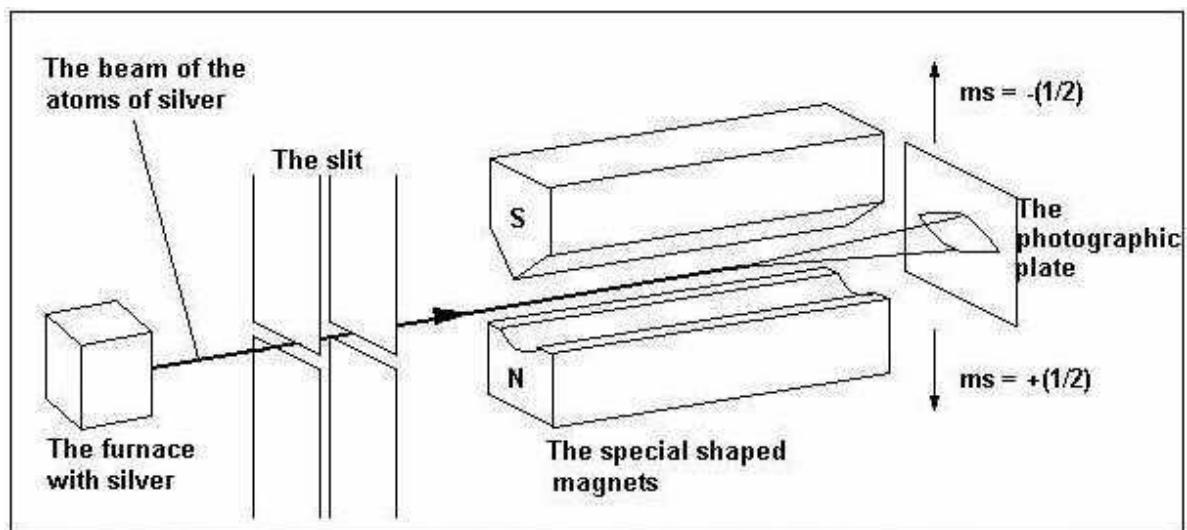


## Chapter Five: Many electron atom

### 5.1 The Stern-Gerlach experiment and spin

Experiments in the early 1920s discovered a new aspect of nature and at the same time found the simplest quantum system in existence. In the Stern-Gerlach experiment, a beam of hot atoms is passed through a nonuniform magnetic field. This field would interact with the magnetic dipole moment of the atom, if any, and deflect it.



The Stern-Gerlach experiment. On the photographic plate are two clear tracks.

- This experiment discovered two surprising things. The atoms specifically, the unpaired outer electron did have a magnetic dipole moment. In effect, in addition to being charged, electrons acted like tiny bar magnets. They also, as it developed, have a tiny intrinsic amount of angular momentum, equal to  $\hbar/2$ . (This quantity is called spin, and all known elementary particles have nonzero spin.) Electrons are called spin-1/2 particles.

- The second surprising thing was how much the path of the electrons was deflected. If electrons were really bar magnets, they could be oriented in any direction. The component oriented along the magnetic field gradient (say the  $Z$  direction) would determine the force on the electron, and hence how much it would be deflected.
- If electrons were like ordinary magnets with random orientations, they would show a continuous distribution of paths. The photographic plate in the Stern-Gerlach experiment would have shown a continuous distribution of impact positions.
- What was observed was quite different. The electrons were deflected either up or down by a constant amount, in roughly equal numbers. Apparently, the  $Z$  component of the electron's spin is quantized: it can take only one of two discrete values. We say that the spin is either up or down in the  $Z$  direction.

## 5.2 Quantum Numbers and Atomic Orbitals

From the solution of Schrödinger equation for hydrogen atom in spherical coordinates, we obtained a set of mathematical equations, called wave functions, which describe the probability of finding electrons at certain energy levels within an atom.

A wave function for an electron in an atom is called an *atomic orbital*; this atomic orbital describes a region of space in which there is a high probability of finding the electron. Energy changes within an atom are the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy (usually accompanied by the absorption or emission of a photon of light).

Each electron in an atom is described by four different quantum numbers. The first three ( $n, \lambda, m_\lambda$ ) specify the particular orbital of interest, and the fourth ( $m_s$ ) specifies how many electrons can occupy that orbital.

**1. Principal Quantum Number ( $n$ ):  $n = 1, 2, 3, \dots, \infty$**

Specifies the energy of an electron and the size of the orbital (the distance from the nucleus of the peak in a radial probability distribution plot). All orbitals that have the same value of  $n$  are said to be in the same shell (level). For a hydrogen atom with  $n=1$ , the electron is in its *ground state*; if the electron is in the  $n=2$  orbital, it is in an *excited state*. The total number of orbitals for a given  $n$  value is  $n^2$ .

**2. Angular Momentum (Secondary, Azimunthal) Quantum Number**

( $\lambda$ ):  $\lambda = 0, 1, \dots, (n-1)$ .

Specifies the shape of an orbital with a particular principal quantum number. The secondary quantum number divides the shells into smaller groups of orbitals called subshells (sublevels). Usually, a letter code is used to identify ( $\lambda$ ) to avoid confusion with ( $n$ ):

$\lambda$     0   1   2   3   4   5   ...

Letter *s*   *p*   *d*   *f*   *g*   *h*   ...

**3. Magnetic Quantum Number ( $m_\lambda$ ):  $m_\lambda = -\lambda, \dots, 0, \dots, +\lambda$**

Specifies the orientation in space of an orbital of a given energy ( $n$ ) and shape ( $\lambda$ ). This number divides the subshell into individual orbitals which

hold the electrons; there are  $(2\lambda+1)$  orbitals in each subshell. Thus the  $s$  subshell has only one orbital, the  $p$  subshell has three orbitals, and so on.

4. Spin Quantum Number ( $m_s$ ):  $m_s=+1/2$  or  $-1/2$ .

Specifies the orientation of the spin axis of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).

The Pauli exclusion principle (Wolfgang Pauli, Nobel Prize 1945) states that “*no two electrons in the same atom can have identical values for all four of their quantum numbers.*” , What this means is that no more than two electrons can occupy the same orbital, and that two electrons in the same orbital must have opposite spins.

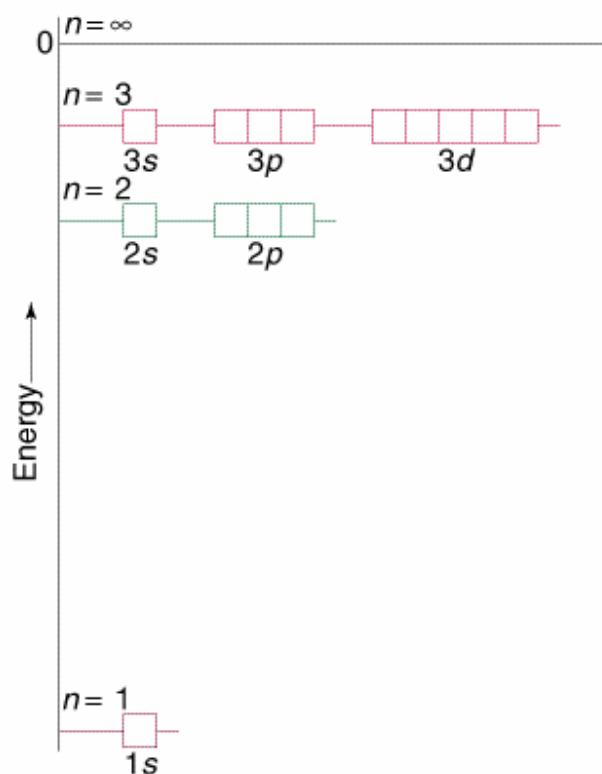
Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be paired. These substances are not attracted to magnets and are said to be *diamagnetic*. Atoms with more electrons that spin in one direction than another contain unpaired electrons. These substances are weakly attracted to magnets and are said to be *paramagnetic*.

## Table of Allowed Quantum Numbers

Relationship Among Values of  $n$ ,  $l$ , and  $m_l$  Through  $n = 4$

$n$	Possible Values of $l$	Subshell Designation	Possible Values of $m_l$	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	9
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	16
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	

The energy of the orbitals of a one-electron atom depends only on  $1/n^2$ , so the energy spectrum looks like this, where all orbitals with the same  $n$  quantum number 'shell' are *degenerate* (i.e. have the same energy).

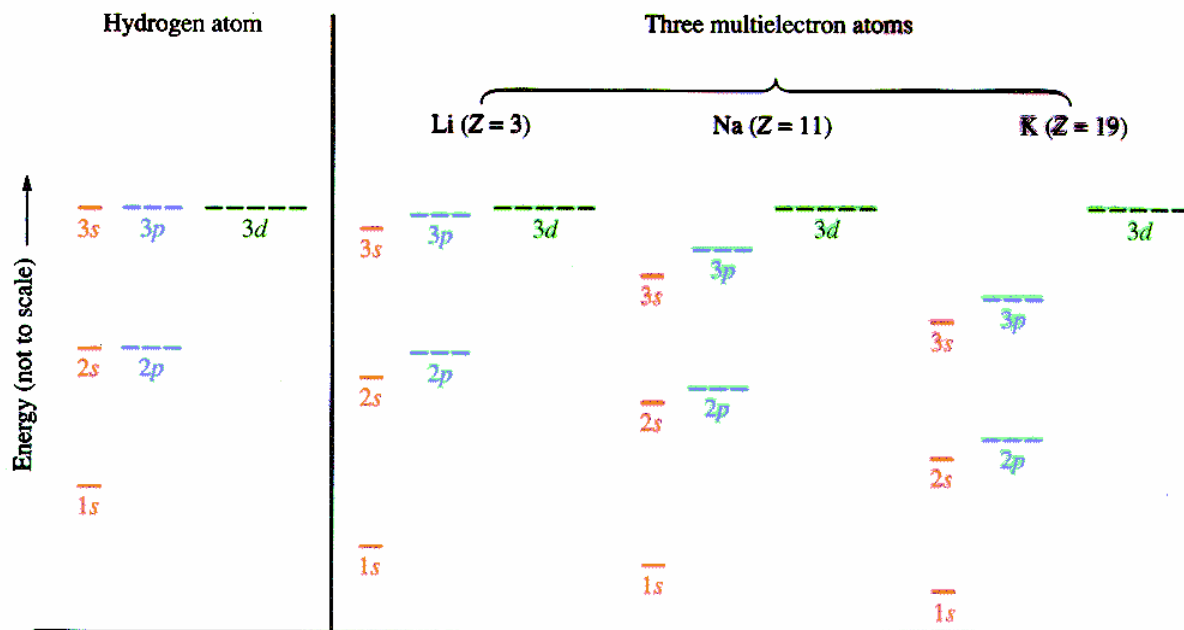


When describing any element other than Hydrogen, the structure of that atom will be more complicated than the simple Bohr picture can predict.

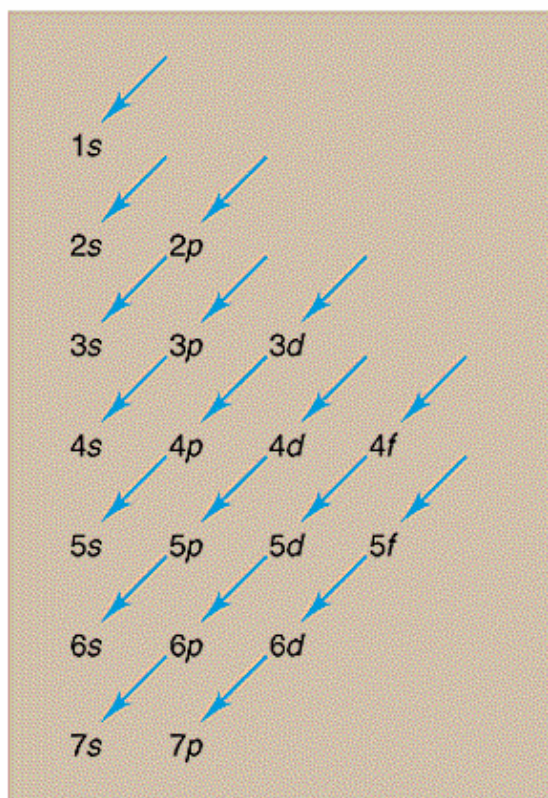
- First, the charge on the nucleus will be larger than  $+1e$ . The increased electrostatic attraction of the electrons to the nucleus will have a tendency to draw those electrons closer to the nucleus (and as a result closer to each other). This will lower the total energy of the atom (the Bohr model can handle this effect)
- Except for positive ions that contain only a single electron, the electrons of the atom or ion will interact with each other *repulsively*, since they have like charges. This will raise the total energy of the atom and 'spread out' the electrons. The Bohr model cannot describe electron-electron repulsion and therefore fails for any multiple electron atom or ion

The description of how most elemental atoms and ions behave is a balance of the two above phenomena.

We will treat the way in which the whole atom behaves as the cumulative behavior of each individual electron. Each individual electron is a 'wave' and has a [wavefunction](#), which may be described approximately with the orbitals of Hydrogen. The energy of each of these wavefunctions (orbitals) is qualitatively different from that of the one-electron atom, however, because of the discriminatory effects of electron-electron repulsion.



The order of filling of the orbitals (the order in energy from low to high) can be remembered by the following chart:



We can now 'build' atoms by filling the orbitals expected from a one-electron model 'perturbed' by what we know about electron-electron repulsion. This is called atomic 'Aufbau'. The first elements are easy if we postulate two 'rules':

- Each electron has one of two possible 'flavors': up or down which are described by a quantum number called  $m_s$ , which has values  $+1/2$  or  $-1/2$ , respectively.
- Electrons 'exclude' each other in that no two electrons can occupy the same 'state' at the same time. Thus, no two electrons in the same atom can have the same quantum numbers. This is called the *Pauli Exclusion Principle*.

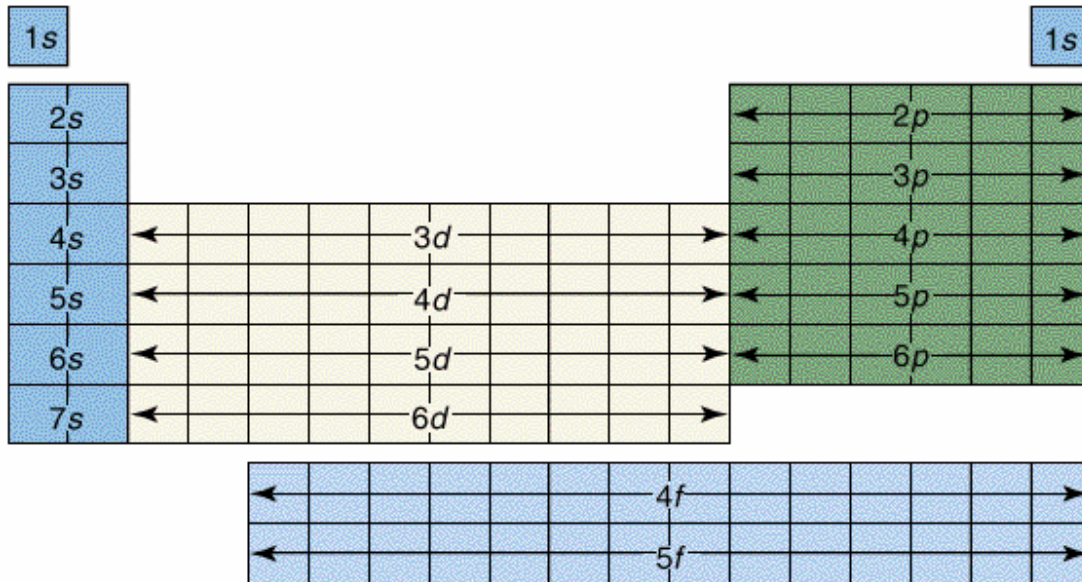
If it were not for the *spin* (the 'up' or 'down' flavor) of the electron, many electron atoms would be filled by putting one electron in each hydrogen-like orbital, to satisfy the Pauli exclusion principle. But, as it is, each spatial orbital can two electrons in it, as long as they are spin paired (one up, one down).

Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
Li	3	$\uparrow\downarrow$	$\uparrow$	$\square$ $\square$ $\square$	$\square$	$1s^2 2s^1$
Be	4	$\uparrow\downarrow$	$\uparrow\downarrow$	$\square$ $\square$ $\square$	$\square$	$1s^2 2s^2$
B	5	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\square$ $\square$	$\square$	$1s^2 2s^2 2p^1$
C	6	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\square$	$\square$	$1s^2 2s^2 2p^2$
N	7	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$	$\square$	$1s^2 2s^2 2p^3$
NE	10	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\square$	$1s^2 2s^2 2p^6$
Na	11	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow$	$1s^2 2s^2 2p^6 3s^1$



The electron configuration of the elements are what give rise to the shape of the periodic table and the names of the blocks that compose it.



### 5.3 The Zeeman Effect

(Classical treatment)

We consider the effect of a weak magnetic field on an electron performing circular motion in a planar orbit. We assume the magnetic field is applied along the z axis and the angular momentum is oriented at an angle  $\theta$  with respect to the z - axis, as shown in (Fig.5.1) below:

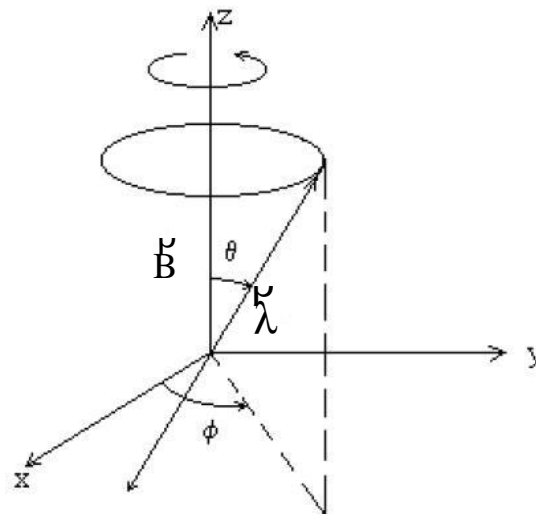


Fig. 5.1: The Precession of the Angular Momentum Vector in a Magnetic Field

The torque on  $\vec{\lambda}$  is given by

$$\vec{\tau}_\lambda = \vec{\mu}_\lambda \times \vec{B} \quad \dots(5.1)$$

This is directed into the plane of the page, in the  $\phi$ -direction

Now, the torque also equals the rate of change of the angular momentum, so we have,

$$\vec{\tau}_\lambda = \frac{d\vec{\lambda}}{dt} = \vec{\mu}_\lambda \times \vec{B} = \gamma_\lambda \vec{\lambda} \times \vec{B} \quad \dots(5.2)$$

But,

$$|d\vec{\lambda}| = \lambda \sin \theta d\phi \quad \dots(5.3)$$

so that the scalar form of Eq.5.3 becomes,

$$\lambda \sin \theta \cdot \frac{d\phi}{dt} = \gamma_\lambda \lambda B \sin \theta \quad \dots(5.4)$$

We define the precessional velocity by

$$\omega_L = \frac{d\phi}{dt}$$

So that (Eq.5.4) becomes,

$$\omega_L = \gamma_\lambda B = \frac{e}{2m} B \quad \dots(5.5)$$

The angular velocity  $\omega_L$  is called the Larmor frequency.

Thus, the angular momentum vector precesses about the z-axis at the Larmor frequency as a result of the torque produced by the action of a magnetic field on its associated magnetic moment.

Using the Planck relation, the energy associated with the Larmor frequency is

$$\Delta E = \pm \omega_L \eta = \pm \frac{e\eta B}{2m} = \pm \mu_B B \quad \dots(5.6)$$

where  $\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ JT}^{-1}$  is called Bohr magneton

where the signs refer to the sense of the rotation. It will be observed that this energy difference is the potential energy of a magnetic dipole whose moment is one Bohr magneton.

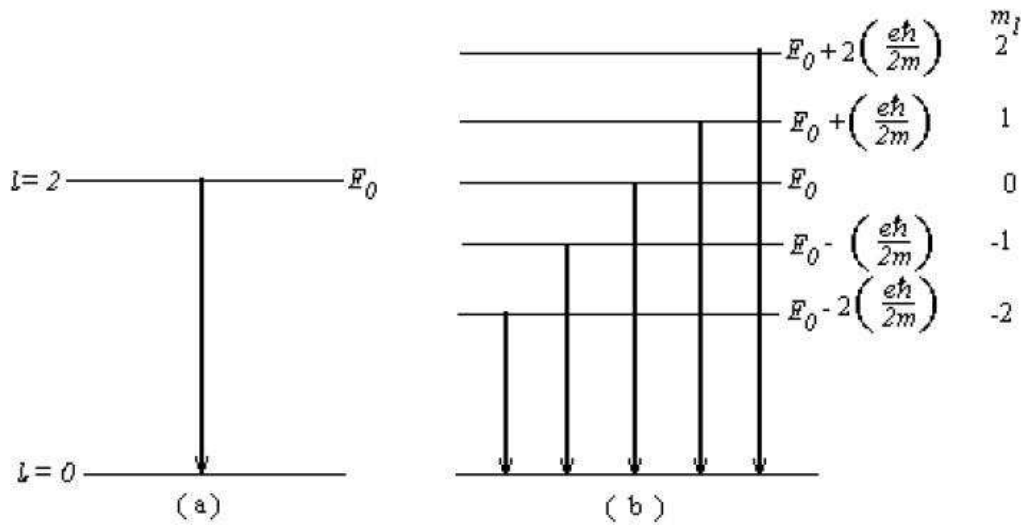
Recall that the dipolar energy is given by

$$\Delta E = -\vec{\mu} \cdot \vec{B}$$

In Eq.5.6, the positive sign corresponds to antiparallel alignment while the negative sign (lower energy) indicates parallel alignment.

The overall effect of this energy associated with the Larmor frequency is that, if the energy of an electron having a moment  $\mu_B$  is  $E_0$  in the absence of an applied field, then it can take on one of the energies

$$E_0 \pm \mu_B B \quad \text{in a magnetic field } B.$$



(a) Single Transition without an applied Magnetic Field

(b) Five transitions with an applied external magnetic field

## Homework Ch.5

Q.1) Rank the following electrons with quantum numbers  $(n, l, m_l, m_s)$  from lowest energy to highest energy.

- A.  $(2, 1, 1, +1/2)$
- B.  $(1, 0, 0, -1/2)$
- C.  $(4, 1, -1, +1/2)$
- D.  $(4, 2, -1, +1/2)$
- E.  $(3, 2, -1, +1/2)$
- F.  $(4, 0, 0, +1/2)$
- G.  $(2, 1, -1, +1/2)$
- H.  $(3, 1, 0, +1/2)$

Q.2) Refer to the electrons from (Q.1) to answer the following questions:

- A.  $(2, 1, 1, +1/2)$
- B.  $(1, 0, 0, -1/2)$
- C.  $(4, 1, -1, +1/2)$
- D.  $(4, 2, -1, +1/2)$

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

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

G. (2, 1, -1, +1/2)

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

- a. Which electron is spinning in a direction different from that of the others?
- b. Which electron is in a spherically shaped orbital?
- c. Which electron is in a  $p$  orbital?
- d. Which electron is in a  $d$  orbital?
- e. Which electron is furthest from the nucleus?
- f. Which two electrons are in the same orbital?
- g. Which two electrons differ only by the orientation of their orbitals?
- h. Which two electrons cannot exist in the same atom?
- i. Which electrons are degenerate?
- j. Which electrons are in an  $f$  orbital?

**Q.3) What is wrong with the quantum numbers ( $n, l, m_l, m_s$ ) of the following electrons?**

- a. (2, 2, 0, +1/2)
- b. (3, 1, -1, -1/2)
- c. (3, 1, -2, 1)
- d. (4, 0, 1, +1/2)
- e. (+1/2, 1, 1, 1)

**Q.4) Rank the following from highest energy to lowest energy.**

$3s, 5p, 4d, 1s, 5d, 3p$