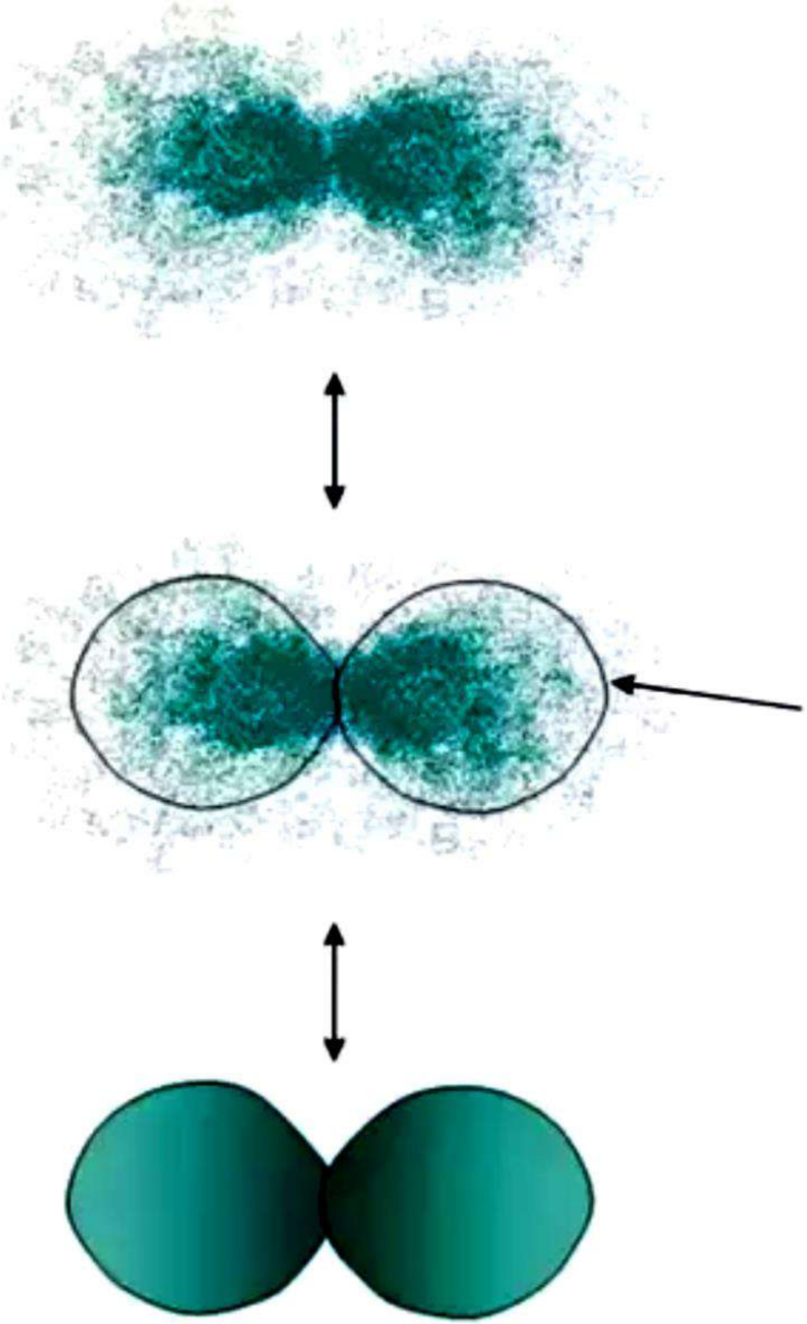
General chemistry

Chapter 4
The Electronic Structure of Atoms

Introduction

- An electron possesses both particle (has a mass) and wave properties (an electron move around the nucleus as standing waves).
- **Atomic orbitals** defines the distribution of electron density in three-dimensional space around the nucleus.
- An atomic orbital has a characteristic energy, as well as a characteristic distribution of electron density.



the electron density in an electron wave

90% of the electron density is inside the two lobes drawn on the electron wave

these balloons represent the region of space which contains 90% of the electron density for this particular electron wave

Quantum numbers

- Quantum numbers describe the distribution of electrons in atomic orbitals and label electrons that reside in them in terms of its wave characters.
- In quantum mechanics, three quantum numbers are required to describe the distribution of electrons in atoms. They are called the ***principal quantum number***, the ***angular momentum quantum number***, and the ***magnetic quantum number***. A fourth quantum number— the ***spin quantum number***—describes the behavior of a specific electron and completes the description of electrons in atoms.

The Principal Quantum Number (n)

- The principal quantum number (n) can have integral values 1, 2, 3, and so forth.
- It describes the shell or the level to which the electron belongs.
- The principal quantum number relates to the average distance of the electron from the nucleus in a particular orbital.
- The larger n is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.

The Angular Momentum Quantum Number (*l*) or subsidiary Quantum Number

- Each shell is divided into subshell or sublevels assigned *l* number.
- Each shell or principal level of quantum number *n* contains *n* subshells. For example, if $n = 2$, then there are two subshells (two values of *l*)
- The values of *l* depend on the value of n. For a given value of n, *l* has possible integral values from 0 to (n -1).
- It tells us the "shape" of the orbitals.
- Thus, if l=0, we have an s orbital; if l =1, we have a p orbital; and so on.

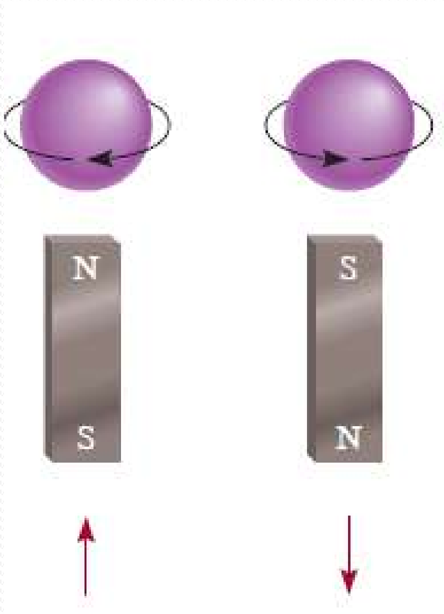
ℓ	0	1	2	3	4	5
Name of orbital	*s*	*p*	*d*	*f*	*g*	*h*

The Magnetic Quantum Number (m_l)

- The magnetic quantum number m_l describes the orientation of the orbital in space
- The values of m_l can vary from - l to l.
- The number of m_l values indicates the number of orbitals in a subshell with a particular l value.
- There are ($2\,l$ +1) integral values of m_l as follows: if l =0, then there are ($2\,l$ + 1)= 1 orbital and the value of m_l = 0. If l = 1, then there are ($2\,l$ + 1)= 3 orbitals have three values of m_l, namely, -1, 0, 1 and so on.

The Electron Spin Quantum Number (m_s)

- Electrons spin on their own axes, so can generate a magnetic field, and it is this motion that causes an electron to behave like a magnet.
- There are two possible spinning motions of an electron, one clockwise and the other counterclockwise.
- The electron spin quantum number (m_s), describe electron spinning and has a value of $+\frac{1}{2}$ or $-\frac{1}{2}$.



Summary

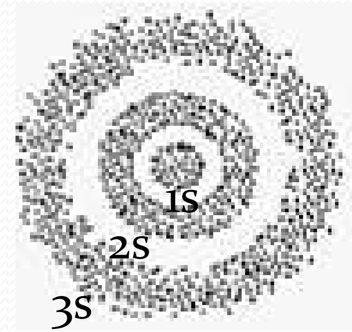
n (shell)	*l* (sub-shell) (0 to n-1)	symbol of *l* subshell	m_l ($-l$ to $+l$)	no. of orbitals in the subshell ($2l+1$)	Total no. of orbitals in the shell (n^2)	Total no. of electrons in the shell ($2n^2$)
1	0	s	0	1	1	2
2	0	s	0	1	4	8
	1	p	-1,0,+1	3		
3	0	s	0	1	9	18
	1	p	-1,0,+1	3		
	2	d	-2,-1,0,+1,+2	5		
4	0	s	0	1	16	32
	1	p	-1,0,+1	3		
	2	d	-2,-1,0,+1,+2	5		
	3	f	-3,-2,-1,0,+1,+2,+3	7		

Atomic Orbitals

- **s Orbitals**

All s orbitals are spherical.

They increase in size as n increases, so 1s< 2s <3s

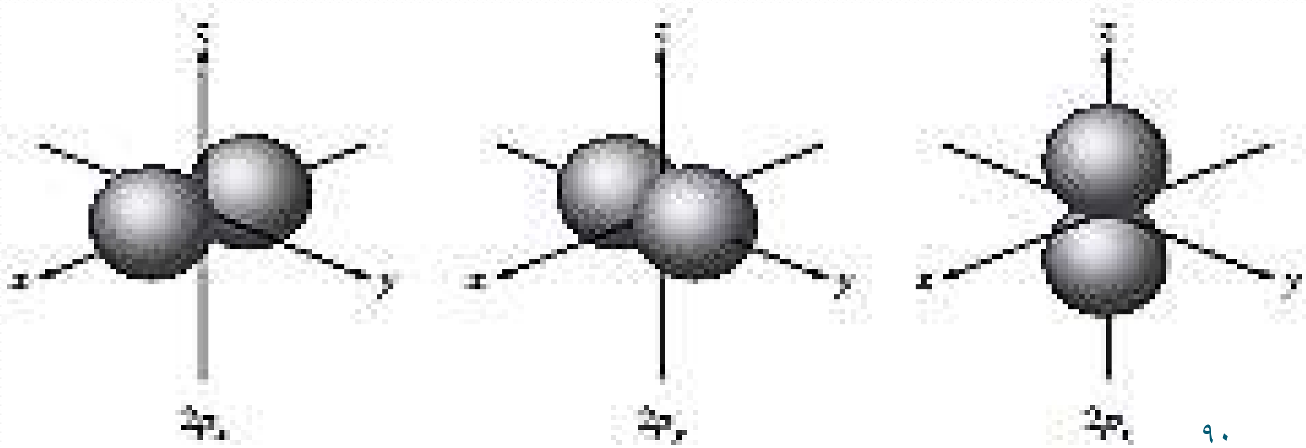


- **p Orbitals**

These three p orbitals are identical in size, shape, and energy; they differ from one another only in orientation.

Each p orbital can be thought of as two lobes on opposite sides of the nucleus.

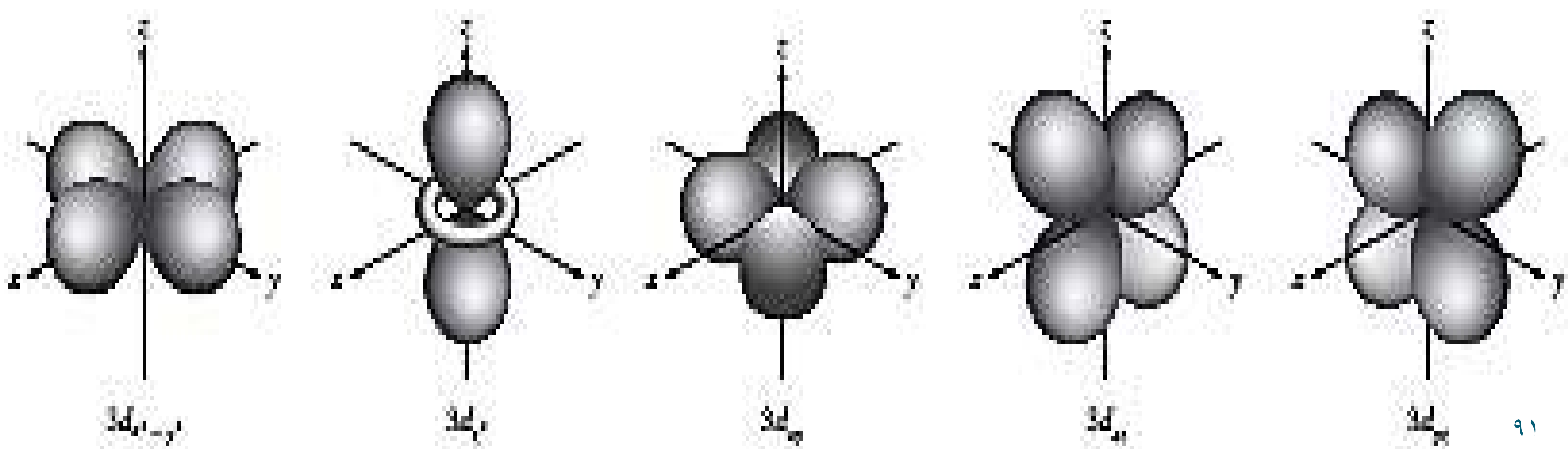
They increase in size as n increases, so 2p< 3p< 4p.



Atomic Orbitals

d Orbitals

All the five d orbitals in an atom are identical in energy. They differ from one another in orientation. They increase in size as n increases.



Notes

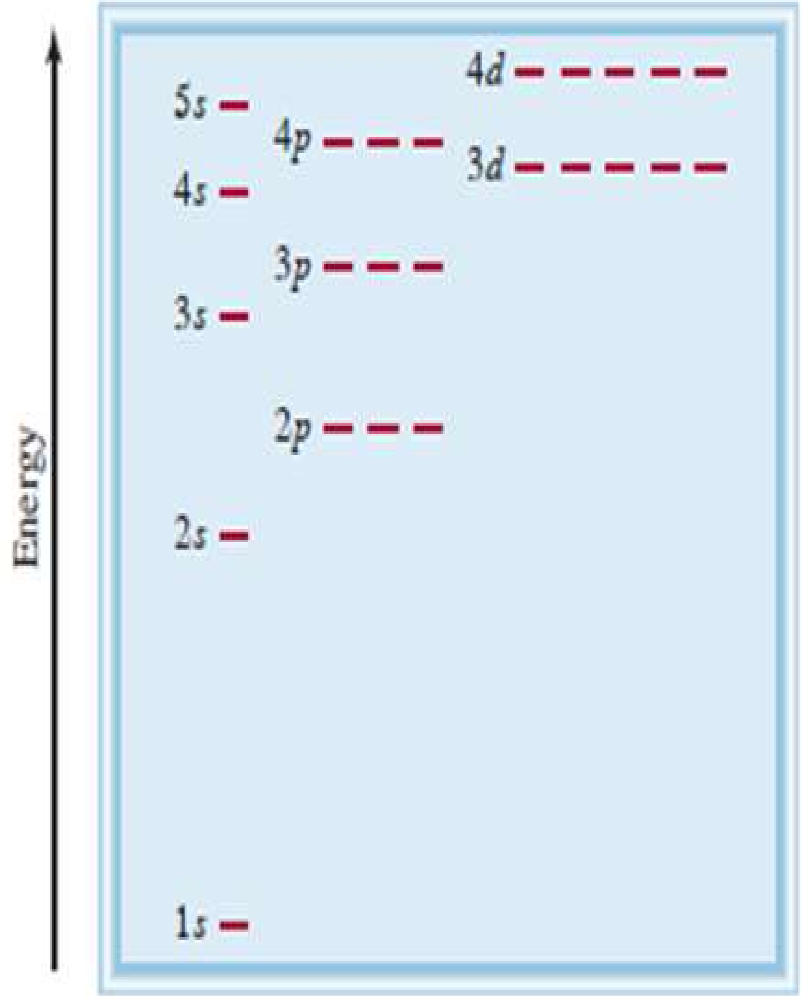
- When we write the subshell, we write first the n number followed by the symbol of the l number.
- **For example:**

In 2s and 2p subshells, 2 denotes the value of n, and s and p denote the symbol of l number.

- The four quantum numbers n, l , m_l , and m_s enable us to label completely an electron in any orbital in any atom.
- In a sense, we can regard the set of four quantum numbers as the "address" of an electron in an atom.
- We use the simplified notation (n, l , m_l, m_s).

The Energies of Orbitals

- The energy of an electron in many-electron atoms in such an atom depends on ***n*** and ***l*** values.
- For the same subshell (l), the energy increases as n increase. (1s<2s<3s).
- In the same shell (n), the energy increase as l increase (3s<3p<3d).
- Between subshells in different shells, there are overlap. For example, the 3d energy level is very close to the 4s energy level.
- It turns out that the total energy of an atom is lower when the 4s subshell is filled before a 3d subshell (the energy of repulsion between the electrons in d orbitals make increase in the atom energy).

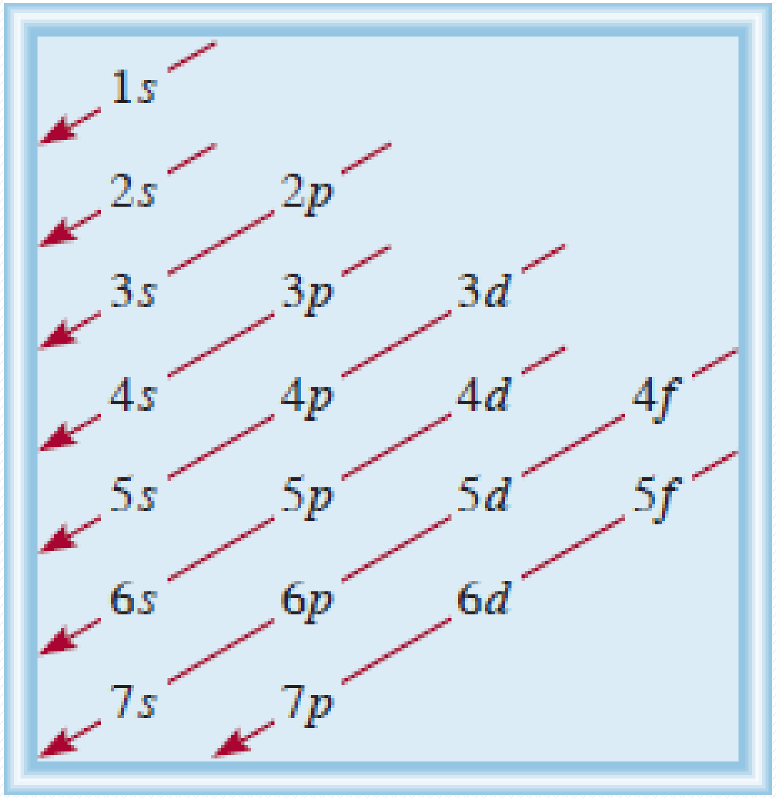


Ground state and excited state

- A **ground state** of an atom is the lowest possible energy (stable state) of an atom in which all the electrons in the atom are as close to the nucleus as possible.
- An **excited state** of an atom in which the electronic configurations gives the atom a higher energy than the ground state.

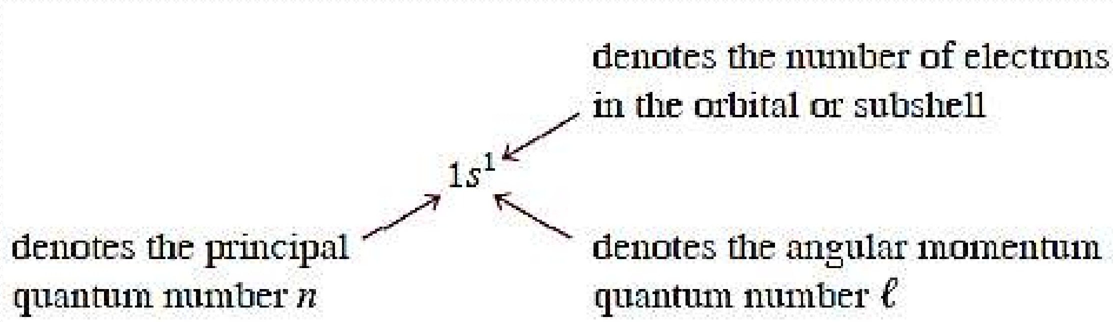
Ground state Electron Configuration

- The **Ground state electron configuration** of the atom determines how the electrons are distributed among the various atomic orbitals. It is important to understand electronic behavior.
- The next figure shows the order in which atomic subshells are filled in a many-electron atom.
- Start with the 1s orbital and move downward, following the direction of the arrows.

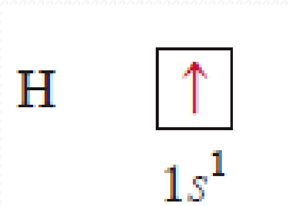


Electron Configuration

- To write the electron configuration we write the symbol of the subshell (n+ symbol of *l*) and provide the number of its electrons in the superscript as follows:



- The electron configuration can also be represented by an *orbital diagram* that shows the spin of the electron:



- The upward arrow denotes one of the two possible spinning motions of the electron. (Alternatively, we could have represented the electron with a downward arrow.) The box represents an atomic orbital.

The Building-Up Principle

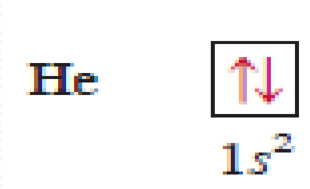
- It is used in writing electron configurations for the elements. This process is based on the Aufbau principle.
- The **Aufbau principle** dictates that as protons are added one by one to the nucleus (as Z increase) to build up the elements, electrons are similarly added to the atomic orbitals.
- The electron configurations of elements (except hydrogen and helium) could be represented by a **noble gas core,** which shows in brackets the noble gas element that most nearly precedes the element being considered, followed by the symbol for the highest filled subshells in the outermost shells.

1	H	$1s^1$
2	He	$1s^2$
3	Li	$[He]2s^1$
4	Be	$[He]2s^2$
5	B	$[He]2s^22p^1$
6	C	$[He]2s^22p^2$
7	N	$[He]2s^22p^3$
8	O	$[He]2s^22p^4$
9	F	$[He]2s^22p^5$
10	Ne	$[He]2s^22p^6$
11	Na	$[Ne]3s^1$
12	Mg	$[Ne]3s^2$
13	Al	$[Ne]3s^23p^1$
14	Si	$[Ne]3s^23p^2$
15	P	$[Ne]3s^23p^3$
16	S	$[Ne]3s^23p^4$
17	Cl	$[Ne]3s^23p^5$
18	Ar	$[Ne]3s^23p^6$

The Pauli Exclusion Principle

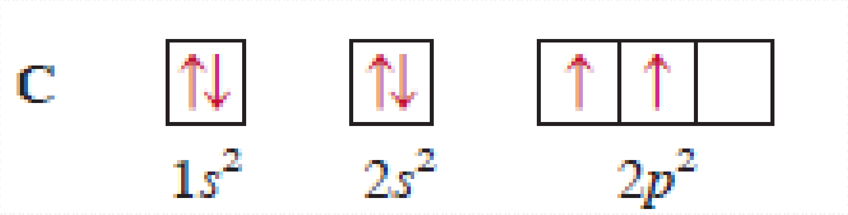
- This principle states that no two electrons in an atom can have the same four quantum numbers.
- If two electrons in an atom should have the same n, l , and m_l values (that is, these two electrons are in the *same* atomic orbital), then they must have different values of m_s.
- In other words, only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins.
- Consider the helium atom, which has two electrons. The right way of placing two electrons in the

1*s* orbital are as follows:



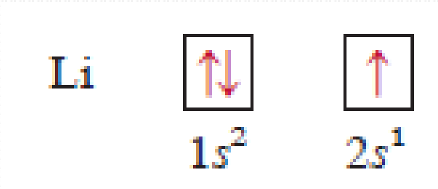
Hund's rule

- This rule states that the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins.

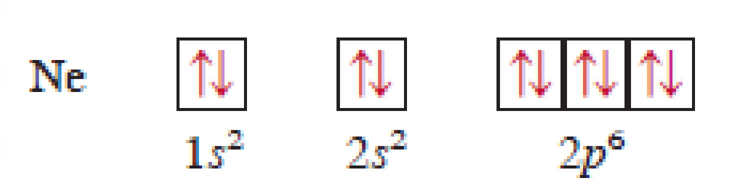


Paramagnetism & diamagnetism

- Atoms in which one or more electrons are unpaired and are attracted by a magnet are paramagnetic.



- Atoms in which all the electron spins are paired (cancel each other) and are slightly repelled by a magnet are diamagnetic.



Irregularities

- The electron configuration of chromium ($Z=24$) is $[Ar]4s^1 3d^5$ and not $[Ar]4s^2 3d^4$, as we might expect. A similar break in the pattern is observed for copper ($Z=29$), whose electron configuration is $[Ar]4s^1 3d^{10}$ rather than $[Ar]4s^2 3d^9$.
- The reason for these irregularities is that a slightly greater stability is associated with the half-filled ($3d^5$) and completely filled ($3d^{10}$) subshells.
- The electron configuration of gadolinium ($Z=64$) is $[Xe]6s^2 4f^7 5d^1$ rather than $[Xe]6s^2 4f^8$. Like chromium, gadolinium gains extra stability by having a half-filled subshell ($4f^7$).

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^24d^5$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $6s^25d^1$	72 **Hf** $6s^25d^2$	73 **Ta** $6s^25d^3$	74 **W** $6s^25d^4$	75 **Re** $6s^25d^5$	76 **Os** $6s^25d^6$	77 **Ir** $6s^25d^7$	78 **Pt** $6s^15d^9$	79 **Au** $6s^15d^{10}$	80 **Hg** $6s^25d^{10}$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $7s^26d^1$	104 **Rf** $7s^26d^2$	105 **Db** $7s^26d^3$	106 **Sg** $7s^26d^4$	107 **Bh** $7s^26d^5$	108 **Hs** $7s^26d^6$	109 **Mt** $7s^26d^7$	110 **Ds** $7s^26d^8$	111 **Rg** $7s^26d^9$	112 $7s^26d^{10}$	(113)	114 $7s^27p^2$	(115)	116 $7s^27p^4$	(117)	(118)

58 **Ce** $6s^24f^15d^1$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$	71 **Lu** $6s^24f^{14}5d^1$
90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^9$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$	103 **Lr** $7s^25f^{14}6d^1$

Summary
General Rules for Assigning Electrons to Atomic Orbitals

- Each shell or principal level of quantum number n contains n subshells. For example, if $n = 2$, then there are two subshells (two values of l) of angular momentum quantum numbers 0 and 1.
- Each subshell of quantum number l contains $(2l + 1)$ orbitals. For example, if $l = 1$, then there are three p orbitals.
- No more than two electrons can be placed in each orbital. They must have opposite spins, or different electron spin quantum numbers. Therefore, the maximum number of electrons is simply twice the number of orbitals that are employed.
- A quick way to determine the maximum number of electrons that an atom can have in a principal level n is to use the formula $2n^2$.
- No two electrons in the same atom can have the same four quantum numbers. (This is the Pauli exclusion principle).
- The most stable arrangement of electrons in a subshell is the one that has the greatest number of parallel spins. This is Hund's rule.
- Atoms in which one or more electrons are unpaired are paramagnetic. Atoms in which all the electron spins are paired are diamagnetic.
- In a hydrogen atom, the energy of the electron depends only on its principal quantum number n. In a many-electron atom, the energy of an electron depends on both n and its angular momentum quantum number l.