**Quantum Mechanics – Part II**

**THE INFINITE SQUARE WELL POTENTIAL (3-D case)**

Now we shall discuss one of the simplest potentials having this property, the infinite *square*

*well potential.* The potential can be written as,

**It has the feature that it will bind a particle with any finite total energy *E >* 0. In *classical mechanics, any* of these energies are possible, but in *quantum mechanics* only *certain* discrete eigenvaluesare allowed.**

We shall see that it is very easy to find simple and concise expressions for the eigenvalues and eigenfunctions of this potential because the time-independent Schrödinger equation happens to have simple solutions.

Since as per (26), V(x,y,z) =0 within 0<x<a,0<y<b and 0<z<c , and outside this region V(x,y,z)=∞

**Therefore, it’s not possible for the particle to cross the boundary, thus φ(x,y,z) must vanish at the boundary and outside.**

Thus, the boundary conditions are,

**φ(0,y,z) = 0 and φ(a,y,z) = 0 ….(27)**

**φ(x,0,z) = 0 and φ(x,b,z) = 0 ….(28)**

**φ(x,y,0) = 0 and φ(x,y,c) = 0 ….(29)**

In this case, time-independent Schrödinger equation becomes,

**30)**

Let us consider**, ……. (31),** which gives,

**And**

Thus, equation (30) becomes,

Or, dividing both side by

Therefore,

where,

Solution of equation (32), (33) and (34) can be written as,

X(x) = A sin αxx + B cos αxx …..(36)

Y(y) = C sin αyy + D cos αyy .….(37)

Z(z) = E sin αzz + F cos αzz ...…(38)

Boundary conditions (equation 27) gives**, X(0) = 0, therefore, B = 0** and **X(a) = 0 or,**

**A sin αxa = 0 = sin nxπ,** Therefore, **αxa= nxπ, or αx= nxπ/a,** where **n = 1,2,3 …..**

Thus, **…(39)**

Similarly, equation (28) gives, **Y(0) = 0,** therefore, **D = 0** and **Y(b)=0** gives, **αy= nyπ/b**

Thus, **…(40)**

And, equation (29) gives**, Z(0) = 0,** therefore**, F = 0** and **Z(c)=0** gives**, αz = nzπ/c**

Thus, **…(40)**

Therefore, combining equation (31) with equation (38), (39) and (40) we obtain the energy eigen function as,

**[Here, nx =ny=nz=0 are not considered as they give the trivial solution and will represent that the particle does not exist, which is in contrary to our problem. nx=ny= nz =0 indicates E=0. Therefore particle with zero energy can’t be present within the potential well. ]**

**As both the eigen function and the energy eigen values are dependent on nx, ny, nz, so we will represent them as and respectively.**

We can evaluate the constant **N=ACE** by applying the normalization procedure to equation (41) ,

,

or,

**Evaluating (42) we get, ,**

**thus the normalized eigen function (41) becomes,**

And the corresponding energy values are obtained from the relation (35) a**s,**

**, which shows the quantization of energy due to the bound states.**

**Degeneracy of energy states (Important)**

Consider a 3-D potential well for which **a=b=c = L(say),** thus equ (43) and (44) becomes,

and **,**

It is now clear form equation (46) that, the particle can have the same value of energy for more than one set of (**nx, ny, nz) and these various energy states corresponding to each set of** (**nx, ny, nz) which result in the same energy eigen-value are termed as degenerate states.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Energy State | Value of **nx** | Value of **ny** | Value of **nz** | Energy Eigen value, | Degree of degeneracy |
| Ground state | **1** | **1** | **1** |  | **1** |
| 1st Excited state | **2** | **1** | **1** |  | **3** |
| **1** | **2** | **1** |
| **1** | **1** | **2** |
| 2nd Excited state | **2** | **2** | **1** |  | **3** |
| **1** | **2** | **2** |
| **2** | **1** | **2** |
| 3rd Excited state | **3** | **1** | **1** |  | **3** |
| **1** | **3** | **1** |
| **1** | **1** | **3** |
| 4th Excited state | **2** | **2** | **2** |  | **1** |

**Operators**

In mathematics, operators provide us with tools for obtaining new functions from a given function. An operator operating on the function f(x) generates a new function g(x):

As an example let,

Then,

**In quantum mechanics each dynamical variable (which represents a measurable quantity like, position, linear momentum, total energy etc.) is represented by an operator.**

Form of the operators of different dynamical variables is provided in the table below:

|  |  |
| --- | --- |
| Dynamical Variable | Corresponding Operator |
| Position |  |
|  |
|  |
| Linear Momentum  (Component wise) |  |
|  |
|  |
| Kinetic Energy  (in 1-D) |  |
| Angular Momentum (**L=r x p**) |  |
|  |
|  |
| Potential Energy |  |
| Hamiltonian |  |

**Linear Operator :** An operator is said to be linear if it satisfies the following two conditions:

**(a)**

Example : ***d/dx*** is a linear operator where ***log*** is not .

**Hermitian Operator**

An operator is said to be Hermitian if it satisfies the following conditions:

**, where \* denotes the complex conjugate**

**All quantum mechanical operators are Hermitian and Linear.**

**Eigen Value and Eigen Function**

In general if we consider an operator which operating on a function **φ(x)** multiplies the latter by a constant ***a***, then **φ(x)** is called an eigenfunction of belonging to the eiegenvalue ***a*.**

**To each operator, there belongs in general a set of eigenvalues *an* and a set of eigenfunctions φn defined by the equation**

**Eigenvalue represents the result of a measurement of the corresponding dynamical variable.**

**Problem:** Find the eigenfunction of the momentum operator corresponding to the eigenvalue ***p*.**

**Answer:** As per the given problem,

Or, + C

Or,

Or**,**

**Eigenvalues of a Hermitian operator are real.**

**Proof:** Let is a Hermitian operator which satisfies the following eigenvalue equation:

,

Therefore, the complex conjugate of the previous equations gives,

As is a Hermitian, then it must obey equation (49), thus replacing equ (51a) and (51 b) in equ(49), we get,

Or,

As, **denotes the total probability, therefore it can’t be zero. Thus,**

**or, . Therefore,**

In 1-D Time-Independent Schrödinger equation is given by,

**Or,**

**Or,**

We have seen before [for example :1-D and 3-D infinite potential well], that equation (52) gives rise to different possible solutions, with different eigenvalues.

**Time-Independent Schrödinger equation represents an eigenvalue equation for Hamiltonian operator** (**: solution of which gives the enegy eigenvalues (En) and the energy eigenfunctions (φn).**

Therefore, the general wave-function **[ψ(x,t)]** will be a linear superposition of all possible eigenfunctions (eigenstates): **,** where Cn are constants.

**[**In the process of deduction of time-independent Schrödinger equation from time-dependent Schrödinger equation, we considered the wavefunction

**]**

**Solutions of time-independent Schrödinger equation represents the stationary states as the probability density, is independent of time.**

**Orthogonality of eigenfunctions (Proof not required)**

A complete set of eigenfunctions of a Hamiltonian operator are orthogonal which can be expressed (in 1-D) by the following relation:

……..(54) ,

**Orthonormality of wavefunction**

If  **are orthogonal as well as normalized (orthonormal), then they must follow**

….(55)

Therefore, equation (53) gives us,

Or,

Or,

Or,

Or, **..(56)**

**[Summation of probabilities of occurrence of all the eigenstates: total probability is one]**

[ As orthogonality of eigenfunction demands (equation(54)),

**The probability of occurrence of the eigenstate φm is given by .**

**Expectation Value**

The expectation value or the expected average of the results of a large number of measurements of a physical property α, is given by,

**Note: Expectation value of different operators (in 1-D),**

**Position : …..(58)**

Linear Momentum:

**….(61)**

Hamiltonian:

**Important: Expectation value of Hamiltonian operator gives the energy expectation value.**

**Problem (important)** : A system has two energy eigenstates ***ε0*** and ***3ε0*** . **φ1 and φ2** are the corresponding normalized eigenfunction. At an instant the system is in a superposed state,

**φ = c1 φ1 + c2 φ2 and c1 = 1/√2.**

i) Find **c2** if φ is normalized.

ii) What is the **probability** that an energy measurement would yield a value ***3ε0.***  
iii) Find out the **energy expectation** value.

**Answer: i)** As **φ is normalized,** then equation **(56)** gives that

It is given that, **c1 = 1/√2, therefore c2 = 1/√2…(63)**

**ii)** Since **φ2 is the energy eigenstate corresponding to the enrgy eigenvalue *3ε0***, therefore the probability of occurrence of that state (ie. An energy measurement would yield a value of ***3ε0***) is given by [using equ (63)]

**iii)** As per the problem**, φ1** and **φ2** satisfy the followingeigenvalue equations,

Thus, the energy expectation value can be evaluated as (equ (62))

Or,

Or,

[where, orthogonality of eigenfunction gives,

**To do**

**1a)** Eigenfunction of a particle in 1-D infinite potential well of length L is given by,

. For the ground state eigenfunction (n=1) show that

i) **, ii)** , iii)  **and Important**

**Hint: ii)**

Or, .

**1b)** Prove that the eigenfunctions are orthogonal to each other. **Important**

**Hint:**

**---------------------------------------------------------------------------------------------------------------------**

**Commutator**

The commutator of two operators is defined as,.

If,

**If two operators commute then they will have simultaneous eigenfunctions**

**Proof:** Let us consider that two operators have a common eigenfunction φ corresponding to different eigenvalues ***a*** and ***b***, thus their eigenvalue equations become,

….… (64)

We will now prove that

Operating we get,

(

Therefore,  **….(65)**

Properties of commutator

**1) …(66)**

**2) …(67)**

**3) …(68)**

**4) ….(69)**

**5) ….(70)**

Evaluate the following commutators

1) ….(71) **Important**

**Ans.**

Or,  **[** follows **uncertainty principle]**

Similarly,

**2)** **[**have **simultaneous eigenfunctions**, equation (65) ]

**Ans.**

Similarly,

3) **Important**

**Ans.** Let us put n=1, (from equ (71))

For n=2,  **=** 69)

(equn(71)) …….(72)

For n=3,  **=**

Thus, method of induction proves that,

4) **Important**

**Ans.** Let us put n=1, (from equ (71))

For n=2,  **=** 68)

(equn(71)) …….(72)

For n=3,  **=**

Thus, method of induction proves that,

5)  **(Important)**

Thus, **.**

Similarly,

6) **To do,**

7) Given,

Prove that**,** where**, ++. (Important)**

**Ans.** )

Or, + + + (using equation (69))

Or, + {since, **}**

**Postulates of Quantum Mechanics**

**I]** There is a **wave function ψ(x,y,z,t)** which completely describes the space-time behavior of the particle, consistent with the uncertainty principle**.**

**II]** Dynamical variables or **observables** which are the **physically measurable (like position, momentum, energy etc)** properties of the particle are represented by **mathematical operators** in quantum mechanics**. These operators are linear and Hermitian.**

**III] The only possible result of measurement** of a dynamical variable **α** are the **eigenvalues of the operator ,** satisfying the eigen value equation **,** where **φn** is the **eigen function** of the operator **,** belonging to **the eigen value *an*.**

The eigen functions are well-behaved, i.e., **they must be single-valued and square-integrable (for bound state) (means eigen-function must vanish at boundaries).** They also form a **complete set** and are **orthogonal.**

The **eigen value equation** satisfied by the **Hamiltonian operator** is known as the **Schrödinger** equation and can be written as**, ,** where **En** isthe **energy of the system.**

**IV]** The probability **Pdv** of finding a particle in the volume element **dv** is given by,

**,** where

In a finite region of space the probability of finding the particle is obtained by integrating the above expression over the volume under consideration**,**

The integral r.h.s must always remain **finite since the probability must be finite** for any physically admissible state. In particular if **we multiply ψ by a suitable complex number**, we can make the total probability of finding the particle somewhere in space as unity, so that we get,

**,** the **wave function ψ** is said to be **normalized** in this case**.**

**V]** The **expectation value** or the expected average of the results of a large number of measurements of a physical property α, is given by,

If , then the expectation value is given by,

**VI]** It may be noted that the state (general wave function) ψ of the system can be built up by applying the **principle of superposition**, thus

where, are the solutions of the 3-D Time-independent Schrödinger equation (eigenvalue equation) and ’s are the complex numbers such that gives the **probability of finding the particle in the eigenstate** represented by the **eigen function** . They can evaluated by utilizing the orthogonality property of eigen functions.