

Introduction to Periodicity & Periodic Table

The concept of chemical periodicity is central to the study of inorganic chemistry. No other generalization rivals the periodic table of the elements in 'its ability to systematize and rationalize known chemical facts or to predict new ones and suggest fruitful areas for further study. Chemical periodicity and the periodic table now find their natural interpretation in the detailed electronic structure of the atom; indeed, they played a major role at the turn of the century in elucidating the mysterious phenomena of radioactivity and the quantum effects, which led ultimately to Bohr's theory of the hydrogen atom. Because ~ this central position it is perhaps not surprising that innumerable articles and books have been written on the subject since these seminal papers by Mendeleev in 1869, and some 700 forms of the periodic table classified into 146 different types or subtypes) have been proposed.

There is no single best for of the periodic table since the choice depends upon the purpose for the periodic table to be used. That is why there have been a debate in the past upon the best numbering system to be used for individual purposes. This have lead towards the best one, long form of periodic table used so far to study the elements.

The Electronic Structure of Atoms

The ubiquitous electron was discovered by J.I. Thompson in 1897 some 25y after the original work on chemical periodicity by OJ. Mendeleev and Lothar Meyer; however, a further 20 Y. were to pass before G.N. Lewis and then I. Langmuir connected the electron with valency and chemical bonding. Refinements continued via wave mechanics and molecular orbital theory, and the symbiotic relation between experiment and theory Still continues today. It should always be remembered, however, that it is incorrect to "deduce" known chemical phenomena

from known theoretical models; the proper relationship is that the currently accepted models and interprets the facts leading towards modification (discarded or replaced) based upon new result discovery. Since theories can never be proved, only the best one gets implemented, more consistent with wide range of experiments. The logical interpretations is based upon the fruitful source of new experiments.

Our present views 'on the electronic structure of atoms are based on a variety of experimental results and theoretical models, which are fully discussed in many elementary texts. In summary, an atom comprises a central, massive positively charged nucleus surrounded by a more tenuous envelope of negative electrons. The nucleus is composed of neutrons (n) and protons (i.e. H^+) of approximately equal mass tightly bound by the force field of mesons. The number of protons (Z) is called the atomic number and this, together with the number of neutrons (N), gives the atomic mass number of the nuclide ($A= N + Z$). An element consists of atoms all of which have the same number of protons (Z) and this number determines the position of the elements in the periodic table (H.GJ, Moseley, 1913). Isotopes of an element all have the same value of Z but differ in the number of neutrons in their nuclei. The charge on the electron (e-I) is equal in size but opposite in sign to that of the proton and the ratio of their masses is 1/1836.20.

Concept of Atomic Orbital

If a line is drawn enclosing a region where an electron can be found, say 90 to 95% of time, such a region or space is called an atomic orbital. Thus:

"The three-dimensional region or space around the nucleus of an atom where there is maximum probability of finding an electron having certain energy is called atomic orbital."

OR

"An atomic orbital represents the space around the nucleus in an atom where the electron spends most of its time while in constant motion."

To clarify the concept of electron probability, let us assume that we take a set of instantaneous pictures of an electron with specific energy moving around a nucleus. If all these sequential pictures, with the electron appearing as small dot in each picture were superimposed, a cloud would result as shown in Fig 1.

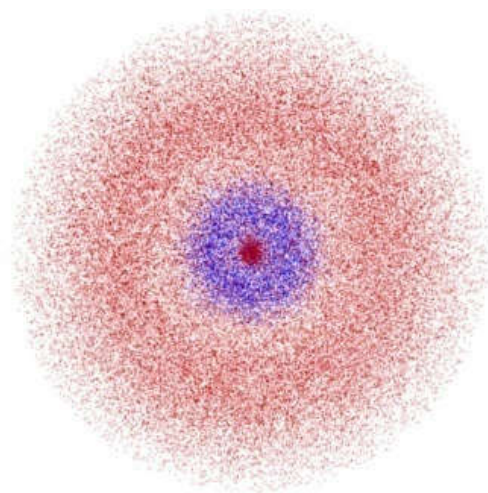


Fig 1. The dot population picture of an orbital

This picture is called an electron density representation. The density of dots in a given spatial region' is a pictorial representation of the probability density in that region.

Shapes of Orbitals

The shapes of orbitals depend on the quantum numbers l and m .

s-orbitals

s-orbitals are shown in Fig 2. The important points regarding their shapes are:

1. All s-orbitals are spherically symmetrical.
2. The effective size of s-orbitals increases as n increases.

3. Each orbital has regions of high electron density (shown as spherical shells)

equal to n .

4. In between the spherical shells there are nodes (having zero probability) equal to

$-n-l$.

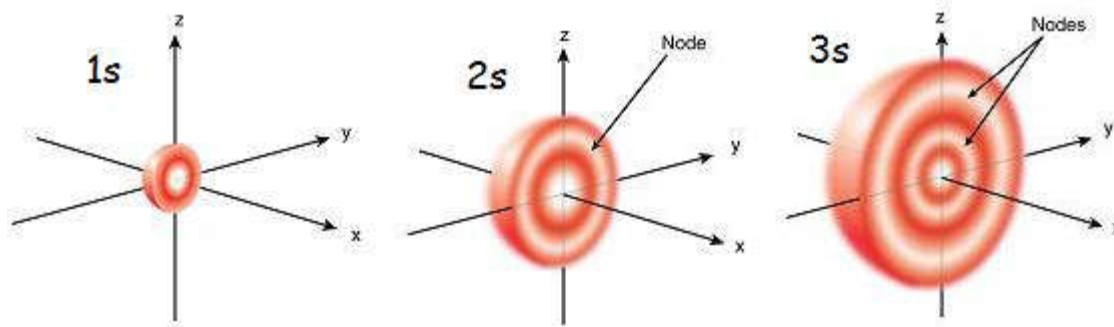


Fig 2. The shapes of s-orbitals with their nodal plane

p-orbitals

There are three p-orbitals, designated as p_x , p_y , and p_z , which are oriented along the three mutually perpendicular axes x , y and z . Each orbital consists of two lobes symmetrical about a particular axis and has dumb bell shape. The two lobes are separated by a nodal plane. Higher p-orbitals have similar shapes except that they have additional smaller regions of high electron density (called lobes) separated from the major lobes by the nodal surface. The number of such regions is $(n - 2)$ on each side.

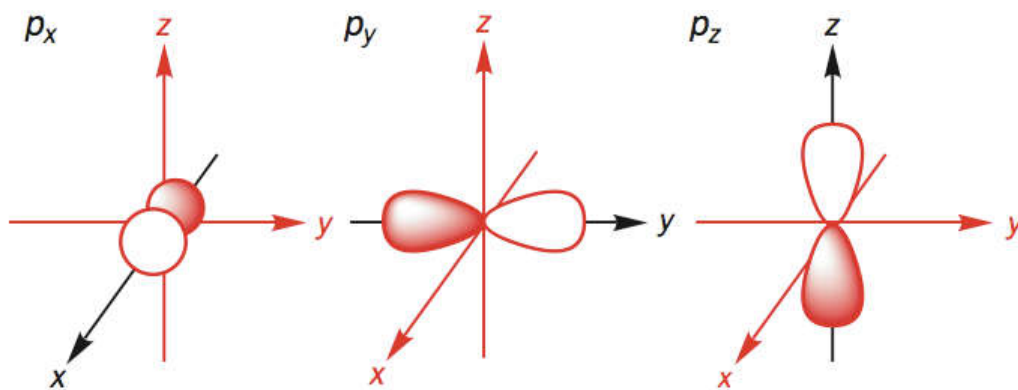


Fig 3. Shapes of p - orbital

d-orbitals

There are five d-orbitals designated as d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} . These are shown in Fig. 4.

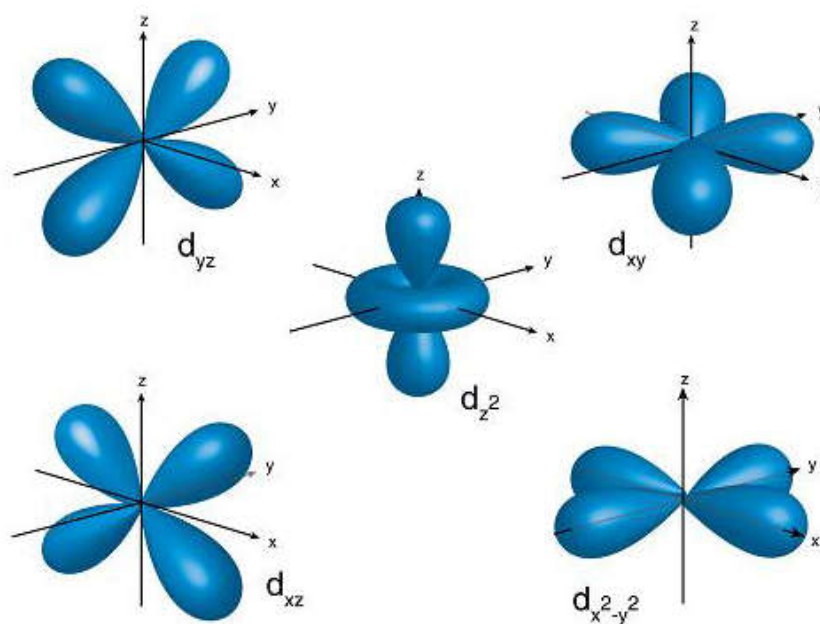


Fig 4. Shapes of d-orbital

QUANTUM NUMBERS

The term quantum number is used to identify the various energy levels available with the atom in which the electron of the atom can reside. The word quantum is used to signify that all the energy which are available to an electron are governed by laws of quantum mechanics.

Just as a college student is identified by (i) his name (ii) the name of his college (iii) class in which he is studying and (iv) the locality of his college, an electron in an atom is completely described by its four quantum numbers. Thus the quantum numbers serve as identification numbers which completely define the electron in an atom i.e., these numbers

- (i) specify the position (or location) of an electron in an atom.
- (ii) predict the direction of spin or self-rotation of the electron, and
- (iii) determine the energy and angular momentum of the electron.

Four quantum numbers which are required to completely specify the character of an electron are:

1. Principal quantum number (n)
2. Azimuthal quantum number (l)
3. Magnetic quantum number (m)
4. Spin quantum number (m_s)

Each quantum number refers to a particular character of an electron in an atom.

1. Principal Quantum Number (n)

This quantum number defines the energy level or shell in which the electron is

present. The average distance of the electron from the nucleus, and the energy associated, depend on n . It can have whole number values as

$$n = 1, 2, 3, 4, \dots$$

2. Azimuthal or Angular Quantum Number (l)

Azimuthal quantum number denotes the sublevel or subshell in a given principal energy level. This quantum number is related to the angular momentum of the electron. In multi-electron atoms, the energy, besides depending on n also depends on l . Corresponding to each value of n there are n possible values of l .

$$l = 0, 1, 2, 3, \dots, (n - 1)$$

These various sub shells are called s, p, d, f depending upon the value of l .

Value of l	0	1	2	3
Sublevel	s	p	d	f

3. Magnetic Quantum Number (m)

The third quantum number m is called the magnetic quantum number for it is only in an applied magnetic field that it is possible to define a direction within the atom with respect to which the orbital can be directed. In general, the magnetic quantum number can take up $2l+1$ values (i.e. $0, \pm 1, \dots, \pm l$), thus an s electron (which is spherically symmetrical and has zero orbital angular momentum) can have only one orientation, but a p electron can have three (frequently chosen x, y and z directions in Cartesian coordinates). Likewise there are five possibilities for the d -orbitals and seven for f - orbitals.

4. Spin Quantum Number (m_s)

This is designated by m_s , and describes the spin orientation of the electron. Since

the electron can spin only in two ways - clockwise and anticlockwise, s can have only two values: $+\frac{1}{2}$ and $-\frac{1}{2}$, which are also expressed by arrows pointing up (\uparrow) and down (\downarrow), respectively. It determines the orientation of spin angular momentum.

It can now be seen that there is a direct and simple correspondence between this description of electronic structure and the form of the periodic table. Hydrogen with 1 proton and 1 electron is the first element, and, in the ground state it has the electronic configuration $1s^1$ with zero orbital angular momentum. Helium, $Z = 2$, has the configuration $1s^2$, and this completes the first period since no other unique combination of $n = 1$, $l = m = 0$, $m_s = \pm \frac{1}{2}$ exists. The second period begins with lithium ($Z = 3$), the least tightly bound electron having the configuration $2s^1$. The same situation obtains for each of other periods.

In so far as the chemical (and physical) properties of an element derive from its electronic configuration, and especially the configuration of its least tightly bound electrons, it follows that chemical periodicity and the form of the periodic table can be elegantly interpreted in terms of electronic structure. A summary of all quantum numbers is given as;

Table 1: Summary of all quantum numbers

	n	l	m	s
1s	1	0	0	$\frac{1}{2}, -\frac{1}{2}$
2s	2	0	0	$\frac{1}{2}, -\frac{1}{2}$
2p	2	1	1, 0, -1	$\frac{1}{2}, -\frac{1}{2}$
3s	3	0	0	$\frac{1}{2}, -\frac{1}{2}$
3p	3	1	1, 0, -1	$\frac{1}{2}, -\frac{1}{2}$
3d	3	2	2, 1, 0, -1, -2	$\frac{1}{2}, -\frac{1}{2}$
4s	4	0	0	$\frac{1}{2}, -\frac{1}{2}$
4p	4	1	1, 0, -1	$\frac{1}{2}, -\frac{1}{2}$
4d	4	2	2, 1, 0, -1, -2	$\frac{1}{2}, -\frac{1}{2}$
4f	4	3	3, 2, 1, 0, -1, -2, -3	$\frac{1}{2}, -\frac{1}{2}$

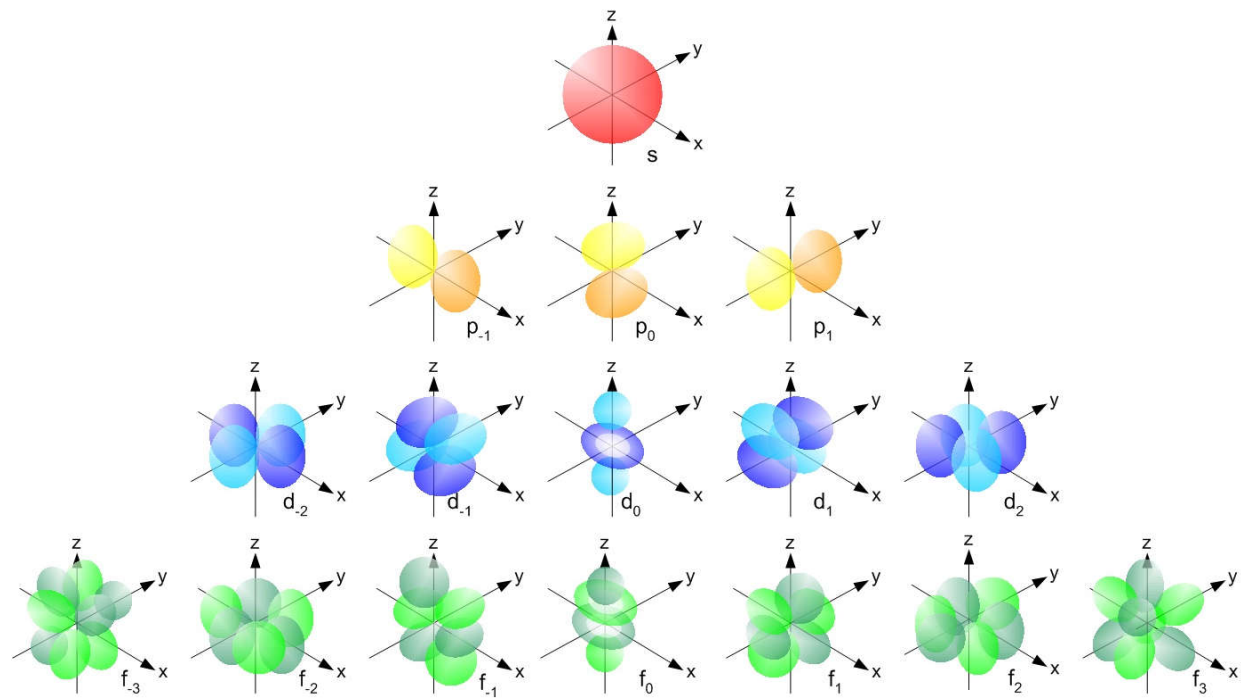


Fig 5. A overview of all the subshells or sub energy levels