CHM 121: Foundation Chemistry I
1st Semester 2020/2021
Lecture Note

<u>Quantum Numbers</u>

Introduction

The atom is the smallest part of matter that represents a particular element. For quite a while, the atom was thought to be the smallest part of matter that could exist. But in the latter part of the 19th century and early part of the 20th, scientists discovered that atoms are composed of certain subatomic particles and that no matter what the element, the same subatomic particles make up the atom. The number of the various subatomic particles is the only thing that varies. Scientists now recognize that there are many subatomic particles. But chemists are generally concerned with the three major subatomic particles namely: Protons, Neutrons and Electrons. Atoms have a nucleus — a centre — containing protons and neutrons.

Many of the important topics in chemistry, such as chemical bonding, the shape of molecules, and so on, are based on where the electrons in an atom are located. Three things are important to understand how electron distributes itself in atom; the shape of the orbital in which it is located, its size, and its orientation in space relative to other orbitals. Thus, simply saying that the electrons are located outside the nucleus is not good enough.

The quantum mechanical model

Early models of the atom had electrons going around the nucleus in a random fashion. But later discoveries have shown that this representation was not accurate. Today, scientists use the quantum mechanical model, a highly mathematical model, to represent the structure of the atom.

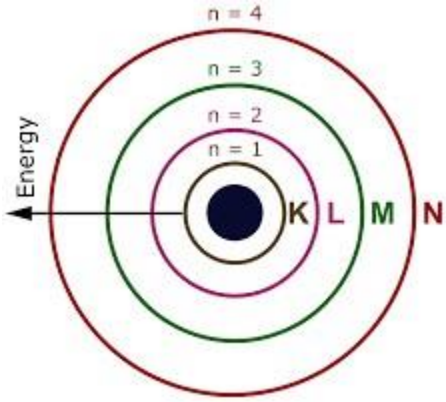
This model is based on quantum theory, which says that matter also has properties associated with waves. According to quantum theory, it is impossible to know an electron's exact position and momentum (speed and direction, multiplied by mass) at the same time. This is known as the uncertainty principle. Based on this, scientists developed the concept of orbitals which are volumes of space in which an electron is likely present.

The quantum mechanical model of the atom uses complex shapes of orbitals and four numbers, called quantum numbers, to describe the characteristics of electrons and their orbitals. Accordingly, an electron in an atom can be described by four quantum numbers based on this model. This are namely:

i. Principal quantum number (n) ii.
Angular momentum quantum number (l)
iii. Magnetic quantum number (ml) iv.
Spin quantum number (ms)

Principal quantum number (n)

The principal quantum number **n** describes the average distance of the orbital from the nucleus — and the energy of the electron in an atom. **n** represents the number of the shell (orbit) or main energy level in which the electron revolves round the nucleus. It can have only positive integer (whole number) values: 1, 2, 3, 4, etc. which represents 1st(K), 2nd(L), 3rd(M), 4th(N) etc. shells. The larger the value of n, the higher the energy and the larger the orbital, or electron shell.



Principal quantum number (n)

Angular momentum quantum number (l)

The Angular momentum or Azimuthal quantum number describes the shape of the orbital occupied by the electron. The possible values which l can have depend on the value of n. l may have values from 0 to (n-1), i.e. 0, 1, 2, … (n – 1). Each value of l represents a particular sub-shell within the principal sub-shell. Thus:

When l = 0, the orbital is spherical and is called an s orbital.

When l = 1, the orbital is dumbbell-shaped and is called a p orbital. When l = 2, the orbital is double dumbbell-shaped and is called a d orbital

When l = 3 a more complicated f orbital is formed.

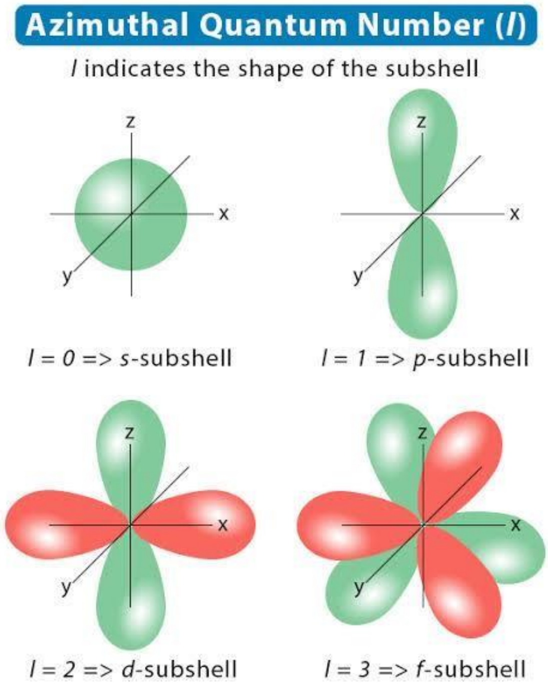
Each shell also has one or more subshells which depend on the value of n. Thus the total number of l values gives us the total number of subshells within a given main shell. i.e., .

When n =1, there is only one subshell corresponding to l = 0. i.e. 1s orbital

When n = 2, there are two subshells corresponding to l = 0, 1. i.e. 2s and 2p orbitals

When n = 3, there are three subshells corresponding to l = 0, 1, 2. i.e. 3s, 3p, and 3d orbitals.

When n = 4, there are four subshells corresponding to l = 0, 1, 2, 3 . i.e. s, p, d and f orbitals.



When a particular subshell in an atom is being described, both the *n* value and the subshell letter can be used e.g., 1s, 2p, 3d, and so on. Normally, a subshell value of 4 is the largest needed to describe a particular subshell.

The magnetic quantum number (ml)

The magnetic quantum number **ml** describes how the various orbitals are oriented in space. The value of ml depends on the value of l. It is given by the formula 2l + 1. The values allowed are integers from –l to 0 to +l. 2

For example, if the value of l = 1 (p orbital), you can write three values for ml: –1, 0, and +1. This means that there are three different p subshells for a particular orbital. For l = 2 (d orbital), you can write five values for ml: -2,1,0,1,2 This means that there are five different d subshells for a particular orbital. The subshells have the same energy but different orientations in space as shown below.

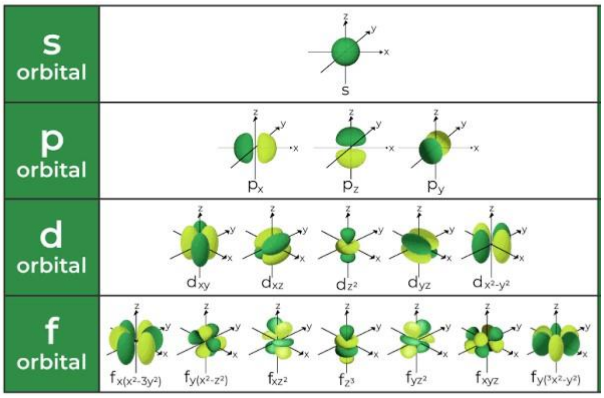


Table 1.1 below gives the different values of n, l and ml.

Principal quantum number n	Subsidiary quantum number l	Magnetic quantum numbers m_e	Symbol
1	0	0	1*s* (one orbital)
2	0	0	2*s* (one orbital)
2	1	−1, 0, +1	2*p* (three orbitals)
3	0	0	3*s* (one orbital)
3	1	−1, 0, +1	3*p* (three orbitals)
3	2	−2, −1, 0, +1, +2	3*d* (five orbitals)
4	0	0	4*s* (one orbital)
4	1	−1, 0, +1	4*p* (three orbitals)
4	2	−2, −1, 0, +1, +2	4*d* (five orbitals)
4	3	−3, −2, −1, 0, +1, +2, −3	4*f* (seven orbitals)

The spin quantum number (ms)

The fourth and final quantum number is the spin quantum number **ms**. It describes the direction the electron is spinning in a magnetic field — either clockwise or counterclockwise. Only two values are allowed for ms: +½ or –½. For each subshell, there can be only two electrons, one with a spin of +½ and another with a spin of –½. Table 1.1 below summarises summarizes the four quantum numbers. When they're all put together, they give a good description of the characteristics of a particular electron.

Table. 1.3 Summary of the Quantum Numbers

Name	***Symbol***	***Description***	***Allowed Values***
Principal	n	Orbital energy	Positive integers (1, 2, 3, and so on)
Angular momentum	l	Orbital shape	Integers from 0 to $n - 1$
Magnetic	m_l	Orientation	Integers from $-l$ to $+l$
Spin	m_s	Electron spin	+½ or –½

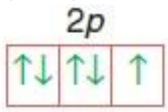
Solved Examples

1. Determine the four quantum numbers for the following:
   (a) the last electron in $2p^5$
   (b) the last electron in $3d^6$

Solution

1(a) For $2p^5$

Principal quantum number n = 2.
Angular momentum quantum number l = 1.
Magnetic quantum number ml = 0, since for l =1 (p orbital), the three values for ml are –1, 0, and +1. And the last electron will be placed under py i.e ml of 0
Spin quantum number ms = +½ i.e



1(b) For $3d^6$

Principal quantum number n = 3
Angular momentum quantum number l = 2
Magnetic quantum number ml = -2
Spin quantum number ms = -½

Electronic Arrangements of Atoms

Aufbau Principle

In the case of atoms, electrons occupy the available orbitals in the subshells of lowest energy. This is known as the Aufbau principle. The assignment of all the electrons in an atom into specific shells and subshells is known as the element's electron configuration (Fig. 2.0).
It is important to know the sequence in which the energy levels are filled. i.e 1s,

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

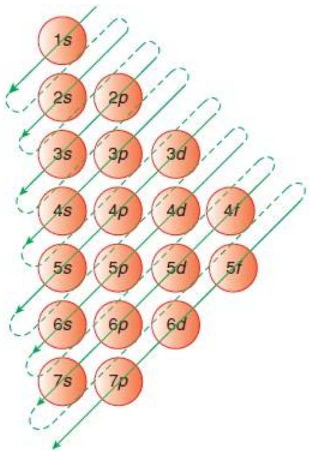


Figure 2.0 Sequence of filling energy levels.

The (n + l) rule

1. Higher the value of (n + l) for a given orbital, greater is it's energy. For example, 4s (n + l = 4 + 0 = 4) is has higher energy than 3s (n + l = 3 + 0 = 3)
2. If (n + l) value for two orbitals are same, then the orbital with higher value of n will have higher energy. For example 4s (n + l = 4 + 0 = 4) and 3p (n + l = 3 + 1 = 4) have same (n + l) values, therefore 4s will have higher energy than 3p orbital due to higher value of n.

Hund's Rule of Maximum Multiplicity

Hund's rule states that where orbitals are available in degenerate sets, maximum multiplicity is preserved; that is, electrons are not paired until each orbital in a degenerate set has been half-filled. This is an empirical rule that determines the lowest energy arrangement of electrons in a subshell. It implies that pairing of electrons in orbitals of p, d and f subshells does not take place till each orbital belonging to that subshell has got one electron each.

Since there are three p, five d and seven f orbitals, the pairing of electrons in them would begin with the 4th, 6th and 8th electron, respectively. This is because half-filled and completely filled states are associated with extra stability.

Pauli's Exclusion Principle

Three quantum numbers n, l and ml are needed to dene an orbital. Each orbital may hold up to two electrons, provided they have opposite spins. An extra quantum number is required to define the spin of an electron in an orbital. Thus, four quantum numbers are needed to define the energy of an electron in an atom. The Pauli exclusion principle states that no two electrons in one atom can have all four quantum numbers the same. By permutating the quantum numbers, the maximum number of electrons which can be contained in each main energy level can be calculated.

Subshell	Number of Orbitals	Maximum Number of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

The maximum electron population per shell is shown below.

Shell	Subshell	Maximum	Shell Population
1	1*s*	2	2
2	2*s* 2*p*	8	(2 + 6)
3	3*s* 3*p* 3*d*	18	(2 + 6 + 10)
4	4*s* 4*p* 4*d* 4*f*	32	(2 + 6 + 10 + 14)

This trend shows that the maximum electron population of a shell is $2n^2$.

Electronic arrangement in the first twenty elements

Electronic configuration of atoms is the distribution of electrons into atomic orbitals. When atoms are in their ground state, the electrons occupy the lowest possible energy levels. This is illustrated in fig 2.1 for n values of 1 to 3.

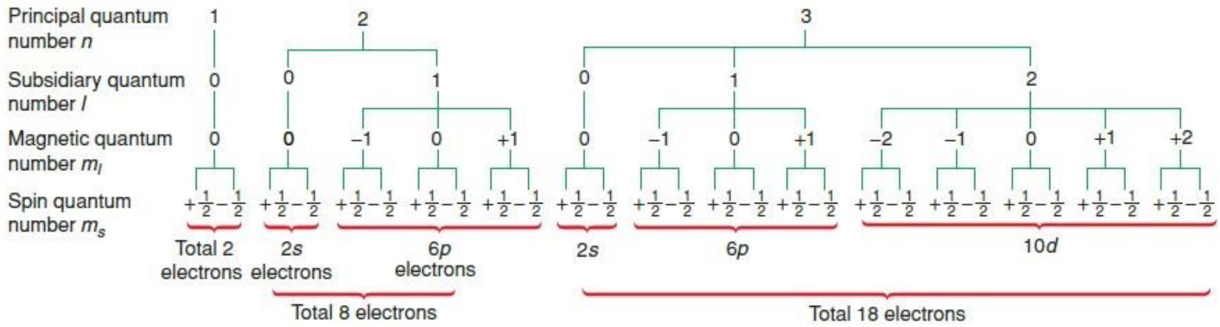


Figure 2.1 Quantum numbers, the permissible number of electrons and the shape of the periodic table.

To show the positions of the electrons in an atom, the symbols 1s, 2s, 2p, etc. are used to denote the main energy level and sublevel. A superscript indicates the number of electrons in each set of orbitals. Thus for hydrogen, the 1s orbital contains one electron, and this is shown as $1s^1$. For helium, the 1s orbital contains two electrons, denoted $1s^2$. After the 1s, 2s, 2p, 3s and 3p levels have been filled at argon, the next two electrons go into the 4s level. This gives the elements potassium and calcium. The electronic structures of the first twenty atoms in the periodic table may be written as shown.

1 H (#e⁻ = 1) $1s^1$							2 He (#e⁻ = 2) $1s^2$
3 Li $1s^2\,2s^1$	4 Be $1s^2\,2s^2$	5 B $1s^2\,2s^2\,2p^1$	6 C $1s^2\,2s^2\,2p^2$	7 N $1s^2\,2s^2\,2p^3$	8 O $1s^2\,2s^2\,2p^4$	9 F $1s^2\,2s^2\,2p^5$	10 Ne $1s^2\,2s^2\,2p^6$
11 Na $1s^2\,2s^2\,2p^6\,3s^1$	12 Mg $1s^2\,2s^2\,2p^6\,3s^2$	13 Al $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$	14 Si $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$	15 P $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$	16 S $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$	17 Cl $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$	18 Ar $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$
19 K $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$	20 Ca $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$	31 Ga $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^1$	32 Ge $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^2$	33 As $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^3$	34 Se $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^4$	35 Br $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^5$	36 Kr $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6$

Figure 2.2: Periodic table of elements listing the electronic configurations

An alternative way of showing the electronic structure of an atom is to draw boxes for orbitals, and arrows for the electrons (Fig. 2.3.). By convention, electron spins are represented by arrows pointing up (↑) or down (↓). The orbital diagram for electronic configuration is more beneficial as all the four quantum numbers are represented by it.

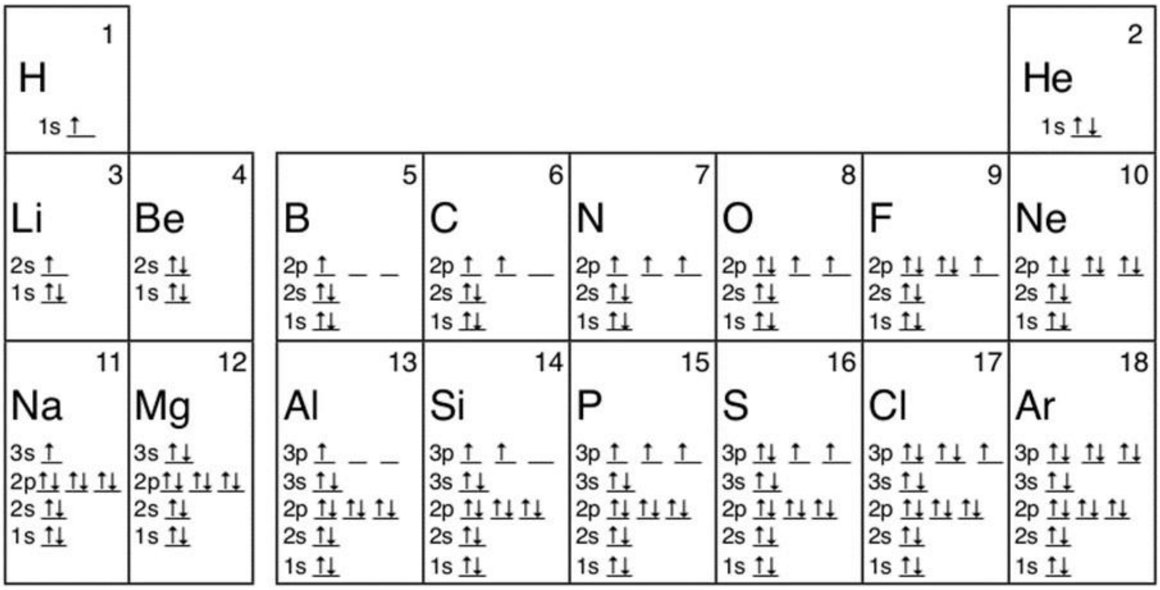


Figure 2.3: Periodic table of elements listing the electronic structure of an atom

Sometimes, the electronic configuration of an element is written in a shorthand form. This is because we are interested primarily in the electrons of the outer shell, thus, we often write electron configurations in an abbreviated or shorthand form. To write the shorthand configuration for an element we indicate what the core is by placing in brackets the symbol of the noble gas whose electron configuration is the same as the core configuration. This is followed by the configuration of the outer electrons for the particular element. Thus, for sodium and magnesium we write:

Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$ Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$

Na: [Ne] $3s^1$ Mg: [Ne] $3s^2$

Assignment

1. Determine the four quantum numbers for the last electron in a $3d^7$ orbital.
2. An electron is in 6f orbital. What possible values of quantum numbers n, l, ml and ms can it have?
3. What designation is given to an orbital having:
   (a) n = 2, l = 1
   (b) n = 3, l = 0
4. Which of the following orbital diagrams is excluded by the Aufbau principle? Which by the Pauli exclusion principle? Which by Hund's rule? Which is correct?

	1s	2s	2p		
(a)	↓↑	↑↓	↑↓	↑	
(b)	↓↑	↑↓	↑	↑	↑
(c)	↓↑	↑	↑↓	↑	↑
(d)	↓↑	↑↑	↑	↑	↑

5. Using s, p, d, f notations, describe the orbital with the following quantum numbers:
   (a) n = 2, l = 1
   (b) n = 4, l = 0
   (c) n = 5, l = 3
   (d) n = 3, l = 2

6. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2?