THE POSTULATES OF QUANTUM MECHANICS

(time-independent)

Postulate 1: The state of a system is completely described by a wavefunction $\psi(\mathbf{r},t)$.

Postulate 2: All measurable quantities (observables) are described by Hermitian linear operators.

Postulate 3: The only values that are obtained in a measurement of an observable "A" are the eigenvalues "a_n" of the corresponding operator "$\hat{A}$". The measurement changes the state of the system to the eigenfunction of $\hat{A}$ with eigenvalue a_n.

Postulate 4: If a system is described by a normalized wavefunction ψ, then the average value of an observable corresponding to $\hat{A}$ is

$$\langle a \rangle = \int \psi^* \hat{A} \psi \, d\tau$$

<u>Implications and elaborations on Postulates</u>

#1] (a) The physically relevant quantity is $|\psi|^2$

$$\psi^*(\mathbf{r},t)\psi(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 \quad \equiv \quad \text{probability density at time } t \text{ and position } \mathbf{r}$$

(b) $\psi(\mathbf{r},t)$ must be normalized

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

(c) $\psi(\mathbf{r},t)$ must be <u>well behaved</u>

(i) Single valued
(ii) ψ and ψ' continuous
(iii) Finite

#2] (a) Example: Particle in a box eigenfunctions of $\hat{H}$

$$\hat{H}(x)\psi_n(x) = E_n\psi_n(x) \qquad \psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$$

But if ψ is <u>not</u> an eigenfunction of the operator, then the statement is not true.

e.g. $\psi_n(x)$ above with momentum operator

$$\hat{p}_n\psi_n(x) = -i\hbar\frac{d}{dx}\psi_n(x) = -i\hbar\frac{d}{dx}\left[\left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)\right]$$

$$\neq p_n\left[\left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)\right]$$

(b) In order to create a Q.M. operator from a classical observable, use $\hat{x} = x$ and $\hat{p}_x = -i\hbar\frac{d}{dx}$ and replace in classical expression.

e.g.

$$\text{K.E.} = \frac{1}{2m}\hat{p}^2 = \frac{1}{2m}(\hat{p})(\hat{p}) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \quad \text{(1D)}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \quad \text{(3D)}$$

Another 3D example: Angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$

$$l_x = yp_z - zp_y = -i\hbar\left(y\frac{d}{dz} - z\frac{d}{dy}\right)$$

$$l_y = zp_x - xp_z = -i\hbar\left(z\frac{d}{dx} - x\frac{d}{dz}\right)$$

$$l_z = xp_y - yp_x = -i\hbar\left(x\frac{d}{dy} - y\frac{d}{dx}\right)$$

(c) Linear means

$$\hat{A}\left[f(x) + g(x)\right] = \hat{A}f(x) + \hat{A}g(x) \qquad \text{and}$$

$$\hat{A}\left[cf(x)\right] = c\hat{A}\left[f(x)\right]$$

(d) Hermitian means that

$$\int \psi_1^* \hat{A}\psi_2 d\tau = \int \psi_2 \left(\hat{A}\psi_1\right)^* d\tau$$

and implies that the eigenvalues of $\hat{A}$ are <u>real</u>. This is important!! Observables should be represented as real numbers.

Proof: Take $\hat{A}\psi = a\psi$

$$\int \psi^* \left(\hat{A}\psi\right) d\tau = \int \psi \left(\hat{A}\psi\right)^* d\tau$$

$$\int \psi^* a\psi d\tau = \int \psi \left(a\psi\right)^* d\tau$$

$$\Rightarrow \quad a = a^*$$

true only if a is real

(e) Eigenfunctions of Hermitian operators are <u>orthogonal</u>

i.e. if $\hat{A}\psi_m = a_m\psi_m$ and $\hat{A}\psi_n = a_n\psi_n$

then $\boxed{\int \psi_m^* \psi_n d\tau = 0 \quad \text{if } m \neq n}$

Proof:

$$\int \psi_m^* \hat{A} \psi_n d\tau = \int \psi_n \left(\hat{A} \psi_m \right)^* d\tau$$

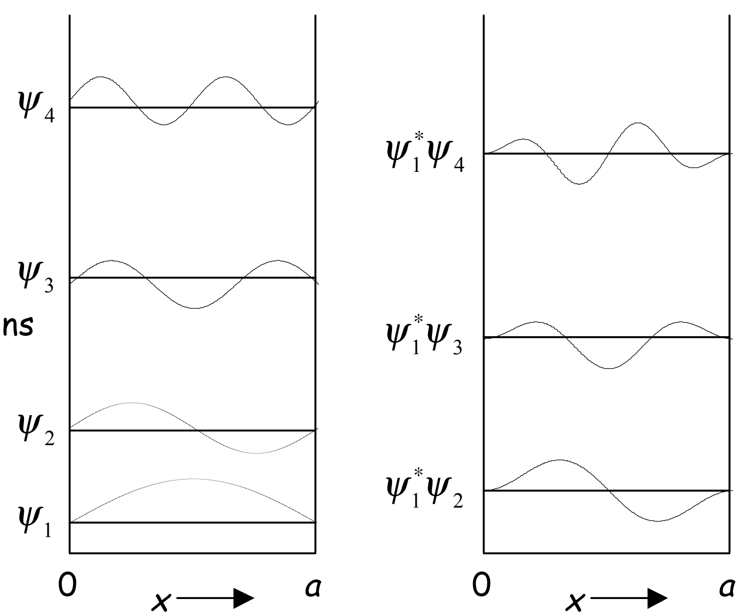
$$a_n \int \psi_m^* \psi_n d\tau = a_m^* \int \psi_n \psi_m^* d\tau$$

$$\Rightarrow \quad \left(a_n - a_m^* \right) \int \psi_m^* \psi_n d\tau = 0$$

$$\underbrace{\left(a_n - a_m^* \right)}_{=\ 0 \text{ if } n = m} \underbrace{\int \psi_m^* \psi_n d\tau}_{=\ 0 \text{ if } n \neq m} = 0$$

Example: Particle in a box

Eigenfunctions of



As much + as - area

$\Rightarrow$

In addition, if eigenfunctions of $\hat{A}$ are <u>normalized</u>, then they are <u>orthonormal</u>

$$\int \psi_m^* \psi_n d\tau = \delta_{mn}$$

↑ Krönecker delta

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \quad \text{(normalization)} \\ 0 & \text{if } m \neq n \quad \text{(orthogonality)} \end{cases}$$

#3] If ψ is an eigenfunction of the operator, then it's easy, e.g.

$\hat{H}\psi_n = E_n\psi_n$ measurement of energy yields value

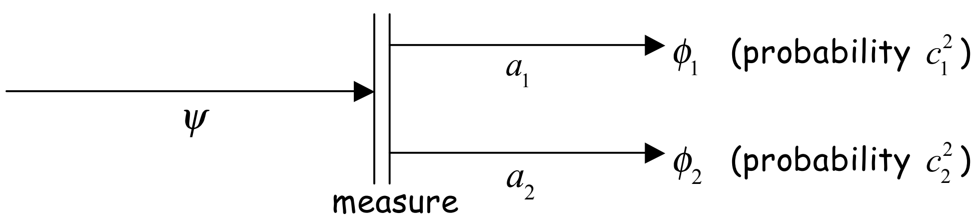
But what if ψ is not an eigenfunction of the operator?

e.g. ψ could be a superposition of eigenfunctions

$$\psi = c_1\phi_1 + c_2\phi_2$$

where $\hat{A}\phi_1 = a_1\phi_1$ and $\hat{A}\phi_2 = a_2\phi_2$

Then a measurement of A returns either a_1 or a_2, with probability c_1^2 or c_2^2 respectively, and making the measurement changes the state to either ϕ_1 or ϕ_2.



#4] This connects to the expectation value

(i) If ψ_n is an eigenfunction of $\hat{A}$, then $\hat{A}\psi_n = a_n\psi_n$

$$\langle a \rangle = \int \psi_n^* \hat{A}\psi_n d\tau = a_n \int \psi_n^*\psi_n d\tau = a_n$$

$\langle a \rangle = a_n$ only value possible

(ii) If $\psi = c_1\phi_1 + c_2\phi_2$ as above

$$\langle a \rangle = \int \psi^* \hat{A} \psi \, d\tau = \int \left(c_1\phi_1 + c_2\phi_2 \right)^* \hat{A} \left(c_1\phi_1 + c_2\phi_2 \right) d\tau = c_1^2 a_1 + c_2^2 a_2$$

c_1^2 is the probability of measuring a_1

$\langle a \rangle$ = average of possible values weighted by their probabilities