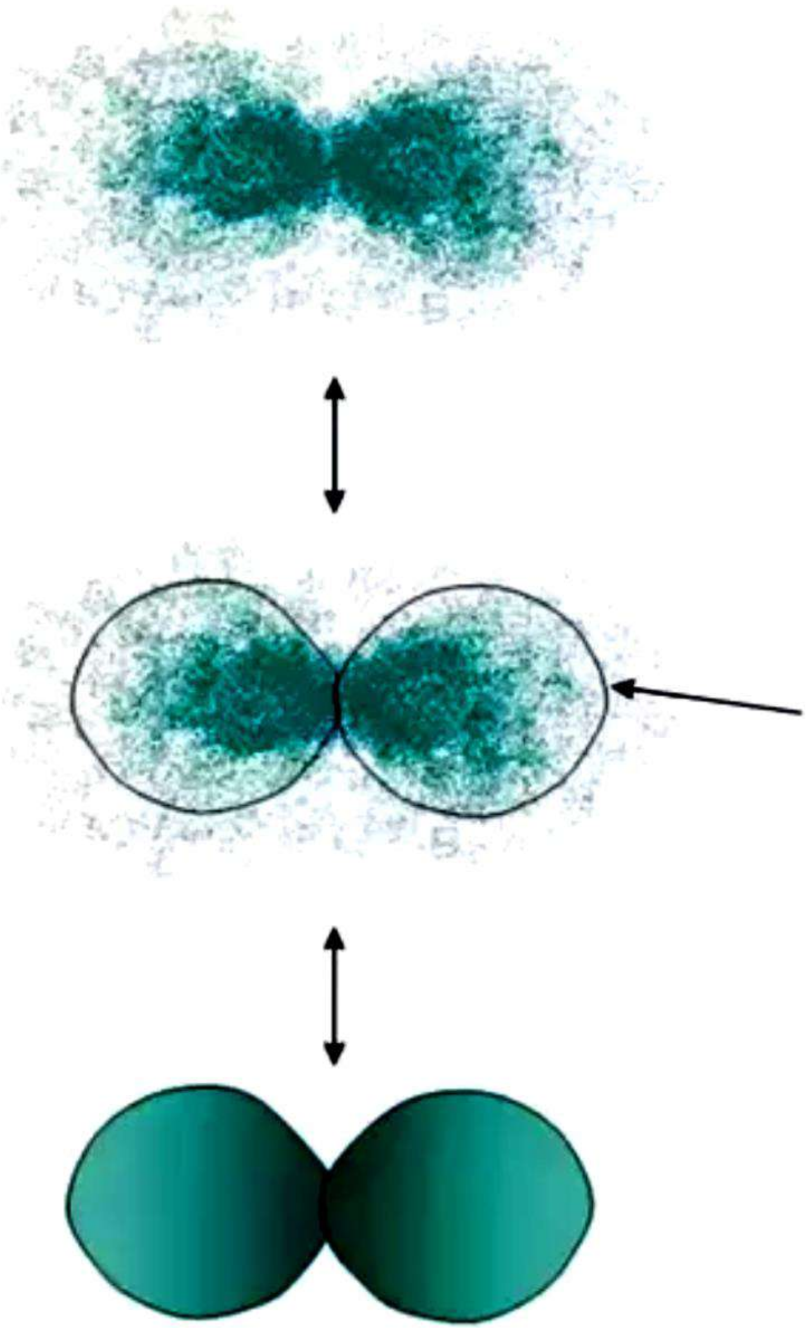
General chemistry

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).
- These waves correspond to definite energy states (orbitals).
- It is impossible to know the precise description of the path of an electron in an atom, so we use the term of **atomic orbital.**
- Orbitals defines the distribution of electron density in three-dimensional space around the nucleus. Electron density gives the probability that an electron will be found in a particular region of an atom.
- 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.
- 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.

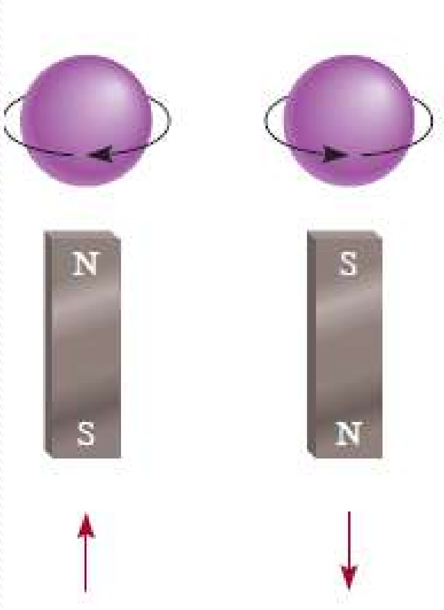
ℓ	0	1	2	3	4	5
Name of orbital	*s*	*p*	*d*	*f*	*g*	*h*

The Magnetic Quantum Number (m_l)

- The magnetic quantum number $\boldsymbol{m_l}$ describes the orientation of the orbital in space
- The values of $\boldsymbol{m_l}$ can vary from - l to l.
- The number of $\boldsymbol{m_l}$ values indicates the number of orbitals in a subshell with a particular l value.
- There are ($2l$ +1) integral values of $\boldsymbol{m_l}$ as follows: if l =0, then there are ($2l$ + 1)= 1 orbital and the value of $\boldsymbol{m_l}$ = 0. If l = 1, then there are ($2l$ + 1)= 3 orbitals have three values of $\boldsymbol{m_l}$، 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 1	s p	0 -1,0,+1	1 3	4	8
3	0 1 2	s p d	0 -1,0,+1 -2,-1,0,+1,+2	1 3 5	9	18
4	0 1 2 3	s p d f	0 -1,0,+1 -2,-1,0,+1,+2 -3,-2,-1,0,+1,+2,+3	1 3 5 7	16	32

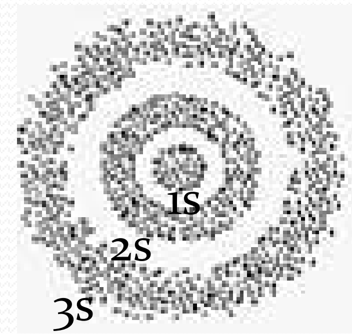
Atomic Orbitals

- **s Orbitals**

All s orbitals are spherical.

They increase in size as n

increases, so 1s< 2s <3s



- **p Orbitals**

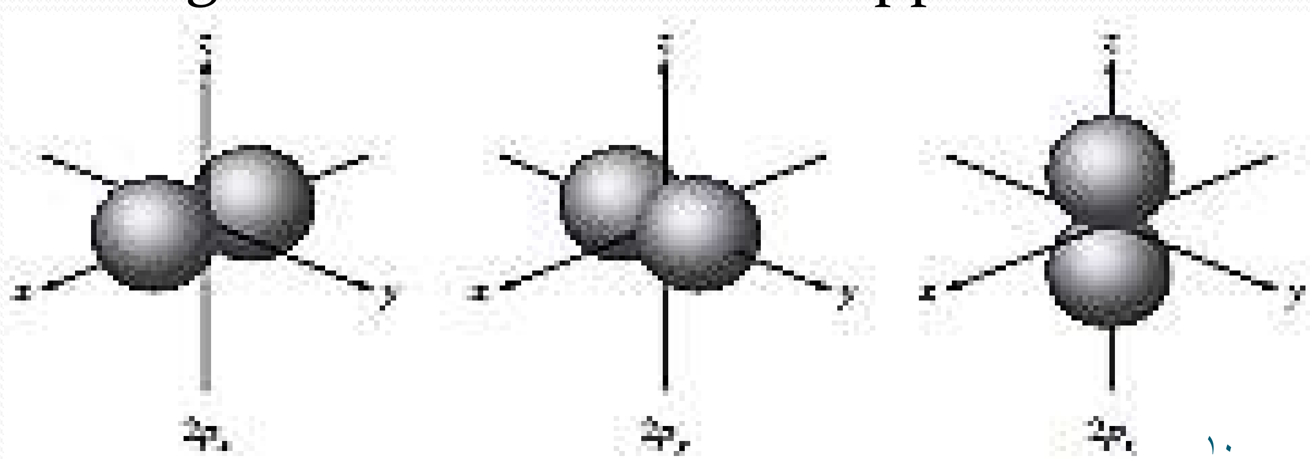
These three p orbitals are identical in size, shape, and energy; they differ from one another only in orientation.

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

They increase in size

as n increases, so

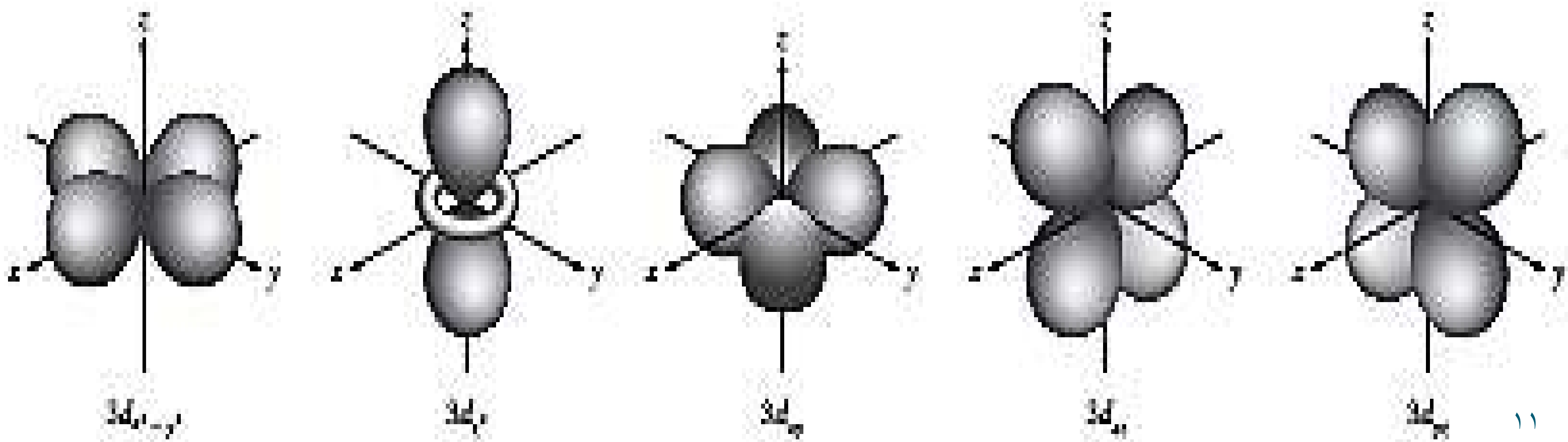
2p< 3p< 4p.



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, 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, m_s).

Problems

- **List the possible quantum numbers of electron in the 2*p* subshell.**

(2, 1, -1, +1/2), (2, 1, -1, -1/2), (2, 1, 0, +1/2), (2, 1, 0, -1/2),
(2, 1, +1, +1/2), (2, 1, +1, -1/2)

- **List the possible quantum numbers of electron in the 3*s* subshell.**

(3, 0, 0, +1/2), (3, 0, 0, -1/2).

- **List the possible quantum numbers of electron in the 4d subshell.**

(4, 2, -2, +1/2), (4, 2, -2, -1/2),
(4, 2, -1, +1/2), (4, 2, -1, -1/2),
(4, 2, 0, +1/2), (4, 2, 0, -1/2),
(4, 2, +1, +1/2), (4, 2, +1, -1/2),
(4, 2, +2, +1/2), (4, 2, +2, -1/2).

Problems

- **Provide the missing quantum number:** (**there may be more than one choice**)**:**

(2,….., 0,….), (1,….,….., ……), (3,….., -2 ,…..), (3,…., -1,…..)

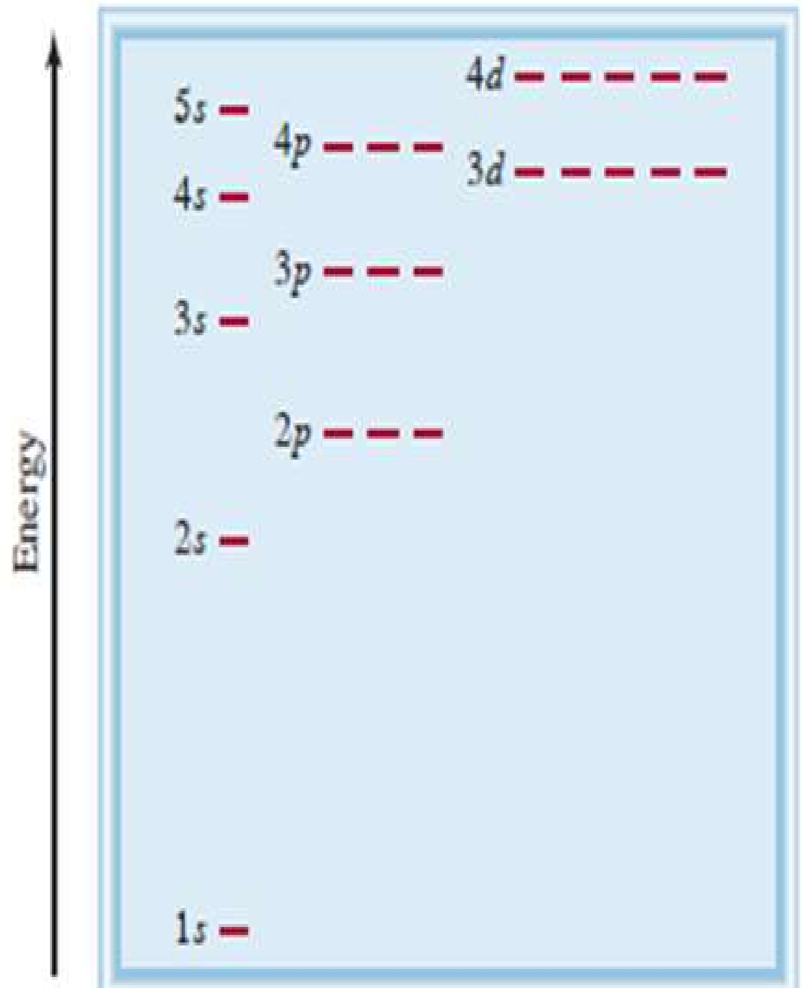
(2, 1,…., …..), (….., 2, +1,……)

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.

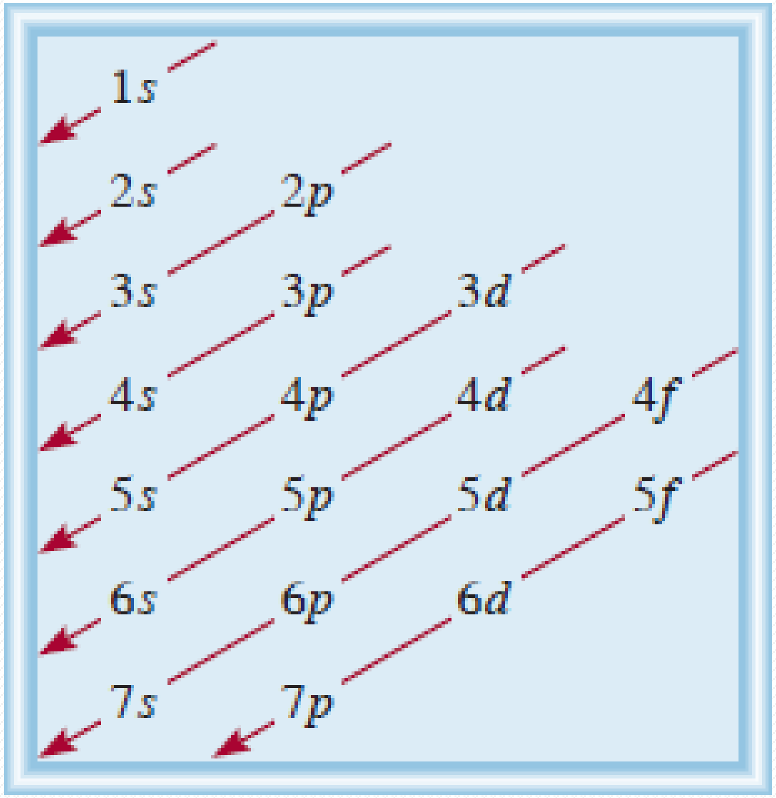
The Energies of Orbitals

- 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).



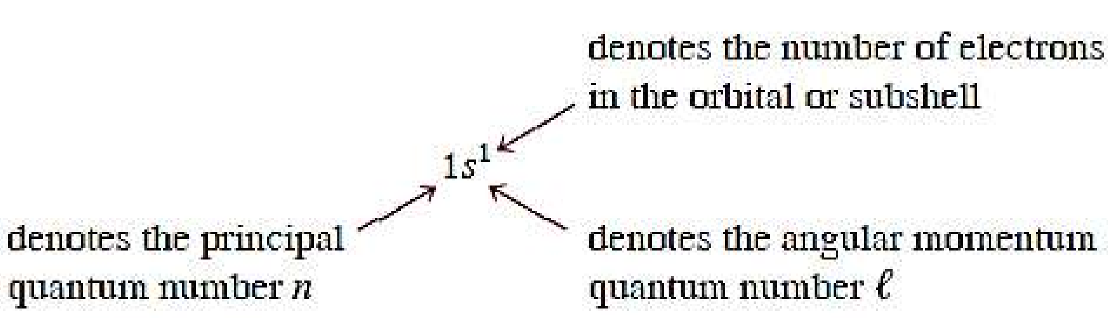
Ground state Electron Configuration

- 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.

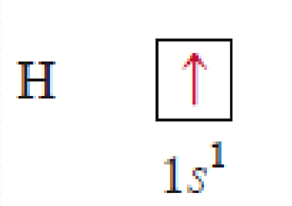


Electron Configuration

- 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

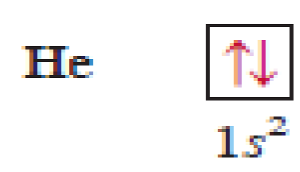
- It is used in writing electron configurations for the elements. This process is based on the Aufbau principle.
- The **Aufbau principle** dictates that as protons are added one by one to the nucleus (as Z increase) to build up the elements, electrons are similarly added to the atomic orbitals.
- The 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

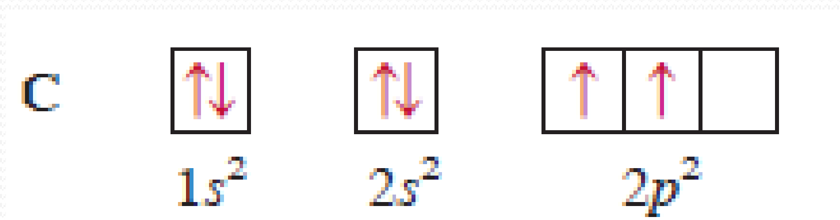
- This principle states that no two electrons in an atom can have the same four quantum numbers.
- If two electrons in an atom should have the same n, l , and m_l values (that is, these two electrons are in the *same* atomic orbital), then they must have different values of m_s.
- In other words, only 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:



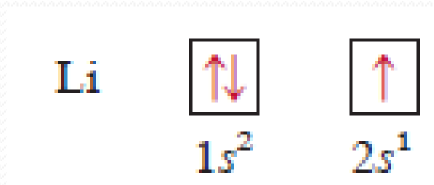
Hund’s rule

- 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 ($4f^7$).

Irregularities

- Elements that require particular care are the transition metals, the lanthanides, and the actinides.
- As we noted earlier, at larger values of the principal quantum number n, the order of subshell filling may reverse from one element to the next.

Problems

- Write the ground-state electron configurations for (a) sulfur (S) and (b) palladium (Pd), which is diamagnetic. (discussion with referring to the periodic table in the next slide).

	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** $7s^25f^{14}6d^1$