MATHEMATICAL & PHYSICAL CONCEPTS IN QUANTUM MECHANICS

Operators

An operator is a symbol which defines the mathematical operation to be cartried out on a function.

Examples of operators:

d/dx = first derivative with respect to x

√ = take the square root of

3 = multiply by 3

Operations with operators:

If A & B are operators & f is a function, then

$(A + B)\, f = Af + Bf$

$A = d/dx,\ B = 3,\ f = f = x^2$

$(d/dx + 3)\, x^2 = dx^2/dx + 3x^2 = 2x + 3\, x^2$

$ABf = A\,(Bf)$

$d/dx\,(3\, x^2) = 6x$

Note that A(Bf) is not necessarily equal to B(Af):

$A = d/dx,\ B = x,\ f = x^2$

$A\,(Bf) = d/dx(x\cdot x^2) = d/dx\,(x^3) = 3\, x^2$

$B\ (Af) = x\ (d/dx\ x^2) = 2\ x^2$

In general, $d/dx\ (xf) = f + x\ df/dx = (1 + x\ d/dx)f$

So $d/dx\ x = 1 + x\ d/dx$

Since A & B are operators rather than numbers, they don't necessarily *commute*. If two operators A & B commute, then

$AB = BA$

and their commutator = 0:

$[A,B] = AB - BA = 0$

(Numbers always commute: $2 \cdot 3\ f = 3 \cdot 2\ f$; $[2,3] = 0$)

What is the commutator of d/dx & x?

$[d/dx,x] = ?$

Since we have shown that $d/dx\ x = 1 + x\ d/dx$, then

$[d/dx,x] = d/dx\ x - x\ d/dx = 1$

What is the commutator of 3 & d/dx?

$[3,d/dx]\ f = 3\ d/dx\ f - d/dx\ 3\ f = 3\ d/dx\ f - 3\ d/dx\ f = 0 =$

$[d/dx,3]$

Equality of operators: If $Af = Bf$, then $A = B$

Associative Law: $A(BC) = (AB)C$

Square of an operator: Apply the operator twice $A^2 = A\,A$

$(d/dx)^2 = d/dx\ d/dx = d^2/dx^2$

C = take the complex conjugate; $f = e^{ix}$

$C\,f = (e^{ix})^* = e^{-ix}$

$C^2 f = C\,(Cf) = C\,(e^{-ix}) = (e^{-ix})^* = e^{ix} = f$

If $C^2 f = f$, then $C^2 = 1$

Linear Operator: A is a linear operator if

$A(f + g) = Af + Ag$

$A(cf) = c\,(Af)$

where f & g are functions & c is a constant.

Examples of linear operators:

$d/dx\,(f + g) = df/dx + dg/dx$

$3(f + g) = 3f + 3g$

Examples of nonlinear operators:

$\sqrt{(f + g)}$ is not equal to $\sqrt{f} + \sqrt{g}$

inverse $(f + g) = 1/(f + g)$ is not equal to $1/f + 1/g$

Cautionary note: When trying to determine the result of operations with operators that include partial derivatives, always using a function as a "place holder". For example, what is $(d/dx + x)^2$?

$$(d/dx + x)^2 f = (d/dx + x)\,(d/dx + x)\,f$$

$$= (d/dx + x)\,(df/dx + xf)$$

$$= d/dx\,(df/dx + xf) + x\,(df/dx + xf)$$

$$= d^2f/dx^2 + d/dx\,(xf) + x\,(df/dx) + x^2 f$$

$$= d^2f/dx^2 + x\,df/dx + f + x\,(df/dx) + x^2 f$$

$$= (d^2/dx^2 + 2x\,d/dx + 1 + x^2)f$$

So $(d/dx + x)^2 = (d^2/dx^2 + 2x\,d/dx + 1 + x^2)$

Eigenfunction/Eigenvalue Relationship:

When an operator operating on a function results in a constant times the function, the function is called an eigenfunction of the operator & the constant is called the eigenvalue

$$A\,f(x) = k\,f(x)$$

$f(x)$ is the eigenfunction & k is the eigenvalue

Example: $d/dx(e^{2x}) = 2\,e^{2x}$

e^{2x} is the eigenfunction; 2 is the eigenvalue

How many different eigenfunctions are there for the operator d/dx?

$$df(x)/dx = k\,f(x)$$

Rearrange the eq. to give: $df(x)/f(x) = k\ dx$

and integrate both sides: $\int df(x)/f(x) = \int k\ dx$

to give: $\ln f = kx + C$

$$f = e^{kx+C} = e^{kx}\, e^{C} = e^{kx}\, C',\ C' = e^{C}$$

Since there are no restrictions on k, there are an infinite number of eigenfunctions of d/dx of this form.

C' is an arbitrary constant. Each choice of k leads to a different solution. Each choice of C' leads to multiples of the same solution.

Any eigenfunction of a linear operator can be multiplied by a constant and still be an eigenfunction of the operator. This means that if f(x) is an eigenfunction of A with eigenvalue k, then cf(x) is also an eigenfunction of A with eigenvalue k. Prove it:

$$A\, f(x) = k\, f(x)$$

$$A\, [cf(x)] = c\, [Af(x)] = c\, [kf(x)] = k\, [cf(x)]$$

To specify the type of eigenfunction of d/dx more definitively, one can apply a physical constraint on the eigenfunction, as we did with the Particle in a Box:

$$c\, e^{kx} \text{ must be finite as } x \rightarrow \pm\infty$$

The most general k is a complex number: $k = a + ib$

Then $c\, e^{kx} = ce^{(a+ib)x} = c\, e^{ax}\, e^{ibx} = c\, e^{ax}\, (\cos bx + i\sin bx)$

Since $e^{ax} \rightarrow \infty$ for $x \rightarrow \pm\infty$, a must be 0

b can be any number

So $c\ e^{ibx}$ is the correct eigenfunction of d/dx.

Relationship of Quantum Mechanical Operators to Classical Mechanical Operators

In the 1-dimensional Schrödinger Eq.

$$[(-\hbar^2/2m)\ d^2/dx^2 + V(x)]\ \psi(x) = E\ \psi(x),$$

$\psi(x)$ is the eigenfunction, E is the eigenvalue, & the Hamiltonian operator is

$$(-\hbar^2/2m)\ d^2/dx^2 + V(x)$$

The Hamiltonian function was originally defined in classical mechanics for systems where the total energy was conserved. This occurs when the potential energy is a function of the coordinates only. this is the type of system to be studied with quantum mechanics.

The classical Hamiltonian expressed Newton's Eq. of Motion such that the energy was a function of the coordinates (x,y,z) & conjugate momentum (p_x, p_y, p_z) where

$$p_x = m\ v_x \qquad\qquad v_x = p_x/m$$

with m = mass & v_x = velocity in the x-direction

Classical kinetic energy (KE) is defined as

$$KE_x = (1/2)\ m\ v_x^2 = p_x^2/(2m)$$

The classical Hamiltonian function is defined as the sum of the kinetic energy (a function of momentum) & the potential energy (a function of cordinates)

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

for a 1-dimensional system

Comparison to the Schrödinger Eq. shows that

$$(-\underline{h}^2/2m)\ d^2/dx^2 \leftrightarrow p_x^2/(2m)$$

Some Postulates of Quantum Mechanics:

<u>(1) Postulate: For every physical property, there is a quantum mechanical operator</u>

<u>(2) Postulate: To find the operator, write the classical mechanical expression for the property</u>

$$F(x,y,z,p_x, p_y, p_z)$$

<u>then substitute as follows:</u>

Each coordinate operator, q, is replaced by multiplication by the coordinate

$$\text{operator } q = q\cdot \qquad\qquad q=x,y,z$$

Each Cartesian component of momentum (p_x, p_y, p_z) is replaced by the operator

$$p_q = (\underline{h}/i)\ \partial/\partial q = -i\ \underline{h}\ \partial/\partial q, \qquad\qquad q=x,y,z$$

So operator $x = x\cdot$, etc. , $p_x = -i\underline{h}\ \partial/\partial x$, etc.

Then $p_x^{\ 2} = (-i\underline{h}\ \partial/\partial x)^{\ 2} = (i)^{\ 2}\underline{h}^2\ \partial^2/\partial x^2 = -\ \underline{h}^2\ \partial^2/\partial x^2$

Potential energy functions are usually functions of the coordinates, such as

$$V(x) = a\ x^2$$

In general, the operator V(x) is replaced by multiplication by V(x): $V(x)\ \cdot$

In summary

Classical mechanics (1-dimension)

$$H = T + V = KE + PE = p_x^{\ 2}/(2m) + V(x)$$

Quantum mechanics (1-dimension)

H (operator) = T (operator) + V (operator)

$$= -\ (\underline{h}^2/2m)\ d^2/dx^2 + V(x)$$

<u>(3) Postulate: The eigenvalues of a system are the only value a property can have</u>

H = Hamiltonian energy operator = $-\ (\underline{h}^2/2m)\ d^2/dx^2 + V(x)$

$H\ \psi_i = E_{\ i}\ \psi_i$ i=1,2,.. different states

Measurement of the energy of the system will result in one of the $E_{\ i}$ (eigenvalues, observables)

Example: Is $\Psi(x,t)$ an eigenfunction of the p_x operator for the 1-dimensional particle in a box?

$\Psi(x,t) = e^{iEt/\underline{h}}\,\psi(x)$ state function

$\psi(x) = \sqrt{(2/L)}\,\sin(n\pi x/L)$, $E_n = n^2h^2/(8mL^2)$

$p_x = -i\underline{h}\partial/\partial x$

For $\Psi(x,t)$ to be an eigenfunction of p_x, must have

$$p_x\Psi(x,t) = c\,\Psi(x,t)$$

But $d/dx \sin(Ax) = A\cos(Ax)$, so $\Psi(x,t)$ is not an eigenfunction of p_x

Example: Is $\Psi(x,t)$ an eigenfunction of the p_x^2 operator for the 1-dimensional particle in a box?

$$p_x^2\,\Psi(x,t) = -\underline{h}^2(d^2/dx^2)\,\{e^{iEt/\underline{h}}\sqrt{(2/L)}\,\sin(n\pi x/L)\}$$

$$= -\underline{h}^2\,e^{iEt/\underline{h}}\sqrt{(2/L)}\,(n\pi/L)\,d/dx\cos(n\pi x/L)$$

$$= \underline{h}^2\,e^{iEt/\underline{h}}\sqrt{(2/L)}\,(n\pi/L)^2\sin(n\pi x/L)$$

$$= \underline{h}^2\,(n\pi/L)^2\{e^{iEt/\underline{h}}\sqrt{(2/L)}\,\sin(n\pi x/L)\}$$

$$= \underline{h}^2\,(n\pi/L)^2\,\Psi(x,t)$$

$$= h^2\,(n^2/(4L^2))\,\Psi(x,t)$$ Yes

Since n=1,2,.., the eigenvalue $h^2\,(n^2/(4L^2))$ is quantized.

Find the eigenfunctions of p_x.

$$p_x\, g(x) = k\, g(x)$$

$$-i\hbar\, dg/dx = k\, g$$

$$dg/g = (ik/\hbar)\, dx$$

$$\ln g = (ik/\hbar)x + C$$

$$g = A\, e^{(ik/\hbar)x}$$

To keep g well-behaved as $x \to \pm\, \infty$, k must be real. So the eigenvalues of p_x are all the real numbers k, $-\infty < k < \infty$.

Forms of Operators in 3-Dimensions & More Than 1 Particle

One particle in 3-dimensions:

$$T = (-\hbar^2/2m)\, (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$$

$$= (-\hbar^2/2m)\, \nabla^2 \qquad \nabla^2 \text{ is the Laplacian operator}$$

$$H\, \psi(x,y,z) = \{(-\hbar^2/2m)\nabla^2 + V(x,y,z)\}\psi(x,y,z) = E\, \psi(x,y,z)$$

The probability of finding the particle at time t in a region bounded by (x,y,z) & (x+dx,y+dy,z+dz) is

$$|\psi(x,y,z,t)|^2 dx\, dy\, dz \qquad d\tau = dx\, dy\, dz$$

$$1 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z,t)|^2 d\tau$$

n particles in 3-dimensions:

Particle i has mass m_i, position (x_i, y_i, z_i) and momentum (p_{xi}, p_{yi}, p_{zi})

$$T = (-\underline{h}^2/2m_1)\,(\partial^2/\partial x_1{}^2 + \partial^2/\partial y_1{}^2 + \partial^2/\partial z_1{}^2) +$$

$$(-\underline{h}^2/2m_2)\,(\partial^2/\partial x_2{}^2 + \partial^2/\partial y_2{}^2 + \partial^2/\partial z_2{}^2) + \ldots +$$

$$(-\underline{h}^2/2m_n)\,(\partial^2/\partial x_n{}^2 + \partial^2/\partial y_n{}^2 + \partial^2/\partial z_n{}^2)$$

$$= \sum_{i=1}^{n} (-\underline{h}^2/2m_i)\,\nabla_i{}^2$$

If V depends only on the Cartesian coordinates,

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

Then $\psi = \psi\,(x_1,y_1,z_1, \ldots, x_n,y_n,z_n)$ and

$$H\,\psi = \{\sum_{i=1}^{n} (-\underline{h}^2/2m_i)\,\nabla_i{}^2 + V\,(x_1, \ldots, z_n)\}\psi = E\,\psi$$

The probability of finding the first particle in a region bounded by (x_1,y_1,z_1) & $(x_1+dx_1,y_1+dy_1,z_1+dz_1)$, the second particle in a region bounded by (x_2,y_2,z_2) & $(x_2+dx_2,y_2+dy_2,z_2+dz_2)$, etc. is

$$|\psi(x_1,y_1,z_1,\ldots, x_n,y_n,z_n, t)|^2 d\tau$$

$$d\tau = dx_1dy_1dz_1 \ldots dx_ndy_ndz_n$$

$$1 = \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} |\psi(x_1,y_1,z_1,\ldots, x_n,y_n,z_n, t)|^2 d\tau$$

Particle in a 3-Dimensional Box:

$$V(x,y,z) = 0 \quad 0 < x < a,\ 0 < y < b,\ 0 < z < c$$

$\psi = 0$ outside the box, as in the 1-dimensional case

Inside the box: $H\,\psi = E\,\psi$

$$(-\underline{h}^2/2m)\,(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) = E\,\psi$$

Solve by Method of Separation of Variables: Assume that ψ is a product of functions, each depending only on one variable. This is a reasonable assumption because the potential has no cross terms (i.e. terms including products of variables)

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

$$H\,\psi = (-\underline{h}^2/2m)\,\{g\,h\,d^2f/dx^2 + f\,h\,d^2g/dy^2 + f\,g\,d^2h/dz^2\} =$$

$$E\,f(x)\,g(y)\,h(z)$$

Dividing both sides by f(x) g(y) h(z) gives:

$$(-\underline{h}^2/2m)\{\,(1/f)\,d^2f/dx^2 + (1/g)\,d^2g/dy^2 + (1/h)\,d^2h/dz^2\} = E$$

Can rewrite so that the left-hand side depends only on x & the right-hand side depends only on y & z:

$$(1/f)\,d^2f/dx^2 = -\,(1/g)\,d^2g/dy^2 - (1/h)\,d^2h/dz^2 - 2mE/\underline{h}^2$$

But this means that the left & right-hand sides must be equal to a constant.

Let $k_x = (1/f)\,d^2f/dx^2$

Could rewrite the eq. so that the left-hand side depends only on y, etc. and get

$k_y = (1/g)\,d^2g/dy^2$ $\qquad$ $k_z = (1/h)\,d^2h/dz^2$

with $k_x + k_y + k_z = -2mE/\hbar^2$

Can redefine the energy components as

$k_x = -2mE_x/\hbar^2$, etc.

So that $E_x + E_y + E_z = E$

and $(1/f)\, d^2f/dx^2 = -2mE_x/\hbar^2$, etc.

Then $d^2f/dx^2 + 2mE_x/\hbar^2 f = 0$

$d^2g/dy^2 + 2mE_y/\hbar^2 g = 0$

$d^2h/dz^2 + 2mE_z/\hbar^2 h = 0$

Boundary Conditions: Functions must be zero at the walls.

$f(x) = 0$ at $x = 0, a$

$g(y) = 0$ at $y = 0, b$

$h(z) = 0$ at $z = 0, c$

So the solutions are the same as for the 1-dimensional particle in a box:

$f(x) = \sqrt{(2/a)} \sin (n_x\pi x/a)$, $E_x = (n_x^2h^2)/(8ma^2)$, $n_x=1,2,...$

$g(y) = \sqrt{(2/b)} \sin (n_y\pi y/b)$, $E_y = (n_y^2h^2)/(8mb^2)$, $n_y=1,2,...$

$h(z) = \sqrt{(2/c)} \sin (n_z\pi z/c)$, $E_z = (n_z^2h^2)/(8mc^2)$, $n_z=1,2,...$

$E = E_x + E_y + E_z = (h^2)/(8m)\ \{n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2\}$

with the quantum numbers n_x, n_y, n_z varying independently

$$\psi(x,y,z) = \sqrt{[8/(abc)]}\sin(n_x\pi x/a)\sin(n_y\pi y/b)\sin(n_z\pi z/c)$$

Normalize ψ:

$$1 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z,t)|^2 d\tau$$

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

But each function is separately normalized

$$1 = \int_0^a dx\ |f(x)|^2, \text{ etc.}$$

so ψ is automatically normalized.

<u>Consider a particle in a cube</u>: a = b = c,

$$E = (h^2)/(8m\ a^2)\ \{n_x^2 + n_y^2 + n_z^2\}$$

$$\text{or } \{n_x^2 + n_y^2 + n_z^2\} = (E\ 8m\ a^2)/h^2$$

Tabulate

n_x n_y n_z	111	211	121	112	122	221	212
$\{n_x^2 + n_y^2 + n_z^2\}$	3	6	6	6	9	9	9

n_x n_y n_z	113	131	311	222	etc
$\{n_x^2 + n_y^2 + n_z^2\}$	11	11	11	12	

Degeneracy occurs when two or more independent wavefunctions correspond to states with the same energy eigenvalue

Each set of (n_x n_y n_z) corrsponds to an independent wavefunction. Since there are 3 independent wavefunctions which give $\{n_x^2 + n_y^2 + n_z^2\} = 6$, the corresponding energy level is said to be 3-fold degenerate.

A rectangular box wouldn't have degenerate energy levels. Degeneracy is related to the symmetry of the system.

The *degree of degeneracy* of an energy level equals the number of linearly independent wavefunctions corresponding to that value of the energy.

A set of n functions is said to be *linearly independent* if no member of the set can be written as a linear combination of the others.

ψ_1, ψ_2, ψ_3, etc are linearly independent if

$c_1\psi_1 + c_2\psi_2 + ... + c_n\psi_n = 0$ only if $c_1 = c_2 = ... = c_n = 0$

Example: $f_1 = 3x$, $f_2 = 5x^2 - x$, $f_3 = x^2$

$f_2 = 5 f_3 - f_1/3$ not linearly independent

Example: $f_1 = 1$, $f_2 = x$, $f_3 = x^2$ linearly independent

Theorem: For any set of linearly independent eigenfunctions of the Hamiltonian operator, ($\psi_1, \psi_2, ..., \psi_n$), with eigenvalue ω, any linear combination of these eigenfunctions is also an eigenfunction of H with eigenvalue ω.

Prove that for

If $\phi = c_1 \psi_1 + c_2 \psi_2 + ... + c_n \psi_n$, and $H \psi_i = \omega \psi_i$ for $i = 1,...,n$

then $H \phi = \omega \phi$

Proof: $H \phi = H (c_1 \psi_1 + c_2 \psi_2 +...+ c_n \psi_n)$

$$= c_1 H\psi_1 + c_2 H \psi_2 +...+ c_n H \psi_n$$
$$= c_1 \omega\psi_1 + c_2 \omega \psi_2 +...+ c_n \omega \psi_n$$

$$= \omega (c_1 \psi_1 + c_2 \psi_2 +...+ c_n \psi_n)$$

$$= \omega \phi$$

Note that the degree of degeneracy of energy level ω is the number of linearly independent eigenfunctions (n) belonging to that level.

Average (or Expectation) Value of a Physical Property:

For a quantity that depends on *discrete* changes in the variables, the average value is defined by a *sum*

F - the physical property
<F> - average value of F
N - the number of systems that are measured
f_i - an observed value of F
n_f - the number of times f is observed
f - a possible value of F

$$\langle F \rangle = \sum_{i=1}^{N} f_i /N = \sum_{i=1}^{N} n_f f /N$$

Example: In a class there are 9 (N=9) students. On a quiz the grades are: 0 (f_1), 20 (f_2), 20 (f_3), 60 (f_4), 60 (f_5), 80

(f_6), 80 (f_7), 80 (f_8), 100 (f_9). There are 5 questions & each question is either all right (20 points) or all wrong (0 points). Calculate the average grade.

$$<F> = \sum_{i=1}^{N} f_i /N = (1/9)\ [0 + 20 + 20 + 60 + 60 + 80 + 80 +$$

$$80 + 100 = 56$$

Alternatively,

$$<F> = \sum^{N} n_f\, f /N$$

The f possible values of F (and n_f number of times f is observed) are:

0 (1), 20 (2), 40 (0), 60 (20), 80 (3), 100 (1)

$$<F> = (1/9)\ [1\cdot 0 + 2\cdot 20 + 0\cdot 40 + 2\cdot 60 + 3\cdot 80 + 1\cdot 100]$$

$$= 56$$

Note that the average grade is not one of the possible or observed grades.

Since the probability, P_f, is defined as n_f /N, then <F> can be written as

$$<F> = \sum_f P_f\, f$$

For quantities that depend on variables that can take on a continuous range of values,

$$P_f = |\psi|^2\, d\tau \qquad\qquad \sum_f \rightarrow \int$$

$\langle F \rangle = \int \Psi^* F \Psi \, d\tau$,

where Ψ is the time-dependent wavefunction

Since F is an operator, cannot write $|\Psi|^2 F$.
Must have $\Psi^* F \Psi$, unless F is a function of coordinates only

$\int d\tau$ is shorthand notation which means integrate over the correct variables & volume element.

For n particles in 3 dimensions, $\int d\tau =$

$$\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dy_1 \int_{-\infty}^{\infty} dz_1 \ldots \int_{-\infty}^{\infty} dx_n \int_{-\infty}^{\infty} dy_n \int_{-\infty}^{\infty} dz_n$$

For 1 particle in 1 dimension, $\int d\tau = \int_{-\infty}^{\infty} dx$

A stationary state is defined as one for which the probability density doesn't vary in time

$$d\,|\Psi|^2/dt = 0$$

For these states (& if F is independent of time), one can show that

$$\Psi^* F \Psi = \psi^* F \psi.$$

This is because

$$\Psi = e^{-iEt/\hbar} \psi$$

So $\quad \Psi^* F \Psi = e^{iEt/\hbar} \psi^* F e^{-iEt/\hbar} \psi$

Since F is independent of time, $F\, e^{-iEt/\hbar}\, \psi = e^{-iEt/\hbar}\, F\, \psi$,

and $\Psi^* F\, \Psi = e^{iEt/\hbar}\, e^{-iEt/\hbar}\, \psi^* F\, \psi = \psi^* F\, \psi$.

The average value of a sum of operators equals the sum of the average values of the operators:

$$< F + G > = <F> + <G>$$

But the average value of a product of operators is *not* equal to the product of the average values of the operators:

$$< F \cdot G > \text{ is not equal to } <F> \cdot <G>$$

Example: Find $<F>$ for $F\, \psi = k\, \psi$.

$$<F> = \int \psi^* F\, \psi\, d\tau = \int \psi^* k\, \psi\, d\tau = k \int \psi^*\, \psi\, d\tau$$

$$= k$$

since $\int \psi^*\, \psi\, d\tau = 1$.