The Formalism of Quantum Mechanics

Our story so far...

- State of physical system: normalizable $\Psi(x,t)$
- Observables: operators $\hat{x}$, $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$, $\hat{H}$
- Dynamics of Ψ: TDSE $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$

To solve, 1st solve TISE: $\hat{H}\psi = E\psi$
sol'ns are stationary states $\psi_n(x)$, E_n
$\Rightarrow$ special sol'ns of TDSE: $\Psi_n(x,t) = \psi_n(x)\, e^{-iE_nt/\hbar}$

TDSE linear $\Rightarrow$ any linear combo. of sol'n is also a solution

Discrete case: $\Psi(x,t) = \sum_n c_n\, e^{-iE_nt/\hbar}\, \psi_n(x)$
$(n = 1,2,3\ldots)$

Continuum case: $\Psi(x,t) = \int dk\, \phi(k)\, e^{-i\omega(k)t}\, \underbrace{\psi_k(x)}_{e^{+ikx}/\sqrt{2\pi}}$
(k any real nbr)

Discrete | Discrete | Continuum | Discrete + Continuum

ψ_n's, ψ_k's form complete, orthonormal sets

$$\int dx\, \psi_m^* \psi_n = \delta_{mn}$$

$$\int dx\, \psi_{k'}^* \psi_k = \frac{1}{2\pi}\int dx\, e^{i(k-k')x} = \delta(k-k')$$

Notice similarity of Ψ's to vectors:

- Vector $\vec{V}$ / complex fn $\Psi(x,t)$
- scalar real number a / complex nbr c

- any linear combination of vectors is a vector

$$\vec{C} = a\vec{A} + b\vec{B} \quad / \quad \Psi = \alpha\Psi_1 + \beta\Psi_2$$

- orthonormal basis vectors

$$\hat{x}\cdot\hat{x} = 1, \quad \hat{x}\cdot\hat{y} = 0 \quad / \quad \int \psi_m^* \psi_n \, dx = \delta_{mn}$$

$$\vec{V} = V_x\hat{x} + V_y\hat{y} + V_z\hat{z} \quad / \quad \Psi = \sum_n c_n \psi_n$$

$$V_x = \hat{x}\cdot\vec{V} \quad / \quad c_n = \int dx\, \psi_n^* \Psi$$

- inner product

$$\vec{A}\cdot\vec{B} = \sum_{i=x,y,z} A_i B_i \quad / \quad \int dx\, \Psi^* \Phi =$$

$$\int dx \left(\sum_m d_m \psi_m\right)^* \left(\sum_n c_n \psi_n\right)$$

$$= \sum_{m,n} d_m^* c_n \underbrace{\int \psi_m^* \psi_n \, dx}_{\delta_{mn}} = \sum_n d_n^* c_n$$

The space of all complex, square-integrable functions $\Psi(x)$ is called Hilbert Space

- Norm $\vec{V}\cdot\vec{V} = |\vec{V}|^2$ / $\int \Psi^* \Psi \, dx < \infty$

Hilbert Space is an infinite-dimensional, vector space w/ complex scalars and normalizable vectors

Postulate 1: Every possible physical state of a system corresponds to a normed vector in Hilbert Space. The correspondence is 1-to 1 except that vectors that differ by a phase factor (scalar of modulus 1) correspond to the same state $\Psi(x,t) \Leftrightarrow e^{i\theta}\Psi(x,t)$

Dirac Notation:

$$\int_{-\infty}^{+\infty} dx\, f^*(x)\, g(x) = \langle f | g \rangle = \text{complex nbr}$$

$$\Rightarrow \langle f | g \rangle = \langle g | f \rangle^*$$

$\langle f | f \rangle$ is real, non-negative

c any complex nbr: $\langle f | c \cdot g \rangle = c \langle f | g \rangle$

$\langle cf | g \rangle = \cancel{c^* \langle f | g \rangle}$

Postulate 2 (to be stated) associates w/ every observable a linear, hermitean operator.

Definition: An operator $\hat{Q}$ is hermitean ~~is~~ if

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle \text{ for all } f, g \text{ in Hilbert space } (\mathcal{H}\text{-space})$$

$$\int dx\, f^* (\hat{Q} g) = \int dx\, (\hat{Q} f)^* g$$

Is $\hat{Q} = \frac{d}{dx}(\ )$ hermitean?

$$\underbrace{\int dx\, f^*\, dg/dx}_{} \stackrel{?}{=} \int dx \left(\frac{df}{dx}\right)^* \cdot g$$

parts: $\underbrace{f^*(x)\, g(x)\Big|_{\infty}^{-\infty}}_{0} - \int \frac{d}{dx}(f^*) \cdot g(x)\, dx = -\int \left(\frac{df}{dx}\right)^* \cdot g(x)\, dx$

(No!)

Is $\hat{Q} = \frac{\hbar}{i}\frac{\partial(\ )}{\partial x}$ hermitean? Ans. <u>Yes</u>

$$\int f^* \frac{\hbar}{i}\frac{\partial g}{\partial x}\, dx \underset{\text{(parts)}}{=} -\int \frac{\hbar}{i}\frac{d}{dx}(f^*)\cdot g = +\int \left(\frac{\hbar}{i}\frac{df}{dx}\right)^* g\, dx$$

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$$

Is $\hat{Q} = c\cdot(\ )$, c = constant hermitean?

$$\underbrace{\langle f | c\cdot g \rangle}_{c\langle f|g\rangle} \overset{?}{=} \langle c\cdot f | g \rangle$$

$$c\langle f|g\rangle \overset{?}{=} c^*\langle f|g\rangle \Rightarrow \text{hermitean only } \underline{\text{if}}\ c\ \underline{\underline{\text{real}}}$$

Why are hermitean operators special? Why only hermitean operators associated w/ physical observables? Because hermitean operators produce <u>real</u> eigenvalues (and measurements of observables always produce <u>real</u> values).

Eigenvalue equation: $\hat{Q}\, \underset{\text{eigenfunction}}{f(x)} = \underset{\text{eigenvalue}}{q}\cdot f(x)$

Theorem: The eigenvalues of a hermitean operator $\hat{Q}$ are real.

Proof: Assume $f(x)$ = eigenfcn: $\hat{Q} f = q f$

$$\langle Q \rangle \equiv \underbrace{\langle f | \hat{Q} f \rangle}_{q\langle f|f\rangle} \underset{\hat{Q}\text{ hermitean}}{=} \underbrace{\langle \hat{Q} f | f \rangle}_{\langle q\cdot f|f\rangle} = q^*\langle f|f\rangle$$

$$\Rightarrow (q - q^*)\langle f|f\rangle = 0 \Rightarrow q = q^* \quad (\text{since } \langle f|f\rangle \neq 0)$$

Theorem: The eigenfns of a hermitean operator w/ distinct (different) eigenvalues are orthogonal.

Proof: Given $\hat{Q} f(x) = q \cdot f(x)$, $\hat{Q} g(x) = q' \cdot g(x)$
w/ $q \neq q'$

$$\underbrace{\langle f | \hat{Q} g \rangle}_{q' \langle f | g \rangle} = \underbrace{\langle \hat{Q} f | g \rangle}_{q^* \langle f | g \rangle} \quad \text{(since } \hat{Q} \text{ hermitean)}$$

$$q' \langle f | g \rangle = q^* \langle f | g \rangle \underset{(q \text{ real})}{=} q \langle f | g \rangle$$

$\Rightarrow (q' - q) \langle f | g \rangle = 0 \Rightarrow \langle f | g \rangle = 0$ since $(q' - q) \neq 0$ by assumption ✓

Postulate 2 (Operator & Observables) This is a long postulate w/ 3 parts, and many texts break this up into 2 or 3 postulates

1) For every physical observable Q (x, p, E, etc) there corresponds a linear hermitean operator $\hat{Q}$ in the Hilbert Space which possesses a complete, orthonormal set of eigenfns $f_n(x)$ and corresponding eigenvalues q_n

$$\hat{Q} f_n(x) = q_n f_n(x) \quad \text{(n could be discrete or continuous)}$$

2) The only possible results of a measurement of Q are one of the eigenvalues $q_n = \{q_1, q_2, q_3, \ldots\}$

3) The momentum operator is $\hat{p} = \frac{\hbar}{i} \partial/\partial x (\ )$
The position operator is $\hat{x} = x \cdot (\ )$
Any function $Q(x, p)$ has operator $\hat{Q} = Q(\hat{x}, \hat{p})$

An example of $\hat{Q} = Q(\hat{x}, \hat{p})$:

energy operator $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(\ ) + V(x)\cdot(\ )$

Sol'ns of $\hat{H}\psi_n = E_n \psi_n$ form an orthonormal set (since H is hermitean!). That ψ_n's form complete set can be proven in some special cases like infinite square well or S.H.O, but, in general, completeness is taken as a postulate.

If energy is measured, only possible results is one of the E_n's.

The momentum eigenstates are sol'ns of:

$$\hat{p}\, f_p(x) = p \cdot f_p(x) \quad , \text{ where } \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

Eigenfcns: $f_p(x) = A e^{ikx}$ (any const A)

Eigenvalues: $p = \hbar k$ (k any real number)

Proof: $\frac{\hbar}{i}\frac{\partial}{\partial x}(A e^{ikx}) = \hbar k (A e^{ikx})$ ✓

In this case, the eigenvalues form a continuum (any real value of $p = \hbar k$ is permitted) and this leads to some mathematical subtleties.

Are the f_p's orthonormal? (Ans: Kind of... yes)

$$\int f_{p'}^*(x) \cdot f_p(x) = \delta(p - p')$$

"Delta function orthogonality"