

CHAPTER 5

Quantum Mechanics – II

❖ Schrodinger Wave Equation for a Particle in a Three Dimensional Box

In the first chapter of this book, we derived and discussed the Schrodinger wave equation for a particle in the one-dimensional box. In this chapter, we will extend that procedure to the particle in a three-dimensional box. In order to do so, consider a particle trapped in a 3-dimensional box of length, breadth, and height as a , b and c , respectively. This means that this particle can travel in any direction i.e. along x -, y - and z -axis. The potential inside the box is 0, while outside to the box it is infinite.

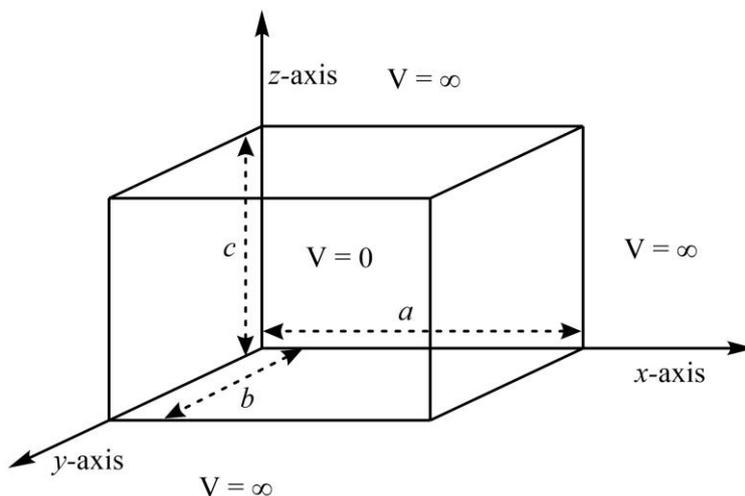


Figure 1. The particle in a three-dimensional box.

So far we have considered a quantum mechanical system of a particle trapped in a three-dimensional box. Now suppose that we need to find various physical properties associated with different states of this system. Had it been a classical system, we would use simple formulas from classical mechanics to determine the value of different physical properties. However, being a quantum mechanical system, we cannot use those expressions because they would give irrational results. Therefore, we need to use the postulates of quantum mechanics to evaluate various physical properties.

Let ψ be the function that describes all the states of the particle in a three-dimensional box. At this point we have no information about the exact mathematical expression of ψ ; nevertheless, we know that there is one operator that does not need the absolute expression of wave function but uses the symbolic form only, the Hamiltonian operator. The operation of Hamiltonian operator over this symbolic form 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 obtained as this second-order differential equation is solved. Mathematically, we can say that

$$\hat{H}\psi = E\psi \quad (1)$$

After putting the value of three-dimensional Hamiltonian in equation (1), we get

$$\left[\frac{-h^2}{8\pi^2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right] \psi = E\psi \quad (2)$$

or

$$\frac{-h^2}{8\pi^2m} \left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \right) + V\psi = E\psi \quad (3)$$

$$\frac{-h^2}{8\pi^2m} \left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \right) + V\psi - E\psi = 0 \quad (4)$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{h^2} (E - V)\psi = 0 \quad (5)$$

The above-mentioned second order differential equation is the Schrodinger wave equation for a particle moving along three dimensions. Since the conditions outside and inside the box are different, the equation (5) must be solved separately for both cases.

1. The solution of Schrodinger wave equation for outside the box: After putting the value of potential outside the box in equation (5) i.e. $V = \infty$, we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{h^2} (E - \infty)\psi = 0 \quad (6)$$

Since E is negligible in comparison to the ∞ , the above equation becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} - \infty\psi = 0 \quad (7)$$

$$\infty\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \quad (8)$$

$$\psi = \frac{1}{\infty} \left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \right) = 0 \quad (9)$$

The physical significance of the equation (9) is that the particle cannot go outside the box, and is always reflected back when it strikes the boundaries. In other words, as the function describing the existence of particles is zero outside the box, the particle cannot exist outside the box.

2. The solution of Schrodinger wave equation for inside the box: After putting the value of potential inside the box in equation (5) i.e. $V = 0$, we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - 0) \psi = 0 \quad (10)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m E}{h^2} \psi = 0 \quad (11)$$

The above equation has three variables and is difficult to solve directly. Therefore, it is better to separate variable, we already know the steps to solve a one-variable equation. To do so, consider that the wave function ψ is the multiplication of three individual functions as

$$\psi(x, y, z) = \psi(x) \times \psi(y) \times \psi(z) = XYZ \quad (12)$$

Using the above expression in equation (11), we get

$$\frac{\partial^2 XYZ}{\partial x^2} + \frac{\partial^2 XYZ}{\partial y^2} + \frac{\partial^2 XYZ}{\partial z^2} + \frac{8\pi^2 m E}{h^2} XYZ = 0 \quad (13)$$

From the rules of partial derivative, the equation (13) takes the form

$$YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m E}{h^2} XYZ = 0 \quad (14)$$

Now divide the above equation by XYZ on both side i.e.

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m E}{h^2} = 0 \quad (15)$$

Assuming

$$k^2 = \frac{8\pi^2 m E}{h^2} \quad (16)$$

The equation (15) becomes

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} + k^2 = 0 \quad (17)$$

Also fragmenting the constant k^2 along three x -, y - and z -axis i.e. $k^2 = k_x^2 + k_y^2 + k_z^2$, the equation (17) can

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} + k_x^2 + k_y^2 + k_z^2 = 0 \quad (18)$$

The above equation can be written as the sum of three equations with only one variable in each i.e.

$$\frac{\partial^2 X}{\partial x^2} + k_x^2 X = 0 \quad (19)$$

$$\frac{\partial^2 Y}{\partial y^2} + k_y^2 Y = 0 \quad (20)$$

$$\frac{\partial^2 Z}{\partial z^2} + k_z^2 Z = 0 \quad (21)$$

The equations (19-21) are simple one-dimensional differential equations whose solutions can be obtained just like in the one-dimensional box. The solution of equation (19) will give the x -dependent wave function as well the energy distribution along x -axis i.e.

$$\psi_{n_x}(x) = X = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \quad \text{and} \quad E_{n_x} = \frac{n_x^2 h^2}{8ma^2} \quad (22)$$

Similarly, the solution of equation (20) will be

$$\psi_{n_y}(y) = Y = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \quad \text{and} \quad E_{n_y} = \frac{n_y^2 h^2}{8mb^2} \quad (23)$$

Just like the above two, the solution of equation (21) will be

$$\psi_{n_z}(z) = Z = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \quad \text{and} \quad E_{n_z} = \frac{n_z^2 h^2}{8mc^2} \quad (24)$$

After putting the expressions of individual wave functions from equation (22-24) in equation (12), the total wave function can be obtained i.e.

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad (25)$$

Since $k^2 = k_x^2 + k_y^2 + k_z^2$, the total energy must be the sum of individual energies i.e.

$$E_{n_x n_y n_z} = \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \frac{h^2}{8m} \quad (26)$$

Where n_x, n_y, n_z are the discrete variable whose permitted values from boundary conditions can be 0, 1, 2, 3, 4... ∞ . Nevertheless, it is worthy to note that even though the $n = 0$ is permitted by the boundary conditions, we still don't use it in equation (25); which is obviously because it makes the whole function zero.

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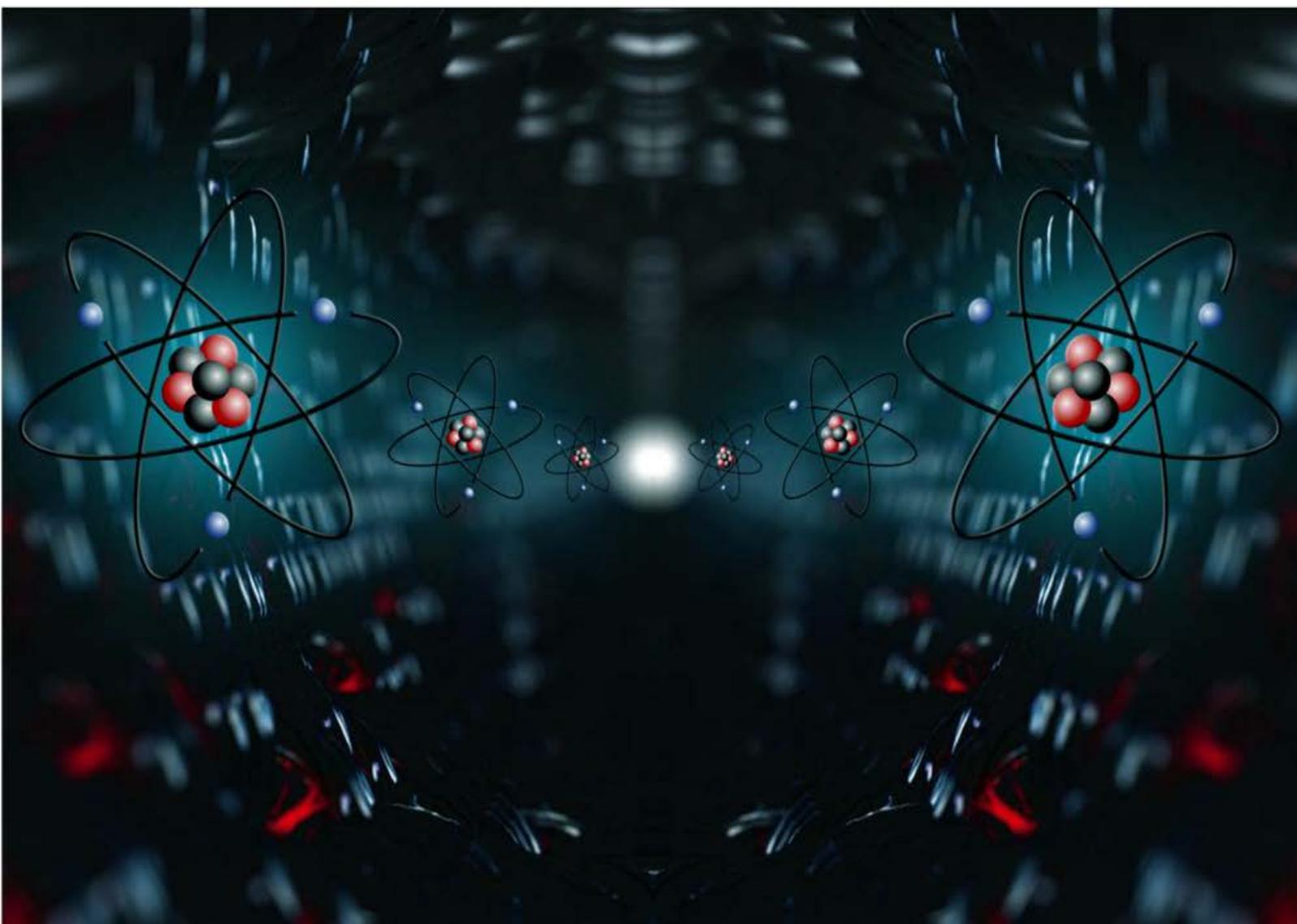
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A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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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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