

## **Lecture 5**

### **Quantum Mechanical Systems and Measurements**

#### **Today's Program:**

1. Wavefunctions in QM
2. Schrodinger's Equation
3. Representing physical quantities: Observables
4. Hermitian operators
5. Principle of spectral decomposition.
6. Predicting the results of measurements, fourth postulate discrete and continuous spectrum.
7. Fifth postulate – the “collapse” of the wavefunction.
8. QM analysis of the particle in a box.

#### **Questions you will be able to answer by the end of today's lecture**

1. Know the qualitative differences between the free particle case and the particle in a box.
2. How to find the projection of a function (vector) onto an eigenfunction (element of the basis)
3. How to expand an arbitrary wavefunction in terms of eigenfunctions?
4. How to predict the probability of obtaining a particular measurement result
5. How to find eigenfunctions and eigenvalues of particle in box
6. How does a measurement effect the state of a quantum mechanical system?

#### **References:**

1. Introductory Quantum and Statistical Mechanics, Hagelstein, Senturia, Orlando.
2. Principles of Quantum Mechanics, Shankar.

In the previous lecture we have learned that the particles can be represented with wavefunctions describing their probability of being at a certain place at a certain time.

**First Postulate of Quantum Mechanics:**

Any quantum mechanical particle or a system in general can be described by a wavefunction  $\psi(\vec{r}, t)$ . (Depending on a system  $\psi$  may be in a vector form). In general we will represent wavefunction in a form of a *ket*:  $|\psi(\vec{r}, t)\rangle$ .

The wavefunctions belong to a state space, which has the properties of a vector space.

The general properties of wavefunctions are:

- (a) Single valued
- (b) Square integrable
- (c) Nowhere infinite (at infinity as well as elsewhere)
- (d) Continuous
- (e) Piecewise continuous first derivative

Now let's consider the simplest wavefunction for a particle. In a free space such as vacuum with no external forces the particle can be approximated as a plane wave:  $e^{ikx-i\omega t}$ , where  $k = \frac{p}{\hbar}$  is the wavevector. Since there is no external forces then the energy of a particle is its kinetic energy:

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

How does this wave propagate in time and space? To answer this question let's consider the change in wavefunction with respect to time and position:

$\frac{\partial}{\partial x} e^{ikx-i\omega t} = ik e^{ikx-i\omega t}$ $\frac{\partial^2}{\partial x^2} e^{ikx-i\omega t} = -k^2 e^{ikx-i\omega t}$ $\frac{\partial^2}{\partial x^2} e^{ikx-i\omega t} = -\frac{p^2}{\hbar^2} e^{ikx-i\omega t}$ $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} e^{ikx-i\omega t} = \frac{p^2}{2m} e^{ikx-i\omega t}$ <div style="text-align: center; margin-top: 5px;"> <math>\xleftrightarrow{E}</math> </div>	$\frac{\partial}{\partial t} e^{ikx-i\omega t} = -i\omega e^{ikx-i\omega t}$ $\frac{\partial}{\partial t} e^{ikx-i\omega t} = -i \frac{E}{\hbar} e^{ikx-i\omega t}$ $i\hbar \frac{\partial}{\partial t} e^{ikx-i\omega t} = E e^{ikx-i\omega t}$
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This exercise results in a curious statement about the propagation of particle ~ plane wave in free space:  $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} e^{ikx-i\omega t} = i\hbar \frac{\partial}{\partial t} e^{ikx-i\omega t}$

In general in the presence of forces in 3D space energy of a particle would be:

$E = \frac{p^2}{2m} + V(x, t)$ , which would yield a following equation for the particle described by a wavefunction  $\psi(\vec{r}, t)$ :

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) + V(x, t) \psi(x, t) = i\hbar \frac{\partial}{\partial t} \psi(x, t)$$

This equation is known as Schrodinger's equation and is usually written in the form:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(x, t) \right] \psi(x, t) = i\hbar \frac{\partial}{\partial t} \psi(x, t)$$

**Sixths Postulate of Quantum Mechanics:** The time evolution of the wavefunction  $\psi(\vec{r}, t)$  is governed by the Schrodinger's equation.

Let's take a closer look at the Schrodinger's equation. During our derivation of the equation we have encountered an intermediate landmark equation:

$$-i\hbar \frac{\partial}{\partial x} e^{ikx - i\omega t} = p e^{ikx - i\omega t}$$

This equation is analogous to an eigenvalue problem:  $A\phi = \lambda\phi$ . Here operator such as a matrix  $A$  acts on it's eigenfunction or an eigenvector  $\phi$ , and  $\lambda$  is the corresponding eigenvalue.

By this logic  $-i\hbar \frac{\partial}{\partial x}$  is an operator with the plane wave being its eigenfunction corresponding to an eigenvalue  $p$ , which is also momentum.

If the eigenvalues of the operator are momenta then it is reasonable to call this operator a

**“momentum operator”**:  $p \rightarrow \hat{p} = -i\hbar \frac{\partial}{\partial x}$

In general:  $\vec{p} = (p_x, p_y, p_z) \rightarrow \hat{\vec{p}} = -i\hbar \vec{\nabla} = -i\hbar \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$

Similarly we can construct a **“position operator”**, which eigenvalues are coordinates:

$$\hat{x} e^{ikx - i\omega t} = x e^{ikx - i\omega t} \Rightarrow x \rightarrow \hat{x} = x$$

In general:  $\vec{r} = (x, y, z) \rightarrow \hat{\vec{r}} = \vec{r} = (x, y, z)$

**Second Postulate of Quantum Mechanics:** Every measurable physical quantity  $a$  is described by an operator  $\hat{A}$  acting on the wavefunction space. This operator is Hermitian and is called an **observable**.

### Properties of Hermitian operators:

1.  $\hat{A}^\dagger = \hat{A}$  (For matrix operators  $(\hat{A}^\dagger)_{ji} = \hat{A}_{ij}$  or  $A_{ji}^* = A_{ij}$ ,  
for function operators  $\int \psi(\hat{A}\varphi)d^3r = \int \varphi(\hat{A}^*\psi)d^3r$ )
2. Eigenvalues are real:  $\hat{A}\varphi_i = \lambda_i\varphi_i$ ,  $\lambda_i \in \mathfrak{R}$
3. Eigenvectors belonging to different eigenvalues are orthogonal.  
 $\lambda_i \neq \lambda_j \Rightarrow \vec{\varphi}_i \cdot \vec{\varphi}_j = 0$  or  $\int \varphi_i^*(\vec{r})\varphi_j(\vec{r})d^3r = 0$
4. Eigenfunctions of the Hermitian operator form a complete basis. This means that any function (or vector if we are working in a vector space) can be represented as a linear combination of eigenfunctions (eigenvectors) of any Hermitian operator.

### How to construct observables?

If a physical quantity  $f$  is a function of position and momentum  $f(\mathbf{x}, \mathbf{p}, t)$ , then we can simply substitute the momentum and position operators into the function  $f$  and obtain the operator  $\hat{f}$  corresponding to the physical quantity  $f$ :  $f = f(\vec{r}, \vec{p}, t) \rightarrow \hat{f} = f(\hat{\vec{r}}, \hat{\vec{p}}, t)$

### Example: *Hamiltonian*

In the first two lectures we have learned how to solve mechanical problems using Hamiltonian approach. Remembering the general form of a Hamiltonian and using our recipe for constructing of observables we can get a Hamiltonian operator:

$$H = \frac{\vec{p}^2}{2m} + V(\vec{r}, t) \rightarrow \hat{H} = -\frac{1}{2m}\hbar^2\vec{\nabla}^2 + V(\vec{r}, t) = \frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r}, t)$$

Now if we look back at the Schrodinger's equation we can see it in the following form:

$$\left[ -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \Rightarrow \hat{H}\psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t)$$

**Akin to a Classical system in Quantum Mechanics knowing the Hamiltonian defines the system and it's evolution in time and space.**

**A special and very important case:** Time-independent Hamiltonian.

If there are no time dependent fields in the system, no time dependent forces, then Hamiltonian does not depend on time explicitly:  $\hat{H}(\vec{r}, \hat{\vec{p}}) = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$

Then the Schrodinger's equation has the following form:

$$\left[ -\frac{\hbar^2}{2m} \bar{\nabla}^2 + V(\vec{r}) \right] \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t)$$

This type of differential equation is separable, i.e. we can look for a solution in the following form:  $\psi(\vec{r}, t) = \varphi(\vec{r}) \xi(t)$ . Let's substitute it into the Schrodinger's equation above:

$$\begin{aligned} \left[ -\frac{\hbar^2}{2m} \bar{\nabla}^2 + V(\vec{r}) \right] \varphi(\vec{r}) \xi(t) &= i\hbar \frac{\partial}{\partial t} \varphi(\vec{r}) \xi(t) \\ \xi(t) \left\{ \left[ -\frac{\hbar^2}{2m} \bar{\nabla}^2 + V(\vec{r}) \right] \varphi(\vec{r}) \right\} &= \varphi(\vec{r}) i\hbar \frac{\partial}{\partial t} \xi(t) \\ \frac{1}{\varphi(\vec{r})} \left\{ \left[ -\frac{\hbar^2}{2m} \bar{\nabla}^2 + V(\vec{r}) \right] \varphi(\vec{r}) \right\} &= \frac{1}{\xi(t)} i\hbar \frac{\partial}{\partial t} \xi(t) \end{aligned}$$

Note that the left side of the equation only depends on position  $\vec{r}$  and the right side of the equation only depends on time  $t$ . This can only be true when both sides of the equation are constant. The units of this constant are  $[\hbar] \frac{1}{[t]} = kg \cdot \frac{m^2}{s^2} = J$  Joules, which are the units of energy.

Let's call this constant  $E$ . Then the equation above splits into the following two equations:

$$\begin{aligned} (I) \quad i\hbar \frac{d}{dt} \xi(t) &= E \xi(t) \\ (II) \quad \left[ -\frac{\hbar^2}{2m} \bar{\nabla}^2 + V(\vec{r}) \right] \varphi(\vec{r}) &= E \varphi(\vec{r}) \end{aligned}$$

The equation (I) has a solution in a form:  $\xi(t) = e^{-\frac{E}{\hbar}t}$ .

The equation (II) is an eigenvalue/eigenfunction problem for the Hamiltonian:  $\hat{H}\varphi(\vec{r}) = E\varphi(\vec{r})$

From the classical Hamiltonian mechanics we remember constructing Hamiltonian based on the sum of potential and kinetic energy of the system. As we constructed quantum mechanical Hamiltonian by analogy with classical Hamiltonian it's eigenvalues correspond to possible energies that our system may have. Since the Hamiltonian does not change in time, the energy in this system is conserved and such system is called "**conservative**". The eigenvalue equation above is called **Time-Independent Schrodinger's** equation.

Suppose eigenvalue equation above has eigenvalues  $E$  and corresponding eigenvectors  $\varphi_E(\vec{r})$ .

Then the solutions to time-dependent Schrodinger's equation will have a form:

$$\psi_E(\vec{r}, t) = \varphi_E(\vec{r}) \xi_E(t) = \varphi_E(\vec{r}) e^{-\frac{E}{\hbar}t}$$

In general, since the Hamiltonian may have many eigenvalues and corresponding eigenfunctions, the solution for this system is a linear combination of all the possible solutions corresponding to different energies:

$\Psi(\vec{r}, t) = \sum_E C_E \varphi_E(\vec{r}) e^{-i\frac{E}{\hbar}t}$ , where  $C_E$  are the coefficients that can be determined from the initial and boundary conditions.

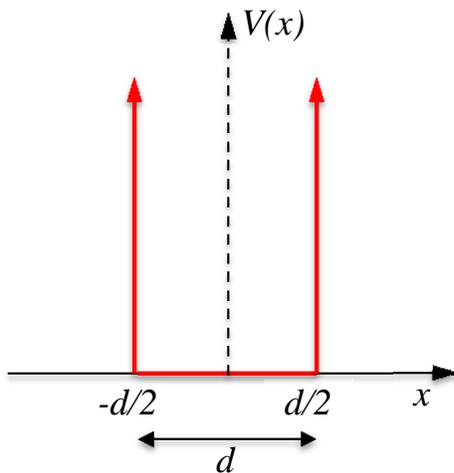
This is a very important result: If we know the special wavefunctions (Hamiltonian eigenfunctions) we can easily find time evolution of this conservative system.

**If we know  $E$  and  $\varphi_E(\vec{r})$  then we know  $\Psi(\vec{r}, t)$  at any time!**

### Example: particle in an infinite potential well

Many of modern materials and devices have dimensions on nanoscale, which results in quantum effects dominating the behavior of such devices. A simplest example of a “nanoscale material” is a quantum dot. Quantum dots are nano-sized single crystals of various semiconductors that have highly efficient and tunable photoluminescence. The most remarkable property of quantum dots is that their optical absorption and photoluminescence spectra shift towards the blue wavelengths as the quantum dot diameter decreases. For example quantum dots of cadmium selenide can be synthesized to achieve photoluminescence spectra spanning all the visible wavelengths by simply changing their diameter from 2 nm to 10 nm. How does that work? The answer lies in one of the most classic examples of Quantum Mechanics – particle in an infinite potential well. The simplest approximation for quantum dot is an infinite potential well where all its electrons are confined.

**I The system:** A particle of mass  $m$  in a potential well with infinitely tall walls:



**II The classical Hamiltonian for this system is:**

$$H(x, p) = \frac{p^2}{2m} + V(x),$$

where the potential energy is defined as follows:

$$V(x) = \begin{cases} 0 & -\frac{d}{2} < x < \frac{d}{2} \\ \infty & x < -\frac{d}{2} \text{ or } x > \frac{d}{2} \end{cases}$$

**III Obtaining the QM Hamiltonian operator:**

$$H(x, p) \rightarrow \hat{H}(\hat{x}, \hat{p}) = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

For now let us restrict our attention to the inside of the well, where potential is zero ( $V(x)=0$ ). Since the Hamiltonian does not depend on time, all we need to do in order to solve this system is to find the eigenfunctions and eigenvalues of the Hamiltonian operator:

$$\hat{H}(\hat{x}, \hat{p}) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

**IV What are the energy eigenfunctions and eigenvalues?**

$$\hat{H}(\hat{x}, \hat{p})u(x) = Eu(x) \Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} u(x) = Eu(x) \Rightarrow \frac{\partial^2 u(x)}{\partial x^2} + \frac{2m}{\hbar^2} Eu(x) = 0$$

$$u_k(x) = ae^{ikx} + be^{-ikx}, \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

**Note:** The undetermined  $a$  and  $b$  coefficients imply that there are an infinite number of allowed eigenfunctions corresponding to every eigenvalue (i.e. determining  $E$  does not determine  $a$  and  $b$ ). We will narrow down this set by using boundary conditions derived from physical insights into our problem. Specifically, we will require that our eigenfunctions will be equal to 0 at the boundary of the well.

The problem of finding the eigenfunctions and eigenvalues of a linear quantum mechanical operator basically is identical to solving a linear differential equation. As such we can apply the techniques and theories, which have been developed to solve differential equations to our problems.

**A differential equation above will have a unique solution as long as we know its value at the boundaries, i.e. we know boundary conditions.**

**As the well has infinitely tall walls the probability of the particle escaping is zero, consequently the boundary conditions in this problem are:**

$$u\left(x = \pm \frac{d}{2}\right) = 0$$

$$u\left(\frac{d}{2}\right) = \left(ae^{+ik\frac{d}{2}} + be^{-ik\frac{d}{2}}\right) = 0 \Rightarrow a\left(\cos\frac{kd}{2} + i\sin\frac{kd}{2}\right) + b\left(\cos\frac{kd}{2} - i\sin\frac{kd}{2}\right) = 0$$

$$\Rightarrow (a+b)\cos\frac{kd}{2} + i(a-b)\sin\frac{kd}{2} = 0$$

$$\Rightarrow a = b, \quad \frac{kd}{2} = n\frac{\pi}{2}, \quad n = 1, 3, 5, \dots \quad \text{or} \quad a = -b, \quad \frac{kd}{2} = n\frac{\pi}{2}, \quad n = 2, 4, 6, \dots$$

Then the solution has the following form:

$$u_E(x) \equiv u_n(x) = \begin{cases} n \text{ odd} & c_n \cos k_n x = c \cos \frac{n\pi x}{d} \\ n \text{ even} & d_n \sin k_n x = d \sin \frac{n\pi x}{d} \end{cases}, \quad k_n = \sqrt{\frac{2mE_n}{\hbar^2}} = \frac{n\pi}{d}$$

Let's check that  $u_n(x)$  are actually indeed the solutions of to the eigenfunction problem and also find the energy eigenvalues.

$$\hat{H}(\hat{x}, \hat{p})\psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} a_n \cos k_n x = \frac{\hbar^2 k_n^2}{2m} a_n \cos k_n x = E_n a_n \cos k_n x = E_n \psi(x)$$

$$\hat{H}(\hat{x}, \hat{p})u_n(x) = E_n u_n(x)$$

Because  $\hat{H}$  is a linear operator any superposition of solutions is also a solution.

The boundary conditions have lead to a quantization of the energy levels:

$$\frac{kd}{2} = n \frac{\pi}{2}, E_n = \frac{1}{2m} \left( \frac{n\pi\hbar}{d} \right)^2 = \frac{n^2 \pi^2 \hbar^2}{2md^2}, \quad n=1,2,3,4,5\dots$$

**V How can we find the coefficients  $c_n$  and  $d_n$ : normalization!**

Since the probability of finding a particle in any state cannot exceed 1, then it is convenient to normalize the eigenfunctions to 1.

$$\int_{-d/2}^{d/2} |c_n|^2 \cos^2 \frac{(2k-1)\pi x}{d} dx = 1 \Rightarrow |c_n|^2 \frac{d}{\pi} \int_{-\pi/2}^{\pi/2} \cos^2 (2k-1)z dz = 1, \quad z = \frac{\pi x}{d} \Rightarrow c_n = \sqrt{\frac{2}{d}}$$

$$\int_{-d/2}^{d/2} |d_n|^2 \sin^2 \frac{(2k)\pi x}{d} dx = 1 \Rightarrow |d_n|^2 \frac{d}{2\pi} \int_{-\pi}^{\pi} \sin^2 ky dy = 1, \quad y = \frac{2\pi x}{d} \Rightarrow d_n = \sqrt{\frac{2}{d}}$$

**Discussion:**

Comparison between the eigenvalues and eigenvectors of the free particle and particle in a box. One has continuous spectrum the other is discrete. The discrete character was a result of the boundary conditions – the fact the particle was confined to a particular region in space.

	Free particle	Particle in a box
Hamiltonian eigenfunctions	$u_k(x) = e^{ikx}$	$u_n(x) = \begin{cases} n \text{ odd} & \sqrt{\frac{2}{d}} \cos k_n x = \sqrt{\frac{2}{d}} \cos \frac{n\pi x}{d} \\ n \text{ even} & \sqrt{\frac{2}{d}} \sin k_n x = \sqrt{\frac{2}{d}} \sin \frac{n\pi x}{d} \end{cases}$
Hamiltonian eigenvalues	$E_k = \frac{\hbar^2 k^2}{2m}$	$E_n = \frac{\hbar^2 k^2}{2m}, \quad k = \frac{n\pi}{d}$

**Important points:**

**1. Discrete vs. continuous spectrum:**

Unlike for the free particle, which can have any energy value, the spectrum of allowed energy states for the particle in the infinite potential well is discrete.

**2. Dependence of energy level separation on size of well.**

What is the distance between the closest energy levels:  $E_n$  and  $E_{n+1}$ :

$$\Delta E_n = E_{n+1} - E_n = \frac{\pi^2 \hbar^2}{2md^2} \left[ (n+1)^2 - n^2 \right] = \frac{\pi^2 \hbar^2}{2md^2} (2n+1)$$

What if we make the well size larger:  $d' > d$ , then the spacing between the energy levels decreases quadratically:  $\frac{1}{d'^2} \sim \Delta E'_n < \Delta E_n \sim \frac{1}{d^2}$

### How is this relevant to quantum dots spectra?

Later in the course we will find out that the spacing between the energy levels defines the wavelength of the absorbed or emitted photons. I.e. absorption and emission of a photon can transfer our system between the energy levels and the larger is the difference between the energy levels the higher the energy of the absorbed or emitted photon. Consequently, smaller quantum dots will absorb and emit higher energy (bluer) photons.

### 3. Number of nodes vs. energy of eigenfunction:

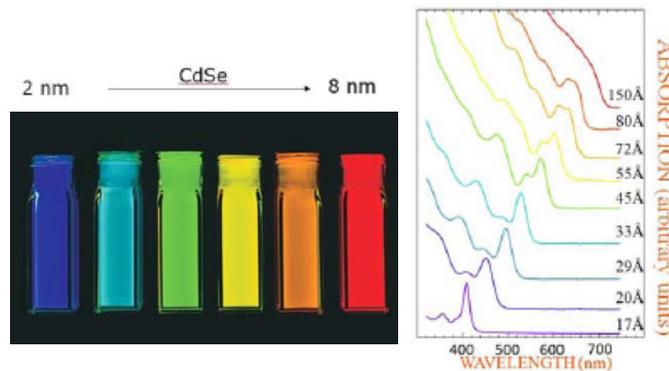


Photo courtesy of Felice Frankel, graph courtesy of Bawendi Lab at MIT. Used with permission.

How many nodes (zeros) will eigenfunction have? For the first eigenvalue:

$$E_1 = \frac{\pi^2 \hbar^2}{2md^2}, \quad u_1(x) = \cos \frac{\pi x}{d} \text{ has 0 nodes between the walls of the well.}$$

$$E_2 = \frac{4\pi^2 \hbar^2}{2md^2}, \quad u_2(x) = \sin \frac{2\pi x}{d} \text{ has 1 node between the walls of the well.}$$

$$E_3 = \frac{9\pi^2 \hbar^2}{2md^2}, \quad u_3(x) = \cos \frac{3\pi x}{d} \text{ has 2 nodes between the walls of the well...}$$

The general trait is that the  $u_n(x)$  has  $n-1$  nodes between the walls of the well.

### 4. Solutions are either odd or even:

The solutions are either symmetric=even ( $\cos \frac{n\pi x}{d}$ ) or antisymmetric=odd ( $\sin \frac{n\pi x}{d}$ ) around the  $x=0$  axis, due to obvious symmetry of the problem.

**5. Lowest energy solution is even:**

Lowest energy solution  $E_1 = \frac{\pi^2 \hbar^2}{2md^2}$ ,  $u_1(x) = \cos \frac{\pi x}{d}$  is even (symmetric around the  $x=0$  axis).

This makes sense: the probability is the highest to find a particle in the middle of the well in the ground state.

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Spring 2013

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