Classical Quantum Mechanics

Introduction: Classical particle, which you can use Newton's law of motion, is something large so you can see, i.e. it has mass, volume, position, etc. It is ***localized*** in space and ***distinguishable***. Classical wave, which you can use Maxwell's equations, has wave length, frequency, velocity, amplitude, intensity, energy, and momentum. It is spread out and occupies a relatively large portion of space.

Blanck's postulate (1900): Quantization of E. M. energy,
"Energy of radiation with frequency ν exists only in multiples of $h\nu$. A quantum of radiation of energy $h\nu$ is called a photon, $E = h\nu = \hbar\omega$". The properties of the photon gas could be easily recalled. For examples: the Plank radiation formula is:

$$u(\nu)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3 d\nu}{e^{h\nu/kT}-1} \to \frac{8\pi h\nu^2}{c^3}kT \quad (\text{as h} \to 0),$$

with c is the speed of light and ν is the frequency; the total energy density (energy per unit volume) is $u = \frac{1}{V}\int U(\nu)d\nu = aT^4, \qquad a = \frac{8\pi^5 k^4}{15h^3c^3} = 7.55\times10^{-16}\,\text{Jm}^{-3}\text{K}^{-4}$.

Einstein's postulate (1905): "*Light is composed of localized bundles of electromagnetic energy called quanta or photons*".
Comments: For photon, with rest mass $m_o = 0$, the energy from the general theory of relativity and wave theory are: $E = mc^2$, and $E = h\nu \quad \Rightarrow mc^2 = h\nu$
Since $c = \lambda\nu$, , (that is, the speed of light equal its frequency times its wavelength), then: $mc^2 = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{h}{mc} = \frac{h}{p}$, where p is the momentum.

de Broglie postulate (1922): Wave aspect of particles ***Duality***.
"If there is a particle of momentum p, its motion is associated with (or guided by) a wave of wavelength $\lambda = \frac{h}{p} = \frac{h}{mv}$".

Examples:

i. for a ball of mass of 0.15 kg, and speed of 41.6 m/s, the wavelength associated with the mass will be: $\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\text{ J.s}}{(0.15\text{ kg})(41.6\text{ m/s})} = 1.06\times10^{-34}\,\text{m}$.

ii. For an electron of $9.01\text{x}10^{-31}$ kg, and speed of 41.6 m/s, the wavelength associated with the electron will be: $\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\text{ J.s}}{(9.109\times10^{-31}\text{ kg})(41.6\text{ m/s})} = 1.75\times10^{-5}\,\text{m}$. . This is corresponding to infrared region of light and could be detected.

In Summary:

	Wave	Matter
Energy (*E*=)	$h\nu = \hbar w = \frac{hc}{\lambda}$	$\frac{1}{2}mv^2$
Momentum (*p*=)	$\frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}$	mv
Wavelength ($\lambda =$)	$\frac{c}{\nu}$	$\frac{h}{p} = \frac{h}{mv}$

Compton effect (1922): Interaction of radiation with matter.

1- Wave theory description:- When E. M. radiation is scattered from a charged particle (such as an electron), the scattered radiation will have the same frequency as the incident radiation in all directions (Isotropic), i.e. $E_{scattering} = E_{incident}$

2- Quantum Mechanics description}: The scattered radiation will have a frequency that is smaller than the incident radiation's and that also depends on the angle of scattering θ, i.e. $E_{scattering} \prec E_{incident}$. The shift in wave length, $\Delta\lambda$ is given by

$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_o c}(1-\cos\theta)$ where $\frac{h}{m_o c}$ is the Compton wave length $= 0.024\times 10^{-8}$ m for electron.

Conclusion: E. M. radiation has particle characteristic which describe the photo-electric effect, Compton effect, etc. It also has wave characteristic which describe the diffraction, interference, etc.

Bohr's principle of complementarity's: "The wave and particle aspects of E. M. radiation are complementary". That is, any given experimental measurement involving E. M. radiation can be completely explained by one model or the other, but not both".

Postulate of Quantum Mechanics:

1- "*A state function ψ is associated with each physical system*"

ψ must be ***well-behaved***, specifies all that can be known about the system. By well-behaved we mean that ψ should be:

i. single valued,
ii. finite,
iii. continuous everywhere as well as its first derivative (except at the infinite jump).
iv. must vanish at infinity, i.e. $\psi(r) \to 0$ as $r \to \pm\infty$, and
v. satisfy the normalization condition $\int_{\text{all space}} \psi^*(r)\psi(r)dr = 1$. An integral without specified limits will be understood to extent over the domain of the function.

The wave function, ψ, has no physical meaning, it could be complex, but the quantity $\psi^*(\mathrm{r},t)\psi(\mathrm{r},t)d\tau = |\psi(\mathrm{r},t)|^2 d\tau$, where ψ^* is the complex conjugate of ψ gives the probability of observing a particle in the interval $d\tau$ at a time *t*. $d\tau = dx$ in one dimensional coordinate. In three dimension $d\tau = dxdydz$ Cartesian coordinates and $d\tau = r^2 \sin\theta dr d\theta d\varphi$ in spherical coordinates.

Quantity	Classical definition	Quantum operator
position	r	r
Momentum	p	$-i\hbar\nabla$
Angular momentum	$\vec{r}\times\vec{p}$	$-i\hbar\vec{r}\times\nabla$
Kinetic energy	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2$
Total energy (Hamiltonian)	$\frac{p^2}{2m}+V$	$-\frac{\hbar^2}{2m}\nabla^2+\hat{V}$

2- "*For every observable quantity there is an operator**"

Observable quantity such as t, p, E, etc, and operators such as +, -, x, integration, differentiation, etc. The choice of the operator is arbitrary, but it must satisfy the condition that when it operates on a wave function it gives the observable quantity times the wave function, i.e.

$$\underbrace{\hat{A}}_{\text{operator}} \; \underbrace{\psi_n}_{\text{eigenfunctions}} = \underbrace{a_n}_{\text{eigenvalues}} \; \underbrace{\psi_n}_{\text{same eigenfunctions}} .$$

The set a_n may be discrete or continuous.

*An operator is, loosely speaking, some instruction that, when applied to a function, changes (maps) it into another function. Usually the operator is designate by a "hat" symbol over the letter.

Examples:

i.

$$\hat{D}e^{3x} = \frac{d}{dx}e^{3x} = 3e^{3x}$$

Operator: differential operator

Eigenfunction: e^{3x}

Eigenvalue: 3

ii.

$$\hat{D}3x^2 = \frac{d}{dx}3x^2 = 6x$$

Operator: differential operator

$3x^2$ **is NOT an eigenfunction.**

iii. The equation $\frac{d^2}{dx^2}\sin\left(\frac{\pi x}{2}\right) = -\frac{\pi^2}{4}\sin\left(\frac{\pi x}{2}\right)$, is an eigenvalue equation with an eigenvalue $= -\frac{\pi^2}{4}$

iv. This equation $\frac{d}{dx}\sin\left(\frac{\pi x}{2}\right) = \frac{\pi}{2}\cos\left(\frac{\pi x}{2}\right)$, is not an eigenvalue equation.

v. Find the explicit expressions for the operator $\hat{A} = \frac{\partial}{\partial x}x$.

Answer: $\hat{A}\psi = \left(\frac{\partial}{\partial x}x\right)\psi = \psi\left(\frac{\partial x}{\partial x}\right) + x\left(\frac{\partial \psi}{\partial x}\right) = (1 + x\frac{\partial}{\partial x})\psi \quad \Rightarrow \hat{A} = (1 + x\frac{\partial}{\partial x})$

3- "*If a system in a state described by a normalized wavefunction ψ_n, then the average value of the observable corresponding to $\hat{A}$ is given by*

$$\langle a \rangle = \int_{\text{all space}} \psi^*(r)\hat{A}\,\psi(r)dr \, .$$

Getting Information from the Wavefunction

The wavefunction contains our knowledge of the system at time *t*, and using the standard methods of quantum mechanics we can obtain a probability distribution for the result of any measurement at any time. For example

$$|\Psi(x,t)|^2$$

is the probability distribution for the position *x* of the particle at time *t*.
We can then find the mean and standard deviation of this probability distribution:

$$\langle x\rangle = \int x\,|\Psi(x,t)|^2\,dx$$

$$\langle x^2\rangle = \int x^2\,|\Psi(x,t)|^2\,dx$$

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

The corresponding results for momentum *p* are:

$$\langle p\rangle = -i\hbar \int \Psi(x,t)^{\star}\frac{\partial \Psi}{\partial x}\,dx$$

$$\langle p^2\rangle = -\hbar^2 \int \Psi(x,t)^{\star}\frac{\partial^2 \Psi}{\partial x^2}\,dx$$

$$\Delta p = \sqrt{\langle p^2\rangle - \langle p\rangle^2}$$

Delta x and *Delta p* are constrained by the uncertainty principle:

$$\frac{\Delta x\,\Delta p}{\hbar} \geq \frac{1}{2}$$

Example: A particle is represented by the normalized wave $\sqrt{2}\sin(\pi x)$ in the range {0, 1}. Calculate the probability that a particle is found in the range:

a) $0 \rightarrow 0.5$ b) $0.25 \rightarrow 0.75$.

Answer:

a) In general:

$$\text{Prob. } \{a \le x \le b\} = \int_a^b \psi^*_n(x)\,\psi_n(x)dx = \int_a^b \sqrt{2}\sin(\pi x)\sqrt{2}\sin(\pi x)dx = 2\int_a^b \sin^2(\pi x)dx = \left|x - \frac{1}{2\pi}\sin(2\pi x)\right|_a^b$$

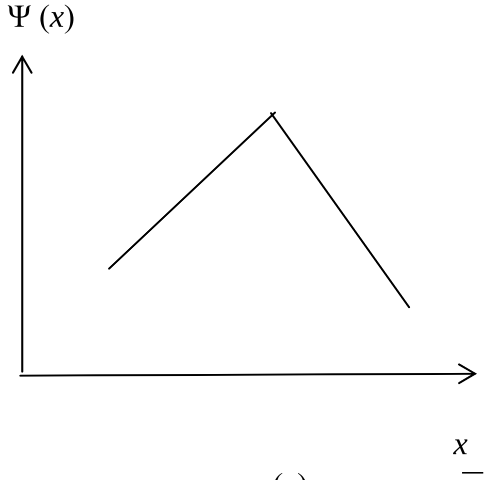
so,

$$\text{Prob. } \{0 \le x \le 0.5\} = \left|x - \frac{1}{2\pi}\sin(2\pi x)\right|_0^{0.5} = 0.5$$

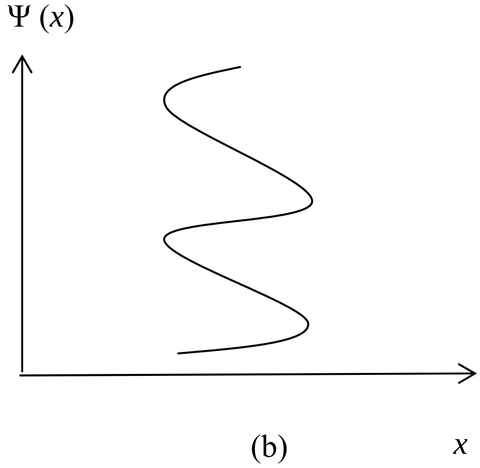
b) $$\text{Prob. } \{0.25 \le x \le 0.75\} = \left|x - \frac{1}{2\pi}\sin(2\pi x)\right|_{0.25}^{0.75} = 0.818$$

Example: Determine whether each of the following functions is acceptable or not as a state function over the indicated intervals:
Answer:

- ***a*- Not acceptable, the derivative is not continuous in the middle.**
- ***b*- Not acceptable, it is a multivalued function.**
- ***c*- Acceptable in that range.**
- ***d*- Acceptable in that range.**
- ***e*- Acceptable in that range.**
- ***f*- Not acceptable, the function itself is not continuous.**



(a)



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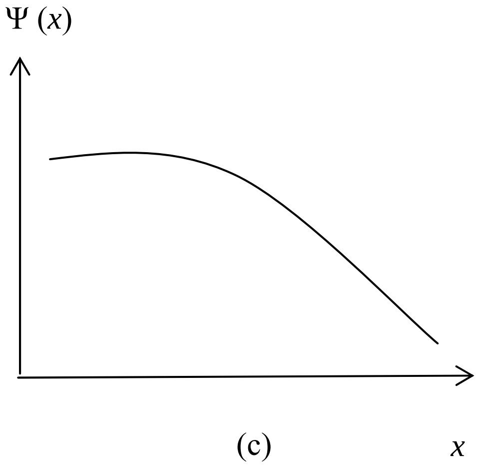

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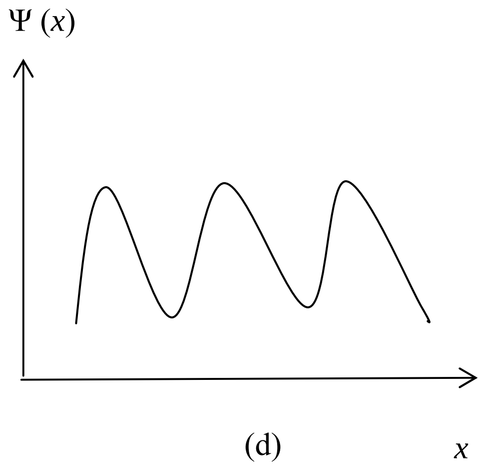

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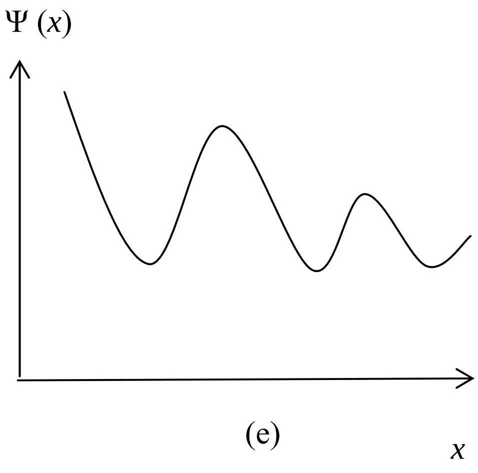

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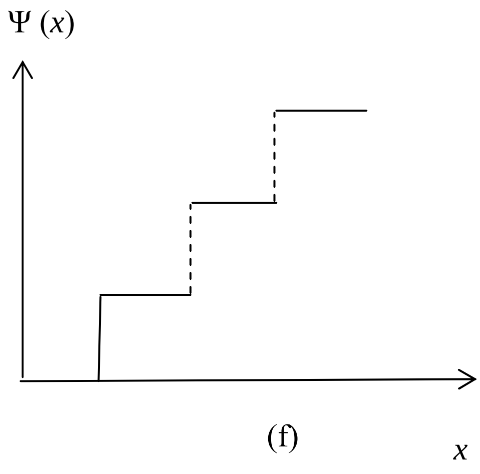


(f)

The Schrödinger Wave Equation in one Dimension

With the help of Bohr's complementarity's principle, superposition principle and de-Broglei duality of waves and matter, Schrödinger described the amplitude of a wave matter by a complex wavefunction $\psi(x,y,z,t)$ in which $|\psi(x,y,z,t)|^2 d\tau$ represent the probability of observing a particle in a volume $d\tau$ at the time *t*. Consider a one dimensional plane wave in the form:

$$\psi = e^{i(kx-wt)} = e^{\frac{i}{\hbar}(Px-Et)} = f(x)f(t) \tag{1}$$

Let us differentiate (1) with respect to *t*:

$$\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar}E\psi \Rightarrow i\hbar\frac{\partial}{\partial t}\psi = E\psi, \tag{2}$$

this has the form of an eigenvalue equation with the operator $\hat{E} = i\hbar\frac{\partial}{\partial t}$.

Let us differentiate (1) with respect to *x*:

$$\begin{aligned} &\frac{\partial\psi}{\partial x} = \frac{i}{\hbar}Pe^{\frac{i}{\hbar}(Px-Et)} = \frac{i}{\hbar}P\psi \quad \Rightarrow \quad \hat{P} = -i\hbar\frac{\partial}{\partial x}, \\ &\frac{\partial^2\psi}{\partial x^2} = -\frac{1}{\hbar^2}P^2e^{\frac{i}{\hbar}(Px-Et)} = -\frac{1}{\hbar^2}P^2\psi \Rightarrow \hat{P}^2 = -\hbar^2\frac{\partial^2}{\partial x^2}, \end{aligned}, \tag{3}$$

which has the form of an eigenvalue equation with the operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, or $\hat{p}^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$.

Since $E = \frac{P^2}{2m} \Rightarrow \hat{E}\psi = \frac{\hat{P}^2}{2m}\psi \Rightarrow i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$. In general, if $E = \frac{P^2}{2m} + V$,

$$\hat{H}\psi = \hat{E}\psi, \tag{4}$$

where $\hat{H}$ is called the Hamiltonian operator (also called the energy operator),

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}\right), \quad \hat{E} = i\hbar\frac{\partial}{\partial t} \tag{5}$$

$V = 0$ for a free particle.

Question: Why did we choose $e^{i(kx-wt)}$ rather than $\cos(kx-wt)$ or $\sin(kx-wt)$?

Answer: Suppose we choose $\psi_1 = \sin(kx-wt)$, and $\psi_2 = \sin(kx+wt)$, the superposition of the two waves gives $\psi_1 + \psi_2 = 2\sin(wt)\cos(kx)$. At t=0 the superposition will be canceled and gives non-physical situation. On the other side, if we choose $\psi_1 = e^{-i(kx-wt)}$ and $\psi_2 = e^{-i(kx+wt)}$ the superposition never vanishes identically everywhere and is acceptable wavefunction.

Solution of Schrödinger's Equation

The Schrödinger Equation for the wavefunction of a particle with Hamiltonian H is

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

This can be solved by separation of variables. Consider a separable solution:

$$\Psi(x,t) = u(x)T(t)$$

The separated functions satisfy

$$H\,u(x) = E\,u(x) \qquad i\hbar\frac{dT(t)}{dt} = E\,T(t)$$

The equation for u is the time-independent Schrödinger equation, and is also the eigenvalue equation for H, where E is the eigenvalue.
It has a set of solutions $u_n(x)$ with eigenvalues E_n.
The equation for T has the solution

$$T(t) = \exp\left(-iE_n t/\hbar\right)$$

We therefore obtain a set of separated solutions

$$\Psi_n(x,t) = u_n(x)\exp\left(-iE_n t/\hbar\right)$$

Because of the linearity of the Schrödinger equation any sum of these with complex constant coefficients is also a solution.
The general solution of the Time Dependent Schrödinger Equation (with a Hamiltonian independent of time) is thus

$$\Psi(x,t) = \sum_n C_n\,u_n(x)\exp\left(-iE_n t/\hbar\right)$$

Applications of the Schrödinger Equation in one Dimension

a- A Free Particle

A free particle implies no potential energy (V=0), i.e. total energy = Kinetic energy. The Schrödinger equation will reduced to

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \Rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi, \qquad k^2 = \frac{2mE}{\hbar^2}.$$

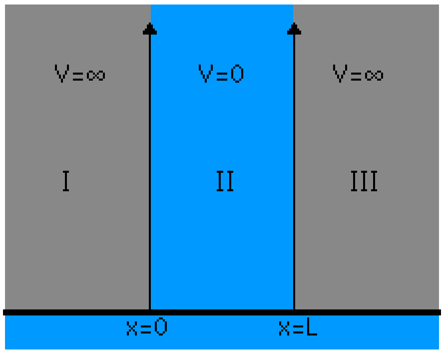
with the solution $\psi(x) = Ae^{\pm ikx}$, where A is the normalization constant. Check that.

b- An Analytic Solution: Particle-in-a-Box

Problem: Consider a particle of mass m held in a one dimensional infinite potential well of width L as:

$$V(x) = \begin{cases} 0, & 0 \langle x \langle L \\ \infty, & \text{otherwise} \end{cases}. \qquad (1)$$

Find the eigenfunctions of the Hamiltonian (i.e. the stationary states) and the corresponding eigenvalues.



Answer

***The strategy to solve the Schrödinger equation should be as follows*:**

First step: *Set up the Schrödinger equation*. In the region $0 \le x \le L$, one has:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \Rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi, \qquad k^2 = \frac{2mE}{\hbar^2} \qquad (2)$$

Second step: Suggest the best solution. Equation (2) is an equation of a simple harmonic and has a solution in the form

$$\psi(x) = ae^{-ikx} + be^{ikx} = \qquad (3.a)$$

$$= A\sin kx + B\cos kx \qquad (3.b)$$

We can pick any solution, let us try the sin and cos solution.

Third step: Wisely use the boundary conditions.

$$\psi(0) = 0 \quad \Rightarrow \quad B \to 0. \qquad (4)$$

So the eigenfunction will take the form $\psi(x) = A\sin kx$

Fourth step: Calculate the constants (coefficients).

i. To calculate k, use one of boundary conditions, i.e.

$$\psi(L) = 0 \quad \Rightarrow \quad A\sin kL = 0 \quad \Rightarrow k_n = \frac{n\pi}{L}, \quad n = 1, 2, \cdots, \qquad (5)$$

n is called the quantum number. n = 0 not included here because it is a trivial solution, i.e. it does not give any new physical behavior. Use of negative integers adds nothing new to the solution, so they are ignored. This is not always be the case. Equation (5) gives the eigenvalues in the form:

$$E_n = \frac{P^2}{2m} = \frac{(\hbar k_n)^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}, \qquad n = 1, 2, \cdots \tag{6}$$

So, the energy of the particle in the box is quantized, since the energy value is restricted to having only certain values. The corresponding eigenfunction as:

$$\psi_n(x) = A \sin k_n x = A \sin\left(\frac{n\pi}{L} x\right), \qquad n = 1, 2, \cdots \tag{7}$$

ii. To calculate *A*, use the normalization condition, i.e.

$$\int_0^L \psi_n^*(x) \psi_m(x) dx = \delta_{nm} \quad \Rightarrow A = \sqrt{\frac{2}{L}} \quad . \tag{8}$$

Finally, the eigenfunctions take the form:

$$\psi_n(x) = A \sin k_n x = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right), \qquad n = 1, 2, \cdots \tag{9}$$

Solved problems:

1- Use Equation (6) to calculate the ground energy of an electron confined in an atom. Take the diameter of the atom as $a = 10^{-8}$ m .

Answer: $E_1 = \left(\frac{\hbar^2 \pi^2}{2mL^2}\right) = \left(\frac{(3.14)^2 (1.054\times 10^{-34} \text{ J-s})^2}{2(9.1\times 10^{-31} \text{ kg})(10^{-10})^2}\right)$

$$= 0.605\times 10^{-17} \text{ J} = 37 \text{ eV}.$$

2- Calculate the probability that a particle in a one dimensional box of length *L* is found to be between *L* and *L*/2.

Answer: The probability is given by

$$\text{Prob. } \{a \le x \le b\} = \int_a^b \psi^*_n(x)\, \psi_n(x) dx = \int_a^b \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) dx$$

$$= \frac{2}{L} \int_a^b \sin^2\left(\frac{n\pi}{L} x\right) dx = \left| \frac{x}{L} - \frac{1}{2\pi n} \sin(\frac{2n\pi x}{L}) \right|_a^b$$

To do it, let us take $z = \frac{n\pi}{L} x$, then

$$\text{Prob. } \{0 \le x \le L/2\} = \frac{2}{n\pi} \int_0^{n\pi/2} \sin^2 z\, dz = \frac{2}{n\pi} \left| \frac{z}{2} - \sin(\frac{2z}{4}) \right|_0^{n\pi/2}$$

$$= \frac{2}{n\pi} \left(\frac{n\pi}{4} - \frac{\sin(n\pi)}{4} \right) = \frac{1}{2} \qquad \text{(for all } n\text{)}$$

Thus the probability that the particle lies in one half of the interval (0,*L*) is 1/2 and does not depend on *n*.

3- For the wavefunction: $\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi}{L} x\right), \qquad 0 \le x \le L$, Calculate:

$\prec x \succ$, $\prec x^2 \succ$, $\sigma_x = \sqrt{\prec x^2 \succ - \prec x \succ^2}$, $\prec p \succ$, $\prec p^2 \succ$, σ_p, $\sigma_x \sigma_p$, and $\prec E \succ$

Answer: In the following, we are going to use the general expression of the wavefunction. To have our value put *n*=1.

$$\langle x \rangle = \int_0^L \psi^*_n(x)\, x\, \psi_n(x) dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) .x. \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) dx = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi}{L}x\right) dx$$

$$= \frac{L}{2}$$

Thus, this particle having the given wavefunction has an average position in the middle of the box. The answer does not depend on *n*.

$$\langle x^2 \rangle = \int_0^L \psi^*_n(x)\, x^2\, \psi_n(x) dx = \frac{2}{L}\int_0^L x^2 \sin^2\left(\frac{n\pi}{L}x\right) dx = \frac{L^2}{6n^2}\left(\frac{2\pi^2 n^2 - 3}{\pi^2}\right)$$

$$\langle \hat{p} \rangle = \int_0^L \psi^*_n(x)\, \hat{p}\, \psi_n(x) dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi}{L}x\right)(-i\hbar\frac{\partial}{\partial x}) \sin\left(\frac{n\pi}{L}x\right) dx = 0$$

Note: $\langle \hat{p} \rangle = 0$ implies that the particles will be moving toward the positive (right) *x*-axis just as much as it moves toward negative (left) *x*-axis. It does not imply a lack of motion.

$$\langle \hat{p}^2 \rangle = \int_0^L \psi^*_n(x)\, \hat{p}^2\, \psi_n(x) dx = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi}{L}x\right)(\hbar^2\frac{\partial^2}{\partial x^2}) \sin\left(\frac{n\pi}{L}x\right) dx = \frac{n^2\hbar^2\pi^2}{L^2}$$

$$\sigma_x = \sqrt{\prec x^2 \succ - \prec x \succ^2} = \sqrt{\frac{L^2}{6n^2}\left(\frac{2n^2\pi^2 - 3}{\pi^2}\right) - \frac{L^2}{4}} =$$

$$\sigma_p = \sqrt{\prec p^2 \succ - \prec p \succ^2} = \sqrt{\frac{n^2\hbar^2\pi^2}{L^2}}$$

$$\sigma_x \sigma_p = \frac{\hbar}{2}\sqrt{\frac{\pi^2 n^2 - 2}{3}} = .57\hbar \rangle \frac{\hbar}{2}$$

Applications of the Schrödinger Equation in Three Dimensions

Problem: Consider a particle of mass m held in a three dimensional infinite potential well in the form:

$$V(x,y,z)=\begin{cases} 0, & 0\langle x\langle a,\ 0\langle y\langle b,\ 0\langle z\langle c \\ & . \\ \infty, & \text{otherwise} \end{cases} \qquad (1)$$

Find the eigenfunctions of the Hamiltonian (i.e. the stationary states) and the corresponding eigenvalues.

Answer

First step: *Set up the Schrödinger equation*. Construct the Schrödinger equation. In the region $(0,0,0)\langle (x,y,z)\langle (a,b,c)$, one has:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)=E\psi(x,y,z) \qquad (2)$$

To solve equation (2), we have to use a method called *separation of variables*. This could be done as follows:

i- Assuming that

$$\psi(x,y,z)=X(x)Y(y)Z(z) \qquad (3)$$

ii- Substitute (3) in (2), and use $E=E_x+E_y+E_z$, one can reaches:

$$\frac{d^2X(x)}{dx^2}+k_x{}^2X(x)=0, \quad k_x{}^2=\frac{2mE_x}{\hbar^2},$$

$$\frac{d^2Y(y)}{dy^2}+k_x{}^2Y(y)=0, \quad k_y{}^2=\frac{2mE_y}{\hbar^2},$$

$$\frac{d^2Z(z)}{dz^2}+k_x{}^2Z(z)=0, \quad k_z{}^2=\frac{2mE_z}{\hbar^2}.$$

Thus, we have changed the partial differential equation in three variables into three ordinary differential equations. They are exactly looks like the particle in a one dimensional box.

Second step: Suggest the best solution, following the solution of particle in a one dimensional box with the boundary conditions

$$\psi(0,y,z)=\psi(a,y,z) \quad \text{for all } y,\ \text{and } z$$

$$\psi(x,0,z)=\psi(x,b,z) \quad \text{for all } x,\ \text{and } z\ ,$$

$$\psi(x,y,0)=\psi(x,y,c) \quad \text{for all } x,\ \text{and } y$$

we have:

$$X(x)=\sqrt{\frac{2}{a}}\sin k_x x, \quad k_x=\frac{n_x\pi}{a}, \quad n_x=1,2,\cdots$$

$$Y(y)=\sqrt{\frac{2}{b}}\sin k_y y, \quad k_y=\frac{n_y\pi}{b}, \quad n_y=1,2,\cdots \qquad (5)$$

$$Z(z)=\sqrt{\frac{2}{c}}\sin k_z Z \quad k_z=\frac{n_z\pi}{c}, \quad n_z=1,2,\cdots$$

So,

$$E=E_x+E_y+E_z=\frac{\hbar^2\pi^2}{2m}\left(\frac{n_x{}^2}{a^2}+\frac{n_y{}^2}{b^2}+\frac{n_z{}^2}{c^2}\right) \qquad (6)$$

So, the energy of the particle in the box is quantized, since the energy value is restricted to having only certain values. The corresponding eigenfunction as:

$$\psi(x,y,z)=\sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right), \qquad n_i=1,2,\cdots \quad (7)$$

Notes:

iii. The three quantum numbers vary independently of one another.

iv. The normalization condition of the wave function implies.

$$\int_{-\infty}^{\infty}|\psi|^2 dxdydz=\int_0^a |X(x)|^2dx\int_0^a |Y(y)|^2dy\int_0^a |Z(z)|^2dz=1 \quad . \qquad (8)$$

v. As $a=b=c$, one can has

$$E=\frac{\hbar^2\pi^2}{2ma^2}\left(n_x{}^2+n_y{}^2+n_z{}^2\right) \qquad (9)$$

vi. By tabulating the allowed energies of a particle confined to a cube with infinitely rigid walls, we can have different quantum numbers may have the same energy, which is called degeneracy.

n_x	n_y	n_z	n^2	Degeneracy
1	1	1	3	None
1	1	2	6	
1	2	1	6	Threefold
2	1	1	6	
1	2	2	9	
2	1	2	9	Threefold
2	2	1	9	
1	1	3	11	
1	3	1	11	Threefold
3	1	1	11	
2	2	2	12	None

The degree of degeneracy of an energy level is the number of states that have that energy. The degeneracy appears due to the high degree of symmetry associated with the cubic shape of the box. The degeneracy will be removed, or lifted, if the side of the box were of unequal length.

Home Work

1-If The following operators and functions are defined as: $\hat{A}=\frac{d}{dx}(\ )$, $\hat{C}=\frac{1}{(\ )}$, and $\psi = 45xy^2$, calculate i. $\hat{A}(\hat{C}\psi)$, and ii. $\hat{C}(\hat{A}\psi)$.

2-Which of the following functions

$i.\ e^{ax+x^2/2}$ $\quad ii.\ e^{ax+x^2}$ $\quad iii.\ e^{ax-x^2/2}$ $\quad iv.\ e^{ax-x^2}$ $\quad v.\ e^{x-x^2/2}$

is the eigenfunction of $x+\frac{d}{dx}$ with eigenvalue *a*?

3-Which of the following functions

$i.\ e^{ax^2}$ $\quad ii.\ e^{ax}$ $\quad iii.\ x^2$ $\quad iv.\ ax+b$ $\quad v.\ \sin x$

are eigenfunctions of both $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$?

4-Indicate which of the following expressions yield eigenvalue equations, and indicate the eigenvalue. i. $\frac{d}{dx}\sin^2\left(\frac{\pi x}{2}\right)$ ii. $\frac{d}{dx}e^{-kx^2}$ iii. $\frac{d}{dx}e^{-kx}$, k is a constant

5-Check whether each of the following operators are linear or non-linear:

i. $\hat{A}f(x) = \text{Sqrt}\left[f(x)\right]$ $\quad$ ii. $\hat{A}f(x) = x^2 f(x)$

6-Find the explicit expressions for the following operators:

ii. $\left(\frac{d}{dx}+x\right)^2$ $\quad$ ii. $\left(\frac{d}{dx}+\frac{1}{x}\right)^3$ $\quad$ iii. $\left(x\frac{d}{dx}\right)^2$ $\quad$ iv. $\left(\frac{d}{dx}x\right)^2$

7- Determine whether each of the following functions is acceptable or not as a state function over the indicated intervals:

iii. $e^{-x}\ (0,\infty)$ $\quad$ ii. $e^{-|x|}\ (-\infty,\infty)$ $\quad$ iii. $\frac{\sin(x)}{x}\ (0,\infty)$ $\quad$ iv. $\sin^{-1}(x)\ (-1,1)$

v. $e^{-x^2}\ (-\infty,\infty)$

$\psi(x)$	Integrable	continuous	$\frac{d\psi}{dx}$ cont.	single-value
$e^{-x}\ (0,\infty)$				
$e^{-\|x\|}\ (-\infty,\infty)$				
$\frac{\sin(x)}{x}\ (0,\infty)$				
$\sin^{-1}(x)\ (-1,1)$				
$e^{-x^2}\ (-\infty,\infty)$				

8-For the following function:

$$\psi(x)=\begin{cases} A, & a\le x\le b \\ 0, & otherwise \end{cases}$$

calculate $A, \prec x\succ, \prec x^2\succ, \sigma_x^{\;2}=\prec x^2\succ-\prec x\succ^2, \sigma_x, \sigma_p$, and $\prec E=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\succ$

9-Calculate the normalization constant "*N*" in the wave-function:

$$\psi = N\; x\, e^{-ar}, \qquad -\infty\le x\le\infty .$$

(use the standard integrals: $\int_0^\infty x^n e^{-ax}dx=\frac{n!}{a^{n+1}}$; $\int_0^\infty \cos^n\theta\sin\theta d\theta=\frac{\{1+(-1)^n\}}{n+1}$;
and the spherical coordinates, in which $d\tau=r^2\sin\theta d\theta d\varphi, x=r\sin\theta\cos\varphi$).

10- For the Gaussian wave-function:

$$\psi(x)=Ne^{-x^2/2a}, \qquad -\infty\le x\le\infty$$

find $N, \prec x\succ, \prec x^2\succ, \sigma_x^{\;2}=\prec x^2\succ-\prec x\succ^2, \sigma_x, \sigma_p$, and $\prec E=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\succ$

(Useful integrals $\int_{-\infty}^{\infty} e^{-ax^2}dx=\sqrt{\frac{\pi}{a}}$, $\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx=\frac{1}{2}\sqrt{\frac{\pi}{a^3}}$,)

11- For the following function:

$$f(x)=\begin{cases} cx(a-x), & 0\le x\le a \\ 0, & otherwise \end{cases}$$

find $c, \prec x\succ, \prec x^2\succ, \sigma_x^{\;2}=\prec x^2\succ-\prec x\succ^2, \sigma_x, \sigma_p$, and $\prec E=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\succ$

(Useful integral $\int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2}dx=\frac{n!}{2a^{n+1}}$, $n=0,1,2,..$)

12- For the wavefunction: $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right), \quad 0 \le x \le L$, Calculate:

$$\prec x \succ, \prec x^2 \succ, \sigma_x, \prec p \succ, \prec p^2 \succ, \sigma_p, \sigma_x \sigma_p, \text{ and } \prec E \succ$$

13- Consider a particle of mass m held in a one dimensional infinite potential well of width L as:

$$V(x) = \begin{cases} 0, & |x| \le L/2 \\ \infty, & \text{otherwise} \end{cases}.$$

Find the eigenfunctions of the Hamiltonian (i.e. the stationary states) and the corresponding eigenvalues.

14- Find the commutation relations for the following operators::

x and $\frac{d}{dx}$ ii. $\frac{\partial}{\partial \varphi}$ and $f(r,\theta,\varphi)$ iii. $\frac{d^2}{dx^2}$ and x iv. $\int_0^x dx'$ and $\frac{d}{dx}$