Chem C1403 Lecture 11. Wednesday, October 12, 2005
End of Chapter 16, into Chapter 17

Magic (Quantum) numbers from the solutions of the wave equation: orbitals of the H atom: n, l and m_l.

The size, shape and orientation of orbitals

Electron spin

Multielectron atoms

Electron configurations of multielectron atoms

Electron configurations of multielectron atoms and the periodic properties of atoms.

Shorthand notation (nicknames) for orbitals:

l = 0, s orbital;

l = 1, p orbital;

l = 2, d orbital;

l = 3, f orbital

Relative energies of the orbitals of a one electron atom:

1s << 2s = 2p < 3s = 3p = 3d, etc.

All orbitals of the same value of n have the same energy!

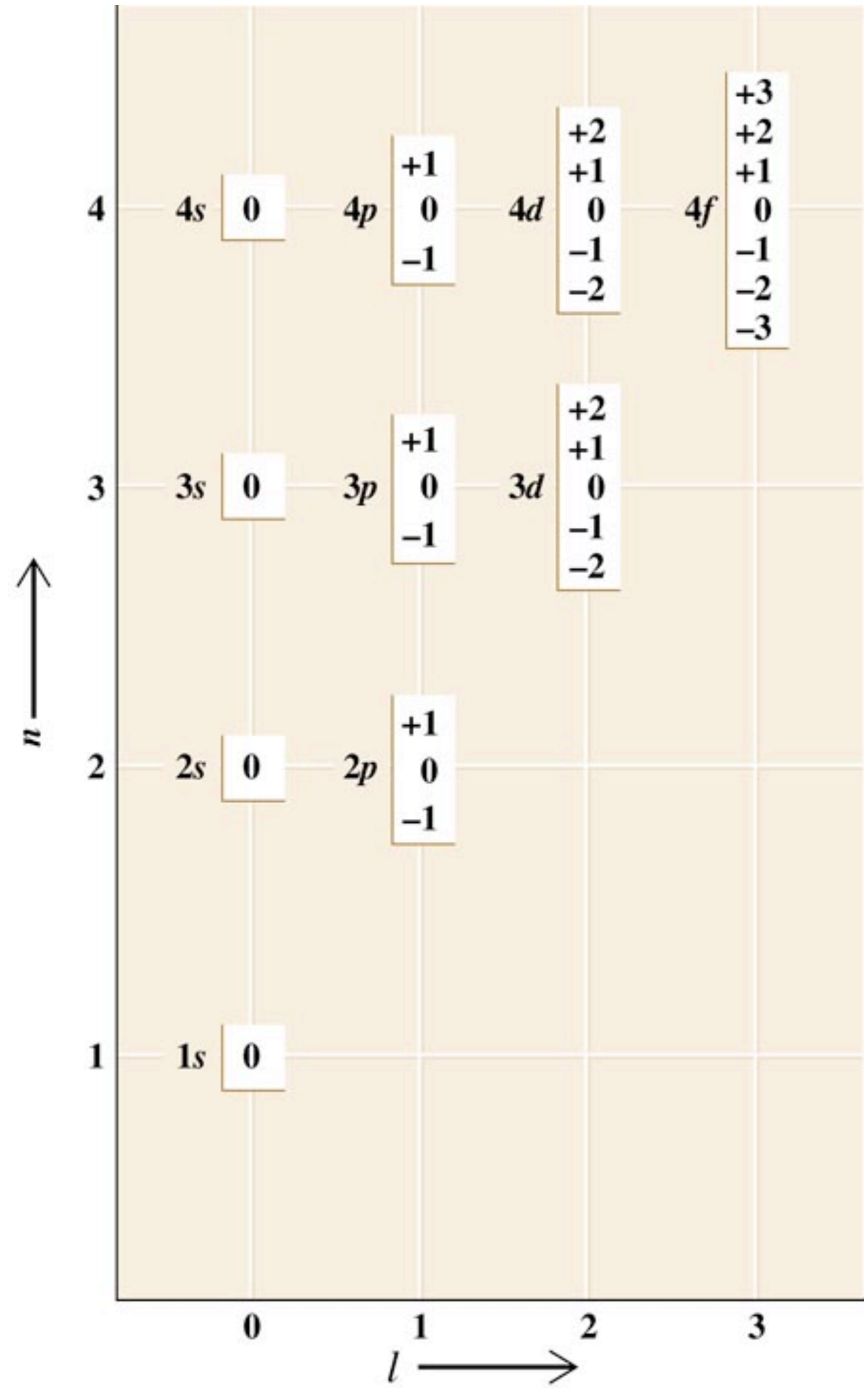
For a one electron atom the energy of an electron in an orbital only depends on n.

Thus,
1s (only orbital)

2s = 2p

3s = 3p = 3d

4s = 4p = 4d = 4f



The relative energies of orbitals of the H atom follow the same pattern as the energies of the orbits of the H atom.

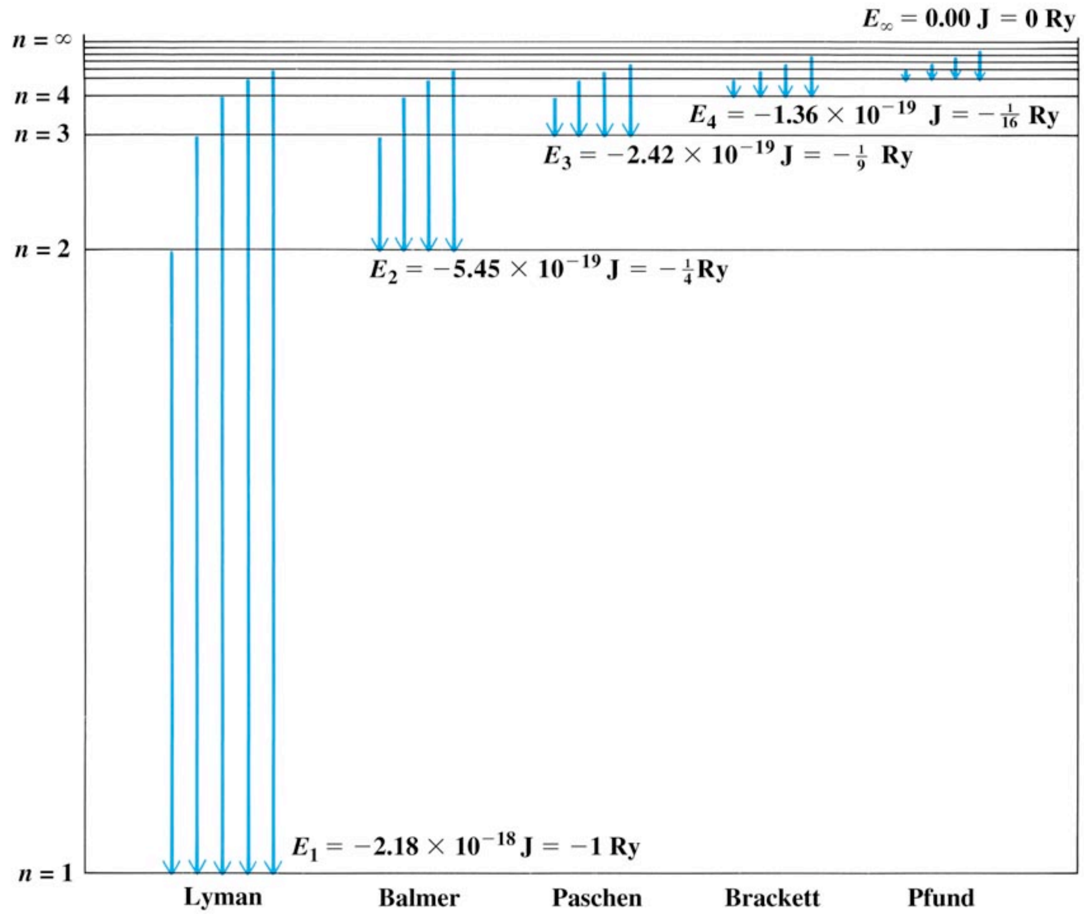
Schroedinger
H atom

Bohr
H atom

4s, 4p, 4d, 4f
3s, 3p, 3d

2s, 2p

1s

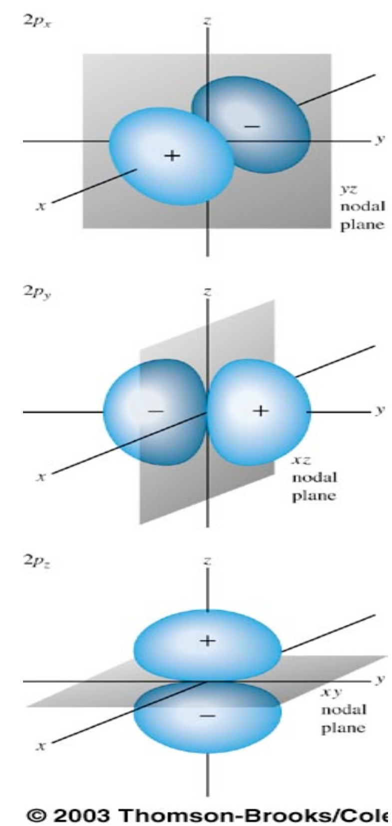


Obital: A wavefunction defined by the quantum numbers n, l and m_l (which are solutions of the wave equation)

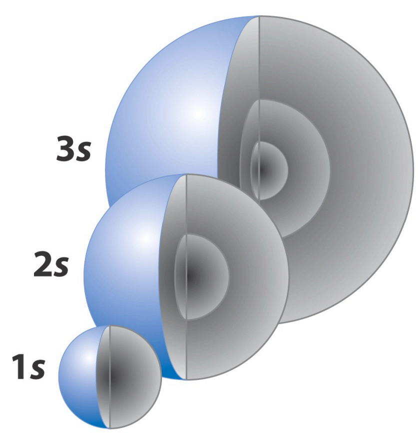
An orbital is a region of space occupied by an electron

Orbitals has energies, shapes and orientation in space

np orbitals



ns orbitals



n determines size and energy;
l determines shape;
m_l determines orientation

The hydrogen s orbitals (solutions to the Schroedinger equation)

Radius of 90% Boundary sphere:
r_{1s} = 1.4 Å
r_{2s} = 3.3 Å
r_{3s} = 10 Å

Value of Ψ as a function of the distance r from the nucleus

Probability of finding an electron in a spherical shell or radius r from the nucleus ($\Psi^2 4\pi r^2$). r^2 captures volume.

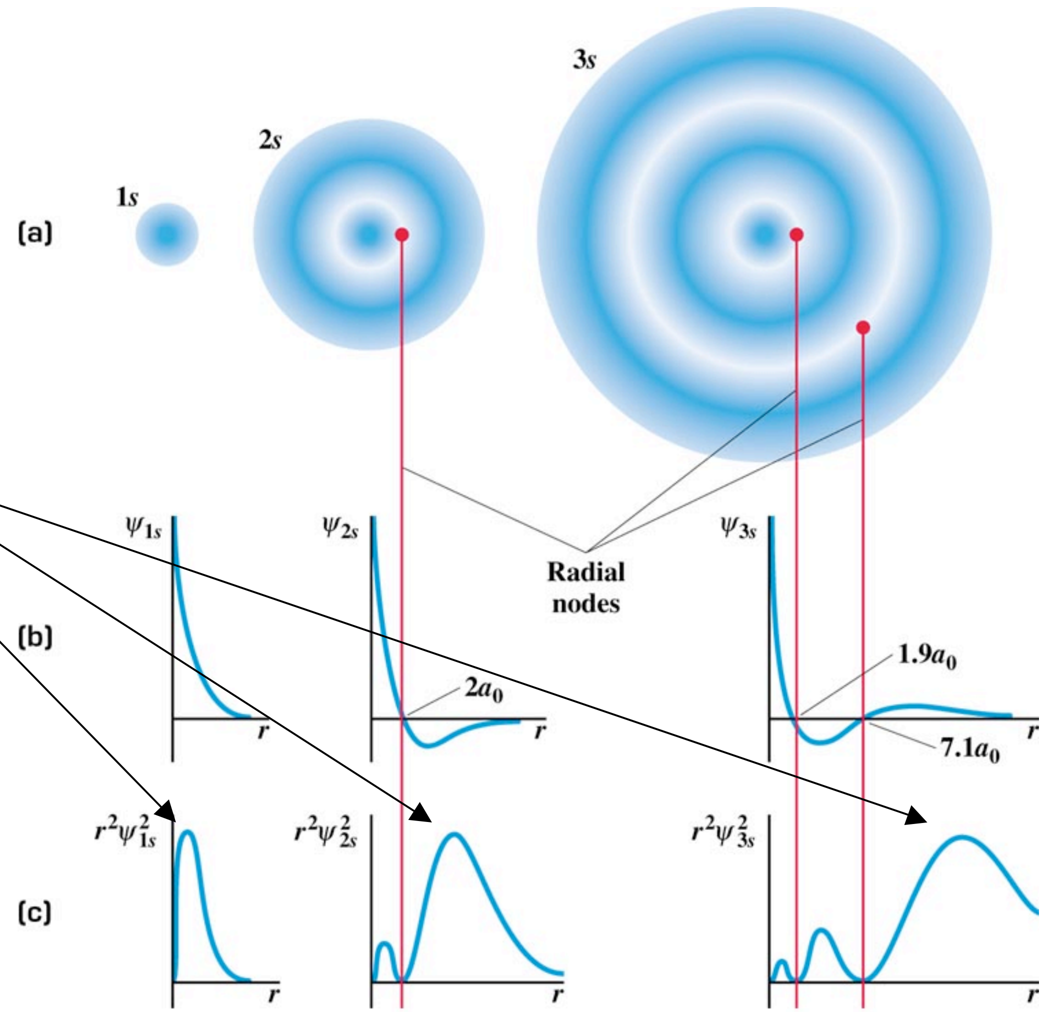
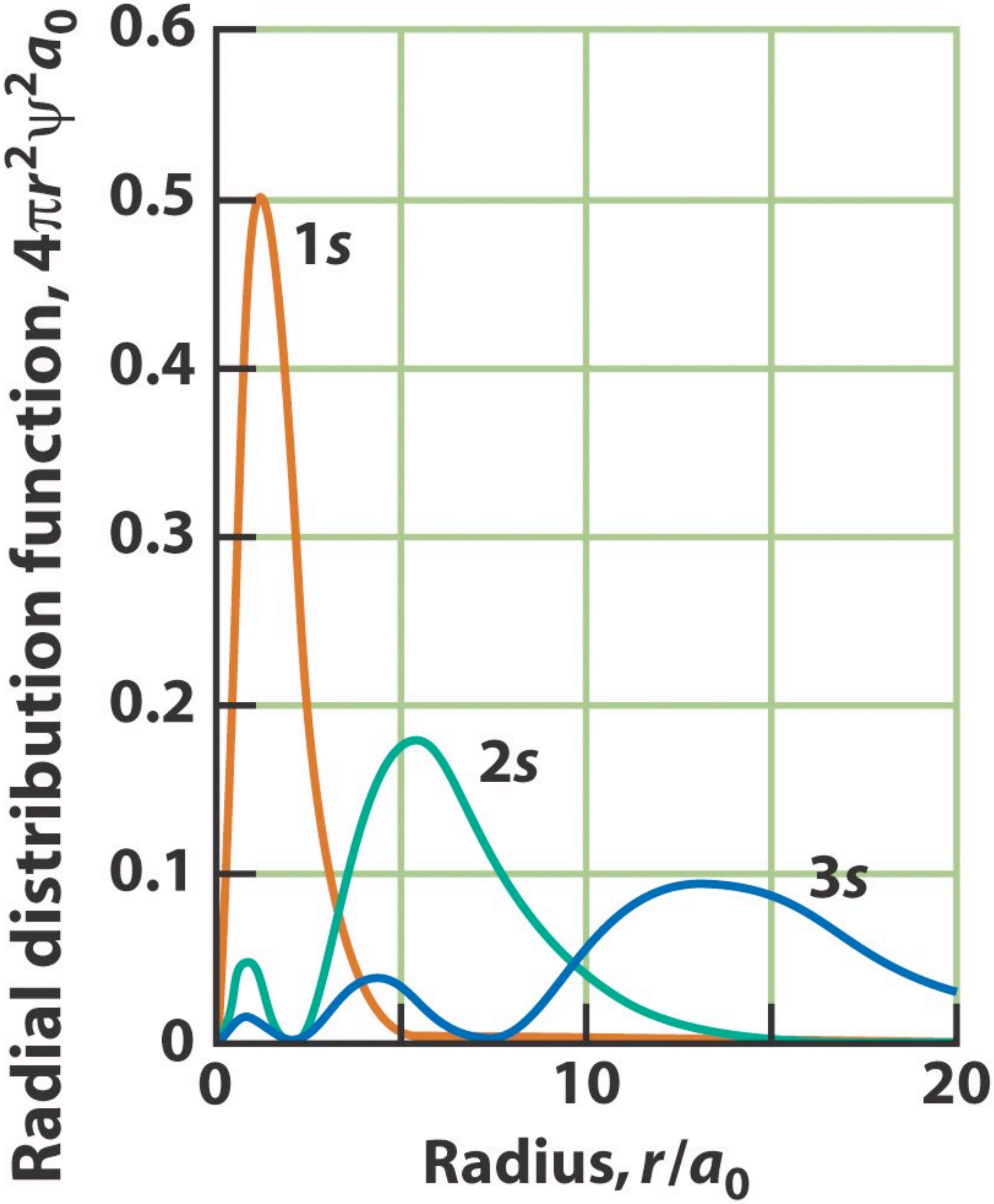


Fig 16-19



Electron probability x space occupied as a function of distance from the nucleus

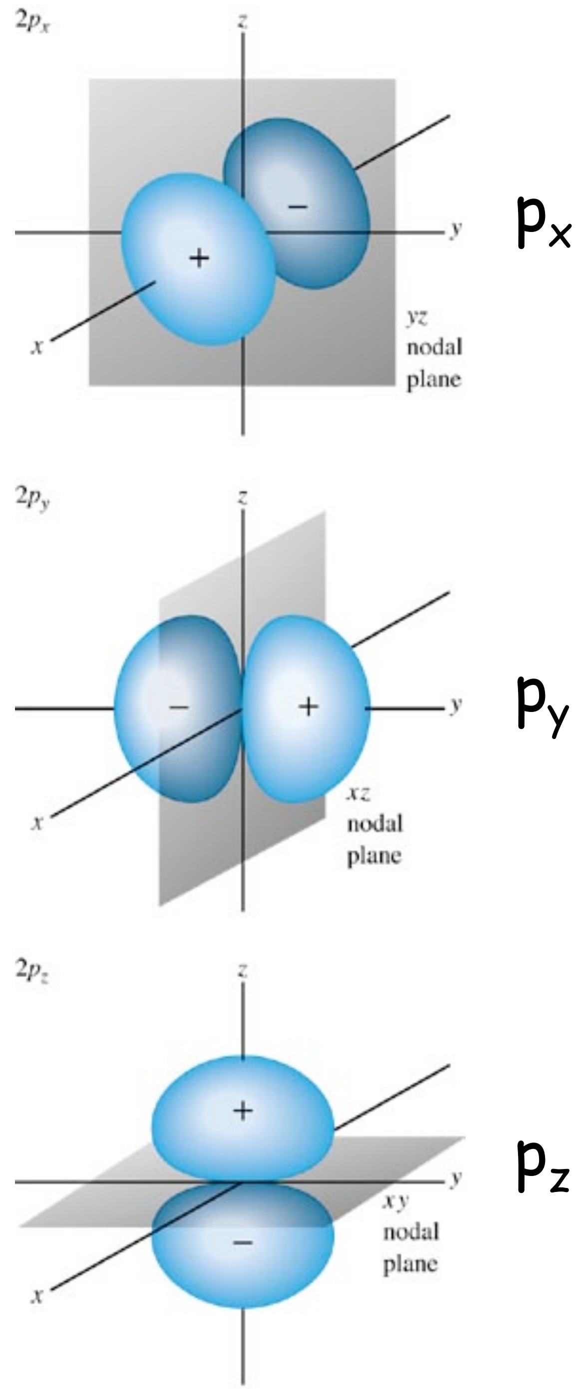
The larger the number of nodes in an orbital, the higher the energy of the orbital

Nodes in orbitals: 2p orbitals: angular node that passes through the nucleus

Orbital is "dumb bell" shaped

Important: the + and - that is shown for a p orbital refers to the mathematical sign of the wavefunction, not electric charge!

Important: The picture of an orbital refers to the space occupied by a SINGLE electron.

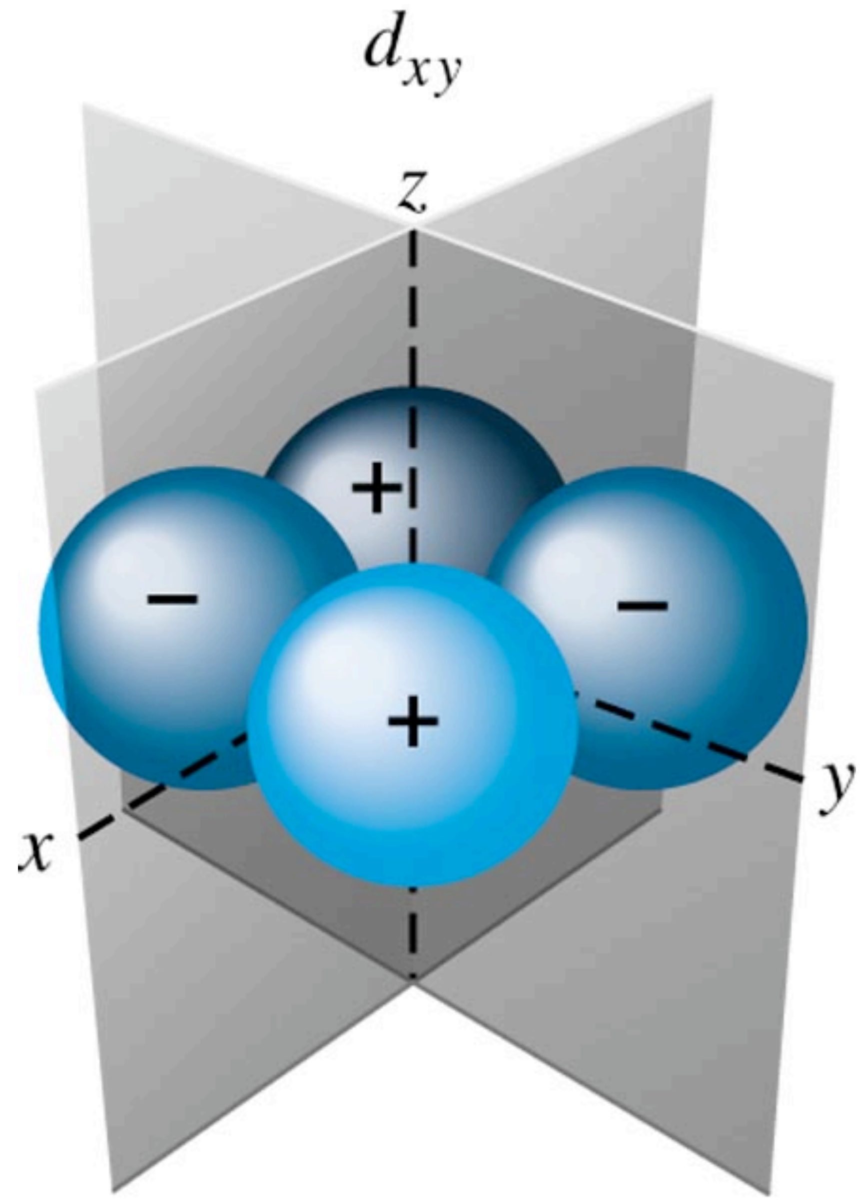


d orbitals

Nodes in
3d orbitals:
two angular nodes that
passes through the
nucleus

Orbital is "four leaf
clover" shaped

d orbitals are important for
metals
(Chapter 19)



(a)

The five d orbitals of a one electron atom

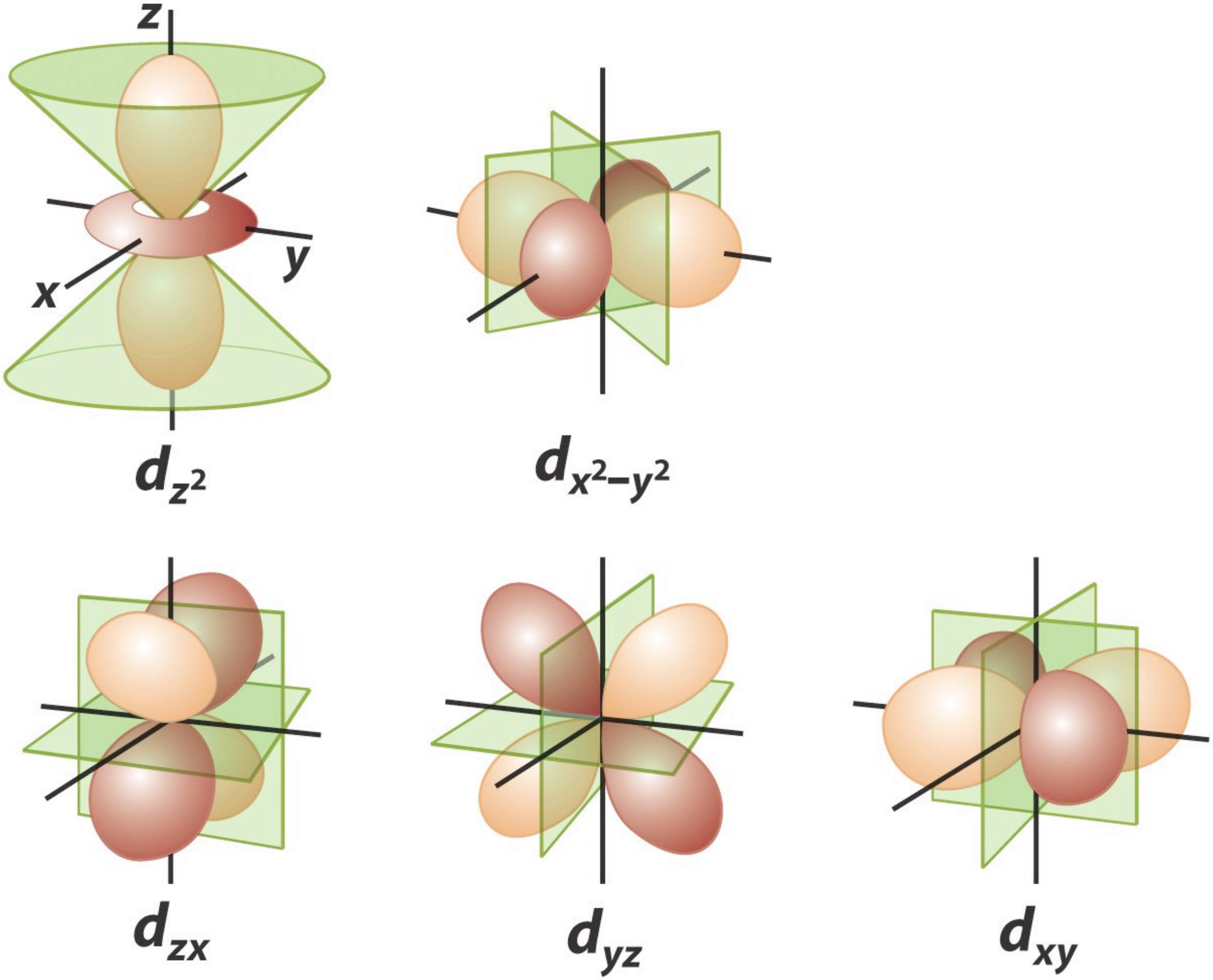
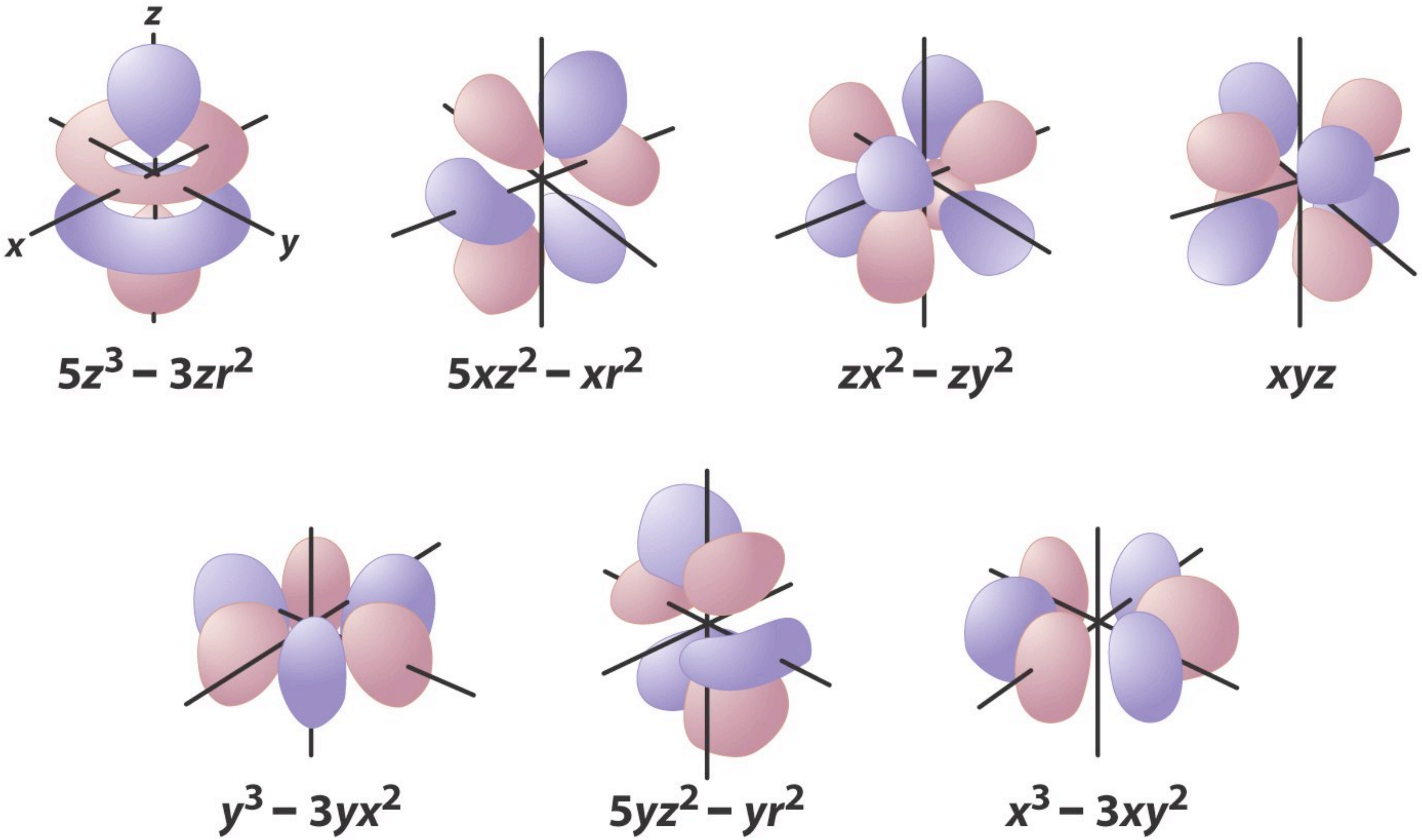


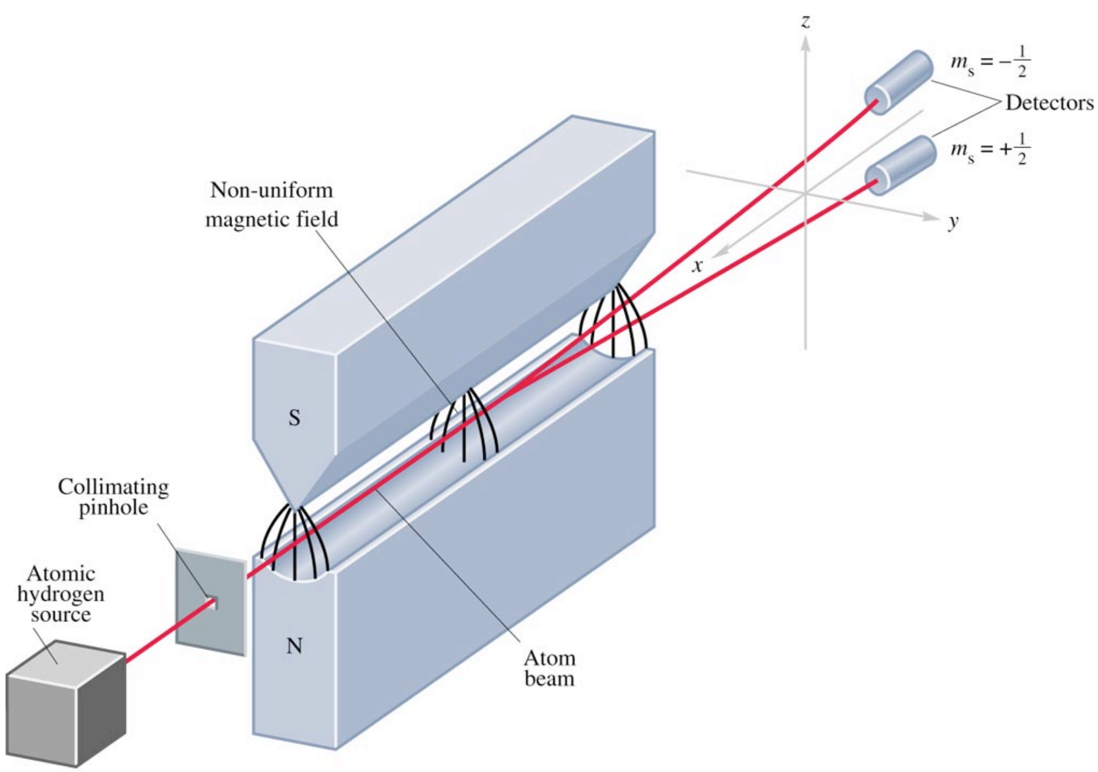
Fig 16-2_

The f orbitals of a one electron atom



This is getting a little complicated!

A need for a fourth quantum number: electron spin



A beam of H atoms in the 1s state is split into two beams when passed through a magnetic field. There must be two states of H which have a different energy in a magnetic field.

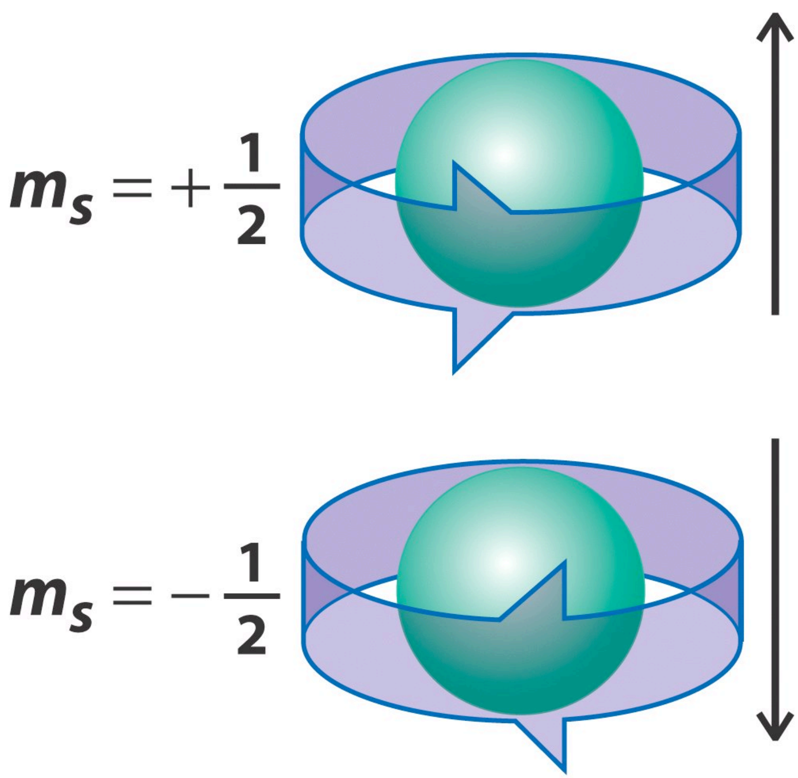
Conclusion: one more quantum number is needed.

The fourth quantum number: Electron Spin

m_s = +1/2 (spin up) or -1/2 (spin down)

Spin: a fundamental property of electrons, like charge and mass.

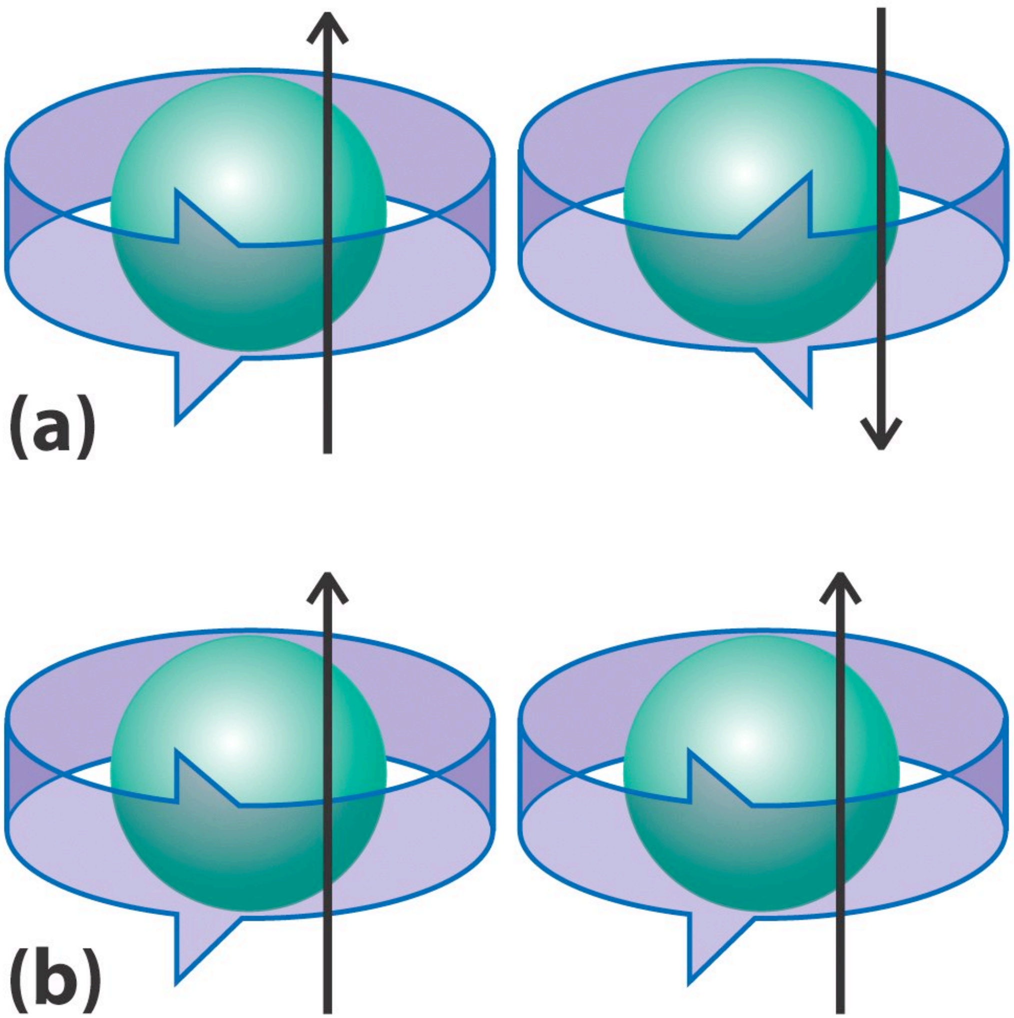
Spin: another manifestation of angular momentum at the quantum level!



(spin up)

(spin down)

Two electron spins can "couple" with one another to produce singlet states and triplet states.



A singlet state:
one spin up, one spin down

A triplet state:
both spins up or both spins down

Two electrons in a single orbital must have different values of m_s

This is the Pauli Exclusion Principle

This statement demands that if there are two electrons in an orbital one must have m_s = +1/2 (spin up ↑) and the other must have m_s = -1/2 (spin down ↓)

An empty orbital is fully described by the three quantum numbers: n, *l* and m_l

An electron in an orbital is fully described by the four quantum numbers: n, *l*, m_l and m_s

Shells and subshells define energy of the electrons in atoms.

Shell	n	ℓ	Symbol	Maximum Number of Pairs
1st shell	1	0	$1s$	1 pair
2nd shell	2	0	$2s$	1 pair
	2	1	$2p$	3 pairs
3rd shell	3	0	$3s$	1 pair
	3	1	$3p$	3 pairs
	3	2	$3d$	5 pairs
4th shell	4	0	$4s$	1 pair
	4	1	$4p$	3 pairs
	4	2	$4d$	5 pairs
	4	3	$4f$	7 pairs

Magic numbers of electrons

Pauli Exclusion Principle says in effect that no two electrons in the same atom can have the same four quantum numbers (states) this leads to a $2(n)^2$ rule for the number of electrons in a given shell:

n=1	2e
n=2	8e
n=3	18e
n=4	32
n=5	50

Wolfgang Pauli
Nobel Prize for 1945
for the discovery of the Exclusion Principle

Exercises using quantum numbers:

Are the following orbitals possible or impossible?

(1) A 2d orbital

(2) A 5s orbital

(1) Is a 2d orbital possible?

The possible values of l can be range from n - 1 to 0.

If n = 2, the possible values of l are 1 (= n -1) and 0.

This means that 2s (l = 0) and 2p (l = 1) orbitals are possible, but 2d (l = 2) is impossible.

The first d orbitals are possible for n = 3.

(2) Is a 5s orbital possible?

For n = 5, the possible values of *l* are 4 (g), 3 (f), 2 (d), 1 (p) and 0 (s).

So 5s, 5p, 5d, 5f and 5g orbitals are possible.

Is the electron configuration $1s^2 2s^3$ possible?

The Pauli exclusion principle forbids any orbital from having more than two electrons under any circumstances.

Since any s orbital can have a maximum of two electrons, a $1s^2 2s^3$ electronic configuration is impossible, since $2s^3$ means that there are THREE electrons in the 2s orbital.

Summary of quantum numbers and their interpretation

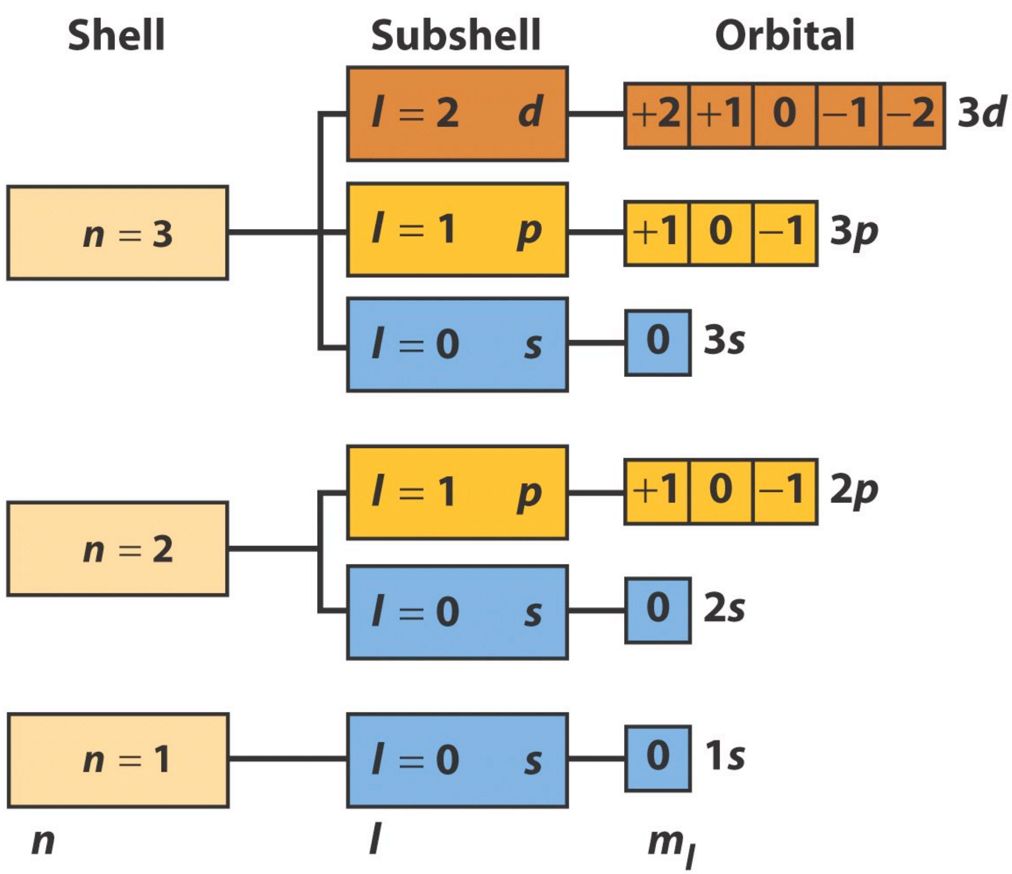
TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	$0, 1, \ldots, n-1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ $s, p, d, f, g, \ldots$	shape
magnetic	m_l	$l, l-1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the *azimuthal quantum number.*

Summary: The energy of an orbital of a hydrogen atom or any one electron atom only depends on the value of n

shell = all orbitals with the same value of n
subshell = all orbitals with the same value of n and *l*
an orbital is fully defined by three quantum numbers, n, *l*, and m_l



Each shell of QN = n contains n subshells

n = 1, one subshell
n= 2, two subshells, etc

Each subshell of QN = *l*, contains 2*l* + 1 orbitals

l = 0, 2(0) + 1 = 1
l = 1, 2(1) + 1 = 3

Chapter 17 Many-Electron Atoms and Chemical Bonding

17.1 Many-Electron Atoms and the Periodic Table
17.2 Experimental Measures of Orbital Energies
17.3 Sizes of Atoms and Ions
17.4 Properties of the Chemical Bond
17.5 Ionic and Covalent Bonds
17.6 Oxidation States and Chemical Bonding

The Original Periodic Table

"The Periodic Table."

Learning Goals: Construct the periodic table based on quantum numbers

Solve the wave equation exactly for the H atom

Use the exact orbitals for the H atom as a starting approximation for the many electron atom

Use quantum numbers obtained for H atom used to describe the many electron atom and build the electron configurations of atoms: periodic table

Quantum mechanics: makes quantitative, experimentally verifiable prediction about the properties of one electron, hydrogen orbital like atoms: atomic sizes, oxidation states and bonding through out the periodic table.

For atoms with more than one electron, approximations are required in order to make quantitative quantum mechical approximations.

The orbital approximation: The electron density of an isolated many-electron atom is approximately the sum of the electron densities of each of the individual electrons taken separately.

The Pauli exclusion principle and magic number of electrons.

Two equivalent statements of the exclusion principle:

(1) No two electrons may have the same set of four quantum numbers;
(2) No more than two electrons may occupy the same orbital.

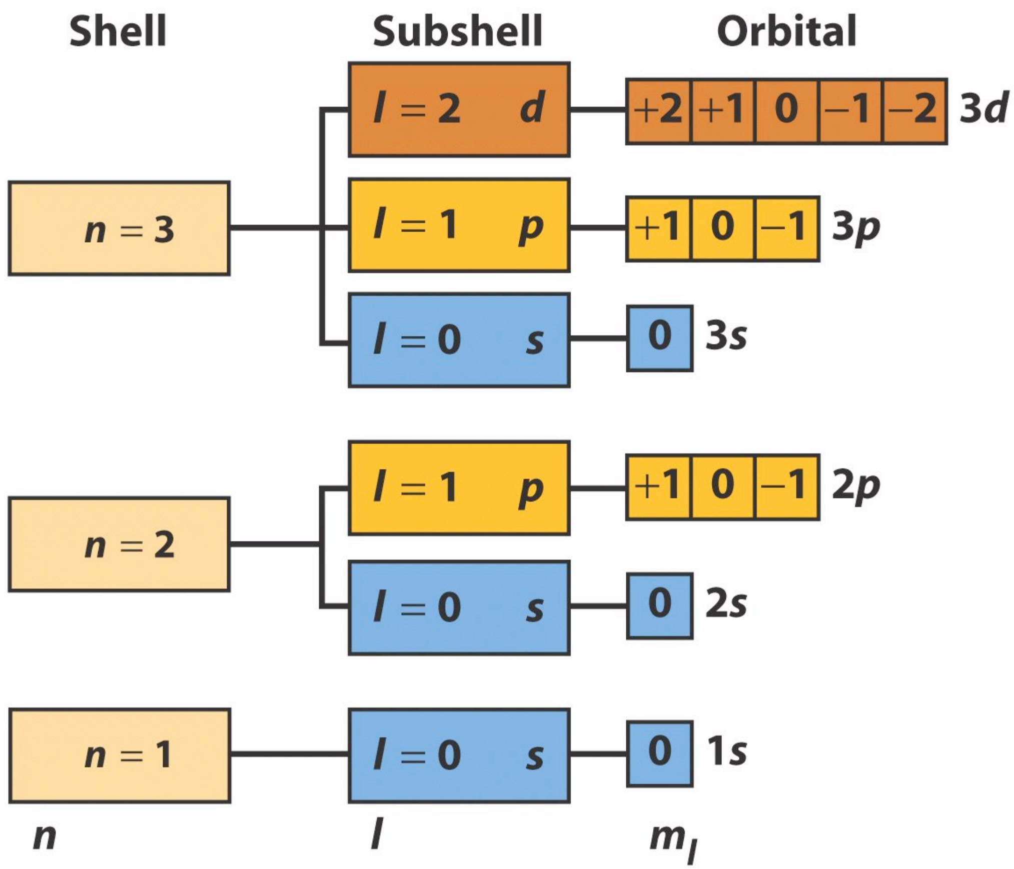
Because of the Pauli exclusion principle, outer electrons do not “fall” into the inner shell. Thus, the atom is stable.

The energy of an orbital of a hydrogen atom or any one electron atom only depends on the value of n

shell = all orbitals with the same value of n

subshell = all orbitals with the same value of n and l

an orbital is fully defined by three quantum numbers, n, l, and m_l

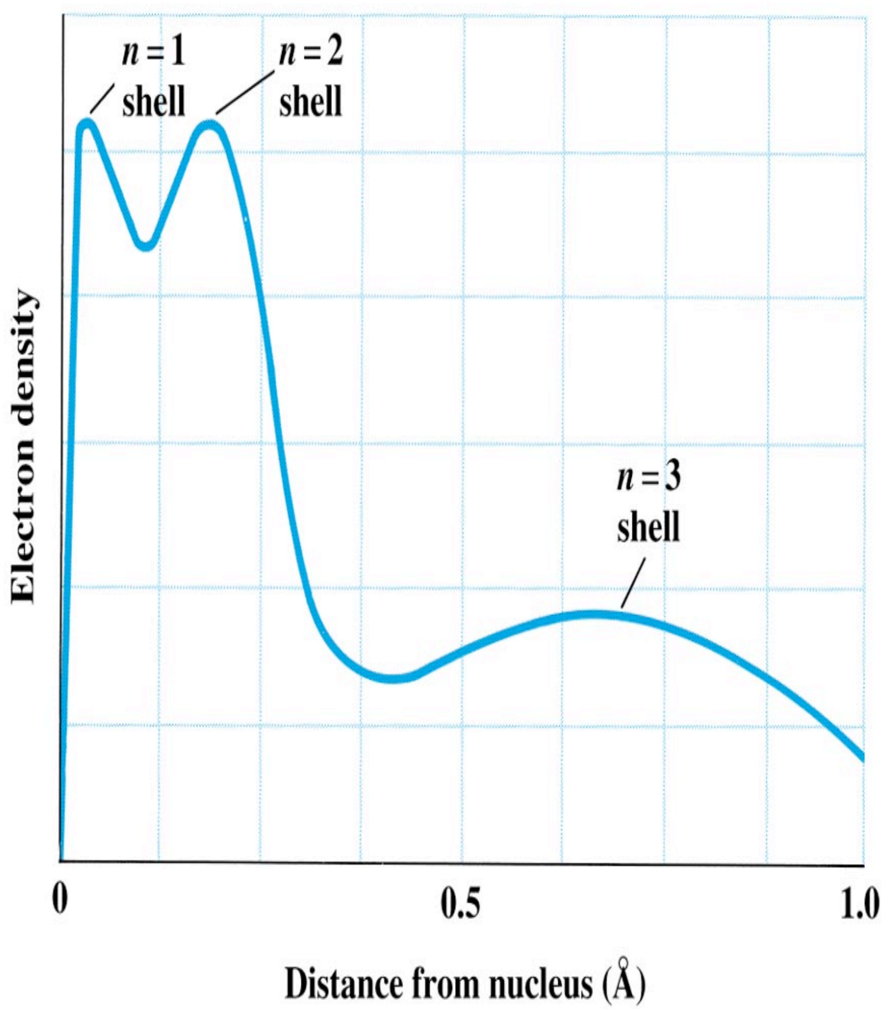


Classification of orbitals of a many electron atom according to their energies.

Orbitals with same value of n and different value of l comprise a shell.
Example: 2s and 2p comprise a shell.

A group of orbitals with exactly equal energies comprise a subshell.
Example: $2p_x$, $2p_y$ and $2p_z$

The orbital approximation ignores electron-electron repulsion, but takes into account Hund's rule: electrons with parallel spins (↑↑) tend to stay apart compared to electrons with antiparallel spins (↑↓).



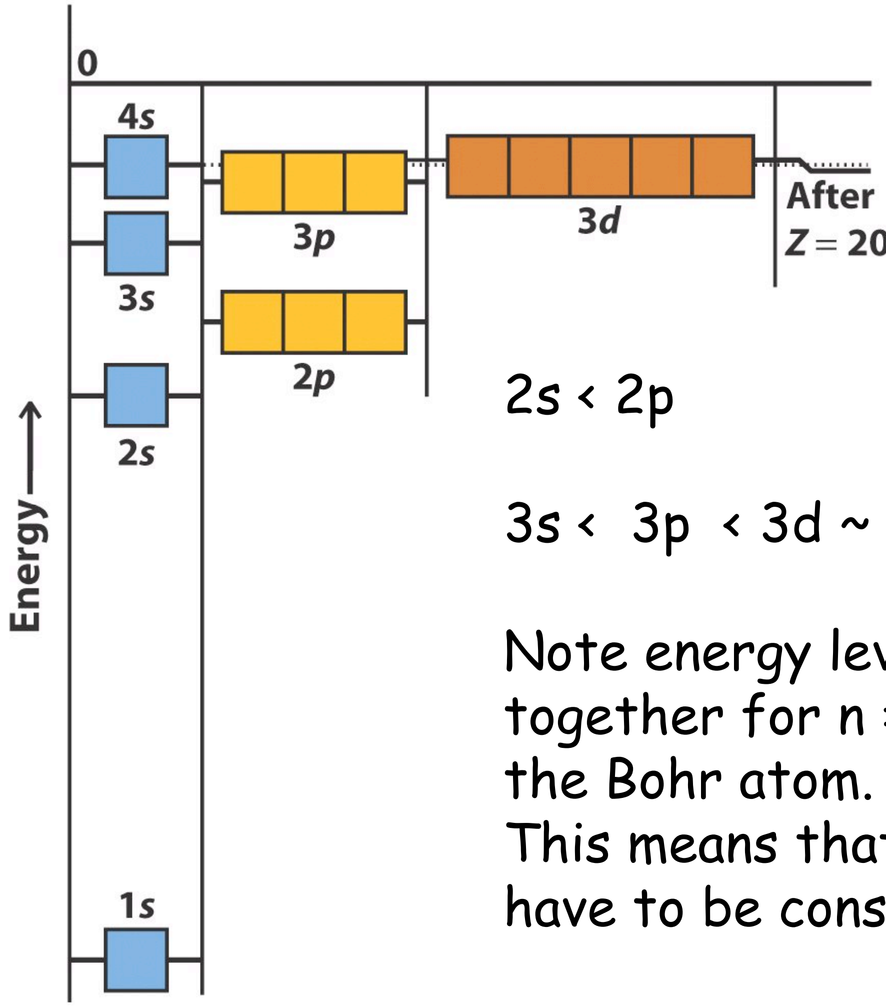
Orbital shells and the building up of the periodic table

A shell is a set of orbitals with the same value of n and *l* for a H atom.

The Ar atom has shells as shown (left) in the profile of electron density as a function of distance from the nucleus

The last shell are the valence electrons of our Lewis structures!

Relative orbital energies for the multielectron atom. The energy of an orbital of a multielectron atom depends on n and *l* (but not m_l)



2s < 2p

3s < 3p < 3d ~ 4s (may switch with Z)

Note energy levels are getting closer together for n = 3 as expected from the Bohr atom.
This means that factors ignored may have to be considered

Electron configuration: **a list of the orbitals that contain electrons and the number of electrons in each occupied orbital.**

The number of electrons are specified with a superscript: What is the electron configuration of ^{9}F?

^{9}F: nine electrons total

Electron configuration of $^{9}F = 1s^{2}2s^{2}2p^{5}$

Electrons fill orbitals of different energies by filling the lowest energy first. The energies of orbitals of multielectron atoms follow the $(n + l)$ rule: the lowest value of $(n + l)$ has the lowest energy.

Isoelectronic atoms: Atoms which have the same number of electrons.

Examples: ^{10}Ne (Z = 10), $^{9}F^{1-}$, $^{8}O^{2-}$, $^{11}Na^{1+}$, $^{12}Mg^{2+}$

Each atom or ions has a *closed shell of* $1s^2 2s^2 2p^6$ electrons.

Shorthand for writing electronic configurations of atoms:

Let $1s^2$ = [He] and $1s^2 2s^2 2p^6$ = [Ne]

Then F = [He]$2s^2 2p^5$, O = [He]$2s^2 2p^4$

Na = [Ne]3s, Mg = [Ne]$3s^2$

The Pauli principle imposes structure on the many electron atom.

Without it, all the electrons might be expected to crowd into the low energy orbitals. With it the electrons are organized, filled orbitals with no more than two electrons.

The ground state is the lowest energy organization of electrons around the nucleus. The electron organization is described by electron configurations.

The ground state of an atom corresponds to the lowest energy electron configuration.

Ground state electron configuration of a many electron atom: Governs reactivity of atoms under normal condition

Imagine a bare nucleus of charge +Z

Imagine empty orbitals surrounding the nucleus

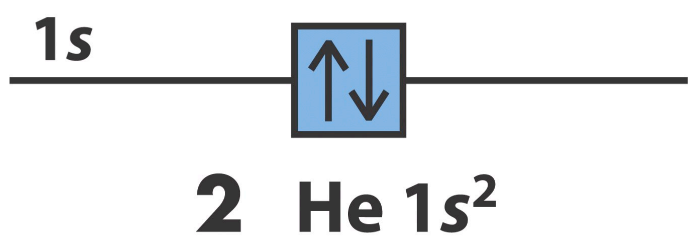
Fill the orbitals with Z electrons for the neutral atom following two principles:

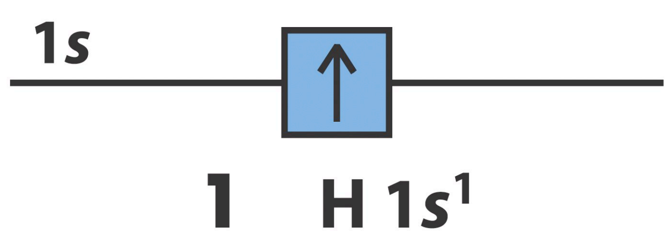
Aufbau principle: fill lowest energy orbitals first

Pauli exclusion principle: each electron must have four different quantum numbers (maximum of 2 electrons in an orbital).

Constructing the periodic table by filling orbitals with electrons (electron configurations).

Construction of the first row of the periodic table. Electron configurations: ^{1}H and ^{2}He.





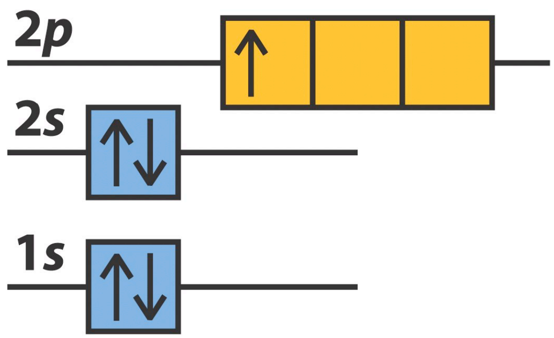
Aufbau: Fill 1s orbital first

Pauli: no more than two electrons in the 1s orbital

The basis of the duet rule: filling a shell

1s subshell filled with ^{2}He = stable electron core given symbol [He].

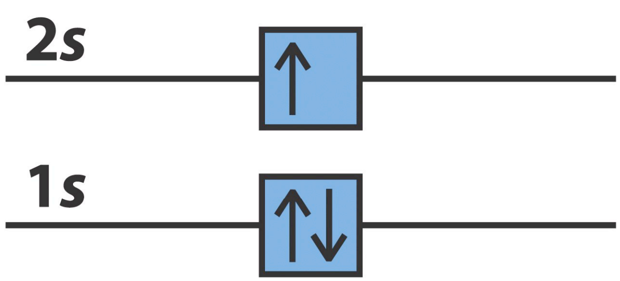
Filling the orbitals of ${}^{3}Li$, ${}^{4}Be$ and ${}^{5}B$



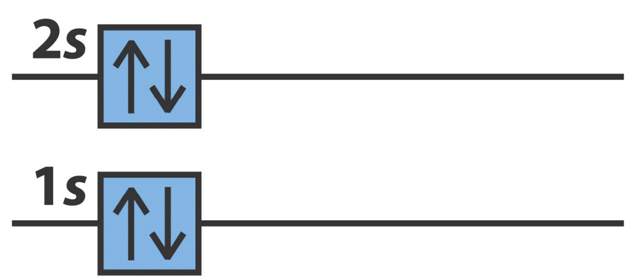
5 B $1s^22s^22p^1$, [He]$2s^22p^1$

Aufbau: Fill 1s orbital first, then 2s, then 2p.
Pauli: no more than two electrons in the 1s orbital.

2s subshell filled with ${}^{4}Be$.

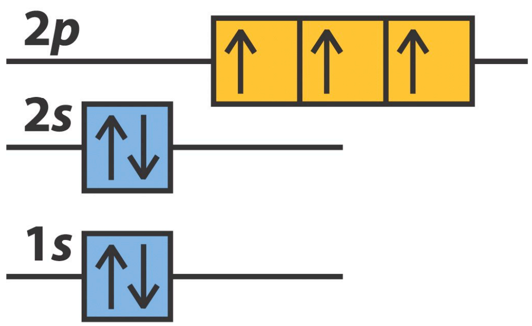


3 Li $1s^22s^1$, [He]$2s^1$



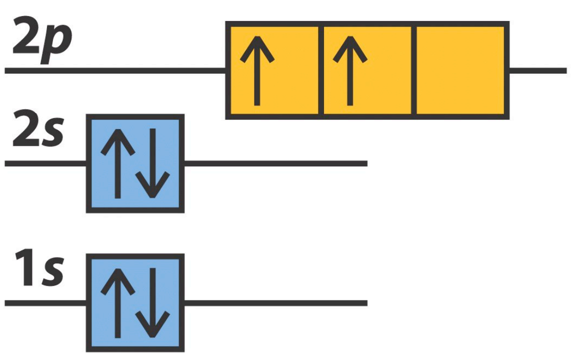
4 Be $1s^22s^2$, [He]$2s^2$

Filling the orbitals of ^6C and ^7N. The need for a third rule (Hund's rule):



7 N $1s^2 2s^2 2p^3$, [He]$2s^2 2p^3$

When electrons occupy orbitals of the same energy, the lowest energy state corresponds to the configuration with the ***greatest number of orbitally and spin unpaired electrons.***



6 C $1s^2 2s^2 2p^2$, [He]$2s^2 2p^2$

This electron configutation avoids electron-electron repulsion and lowers the atom's energy

Hund's rule refers to the lowest energy of electron configurations allowed by the Pauli exclusions principle. It does not forbid the existence of any of the Pauli allowed configurations. If there are more than electron configurations one allowed Pauli configuration, the lower energy on will be predicted by Hund's rule and the others will be excited states.

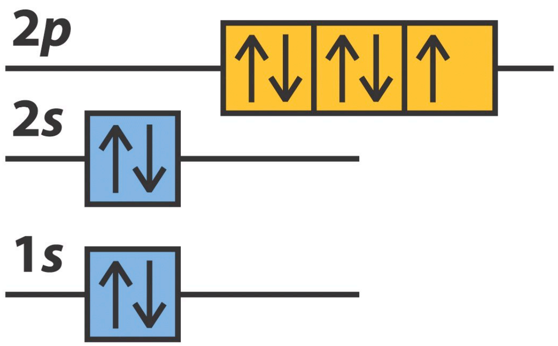
Are the following two states allowed for N by the Pauli principle?

$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ or $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$

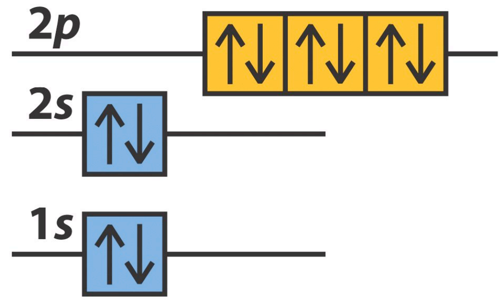
Which is more stable?

$1s^2 2s^2 2p_x(\uparrow) 2p_y(\uparrow) 2p_z(\uparrow)$ is more stable than $1s^2 2s^2 2p_x(\uparrow\downarrow) 2p_y(\uparrow) 2p_z()$

Filling the orbitals of ^{8}O, ^{9}F and ^{10}Ne

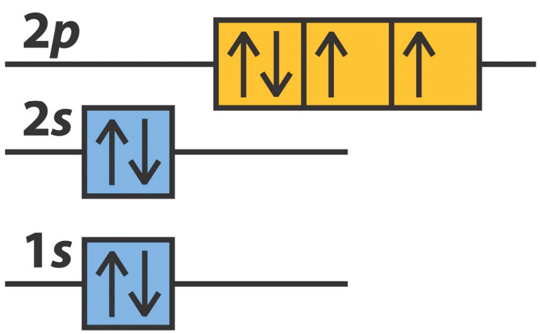


9 F $1s^2 2s^2 2p^5$, [He]$2s^2 2p^5$



10 Ne $1s^2 2s^2 2p^6$, [He]$2s^2 2p^6$

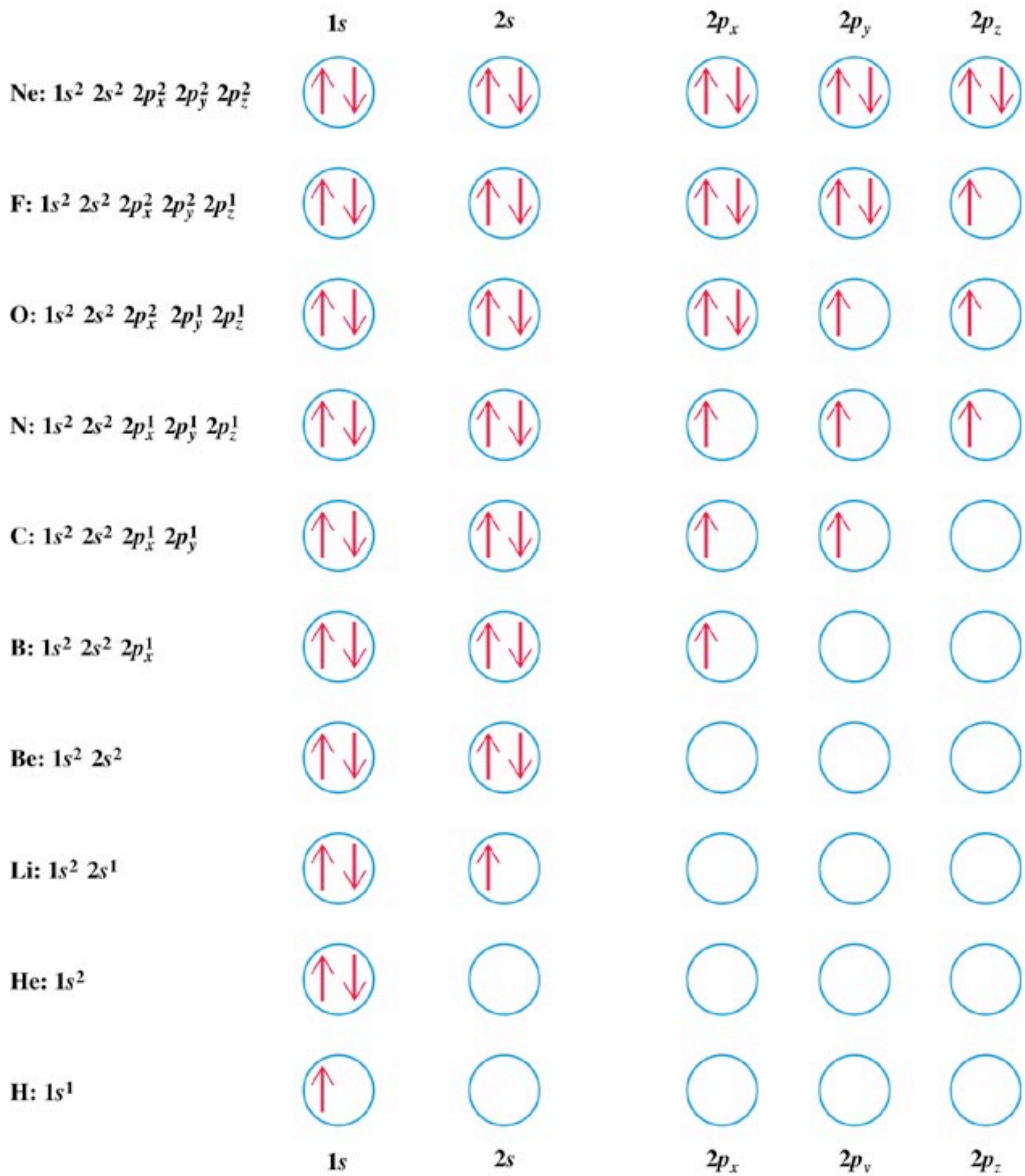
Filling the 2p subshell produces another stable configuration of electrons which serves as the core shell of the third row: symbol [Ne]



8 O $1s^2 2s^2 2p^4$, [He]$2s^2 2p^4$

Summary: Electron configurations from ^{1}H to ^{10}Ne.

No new features for the electron configurations from ^{11}Na to ^{18}Ar.



Ionization energies (ionization potentials):

The ionization energy (IE) of an atom is the minimun energy required to remove an electron from a gaseous atom.

$$X(g) \longrightarrow X^{+}(g) + e^{-}$$

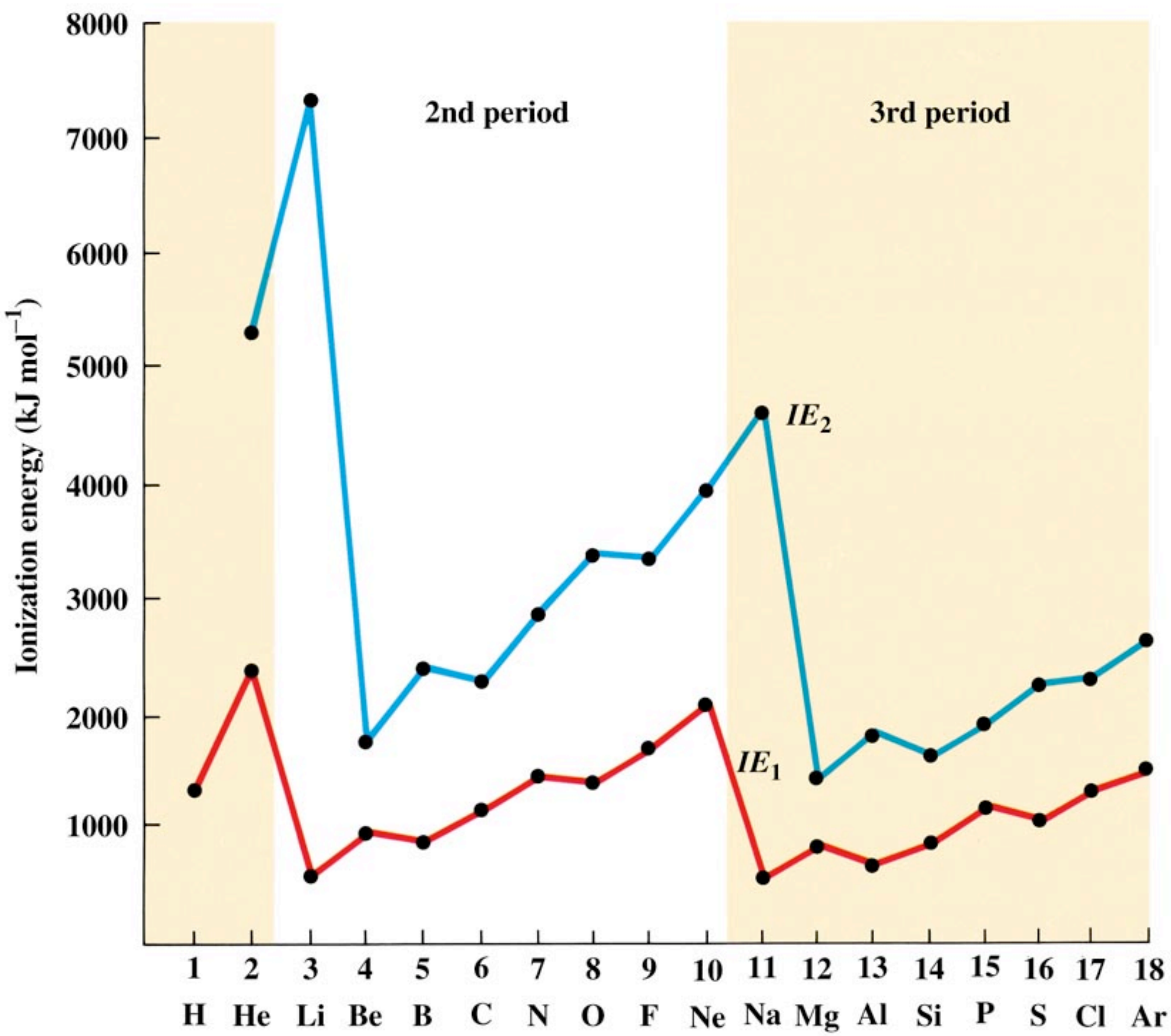
The first ionization energy IE_1 is the energy required to remove the first electron from the atom, the second ionization energy IE_2, is the energy required to remove the second electron from the +1 positive ion of the atom and so on.

Conclusions from experimental IE values:
An abrupt change in IE in going along a row or column of the periodic table indicates a change in the valence electron shell or subshell. Let's take a look:

Ionization energies in tabular form

Z	Element	1st	2nd	3rd	4th	5th	6th	7th	8th
1	H	13.6	(13.6×2^2)						
2	He	24.6	54.4	(13.6×3^2)					
3	Li	5.4	75.6	122	(13.6×4^2)				
4	Be	9.3	18.2	154	218	(13.6×5^2)			
5	B	8.3	25.1	38	259	340	(13.6×6^2)		
6	C	11.3	24.4	48	64	392	490	(13.6×7^2)	
7	N	14.5	29.6	47	77	98	552	667	(13.6×8^2)
8	O	13.6	35.1	55	77	114	138	739	871
9	F	17.4	35.0	63	87	114	157	185	954
10	Ne	21.6	41.1	64	97	126	158	207	238
11	Na	5.1	47.3	72	99	138	172	208	264
12	Mg	7.6	15.0	80	109	141	186	225	266
13	Al	6.0	18.8	28	120	154	190	241	285
14	Si	8.1	16.3	33	45	167	205	246	303
15	P	10.5	19.7	30	51	65	220	263	309
16	S	10.4	23.4	35	47	72	88	281	329
17	Cl	13.0	23.8	40	54	68	97	114	348
18	Ar	15.8	27.6	41	60	75	91	124	143

Ionization energies in graphical form



Periodic trends of the first ionization energies of the representative elements: What are the correlations across and down?

Group

Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1				H 1310				He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

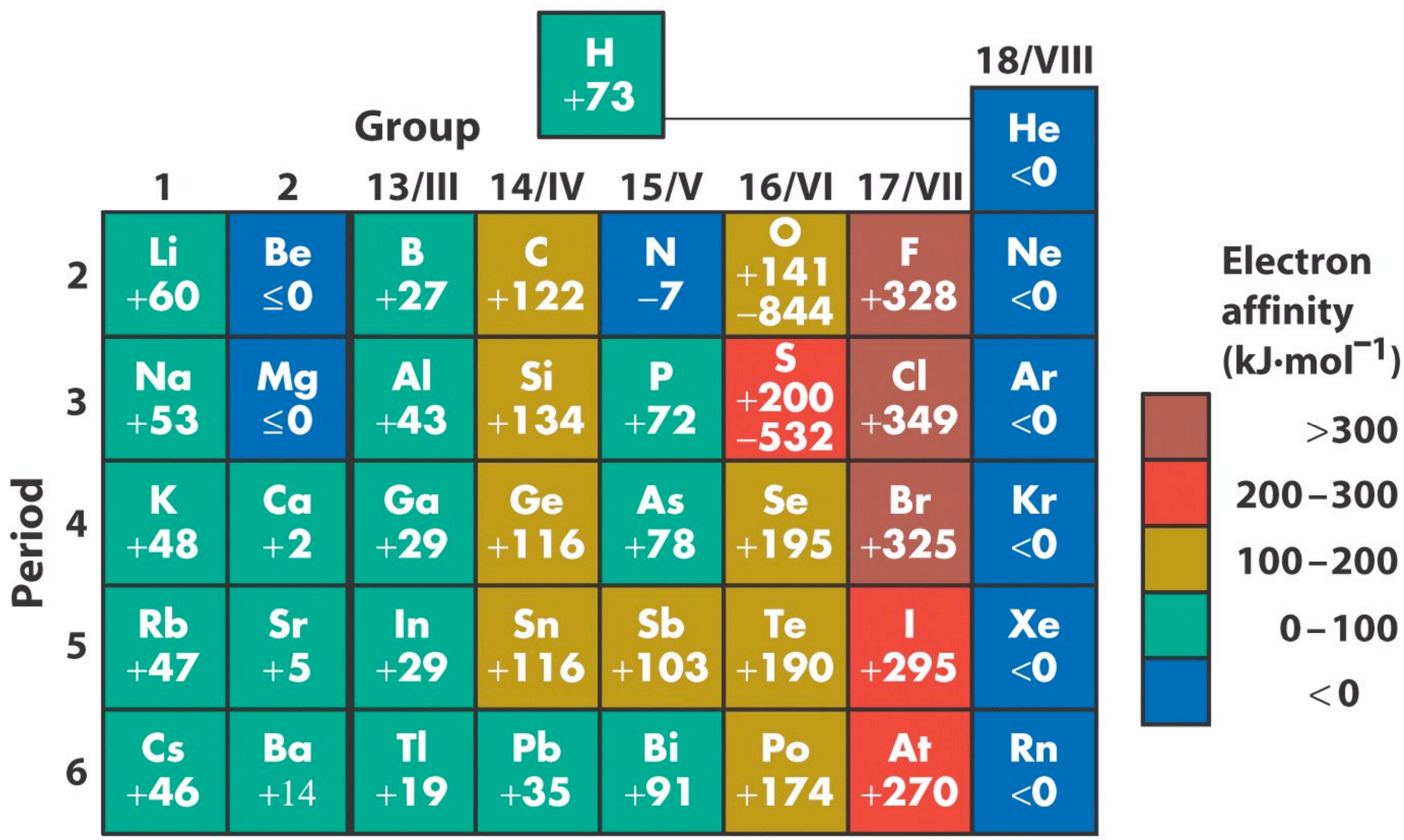
Ionization energy ($kJ \cdot mol^{-1}$)

- 2001–2500
- 1501–2000
- 1001–1500
- 501–1000
- 1–500

The electron affinity (EA) of an atom is the energy change which occurs when an atom gains an electron.

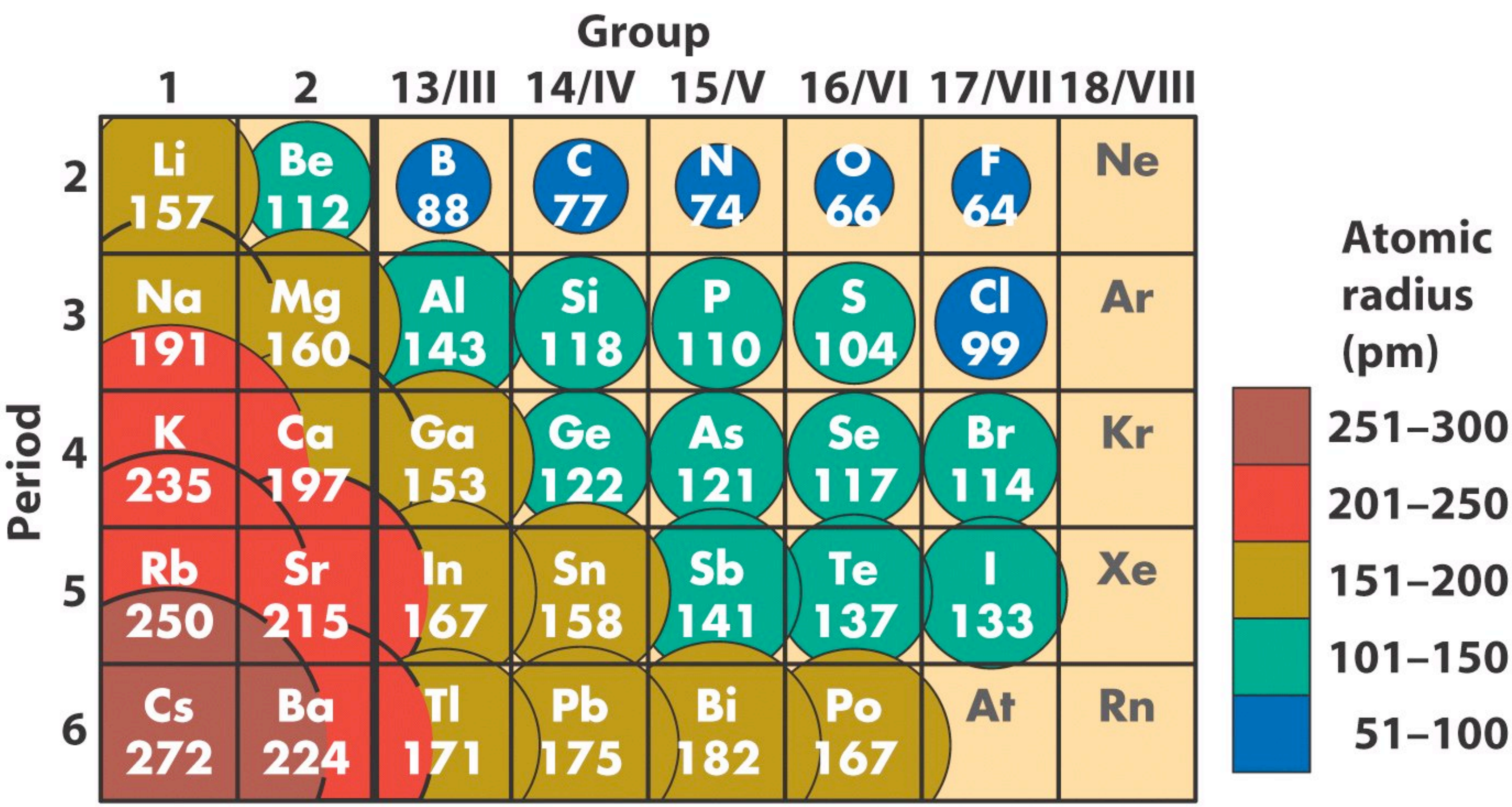
$$X(g) \; + \; e^- \longrightarrow Xe^- \; (g)$$

Electron affinities of the representative elements:
What are the correlations across and down?

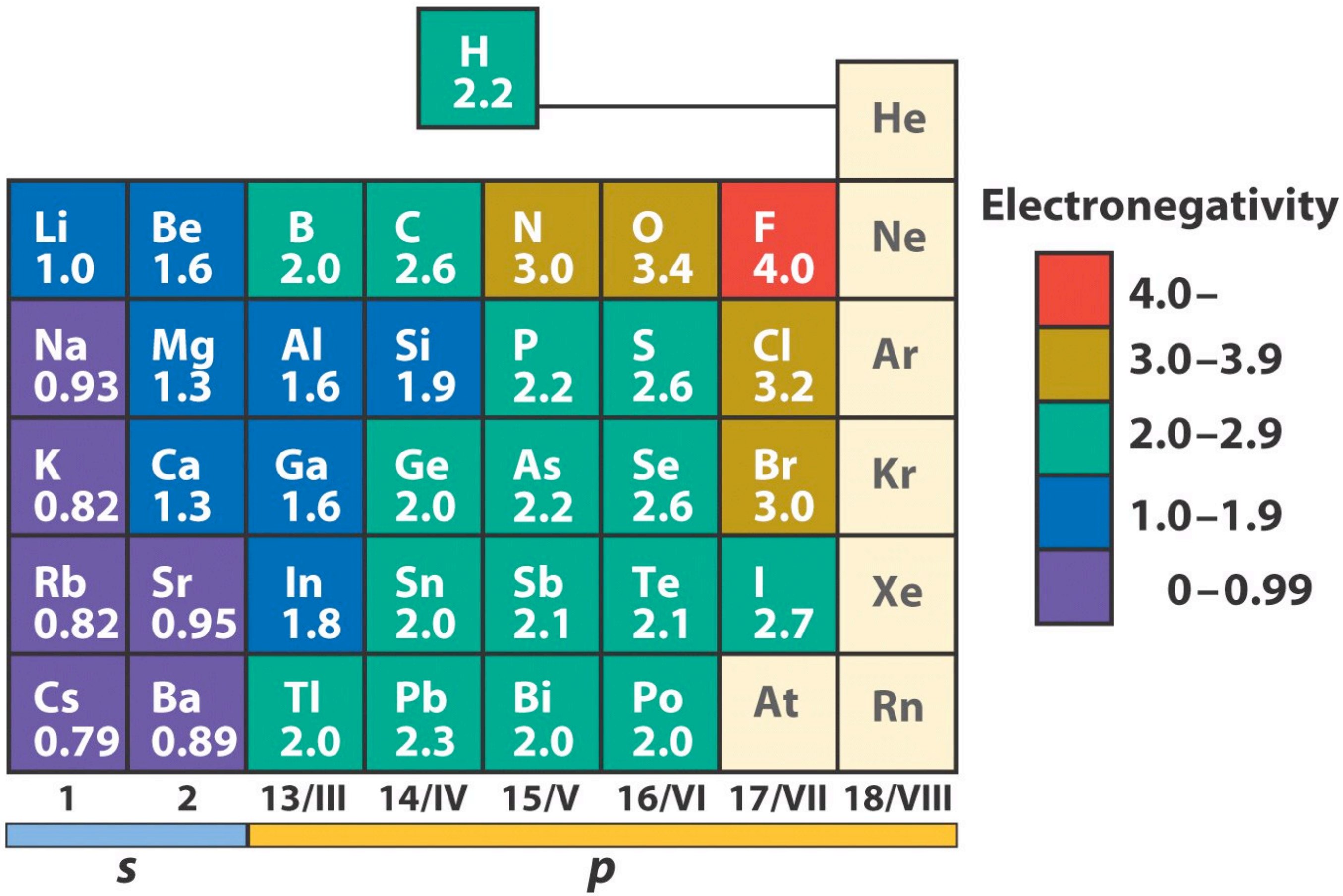


Periodic properties of atomic radius:
What are the correlations?

General Rule: The size of an atom decreases in a row as the nuclear charge increases and the size of an atom increases in a column as the nuclear charge increases



Electronegativity (EN): a measure of the ability of an atom to attract electrons to itself in competition with other atoms



Electronic structure and the periodic table

Electrons in the outermost shell of an atom are the most important in determining chemical properties. Chemical reactions involve only the outer (valence) electrons. The inner (core) electrons are not involved in chemical reactions.

Elements in a given vertical column (families) of the periodic table have similar outer-shell electron configurations and similar properties. They are isoelectronic with respect to the number of valence electrons.

Elements in a row show regular trends in their properties due to the continuing increase in the number of valence electrons until a shell is filled.

Electronic structure of atoms of the elements:

(1) Atoms of the various elements differ from each other in their values of Z and electrons.

(2) Electrons in atoms are arranged in orbitals and shells.

(3) Orbitals are characterized by the quantum numbers n, l and m_l.

(4) Orbitals having the same value of n are said to be in the same shell. Orbitals having the same values of n and l are said to be in the same subshell.