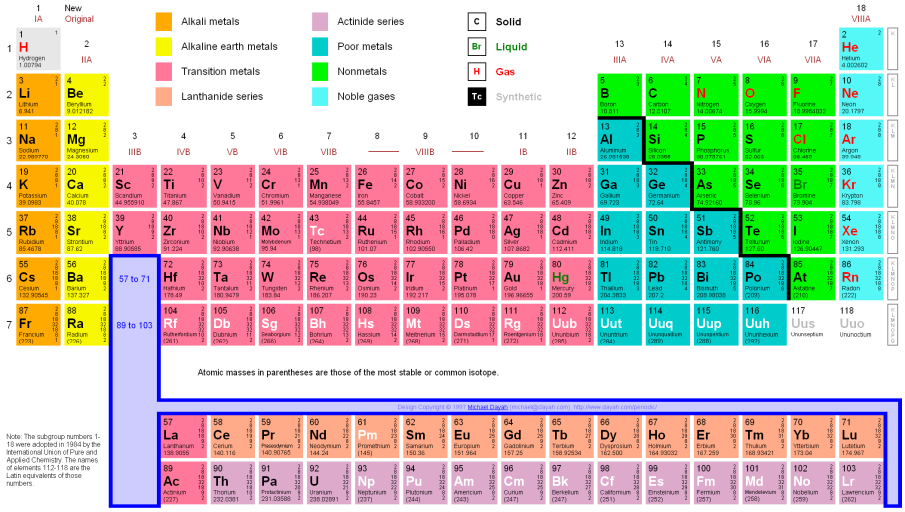
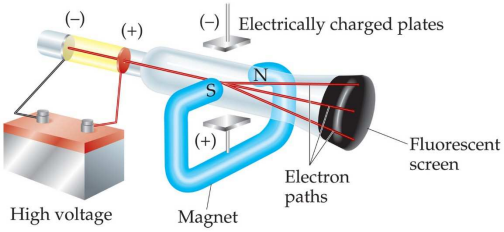
Chapter 1 - Basic Concepts: atoms

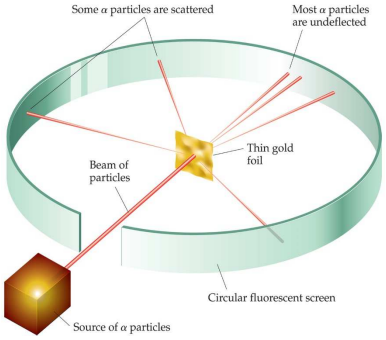


Discovery of atomic structure

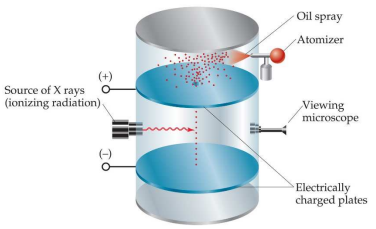
JJ Thomson (1897)



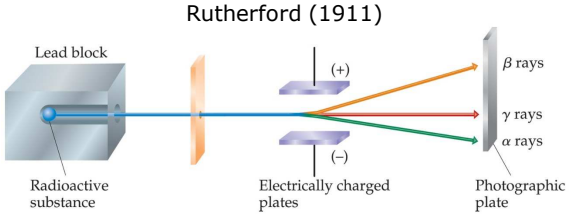
Rutherford (1910)

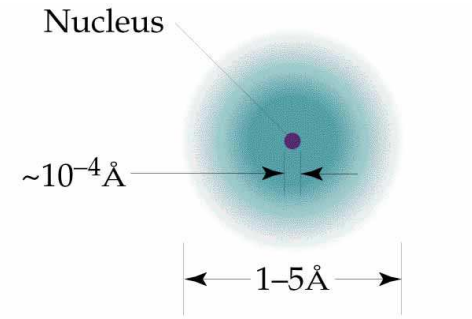


Milliken (1909)



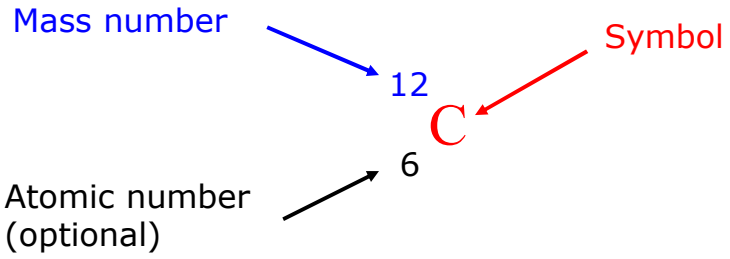
Rutherford (1911)





	Proton	Electron	Neutron
Charge / C	$+1.602 \times 10^{-19}$	-1.602×10^{-19}	0
Charge number (relative charge)	1	−1	0
Rest mass / kg	1.673×10^{-27}	9.109×10^{-31}	1.675×10^{-27}
Relative mass	1837	1	1839
Symbol	p^+	e^-	n^0
Mass (amu)	1.00732	0.000549	1.00870
Discovery	1919, Rutherford	1897, Thomson	1932, Chadwick

Atomic and Mass Numbers



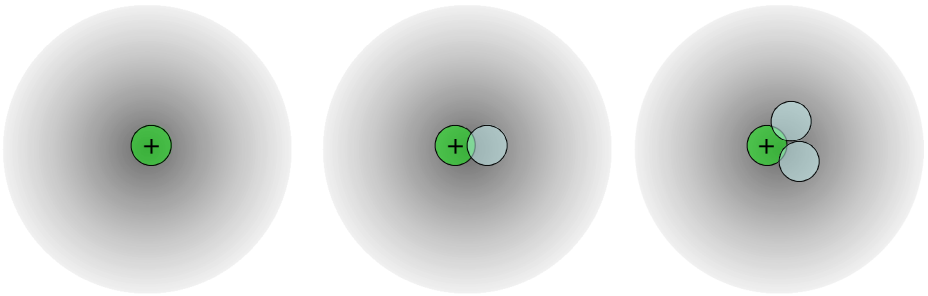
Atomic number (*Z*): equal to the number of protons in the nucleus. All atoms of the same element have the same number of protons.

$$ {}^{A}_{Z}\mathrm{E} $$

Mass number (*A*): equal to the sum of the number of protons and neutrons for an atom.

Atomic mass unit (amu) is 1/12 the mass of ^{12}C (1.660×10^{-27} kg)

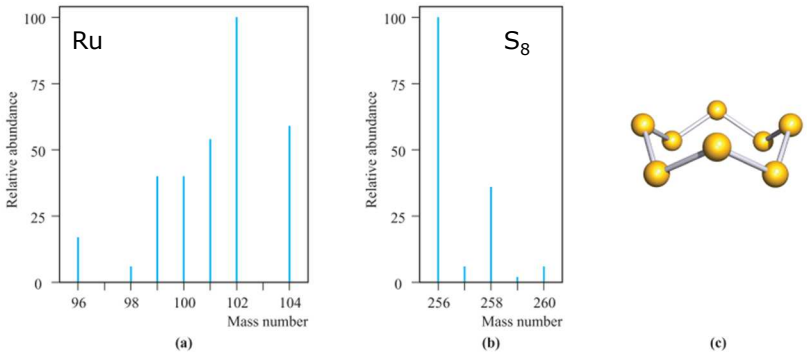
Isotopes of Hydrogen

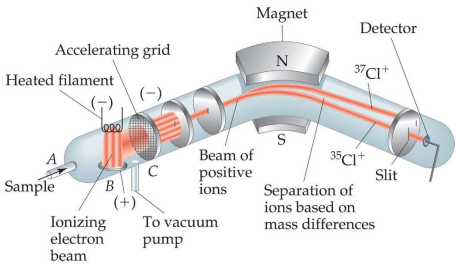


Hydrogen
1 proton
1 electron

Deuterium
1 proton
1 neutron
1 electron

Tritium
1 proton
2 neutrons
1 electron



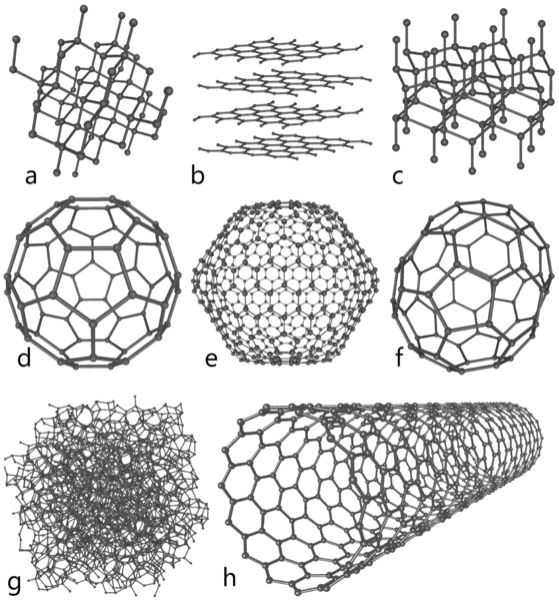


The **atomic mass** is the weighted average mass, of the naturally occurring element. It is calculated from the isotopes of an element weighted by their relative abundances.

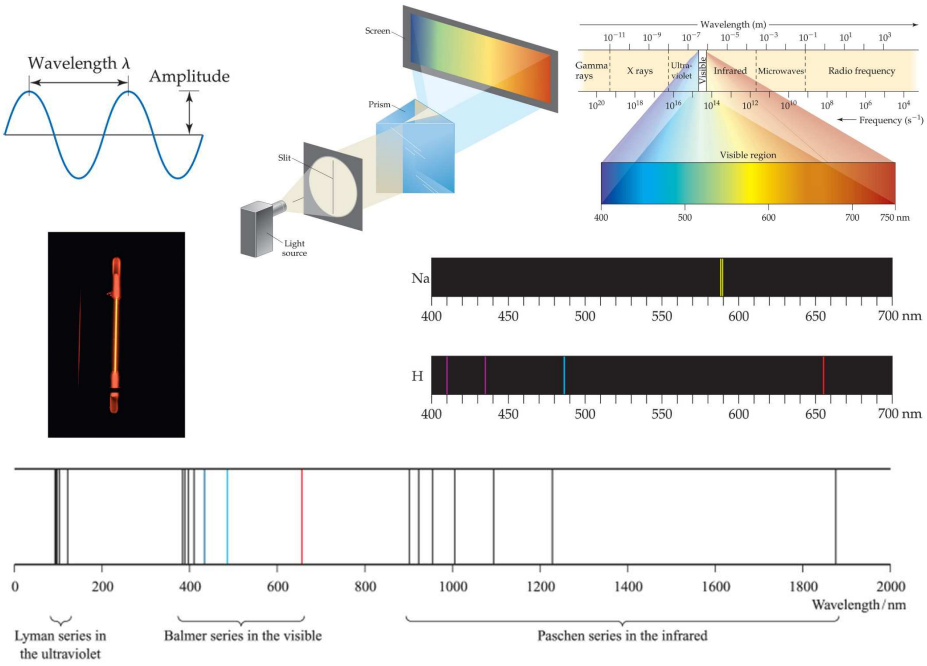
atomic mass = fraction$_A m_A$ + fraction$_B m_B$ + ...

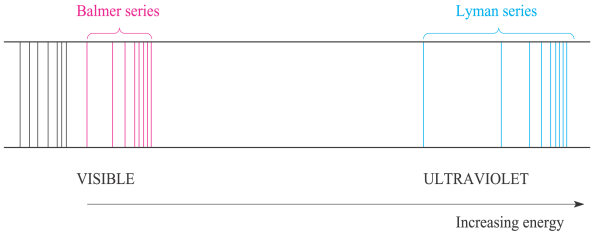
Allotropes

element's atoms are bonded together in a different manner



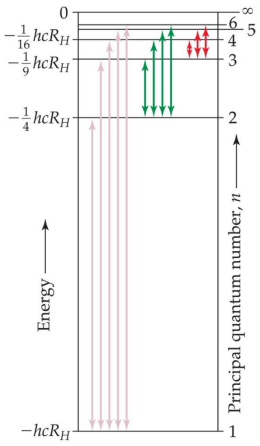
Successes in early quantum theory

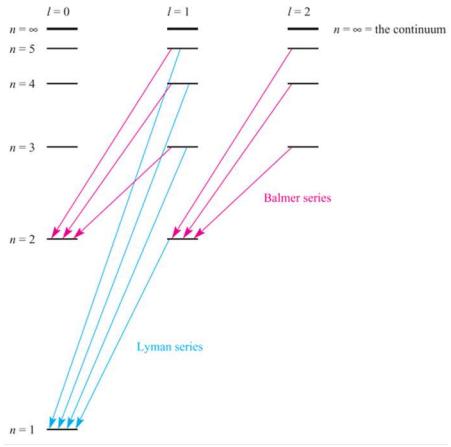




$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

where R is the Rydberg constant for H, 1.097×10^5 cm^{-1}

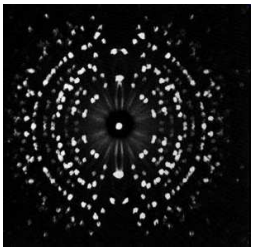




Wave Nature of Matter

$$\lambda = \frac{h}{mv}$$

where *h* is Planck's constant, 6.626×10^{-34} Js



Uncertainty Principle

$$(\Delta x)\,(\Delta mv) \geq \frac{h}{4\pi}$$

Schrödinger wave equation

The probability of finding an electron at a given point in space is determined from the function ψ^2 where ψ is the wavefunction.

1d $$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

where m = mass, E = total energy, and V = potential energy of the particle

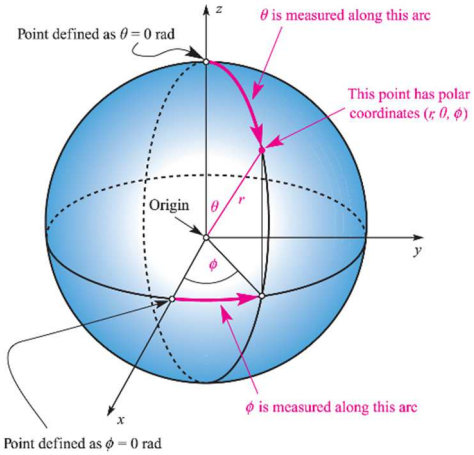
3d $$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

where m = mass, E = total energy, and V = potential energy of the particle

It is convenient to use spherical polar coordinates, with radial and angular parts of the wavefunction.

$$\psi_{Cartesian}(x,y,z)\equiv\psi_{radial}(r)\psi_{angular}(\theta,\phi)=R(r)A(\theta,\phi)$$

Definition of the polar coordinates (r, θ, ϕ)



- The wave function ψ is a solution of the Schrodinger equation and describes the behavior of an electron in a region of space called the atomic orbital.
- We can find energy values that are associated with particular wavefunctions.
- *Quantization* of energy levels arises naturally from the Schrodinger equation.

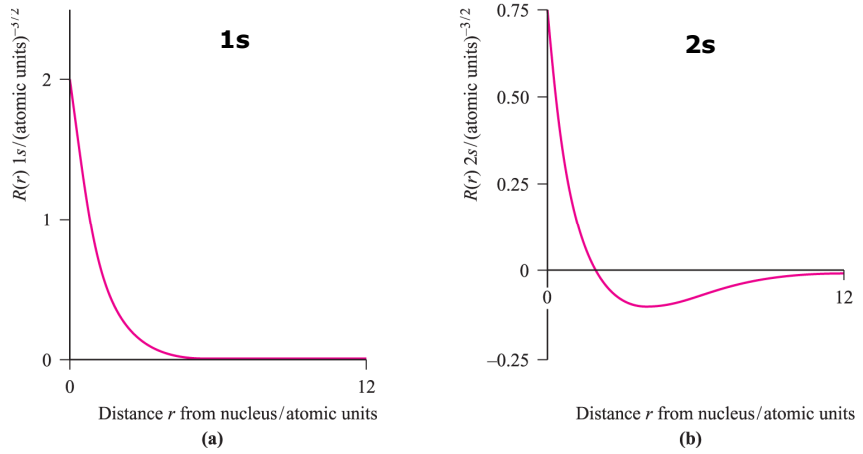
Atomic Orbital	n	l	m_l	Radial part of the wavefunction, R(r)	Angular part of the wavefunction, A(θ,φ)
1*s*	1	0	0	$2e^{-r}$	$\frac{1}{2\sqrt{\pi}}$
2*s*	2	0	0	$\frac{1}{2\sqrt{2}}(2-r)e^{-r/2}$	$\frac{1}{2\sqrt{\pi}}$
$2p_x$	2	1	+1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\cos\phi)}{2\sqrt{\pi}}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\cos\theta)}{2\sqrt{\pi}}$
$2p_y$	2	1	-1	$\frac{1}{2\sqrt{6}}re^{-r/2}$	$\frac{\sqrt{3}(\sin\theta\sin\phi)}{2\sqrt{\pi}}$

Atomic Orbitals

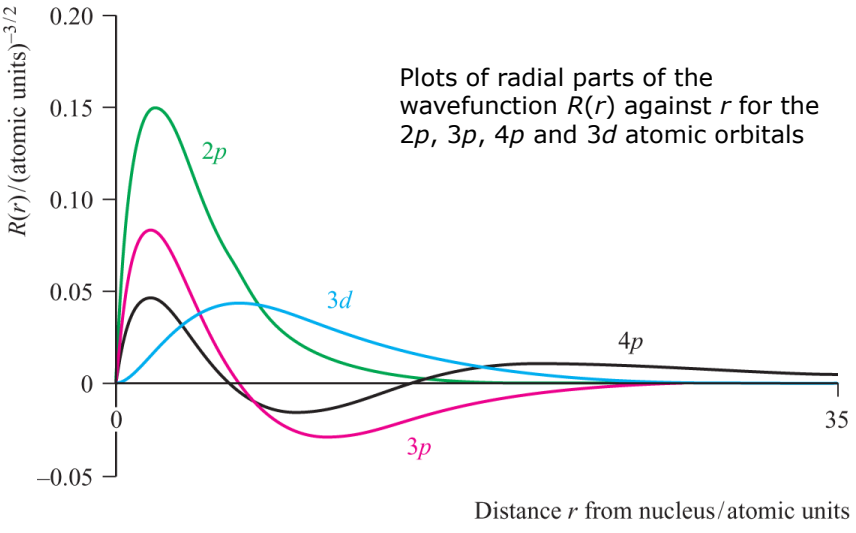
A wavefunction ψ is a mathematical function that contains detailed information about the behavior of an electron. An atomic wavefunction consists of a radial component *R(r)*, and an angular component *A(θ,φ)*. The region of space defined by a wavefunction is called an *atomic orbital*.

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

Degenerate orbitals possess the same energy.



Plot of the *radial* part of the wavefunction against distance (r) from the nucleus

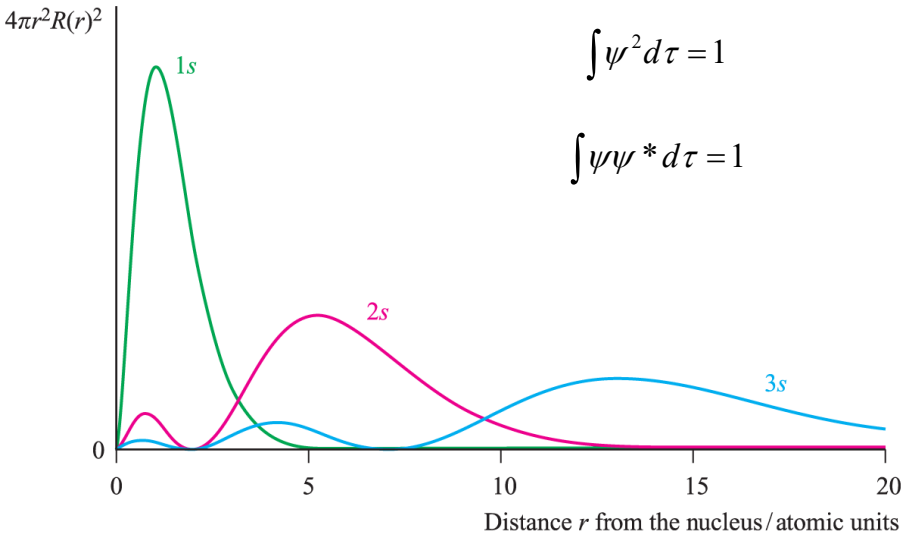


Plots of radial parts of the wavefunction $R(r)$ against r for the $2p$, $3p$, $4p$ and $3d$ atomic orbitals

(n-l-1) radial nodes

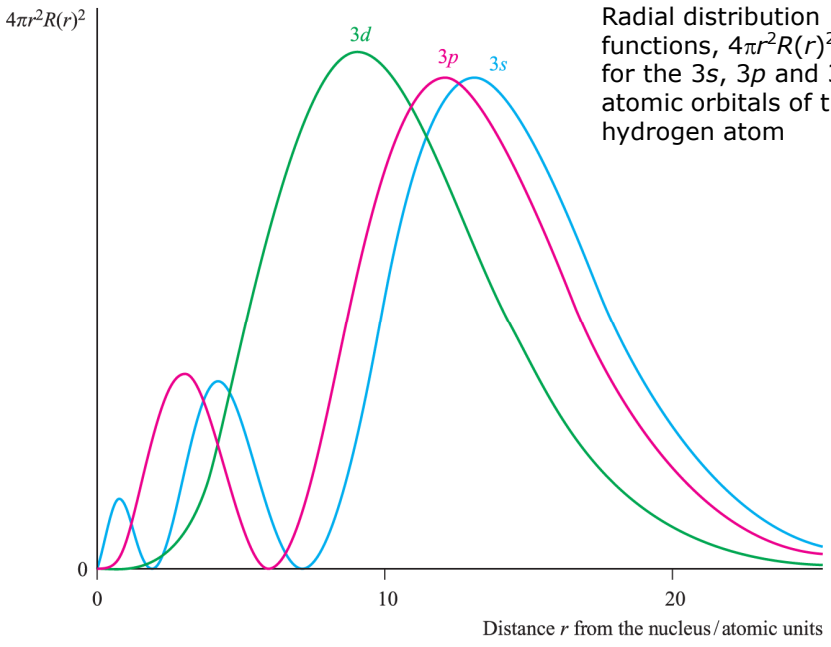
ns orbitals have (n-1 radial nodes), *np* orbitals have (n-2 radial nodes), *nd* orbitals have (n-3 radial nodes), *nf* orbitals have (n-4 radial nodes).

Radial Distribution Function,
$4\pi r^2 R(r)^2$



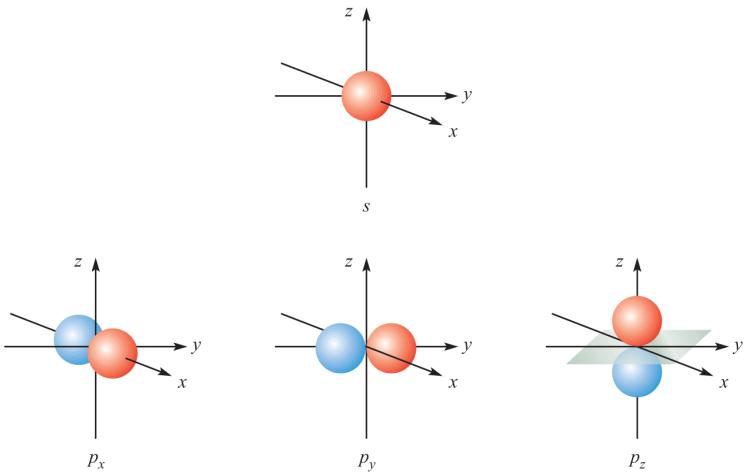
$$\int \psi^2 d\tau = 1$$

$$\int \psi\psi^* d\tau = 1$$



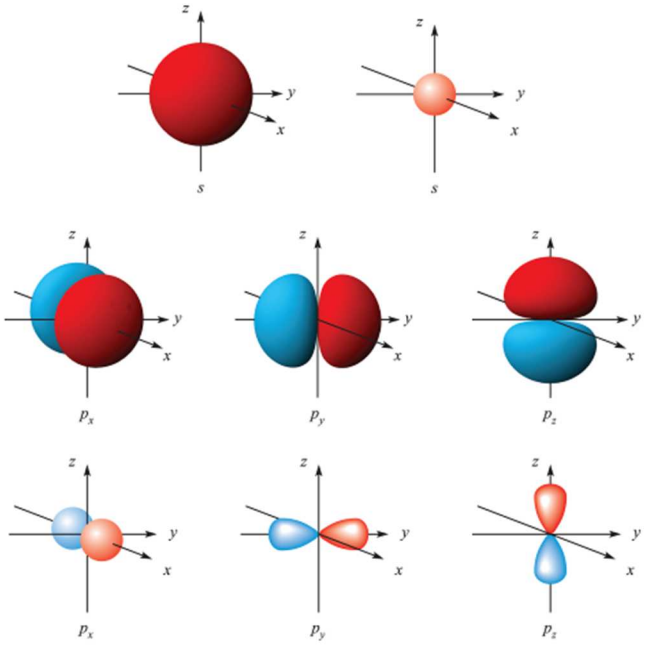
Radial distribution functions, $4\pi r^2 R(r)^2$, for the 3*s*, 3*p* and 3*d* atomic orbitals of the hydrogen atom

Boundary surfaces for angular part of wavefunction, A(θ,φ)

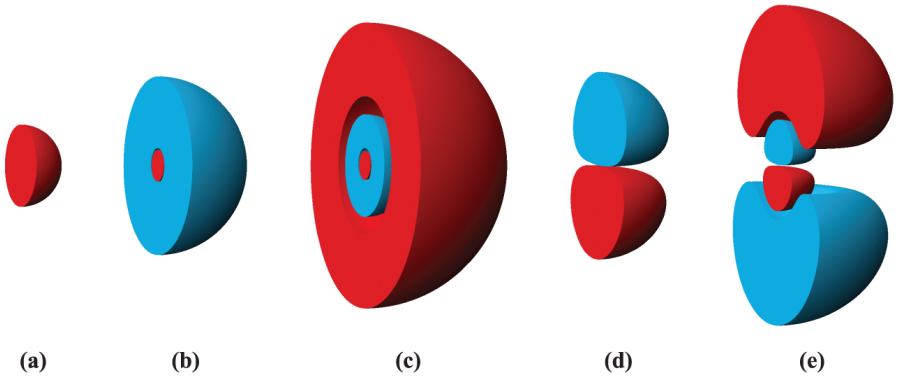


Different colors of lobes are significant

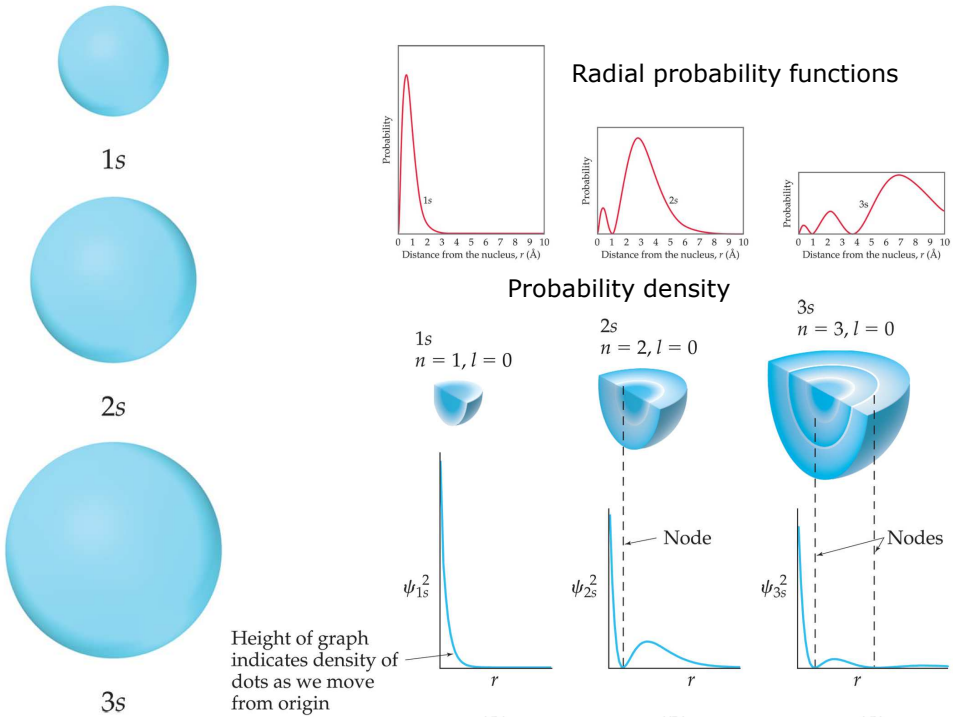
- For s orbital it has constant phase i.e. the amplitude of the wavefunction has a constant sign
- For a p orbital, there is one phase change with respect to the boundary surface. This phase change occurs at a nodal plane.

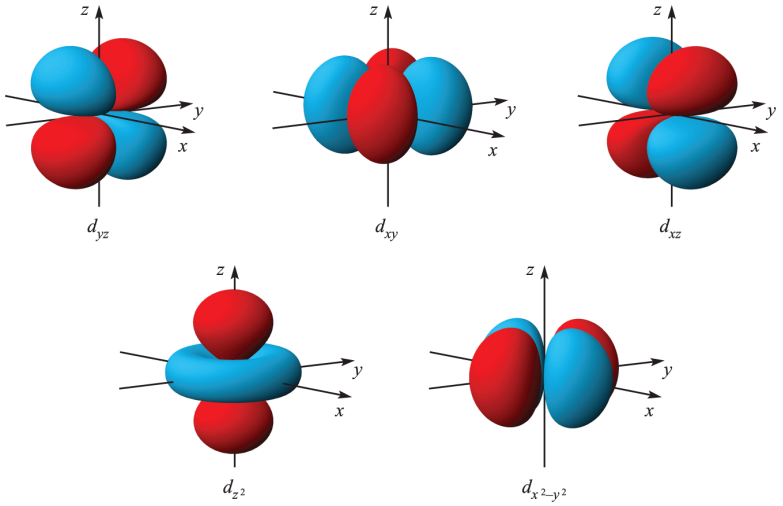


Representations of an *s* and a set of three degenerate *p* atomic orbitals.



Cross-sections through the (a) 1*s* (no radial nodes), (b) 2*s* (one radial node), (c) 3*s* (two radial nodes), (d) 2*p* (no radial nodes) and (e) 3*p* (one radial node) atomic orbitals of hydrogen.





set of five degenerate *d* atomic orbitals

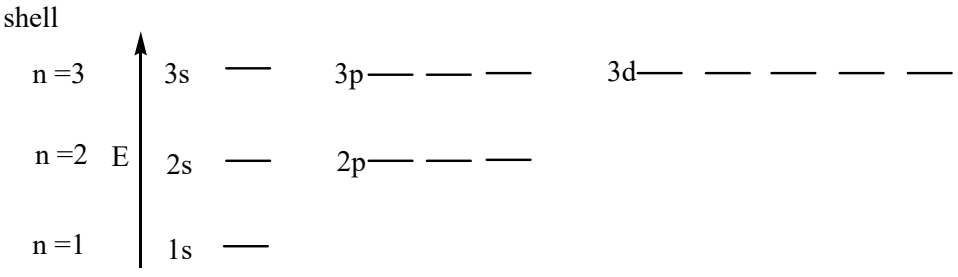
Orbitals energies in hydrogen-like species

$$E = -\frac{kZ^2}{n^2}$$

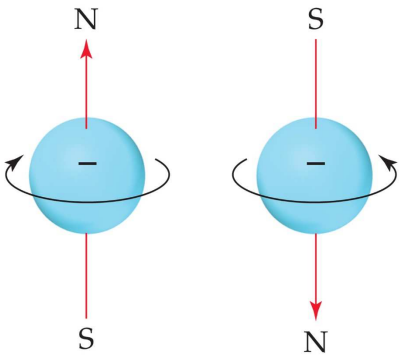
k = 1.312×10^3 kJ mol^{-1}

Z = atomic number

In the absence of an electric or magnetic field these atomic orbital energy levels are **degenerate**; that is they are identical in energy.



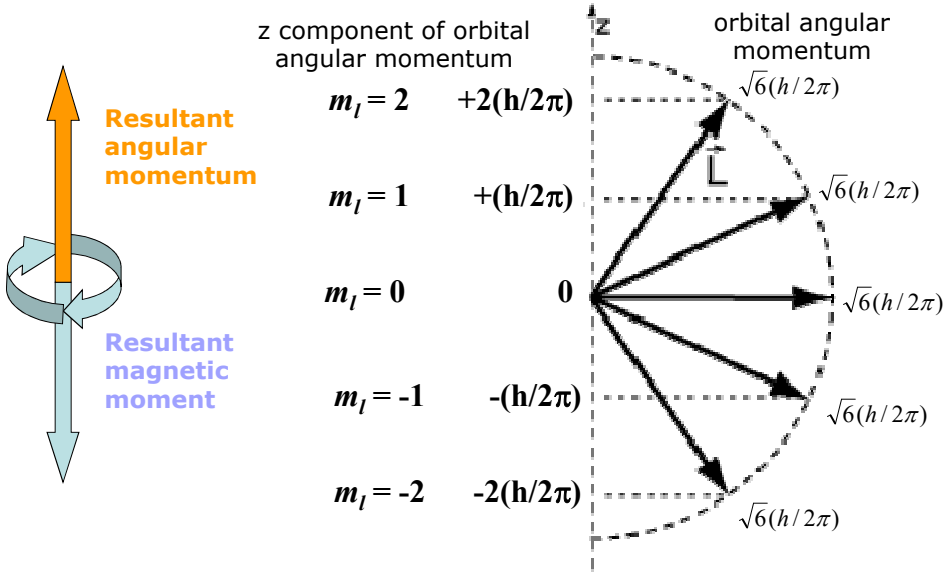
Spin Quantum Number, m_s



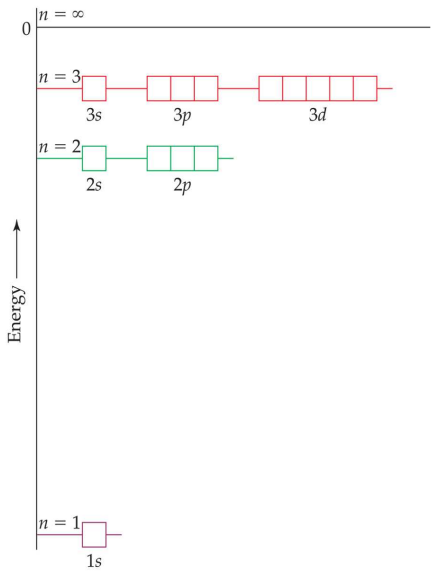
- Spin angular number, s, determines the *magnitude* of the spin angular momentum of a electron and has a value of ½.
- Since angular momentum is a vector quantity, it must have direction
  - Magnetic spin quantum number, m_s, can have values +1/2 or -1/2.

An orbital is fully occupied when it contains two electrons which are spin paired; one electron has a value of m_s = +1/2 and the other -1/2

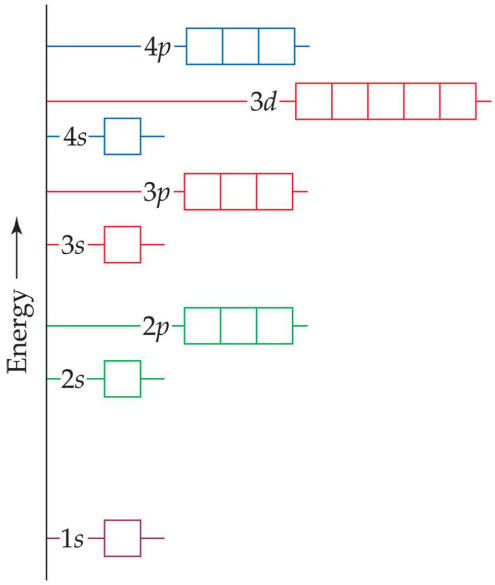
Angular momentum, the inner quantum number, j, spin-orbit coupling



^{1}H – ground state



Many-electron atom



Ground State Electronic Configurations

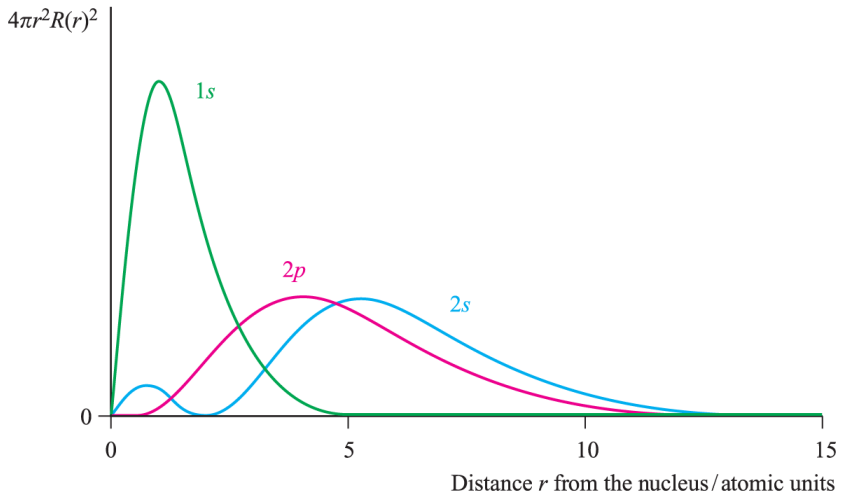
Atomic number	Element	Ground state electronic configuration	Atomic number	Element	Ground state electronic configuration
1	H	$1s^1$	53	I	$[Kr]5s^24d^{10}5p^5$
2	He	$1s^2 = [He]$	54	Xe	$[Kr]5s^24d^{10}5p^6 = [Xe]$
3	Li	$[He]2s^1$	55	Cs	$[Xe]6s^1$
4	Be	$[He]2s^2$	56	Ba	$[Xe]6s^2$
5	B	$[He]2s^22p^1$	57	La	$[Xe]6s^25d^1$
6	C	$[He]2s^22p^2$	58	Ce	$[Xe]4f^16s^25d^1$
7	N	$[He]2s^22p^3$	59	Pr	$[Xe]4f^36s^2$
8	O	$[He]2s^22p^4$	60	Nd	$[Xe]4f^46s^2$
9	F	$[He]2s^22p^5$	61	Pm	$[Xe]4f^56s^2$
10	Ne	$[He]2s^22p^6 = [Ne]$	62	Sm	$[Xe]4f^66s^2$
11	Na	$[Ne]3s^1$	63	Eu	$[Xe]4f^76s^2$
12	Mg	$[Ne]3s^2$	64	Gd	$[Xe]4f^75d^16s^2$
13	Al	$[Ne]3s^23p^1$	65	Tb	$[Xe]4f^96s^2$
14	Si	$[Ne]3s^23p^2$	66	Dy	$[Xe]4f^{10}6s^2$
15	P	$[Ne]3s^23p^3$	67	Ho	$[Xe]4f^{11}6s^2$
16	S	$[Ne]3s^23p^4$	68	Er	$[Xe]4f^{12}6s^2$
17	Cl	$[Ne]3s^23p^5$	69	Tm	$[Xe]4f^{13}6s^2$
18	Ar	$[Ne]3s^23p^6 = [Ar]$	70	Yb	$[Xe]4f^{14}6s^2$
19	K	$[Ar]4s^1$	71	Lu	$[Xe]4f^{14}6s^25d^1$
20	Ca	$[Ar]4s^2$	72	Hf	$[Xe]4f^{14}6s^25d^2$
21	Sc	$[Ar]4s^23d^1$	73	Ta	$[Xe]4f^{14}6s^25d^3$
22	Ti	$[Ar]4s^23d^2$	74	W	$[Xe]4f^{14}6s^25d^4$
23	V	$[Ar]4s^23d^3$	75	Re	$[Xe]4f^{14}6s^25d^5$
24	Cr	$[Ar]4s^13d^5$	76	Os	$[Xe]4f^{14}6s^25d^6$
25	Mn	$[Ar]4s^23d^5$	77	Ir	$[Xe]4f^{14}6s^25d^7$

The sequence that approximately describes the relative energies or orbitals in ***neutral*** atoms:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p< 5s < 4d < 5p < 6s <5d≈4f < 6p < 7s < 6d≈5f

Atomic number	Element	Ground state electronic configuration	Atomic number	Element	Ground state electronic configuration
26	Fe	$[Ar]4s^2 3d^6$	78	Pt	$[Xe]4f^{14} 6s^1 5d^9$
27	Co	$[Ar]4s^2 3d^7$	79	Au	$[Xe]4f^{14} 6s^1 5d^{10}$
28	Ni	$[Ar]4s^2 3d^8$	80	Hg	$[Xe]4f^{14} 6s^2 5d^{10}$
29	Cu	$[Ar]4s^1 3d^{10}$	81	Tl	$[Xe]4f^{14} 6s^2 5d^{10} 6p^1$
30	Zn	$[Ar]4s^2 3d^{10}$	82	Pb	$[Xe]4f^{14} 6s^2 5d^{10} 6p^2$
31	Ga	$[Ar]4s^2 3d^{10} 4p^1$	83	Bi	$[Xe]4f^{14} 6s^2 5d^{10} 6p^3$
32	Ge	$[Ar]4s^2 3d^{10} 4p^2$	84	Po	$[Xe]4f^{14} 6s^2 5d^{10} 6p^4$
33	As	$[Ar]4s^2 3d^{10} 4p^3$	85	At	$[Xe]4f^{14} 6s^2 5d^{10} 6p^5$
34	Se	$[Ar]4s^2 3d^{10} 4p^4$	86	Rn	$[Xe]4f^{14} 6s^2 5d^{10} 6p^6$ = [Rn]
35	Br	$[Ar]4s^2 3d^{10} 4p^5$	87	Fr	$[Rn]7s^1$
36	Kr	$[Ar]4s^2 3d^{10} 4p^6$ = [Kr]	88	Ra	$[Rn]7s^2$
37	Rb	$[Kr]5s^1$	89	Ac	$[Rn]6d^1 7s^2$
38	Sr	$[Kr]5s^2$	90	Th	$[Rn]6d^2 7s^2$
39	Y	$[Kr]5s^2 4d^1$	91	Pa	$[Rn]5f^2 7s^2 6d^1$
40	Zr	$[Kr]5s^2 4d^2$	92	U	$[Rn]5f^3 7s^2 6d^1$
41	Nb	$[Kr]5s^1 4d^4$	93	Np	$[Rn]5f^4 7s^2 6d^1$
42	Mo	$[Kr]5s^1 4d^5$	94	Pu	$[Rn]5f^6 7s^2$
43	Tc	$[Kr]5s^2 4d^5$	95	Am	$[Rn]5f^7 7s^2$
44	Ru	$[Kr]5s^1 4d^7$	96	Cm	$[Rn]5f^7 7s^2 6d^1$
45	Rh	$[Kr]5s^1 4d^8$	97	Bk	$[Rn]5f^9 7s^2$
46	Pd	$[Kr]5s^0 4d^{10}$	98	Cf	$[Rn]5f^{10} 7s^2$
47	Ag	$[Kr]5s^1 4d^{10}$	99	Es	$[Rn]5f^{11} 7s^2$
48	Cd	$[Kr]5s^2 4d^{10}$	100	Fm	$[Rn]5f^{12} 7s^2$
49	In	$[Kr]5s^2 4d^{10} 5p^1$	101	Md	$[Rn]5f^{13} 7s^2$
50	Sn	$[Kr]5s^2 4d^{10} 5p^2$	102	No	$[Rn]5f^{14} 7s^2$
51	Sb	$[Kr]5s^2 4d^{10} 5p^3$	103	Lr	$[Rn]5f^{14} 7s^2 6d^1$
52	Te	$[Kr]5s^2 4d^{10} 5p^4$			

Penetration and shielding



Radial distribution functions, $4\pi r^2 R(r)^2$, for the 1*s*, 2*s* and 2*p* atomic orbitals of H.

Slater's Rules for Calculating Shielding

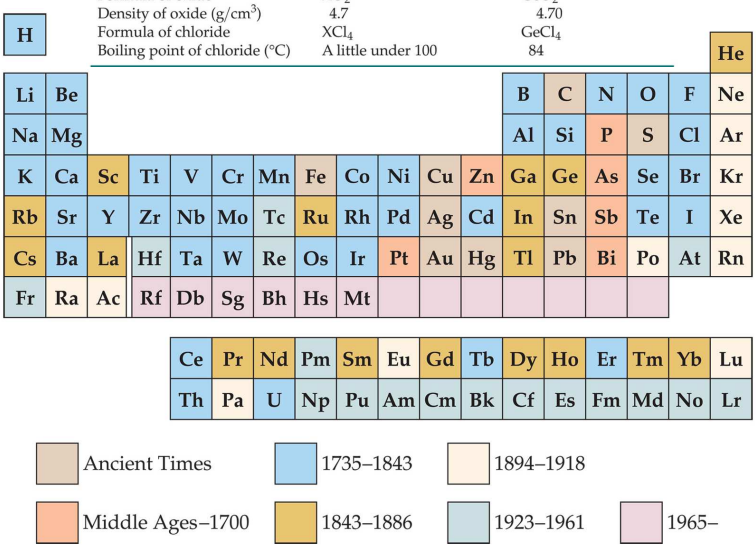
Effective nuclear charge

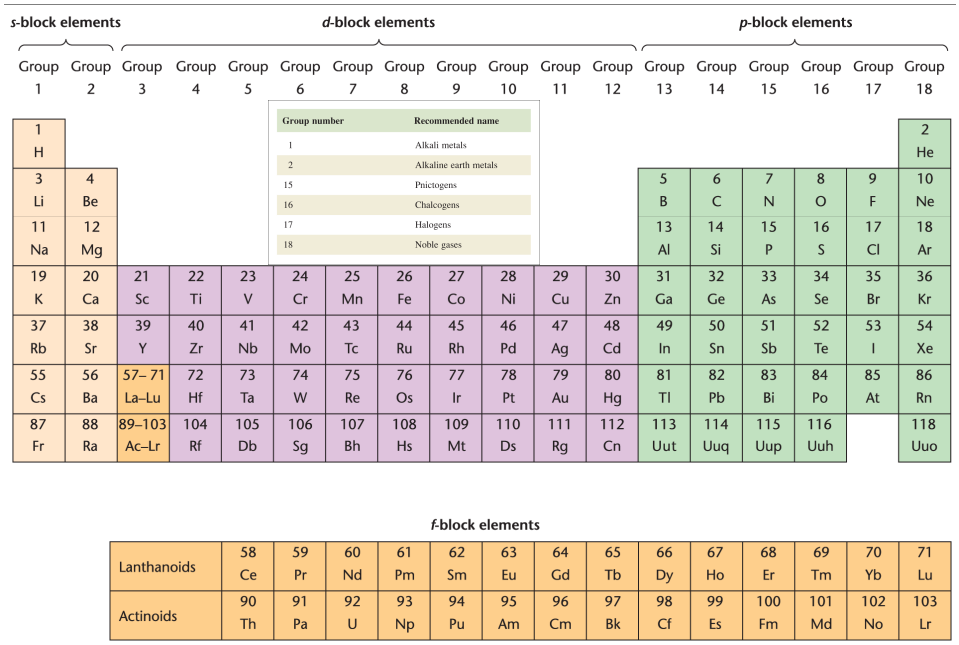
$$Z_{eff} = Z - S$$

1. Write out electron configuration of the element [1s][2s,2p][3s,3p][3d][4s,4p][4d][4f] [5s,5p] etc*
2. Electrons in an group higher in this sequence contribute nothing to *S*.
3. For an electron in *ns* or *np* orbital
   i. Each of the other electrons of same *group* contributes *S* = 0.35 each (except in 1s, *S* = 0.3)
   ii. Each electron in (n – 1) *shell*, contributes *S* = 0.85
   iii. Each electron in (n – 2) or lower *shell*, contributes *S* = 1.00
4. For an electron in an *nd* or *nf* group
   i. Each of the other electrons of same *nd* or *nf group* contributes *S* = 0.35 each
   ii. Each electron in a lower *group*, contributes *S* = 1.00

*A bracket indicates a group and *n* is the principle quantum number of a shell

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-k)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84





s-block elements | *d*-block elements | *p*-block elements

Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57–71 La–Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89–103 Ac–Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh		118 Uuo

Group number	Recommended name
1	Alkali metals
2	Alkaline earth metals
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases

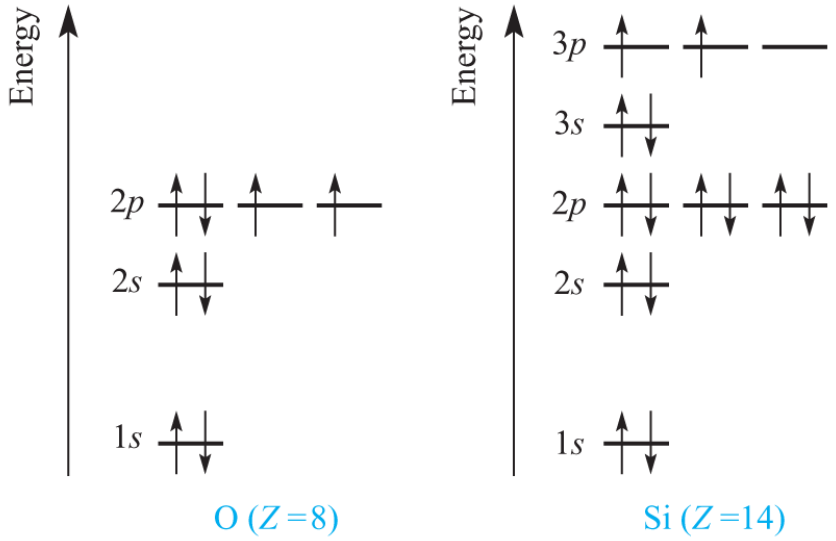
f-block elements

Lanthanoids	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoids	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

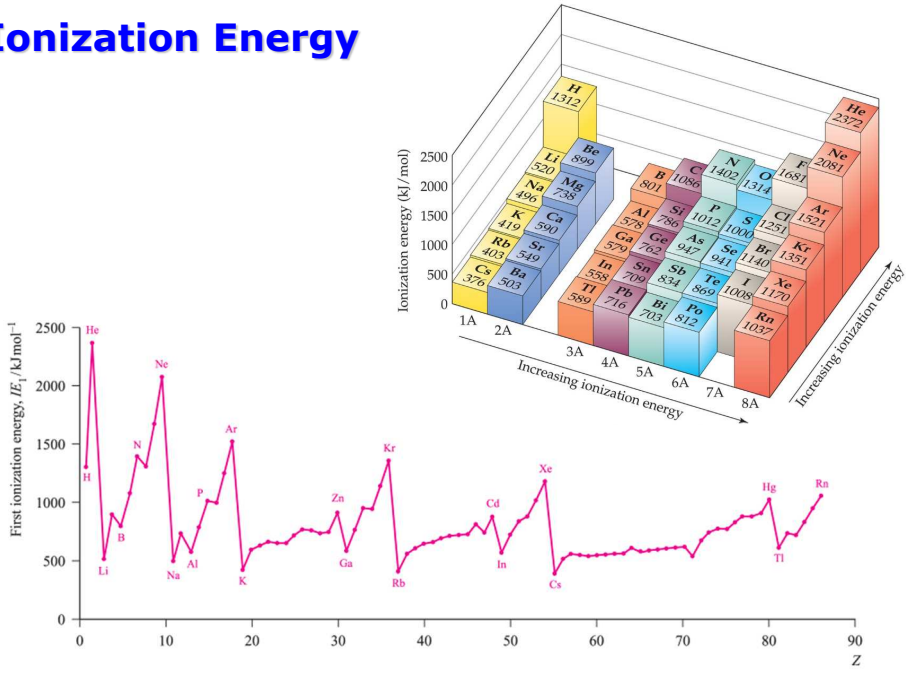
The aufbau principle

- Orbitals are filled in the order of energy, the lowest energy orbitals being filled first.
- Hund's first rule: in a set of degenerate orbitals, electrons may not be spin paired in an orbital until each orbital in the set contains one electron; electrons singly occupying orbitals in a degenerate set have parallel spins, i.e. have the same values of m_s.
- Pauli Exclusion Principle : no two electrons in the same atom can have identical sets of quantum numbers *n, l,* m_l, m_s; each orbital can accommodate a maximum of two electrons with different m_s.

Valence and core electrons



Ionization Energy



Ionization Energy

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4562	(inner-shell electrons)				
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

Electron Affinity

Electron affinity is defined as minus the change in internal energy for the gain of an electron by a gaseous atom.

EA = -ΔU(0K)

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0

Process	$\approx \Delta_{EA}H$/kJ mol^{-1}
$H(g) + e^- \rightarrow H^-(g)$	−73
$Li(g) + e^- \rightarrow Li^-(g)$	−60
$Na(g) + e^- \rightarrow Na^-(g)$	−53
$K(g) + e^- \rightarrow K^-(g)$	−48
$N(g) + e^- \rightarrow N^-(g)$	≈0
$P(g) + e^- \rightarrow P^-(g)$	−72
$O(g) + e^- \rightarrow O^-(g)$	−141
$O^-(g) + e^- \rightarrow O^{2-}(g)$	+798
$S(g) + e^- \rightarrow S^-(g)$	−201
$S^-(g) + e^- \rightarrow S^{2-}(g)$	+640
$F(g) + e^- \rightarrow F^-(g)$	−328
$Cl(g) + e^- \rightarrow Cl^-(g)$	−349
$Br(g) + e^- \rightarrow Br^-(g)$	−325
$I(g) + e^- \rightarrow I^-(g)$	−295

† Tables of data differ in whether they list values of EA or $\Delta_{EA}H$ and it is essential to note which is being used.