Electronic Configuration of Atoms

What is Electronic Configuration ?

The distribution of electrons in various shells, sub-shells and orbitals of an atom is called its *complete electronic configuration* or simply *electronic configuration*.

What is Valence-shell Configuration ?

The distribution of electrons in various sub-shells and orbitals of the valence-shell (or outermost shell) is called *valence-shell configuration*.

Representation of Electronic Configuration

The electronic configuration of an atom is written in terms of nl^x notation where l indicates the sub-shell as given below :

Value of l	:	*0*	*1*	*2*	*3*	....
Sub-shell	:	*s*	*p*	*d*	*f*	....

In the notation nl^x, super-script x written at the top of l indicates the number of electrons present in the sub-shell given by l, while n written to the left of l^x indicates the number of the shell to which the sub-shell denoted by l belongs. For example $3p^2$ in which $n = 3$, $x = 2$ and $l = 1$ (p sub-shell) indicates that two electrons ($x = 2$) are present in p sub-shell ($l = 1$) which belongs to *3rd* main shell ($n = 3$). (Fig. 3.1).

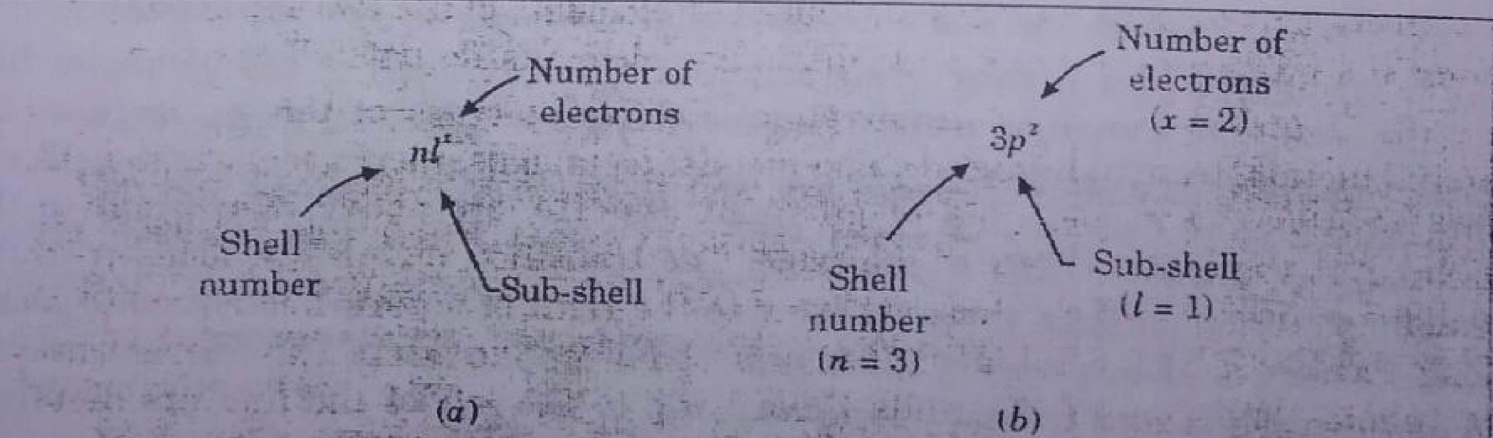


Fig. 3.1. (*a*) Representation of electronic configuration of an atom. (*b*) Representation of electronic configuration of an atom containing two electrons ($x = 2$) in p sub-sell ($l = 1$) belonging to *3rd* shell ($n = 3$).

Rules for Writing Electronic Configuration of a Given Atom

The rules used for writing the electronic configurations of the atoms of the elements in the ground state are :

1. Maximum number of electrons in a shell. According to *Bohr-Bury scheme* the maximum number of electrons that a shell can hold is equal to $2n^2$ where n is the number of the shell (*i.e.*, principal quantum number). Thus :

The maximum number of electrons in 1st shell (n = 1) = 2 × 1^2 = 2

The maximum number of electrons in 2nd shell (n = 2) = 2 × 2^2 = 8

The maximum number of electrons in 3rd shell (n = 3) = 2 × 3^2 = 18

The maximum number of electrons in 4th shell (n = 4) = 2 × 4^2 = 32

2. **Maximum number of electrons in a sub-shell.** We have seen during the study of azimuthal quantum number that the maximum number of electrons in a sub-shell is equal to $2(2l + 1)$ where l = 0, 1, 2 or 3 for *s*, *p*, *d* or *f* sub-shells respectively. Thus :

Value of l	:	0	1	2	3
Sub-shell	:	s	p	d	f
Max. number of electrons = $2(2l + 1)$	:	2	6	10	14

3. **Aufbau principle.** Aufbau is a German word which means *build up* or *construction*. It is for this reason that the principle is also often called *building up principle* or *construction principle*. It is pronounced as *of bow*. This principle gives us a sequence in which various orbitals are filled with electrons. This principle states as follows :

The orbitals are filled up with electrons in the increasing order of their energy.

The principle can also be restated in any of the following forms :

(*i*) *The orbitals of minimum energy are filled up first with electrons and then the orbitals of higher energy start to fill.*

(*ii*) *Electrons occupy the orbitals of minimum energy first and then they occupy the orbitals of higher enegry.*

(*iii*) *Orbitals with lowest energy are better seats for electrons and are, therefore, occupied first.*

The energy of various orbitals of an atom *a multi-electron atom* increases as :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < 8s \ldots$$

Thus the sequence in which various orbitals are filled up with electrons is the same as the relative order of the energy of orbitals. Thus the orbitals will be filled up with electrons in the following sequence :

Orbitals being filled →

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, ...

The sequence given above is represented diagramatically in Fig. 3.2.

Limitations (Deviations) of Aufbau principle. There are some elements in which the extra electron, while entering the orbital, does not obey Aufbau principle as shown by the following examples :

(*i*) ***Configuration of La (Z = 57) atom.*** We know that, according to Afbau principle, the configuration of Ba (Z = 56) atom is $[Xe]_{54}\ 6s^2$ where $[Xe]_{54}$ indicates the configuration of Xe (Z = 54) atom which is 2, 8, 18, 18, 8.

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	37	Rb	[Kr]$5s^1$	73	Ta	[Xe]$6s^24f^{14}5d^3$
2	He	$1s^2$	38	Sr	[Kr]$5s^2$	74	W	[Xe]$6s^24f^{14}5d^4$
3	Li	[He]$2s^1$	39	Y	[Kr]$5s^24d^1$	75	Re	[Xe]$6s^24f^{14}5d^5$
4	Be	[He]$2s^2$	40	Zr	[Kr]$5s^24d^2$	76	Os	[Xe]$6s^24f^{14}5d^6$
5	B	[He]$2s^22p^1$	41	Nb	[Kr]$5s^14d^4$	77	Ir	[Xe]$6s^24f^{14}5d^7$
6	C	[He]$2s^22p^2$	42	Mo	[Kr]$5s^14d^5$	78	Pt	[Xe]$6s^14f^{14}5d^9$
7	N	[He]$2s^22p^3$	43	Tc	[Kr]$5s^24d^5$	79	Au	[Xe]$6s^14f^{14}5d^{10}$
8	O	[He]$2s^22p^4$	44	Ru	[Kr]$5s^14d^7$	80	Hg	[Xe]$6s^24f^{14}5d^{10}$
9	F	[He]$2s^22p^5$	45	Rh	[Kr]$5s^14d^8$	81	Tl	[Xe]$6s^24f^{14}5d^{10}6p^1$
10	Ne	[He]$2s^22p^6$	46	Pd	[Kr]$4d^{10}$	82	Pb	[Xe]$6s^24f^{14}5d^{10}6p^2$
11	Na	[Ne]$3s^1$	47	Ag	[Kr]$5s^14d^{10}$	83	Bi	[Xe]$6s^24f^{14}5d^{10}6p^3$
12	Mg	[Ne]$3s^2$	48	Cd	[Kr]$5s^24d^{10}$	84	Po	[Xe]$6s^24f^{14}5d^{10}6p^4$
13	Al	[Ne]$3s^23p^1$	49	In	[Kr]$5s^24d^{10}5p^1$	85	At	[Xe]$6s^24f^{14}5d^{10}6p^5$
14	Si	[Ne]$3s^23p^2$	50	Sn	[Kr]$5s^24d^{10}5p^2$	86	Rn	[Xe]$6s^24f^{14}5d^{10}6p^6$
15	P	[Ne]$3s^23p^3$	51	Sb	[Kr]$5s^24d^{10}5p^3$	87	Fr	[Rn]$7s^1$
16	S	[Ne]$3s^23p^4$	52	Te	[Kr]$5s^24d^{10}5p^4$	88	Ra	[Rn]$7s^2$
17	Cl	[Ne]$3s^23p^5$	53	I	[Kr]$5s^24d^{10}5p^5$	89	Ac	[Rn]$7s^26d^1$
18	Ar	[Ne]$3s^23p^6$	54	Xe	[Kr]$5s^24d^{10}5p^6$	90	Th	[Rn]$7s^26d^2$
19	K	[Ar]$4s^1$	55	Cs	[Xe]$6s^1$	91	Pa	[Rn]$7s^25f^26d^1$
20	Ca	[Ar]$4s^2$	56	Ba	[Xe]$6s^2$	92	U	[Rn]$7s^25f^36d^1$
21	Sc	[Ar]$4s^23d^1$	57	La	[Xe]$6s^25d^1$	93	Np	[Rn]$7s^25f^46d^1$
22	Ti	[Ar]$4s^23d^2$	58	Ce	[Xe]$6s^24f^15d^1$	94	Pu	[Rn]$7s^25f^6$
23	V	[Ar]$4s^23d^3$	59	Pr	[Xe]$6s^24f^3$	95	Am	[Rn]$7s^25f^7$
24	Cr	[Ar]$4s^13d^5$	60	Nd	[Xe]$6s^24f^4$	96	Cm	[Rn]$7s^25f^76d^1$
25	Mn	[Ar]$4s^23d^5$	61	Pm	[Xe]$6s^24f^5$	97	Bk	[Rn]$7s^25f^9$
26	Fe	[Ar]$4s^23d^6$	62	Sm	[Xe]$6s^24f^6$	98	Cf	[Rn]$7s^25f^{10}$
27	Co	[Ar]$4s^23d^7$	63	Eu	[Xe]$6s^24f^7$	99	Es	[Rn]$7s^25f^{11}$
28	Ni	[Ar]$4s^23d^8$	64	Gd	[Xe]$6s^24f^75d^1$	100	Fm	[Rn]$7s^25f^{12}$
29	Cu	[Ar]$4s^13d^{10}$	65	Tb	[Xe]$6s^24f^9$	101	Md	[Rn]$7s^25f^{13}$
30	Zn	[Ar]$4s^23d^{10}$	66	Dy	[Xe]$6s^24f^{10}$	102	No	[Rn]$7s^25f^{14}$
31	Ga	[Ar]$4s^23d^{10}4p^1$	67	Ho	[Xe]$6s^24f^{11}$	103	Lr	[Rn]$7s^25f^{14}6d^1$
32	Ge	[Ar]$4s^23d^{10}4p^2$	68	Er	[Xe]$6s^24f^{12}$	104	Rf	[Rn]$7s^25f^{14}6d^2$
33	As	[Ar]$4s^23d^{10}4p^3$	69	Tm	[Xe]$6s^24f^{13}$	105	Db	[Rn]$7s^25f^{14}6d^3$
34	Se	[Ar]$4s^23d^{10}4p^4$	70	Yb	[Xe]$6s^24f^{14}$	106	Sg	[Rn]$7s^25f^{14}6d^4$
35	Br	[Ar]$4s^23d^{10}4p^5$	71	Lu	[Xe]$6s^24f^{14}5d^1$	107	Bh	[Rn]$7s^25f^{14}6d^5$
36	Kr	[Ar]$4s^23d^{10}4p^6$	72	Hf	[Xe]$6s^24f^{14}5d^2$	108	Hs	[Rn]$7s^25f^{14}6d^6$
						109	Mt	[Rn]$7s^25f^{14}6d^7$
						110	Ds	[Rn]$7s^15f^{14}6d^9$
						111	Rg	[Rn]$7s^15f^{14}6d^{10}$

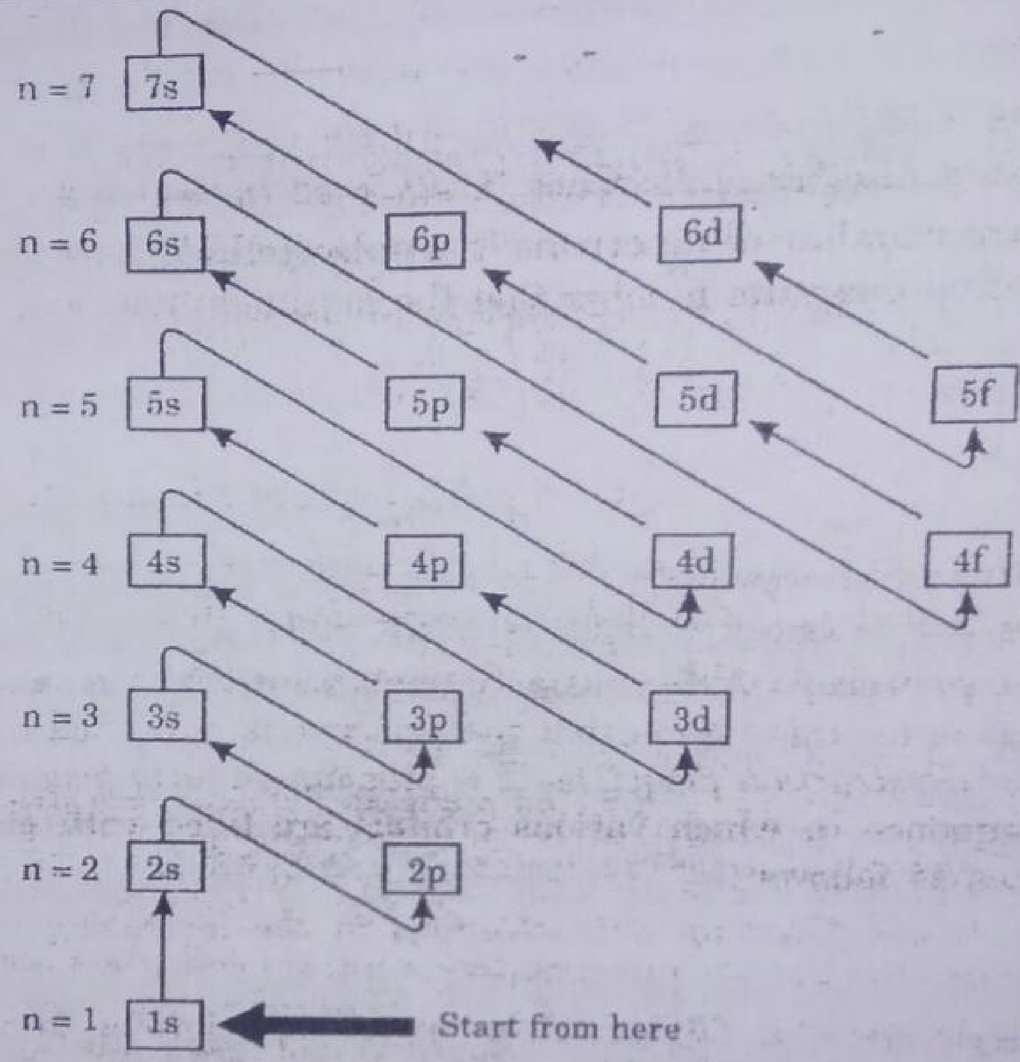


Fig. 3.2. The sequence in which various orbitals are filled up with electrons.

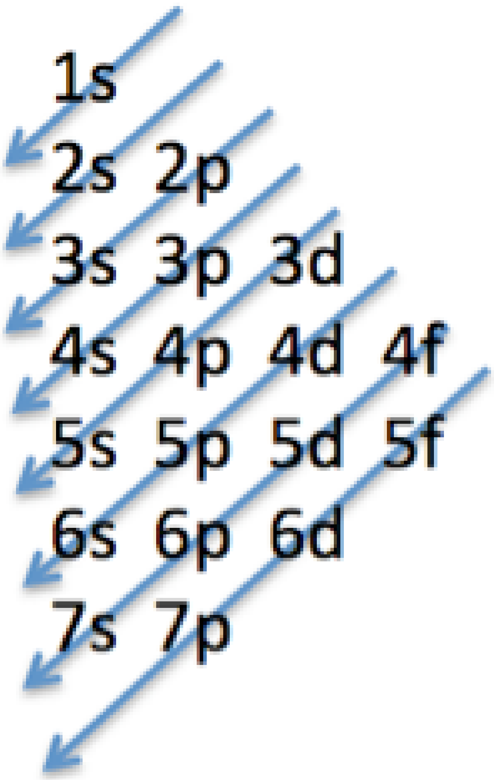
Now after 6s orbital has been completely filled at Ba, the next electron, according to Aufbau principle, must enter $4f$ orbital in La atom to give $[Xe]_{54}4f^1 5d^{\circ} 6s^2$ configuration to La atom; but it has been observed that the extra electron enters $5d$ orbital (instead of $4f$ orbital) to give $[Xe]_{54}4f^{\circ}5d^1 6s^2$ configuration to La atom as shown below :

La (Z = 57) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 5d^1$
→ $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^6d^1, 6s^2$
→ 2, 8, 18, 18, 9, 2
→ $[Xe]_{54}\ 4f^{\circ}5d^1 6s^2$

Why the extra electron goes to $5d$ orbital, instead of $4f$ orbital in La atom has been explained on the basis that at La, $5d$ and $4f$ orbitals are supposed to have almost the same energy and hence the extra electron is free to occupy any of these two orbitals.

(ii) Configuration of Ac (Z = 89) atom. We know that, according to Aufbau principle, the configuration of Ra (Z = 88) atom is $[Rn]_{86}\ 7s^2$ where $[Rn]_{86}$ is the configuration of Rn (Z = 86) atom which is 2, 8, 18, 32, 18, 8.

Now after $7s$ orbital has been completely filled at Ra, the next electron according to Aufbau principle, must enter $5f$ orbital in Ac atom; but it has been observed that the extra electron enters 6d orbital (instead of $5f$ orbital) to give $[Rn]_{86}\ 5f^{\circ}.6d^1.7s^2$ configuration to Ac atom as shown below :



$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
$3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2$
$4f^{14}\ 5d^{10}\ 6p^6\ 7s^2\ 5f^{14}\ 6d^{10}\ 7p^6$

Diagonal Rule

(n+l) Rule. The relative order of energy of different orbitals (or the sequence in which various orbitals are filled up with electrons) can also be determined with the help of $(n + l)$ value for a given orbital (n = principal quantum number, l = azimuthal quantum number). This rule is called $(n + l)$ rule. According to this rule :

The orbital having the lowest value of $(n + l)$ has the lowest energy and hence is filled up first with electrons. When two or more orbitals have the same value of $(n + l)$, the orbital with lower value of n is lower in energy and hence is filled up first with electrons.

Thus the order of energies of, for example, 3*d*, 4*p* and 5*s* orbitals for all of which $(n + l) = 5$ is as : 3*d* $(n = 3) <$ 4p $(n=4) <$ 5s $(n=5)$, since n for these orbitals is 3, 4 and 5 respectively. Thus orbitals will be filled up with electrons in the following sequence :