Operators

$$\hat{O}f = g$$

$\hat{O}$ is an operator.

f and g are functions

Consider applying two operators in succession

if $\hat{A}\hat{B}f = \hat{B}\hat{A}f$, the operators commute

if $\hat{A}\hat{B}f \neq \hat{B}\hat{A}f$, the operators do not commute

We use $\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$ as shorthand for the commutator

$\left[\hat{A},\hat{B}\right] = 0$ If the operators commute

Let: $\hat{A} = \dfrac{d}{dx}$, $\hat{B} = x$

$$\hat{A}\hat{B}f = \frac{d}{dx}xf = f + xf'$$

$$\hat{B}\hat{A}f = x\frac{d}{dx}f = xf'$$

$$\left[\hat{A}\hat{B} - \hat{B}\hat{A}\right]f = f \Rightarrow \hat{A}\hat{B} - \hat{B}\hat{A} = 1$$

Note if: $\hat{A} = \dfrac{d}{dx}$, $\hat{B} = y$,

then the operators do commute

Linear Operators

$$\hat{A}[f+g] = \hat{A}f + \hat{A}g$$

$$\hat{A}[cf] = c\hat{A}f$$

examples:

$$x, x^2, \frac{d}{dx}, \frac{d^2}{dx^2}$$

C is a constant

Eigenvalue problem

$\hat{A}f = af$, where a is a constant

In general, a QM Operator $\hat{B}$ will have many eigenfunctions

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

A measurement of *B* must give one of the b_i

Consider the Schrödinger Eq. $\hat{H}\psi_i = E_i\psi_i$

If we measure energy we get one of the E_i

If the system starts in an energy eigenstate E_i a measurement of the energy necessarily gives E_i

Now suppose the system is in a superposition of two energy eigenstates.

$$\hat{H}\psi_1 = E_1\psi_1, \ \hat{H}\psi_2 = E_2\psi_2$$

$$\psi = c_1\psi_1 + c_2\psi_2$$

Assume ψ is normalized: $$|c_1|^2 + |c_2|^2 = 1$$

If we do many measurements on identically prepared systems. We will get E_1 a fraction $|c_1|^2$ of the time and E_2 a fraction $|c_2|^2$ of the time.

Correspondence principle between classical observables and QM operators

Classical H: $$H = \frac{p_x^2}{2m} + V(x)$$

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

$$\Rightarrow \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

In general, there can be multiple operators, e.g., energy, linear angular momentum, momentum, spin, various symmetry operations.

Each has its own eigenvalues and eigenfunctions.

E.g., for the particle in the box problem, the energy eigenfunctions are not momentum eigenfunctions.

What do we get if we do an isolated measurement of the momentum?

3D SE for a single particle

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

∇^2 ← Laplacian operator

If there are n particles

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

For a 3D 1-particle system

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\psi(x,y,z)\right|^2 dxdydz = 1$$

if ψ is normalized

For a 3D, n-particle system ψ depends on $x_1,\ldots,z_n$ and we need to $\int$ over all degrees of freedom.

$\int |\psi|^2 d\tau = 1$, $d\tau \Rightarrow$ integrate over all degrees of freedom

Particle in a 3D Box

$$\left.\begin{array}{l} 0 \le x \le a \\ 0 \le y \le b \\ 0 \le z \le c \end{array}\right\}$$

V = 0 inside box

V = ∞ outside box

Inside the box

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

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

$$\frac{-\hbar^2}{2m}\left[f''gh + fg''h + fgh''\right] = Efgh$$

$$\frac{-\hbar^2}{2m}\left[\frac{f''}{f} + \frac{g''}{g} + \frac{h''}{h}\right] = E$$

$$\frac{-\hbar^2}{2m}\frac{f''}{f} = -\frac{\hbar^2}{2m}\left[\frac{g''}{g} + \frac{h''}{h}\right] + E$$

depends only on *x* depends only on *y, z*

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{f''}{f} =$$ A constant that we choose to be E_x

So $E = E_x + E_y + E_z$

This leads to three separate one-D particle-in-the-box problems

$$\frac{\partial^2\psi}{\partial x^2} = f''gh,$$

$$\frac{\partial^2\psi}{\partial y^2} = fg''h,$$

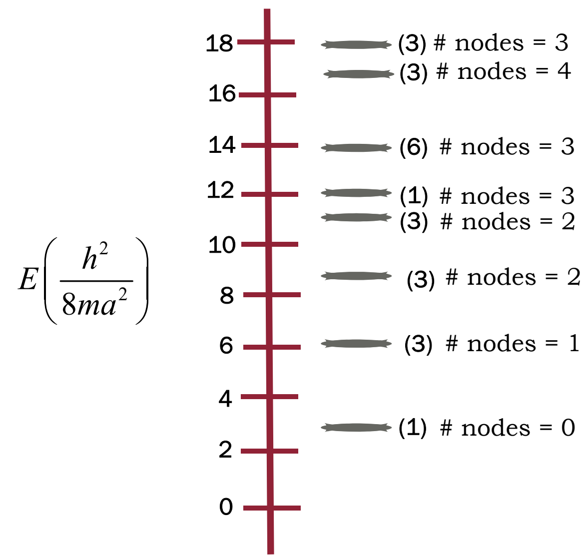
$$\frac{\partial^2\psi}{\partial z^2} = fgh''$$

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

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

Suppose the box is cubic with $a = b = c$

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^{\,2} + n_y^{\,2} + n_z^{\,2}\right)$$



Energy Levels

$$(n_x, n_y, n_z) = (111) \rightarrow E_{111} = \frac{3h^2}{8ma^2}$$

$$= (211), (121), (112) \rightarrow E_{211} = \frac{6h^2}{8ma^2}$$

$$= (221), (212), (122) \rightarrow E_{221} = \frac{9h^2}{8ma^2}$$

(111) is nondegenerate, (211) is triply degenerate, (123) is six-fold degenerate

Group theory leads us to expect at most a 3-fold degeneracy in the cubic group

There are degeneracies caused by symmetry and also those that are accidental (not symmetry caused).

The cubic box clearly has two special situations of "accidental" degeneracies.

(1) The 6-fold degeneracy of the (1,2,3) level

(2) the degeneracy between (3,3,3) and the various (1,1,5) combinations.

Why many texts and lectures label these as accidental, the problem is actually much more interesting than that, due to the presence of hidden symmetries, i.e., operators not contained in the point group that commute with H.

See F.M. Fernández, Acta Polytech., 54 (2) (2014), pp. 113-115 (you can also find this on arXiv archive).

Compare with the H atom

$3s,\ 3p,\ 3d$	degeneracy = 1 + 3 + 5
$2s,\ 2p$	degeneracy = 1 + 3
$1s$	degeneracy = *1*

But there is an interesting difference. Even though the Schrödinger Eq. for the H atom separates into r, θ, and ϕ equations, the energy depends only on the radial equation

Degeneracies often related to symmetry.

If ψ_1 and ψ_2 are degenerate eigenfunctions then $c_1\psi_1 + c_2\psi_2$ has the same energy as ψ_1 and ψ_2 alone

Thus, there is an infinite # of combinations that give the same energy

If the linearly independent combinations $\{f_i\}$ span a space, then any other functions possible in that space can be represented in terms of the $\{f_i\}$.

Acceptable wave functions

1. ψ continuous
2. ψ' continuous
3. ψ is normalizable $\Rightarrow \int |\psi|^2 d\tau$ is finite. (ψ is quadratically integrable)
4. $|\psi|^2$ is single valued

Note: ψ' is not continuous at the walls of the particle in the box problem. But real potentials don't have discontinuous jumps in energy.

Note: ψ is not quadratically integrable for unbound states.

For every observable B, there is an operator $\hat{B}$

Measurements of the observable B must give an eigenvalue of $\hat{B}$

Measurements of QM observables give real results.

Average (expectation value) of an operator

Average of operator $\hat{B}$ is $\langle \bar{B} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{B} \psi \, d\tau$

What happens if ψ is an eigenfunction of $\hat{B}$ with $\hat{B}\psi = k\psi$?

$$\langle B \rangle = \int_{-\infty}^{\infty} \psi^* \hat{B} \psi \, d\tau = k \int_{-\infty}^{\infty} \psi^* \psi \, d\tau = k$$

All measurements give the same value, k

Note: $\hat{B}\psi^* \psi \neq \psi^* \psi \hat{B} \neq \psi^* \hat{B} \psi$

if $\hat{B}$ e.g. involves derivatives

Finite # of measurements

$$\langle B \rangle = \frac{\sum_b b n_b}{N},$$

b is a specific eigenvalue n_b is the # of times it is observed

$$= \sum_b P_b b,$$

P_b is the probability of observable b

For 3D particle in box

$$\langle \hat{p}_x \rangle = \int_o^a f^* \hat{p}_x f dx \int_o^b g^* g dy \int_o^c h^* h dz$$

$$= \int_o^a f^* \hat{p}_x f dx = \frac{\hbar}{i} \int_o^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \sqrt{\frac{2}{a}} \frac{n\pi}{a} \cos\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{\hbar}{i} \frac{2}{a} \frac{n\pi}{a} \int_o^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) dx = 0$$

How can we show this?