❖ Schrodinger Wave Equation for Three Dimensional Rigid Rotator

In order to study the rotational behavior of a diatomic molecule, consider a system two masses m_1 and m_2 joined by a rigid rod of length "r". Now assume that this dumbbell type geometry rotates about an axis that is perpendicular to r and passes through the center of mass.

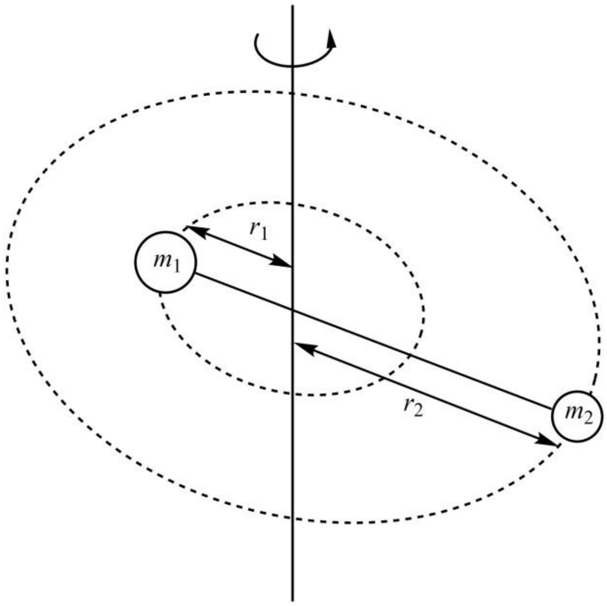

Figure 7. The pictorial representation of the diatomic rigid rotator in classical mechanics.

If v_1 and v_2 are the velocities of the mass m_1 and m_2 revolving about the axis of rotation, the total kinetic energy (T) of the rotator can be given by the following relation.

$$T = \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 \quad (121)$$

Since we know that linear velocity v is simply equal to the angular velocity ω multiplied by the radius of rotation r i.e. $v = \omega r$, the equation (121) takes the form

$$T = \frac{1}{2}m_1(r_1\omega)^2 + \frac{1}{2}m_2(r_2\omega)^2 \quad (122)$$

$$T = \frac{1}{2}(m_1 r_1^2 + m_2 r_2^2)\omega^2 \quad (123)$$

$$T = \frac{1}{2}I\omega^2 \quad (123)$$

Where I is the moment of inertia with definition $I = \sum m_i r_i^2$. Furthermore, we know from mass-center that

$$m_1r_1 = m_2r_2 \tag{124}$$

Now since $r = r_1 + r_2$, we rearrange equation (124) to give

$$r_1 = \frac{m_2}{m_1 + m_2}r \qquad and \qquad r_2 = \frac{m_1}{m_1 + m_2}r \tag{125}$$

In the two-mass system $I = m_1r_1^2 + m_2r_2^2$, so have

$$I = m_1\left(\frac{m_2}{m_1 + m_2}r\right)^2 + m_2\left(\frac{m_1}{m_1 + m_2}r\right)^2 \tag{126}$$

$$I = \left(\frac{m_1m_2}{m_1 + m_2}\right)r^2 \tag{127}$$

$$I = \mu r^2 \tag{128}$$

Where $\mu = m_1m_2/m_1 + m_2$ is the reduced mass of the rigid diatomic system. Since we that the kinetic energy and linear moment of a particle of mass m moving with velocity v are

$$T = \frac{1}{2}mv^2 \qquad and \qquad p = mv \tag{129}$$

The counterparts in the angular motion can be written as

$$T = \frac{1}{2}I\omega^2 \qquad and \qquad L = I\omega \tag{130}$$

Multiplying and dividing the rotational kinetic energy by I, we have

$$T = \frac{I^2\omega^2}{2I} = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{131}$$

It is clear from the above equation that the kinetic energy of a classical rotator can have any value because the value-domain of angular velocity is continuous. Moreover, as no external force is working on the rotator, the potential can be set to zero. In other words, the Hamiltonian for diatomic rigid rotator can be given as

$$\hat{H} = \hat{T} + \hat{V} \tag{132}$$

$$\hat{H} = \frac{\hat{L}^2}{2I} + 0 \tag{133}$$

The expression for the operator $\hat{L}^2$ in polar coordinates is

$$L^2 = -\frac{h^2}{4\pi^2}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial}{\partial\phi}\right] \tag{134}$$

Using equation (134) in equation (133), the Hamiltonian operator takes the form

$$\hat{H} = -\frac{h^2}{8\pi^2 I}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial}{\partial\phi}\right] + 0 \tag{135}$$

Now, let ψ be the function that describes all the rotational states of the diatomic rigid rotator. The operation of Hamiltonian operator over ψ can be rearranged to give to construct the Schrodinger wave equation; and we all know that the wave function as well the energy, both are the obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\hat{H}\psi = E\psi \tag{136}$$

After putting the expression of the Hamiltonian operator from equation (135) in equation (136), we get

$$-\frac{h^2}{8\pi^2 I}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial}{\partial\phi}\right]\psi = E\psi \tag{137}$$

or

$$-\frac{h^2}{8\pi^2 I}\left[\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi}\right] = E\psi \tag{138}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi} = -\frac{8\pi^2 IE\psi}{h^2} \tag{139}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\psi}{\partial\phi} + \frac{8\pi^2 IE\psi}{h^2} = 0 \tag{140}$$

The above differential equation contains two variable ϕ and θ, and therefore, is difficult to solve. Thus, we need to use the same mathematical technique we used to study particle in a 3-dimensional box i.e. the separation of variables. To do so, consider the total wavefunction as the product of two independent, one θ-dependent and other as a ϕ-dependent function only i.e.

$$\psi(\theta,\phi) = \psi(\theta)\times\psi(\phi) = \Theta\times\Phi \tag{141}$$

After putting the value of equation (141) in equation (140), we get

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta\Phi}{\partial\theta}\right) + \frac{1}{Sin^2\,\theta}\frac{\partial\Theta\Phi}{\partial\phi} + \frac{8\pi^2 IE\Theta\Phi}{h^2} = 0 \tag{142}$$

Since the first and second terms contain the partial derivatives w.r.t. θ and ϕ, respectively; function Φ and Θ must be kept constant correspondingly, i.e.,

$$\Phi\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\frac{1}{Sin^2\,\theta}\frac{\partial\Phi}{\partial\phi}+\frac{8\pi^2IE\Theta\Phi}{h^2}=0 \tag{143}$$

Dividing the above equation by $\Theta\Phi$, the equation (143) takes the form

$$\frac{1}{\Theta}\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{Sin^2\,\theta}\frac{\partial\Phi}{\partial\phi}+\frac{8\pi^2IE}{h^2}=0 \tag{144}$$

After multiplying equation (144) by $Sin^2\theta$, we get

$$\frac{Sin\,\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial\Phi}{\partial\phi}+\frac{8\pi^2IE}{h^2}Sin^2\theta=0 \tag{145}$$

Rearranging

$$\frac{Sin\,\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2IE}{h^2}Sin^2\theta=-\frac{1}{\Phi}\frac{\partial\Phi}{\partial\phi} \tag{146}$$

At this point, we can set both sides equal to constant m^2 i.e.

$$\frac{Sin\,\theta}{\Theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2IE}{h^2}Sin^2\theta=m^2=-\frac{1}{\Phi}\frac{\partial\Phi}{\partial\phi} \tag{147}$$

The equation (147) can be fragmented into two equations, each containing a single variable i.e.

$$\frac{\partial\Phi}{\partial\phi}+m^2\Phi=0 \tag{148}$$

And

$$Sin\,\theta\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\frac{8\pi^2IE}{h^2}Sin^2\theta-m^2\Theta=0 \tag{149}$$

Now dividing the above equation by $Sin^2\theta$, we get

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\Theta\frac{8\pi^2IE}{h^2}-\frac{m^2\Theta}{Sin^2\theta}=0 \tag{150}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\frac{8\pi^2IE}{h^2}-\frac{m^2}{Sin^2\theta}\right)\Theta=0 \tag{151}$$

or

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{Sin^2\theta}\right)\Theta=0 \tag{152}$$

Where the constant β is defined as

$$\beta = \frac{8\pi^2 IE}{h^2} \tag{153}$$

The solution of Φ equation: Recall the differential equation obtained after separation of variables having ϕ dependence i.e.

$$\frac{\partial \Phi}{\partial \phi} + m^2 \Phi = 0 \tag{154}$$

The general solution of such an equation is

$$\Phi(\phi) = N e^{im\phi} \tag{155}$$

Where N represents the normalization constant. The wavefunction given above will be acceptable only if m has integer value i.e. $0, \pm 1, \pm 2$, etc. This can be understood in terms of single-valued, continuous and finite nature of quantum states.

i) The boundary condition for function Φ: If we replace the angle "ϕ" with "$\phi + 2\pi$", the position of the point under consideration should remain the same i.e.

$$\Phi(\phi + 2\pi) = \Phi(\phi) \tag{156}$$

Therefore

$$N e^{im(\phi+2\pi)} = N e^{im\phi} \tag{157}$$

or

$$e^{im(\phi+2\pi)} = e^{im\phi} \tag{158}$$

$$e^{im\phi}.e^{im2\pi} = e^{im\phi} \tag{159}$$

$$e^{im2\pi} = e^{im\phi} e^{-im\phi} \tag{160}$$

$$e^{im2\pi} = e^{im\phi - im\phi} = e^0 \tag{161}$$

$$e^{im2\pi} = 1 \tag{162}$$

Since we know from the Euler's expansion $e^{ix} = Cos\ x + i\ Sin\ x$, the equation (162) takes the form

$$e^{im2\pi} = Cos\ 2\pi m + i\ Sin\ 2\pi m \tag{163}$$

After putting the value of equation (163) in equation (162), we get

$$Cos\ 2\pi m + i\ Sin\ 2\pi m = 1 \tag{164}$$

The relation holds true only when we use $m = 0, \pm 1, \pm 2, \pm 3, \pm 4$, etc.

ii) The normalization constant for function Φ: In order to determine the normalization constant for the Φ function, we must put the squared-integral over whole configuration space as unity i.e.

$$\int_0^{2\pi} \Phi^*\Phi \, d\phi = 1 \tag{165}$$

or

$$N^2 \int_0^{2\pi} e^{im\phi}.e^{-im\phi} \, d\phi = 1 \tag{166}$$

$$N^2 \int_0^{2\pi} e^{im\phi-im\phi} \, d\phi = N^2 \int_0^{2\pi} e^0 \, d\phi = 1 \tag{167}$$

$$N^2[\phi]_0^{2\pi} = N^2[2\pi] = 1 \tag{168}$$

$$N = \sqrt{\frac{1}{2\pi}} \tag{169}$$

After using the value of normalization constant in equation (155), we get

$$\Phi(\phi) = \sqrt{\frac{1}{2\pi}} e^{\pm im\phi} \tag{170}$$

Solution of Θ equation: Recall the differential equation obtained after separation of variables having θ dependence i.e.

$$\frac{1}{Sin\,\theta}\frac{\partial}{\partial\theta}\left(Sin\,\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{Sin^2\theta}\right)\Theta = 0 \tag{171}$$

After defining a new variable $x = Cos\,\theta$, we have

$$Sin^2\theta + Cos^2\theta = 1 \tag{172}$$

$$Sin^2\theta = 1 - Cos^2\theta \tag{173}$$

$$Sin\,\theta = \sqrt{1 - Cos^2\theta} \tag{174}$$

$$Sin\,\theta = \sqrt{1 - x^2} \tag{175}$$

Also, since we assumed $x = Cos\,\theta$, the first derivative w.r.t. θ will be

$$\frac{\partial x}{\partial \theta} = -Sin\,\theta \tag{176}$$

The derivative of Θ function w.r.t. θ can be rewritten as

$$\frac{\partial \Theta}{\partial \theta} = \frac{\partial \Theta}{\partial x} \cdot \frac{\partial x}{\partial \theta} \tag{177}$$

After putting the values of $\partial x/\partial \theta$ from equation (176) in equation (177), we get

$$\frac{\partial \Theta}{\partial \theta} = -Sin\,\theta \frac{\partial \Theta}{\partial x} \tag{178}$$

After removing Θ from both sides

$$\frac{\partial}{\partial \theta} = -Sin\,\theta \frac{\partial}{\partial x} \tag{179}$$

Multiplying both sides of equation (178) by $Sin\,\theta$, we have

$$Sin\,\theta \frac{\partial \Theta}{\partial \theta} = -Sin^2\,\theta \frac{\partial \Theta}{\partial x} \tag{180}$$

$$Sin\,\theta \frac{\partial \Theta}{\partial \theta} = -(1 - x^2) \frac{\partial \Theta}{\partial x} \tag{181}$$

Now, after putting the values of equation (179) and (181) in equation (171), we get

$$\frac{1}{Sin\,\theta}\left(-Sin\,\theta \frac{\partial}{\partial x}\right)\left[-(1 - x^2)\frac{\partial \Theta}{\partial x}\right] + \left(\beta - \frac{m^2}{1 - x^2}\right)\Theta = 0 \tag{182}$$

or

$$\frac{\partial}{\partial x}\left[(1 - x^2)\frac{\partial \Theta}{\partial x}\right] + \left(\beta - \frac{m^2}{1 - x^2}\right)\Theta = 0 \tag{183}$$

The equation given above is a Legendre's polynomial and has physical significance only in the range of $x = +1$ to -1. Therefore, consider that one more form of Θ function so that this condition is satisfied i.e.

$$\Theta(\theta) = (1 - x^2)^{\frac{m}{2}}.X(x) \tag{184}$$

Where X is a function depending upon variable x. The differentiation of the above equation w.r.t. x yields

$$\frac{\partial \Theta}{\partial x} = -mx(1 - x^2)^{\frac{m}{2}-1}.X + (1 - x^2)^{\frac{m}{2}}.\frac{dX}{dx} \tag{185}$$

After multiplying the above equation by $1 - x^2$ and $\partial/\partial x$, we get

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial\Theta}{\partial x}\right]=\frac{\partial}{\partial x}\left[-mx(1-x^2)^{\frac{m}{2}}.X+(1-x^2)^{\frac{m}{2}+1}.\frac{dX}{dx}\right] \tag{186}$$

$$=\left[-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{\frac{m}{2}-1}\right]X-\left[2x(m+1)(1-x^2)^{\frac{m}{2}}\right]X' + \left[(1-x^2)^{\frac{m}{2}+1}\right]X'' \tag{187}$$

Where $\partial/\partial x$ and $\partial^2/\partial x^2$ are represented by the symbol X' and X'', respectively. Now, after using the value of equation (184) and equation (187) in equation (183), we get

$$\left[-m(1-x^2)^{m/2}+m^2x^2(1-x^2)^{\frac{m}{2}-1}\right]X-\left[2x(m+1)(1-x^2)^{\frac{m}{2}}\right]X' + \left[(1-x^2)^{\frac{m}{2}+1}\right]X''+\left(\beta-\frac{m^2}{1-x^2}\right)(1-x^2)^{\frac{m}{2}}.X=0 \tag{188}$$

Dividing above expression by $(1-x^2)^{m/2}$, we have

$$(1-x^2)X''-2(m+1)xX'+[\beta-m(m+1)]X=0 \tag{189}$$

or

$$(1-x^2)X''-2\alpha xX'+\lambda X=0 \tag{190}$$

Where $\alpha=m+1$ and $\lambda=\beta-m(m+1)$. Now assume that the function X can be expressed as a power series expansion as given below.

$$X=a_0+a_1x+a_2x^2+a_3x^3\dots\dots\dots \tag{191}$$

$$X'=a_1+2a_2x+3a_3x^2\dots\dots\dots \tag{192}$$

$$X''=2a_2+6a_3x+12a_4x^2\dots\dots\dots \tag{193}$$

Putting values of equation (191-193) in equation (190), we get

$$(1-x^2)(2a_2+6a_3x+12a_4x^2+20a_5x^3)-2\alpha x(a_1+2a_2x+3a_3x^2+4a_4x^3)+\lambda(a_0+a_1x+a_2x^2+a_3x^3)=0 \tag{194}$$

or

$$(2a_2+\lambda a_0)+[6a_3+(\lambda-2\alpha)a_1]x+[12a_4+(\lambda-2\alpha-2)a_2]x^2\dots\dots\dots=0 \tag{195}$$

The above equation is satisfied only if each term on the left-hand side is individually equal to zero i.e. coefficients of each power of x are vanish. The general expression for the coefficients must follow the condition given below.

$$(n+1)(n+2)a_{n+2}+[\lambda-2n\alpha-n(n-1)]a_n=0 \tag{196}$$

Where $n = 0, 1, 2, 3$ etc. Summarizing the result, we can write

$$a_{n+2} = \frac{2n\alpha + n(n-1) - \lambda}{(n+1)(n+2)} a_n \quad (197)$$

After putting values of α and λ in equation (197), we get

$$\frac{a_{n+2}}{a_n} = \frac{(n+m)(n+m+1) - \beta}{(n+1)(n+2)} \quad (198)$$

Which is the Recursion formula for the coefficients of the power of x. Now, in order to obtain a valid wavefunction, the power series must contain a finite number of terms which is possible only if numerator becomes zero i.e.

$$(n+m)(n+m+1) - \beta = 0 \quad (199)$$

$$\beta = (n+m)(n+m+1) \quad (200)$$

Since we know that m as well n both are the whole numbers, their sum must also be a whole number. Therefore, the sum of n and m can be replaced by another whole number symbolized by l i.e.

$$\beta = l(l+1) \quad (201)$$

Where $l = 0, 1, 2, 3$ etc. After putting the value of β from equation (201) in equation (183), we get

$$\frac{\partial}{\partial x}\left[(1-x^2)\frac{\partial\Theta}{\partial x}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]\Theta = 0 \quad (202)$$

The general solution of equation (202) is

$$\Theta = NP_l^m(x) = NP_l^m(Cos\ \theta) \quad (203)$$

Where N is the normalization constant and $P_l^m(x)$ is the associated "Legendre function" which is defined as given below.

$$P_l^m(x) = (1-x^2)^{m/2}\frac{d^m P_l(x)}{dx^m} \quad (204)$$

Where $P_l(x)$ is the Legendre polynomial given by

$$P_l(x) = \frac{1}{2^l\, l!}\frac{d^l(x^2-1)^l}{dx^l} \quad (205)$$

In order to proceed further, we must discuss the concept of orthogonality and the normalization of the "Legendre's function".

i) Orthogonality of associated Legendre's function: The orthogonality of the associated Legendre's polynomial follows the conditions given below.

$$\int_{-1}^{+1} P_k^m(x)\, P_l^m(x) = 0 \qquad if\ k \neq l \tag{206}$$

$$\int_{-1}^{+1} P_k^m(x)\, P_l^m(x) = \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} \qquad if\ k = l \tag{207}$$

ii) Normalization of associated Legendre's function: The normalization of the associated Legendre's polynomial follows the conditions given below.

$$\int_{-1}^{+1} \Theta_{m,l}\, \Theta_{m,l}^*(d\theta) = 1 \tag{208}$$

$$N^2 \int_{-1}^{+1} P_k^m(x)\, P_l^m(x)\, dx = 1 \tag{209}$$

After solving the integral, we get

$$N^2 . \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} = 1 \tag{210}$$

$$N = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} \tag{211}$$

Using the value of normalization constant in equation (203), we get

$$\Theta(\theta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\ \theta) \tag{212}$$

The complete eigenfunction of rigid rotator: The total eigenfunction for the rigid rotator now can be obtained by simply multiplying the solution of ϕ-dependent and θ-dependent differential equations i.e. equation (170) and equation (203).

$$\psi_{l,m}(\theta,\phi) = \Theta_{l,m}(\theta)\Phi_m(\phi) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\ \theta). \sqrt{\frac{1}{2\pi}}\, e^{\pm im\phi} \tag{213}$$

$$\psi_{l,m}(\theta,\phi) = \sqrt{\frac{1}{2\pi}} \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} . P_l^m(Cos\ \theta). e^{\pm im\phi} \tag{214}$$

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Volume I

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