Schrodinger Wave Equation for a Particle in One Dimensional Box

In the first section of this chapter, we discussed the postulates of quantum mechanics i.e. the step-by-step procedure to solve a quantum mechanical problem. Now it’s the time to implement those rules to the simplest quantum mechanical problem i.e. particle in a one-dimensional box. Consider a particle trapped in a one-dimensional box of length “a”, which means that this particle can travel in only one direction only, say along x-axis. The potential inside the box is V, while outside to the box it is infinite.

One other popular depiction of the particle in a one-dimensional box is also given in which the potential is shown vertically while the displacement is projected along the horizontal line.

So far we have considered a quantum mechanical system of a particle trapped in a one-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 \( \psi \) be the function that describes all the states of the particle in a one-dimensional box. At this point we have no information about the exact mathematical expression of \( \psi \); 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 the obtained as this second-order differential equation is solved. Mathematically, we can say that
\[ \hat{H}\psi = E\psi \quad (415) \]

After putting the value of one-dimensional Hamiltonian in equation (415), we get

\[ \left[ -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} + V \right] \psi = E\psi \quad (416) \]

or

\[ -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi \quad (417) \]

\[ -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2\psi}{\partial x^2} + V\psi - E\psi = 0 \quad (418) \]

or

\[ \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} V\psi = 0 \quad (419) \]

or

\[ \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} (E - V)\psi = 0 \quad (420) \]

The above-mentioned second order differential equation is the Schrödinger wave equation for a particle moving along one dimension only. Since the conditions outside and inside the box are different, the equation (420) 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 (420) i.e. \( V = \infty \), we get

\[ \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} (E - \infty)\psi = 0 \quad (421) \]

Since \( E \) is negligible in comparison to the \( \infty \), the above equation becomes

\[ \frac{\partial^2\psi}{\partial x^2} - \infty\psi = 0 \quad (422) \]

\[ \infty\psi = \frac{\partial^2\psi}{\partial x^2} \quad (423) \]

\[ \psi = \frac{1}{\infty} \frac{\partial^2\psi}{\partial x^2} = 0 \quad (424) \]

The physical significance of the equation (424) 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. Solution of Schrödinger wave equation for inside the box: After putting the value of potential inside the box in equation (420) i.e. $V = 0$, we get

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

(425)

or

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 mE}{h^2} \psi = 0$$

(426)

Now consider

$$k^2 = \frac{8\pi^2 mE}{h^2}$$

(427)

After using the value from equation (427) in equation (426), we get

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$$

(428)

The general solution of the above equation is

$$\psi = A \sin kx + B \cos kx$$

(429)

Hence, from just the symbolic form we have obtained some kind of expression for the wave function defining quantum mechanical states. However, the function given by equation (429) cannot be used to find different physical properties or the nature of corresponding quantum mechanical states. The reason is that this expression does have some unknown parameters like $A$, $B$ and $k$. Since the function describing any quantum mechanical state must be single-valued, finite and continuous, the function $\psi$ must also follow these conditions to become a “wave-function”. Therefore, these boundary conditions are fulfilled only if the magnitude of $\psi$ is zero at the start and at the end of the box (function outside is zero).

i) The first boundary condition: $\psi$ must vanish when $x = 0$ i.e.

$$0 = A \sin k(0) + B \cos k(0)$$

(430)

$$0 = 0 + B \cos k(0)$$

(431)

$$B = 0$$

(432)

So, the function $\psi$ is acceptable only if the value of the constant $B$ is zero. After putting the value of $B$ in equation (429), we get

$$\psi = A \sin kx + (0) \cos kx$$

(433)

$$\psi = A \sin kx$$

(434)
ii) The second boundary condition: \( \psi \) must vanish when \( x = a \), i.e.,

\[
0 = A \sin ka
\]

\[
\sin ka = 0
\] (435) (436)

Moreover, as we know that

\[
\sin 0 = 0 \quad \text{or} \quad \sin 0\pi = 0
\]

\[
\sin 180 = 0 \quad \text{or} \quad \sin 1\pi = 0
\]

\[
\sin 360 = 0 \quad \text{or} \quad \sin 2\pi = 0
\]

\[
\sin 540 = 0 \quad \text{or} \quad \sin 3\pi = 0
\]

or

\[
\sin n\pi = 0
\] (437) (438) (439) (440)

Where \( n = 0, 1, 2, 3, 4, 5 \ldots \infty \). Comparing equation (436) and equation (441), we conclude that

\[
\sin ka = \sin n\pi = 0
\] (441)

Which eventually means that

\[
ka = n\pi
\]

\[
k = \frac{n\pi}{a}
\] (442) (443) (444)

After putting the value of \( k \) in equation (434), we get

\[
\psi = A \sin \frac{n\pi x}{a}
\] (445)

The only parameters that is still unknown in equation (445) is \( A \), which can also be obtained by the condition of normalization i.e. the function must define the state completely. Therefore, we can say that

\[
\int_0^a \psi^2 = A^2 \int_0^a \sin^2 \left( \frac{n\pi x}{a} \right) = 1
\]

\[
A^2 \cdot \frac{a}{2} = 1
\] (446) (447)

\[
A^2 = \frac{2}{a} \quad \text{or} \quad A = \sqrt{\frac{2}{a}}
\] (448)

After putting the value of \( A \) in equation (445), we get
\[ \psi = \frac{\sqrt{2}}{a} \sin \frac{n\pi x}{a} \]  
(449)

Since the function \( \psi \) also depends upon the discrete variable \( n \), it is better to write the above equation given as

\[ \psi_n = \frac{\sqrt{2}}{a} \sin \frac{n\pi x}{a} \]  
(450)

The equation (450) represents all the quantum mechanical states of a particle in one-dimensional box. We can obtain functions for individual states just by putting different values of “\( n \)” allowed by the boundary conditions.

For first quantum mechanical state i.e \( n = 1 \)

\[ \psi_1 = \frac{\sqrt{2}}{a} \sin \frac{\pi x}{a} \]  
(451)

For second quantum mechanical state i.e \( n = 2 \)

\[ \psi_2 = \frac{\sqrt{2}}{a} \sin \frac{2\pi x}{a} \]  
(452)

For third quantum mechanical state i.e \( n = 3 \)

\[ \psi_3 = \frac{\sqrt{2}}{a} \sin \frac{3\pi x}{a} \]  
(453)

Similarly, we can write the expression for \( \psi_4, \psi_5, \psi_6 \) and so on. It is also worthy to note that even though the \( n = 0 \) is permitted by the boundary condition, we still didn’t use it in equation (450); which is obviously because it makes the whole function to collapse to zero.

One of the most remarkable results of this procedure that we have not discussed yet is the correlation of equation (427) and equation (444).

\[ k^2 = \frac{8\pi^2 m E}{\hbar^2} = \frac{n^2 \pi^2}{a^2} \]  
(454)

\[ E_n = \frac{n^2 \hbar^2}{8ma^2} \]  
(455)

The energy of different quantum mechanical states can be obtained by putting \( n = 1, 2, 3, \ldots \infty \) in equation (455). Hence, we have obtained the wave-function as well as the energy for a particle in one-dimensional box.
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# Table of Contents

## CHAPTER 1

**Quantum Mechanics – I**

- 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

**Thermodynamics – I**

- 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 (\(\Lambda\)) 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
Schroedinger 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
Schroedinger Wave Equation for Three Dimensional Rigid Rotator ........................................ 231
Energy of Rigid Rotator ........................................................................................................ 241
Space Quantization ................................................................................................................ 243
Schroedinger 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 (s, p & d)......................................................................................... 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,B 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
Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands).

Mandeep Dalal  
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)  
Founder & Director, Dalal Institute  
Contact No: +91-9802825820  
Homepage: www.mandeepdalal.com  
E-Mail: dr.mandeep.dalal@gmail.com

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