

❖ Principal, Azimuthal and Magnetic Quantum Numbers and the Magnitude of Their Values

The Schrodinger wave equation for hydrogen and hydrogen-like species in the polar coordinates can be written as:

$$\frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + \frac{8\pi^2 \mu}{h^2} \left(E + \frac{Ze^2}{r} \right) \psi = 0 \quad (406)$$

After separating the variables present in the equation given above, the solution of the differential equation was found to be

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l} \cdot \Theta_{l,m} \cdot \Phi_m \quad (407)$$

$$= \sqrt{\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}} \cdot \exp\left(-\frac{Zr}{na_0}\right) \cdot \left(\frac{2Zr}{na_0} \right)^l \cdot \sum_{k=0}^{k=n-l-1} \frac{(-1)^{k+1} [(n+l)!]^2 \left(\frac{2Zr}{na_0} \right)^k}{(n-l-1-k)! (2l+1+k)! k!} \quad (408)$$

$$\times \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \cdot P_l^m(\cos \theta) \times \sqrt{\frac{1}{2\pi}} e^{im\phi}$$

It is obvious that the solution of equation (406) contains three discrete (n, l, m) and three continuous (r, θ, ϕ) variables. In order to be a well-behaved function, there are some conditions over the values of discrete variables that must be followed i.e. boundary conditions. Therefore, we can conclude that principal (n), azimuthal (l) and magnetic (m) quantum numbers are obtained as a solution of the Schrodinger wave equation for hydrogen atom; and these quantum numbers are used to define various quantum mechanical states. In this section, we will discuss the properties and significance of all these three quantum numbers one by one.

➤ Principal Quantum Number

The principal quantum number is denoted by the symbol n ; and can have value 1, 2, 3, 4, 5, ..., ∞ . The label “principal” is allotted because valid values of l and m can be defined only after defining an acceptable value of n . Some of the most important significances of the principal quantum number are given below.

1. The energy of an electron in hydrogen-like systems: The principal quantum number gives the energy of the electron in all hydrogen and hydrogen-like species by the following relation.

$$E_n = -\frac{\mu Z^2 e^4}{2 n^2 \hbar^2} \quad (409)$$

Where μ is the reduced mass of the system while e represents the electronic charge. The symbol Z represents the nuclear charge of the one-electron system. Now since main shells are nothing but the classification of different quantum mechanical states of electron on the basis of energy only, we can also say that n tells about the main shells in the modern wave mechanical model of the atom.

2. Degeneracy in hydrogen-like systems: Since the total number of wave functions that can be written for a given value of n are n^2 , we can say that the degeneracy of any energy level is also n^2 . In other words, we can say that because the energy depends only upon the value of n , all wave functions with the same value of n must possess the same energy. For instance, if we $n = 2$, a total of four wave-functions can be written i.e. $\psi_{2,0,0}$, $\psi_{2,1,0}$, $\psi_{2,1,+1}$ and $\psi_{2,1,-1}$. Owing to the same value of n , all of these states are bound to have the same energy, and thus, are degenerate.

3. The maximum number of electrons per unit cell: Since two electrons can have the same set of principal, orbital and magnetic quantum numbers via opposite spins, the maximum number of electrons per unit cell will be $2n^2$ i.e. the double of the degeneracy. For instance, if we $n = 2$, the maximum number of electrons that can be filled in the second main shell is $2 \times 2^2 = 8$. Similarly, if we $n = 3$, the maximum number of electrons that can be filled in the third main shell is $2 \times 3^2 = 18$.

4. Spectra of elemental hydrogen: In order to understand this concept, recall the energy expression for the hydrogen atom i.e.

$$E_n = -\frac{m e^4}{2 n^2 \hbar^2} = -\frac{4\pi^2 m e^4}{2 n^2 h^2} \quad (410)$$

In the SI system, the above equation needs to be corrected for permittivity factor ($4\pi\epsilon_0$) i.e.

$$E_n = -\frac{4\pi^2 m e^4}{2 n^2 h^2 (4\pi\epsilon_0)^2} \text{ Joules} = -\frac{4\pi^2 m e^4}{32 \pi^2 n^2 h^2 \epsilon_0^2} \text{ Joules} \quad (411)$$

or

$$E_n = -\frac{m e^4}{8 n^2 h^2 \epsilon_0^2} \text{ Joules} \quad (412)$$

Converting Joules into cm^{-1} (dividing by hc) the above equation takes the form

$$\bar{\nu}_n = -\frac{m e^4}{8 n^2 h^3 c \epsilon_0^2} \text{ cm}^{-1} = -\frac{R}{n^2} \text{ cm}^{-1} \quad (413)$$

Now the selection rules for electronic transitions are

$$\Delta n = \text{anything} \quad \text{and} \quad \Delta l = \pm 1 \quad (414)$$

This means that electron can move from s to p -orbital only; and all $s-s$, $p-p$, $d-d$ and $f-f$ transitions are Laporte forbidden. Now assume that electron shows a transition from an initial quantum mechanical state (n_1) to the final quantum mechanical state (n_2). The energy of absorption can be formulated as:

$$\Delta \bar{\nu} = \bar{\nu}_{n_2} - \bar{\nu}_{n_1} = \left(-\frac{R}{n_2^2} \right) - \left(-\frac{R}{n_1^2} \right) \text{ cm}^{-1} \quad (415)$$

or

$$\Delta\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1} \quad (416)$$

The above equation can also be used to determine the wavenumber of the emission spectral line of the hydrogen atom. All the possibilities and corresponding series are given below.

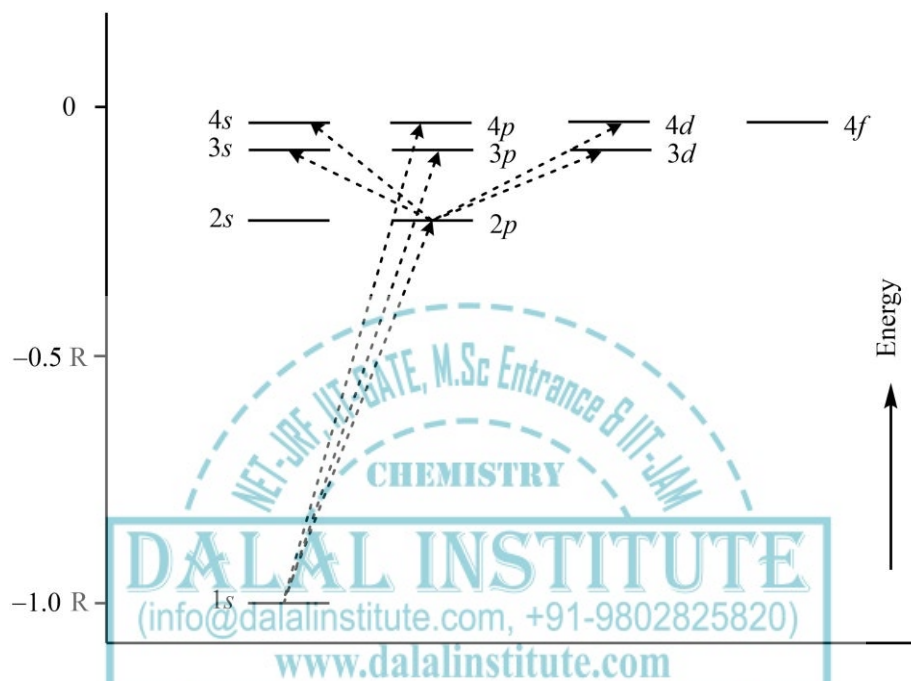


Figure 15. Energy level diagram of the hydrogen atom in the units of Rydberg constant.

At this stage, we must consider all the possibilities that may arise from the transitioning of the electron from different quantum mechanical states. These transitions are grouped in various series labeled as Lyman, Balmer, Paschen, Brackett and Pfund series.

Table 5. Different spectral series in the hydrogen atom.

Series name	Lower state (n_1)	Higher state (n_2)	Region
Lyman	1	2, 3, 4, 5, ∞	UV
Balmer	2	3, 4, 5, 6, ∞	Visible
Paschen	3	4, 5, 6, 7, ∞	Near IR
Brackett	4	5, 6, 7, 8, ∞	Mid IR
Pfund	5	6, 7, 8, 9, ∞	Far IR

➤ **Azimuthal Quantum Number**

The azimuthal quantum number is denoted by the symbol l ; and can have value $n-1, n-2, n-3, \dots, 0$. The label azimuthal quantum number is also called as “angular momentum quantum number” because the values of l also govern the orbital angular momentum of the electron in a particular quantum mechanical state. Some of the most important significances of the principal quantum number are given below.

1. Orbital angular momentum of the electron: The azimuthal quantum number gives the angular momentum of the electron in all hydrogen and hydrogen-like species by the following relation.

$$\langle L \rangle = \oint \psi_{n,l,m}(r, \theta, \phi) \hat{L} \psi_{n,l,m}(r, \theta, \phi) \quad (417)$$

$$= \sqrt{l(l+1)} \frac{h}{2\pi} \quad (418)$$

After looking at the equation (418), it is obvious that it's only the ' l ' quantum number that controls the magnitude of the orbital angular momentum quantum number. Furthermore, owing to the quantized nature of ' l ' quantum number, the angular momentum of an electron in an atom is also quantized. For instance, if we use $l = 0, 1, 2, 3$ in equation (418), we will get $0, \sqrt{2}, \sqrt{6}$ and $\sqrt{12}$ units of angular momentum, respectively.

2. Subshells in the main shell: The azimuthal quantum number can also be used to classify different quantum mechanical states on the basis of orbital angular momentum. In other words, subshells are nothing but the classification degenerate quantum mechanical states on the basis of angular momentum.

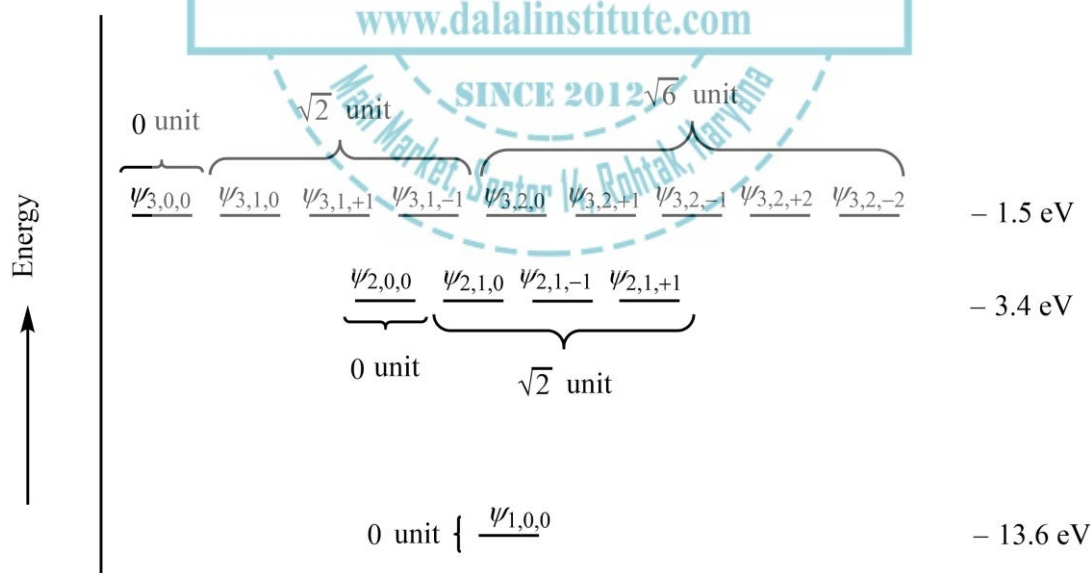


Figure 16. Energy level diagram of the hydrogen atom with further classification.

3. Shape and number of angular nodes in atomic orbital: The angular momentum quantum number, l , also controls the number of angular nodes that pass through the nucleus. An angular node (planar or conical) is observed when the angular part of the wave function passes through zero and changes sign.

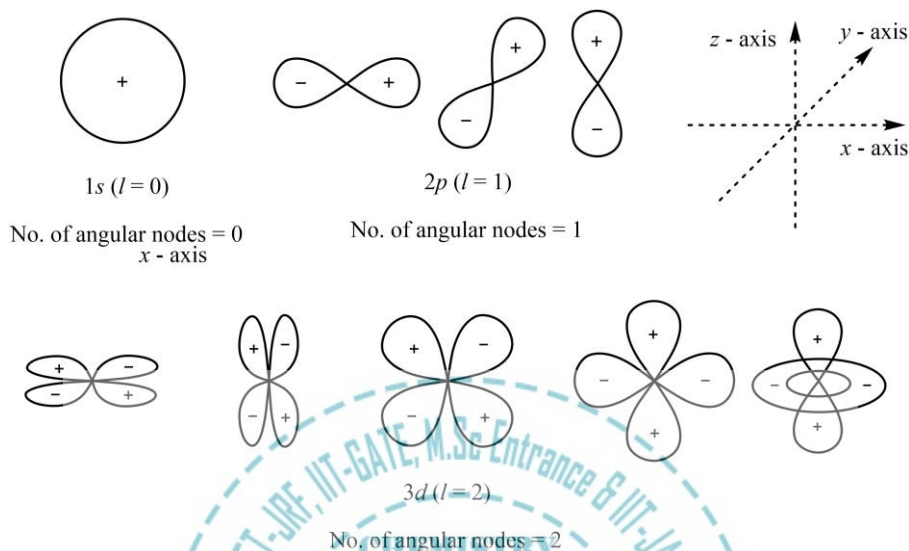


Figure 17. Different orbitals and the corresponding angular nodes.

4. The energy of different subshells in multi-electron atoms: In hydrogen and H-like atoms (i.e. one-electron systems), the energy levels depend only upon the principal quantum number. However, these energy levels also split according to the magnitude of l as well. Quantum states of higher l are placed above than the states with lower l . For instance, the energy of 2s orbital is lower than 2p, 3d exists at higher position than 3p.

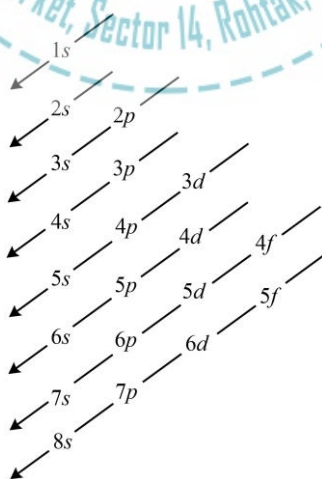


Figure 18. The energy pattern of different subshells in multi-electron atoms.

➤ **Magnetic Quantum Number**

The magnetic quantum number is denoted by the symbol m , and can have values $+l$ to $-l$ in unit steps. In other words, the quantum number m is nothing but the allowed effects of orbital angular momentum in the z -direction. The label “magnetic quantum number” arises because m affects the energy of the electron in an externally applied magnetic field. In the absence of such a field, all spherical harmonics corresponding to the different arbitrary values of m will be equivalent. Some of the most important significances of the principal quantum number are given below.

1. The orientation of orbital angular momentum: The azimuthal quantum number gives the angular momentum of the electron in all hydrogen and hydrogen-like species by the following relation:

$$L_l = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (419)$$

Since $l = 0, 1, 2, 3, 4 \dots (n-1)$ etc., the quantum mechanically allowed values of orbital angular momentum (in the units of $h/2\pi$) are given below.

$$L_0 = \sqrt{0(0+1)} \text{ unit} = 0 \text{ unit} \quad (420)$$

$$L_1 = \sqrt{1(1+1)} \text{ unit} = \sqrt{2} \text{ unit} \quad (421)$$

$$L_2 = \sqrt{2(2+1)} \text{ unit} = \sqrt{6} \text{ unit} \quad (422)$$

$$L_3 = \sqrt{3(3+1)} \text{ unit} = \sqrt{12} \text{ unit} \quad (423)$$

However, there is boundary condition in quantum mechanics that says that only integral effects are allowed reference direction if the angular momentum is generated by integral quantum number and half-integral effects are allowed in reference direction if the momentum is generated by half-integral quantum number.

Since, $L_z = L \cos \theta$, $\sqrt{2}$ units of orbital angular momentum cannot orient itself along z -axis because this makes $\theta = 0^\circ$, and since $\cos 0 = 1$, $\vec{L}_z = L$ i.e. orbital angular momentum effect along the z -axis is also 1.414 unit which is not allowed quantum mechanically. The effects of angular momentum allowed in the z -direction are $+1, 0, -1$; for which angles required are determined as follows.

$$+1 = \sqrt{2} \cos \theta \Rightarrow \theta = \cos^{-1} \frac{1}{\sqrt{2}} = 45^\circ \quad (424)$$

$$0 = \sqrt{2} \cos \theta \Rightarrow \theta = \cos^{-1} \frac{0}{\sqrt{2}} = 90^\circ \quad (425)$$

$$-1 = \sqrt{2} \cos \theta \Rightarrow \theta = \cos^{-1} \frac{-1}{\sqrt{2}} = 135^\circ \quad (426)$$

Hence, we can say that in order to be allowed, the 1.414 units of orbital angular momentum must orient itself only at 45° , 90° and 135° in space from reference direction (z -axis in this case). Since the orientation of angular momentum can orient itself in any direction from the z -axis as far as the effective orbital angular momentum $+1$ unit along z -direction; therefore, we should use a cone around the same at 45° . The same is true for 0 and -1 effects with 90° and 135° , respectively.

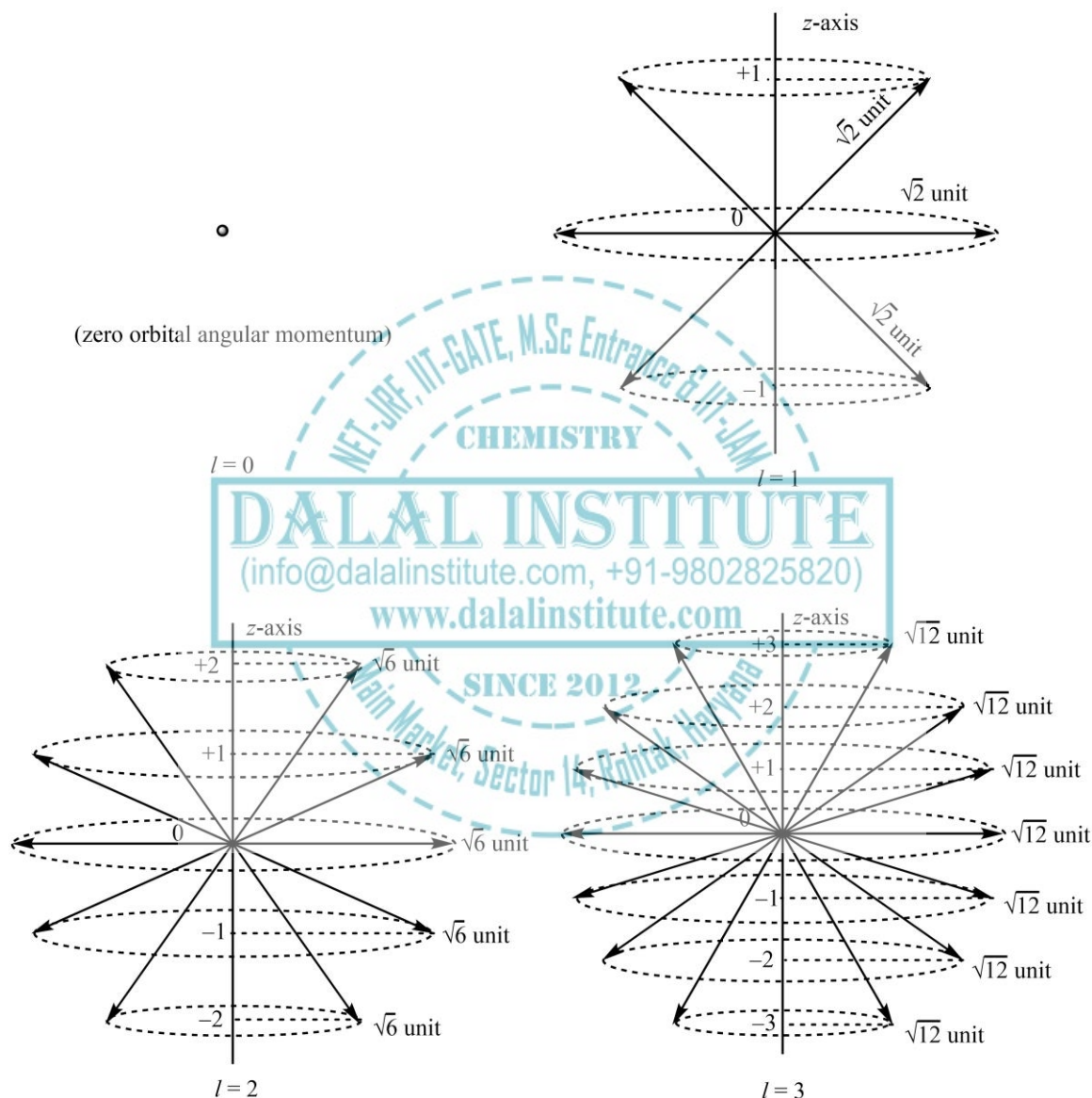


Figure 19. The space quantization of orbital angular momentum of an electron for $l = 0, 1, 2$ and 3 states.

It is also worthy to mention that all the orientations of orbital angular momentum are degenerate in the absence of any externally applied magnetic field.

2. The energy of different orientations: The probability of different orientations of orbital angular momentum, and also the corresponding magnetic fields, are same. However, after applying the magnetic field along the z -direction, the situation will not be the same.

The orientation with a maximum negative value of orbital angular momentum along the z -axis will have magnetic dipole aligned along the applied magnetic field, and thus, will be most stable. Conversely, the orientations with the maximum positive value of orbital angular momentum along the z -axis will have magnetic dipole aligned opposite to the applied magnetic field, and thus, will be least stable. Likewise, the orientations with angular momentum component in between will also have intermediary energies in this case.

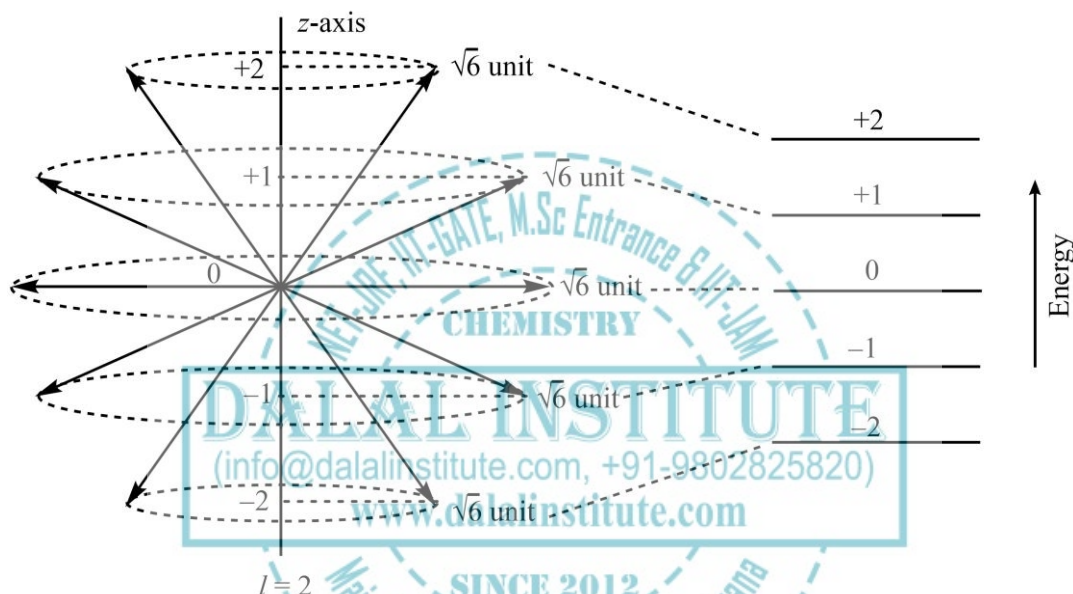


Figure 20. Different orientations of the orbital angular momentum of an electron in a d -subshell and corresponding energies in the applied magnetic field.

To understand this, consider the typical case of d -subshell. The orbital angular momentum for the corresponding electron can be obtained using equation (419) i.e.

$$L = \sqrt{2(2+1)} \frac{h}{2\pi} \quad (427)$$

$$L = \sqrt{6} \frac{h}{2\pi} \quad (428)$$

The allowed effects of orbital angular momentum in the z -direction are $+2, +1, 0, -1, -2$ in the units of $h/2\pi$. Therefore, each spectral line arising from the transition to the d -subshell will split in a quintet in the presence of the externally applied magnetic field.

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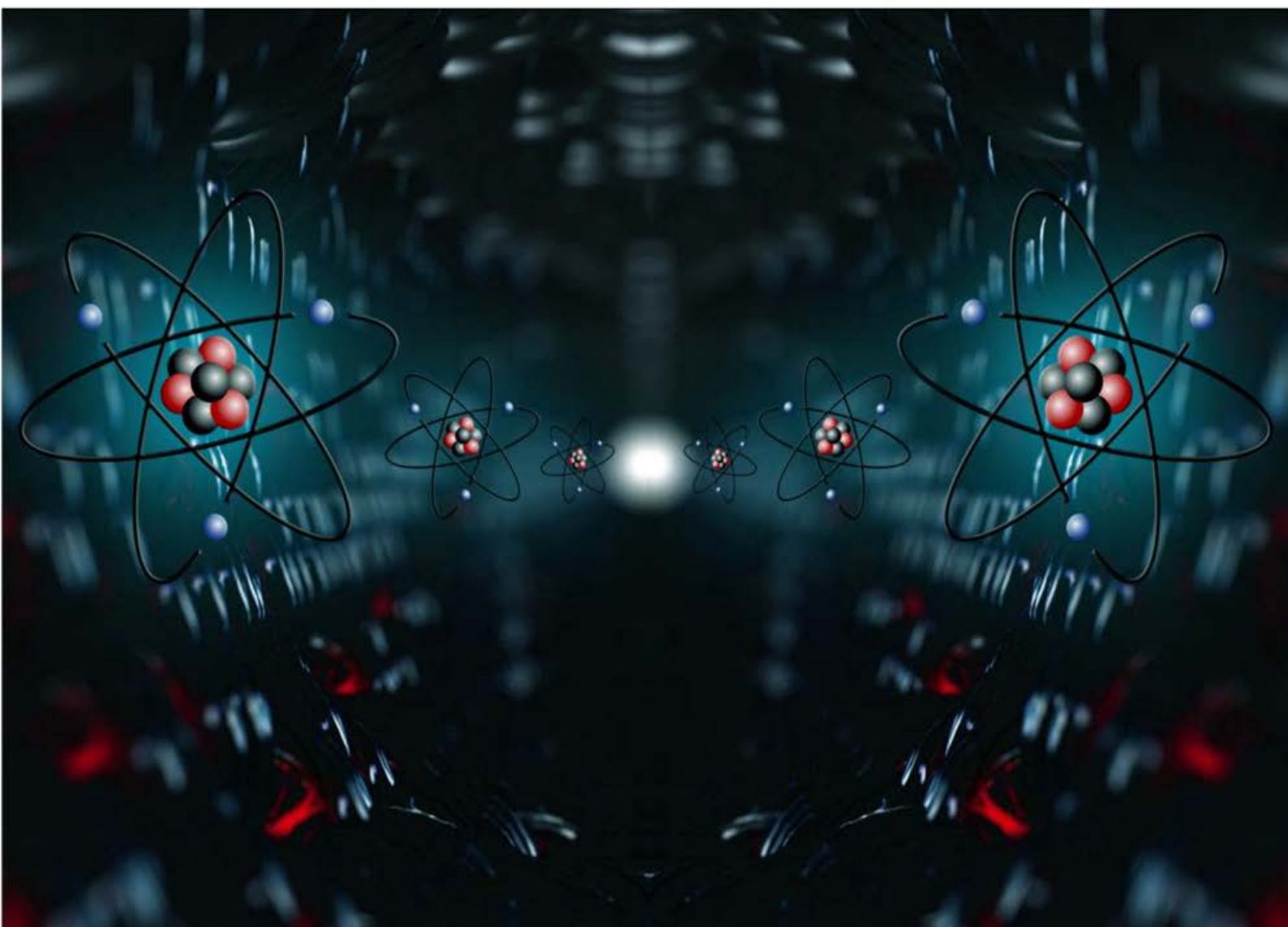
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