:



The orbital and spin angular-momentum vectors L and S precess about J.



In the presence of an external magnetic field B, the total angular-momentum vector J processes about B.

jj coupling: $J_i=L_i+S_i$, $J=\sum J_i$. The scheme holds for heavier atoms and these atoms in a strong magnetic field.

Representation of electron states: $n^{2s+1}L_J$, where L=0(S), 1(P), 2(D), 3(F), 4(G), 5(H), 6(I), …

Eg. Find the values of s, L, and J for the representation of electron states: $^1S_0$, $^3P_2$, $^2D_{3/2}$, $^5F_5$, $^6H_{5/2}$.

(Sol.) $^1S_0$: $1=2s+1 \Rightarrow s=0$; $S \Rightarrow L=0$; $0 \Rightarrow J=0$

$^3P_2$: $3=2s+1 \Rightarrow s=1$; $P \Rightarrow L=1$; $2 \Rightarrow J=2$

$^2D_{3/2}$: $2=2s+1 \Rightarrow s=1/2$; $D \Rightarrow L=2$; $3/2 \Rightarrow J=3/2$

$^5F_5$: $5=2s+1 \Rightarrow s=2$; $F \Rightarrow L=3$; $5 \Rightarrow J=5$

$^6H_{5/2}$: $6=2s+1 \Rightarrow s=5/2$; $H \Rightarrow L=5$; $5/2 \Rightarrow J=5/2$

Selection rules of *LS* coupling: $\triangle L=0, \pm1$, $\triangle J=0, \pm1$ (but J: $0 \rightarrow 0$ is prohibited), $\triangle S=0$

5-2 Pauli's Exclusion Principle and Periodical Table

Pauli's Exclusion Principle: No two electrons in one atom (or in close atoms) can occupy the same quantum state.

Consider that particle 1 is in quantum state a and particle 2 is in quantum state b. The wavefunctions $\Psi_I=\Psi_a(1)\Psi_b(2)$ and $\Psi_{II}=\Psi_a(2)\Psi_b(1)$ are identical to each other if particle 1 and particle 2 are indistinguishable. Let an antisymmetric function be $\Psi_A(1,2)=[\Psi_a(1)\Psi_b(2)-\Psi_a(2)\Psi_b(1)]/\sqrt{2}=-\Psi_A(2,1)$ and a symmetric function be $\Psi_S(1,2)=[\Psi_a(1)\Psi_b(2)+\Psi_a(2)\Psi_b(1)]/\sqrt{2}=\Psi_S(2,1)$. If $a=b$, then $\Psi_A(1,2)=0$. That is, particles 1 and 2 can not exist in the same quantum state.

Antisymmetric wavefunction: $\Psi_A(1,2)=[\Psi_a(1)\Psi_b(2)-\Psi_a(2)\Psi_b(1)]/\sqrt{2}$. It is in agreement with Pauli's Exclusion Principle.

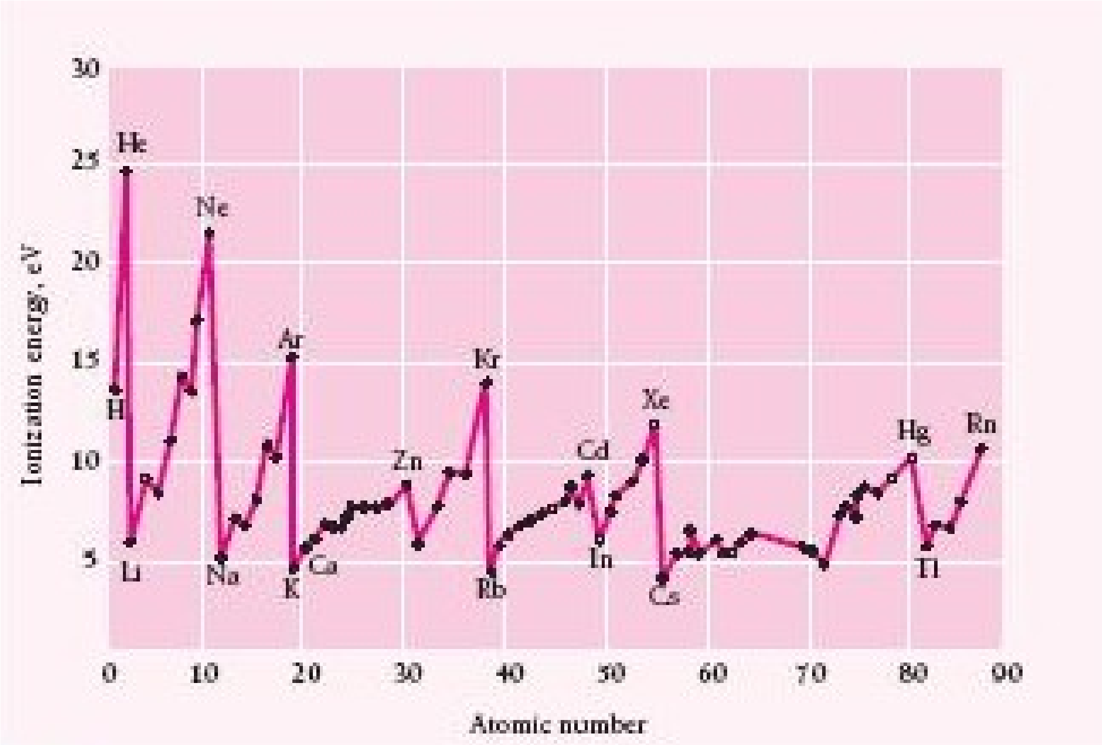
Symmetric wavefunction: $\Psi_S(1,2)=[\Psi_a(1)\Psi_b(2)+\Psi_a(2)\Psi_b(1)]/\sqrt{2}$

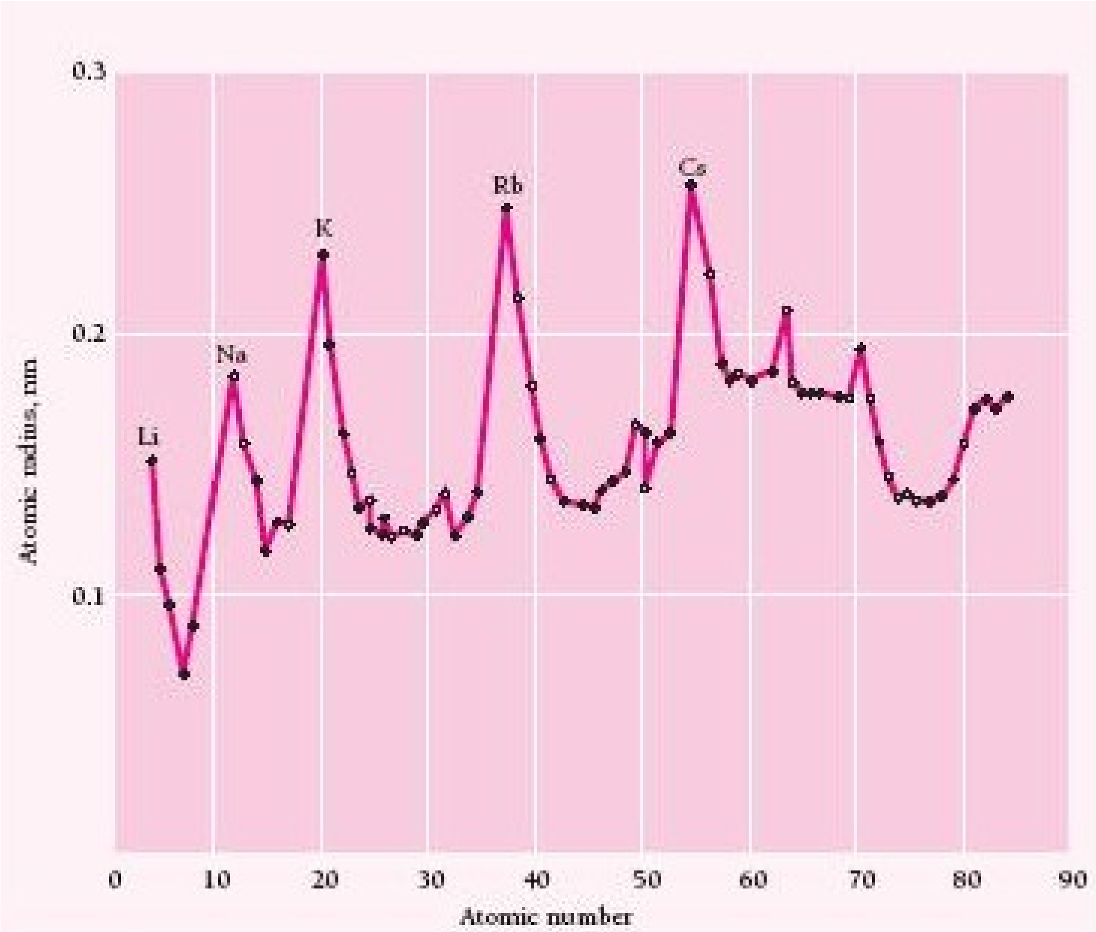
Fermions: Particles of odd half-integral spin have antisymmetric wavefunctions. They obey Pauli's Exclusion Principle.

Eg. Electrons, Protons, Neutrons, etc.

Bosons: Particles of 0 or integral spin have symmetric wavefunctions. They do not obey Pauli's Exclusion Principle.

Eg. Photons, He atom in very low temperature, α-particle, etc.





Magic numbers: There are 2, 10, 18, 36, 54, and 86 electrons in the electron shells such that the electron shells are exceptionally stable.

Periodical Table:

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.

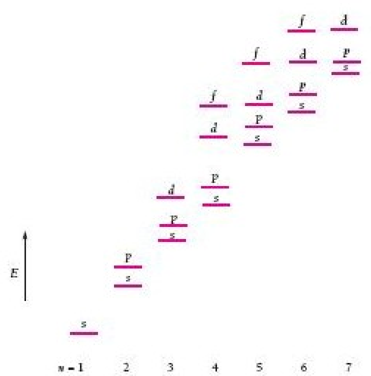
Elements with atomic numbers 110, 111, 112, 114, and 116 have also been created but not yet named.

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											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 131.3
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)									

Alkali metals — Transition metals — Halogens — Inert gases

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 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103



Atomic shells: n=1(K), 2(L), 3(M), 4(N), 5(O), … For a fixed n, l=0, 1, 2, …, n-1. m_l=0, ±1, ±2, …, ±l. $m_s=\pm\frac{1}{2}$. The maximum number of electrons in a shell is $2\sum_{l=0}^{n-1}(2l+1)=2n^2$.

Eg. *n*=1 shell can contain 2 electrons; *n*=2 shell can hold 8 electrons; *n*=3 shell can hold 18 electrons, etc.

Electron configuration: $s(l=0)$, $p(l=1)$, $d(l=2)$, …

Electron Configurations of Elements from $Z = 5$ to $Z = 10$. The p electrons have parallel spins whenever possible, in accord with Hund's rule.

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	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓

Eg. Electron configuration of sodium (Na) is $1s^2 2s^2 2p^6 3s^1$. It means that subshell 1*s* (*n*=1, *l*=0) and subshell 2*s* (*n*=2, *l*=0) contain respective 2 electrons; subshell 2*p* (*n*=2, *l*=1) contains 6 electrons; and subshell 3*s* (*n*=3, *l*=0) contains 1 electron.