

❖ 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.

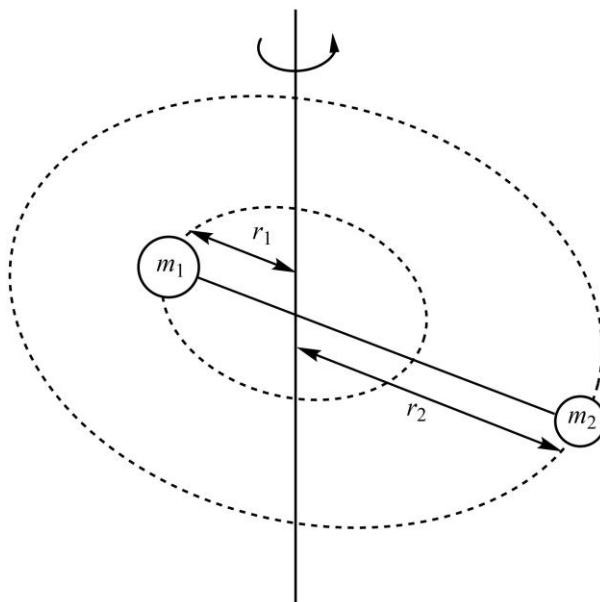


Figure 7. The pictorial representation of the diatomic rigid rotator in classical mechanics.

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.

$$T = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 \quad (121)$$

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

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

$$T = \frac{1}{2}(m_1r_1^2 + m_2r_2^2)\omega^2 \quad (123)$$

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

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

$$m_1 r_1 = m_2 r_2 \quad (124)$$

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

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r \quad (125)$$

In the two-mass system $I = m_1 r_1^2 + m_2 r_2^2$, so have

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

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

$$I = \mu r^2 \quad (128)$$

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

$$T = \frac{1}{2} m v^2 \quad \text{and} \quad p = m v \quad (129)$$

The counterparts in the angular motion can be written as

$$T = \frac{1}{2} I \omega^2 \quad \text{and} \quad L = I \omega \quad (130)$$

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

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

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

$$\hat{H} = \hat{T} + \hat{V} \quad (132)$$

$$\hat{H} = \frac{\hat{L}^2}{2I} + 0 \quad (133)$$

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

$$L^2 = -\frac{\hbar^2}{4\pi^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \right] \quad (134)$$

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

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

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

$$\hat{H}\psi = E\psi \quad (136)$$

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

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

or

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

or

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial \psi}{\partial \phi} - \frac{8\pi^2 I E \psi}{h^2} = 0 \quad (139)$$

or

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial \psi}{\partial \phi} + \frac{8\pi^2 I E \psi}{h^2} = 0 \quad (140)$$

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.

$$\psi(\theta, \phi) = \psi(\theta) \times \psi(\phi) = \Theta \times \Phi \quad (141)$$

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

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta \Phi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial \Theta \Phi}{\partial \phi} + \frac{8\pi^2 I E \Theta \Phi}{h^2} = 0 \quad (142)$$

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.,

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

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

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

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

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

Rearranging

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

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

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

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

$$\frac{\partial \Phi}{\partial \phi} + m^2 \Phi = 0 \quad (148)$$

And

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \theta}{\partial \theta} \right) + \theta \frac{8\pi^2 IE}{h^2} \sin^2 \theta - m^2 \theta = 0 \quad (149)$$

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

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

or

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

or

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \theta}{\partial \theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) \theta = 0 \quad (152)$$

Where the constant β is defined as

$$\beta = \frac{8\pi^2 IE}{h^2} \quad (153)$$

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

$$\frac{\partial \Phi}{\partial \phi} + m^2 \Phi = 0 \quad (154)$$

The general solution of such an equation is

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

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.

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (156)$$

Therefore

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

or

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

$$e^{im\phi} \cdot e^{im2\pi} = e^{im\phi} \quad (159)$$

$$e^{im2\pi} = e^{im\phi} e^{-im\phi} \quad (160)$$

$$e^{im2\pi} = e^{im\phi - im\phi} = e^0 \quad (161)$$

$$e^{im2\pi} = 1 \quad (162)$$

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

$$e^{im2\pi} = \cos 2\pi m + i \sin 2\pi m \quad (163)$$

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

$$\cos 2\pi m + i \sin 2\pi m = 1 \quad (164)$$

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.

$$\int_0^{2\pi} \Phi^* \Phi d\phi = 1 \quad (165)$$

or

$$N^2 \int_0^{2\pi} e^{im\phi} \cdot e^{-im\phi} d\phi = 1 \quad (166)$$

$$N^2 \int_0^{2\pi} e^{im\phi - im\phi} d\phi = N^2 \int_0^{2\pi} e^0 d\phi = 1 \quad (167)$$

$$N^2 [\phi]_0^{2\pi} = N^2 [2\pi] = 1 \quad (168)$$

$$N = \sqrt{\frac{1}{2\pi}} \quad (169)$$

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

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

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

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

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

$$\sin^2 \theta + \cos^2 \theta = 1 \quad (172)$$

$$\sin^2 \theta = 1 - \cos^2 \theta \quad (173)$$

$$\sin \theta = \sqrt{1 - \cos^2 \theta} \quad (174)$$

$$\sin \theta = \sqrt{1 - x^2} \quad (175)$$

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

$$\frac{\partial x}{\partial \theta} = -\sin \theta \quad (176)$$

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

$$\frac{\partial \Theta}{\partial \theta} = \frac{\partial \Theta}{\partial x} \cdot \frac{\partial x}{\partial \theta} \quad (177)$$

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

$$\frac{\partial \Theta}{\partial \theta} = -\sin \theta \frac{\partial \Theta}{\partial x} \quad (178)$$

After removing Θ from both sides

$$\frac{\partial}{\partial \theta} = -\sin \theta \frac{\partial}{\partial x} \quad (179)$$

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

$$\sin \theta \frac{\partial \Theta}{\partial \theta} = -\sin^2 \theta \frac{\partial \Theta}{\partial x} \quad (180)$$

$$\sin \theta \frac{\partial \Theta}{\partial \theta} = -(1-x^2) \frac{\partial \Theta}{\partial x} \quad (181)$$

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

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

or

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

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.

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

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

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

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

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

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

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

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

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

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

or

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

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.

$$X = a_0 + a_1x + a_2x^2 + a_3x^3 + \dots \quad (191)$$

$$X' = a_1 + 2a_2x + 3a_3x^2 + \dots \quad (192)$$

$$X'' = 2a_2 + 6a_3x + 12a_4x^2 + \dots \quad (193)$$

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

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

or

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

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.

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

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.

$$\int_{-1}^{+1} P_k^m(x) P_l^m(x) dx = 0 \quad \text{if } k \neq l \quad (206)$$

$$\int_{-1}^{+1} P_k^m(x) P_l^m(x) dx = \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} \quad \text{if } k = l \quad (207)$$

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

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

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

After solving the integral, we get

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

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

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

$$\theta(\theta) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos \theta) \quad (212)$$

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).

$$\psi_{l,m}(\theta, \phi) = \theta_{l,m}(\theta) \Phi_m(\phi) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos \theta) \cdot \sqrt{\frac{1}{2\pi}} e^{\pm im\phi} \quad (213)$$

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

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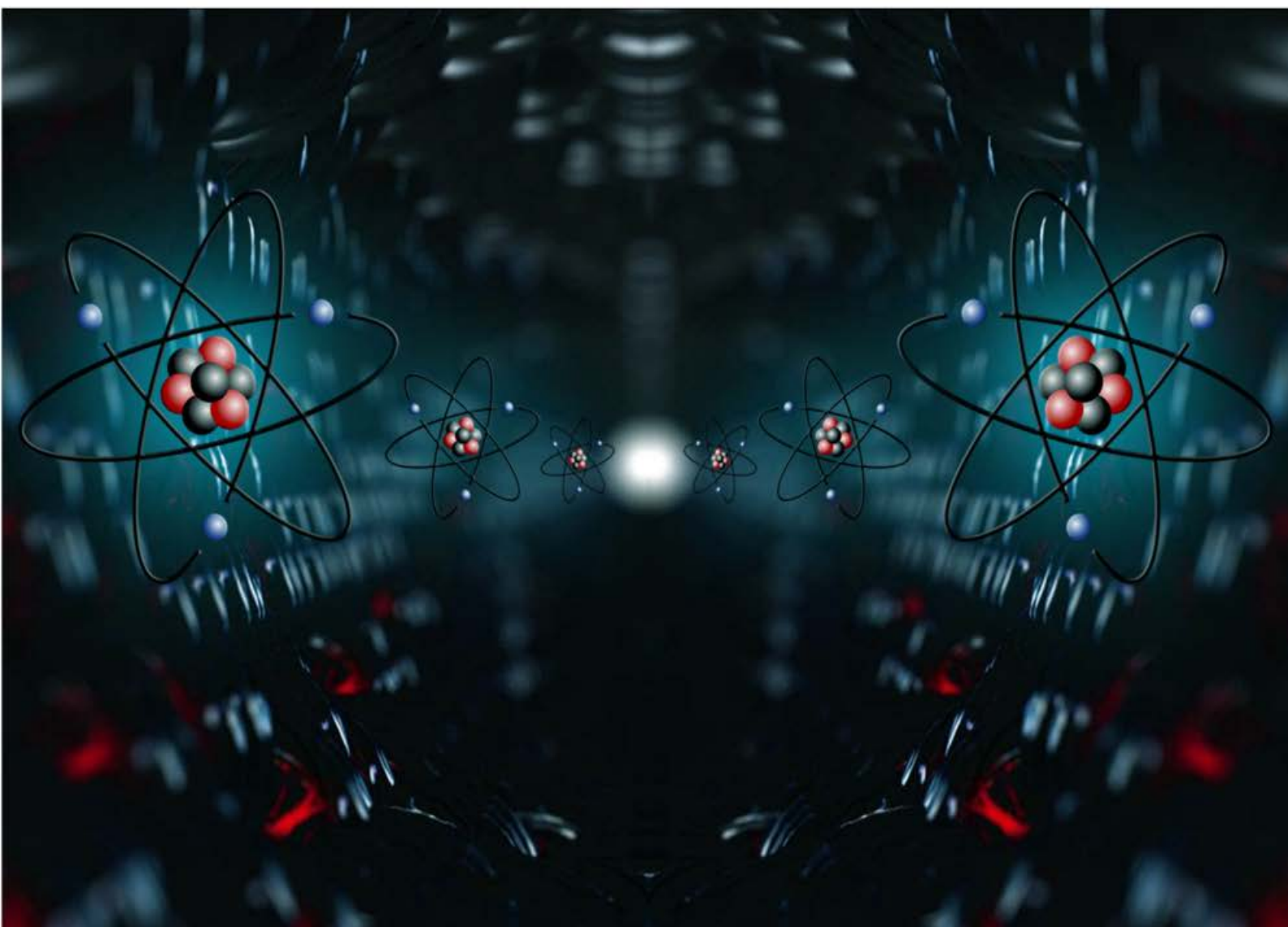
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Volume I

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Table of Contents

CHAPTER 1	11
Quantum Mechanics – I	11
❖ Postulates of Quantum Mechanics	11
❖ Derivation of Schrodinger Wave Equation.....	16
❖ Max-Born Interpretation of Wave Functions	21
❖ The Heisenberg’s Uncertainty Principle.....	24
❖ Quantum Mechanical Operators and Their Commutation Relations.....	29
❖ Hermitian Operators – Elementary Ideas, Quantum Mechanical Operator for Linear Momentum, Angular Momentum and Energy as Hermitian Operator	52
❖ The Average Value of the Square of Hermitian Operators	62
❖ Commuting Operators and Uncertainty Principle (x & p ; E & t).....	63
❖ Schrodinger Wave Equation for a Particle in One Dimensional Box.....	65
❖ Evaluation of Average Position, Average Momentum and Determination of Uncertainty in Position and Momentum and Hence Heisenberg’s Uncertainty Principle.....	70
❖ Pictorial Representation of the Wave Equation of a Particle in One Dimensional Box and Its Influence on the Kinetic Energy of the Particle in Each Successive Quantum Level	75
❖ Lowest Energy of the Particle	80
❖ Problems	82
❖ Bibliography	83
CHAPTER 2	84
Thermodynamics – I	84
❖ Brief Resume of First and Second Law of Thermodynamics.....	84
❖ Entropy Changes in Reversible and Irreversible Processes.....	87
❖ Variation of Entropy with Temperature, Pressure and Volume	92
❖ Entropy Concept as a Measure of Unavailable Energy and Criteria for the Spontaneity of Reaction	94
❖ Free Energy, Enthalpy Functions and Their Significance, Criteria for Spontaneity of a Process ...	98
❖ Partial Molar Quantities (Free Energy, Volume, Heat Concept).....	104
❖ Gibb’s-Duhem Equation.....	108
❖ Problems	111
❖ Bibliography	112

CHAPTER 3	113
Chemical Dynamics – I	113
❖ Effect of Temperature on Reaction Rates.....	113
❖ Rate Law for Opposing Reactions of 1st Order and 2nd Order.....	119
❖ Rate Law for Consecutive & Parallel Reactions of 1st Order Reactions	127
❖ Collision Theory of Reaction Rates and Its Limitations	135
❖ Steric Factor.....	141
❖ Activated Complex Theory	143
❖ Ionic Reactions: Single and Double Sphere Models	147
❖ Influence of Solvent and Ionic Strength.....	152
❖ The Comparison of Collision and Activated Complex Theory	157
❖ Problems.....	158
❖ Bibliography	159
CHAPTER 4	160
Electrochemistry – I: Ion-Ion Interactions	160
❖ The Debye-Huckel Theory of Ion-Ion Interactions	160
❖ Potential and Excess Charge Density as a Function of Distance from the Central Ion.....	168
❖ Debye-Huckel Reciprocal Length	173
❖ Ionic Cloud and Its Contribution to the Total Potential	176
❖ Debye-Huckel Limiting Law of Activity Coefficients and Its Limitations.....	178
❖ Ion-Size Effect on Potential.....	185
❖ Ion-Size Parameter and the Theoretical Mean - Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions.....	187
❖ Debye-Huckel-Onsager Treatment for Aqueous Solutions and Its Limitations.....	190
❖ Debye-Huckel-Onsager Theory for Non-Aqueous Solutions.....	195
❖ The Solvent Effect on the Mobility at Infinite Dilution	196
❖ Equivalent Conductivity (Λ) vs Concentration $C^{1/2}$ as a Function of the Solvent	198
❖ Effect of Ion Association Upon Conductivity (Debye-Huckel-Bjerrum Equation)	200
❖ Problems.....	209
❖ Bibliography	210
CHAPTER 5	211
Quantum Mechanics – II	211
❖ Schrodinger Wave Equation for a Particle in a Three Dimensional Box	211

❖ The Concept of Degeneracy Among Energy Levels for a Particle in Three Dimensional Box	215
❖ Schrodinger Wave Equation for a Linear Harmonic Oscillator & Its Solution by Polynomial Method	217
❖ Zero Point Energy of a Particle Possessing Harmonic Motion and Its Consequence	229
❖ Schrodinger Wave Equation for Three Dimensional Rigid Rotator.....	231
❖ Energy of Rigid Rotator	241
❖ Space Quantization.....	243
❖ Schrodinger Wave Equation for Hydrogen Atom: Separation of Variable in Polar Spherical Coordinates and Its Solution	247
❖ Principal, Azimuthal and Magnetic Quantum Numbers and the Magnitude of Their Values.....	268
❖ Probability Distribution Function.....	276
❖ Radial Distribution Function	278
❖ Shape of Atomic Orbitals (<i>s</i> , <i>p</i> & <i>d</i>).....	281
❖ Problems.....	287
❖ Bibliography	288
CHAPTER 6	289
Thermodynamics – II.....	289
❖ Clausius-Clapeyron Equation.....	289
❖ Law of Mass Action and Its Thermodynamic Derivation	293
❖ Third Law of Thermodynamics (Nernst Heat Theorem, Determination of Absolute Entropy, Unattainability of Absolute Zero) And Its Limitation.....	296
❖ Phase Diagram for Two Completely Miscible Components Systems	304
❖ Eutectic Systems (Calculation of Eutectic Point).....	311
❖ Systems Forming Solid Compounds A_xB_y with Congruent and Incongruent Melting Points	321
❖ Phase Diagram and Thermodynamic Treatment of Solid Solutions.....	332
❖ Problems.....	342
❖ Bibliography	343
CHAPTER 7	344
Chemical Dynamics – II	344
❖ Chain Reactions: Hydrogen-Bromine Reaction, Pyrolysis of Acetaldehyde, Decomposition of Ethane.....	344
❖ Photochemical Reactions (Hydrogen-Bromine & Hydrogen-Chlorine Reactions).....	352
❖ General Treatment of Chain Reactions (Ortho-Para Hydrogen Conversion and Hydrogen-Bromine Reactions).....	358

❖ Apparent Activation Energy of Chain Reactions	362
❖ Chain Length	364
❖ Rice-Herzfeld Mechanism of Organic Molecules Decomposition (Acetaldehyde)	366
❖ Branching Chain Reactions and Explosions (H_2-O_2 Reaction)	368
❖ Kinetics of (One Intermediate) Enzymatic Reaction: Michaelis-Menten Treatment	371
❖ Evaluation of Michaelis's Constant for Enzyme-Substrate Binding by Lineweaver-Burk Plot and Eadie-Hofstee Methods	375
❖ Competitive and Non-Competitive Inhibition	378
❖ Problems	388
❖ Bibliography	389
CHAPTER 8	390
Electrochemistry – II: Ion Transport in Solutions	390
❖ Ionic Movement Under the Influence of an Electric Field	390
❖ Mobility of Ions	393
❖ Ionic Drift Velocity and Its Relation with Current Density	394
❖ Einstein Relation Between the Absolute Mobility and Diffusion Coefficient	398
❖ The Stokes-Einstein Relation	401
❖ The Nernst-Einstein Equation	403
❖ Walden's Rule	404
❖ The Rate-Process Approach to Ionic Migration	406
❖ The Rate-Process Equation for Equivalent Conductivity	410
❖ Total Driving Force for Ionic Transport: Nernst-Planck Flux Equation	412
❖ Ionic Drift and Diffusion Potential	416
❖ The Onsager Phenomenological Equations	418
❖ The Basic Equation for the Diffusion	419
❖ Planck-Henderson Equation for the Diffusion Potential	422
❖ Problems	425
❖ Bibliography	426
INDEX	427



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