

## STRUCTURE OF ATOM

## Aoms:

Atom is the smallest indivisible particle of the matter. Atom is made of electron, proton and neutrons.

PARTICLE	ELECTRON	PROTON	NEUTRON
<b>Discovery</b>	Sir. J. J. Thomson (1869)	Goldstein (1886)	Chadwick (1932)
<b>Nature of charge</b>	Negative	Positive	Neutral
<b>Amount of charge</b>	$1.6 \times 10^{-19}$ Coloumb	$1.6 \times 10^{-19}$ Coloumb	0
<b>Mass</b>	$9.11 \times 10^{-31}$ kg	$1.672614 \times 10^{-27}$ kg	$1.67492 \times 10^{-27}$ kg

Electrons were discovered using cathode ray discharge tube experiment.

Nucleus was discovered by Rutherford in 1911.

Cathode ray discharge tube experiment: A cathode ray discharge tube made of glass is taken with two electrodes. At very low pressure and high voltage, current starts flowing through a stream of particles moving in the tube from cathode to anode. These rays were called cathode rays. When a perforated anode was taken, the cathode rays struck the other end of the glass tube at the fluorescent coating and a bright spot on the coating was developed

**Results of Rutherford experiments:**

- Cathode rays consist of negatively charged electrons.
- Cathode rays themselves are not visible but their behavior can be observed with help of fluorescent or phosphorescent materials.
- In absence of electrical or magnetic field cathode rays travel in straight lines. In presence of electrical or magnetic field, behaviour of cathode rays is similar to that shown by electrons
- The characteristics of the cathode rays do not depend upon the material of the electrodes and the nature of the gas present in the cathode ray tube.

Charge to mass ratio of an electron was determined by Thomson. The charge to mass ratio of an electron as  $1.758820 \times 10^{11}$  C kg<sup>-1</sup>

Charge on an electron was determined by R A Millikan by using an oil drop experiment. The value of the charge on an electron is  $-1.6 \times 10^{-19}$  C.

is considered to be evenly spread over the atom. Thomson model of atom is also called as Plum pudding, raisin pudding or watermelon model. Thomson model of atom was discarded because it could not explain certain experimental results like the scattering of  $\alpha$ -particles by thin metal foils.

### **Observations from $\alpha$ -particles scattering experiment by Rutherford:**

- Most of the  $\alpha$ -particles passed through gold foil undeflected
- A small fraction of  $\alpha$ -particles got deflected through small angles
- Very few  $\alpha$ -particles did not pass through foil but suffered large deflection nearly  $180^\circ$

### **Conclusions Rutherford drew from $\alpha$ -particles scattering experiment:**

- Since most of the  $\alpha$ -particles passed through foil undeflected, it means most of the space in atom is empty
- Since some of the  $\alpha$ -particles are deflected to certain angles, it means that there is positively charged mass present in atom
- Since only some of the  $\alpha$ -particles suffered large deflections, the positively charged mass must be occupying very small space
- Strong deflections or even bouncing back of  $\alpha$ -particles from metal foil were due to direct collision with positively charged mass in atom

### **Rutherford's model of atom :**

This model explained that atom consists of nucleus which is concentrated in a very small volume. The nucleus comprises of protons and neutrons. The electrons revolve around the nucleus in fixed orbits. Electrons and nucleus are held together by electrostatic forces of attraction.

### **Drawbacks of Rutherford's model of atom :**

- According to Rutherford's model of atom, electrons which are negatively charged particles revolve around the nucleus in fixed orbits. Thus,
- the electrons undergo acceleration. According to electromagnetic theory of Maxwell, a charged particle undergoing acceleration should emit electromagnetic radiation. Thus, an electron in an orbit should emit radiation. Thus, the orbit should shrink. But this does not happen.
- The model does not give any information about how electrons are distributed around nucleus and what are energies of these electrons

**Isotopes:** These are the atoms of the same element having the same atomic number but different mass number. e.g.  ${}_1\text{H}^1, {}_1\text{H}^2, {}_1\text{H}^3$

**Isobars:** Isobars are the atoms of different elements having the same mass number but different atomic number. e.g.  ${}_{18}\text{Ar}^{40}, {}_{20}\text{Ca}^{40}$

**Isoelectronic species:** These are those species which have the same number of electrons.

### **Electromagnetic radiations:**

## Planck's Quantum Theory-

o The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy called 'quantum'. In case of light, the quantum of energy is called a 'photon'

o The energy of each quantum is directly proportional to the frequency of the radiation, i.e.  $E \propto \nu$  or

$$E = h\nu \quad \text{where } h = \text{Planck's constant} = 6.626 \times 10^{-27} \text{ Js}$$

o Energy is always emitted or absorbed as integral multiple of this quantum.  $E = nh\nu$  Where  $n = 1, 2, 3, 4, \dots$

**Black body:** An ideal body, which emits and absorbs all frequencies, is called a black body. The radiation emitted by such a body is called black body radiation.

### Photoelectric effect:

The phenomenon of ejection of electrons from the surface of metal when light of suitable frequency strikes it is called photoelectric effect. The ejected electrons are called photoelectrons.

### Experimental results observed for the experiment of Photoelectric effect-

o When beam of light falls on a metal surface electrons are ejected immediately.

o Number of electrons ejected is proportional to intensity or brightness of light

o Threshold frequency ( $\nu_0$ ): For each metal there is a characteristic minimum frequency below which photoelectric effect is not observed. This is called threshold frequency.

o If frequency of light is less than the threshold frequency there is no ejection of electrons no matter how long it falls on surface or how high is its intensity.

**Photoelectric work function ( $W_0$ ):** The minimum energy required to eject electrons is called photoelectric work function.  $W_0 = h\nu_0$

**Energy of the ejected electrons :**

$$h(\nu - \nu_0) = \frac{1}{2} m_e v^2$$

### Dual behavior of electromagnetic radiation

The light possesses both particle and wave like properties, i.e., light has dual behavior. Whenever radiation interacts with matter, it displays particle like properties. (Black body radiation and photoelectric effect) Wave like properties are exhibited when it propagates (interference and diffraction)

### Spectrum :-

When a white light is passed through a prism, it splits into a series of coloured bands known as **spectrum**.

### Spectrum is of two types:

(a) **Continuous and line spectrum** The spectrum which consists of all the wavelengths is called continuous spectrum.

Rydberg equation

$$\bar{\nu} = 109,677 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

R = Rydberg's constant = 109677 cm<sup>-1</sup>

### Bohr's model for hydrogen atom:

- An electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits or energy levels. These orbits are arranged concentrically around the nucleus.
- As long as an electron remains in a particular orbit, it does not lose or gain energy and its energy remains constant.
- When transition occurs between two stationary states that differ in energy, the frequency of the radiation absorbed or emitted can be calculated.

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

- An electron can move only in those orbits for which its angular momentum is an integral multiple of  $h/2\pi$

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$

The radius of the  $n$ th orbit is given by  $r_n = 52.9 \text{ pm} \cdot n^2 / Z$

energy of electron in  $n$ th orbit is :

$$E_n = -2.18 \times 10^{-18} \left( \frac{Z^2}{n^2} \right) \text{ J}$$

### Limitations of Bohr's model of atom:

- Bohr's model failed to account for the finer details of the hydrogen spectrum.
- Bohr's model was also unable to explain spectrum of atoms containing more than one electron.

### Dual behavior of matter:

de Broglie proposed that matter exhibits dual behavior i.e. matter shows both particle and wave nature. de Broglie's relation is

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

### Heisenberg's uncertainty principle:

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. The product of their uncertainties is always equal to or greater than  $h/4\pi$ .

$\Psi$  represents the wave function which is the amplitude of the electron

Wave

### Schrodinger's equation:

For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as:

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) of the electron associated with each energy level. Out of the

possible values, only certain solutions are permitted. Each permitted solution is highly significant as it corresponds to a definite energy state. Thus, we can say that energy is quantized.

**Probability density :**  $\psi$  gives us the amplitude of wave. The value of  $\psi$  has no physical significance.

$\Psi^2$  gives us the region in which the probability of finding an electron is maximum. It is called **probability density**.

**Orbital:** The region of space around the nucleus where the probability of finding an electron is maximum is called an orbital.

### Quantum numbers:

There are a set of four quantum numbers which specify the energy, size, shape and orientation of an orbital. To specify an orbital only three quantum numbers are required while to specify an electron all four quantum numbers are required.

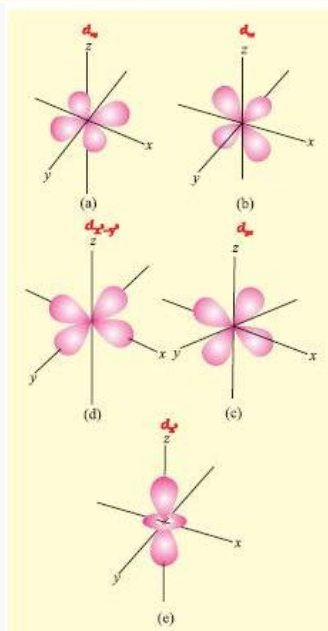
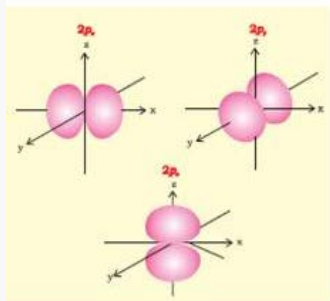
**Principal quantum number (n):** It identifies shell, determines sizes and energy of orbitals

<b>N</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Shell no.:	K	L	M	N
Total number of orbitals in a shell = $n^2$	1	4	9	16
Maximum number of electrons = $2n^2$	2	8	18	32

**Azimuthal quantum number (l):** Azimuthal quantum number. 'l' is also known as orbital angular momentum or subsidiary quantum number. l. It identifies sub-shell, determines the shape of orbitals, energy of orbitals in multi-electron atoms along with principal quantum number and orbital angular

$\sqrt{l(l+1)} \frac{h}{2\pi}$  momentum, i.e., The number of orbitals in a subshell =  $2l + 1$ . For a given value of  $n$ , it can have  $n$  values ranging from 0 to  $n-1$ . Total number of subshells in a particular shell is equal to the value of  $n$ .

Subshell notation	s	p	d	f	g
Value of 'l'	0	1	2	3	4
Number of	1	3	5	7	9



### Shielding effect or screening effect:

Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge on the nucleus. So, due to the screening effect, the net positive charge experienced by the electron from the nucleus is lowered and is known as effective nuclear charge. Effective nuclear charge experienced by the orbital decreases with increase of azimuthal quantum number ( $l$ ).

### Aufbau Principle:

In the ground state of the atoms, the orbitals are filled in order of their increasing energies

**$n+1$  rule**-Orbitals with lower value of  $(n+l)$  have lower energy. If two orbitals have the same value of  $(n+l)$  then orbital with lower value of  $n$  will have lower energy.

SUMMARY

## 2. Structure of Atom

### Some Important Points and Terms of the Chapter

1. The word 'atom' has been derived from the Greek word '**a-tomio**' which means 'uncuttable' or 'non-divisible'.
2. J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately  $10^{-10}$  m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4, NCERT Page 5). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.**
3. **Rutherford's Nuclear Model of Atom:**
  - a) Most of the space in the atom is empty as most of the  $\alpha$ -particles passed through the foil undeflected.
  - b) A few positively charged  $\alpha$ -particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged  $\alpha$ -particles.
  - c) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about  $10^{-10}$  m, while that of nucleus is  $10^{-15}$  m.
  - d) On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom (after the discovery of protons). According to this model :
    - (i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford.
    - (ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.
    - (iii) Electrons and the nucleus are held together by electrostatic forces of attraction.



4. The number of protons present in the nucleus is equal to atomic number ( $Z$ ). The nucleus is equal to atomic number ( $Z$ ). i.e. **Atomic number ( $Z$ )** = number of protons in the nucleus of an atom = number of electrons in a neutral atom
5. Protons and neutrons present in the nucleus are collectively known as nucleons. The total number of nucleons is termed as **mass number ( $A$ )** of the atom. mass number ( $A$ ) = number of protons ( $Z$ ) + number of neutrons ( $n$ )
6. **Isobars** are the atoms with same mass number but different atomic number for example,  ${}_6\text{C}^{14}$  and  ${}_7\text{N}^{14}$ . On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. e.g.  ${}_6\text{C}^{14}$ ,  ${}_6\text{C}^{13}$ ,  ${}_6\text{C}^{12}$  &  ${}_{17}\text{Cl}^{35}$ ,  ${}_{17}\text{Cl}^{37}$
7. **Drawbacks of Rutherford Model** According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only  $10^{-8}$  s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.
8. The frequency ( $\nu$ ), wavelength ( $\lambda$ ) and velocity of light ( $c$ ) are related by the equation (2.5).  $c = \nu \lambda$  The other commonly used quantity specially in spectroscopy, is the wavenumber ( $\bar{\nu}$ ). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e.,  $\text{m}^{-1}$ .
9. H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light. The phenomenon is called Photoelectric effect. **For photoelectric effect** :  $h\nu = h\nu_0 + \frac{1}{2} m v^2$
10. **Planck's quantum theory.** (i) The energy is radiated or absorbed by a body not continuously but discontinuously in form of small packets. (ii) Each packet is called quantum. In case of light, the quantum is called 'photon'. The energy of quantum is directly proportional to the frequency ( $\nu$ ) of the radiation.  $E \propto \nu$   $E = h\nu$ , Where ' $h$ ' is Planck's constant. Its value is  $6.625 \times 10^{-34}$  Joule second.
11. The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

12. An **absorption spectrum** is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths.
13. **Line Spectrum of Hydrogen:** When an electric discharge is passed through gaseous hydrogen, the H<sub>2</sub> molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers.

Series	n <sub>1</sub>	n <sub>2</sub>	Spectral region
<b>Lyman</b>	1	2,3.....	Ultraviolet
<b>Balmer</b>	2	3,4.....	Visible
<b>Paschen</b>	3	4,5.....	Infrared
<b>Brackett</b>	4	5,6.....	Infrared
<b>Pfund</b>	5	6,7.....	Infrared

The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum

$$\bar{\nu} = 109,677 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

could be described by the following expression :

#### 14. Bohr's Model For Hydrogen Atom

- The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- An electron can move only in those orbits for which its angular momentum is integral multiple of  $h/2\pi$  that is why only certain fixed orbits are allowed. The angular momentum of an electron in a given stationary state can be expressed as in equation
 
$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$
- The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.
- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by  $\Delta E$ , is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

15. Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example,  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the

$$E_n = -2.18 \times 10^{-18} \left( \frac{Z^2}{n^2} \right) \text{J}$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{pm}$$

expression

16. **Limitations of Bohr's Model:** It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) or an electric field (**Stark effect**).

17. **Dual Behaviour of Matter:** The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties.

18. The **de Broglie relation**. :de Broglie relation state that the wavelength associated with a moving object or an electron is inversely proportional to the momentum of the particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \text{ where } p \text{ is the momentum of particle} = mv.$$

19. **Heisenberg's Uncertainty Principle.** It is not possible to determine the position and velocity simultaneously for a sub-atomic particle like electron at any given instant to an arbitrary degree of precision. Consequently, it is not possible to talk of path of the electron in which it moves. If 'Δx' is uncertainty in position and 'ΔP' is uncertainty in momentum then

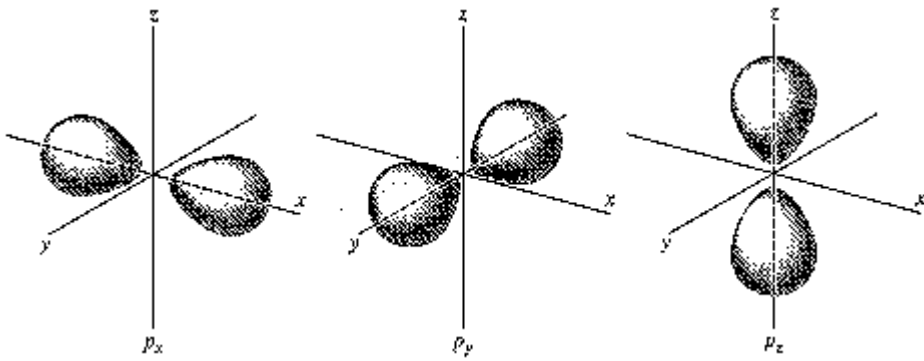
$$\Delta x \cdot \Delta P \geq \frac{h}{4\pi}$$

20. **Orbital.** It is a region or space where there is maximum probability of getting electron.

21. **Quantum numbers.** They are used to get complete information about electron, i.e., location, energy, spin, etc. These quantum numbers also help to designate the electron present in an orbital.

22. **Principal quantum number.** It specifies the location and energy of an electron. It is measure of the effective volume of the electron cloud. It is denoted by 'n'. Its possible values are 1, 2, 3,4 .....

23. **Angular momentum quantum number.** It is also called 'azimuthal quantum number'. It determines the shape of the orbital. It is denoted by ' $l$ '. The permitted values of ' $l$ ' are 0, 1, 2, etc., upto  $n-1$ . For a given value of  $n$ ,  $l = 0$  to  $n - 1$ . e.g., if value of  $n$  is 4,  $l$  can have values 0, 1, 2, 3. It determines angular momentum. 
$$mvr = \sqrt{l(l+1)} \frac{h}{2\pi}$$
24. **Magnetic quantum number.** It is denoted by ' $m$ ' and its value depends on value of ' $l$ ' since magnetism is due to angular momentum. It determines the magnetic orientation of an orbital, i.e., the direction of orbital relative to magnetic field in which it is placed. Its permitted values are  $-l$  to  $+l$  including zero, e.g., when  $l = 1$ , then  $m = -1, 0, +1$ . It has total number of values equal to  $2l + 1$ .
25. **Spin quantum number.** It indicates, the direction in which electron revolves. Spin is magnetic property and is also quantized. It has two permitted values  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . The spin angular momentum of an electron is constant and cannot be changed.
26. **(n+l) rule:** The relative order of energies of various sub-shells in a multi-electron atom can be predicted with the help of (n+l) rule (also called Bohr-Bury rule) According to this rule a sub-shell with lower values of (n+l) has lower energy. In case two sub-shell has equal value of (n+l), the sub-shell with lower value of  $n$  has lower energy
27. **Pauli's Exclusion Principle.** No two electrons in an atom can have all the four quantum numbers same. It can also be stated as – An orbital can have maximum two electrons and they must be of opposite spin quantum numbers.
28. **Aufbau principle.** Electrons are filled in the various orbitals in the increasing order of their energies, i.e., orbital having lowest energy will be filled first and the orbital having highest energy will be filled last. **Increasing energy of atomic orbitals for multi-electron atoms**  
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$
29. **Hund's rule of maximum multiplicity.** No electron pairing takes place in  $p$ ,  $d$  and  $f$  orbitals until each orbital in the given sub-shell contains one electron, e.g., N (7) has electronic configuration  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  according to Hund's rule and not  $1s^2 2s^2 2p_x^2 2p_y^1$ .
30. The valence electronic configurations of Cr and Cu, therefore, are  $3d^5 4s^1$  and  $3d^{10} 4s^1$  respectively and not  $3d^4 4s^2$  and  $3d^9 4s^2$ . It has been found that there is extra stability (Stability of Completely Filled and Half Filled Subshells) associated with these electronic configurations.
31. **Three orbitals of 2p subshell** ( $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals).



32. Five orbitals of 3d subshell ( $3d_{xy}$ ,  $3d_{yz}$ ,  $3d_{zx}$ ,  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbitals).

