# Introduction to Quantum Mechanics



An half semester course on non-relativistic quantum mechanics which is primarily intended for undergraduate chemistry majors.

- **1.** The basic concepts of quantum mechanics
- 2. Simple cases
- **3. Operators**
- 4. Angular Momentum
- 5. The hydrogen atom
- 6. Many-electron atoms
- 7. Approximate methods the Variation Method
- 8. Diatomic molecules

#### Mathematics

You will find almost all the mathematics used in this course surprisingly familiar. The bulk of it is differentiation and integration of standard expressions (such as  $x^2$ , sin x, exp(- $x^2$ ), and so on), plus the usual algebraic manipulation and ...

*Quantum Mechanics 1: Foundations*, N. J. B. Green. Oxford Chemistry Primers, No. 48

*Introduction to Quantum Mechanics*, D.J. Griffiths, 2nd Edition, (Pearson Prentice Hall, Upper Saddle River NJ, 2005).

*Molecular Quantum Mechanics*, P. W. Atkins and R. S. Friedman, Oxford University Press

#### **Chapter 1. The basic concepts of quantum mechanics**

1. Black-Body Radiation

E = nhv

Planck's constant: h =  $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ 

2. <u>The photoelectric effect</u>

A corpuscular theory of light (photons)  $\epsilon = h\nu$  h = Planck's constant  $p = h/\lambda$ 

3. Bohr model

# **Experiments**

Particles Behaving as Waves: Single photon/electron double slit experiment

1801, Young

1920s, Taylor 1974, Merli, Missiroli, Pozz

**Electron Diffraction:** 

1925, Davisson and Germer

Molecular Quantum Mechanics

Waves Behaving as Particles

The photoelectric effect 1905, Einstein

Compton Effect

1923, Compton

#### Introduction and orientation

0.1	Black-body radiation	1
0.2	Heat capacities	2
0.3	The photoelectric and Compton effects	З
0.4	Atomic spectra	4

# **1.1 The wave-particle duality of microscopic particles**

#### De Broglie



De Broglie considered that the wave-particle relationship in light is also applicable to particles of matter, i.e.

$$E = h\nu$$

$$p = h/\lambda$$

$$F = h/\lambda$$

$$h = Planck's constant,$$
  

$$p = particle momentum,$$
  

$$\lambda = de Broglie$$
  
wavelength

The wavelength of a particle could be determined by  $\lambda = h/p = h/mv$ 

Introduction and orientation		
0.1	Black-body radiation	1
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0.5	The duality of matter	5

#### The de Broglie Wavelengths of Several particles

Particles	Mass (g)	Speed (m/s)	λ (m)
Slow electron	9 × 10 <sup>- 28</sup>	1.0	7 × 10 <sup>-4</sup>
Fast electron	$9 \times 10^{-28}$	$5.9 \times 10^{6}$	$1 \times 10^{-10}$
Alpha particle	6.6 × 10 <sup>- 24</sup>	$1.5 \times 10^{7}$	$7 \times 10^{-15}$
One-gram mass	1.0	0.01	7 × 10 <sup>-29</sup>
Baseball	142	25.0	2 × 10 <sup>- 34</sup>
Earth	$6.0  imes 10^{27}$	$3.0 \times 10^{4}$	$4 \times 10^{-63}$

#### The wave-particle duality

- Wave (i.e., light)
  - can be wave-like (diffraction)
  - can be particle-like (p=h/ $\lambda$ )
- Particles
- can be wave-like ( $\lambda = h/p$ )
- can be particle-like (classical)

Wave-particle duality is the concept that every particle may be partly described in terms not only of particles, but also of waves. It expresses the inability of the classical concepts "particle" or "wave" to fully describe the behaviour of quantum-scale objects. Because particles sometimes behave like waves or exhibit wave properties, its hard to measure locations and velocities with precision.

## **The Uncertainty Principle**



--Heisenberg, uncertainty paper, 1927

•<u>Classical</u>: the error in the measurement depends on the precision of the apparatus, could be arbitrarily small.

•Quantum: it is physically impossible to measure simultaneously the exact position and the exact velocity of a particle.

The description of the behavior of electrons in atoms requires a completely new "quantum theory".

#### Example

The speed of an electron is measured to be 1000 m/s to an accuracy of 0.001%. Find the uncertainty in the position of this electron.

 $p = mv = (9.11 \times 10^{-31} \text{ kg}) (1 \times 10^3 \text{ m/s}) = 9.11 \times 10^{-28} \text{ kg.m/s}$   $\Delta p = p \times 0.001\% = 9.11 \times 10^{-33} \text{ kg m/s}$  $\Delta x = h / \Delta p = 6.626 \times 10^{-34} / (9.11 \text{ x } 10^{-33}) = 7.27 \times 10^{-2} \text{ (m)}$ 

The speed of a bullet of mass of 0.01 kg is measured to be 1000 m/s to an accuracy of 0.001%. Find the uncertainty in the position of this bullet.

 $p = mv = (0.01 \text{ kg}) (1 \times 10^3 \text{ m/s}) = 10 \text{ kg.m/s}$   $\Delta p = p \times 0.001\% = 1 \times 10^{-4} \text{ kg m/s}$  $\Delta x = h / \Delta p = 6.626 \times 10^{-34} / (1 \times 10^{-4}) = 6.626 \times 10^{-30} \text{ (m)}$ 





M. Planck (1858-1947)



A. Einstein (1878-1955)

color
 greenhouse effect
 electric resistance

## **1.3 Wavefunctions**

A quantum mechanical system is described by its *wavefunction*, which is a function of the positions of all the particles in the system. The symbol  $\psi$  or  $\Psi$  is commonly used for the wavefunction.

*Example*: We can approximate the vibrational motion of a diatomic molecule by a *harmonic oscillator* with effective mass m, force constant k, and position x. For the lowest-energy state the wavefunction is

$$\psi_0 = N \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)$$
 (1)

where  $\hbar$  is Planck's constant *h* divided by  $2\pi$ , and *N* is a constant. This wavefunction is real, but in general wavefunctions may be complex. We shall see later how to obtain this wavefunction. The wavefunction is a mathematical map of the system: it contains within itself information about **everything** that any experiment on the system can possibly measure. We have to do maths on the wave function to extract this information. The simplest information to obtain is the probability of finding the system at a particular position; this is proportional to the square of the wavefunction (or to its square modulus if complex). For the harmonic oscillator ground-state wavefunction (1) this gives



for the probability of finding the particle between x and x + dx. P(x) is called the *probability density*  we must have  $\int_{-\infty}^{\infty} P(x) dx = 1$ . To achieve this, we need

$$P(x) = \frac{\psi_0^* \psi_0}{\int_{-\infty}^{\infty} \psi_0^* \psi_0 dx} dx$$
(2)

This expression is simplified if  $\int_{-\infty}^{\infty} \psi_0^* \psi_0 dx = 1$ . If this is true, the wavefunction is said to be *normalised*. We can achieve this by a suitable choice of the constant *N*. However *N* is arbitrary — it cancels out of the expression for *P*(*x*) — so normalisation is a convenience, not a necessity. For  $\psi_0$  (eq. (1)), the normalisation condition is

$$\int_{-\infty}^{\infty} N^2 \exp\left(-\frac{\sqrt{km}}{\hbar}x^2\right) dx = 1$$
 (3)

We get 
$$N^2 \sqrt{\frac{\pi\hbar}{\sqrt{km}}} = 1$$
, and  $N = \left[\frac{\sqrt{km}}{\pi\hbar}\right]^{1/4}$ 

The wavefunction  $\psi_0$  (eq. (1)) for the quantum harmonic oscillator is an example of a *time-independent wavefunction*: it does not depend on the time *t*, and neither do any of the physical properties that can be predicted using it. Most of the wavefunctions that are used in chemistry are similarly time-independent. However, sometimes one needs to construct wave functions which do depend on the time.

If we measure the position, we can't predict precisely what the result will be. The wavefunction  $\psi_0(x)$  only tells us the probability of finding any particular value *x*, through the probability density P(x) in eq. (3).

The measurement disturbs the system, so its wavefunction changes, but we can set it up again with the same wavefunction as before and repeat the measurement. We can take a whole series of measurements in this way, and must expect every one of them to be different.

# What is Ψ?



M. Born (1954)  $\Psi$  is a probability amplitude wave!  $|\Psi|^2$  tells us the probability of finding the particle at a given place at a given time. Leads to indeterminancy in the fundamental laws of nature.

- In CM (classical mechanics), the state of a system of N particles is specified totally by giving 3N spatial coordinates (Xi, Yi, Zi) and 3N velocity coordinates (Vxi, Vyi, Vzi).
- In QM, the wave function takes the form y(r, t) that depends on the coordinates of the particle and on the time.

# **1.4 The probability**

 $\psi^*(r,t)\psi(r,t)dxdydz$ 

The probability that the particle lies in the volume element dxdydz, located at r, at time t.

To be generally **normalized** 

$$\int_{-\infty-\infty-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^{*}(r,t)\psi(r,t)dxdydz = 1$$
$$c\int_{-\infty}^{+\infty}|\psi|^{2}d\tau = 1$$
$$c = \frac{1}{\int_{\infty}^{-\infty}|\psi|^{2}d\tau}$$



The average or *expectation value*  $\langle x \rangle$  of a large number of measurements of x is

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = N^2 \int_{-\infty}^{\infty} \psi_0^*(x) x \psi_0(x) dx$$

$$= \frac{\int_{-\infty}^{\infty} \psi_0^*(x) x \psi_0(x) dx}{\int_{-\infty}^{\infty} \psi_0^*(x) \psi_0(x) dx}$$

$$(4)$$

The mean position of an oscillator described by the wavefunction (1) is

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = N^2 \int_{-\infty}^{\infty} x \exp\left(-\frac{\sqrt{km}}{\hbar}x^2\right) dx = 0$$

using the fact that  $\int_{-\infty}^{\infty} x \exp(-ax^2) dx = 0$ .

This is fairly obvious from the fact that the probability distribution is symmetrical about x = 0 (an even function of *x*) so that the integrand is *odd*.



#### **1.6 Operators and measures**

In general, to predict a property of the system, one must apply an *operator* to the wavefunction. Every observable physical quantity, such as position, energy or momentum, is described by an operator.

An operator is a mathematical instruction that converts one function into another. The simplest operator is the operator  $\hat{x}$  which means 'multiply the wavefunction by x'. This is the operator we have just been using to calculate the expectation value of the position and its uncertainty. A similar operator which is almost as simple is the potential energy operator  $\hat{V}$ , which means 'multiply by the function V(x)', i.e.

 $\hat{V}\psi(x) = V(x)\psi(x)$ 

If the system is a harmonic oscillator, then  $V(x) = \frac{1}{2}kx^2$ , in which case  $\hat{V}\psi(x) = \frac{1}{2}kx^2\psi(x)$  Another type of operator is *a differential operator*. For instance, the operator  $\frac{d}{dx}$  changes the function  $\sin x$  into the function  $\cos x$ :  $\frac{d}{dx} \sin x = \cos x$ 

If a particle's position is described by coordinates (x, y, z) then its momentum in the x direction is described by the operator

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

(We have to use partial derivatives here because there are several coordinates.) This equation is one of the fundamental postulates of quantum mechanics. It is by now universally accepted to be true because it leads to results that agree with experiment, with no measurable discrepancies in the 80+ years since it was first proposed. We almost always work with momentum in quantum mechanics rather than velocity. The rules for constructing the operator corresponding to a physical quantity are as follows:

- Write the expression for the physical quantity in terms of position and momentum variables.
- All position variables remain unchanged.
- A momentum in the direction of the coordinate q is replaced by the operator  $-i\hbar\partial/\partial q$ .

The last rule applies to angular coordinates as well as Cartesian ones.

For example, rotation about the z axis can be described using the spherical polar coordinate

 $\varphi$ , and then the angular momentum about the z axis is described by the operator  $-i\hbar \frac{\partial}{\partial \varphi}$ .

#### **Mechanical quantities and their Operators**

To every physical observable there corresponds a linear Hermitian operator. To find this operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates and corresponding linear-momentum components, and then replace each coordinate x by the operator x. and each momentum component  $p_x$  by the operator -  $i\hbar\partial/\partial x$ .

Mechanical quantities	Methematical Operator
X	$\hat{\mathbf{x}} = \mathbf{x}$
$P_x$	$\hat{\mathbf{p}} = -\frac{i\hbar}{2\pi}\frac{\partial}{\partial \mathbf{x}} = -i\hbar\frac{\partial}{\partial \mathbf{x}}$
$T = p^2/2m$	$\hat{\mathbf{T}} = -\frac{h^2}{8\pi^2 \mathbf{m}} \left(\frac{\partial^2}{\partial \mathbf{x}^2} + \frac{\partial^2}{\partial \mathbf{y}^2} + \frac{\partial^2}{\partial \mathbf{z}^2}\right) = -\frac{h^2}{8\pi^2 \mathbf{m}} \nabla^2$
V	$\hat{\mathbf{V}} = \mathbf{V}$
E = T + V	$\hat{\mathbf{H}} = -\frac{h^2}{8\pi^2 \mathbf{m}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{\mathbf{V}}$

#### **Expectation values for general operators**

In quantum mechanics the expectation value of a quantity Q is calculated by the formula  $\langle Q \rangle = \frac{\int \psi^* \hat{Q} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$ where  $\hat{Q}$  is the operator corresponding to Q, and  $\int \dots d\tau$  is a conventional notation meaning that we integrate over *all variables* and over *all space*.

The order of the factors in the numerator is important: operators work to the *right* only, so in this case  $\hat{Q}$  operates only on  $\psi$ , not on  $\psi^*$ . This makes no difference when the operator just multiplies the function, but for differential operators it is crucial.

Notice that  $\langle Q \rangle$  is the same for the function  $c\psi$  as it is for  $\psi$ , where *c* is any number (possibly complex).  $\psi$  and  $c\psi$  are the same as far as any physical predictions are concerned. As we have seen, it is usually convenient to normalize the wavefunction, i.e. to choose *c* so that  $\int \psi * \psi d\tau = 1$ . For a normalized wavefunction,  $\langle Q \rangle = \int \psi^* \hat{Q} \psi d\tau$ 

## **Eigenfunctions and eigenvalues**

Suppose that we have an operator  $\hat{Q}$  representing some measurable physical quantity, and a wavefunction  $\psi_a$  that satisfies the following equation:

 $\hat{Q}\psi_q = q\psi_q$ 

where q is just a number (with the appropriate dimensions).

Let's calculate the uncertainty  $\Delta Q$  for this wavefunction. We need

$$\langle Q \rangle = \frac{\int \psi_q^* \hat{Q} \psi_q d\tau}{\int \psi_q^* \psi_q d\tau} = \frac{\int \psi_q^* q \psi_q d\tau}{\int \psi_q^* \psi_q d\tau} = q$$

$$\langle Q^2 \rangle = \frac{\int \psi_q^* \hat{Q}^2 \psi_q d\tau}{\int \psi_q^* \psi_q d\tau} = \frac{\int \psi_q^* q^2 \psi_q d\tau}{\int \psi_q^* \psi_q d\tau} = q^2$$

(remember that q is just a number) and then  $(\Delta Q)^2 = \langle Q^2 \rangle - \langle Q \rangle^2 = q^2 - q^2 = 0$ 

So *the uncertainty is zero*. This means that whenever we measure Q for a state with the wavefunction  $\psi_q$ , we *always* get the answer q.

A *measurement* of the property Q must be give a result that is one of the *eigenvalues* of the operator  $\hat{Q}$ .

If the state function happens to be an eigenfunction of  $\hat{Q}$  with eigenvalue q, we are *certain* to get q.

$$q = \int_{-\infty}^{\infty} \psi_q^* \hat{Q} \psi_q \mathrm{d}\tau$$

If the state function is NOT one of the eigenfunctions of  $\hat{Q}$ , we will get average value of the physical observable.

$$\overline{q} = \left\langle \hat{Q} \right\rangle = \int_{-\infty}^{\infty} \psi^* \hat{Q} \psi du$$

The uncertainty is not zero

$$\Delta Q = \sqrt{\left\langle \hat{Q}^2 \right\rangle - \left\langle \hat{Q} \right\rangle^2}$$

#### **Uncertainty in position**

The uncertainty  $\Delta x$  in x is defined by

 $\left(\Delta x\right)^{2} = \left\langle \left|x - \left\langle x\right\rangle\right|^{2} \right\rangle = \left\langle x^{2} \right\rangle - \left\langle x\right\rangle^{2}$ 

For the wavefunction  $\psi_0$  (oscillator), we know that  $\langle x \rangle = 0$ . For  $\langle x^2 \rangle$  we have

$$\left\langle x^{2} \right\rangle = \int_{-\infty}^{\infty} x^{2} P(x) dx$$

$$= \frac{\int_{-\infty}^{\infty} \psi_{0}^{*}(x) x^{2} \psi_{0}(x) dx}{\int_{-\infty}^{\infty} \psi_{0}^{*}(x) \psi_{0}(x) dx}$$

$$= \frac{\int_{-\infty}^{\infty} x^{2} \exp(-ax^{2}) dx}{\int_{-\infty}^{\infty} \exp(-ax^{2}) dx} \quad \text{with } a = \sqrt{km}/\hbar$$

$$= \frac{(1/2a)\sqrt{\pi/a}}{\sqrt{\pi/a}} = \frac{1}{2a} = \frac{\hbar}{2\sqrt{km}}$$

$$\Delta x = \left[ \frac{\hbar^{2}}{4km} \right]^{1/4}$$

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$$\Delta x = \left[\hbar^2 / 4km\right]^{1/4}$$

- For mass 100g and force constant 6 N m<sup>-1</sup>,  $\Delta x \approx 8 \times 10^{-8}$ Å. This system would oscillate at about 1 Hz.
- For a diatomic molecule with (reduced) mass 1amu and force constant 600 N m<sup>-1</sup>,  $\Delta x \approx 0.07$ Å.

Notice that the uncertainty in the position of the macroscopic object is much smaller in absolute terms, not just in relative terms.

Uncertainty is a fundamental aspect of quantum mechanics, expressed in its simplest form by Heisenberg's uncertainty principle for position and momentum. If x is a position coordinate and  $p_x$  is the corresponding momentum (formally, the 'momentum conjugate to x', in the jargon), then the uncertainties in x and  $p_x$  satisfy the inequality 1

$$\Delta x \Delta p_x \ge \frac{1}{2}\hbar$$

Note that this relationship has nothing to do with experimental error; it is a fundamental feature of the theory. It tells us that, even in an ideal experiment, it is *impossible* to measure both the momentum and the position of a particle precisely. Why?

$$[\hat{x}, \hat{p}_x] \neq 0$$

## **1.7 The time-independent Schrödinger equation**

 $\hat{Q}\psi_q = q\psi_q$ 

It is an *eigenvalue equation*. The wavefunction  $\psi_q$  is an *eigenfunction*, and q is the corresponding *eigenvalue*.

For which operators does a wave function satisfy an eigenvalue equation? In general this is not an easy question to answer and depends on the system. We will meet various examples in the following lectures. However, there is one operator of which the (time-independent) wave function  $\psi$  is always an eigenfunction. This is the total energy operator, which is called the *Hamiltonian*, and has the symbol H. The resulting eigenvalue equation is

 $H\psi = E\psi$ 

which is the *time-independent Schrödinger equation*. This is the central equation of quantum chemistry, because solving it allows us to calculate  $\psi$ . Because  $\psi$  is an eigenfunction of H, we know that an experiment can measure the energy *E* precisely, with zero uncertainty. H is the sum of the kinetic and potential energy operators  $\hat{T}$  and  $\hat{V}$ :  $H = \hat{T} + \hat{V}$ 

We can not derive or prove Schrödinger equation

Quantum mechanics => Classical mechanics Microscopic Macroscopic

- <u>Macroscopic matter</u> Matter is particulate, energy varies continuously. The motion of a group of particles can be predicted knowing their positions, their velocities and the forces acting between them.
- <u>Microscopic particles</u> microscopic particles such as electrons exhibit a waveparticle "duality", showing both particle-like and wave-like characteristics. The energy level is discrete. ...

#### **Example: the harmonic oscillator Hamiltonian**

As an example we can construct the Hamiltonian for the harmonic oscillator. The kinetic energy  $T = \frac{1}{2}mv^2$  needs to be written in terms of the momentum  $p_x = mv$ , i.e. as  $p_x^2/2m$ . The potential energy for a harmonic oscillator is  $V = \frac{1}{2}kx^2$ . Replacing x and  $p_x$ by their operators gives  $\hat{T} = \frac{1}{2m} \hat{p}_x^2 \qquad \qquad \hat{V} = \frac{1}{2} k \hat{x}^2$  $H = \frac{1}{2m} \hat{p}_x^2 + \frac{1}{2} k \hat{x}^2$ and therefore Substituting  $\hat{x} = x$  and  $\hat{p}_x = -i\hbar d/dx$ , yields  $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$ 

Hence the Schrödinger equation of a harmonic oscillator is  $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \frac{1}{2}kx^2\psi = E\psi$ 

# **Time-dependent** wavefunctions

So far we have discussed time-independent wavefunctions  $\psi$ , which yieldobservables that are independent of time. Almost all of the wavefunctions you will encounter in chemistry are of this type, but it is useful to know that there exists a more general type of *time-dependent* wave function, which we will write  $\Psi(x, t)$ . These functions satisfy the *time-dependent* version of the Schrödinger equation:

$$H\Psi(x,t) = i\hbar \frac{\partial \Psi}{\partial t}$$
(\*)

If the Hamiltonian is independent of time, then there exists a special class of solutions of the form,

 $\Psi(x,t) = \psi(x) e^{-iEt/\hbar}$ 

where  $\psi(x)$  is the time-independent wave function.

If V(x,t) = V(x)

For the wavefunction  $\Psi = \psi(x)e^{-iEt/\hbar}$  the expectation value of any operator which doesn't itself depend on the time takes the form

$$\langle Q \rangle = \frac{\int \Psi^* \hat{Q} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\int (\psi e^{-iEt/\hbar})^* \hat{Q} (\psi e^{-iEt/\hbar}) d\tau}{\int (\psi e^{-iEt/\hbar})^* (\psi e^{-iEt/\hbar}) d\tau} = \frac{\int \psi^* \hat{Q} \psi d\tau}{\int \psi^* \psi d\tau}$$

so the time-dependence cancels out and the expectation value is independent of time. Such a wavefunction is called a *stationary state*, and these are the states that one usually meets in chemistry. We usually ignore the time-dependence contained in  $\exp(-iEt/\hbar)$ , and consider just the time-independent wavefunction  $\psi(x)$ , which satisfies the timeindependent Schrödinger equation.

Note, however, that there are more general time-dependent wave functions, in which the observables do depend on time.

# Continuity

The kinetic energy T involves the square of the momentum, which becomes a second derivative in operator form. The wavefunction has to satisfy the Schrödinger equation

$$H\psi = \hat{T}\psi + \hat{V}\psi = E\psi$$

 $\psi$  remains finite (remember that it describes the probability density) so if *V* is finite then  $\hat{V}\psi$  is finite. Therefore  $\hat{T}\psi$  must remain finite. This means that  $\psi$  and its first derivative must be *continuous*.

If *V* becomes infinite, and  $\psi$  is nonzero, then it is possible (in fact necessary) for  $\hat{T}\psi$  to be infinite also, which means that there is a discontinuity in the derivative of  $\psi$ . However  $\psi$  itself must still b



The time-independent Schrödinger equation is an equation for the second derivative of the wavefunction, which we can interpret informally as its curvature.

(a) The curvature of the wavefunction

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} \Big[ V(x) - E \Big] \psi$$



if  $E < V_{min}$ , then  $\psi$ " and  $\psi$  always have the same sign: If  $\psi$  is positive (negative), then  $\psi$ " is also positive(negative). This means that  $\psi$  always curves away from the axis. However, it has got to go to zero as  $x \rightarrow -\infty$  (else it would not be normalizable). At some point it's got to depart from zero (if it doesn't, it's going to be identically zero everywhere), in the positive direction. At this point its slope is positive, and increasing, so  $\psi$  gets bigger and bigger as x increases. It can't ever "turn over" and head back toward the axis, because that would require a negative second derivative—it always has to bend away from the axis. By the same token, if it starts out heading negative, it just runs more and more negative. In neither case is there any way for it to come back to zero, as it must (at  $x \rightarrow \infty$ ) in order to be normalizable.

#### (b) The emergence of quantization

The Schrödinger equation, being a differential equation, has an infinite number of solutions. It has mathematically acceptable solutions for any value of E. However, the Born interpretation imposes restrictions on the solutions. When the system has boundaries that confine the particle to a finite region, almost all the solutions are unacceptable: acceptable solutions occur only for special values of E. That is, energy quantization is a consequence of boundary conditions.

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#### (3) Superposition Principle

Mathematically, superposition principle means, if you linearly combine any number of solutions of an equation then the linear combination is itself a solution. The basic equation of quantum mechanics is Schrödinger equation, which is a linear differential equation, so its solutions obey superposition principle

A statefunction ( $\Psi$ ) can be expanded as a linear combination of the normalized eigenstates  $(\varphi_n)$  of a particular operator that constitute a basis of the space occupied by  $\Psi$ . For the discrete case:

	QM Statefunction	3-Space Vector
Vector	$  \Psi  angle = \sum_{n=1}^{\infty} \lvert b_n arphi_n  angle$	$\mathbf{A}(x, y, z) = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$
<b>Basis vectors</b>	Eigenstates: $\varphi_n$	Unit vectors: <b>i</b> , <b>j</b> , <b>k</b>
Projections	<i>b</i> <sub>1</sub> , <i>b</i> <sub>2</sub> , <i>b</i> <sub>3</sub> ,	х, y, z
Physical meaning of projections	$ b_n ^2$ = probability of finding the eigenvalue for the eigenstate $\varphi_n$ upon measurement.	Extension in space.
Result of measurement	The state $\Psi$ is destroyed. The system falls to one of the eigenstates $\varphi_n$ after measurement.	No change to <b>A</b> , i.e. all original components of <b>A</b> are intact.

#### **Expectation Value**

As an example, consider the expectation value of energy  $\langle E \rangle$  for a discrete system is in state  $\Psi$ . The normalized eigenfunctions of energy are  $\varphi_n$  and the eigenvalues are  $E_n$ . The expectation (average) value is the sum:

$$\left\langle E\right\rangle = \sum_{n=1}^{\infty} \left|b_n^2\right| E_n$$

where  $|b_n|^2$  is the absolute value of the coefficients of expansion that are given above. This is just the weighted average of the possible values of the observable E.

#### **Probability of Measurement**

From the definition of the expectation value  $\langle E \rangle$ 

we get,

$$\sum_{n=1}^{\infty} P(E_n) E_n = \sum_{n=1}^{\infty} \left| b_n^2 \right| E_n$$

or the probability of obtaining  $E_n$ , when the energy of the system (*in the state Y*) is measured, is equal to  $|b_n|^2$ . Note that since the eigenstates  $j_n$  are normalized,  $\sum |b_n|^2 = 1$ 

#### **The Double-Slit Experiment**

Electrons are fired at the screen. Here, some kind of detector is behind the screen and records the impact (intensity) of the electrons. First slit one is closed, then slit two. The results are illustrated in (a) and (b) respectively. The intensity for the electron passing through the first slot is  $I_1$  and the intensity for the electron passing through the second is  $I_2$ . The result with both slits open is shown in (c), where an interference pattern is observed.



for which the intensity is given by  $I = |\Psi|^2$   $I_1 = |\Psi_1|^2$   $I_2 = |\Psi_2|^2$ 

The resultant wavefunction

 $\Psi = \Psi_1 + \Psi_2$ 

The superposition principle gives the resultant wavefunction for both slots being opened. Until a measurement is made, the system is "in" all possible states. Here, the possible states are the electron going through slot one  $(\Psi_1)$  and the electron going through slot two  $(\Psi_2)$ . The corresponding intensity is,

 $| = | \Psi_1 + \Psi_2 |^2$ 

 $I = |\Psi_1 + \Psi_2|^2 = I_1 + I_2 + \text{Re}(\Psi_1^* \Psi_2) + \text{Re}(\Psi_1 \Psi_2^*)$ 

The final term is called the "interference term." This results in the oscillation pattern in (c).

The superposition of states thus explains the quantum interference pattern. When both slits are open, the description of the system is the superposition of the states when each slot is opened individually (i.e.,  $\Psi = \Psi_1 + \Psi_2$ ) and it is just this superposition that accounts for the interference. This is true until one tries to determine which path is taken by an electron, after which the state of the system collapses.