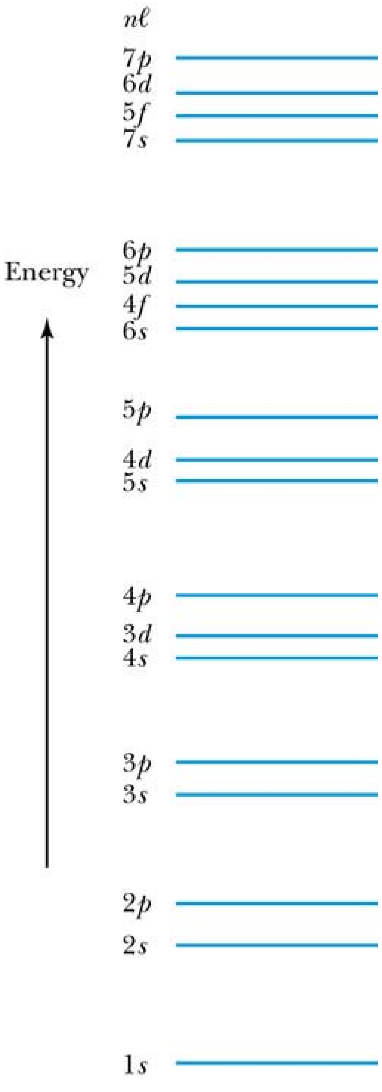
Pauli Exclusion Principle

- To understand multi-electron atoms, Pauli, in 1925, proposed the exclusion principle:

> No two electrons in an atom may have the same set of quantum numbers

- Holds for all fermions – with half integral spins
- This together with the idea that atoms will occupy the lowest energy levels available allows us to understand the Periodic Table
- Imagine building up the elements in the Periodic Table one at a time starting from H

Constructing the Periodic Table



L shell with 2s & 2p subshells

K shell

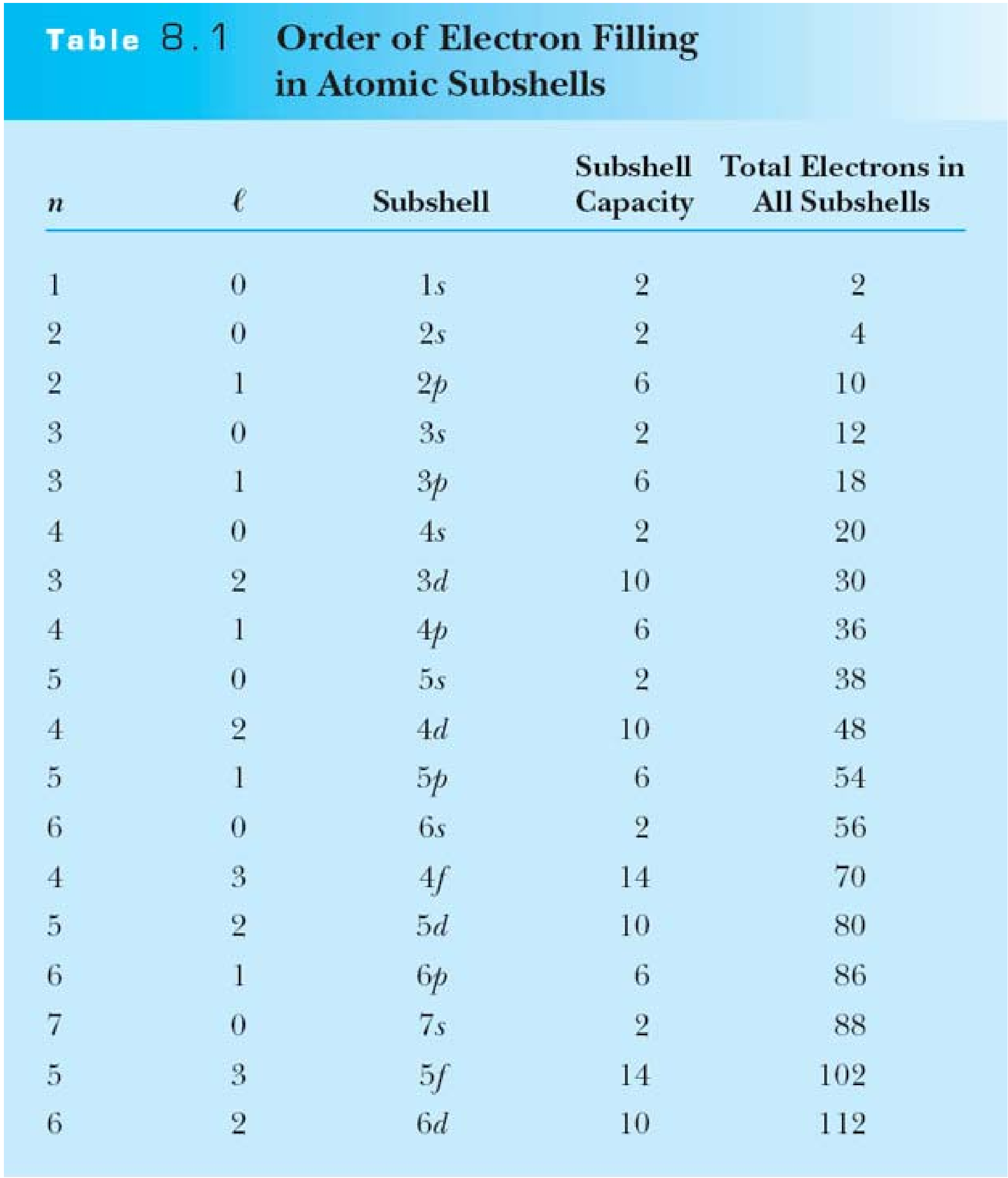
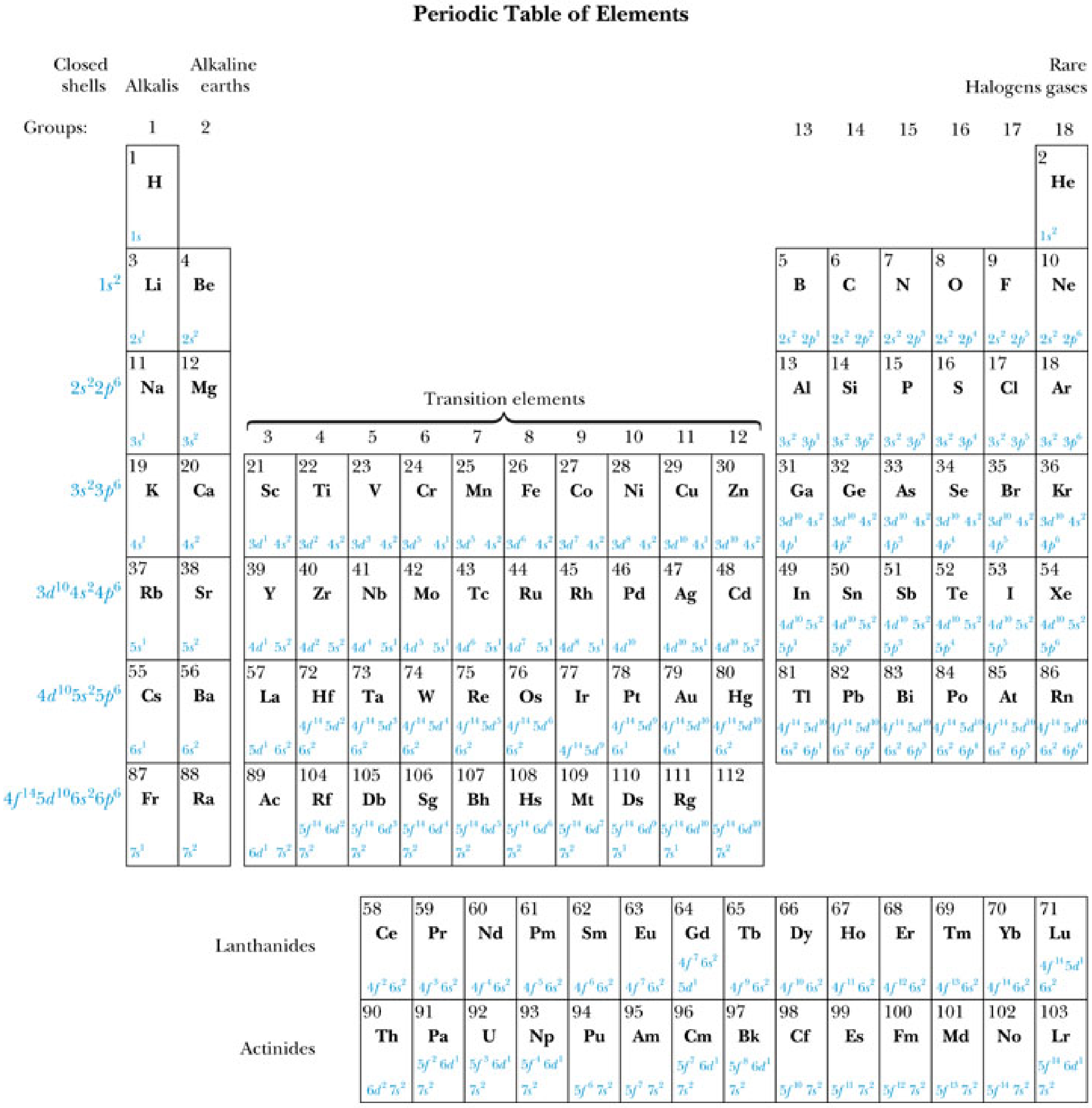


Table 8.1 Order of Electron Filling in Atomic Subshells

n	ℓ	Subshell	Subshell Capacity	Total Electrons in All Subshells
1	0	1s	2	2
2	0	2s	2	4
2	1	2p	6	10
3	0	3s	2	12
3	1	3p	6	18
4	0	4s	2	20
3	2	3d	10	30
4	1	4p	6	36
5	0	5s	2	38
4	2	4d	10	48
5	1	5p	6	54
6	0	6s	2	56
4	3	4f	14	70
5	2	5d	10	80
6	1	6p	6	86
7	0	7s	2	88
5	3	5f	14	102
6	2	6d	10	112

Periodic Table of the Elements



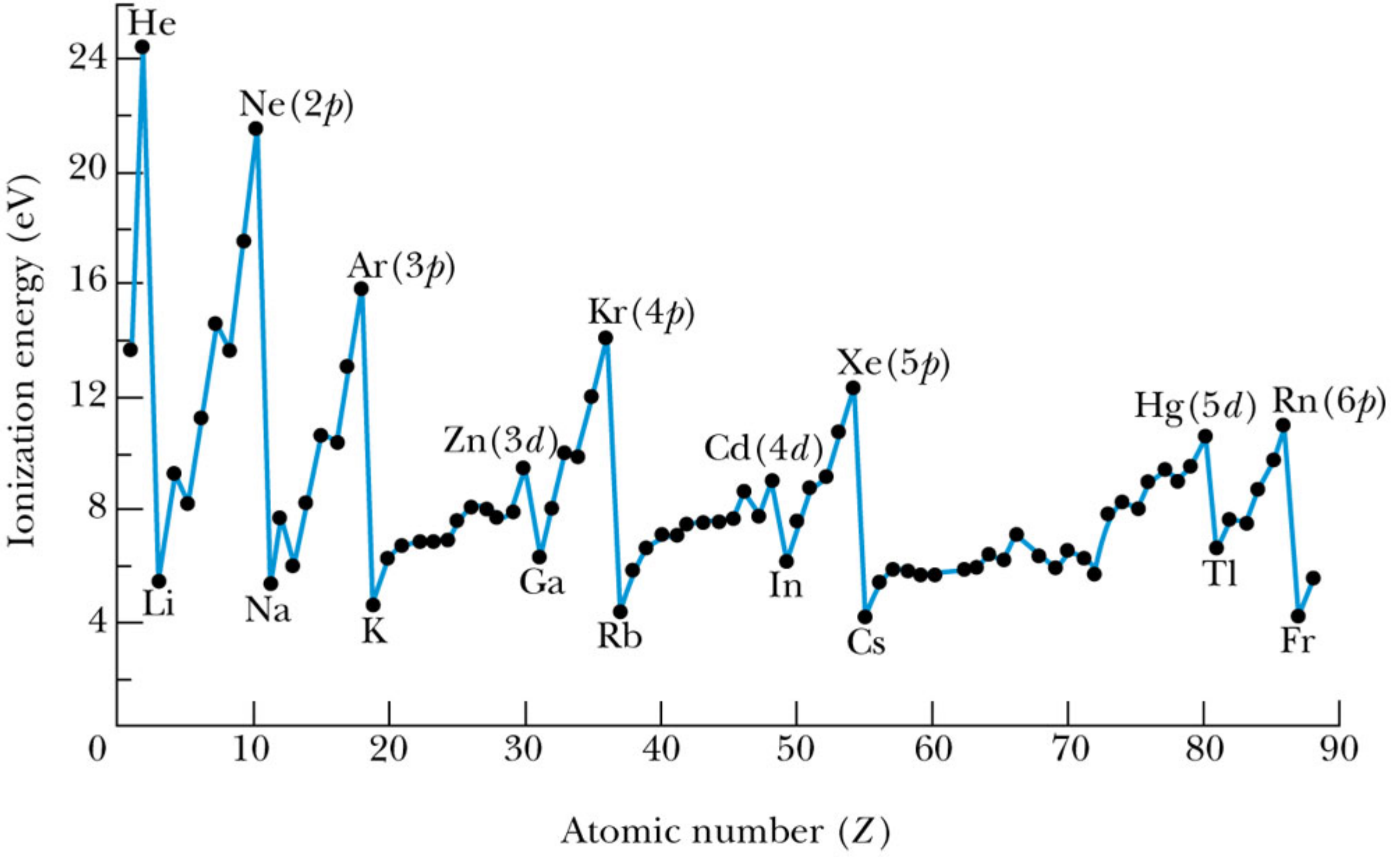
Periodic Table of Elements

Closed shells	Alkalis	Alkaline earths	Transition elements														Halogens	Rare gases
Groups:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1 **H** $1s$																	2 **He** $1s^2$
$1s^2$	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2\ 2p^1$	6 **C** $2s^2\ 2p^2$	7 **N** $2s^2\ 2p^3$	8 **O** $2s^2\ 2p^4$	9 **F** $2s^2\ 2p^5$	10 **Ne** $2s^2\ 2p^6$
$2s^2 2p^6$	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2\ 3p^1$	14 **Si** $3s^2\ 3p^2$	15 **P** $3s^2\ 3p^3$	16 **S** $3s^2\ 3p^4$	17 **Cl** $3s^2\ 3p^5$	18 **Ar** $3s^2\ 3p^6$
$3s^2 3p^6$	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1\ 4s^2$	22 **Ti** $3d^2\ 4s^2$	23 **V** $3d^3\ 4s^2$	24 **Cr** $3d^5\ 4s^1$	25 **Mn** $3d^5\ 4s^2$	26 **Fe** $3d^6\ 4s^2$	27 **Co** $3d^7\ 4s^2$	28 **Ni** $3d^8\ 4s^2$	29 **Cu** $3d^{10}\ 4s^1$	30 **Zn** $3d^{10}\ 4s^2$	31 **Ga** $3d^{10}\ 4s^2$ $4p^1$	32 **Ge** $3d^{10}\ 4s^2$ $4p^2$	33 **As** $3d^{10}\ 4s^2$ $4p^3$	34 **Se** $3d^{10}\ 4s^2$ $4p^4$	35 **Br** $3d^{10}\ 4s^2$ $4p^5$	36 **Kr** $3d^{10}\ 4s^2$ $4p^6$
$3d^{10} 4s^2 4p^6$	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1\ 5s^2$	40 **Zr** $4d^2\ 5s^2$	41 **Nb** $4d^4\ 5s^1$	42 **Mo** $4d^5\ 5s^1$	43 **Tc** $4d^6\ 5s^1$	44 **Ru** $4d^7\ 5s^1$	45 **Rh** $4d^8\ 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}\ 5s^1$	48 **Cd** $4d^{10}\ 5s^2$	49 **In** $4d^{10}\ 5s^2$ $5p^1$	50 **Sn** $4d^{10}\ 5s^2$ $5p^2$	51 **Sb** $4d^{10}\ 5s^2$ $5p^3$	52 **Te** $4d^{10}\ 5s^2$ $5p^4$	53 **I** $4d^{10}\ 5s^2$ $5p^5$	54 **Xe** $4d^{10}\ 5s^2$ $5p^6$
$4d^{10} 5s^2 5p^6$	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $5d^1\ 6s^2$	72 **Hf** $4f^{14}\ 5d^2$ $6s^2$	73 **Ta** $4f^{14}\ 5d^3$ $6s^2$	74 **W** $4f^{14}\ 5d^4$ $6s^2$	75 **Re** $4f^{14}\ 5d^5$ $6s^2$	76 **Os** $4f^{14}\ 5d^6$ $6s^2$	77 **Ir** $4f^{14}\ 5d^9$	78 **Pt** $4f^{14}\ 5d^9$ $6s^1$	79 **Au** $4f^{14}\ 5d^{10}$ $6s^1$	80 **Hg** $4f^{14}\ 5d^{10}$ $6s^2$	81 **Tl** $4f^{14}\ 5d^{10}$ $6s^2\ 6p^1$	82 **Pb** $4f^{14}\ 5d^{10}$ $6s^2\ 6p^2$	83 **Bi** $4f^{14}\ 5d^{10}$ $6s^2\ 6p^3$	84 **Po** $4f^{14}\ 5d^{10}$ $6s^2\ 6p^4$	85 **At** $4f^{14}\ 5d^{10}$ $6s^2\ 6p^5$	86 **Rn** $4f^{14}\ 5d^{10}$ $6s^2\ 6p^6$
$4f^{14} 5d^{10} 6s^2 6p^6$	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $6d^1\ 7s^2$	104 **Rf** $5f^{14}\ 6d^2$ $7s^2$	105 **Db** $5f^{14}\ 6d^3$ $7s^2$	106 **Sg** $5f^{14}\ 6d^4$ $7s^2$	107 **Bh** $5f^{14}\ 6d^5$ $7s^2$	108 **Hs** $5f^{14}\ 6d^6$ $7s^2$	109 **Mt** $5f^{14}\ 6d^7$ $7s^2$	110 **Ds** $5f^{14}\ 6d^9$ $7s^1$	111 **Rg** $5f^{14}\ 6d^{10}$ $7s^1$	112 $5f^{14}\ 6d^{10}$ $7s^2$						

Lanthanides	58 **Ce** $4f^2\ 6s^2$	59 **Pr** $4f^3\ 6s^2$	60 **Nd** $4f^4\ 6s^2$	61 **Pm** $4f^5\ 6s^2$	62 **Sm** $4f^6\ 6s^2$	63 **Eu** $4f^7\ 6s^2$	64 **Gd** $4f^7\ 6s^2$ $5d^1$	65 **Tb** $4f^9\ 6s^2$	66 **Dy** $4f^{10}\ 6s^2$	67 **Ho** $4f^{11}\ 6s^2$	68 **Er** $4f^{12}\ 6s^2$	69 **Tm** $4f^{13}\ 6s^2$	70 **Yb** $4f^{14}\ 6s^2$	71 **Lu** $4f^{14}\ 5d^1$ $6s^2$
Actinides	90 **Th** $6d^2\ 7s^2$	91 **Pa** $5f^2\ 6d^1$ $7s^2$	92 **U** $5f^3\ 6d^1$ $7s^2$	93 **Np** $5f^4\ 6d^1$ $7s^2$	94 **Pu** $5f^6\ 7s^2$	95 **Am** $5f^7\ 7s^2$	96 **Cm** $5f^7\ 6d^1$ $7s^2$	97 **Bk** $5f^8\ 6d^1$ $7s^2$	98 **Cf** $5f^{10}\ 7s^2$	99 **Es** $5f^{11}\ 7s^2$	100 **Fm** $5f^{12}\ 7s^2$	101 **Md** $5f^{13}\ 7s^2$	102 **No** $5f^{14}\ 7s^2$	103 **Lr** $5f^{14}\ 6d^1$ $7s^2$

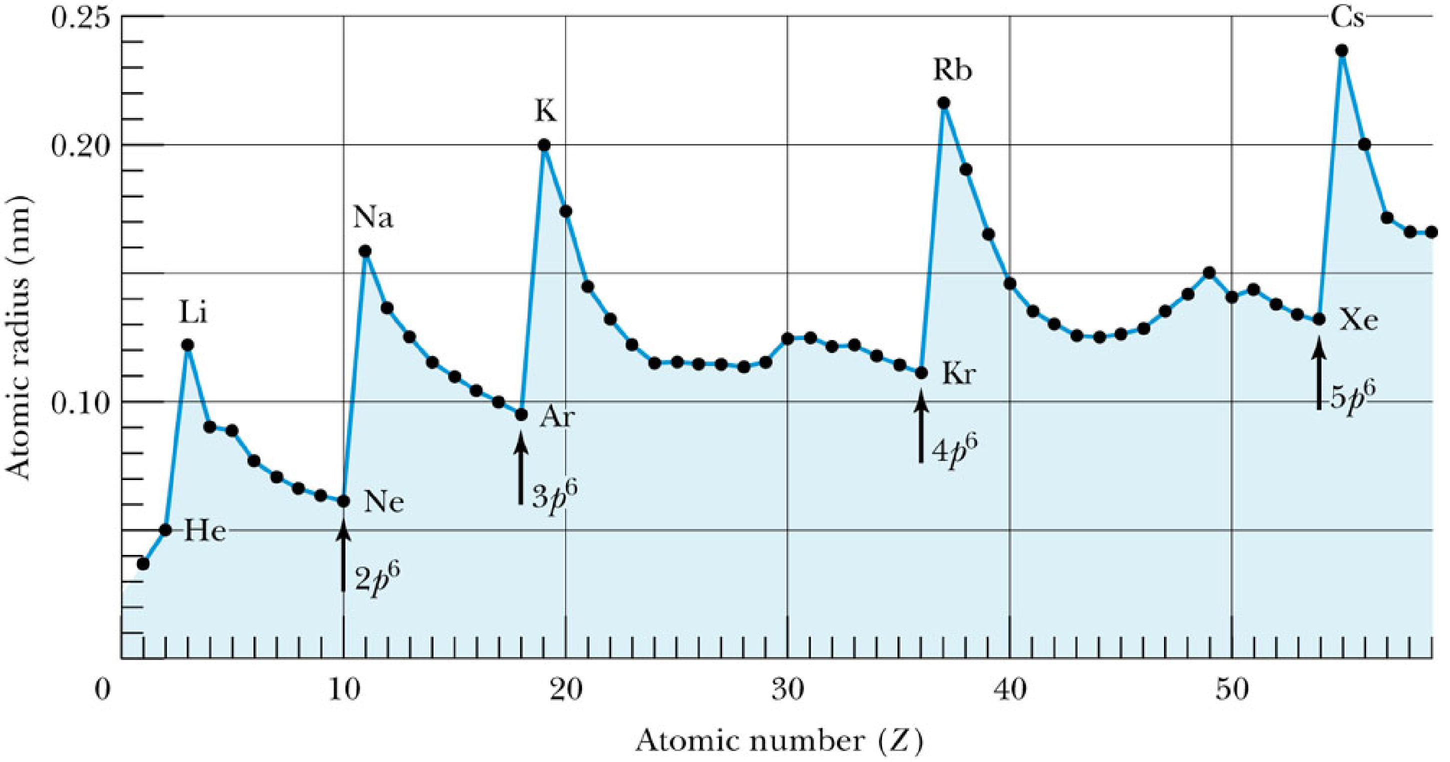
Ionization Energy vs Z

- This is the minimal energy needed to ionize an atom – note the lowest ionization energies are for atoms w/ single electrons in p or d subshells



Atomic radii vs Z

- Note that smallest radii are for noble gases with filled subshells



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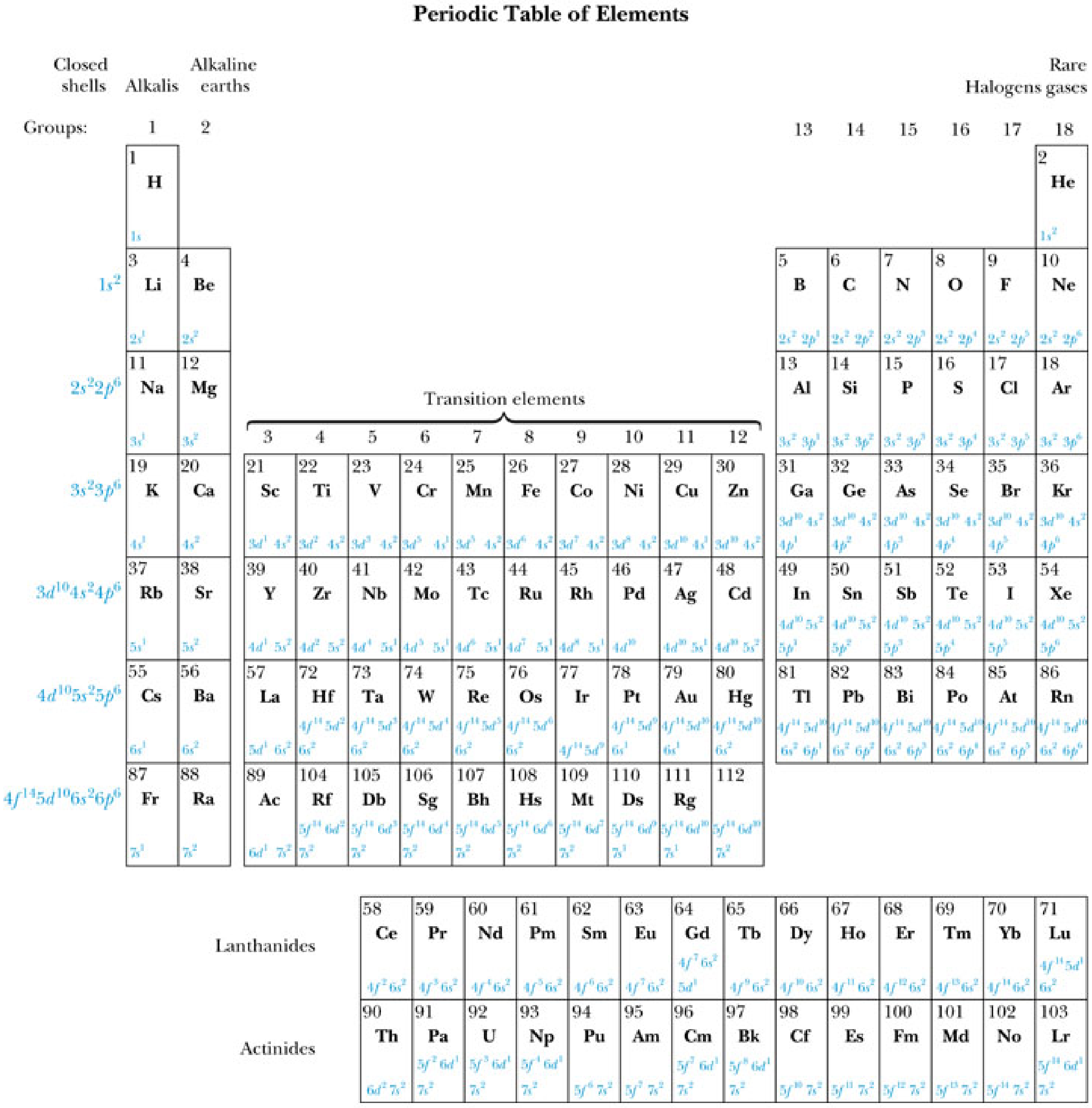
Periodic Table of the Elements



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Assorted Comments on Periodic Table

- Inert gases: last column; closed subshells; no valence e^-; chemically inert; zero net spin; poor electrical conductivity; monoatomic gases at room T
- Alkalis (H and metals): first column; single s valence electron; easily form + ion; good electrical conductors
- Alkaline Earths – 2nd column; 2 s shell e^- can extend far from nucleus so are large in size; ions are +2 charged – easily form (low ionization E) – fairly active chemically
- Halogens – 2nd column from right; chemically very active with valence = -1; form strong ionic bonds
- Transition Metals – 3 rows of 3d, 4d, 5d subshells – have some interesting unpaired spin elements (Fe, Co, Ni) = ferromagnetic
- Lanthanides – or rare earths – also have some unpaired spin elements
- Actinides – all radioactive

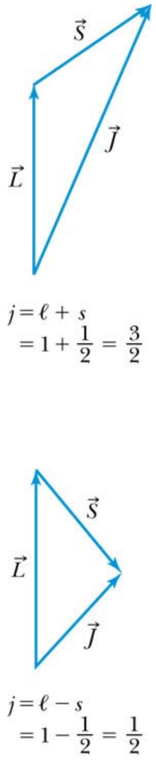
Total Angular Momentum

- Orbital (L) and Spin (S) angular momentum add to produce a total angular momentum (J) where $\vec{J} = \vec{L} + \vec{S}$
- For single electron atoms, s = ½ and ℓ = integer, so m_ℓ = integer and m_s = ½ integer; therefore m_j (ranging from –j to +j) must be ½ integer and j = ℓ ± s = ℓ ± ½
- $\vec{J}$ follows the same rules as other angular momenta; $J = \sqrt{j(j+1)}\,\hbar \quad and \quad J_z = m_J \hbar$
- j and m_j are "better" QN than m_ℓ and m_s because the total angular momentum is conserved

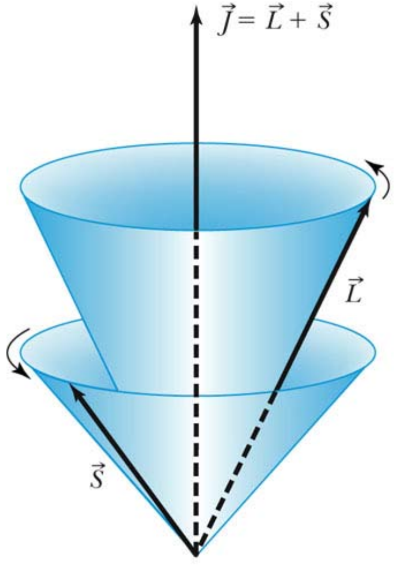
Spin-Orbit Coupling and J

- S and L couple through $V_{s\ell} = -\mu_s \cdot B_{\text{internal}}$
- Magnetic moment ~ S and B_{int} ~ L hence spin-orbit coupling $V_{s\ell} \sim \vec{S} \cdot \vec{L}$
- Addition of L & S for ℓ = 1, s = ½

Two possible net J states

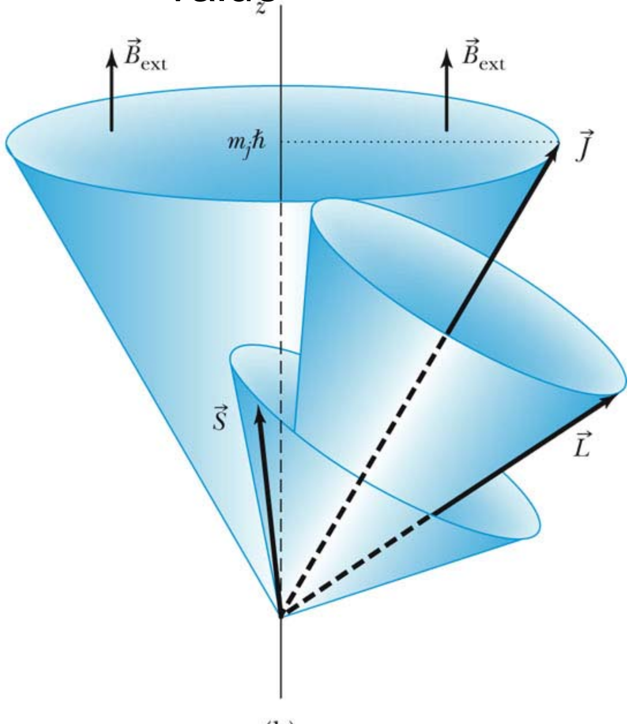


L & S precess around J



(a)

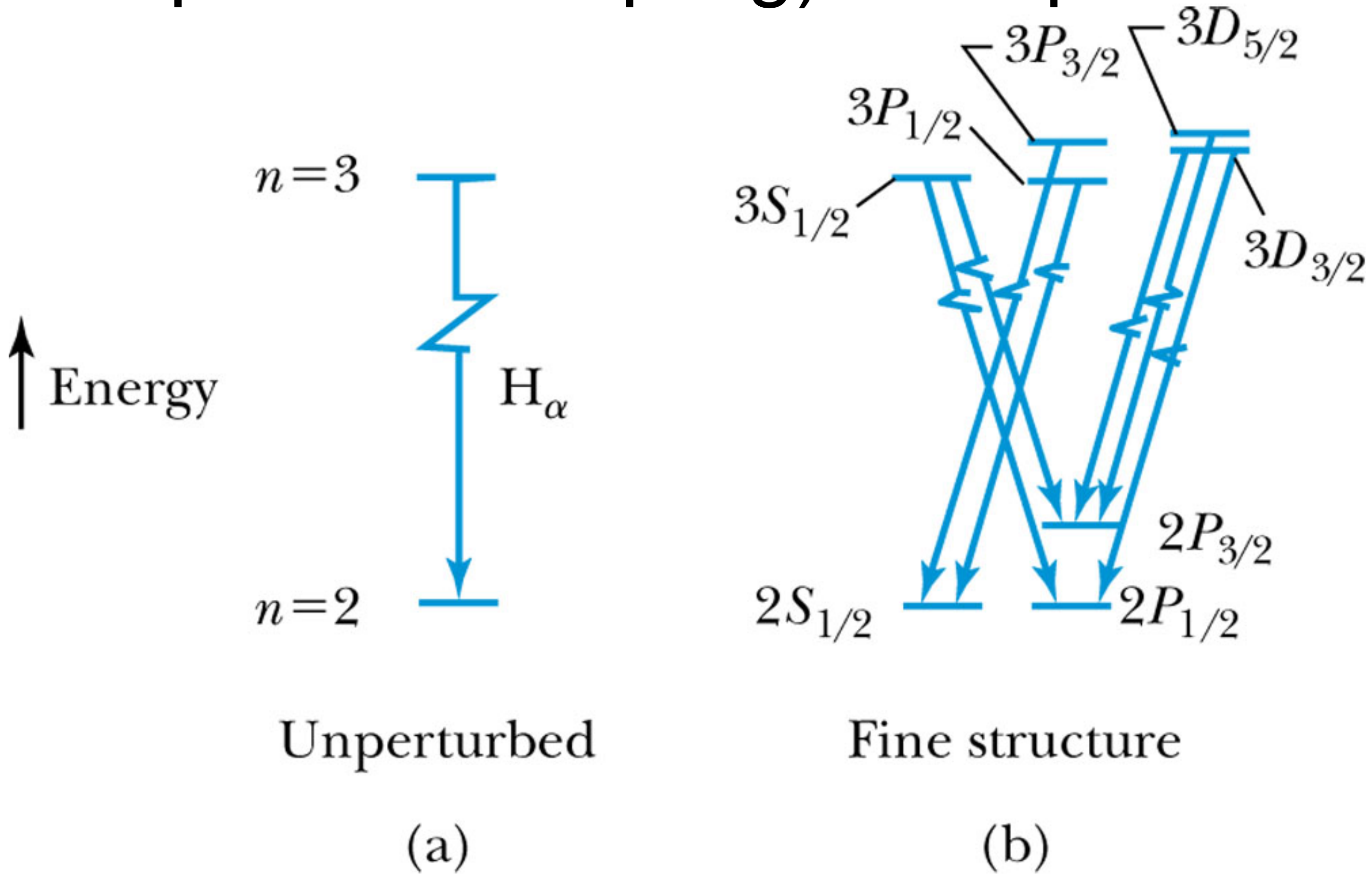
With an external B along z, J_z has a definite value



(b)

Selection Rules for J

- Selection rules are Δm_j and Δj both = 0, ±1
- For Hydrogen fine structure splitting (from spin-orbit coupling) example:

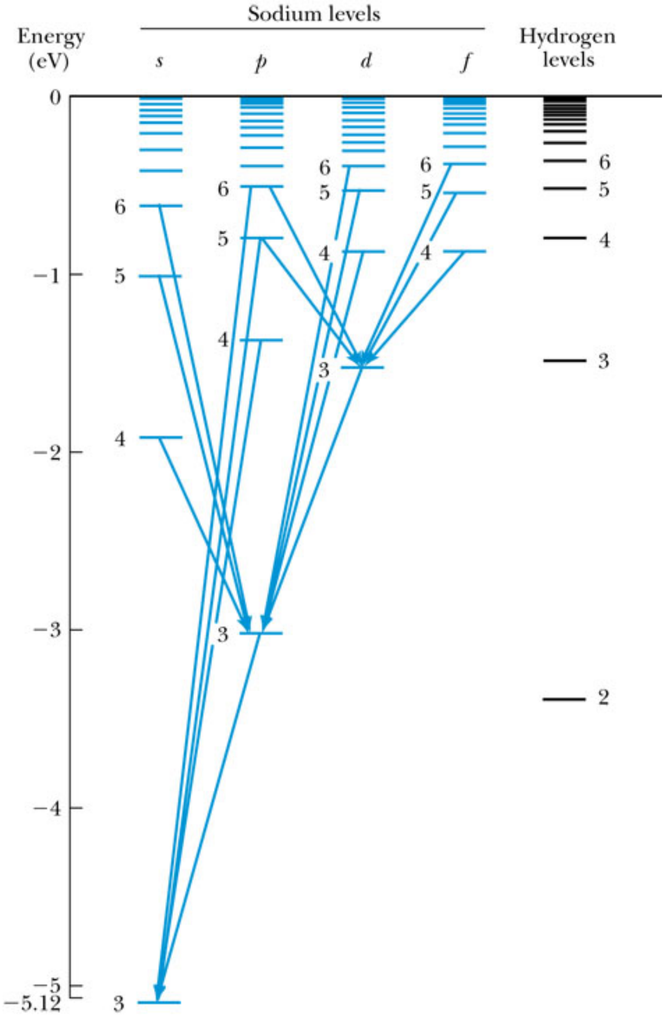


S state has ℓ=0, so j = ½

P & D states are split (ℓ ± ½) giving fine structure with $\Delta E \sim 10^{-4}$ ev

More complex fine structure for Na

- Na (a single e^- atom) energy levels compared to those of H
- Strong attraction of inner electrons causes E levels to be reduced relative to H



LS vs JJ Coupling in multi-e^- atoms

- In adding up the total angular momentum for a multi (2)-electron atom, we could:
  - Add $L = L_1 + L_2$ and $S = S_1 + S_2$ and then think of L and S interacting – so-called LS coupling
  - Or add $J_1 = L_1 + S_1$ and $J_2 = L_2 + S_2$ and think of J_1 and J_2 interacting – so-called JJ coupling
  - In weak B fields and smaller atoms, LS coupling is appropriate while in larger atoms or at higher B fields, JJ coupling theories work better

Two e$^-$ atoms and LS Coupling

- Two spin states – singlet (S=0) and triplet (S=1)
- There are 2S+1 (= multiplicity) states for a given L

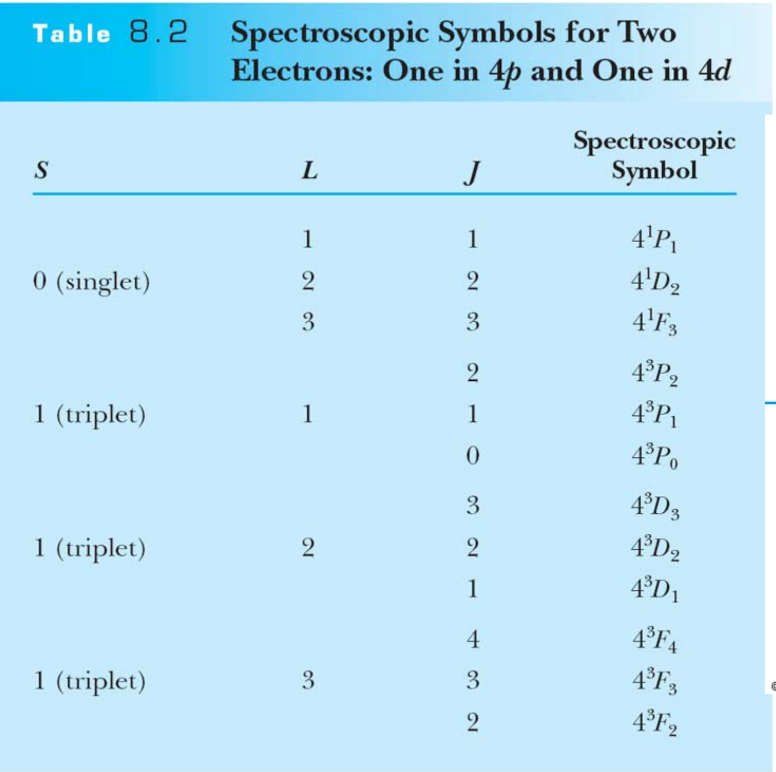


Table 8.2 Spectroscopic Symbols for Two Electrons: One in 4p and One in 4d

S	L	J	Spectroscopic Symbol
0 (singlet)	1	1	4^1P_1
	2	2	4^1D_2
	3	3	4^1F_3
1 (triplet)	1	2	4^3P_2
		1	4^3P_1
		0	4^3P_0
1 (triplet)	2	3	4^3D_3
		2	4^3D_2
		1	4^3D_1
1 (triplet)	3	4	4^3F_4
		3	4^3F_3
		2	4^3F_2