❖ Space Quantization

The solution of the Schrodinger wave equation for the diatomic rigid rotator provided the mathematical descriptions of all the rotational states along with their corresponding energies. The general form of total eigenfunction for the rigid rotator is given below.

$$\psi_{l,m}(\theta,\phi)=\sqrt{\frac{1}{2\pi}}\sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}.P_l^m(Cos\,\theta).e^{\pm im\phi} \tag{227}$$

Where ψ is the mathematical expression defining various quantum mechanical states depending upon two variables θ and ϕ. Furthermore, the most important property of a rigid rotator after energy is the angular momentum which can be obtained using the last postulate of quantum mechanics i.e.

$$<L>=\oint \psi_{l,m}(\theta,\phi)\,\hat{L}\,\psi_{l,m}(\theta,\phi) \tag{228}$$

$$L_l=\sqrt{l(l+1)}\frac{h}{2\pi} \tag{229}$$

Alternatively, we know that the energies of various rotational states of rigid rotators are given by the following relation.

$$E=\frac{h^2}{8\pi^2 I}\,l(l+1) \tag{230}$$

Where $l=0,1,2,3,4$ etc. Also, we know that the angular momentum and energy are related classically as

$$E=\frac{1}{2}\,I\omega^2=\frac{(I\omega)^2}{2I}=\frac{L^2}{2I} \tag{231}$$

or

$$L=\sqrt{2EI} \tag{232}$$

After using the value of energy from equation (230) into equation (232), we get

$$L_l=\sqrt{2I.\frac{h^2}{8\pi^2 I}\,l(l+1)} \tag{233}$$

or

$$L_l=\sqrt{\frac{h^2}{4\pi^2}\,l(l+1)} \tag{234}$$

or

$$L_l = \sqrt{l(l+1)}\,\frac{h}{2\pi} \tag{235}$$

Which is exactly the same as given by equation (229). Since $l = 0, 1, 2, 3, 4$ etc., the quantum mechanically allowed values of angular momentum (in the units of $h/2\pi$) are given below.

$$L_0 = \sqrt{0(0+1)}\text{ unit} = 0\text{ unit} \tag{236}$$

$$L_1 = \sqrt{1(1+1)}\text{ unit} = \sqrt{2}\text{ unit} \tag{237}$$

$$L_2 = \sqrt{2(2+1)}\text{ unit} = \sqrt{6}\text{ unit} \tag{238}$$

$$L_3 = \sqrt{3(3+1)}\text{ unit} = \sqrt{12}\text{ unit} \tag{239}$$

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.

This can be understood by taking the example of a diatomic molecule rotating in the first excited rotational state i.e. $l = 1$. The angular momentum of such a molecule will be $\sqrt{2}$ or 1.414 units. However, since this angular momentum is obtained using an integral quantum number ($l = 1$), only integral effects (i.e. $+1, 0, -1$) are allowed in reference direction. Now if *z*-axis is the reference direction, the effect of any vector $\vec{A}$ in the reference direction is calculated by multiplying its magnitude with the cosine of the angle it makes with reference direction.

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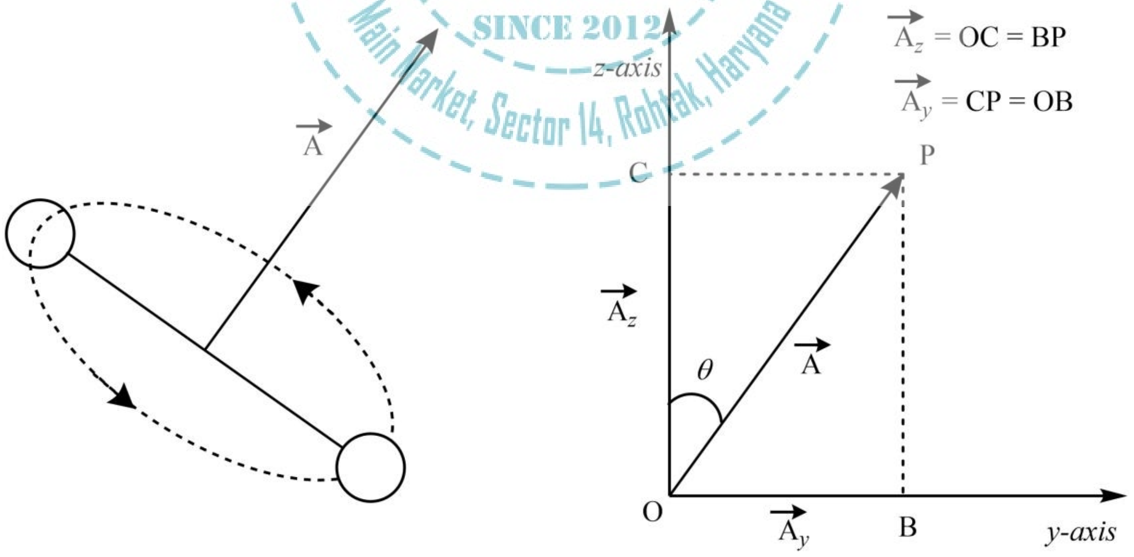

Figure 9. The angular momentum of the diatomic rigid rotator (left) and its rectangular resolution.

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In tringle OPC, the side OC represents the effect of the angular momentum vector $\vec{A}$ along z-axis, can be calculated as given below.

$$\frac{OC}{OP} = Cos\ \theta \tag{240}$$

$$OC = OP.Cos\ \theta \tag{241}$$

$$\vec{A}_z = A\ Cos\ \theta \tag{242}$$

Hence, a diatomic molecule in its first rotational state cannot rotate in xy-plane since it will generate $\sqrt{2}$ or 1.414 units of angular momentum along the z-axis (from right-hand thumb rule). In other words, the $\sqrt{2}$ units of angular momentum cannot orient itself along z-axis because this makes $\theta = 0°$ and since $Cos\ 0 = 1$, $\vec{A}_z = A$ i.e. 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.

$$+1 = \sqrt{2}\,Cos\ \theta \quad \Rightarrow \quad \theta = Cos^{-1}\frac{1}{\sqrt{2}} = 45° \tag{243}$$

$$0 = \sqrt{2}\,Cos\ \theta \quad \Rightarrow \quad \theta = Cos^{-1}\frac{0}{\sqrt{2}} = 90° \tag{244}$$

$$-1 = \sqrt{2}\,Cos\ \theta \quad \Rightarrow \quad \theta = Cos^{-1}\frac{-1}{\sqrt{2}} = 135° \tag{245}$$

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Hence, we can say that in order to be allowed, the 1.414 units of angular momentum must orient itself only at 45°, 90° and 135° in space from reference direction (z-axis in this case).

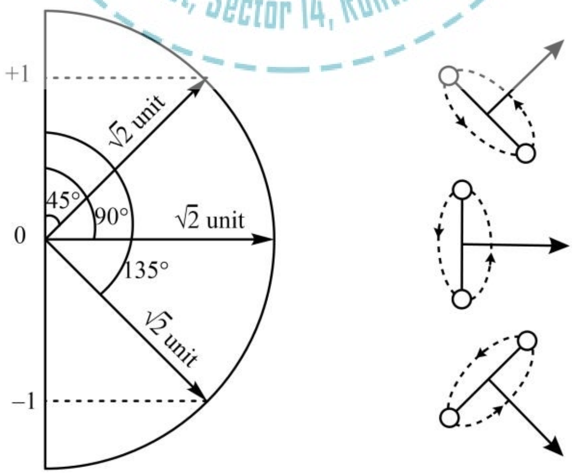

Figure 10. The space quantization of angular momentum of rigid rotator in $l = 1$ rotational state.

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Since the orientation of angular momentum can orient itself in any direction from the *z*-axis as far as the effective 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.

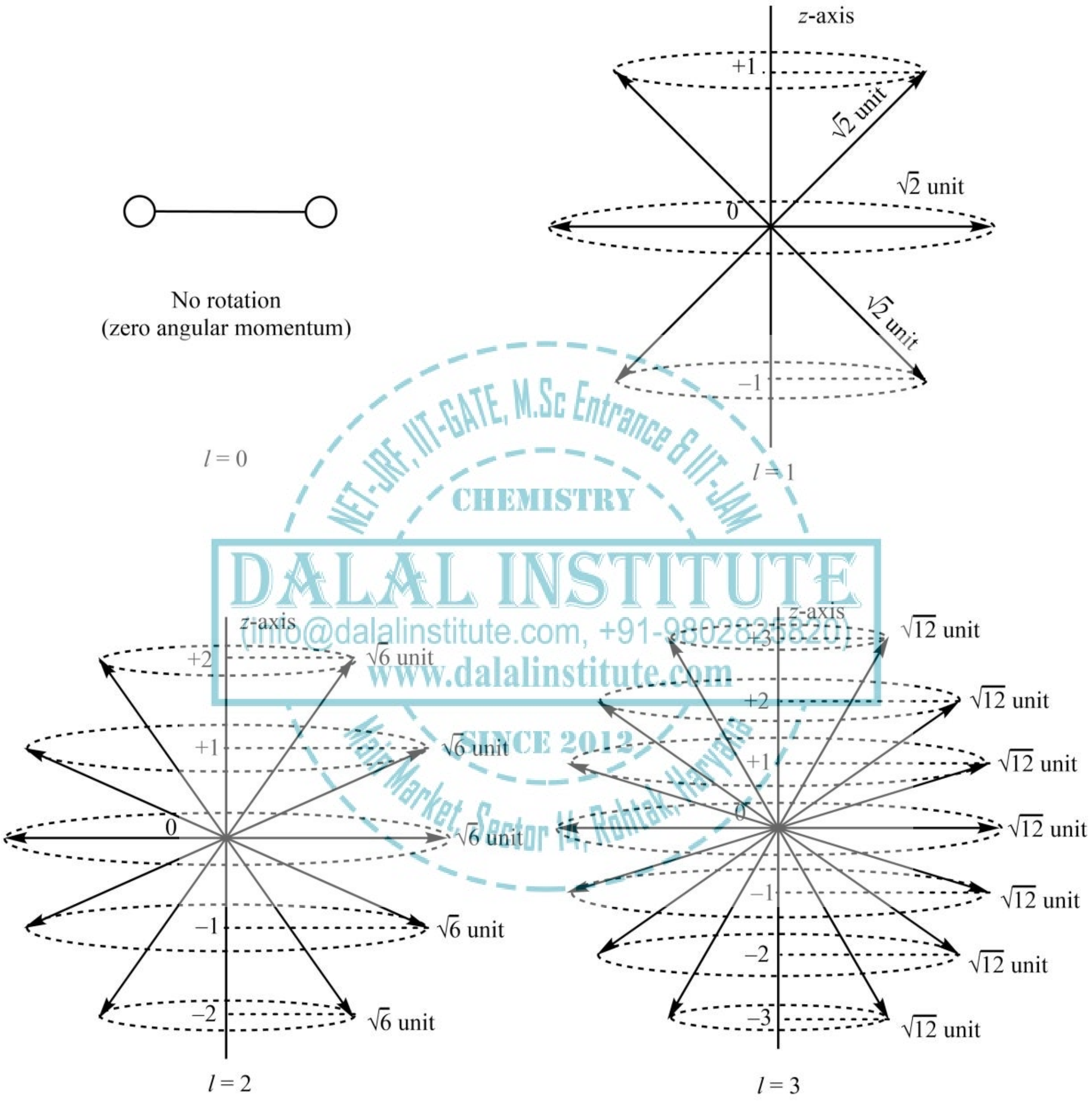

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Figure 11. The space quantization of angular momentum of the rigid rotator in $l = 0, 1, 2$ and 3 states.

It is also worthy to mention that the concept of space quantization is equally applicable to the angular momentums of all other systems also like orbital or spin angular momentum of electrons or nuclei.

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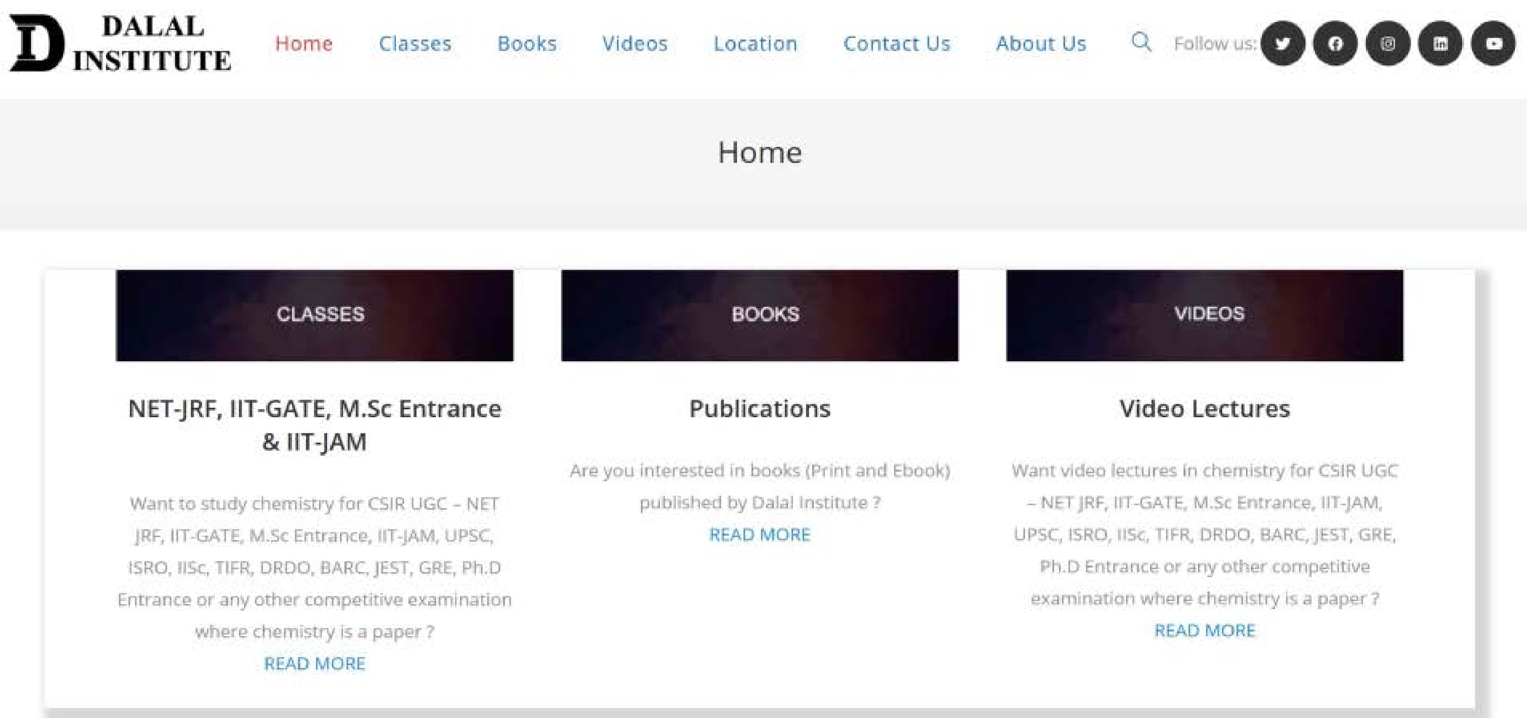

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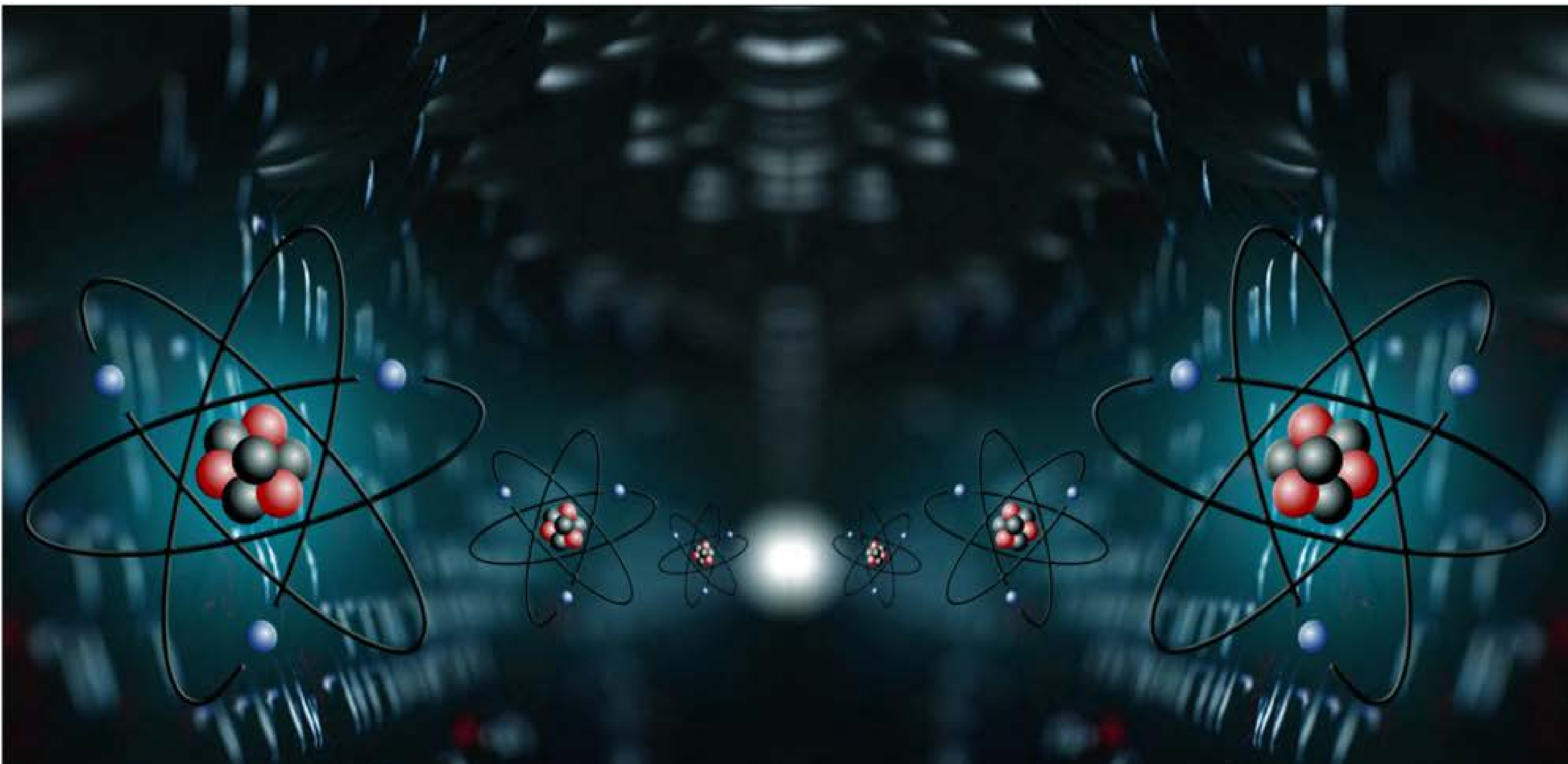

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