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Chapter 3

Operators

Operators:

- Basis of quantum mechanics set up around two things:
  - Wave function, which contains all information about the system.
  - Operators which are rules whereby given some function, we can find another.

Operators:

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

- The entity in brackets is operators. The equation suggests that we have an energy operator, which operating on the wave function, given us the wave function again, but multiplied by the allowed values of the energy.

Operators:

- Operator is a rule that transforms a given function into another function

$$\hat{D}f(x) = f'(x)$$

$$\hat{D}(x^2 + 3e^x) = 2x + 3e^x$$

$$\hat{3}(x^2 + 3e^x) = 3x^2 + 9e^x$$

$$\cos(x^2 + 1)$$

$$\hat{A}f(x) = g(x)$$

Operators:

$$\frac{\hat{\partial}^2}{\partial x^2}$$ is a derivative operator

- $\wedge$ is called circumflex to indicate the operator.
- In quantum mechanics, the momentum operator is:

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

Operators:

The **sum** and the **difference** definition

$$(\hat{A} + \hat{B})f(x) \equiv \hat{A}f(x) + \hat{B}f(x)$$
$$(\hat{A} - \hat{B})f(x) \equiv \hat{A}f(x) - \hat{B}f(x)$$

Example

$$\hat{D} \equiv d/dx$$

$$(\hat{D} + \hat{3})(x^3 - 5) \equiv \hat{D}(x^3 - 5) + 3(x^3 - 5) =$$

$$3x^2 + (3x^3 - 15) = 3x^3 + 3x^2 - 15$$

Operators:

The **product** of Â and B operators

$$\hat{A}\hat{B}f(x) \equiv \hat{A}[\hat{B}f(x)]$$

Example

$$\hat{3}\hat{D}f(x) = \hat{3}[\hat{D}f(x)] = \hat{3}f'(x) = 3f'(x)$$

Maybe: AB ≠ BA

$$\hat{D}\hat{x}f(x) = \frac{d}{dx}[xf(x)] = f(x) + xf'(x) = (\hat{1} + \hat{x}\hat{D})f(x)$$

$$\hat{x}\hat{D}f(x) = \hat{x}\left[\frac{d}{dx}f(x)\right] = xf'(x)$$

Operator algebra

A and B are equal if $\hat{A}f = \hat{B}f$

$$\hat{D}\hat{x} = 1 + \hat{x}\hat{D}$$

Î is the unit operator

Ô is the null operator

We can transform an operator from one side of operator equation to other side

$$\hat{D}\hat{x} - \hat{x}\hat{D} - \hat{1} = 0$$

Operator algebra

Operators obey the association law of multiplication

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

The proof: let Â = d/dx, B = x, and Ĉ = 3.

$$(\hat{A}\hat{B}) = \hat{D}\hat{x} = 1 + \hat{x}\hat{D}, \qquad [(\hat{A}\hat{B})\hat{C}]f = (1 + \hat{x}\hat{D})3f = 3f + 3xf'$$

$$(\hat{B}\hat{C}) = 3\hat{x}, \qquad [\hat{A}(\hat{B}\hat{C})]f = \hat{D}(3xf) = 3f + 3xf'$$

Operator algebra

The major difference between operator algebra and ordinary algebra: Commutation law

Commentator of A and B operators $[\hat{A},\, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$

$[\hat{A}, \hat{B}] = 0$ ⟶ AB = BA → A and B commute

$\hat{A}\hat{B} \neq \hat{B}\hat{A}$ ⟶ A and B do not commute

examples

$$\left[\hat{3},\, \frac{d}{dx}\right] = \hat{3}\frac{d}{dx} - \frac{d}{dx}\hat{3} = 0 \qquad \left[\frac{d}{dx},\, \hat{x}\right] = \hat{D}\hat{x} - \hat{x}\hat{D} = 1$$

Operator algebra

EXAMPLE
Find $[z^3, d/dz]$.
To find $[z^3, d/dz]$, we apply this operator to an arbitrary function g(z). Using the commutator definition and the definitions of the difference and product of two operators, we have

$$[z^3, d/dz]g = [z^3(d/dz) - (d/dz)z^3]g = z^3(d/dz)g - (d/dz)(z^3 g)$$
$$= z^3 g' - 3z^2 g - z^3 g' = -3z^2 g$$

$$[z^3, d/dz] = -3z^2.$$

Operator algebra

The square of an operator is defined as the product with itself

$$\hat{A}^2 = \hat{A}\hat{A}$$

example

$$\hat{D}^2 f(x) = \hat{D}(\hat{D}f) = \hat{D}f' = f''$$

$$\hat{D}^2 = d^2/dx^2$$

Â is a linear operator if and only if:

$$\hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x)$$
$$\hat{A}[cf(x)] = c\hat{A}f(x)$$

Operator algebra

EXAMPLE
Is d/dx a linear operator? Is √ a linear operator?
We have

$$(d/dx)[f(x) + g(x)] = df/dx + dg/dx = (d/dx)f(x) + (d/dx)g(x)$$
$$(d/dx)[cf(x)] = c\,df(x)/dx$$

a linear operator.

$$\sqrt{f(x) + g(x)} \neq \sqrt{f(x)} + \sqrt{g(x)}$$

is nonlinear.

Operator algebra

A linear operator

$$[A_n(x)\hat{D}^n + A_{n-1}(x)\hat{D}^{n-1} + \cdots + A_1(x)\hat{D} + A_0(x)]y(x) = g(x)$$

Useful identities

$$(\hat{A} + \hat{B})\hat{C} = \hat{A}\hat{C} + \hat{B}\hat{C}$$ For all operators

$$\hat{A}(\hat{B} + \hat{C}) = \hat{A}\hat{B} + \hat{A}\hat{C}$$ For linear operators

Prove the above relations:

Operator algebra

EXAMPLE Find the square of the operator $d/dx + \hat{x}$.

$$(\hat{D} + \hat{x})^2 f(x) = (\hat{D} + \hat{x})[(\hat{D} + x)f] = (\hat{D} + \hat{x})(f' + xf)$$
$$= f'' + f + xf' + xf' + x^2 f = (\hat{D}^2 + 2\hat{x}\hat{D} + \hat{x}^2 + 1)f(x)$$
$$(\hat{D} + \hat{x})^2 = \hat{D}^2 + 2\hat{x}\hat{D} + \hat{x}^2 + 1$$

$$(\hat{D} + \hat{x})^2 = (\hat{D} + \hat{x})(\hat{D} + \hat{x}) = \hat{D}(\hat{D} + \hat{x}) + \hat{x}(\hat{D} + \hat{x})$$
$$= \hat{D}^2 + \hat{D}\hat{x} + \hat{x}\hat{D} + \hat{x}^2 = \hat{D}^2 + \hat{x}\hat{D} + 1 + \hat{x}\hat{D} + \hat{x}^2$$
$$= \hat{D}^2 + 2x\hat{D} + x^2 + 1$$

Eigenfunction and Eigenvalue

- Suppose that the effect of operating on some function f(x) with the operator Â is simply to multiply f(x) by a certain constant k:

$$\hat{A}f(x) = kf(x)$$

an eigenfunction of Â — an eigenvalue of Â

(Eigen is a German word meaning Characteristic).

Eigenfunction and Eigenvalue

$$(d/dx)e^{2x} = 2e^{2x}$$

Operator: d/dx **Eigenfunction: e^{2x}** **Eigenvalue: 2**

$$(d/dx)\ (\sin 2x) = 2\cos 2x$$

Operator: d/dx **This is not an Eigenvalue relation**

Example

If f(x) is an eigenfunction of the linear operator $\hat{A}$ and c is any constant, prove that cf(x) is an eigenfunction of $\hat{A}$ with the same eigenvalue as f(x).

The given information:

$$\hat{A}f = kf$$

$$\hat{A}(f+g) = \hat{A}f + \hat{A}g \quad \text{and} \quad \hat{A}(bf) = b\hat{A}f$$

c ≡ a constant

We want to prove:

$$\hat{A}(cf) = k(cf)$$

$$\hat{A}(cf) = c\hat{A}f = ckf = k(cf)$$

Example

(a) Find the eigenfunctions and eigenvalues of the operator d/dx. (b) If we impose the boundary condition that the eigenfunctions remain finite as x → ±∞, find the eigenvalues.

a)

$$df(x)/dx = kf(x)$$
$$df/f = k\,dx$$
$$\ln f = kx + \text{constant}$$
$$f = e^{\text{constant}}e^{kx}$$
$$f = ce^{kx}$$

k ≡ eigenvalue

b) k can be complex **k = a + bi**

$$\left\{\begin{array}{l} \left.\begin{array}{l} a > 0 \\ a < 0 \end{array}\right\} \text{f goes to infinity} \\ a = 0 \end{array}\right.$$

$$\boxed{k = bi}$$

operators and quantum mechanics

- Schrödinger equation is an eigenvalue problem

For a one particle one dimension problem

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]}_{\text{operator}}\underbrace{\psi(x)}_{\text{eigenfunction}} = \underbrace{E}_{\text{eigenvalue}}\psi(x)$$

Hamiltonian operator

operators and quantum mechanics

For conservative systems:

The classical mechanical Hamiltonian function =
the total energy (in terms of coordinates and conjugated momenta)

Conjugated moenta p_x, p_y, and p_z $\longrightarrow$ For Cartesian coordinates x, y, and z

$$p_x \equiv mv_x, \qquad p_y \equiv mv_y, \qquad p_z \equiv mv_z$$

E = Kinetic energy + Potential energy

operators and quantum mechanics

For a particle of mass m moving in one dimension and subject to V(x):

Kinetic energy = $p_x^2/2m$

Potential energy = V(x)

H = Kinetic energy + Potential energy

$$H = \frac{p_x^2}{2m} + V$$ **Hamiltonian function**

For that system:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$ **Hamiltonian operator**

operators and quantum mechanics

- A postulate of quantum mechanics:

  To every physical property there corresponds a quantum-mechanical operator, such that the operator for physical property B is obtained by writing the classical-mechanical expression for B as a function of Cartesian coordinate and corresponding momenta and then making the following replacements

$$\hat{q} = q \cdot \qquad \hat{p}_q = \frac{\hbar}{i}\frac{\partial}{\partial q} = -i\hbar\frac{\partial}{\partial q}$$

$$i = \sqrt{-1} \qquad 1/i = i/i^2 = i/(-1) = -i$$

operators and quantum mechanics

$$\hat{x} = x \cdot \qquad \hat{y} = y \cdot \quad \text{and} \quad \hat{z} = z \cdot$$

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \qquad \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \qquad \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$$

$$\hat{p}_x^2 = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = -\hbar^2\frac{\partial^2}{\partial x^2}$$

$$\hat{V}(x) = ax^2 \cdot \longleftarrow V(x) = ax^2$$

operators and quantum mechanics

For a particle of mass m moving in one dimension and subject to V(x):

$$T = p_x^2/2m$$

The classical-mechanical Expression for kinetics energy

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

The corresponding operator

$$H = T + V = p_x^2/2m + V(x)$$

The classical-mechanical Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

The quantum-mechanical Hamiltonian operator

In agreement with the Schrödinger equation

operators and quantum mechanics

If B is a physical property:

$$\hat{B}f_i = b_i f_i, \qquad i = 1, 2, 3, \ldots$$

A measurement of the property B must yield one of the eigenvalues b_i of the operator $\hat{B}$

For example:

$$\hat{H}\psi_i = E_i\psi_i$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_i = E_i\psi_i$$

operators and quantum mechanics

- It is postulated that:

  If Ψ is an eigenfunction of B with eigenvalues b_k, then a measurement of B is certain to yield the value b_k.

  For example: if B ≡ E

  The eigenfunctions of E are solutions of time-independent Schrödinger equation $\Psi(x)$

operators and quantum mechanics

Suppose the system is in a stationary state:

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

Is $\Psi(x,t)$ an eigenfunction of $\hat{H}$?

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

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

$$\hat{H}\Psi = E\Psi$$

For a stationary state, Ψ is an eigenfunction of $\hat{H}$ and we certain to obtain the E value when we measure the energy.

operators and quantum mechanics

Momentum?

$$\hat{p}_x g = kg$$

$$\frac{\hbar}{i}\frac{dg}{dx} = kg$$

$$g = Ae^{ikx/\hbar}$$

$$-\infty < k < \infty$$

operators and quantum mechanics

The momentum of a particle in a box

$$\Psi(x,t) = e^{-iEt/\hbar}\left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right)$$

$$E = n^2h^2/8ml^2$$

Does the particle have a definite value of p_x?
That is, is Ψ(x,t) an eigenfunction of p_x?

$$\hat{p}_x\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}e^{-iEt/\hbar}\left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right) = \frac{n\pi\hbar}{il}e^{-iEt/\hbar}\left(\frac{2}{l}\right)^{1/2}\cos\left(\frac{n\pi x}{l}\right)$$

$$\boxed{\hat{p}_x\Psi \neq \text{constant}\cdot\Psi}$$

operators and quantum mechanics

Are the particle-in-a-box stationary-state wave functions eigenfunctions of p_x^2 ?

$$\hat{p}_x^2\Psi = -\hbar^2\frac{\partial^2}{\partial x^2}e^{-iEt/\hbar}\left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right)$$

$$= \frac{n^2\pi^2\hbar^2}{l^2}e^{-iEt/\hbar}\left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right)$$

$$\boxed{\hat{p}_x^2\Psi = \frac{n^2h^2}{4l^2}\Psi}$$

$$\hat{H} = \hat{T} + \hat{V} = \hat{T} = \hat{p}_x^2/2m$$

$$\hat{H}\Psi = E\Psi = \frac{\hat{p}_x^2}{2m}\Psi$$

$$\hat{p}_x^2\Psi = 2mE\Psi = 2m\frac{n^2h^2}{8ml^2}\Psi = \frac{n^2h^2}{4l^2}\Psi$$

$$\boxed{p_x^2 = n^2h^2/4l^2}$$

operators and quantum mechanics

Example:
The energy of a particle of mass m in a one-dimensional box of length l is measured. What are the possible values that can result from the measurement if (a) at the time the measurement begins, the particle's state function is $\Psi = (30/l^5)^{1/2}x(l-x)$ for $0 \le x \le l$; (b) at the time the measurement begins, $\Psi = (2/l)^{1/2}\sin(3\pi x/l)$ for $0 \le x \le l$?

$$E = \frac{n^2h^2}{8ml^2}$$

a) $\hat{H}\psi \ne \text{cte} \times \psi$
One of above values

b) n = 3 $E = \dfrac{9h^2}{8ml^2}$

The three dimensional many-particle Schrödinger equation

The time dependent Schrodinger equation for time development of the state function is postulated to have the form:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

$$\hat{H}\psi = E\psi$$

For one-particle, three-dimensional system:

$$H = T + V = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V(x, y, z)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)$$

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Laplacian operator

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

The three dimensional many-particle Schrödinger equation

For three-dimensional, n particle system

$$T = \frac{1}{2m_1}\left(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2\right) + \frac{1}{2m_2}\left(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2\right) + \ldots + \frac{1}{2m_n}\left(p_{x_n}^2 + p_{y_n}^2 + p_{z_n}^2\right)$$

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - \ldots - \frac{\hbar^2}{2m_n}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2}\right)$$

$$\hat{T} = -\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2 \qquad \nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

The three dimensional many-particle Schrödinger equation

$$\hat{T} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i}\nabla_i^2$$

$$V = V(x_1, y_1, z_1, ..., x_n, y_n, z_n)$$

$$\boxed{\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i}\nabla_i^2 + V(x_1, ..., z_n)}$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

If the potential energy depends only on the 3n coordinates

The three dimensional many-particle Schrödinger equation

$$\left[-\sum_{i=1}^{n} \frac{\hbar^2}{2m_i}\nabla_i^2 + V(x_1, ..., z_n)\right]\psi = E\psi$$

$$\psi = \psi(x_1, y_1, z_1, ..., x_n, y_n, z_n)$$

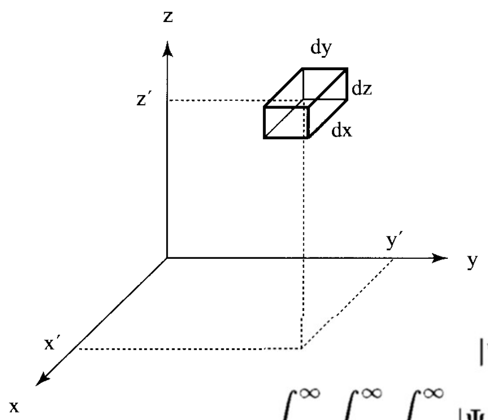
3n coordinate

Two particles interact so that the potential energy is inversely proportional to the distance between them:

$$\left[-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right) + \frac{c}{[(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}}\right]\psi = E\psi$$

$$\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

The three dimensional many-particle Schrödinger equation



Born postulate:

For one-particle, three-dimensional system

$$|\Psi(x', y', z', t)|^2 \, dx \, dy \, dz$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(x, y, z, t)|^2 \, dx \, dy \, dz = 1$$

The three dimensional many-particle Schrödinger equation

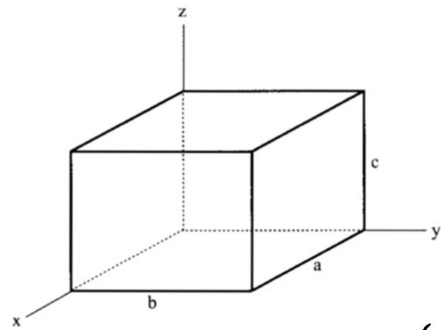
For a three-dimensional, n-particle system:

$$|\Psi(x_1', y_1', z_1', x_2', y_2', z_2', \ldots, x_n', y_n', z_n', t)|^2 dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \cdots dx_n dy_n dz_n$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi|^2 dx_1 \, dy_1 \, dx_1 \cdots dx_n \, dy_n \, dz_n = 1$$

$$\int |\Psi|^2 d\tau = 1 \xrightarrow[|\Psi|^2 = |\psi|^2]{\text{For a stationary state}} \int |\psi|^2 d\tau = 1$$

The particle in a three dimensional box



$V(x, y, z) = 0$ **in the region** $\begin{cases} 0 < x < a \\ 0 < y < b \\ 0 < z < c \end{cases}$

$V = \infty$ **elsewhere**

The particle in a three dimensional box

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

We assume the the solutions can be written as: **Separation of variables**

$$\psi(x,\, y,\, z) = f(x)g(y)h(z)$$

$$\frac{\partial^2\psi}{\partial x^2} = f''(x)g(y)h(z), \quad \frac{\partial^2\psi}{\partial y^2} = f(x)g''(y)h(z), \quad \frac{\partial^2\psi}{\partial z^2} = f(x)g(y)h''(z)$$

$$-(\hbar^2/2m)f''gh - (\hbar^2/2m)fg''h - (\hbar^2/2m)fgh'' - Efgh = 0$$

$$-\frac{\hbar^2 f''}{2mf} - \frac{\hbar^2 g''}{2mg} - \frac{\hbar^2 h''}{2mh} - E = 0$$

The particle in a three dimensional box

$$-\frac{\hbar^2 f''(x)}{2mf(x)} = \frac{\hbar^2 g''(y)}{2mg(y)} + \frac{\hbar^2 h''(z)}{2mh(z)} + E$$

$$E_x \equiv -\hbar^2 f''(x)/2mf(x)$$

$$E_y \equiv -\hbar^2 g''(y)/2mg(y).$$

$$E_z \equiv -\hbar^2 h''(z)/2mh(z)$$

$$E_x + E_y + E_z = E$$

The particle in a three dimensional box

$$\frac{d^2 f(x)}{dx^2} + \frac{2m}{\hbar^2} E_x f(x) = 0 \qquad \begin{cases} f(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \\ E_x = \frac{n_x^2 h^2}{8ma^2}, \quad n_x = 1, 2, 3... \end{cases}$$

$$\frac{d^2 g(y)}{dy^2} + \frac{2m}{\hbar^2} E_y g(y) = 0. \qquad \begin{cases} g(y) = \left(\frac{2}{b}\right)^{1/2} \sin\left(\frac{n_y \pi y}{b}\right) \\ E_y = \frac{n_y^2 h^2}{8mb^2}, \quad n_y = 1, 2, 3... \end{cases}$$

$$\frac{d^2 h(z)}{dz^2} + \frac{2m}{\hbar^2} E_z h(z) = 0 \qquad \begin{cases} h(z) = \left(\frac{2}{c}\right)^{1/2} \sin\left(\frac{n_z \pi z}{c}\right) \\ E_z = \frac{n_z^2 h^2}{8mc^2}, \quad n_z = 1, 2, 3... \end{cases}$$

The particle in a three dimensional box

$$E_x + E_y + E_z = E$$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

$$\psi(x, y, z) = f(x)g(y)h(z)$$

$$\psi(x, y, z) = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

The particle in a three dimensional box

$$\iiint F(x)G(y)H(z)\,dx\,dy\,dz = \int F(x)dx \int G(y)dy \int H(z)dz$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2\,dx\,dy\,dz = \int_0^a |f(x)|^2 dx \int_0^b |g(y)|^2 dy \int_0^c |h(z)|^2 dz = 1$$

Since x, y, and z factors of wave function are each independently normalized, the wave function is normalized:

What are the dimensions of wave function?

The particle in a three dimensional box

If a=b=c $E = (h^2/8ma^2)(n_x^2 + n_y^2 + n_z^2)$

$n_x n_y n_z$	111	211	121	112	122	212	221	113	131	311	222
$E(8ma^2/h^2)$	3	6	6	6	9	9	9	11	11	11	12

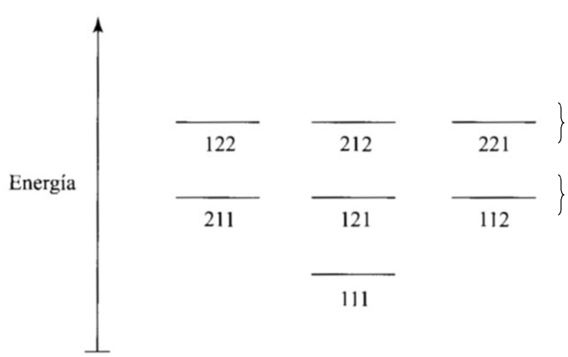
$$\psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

211 $$\psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{2\pi x}{a}\right) \sin\left(\frac{\pi y}{b}\right) \sin\left(\frac{\pi z}{c}\right)$$

121 $$\psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi y}{b}\right) \sin\left(\frac{\pi z}{c}\right)$$

112 $$\psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{b}\right) \sin\left(\frac{2\pi z}{c}\right)$$

The particle in a three dimensional box



these eigenvalues are said to be degenerate

The degree of degeneracy of an energy level is the number of states that have that energy

The degree of degeneracy ≡ Degeneracy

Degeneracy

If $\hat{H}\psi_1 = w\psi_1, \ \hat{H}\psi_2 = w\psi_2, \ \cdots, \ \hat{H}\psi_n = w\psi_n$

Φ will be an eigenfunction of H with eigenvalue w

$$\phi \equiv c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n$$

We must show ĤΦ = wΦ

$$\hat{H}(c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n) = w(c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n)$$

$$\hat{H}(c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n) = \hat{H}(c_1\psi_1) + \hat{H}(c_2\psi_2) + \cdots + \hat{H}(c_n\psi_n)$$

$$\begin{aligned}\hat{H}(c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n) &= c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 + \cdots + c_n\hat{H}\psi_n \\ &= c_1 w\psi_1 + c_2 w\psi_2 + \cdots + c_n w\psi_n\end{aligned}$$

$$\hat{H}(c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n) = w(c_1\psi_1 + c_2\psi_2 + \cdots + c_n\psi_n)$$

Degeneracy

$$\boxed{\begin{aligned}\hat{H}\psi_{211} &= E_2\psi_{211} \\ \hat{H}\psi_{121} &= E_2\psi_{121} \\ \hat{H}\psi_{112} &= E_2\psi_{112}\end{aligned}}$$

$$\Downarrow$$

$$\boxed{\hat{H}(c_1\psi_{211} + c_2\psi_{121} + c_3\psi_{121}) = E_2(c_1\psi_{211} + c_2\psi_{121} + c_3\psi_{121})}$$

$$\hat{H}(c_1\psi_{211} + c_2\psi_{121} + c_3\psi_{121}) = \frac{6h^2}{8ma^2}(c_1\psi_{211} + c_2\psi_{121} + c_3\psi_{121})$$

Degree of degeneracy

Degeneracy

Linearly independent functions

$f_1, \ldots, f_n$ **are independent functions if:**

$c_1 f_1 + \cdots + c_n f_n = 0$

Only be satisfied with all the constants c1, c2, …, c_n equal to zero

$f_1 = 3x,\ f_2 = 5x^2 - x\ ,\ f_3 = x^2$ $\qquad f_2 = 5f_3 - \frac{1}{3}f_1$

$g_1 = 1,\ g_2 = x\ ,\ g_3 = x^2$

Degree of degeneracy ≡ ?

Average values

Probability density for a one-particle one-dimensional system

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

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi(x,t)|^2 dx$$

Probability density for a one-particle three-dimensional system

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

$$\langle x \rangle = \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(x,y,z,y)|^2 dy\, dz\right] x\, dx$$

$$\langle x \rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(x,y,z,t)|^2\, x\, dx\, dy\, dz$$

Average values

The average value of some property B(x,y,z) that is a function of particles coordinates

$$\langle B(x, y, z)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(x, y, z, t)|^2 B(x, y, z)\, dx\, dy\, dz$$

$$\langle B(x, y, z)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi^* B \Psi\, dx\, dy\, dz$$

In general B depends on coordinates and momenta

$$B = B(x, y, z, p_x, p_y, p_z)$$

For the one particle, three-dimensional case

Average values

We ***postulate*** that < B> for a system in state Ψ is :

$$\langle B\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi^* B\left(x, y, z, \frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}\right) \Psi\, dx\, dy\, dz$$

$$\langle B\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi^* \hat{B} \Psi\, dx\, dy\, dz$$

Average values

For the n-particle case:

$$\langle B \rangle = \int \Psi^* \hat{B} \Psi d\tau$$

$\hat{B}\Psi^*\Psi$ and $\Psi^*\Psi\hat{B}$ are not the same as $\Psi^*\hat{B}\Psi$

For a stationary state:

$$\Psi^* \hat{B} \Psi = e^{iEt/\hbar} \psi^* \hat{B} e^{-iEt/\hbar} \psi = e^0 \psi^* \hat{B} \psi = \psi^* \hat{B} \psi$$

$$\langle B \rangle = \int \psi^* \hat{B} \psi d\tau$$

Time independent

Average values

where Ψ is an eigenfunction of B $\qquad \hat{B}\Psi = k\Psi$

$$\langle B \rangle = \int \Psi^* \hat{B} \Psi \, d\tau = \int \Psi^* k \, \Psi \, d\tau = k \int \Psi^* \Psi \, d\tau = k$$

$$\langle B + C \rangle = \langle B \rangle + \langle C \rangle$$

$$\langle BC \rangle \neq \langle B \rangle \langle C \rangle$$

Average values

Example:
Find <x> and <p_x> for the ground stationary state of a particle in a three-dimensional box.

$$\langle x\rangle = \int \psi^* \hat{x} \psi \, d\tau = \int_0^c \int_0^b \int_0^a f^* g^* h^* x f g h \, dx \, dy \, dz$$

$$\langle x\rangle = \int_0^a x |f(x)|^2 \, dx \int_0^b |g(y)|^2 \, dy \int_0^c |h(z)|^2 \, dz = \int_0^a x |f(x)|^2 \, dx$$

$$\langle x\rangle = \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{a}{2}$$

$$\langle p_x\rangle = \int \psi^* \hat{p}_x \psi \, d\tau = \int_0^c \int_0^b \int_0^a f^* g^* h^* \frac{\hbar}{i} \frac{\partial}{\partial x} [f(x) g(y) h(z)] \, dx \, dy \, dz$$

$$\langle p_x\rangle = \frac{\hbar}{i} \int_0^a f^*(x) f'(x) \, dx \int_0^b |g(y)|^2 \, dy \int_0^c |h(z)|^2 \, dz$$

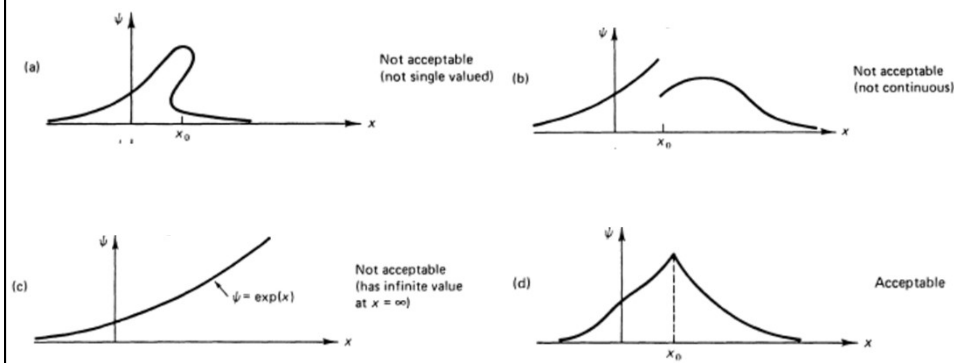
$$\langle p_x\rangle = \frac{\hbar}{i} \int_0^a f(x) f'(x) \, dx = \frac{\hbar}{2i} f^2(x) \Big|_0^a = 0$$

Well-behaved functions

- we require:
  - ψ to be continuous.
  - ψ to be quadratically integrable.
  - it must be single-valued.
  - we usually also require that all the partial derivatives be continuous.
  - it is sometimes stated that the wave function must be finite everywhere, including infinity. (the fundamental requirement is quadratic integrability, rather than finiteness.)

acceptable **(well-behaved) functions.**

Well-behaved functions



(a) ψ is triple valued at x_0. (b) ψ is discontinuous at x_0. (c) ψ grows without limit as x approaches +∞ (i.e., ψ "blows up," or "explodes"). (d) ψ is continuous and has a "cusp" at x_0. Hence, first derivative of ψ is discontinuous at x_0 and is only piecewise continuous. This does not prevent ψ from being acceptable.