Theorems from Postulates:

Now that we have "laws" or better "postulates" we should explore what they imply about working q.m. problems -- Theorems (*Levine 7.2, 7.4*)

Thm 1 -- eigen values of Hermitian operators are real (clearly this fits well with

Post. 2 restriction → we need real observables

let $A | i \rangle = a_i | i \rangle$

$\langle i|A|i\rangle = \langle i|A|i\rangle^*$

$a_i\langle i|i\rangle = a_i^*\langle i|i\rangle$

$(a_i - a_i^*)\langle i|i\rangle = 0 \Longrightarrow a_I = a_i^* \Longrightarrow a_i$ real since $\langle i|i\rangle$ is positive definite

Thm 2 -- eigen function of a Hermitian operator can be chosen to be orthogonal

i.e. $\int f\ g d\tau = 0$ for $f \neq g$

$$\langle j|A|i\rangle = \langle i|A|j\rangle$$

$a_i\langle j|i\rangle = a_j\langle i|j\rangle = a_j\langle i|j\rangle = a_j\langle j|i\rangle$, $a_j^* \rightarrow a_j$ since real, $\langle i|j\rangle$ flip order on complex conj.

$$(a_i - a_j)\langle j|i\rangle = 0$$

either $a_i = a_j$ (same state or degenerate) or orthogonal: $\langle i|j\rangle = 0$

if $|i\rangle$, $|j\rangle$ are degenerate can construct $|1\rangle = c_i|i\rangle + c_j|j\rangle$, $|2\rangle = c_j|i\rangle - c_i|j\rangle$

$\langle 1|2\rangle = 0$, orthogonal by construction and still are degenerate eigen functions

i.e. $A(c_i|i\rangle + c_j|i\rangle) = a_i(c_i|i\rangle + c_j|j\rangle)$

Wednesday--August 29

Applications:

The wave function describing the state of a quantum mechanical system can be described as a superposition of in terms of eigen functions of an operator $\hat{\alpha}$ --$\{f_i\}$, since they form a complete set

You have experience with this from

Taylor series: $f(x-a) = \sum_n \frac{f^{(n)}(a)}{n!}(x-a)^n$ or $f(x) = \sum_n \frac{1}{n!}\frac{\partial^n f}{\partial x^n}\Big|_0 x^n$

so f(x) is represented as linear combination of x^n -- power series

More general is Fourier series : $f(x) = \sum_n [s_n \sin(2\pi nx) + c_n \cos(2\pi nx)]$

where expand in sine and cosine fcts or exponetials: $\sum b_n e^{-i2\pi xn}$

in these cases: x^n, $\sin(2\pi nx)$, $e^{-i2n\pi x}$ form complete sets

(*Note* sin is odd, must add cos if parity not odd, eliminate sin if even)

So what are the coefficients? In Taylor : $\frac{f^{(n)}(x)}{n!}$ but

in q.m. expand in a set $\{g_i\}$ of eigen fct of operator α: $f(x) = \sum_i c_i g_i(x) = \sum_i c_i |i\rangle$

multiply. by g_j^* and integrate : $\langle j|f\rangle = \sum_i c_i \langle j|i\rangle = \sum_i c_i \delta_{ij} = c_j$

Dirac delta function: $\langle i|j\rangle = \delta_{ij} = 1 \quad i = j \qquad = 0 \quad i \neq j$

so $c_i = \langle i|f\rangle$ or $f = \Sigma\, |i\rangle\langle i|f\rangle$,, Where $\Sigma\, |i\rangle\langle i|$ is projection operator picks out (projects) part of $|f\rangle$ that lies along $|i\rangle$ [analogous to dot (scalar) product from vector algebra]

Thm 3 -- if $\{g_i\}$ is set of eigen fcts of α and f is also an eigen fct so that $\hat{\alpha}f = af$ then if $f = \sum_i c_i g_i$ the only non-zero c_i are for g_i which have eigen value of a (degen. with f).

(Alternateively, f must be a linear combination of degenerate g_i with same eigenvalue)

$$\hat{\alpha}f = \hat{\alpha}\sum c_i g_i = \sum c_i a_i g_i = af = a\sum_i c_i g_i$$

$c_i = \langle f|g\rangle$ is only non-zero for f = g_i or f-degenerate with g_i, (otherwise $\langle f|g_i\rangle = 0$, orthog)

alternatively: if g_i are indep fct, only if $a = a_i$ will c_i be non-zero: $\sum_i (a - a_i)c_i g_i = 0$,

Commutation:

A commutator of operators $\hat{\alpha}$, $\hat{\beta}$ is $\left[\hat{\alpha},\hat{\beta}\right] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}$

Note this is familiar: $xp_x - p_x x = i\hbar$ from Post 2

Simple multiplicative or scalar operators commute -- this is your experience

derivative and matrix operators may or may not commute.

if $\left[\hat{\alpha},\hat{\beta}\right] = 0$ we say it commutes

Thm 4 -- if $\hat{\alpha}$, $\hat{\beta}$ are two operators that share a complete set of eigen fcts, $\left[\hat{\alpha},\hat{\beta}\right] = 0$

???error → simple proof not general: let {fi} be eigen fct $\hat{\alpha}$, $\hat{\beta}$

$$\hat{\alpha}\hat{\beta}f_i = \hat{\alpha}b_i f_i = b_i\hat{\alpha}f_i = b_i a_i f_i = a_i(b_i f_i) = a_i\hat{\beta}f_i =$$

$$\hat{\beta}(a_i f_i) = \hat{\beta}\hat{\alpha}f_i \qquad \left[\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}\right]f_i = 0$$

book proof a little more general -- $g = \sum c_i f_i$ uses commutation of constants, a_i, b_i

$$\left[\hat{\alpha}\hat{\beta} - \hat{\beta}\alpha\right]g = \sum_i c_i[\alpha\beta - \beta\alpha]g_i = \sum_i c_i[\hat{\alpha}b_i - \beta a_i]g_i = \sum c_i[b_i a_i - a_i b_i]g_i = 0$$

This theorem very powerful, lets us substitute eigen functions to determine properties.

Also this is uncertainty principle : if $\rightarrow \left[\hat{\alpha},\hat{\beta}\right] = 0$

then we can determine observables corresponding to $\hat{\alpha}$, $\hat{\beta}$ with arbitrary accuracy

if not $\rightarrow$ uncertainty relation tells measurement limitations

$$\left[x, p_x\right] = \left(x \frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x} x\right) = i\hbar$$

recall: operator must act on something:

(d/dx)xf(x) = f(x) + x(df(x)/dx) ➔ Chain rule differentiation leaves a noncancelling term

Reverse form particularly important

Thm 5 -- if $\left[\hat{\alpha},\hat{\beta}\right] = 0$, there exists a common set {f_i} of eigen functions for both $\hat{\alpha}$ and $\hat{\beta}$

let $\hat{\alpha} f_i = a_i f_i$ set of eigen functions

operate β on α eigen eqn: $\hat{\beta}\hat{\alpha} f_i = \hat{\beta} a_i f_i = a_i\left(\beta f_i\right) = \hat{\alpha}\hat{\beta} f_i = \hat{\alpha}\left(\hat{\beta} f_i\right)$, since commute

since equal, (βf_i) must be an eigen function $\hat{\alpha}$

since (βf_i) and (f_i) have same eigen value a_i, they must be degenerate or relate by const

(non-degenerate) *i.e.* $\beta f_i = b_i f_i$ or f_i must be an eigen fct of β

Several general properties that you can prove: (*Atkins 5.4*)

$$\left[\hat{A},\hat{B}\right] = -\left[\hat{B},\hat{A}\right]$$

$$\left[\hat{A}, b\hat{B}\right] = b\left[\hat{A},\hat{B}\right]$$

$$\left[\hat{A},\hat{B}\hat{C}\right] = \left[\hat{A},\hat{B}\right]\hat{C} + \hat{B}\left[\hat{A},\hat{C}\right]$$

$$\left[\hat{A},\hat{B}+\hat{C}\right] = \left[\hat{A},\hat{B}\right] + \left[\hat{B},\hat{C}\right]$$

$$\left[\hat{A},\left[\hat{B},\hat{C}\right]\right] = ABC - BCA - ACB + CBA$$

Commutation has form of uncertainty (recall $xp_x - p_x x = i\hbar$ <==> $\Delta x \Delta p \geq \hbar/2$)

use expectation values $\langle \hat{\alpha} \rangle = \langle \psi | \hat{\alpha} | \psi \rangle$ and mean deviation: $\Delta\hat{\alpha} = \hat{\alpha} - \langle \alpha \rangle$

since $\langle \alpha \rangle$ is a constant: $\left[\Delta\hat{A}, \Delta\hat{B}\right] = \left[\hat{A}, \hat{B}\right] = i\hat{C}$

let iC represent result of commutator can be zero, a constant or <u>operator</u>

then $\left\langle \left(\Delta\hat{A}\right)^2 \right\rangle \left\langle \left(\Delta\hat{\beta}\right)^2 \right\rangle \geq \frac{1}{4} \langle C \rangle$ from: $\left\langle \left(\Delta\hat{A}\right)^2 \right\rangle = \langle \hat{A}^2 \rangle - \langle A \rangle^2$

define root mean square deviation: $\sqrt{\langle \hat{A} \rangle^2 - \langle A \rangle^2} = \delta A$

$\delta A \delta B \geq \frac{1}{2} |\langle \quad \rangle|$ $\hat{C} \geq \left[\hat{A}, \hat{B}\right] / i$

from : $[x,p_x] = ih/2\pi$, $\delta x \delta p_x \geq \hbar/2$ (precise form) but $[x,y] = [x,p_y] = 0$ → no uncertainty

Note: $\Delta E \Delta t \geq h/4\pi$ not a true uncertainty → no true operator, actually from $[x,p_x]$

but a consequence of time dependent Schroedinger Equation

<u>Parity</u> --(*Levine 7.5*)-- functions can be even or odd or neither.

even: f(x) = f(-x) , f(x,y,z) = f(-x, -y, -z)

odd: f(x) = -f(-x)

if system has parity it is even or odd and that can be represented by parity operator $\hat{\pi}$

$\hat{\pi} g_i = c_i g_i$ g_i - odd - $c_i = -1$ g_i eigen fct of $\hat{\pi}$

$= g_i(-x, -y, -z)$ c_i - even - $c_i = 1$ all possible even/odd fct

if $\left[\hat{\pi}, \hat{H}\right] = 0$ these eigen fct of $\hat{H}$ must be even/odd

$[\pi, T] = 0$ $\frac{\partial^2}{\partial(-x)^2} f(-x) = \frac{\partial^2}{\partial x^2} f(x)$

but $\left[\hat{\pi}, \hat{V}\right]$ depends on form of potential e.g. $V = \frac{1}{2}kx^2$ (Hooks law spring) even -- square of coordinate

$V = \frac{-e^2}{r}$ (electrostatic attraction) even --depends only on distance, not direction

$V = -eE(x)$ (change in electric field is directional - odd)

Thm 7 -- If potential V is an even fct, can choose stationary states ψ_i to be even or odd

$$\left[\hat{\pi},\hat{H}\right] = \left[\hat{\pi},\hat{T}+\hat{V}\right] = \left[\hat{\pi},\hat{T}\right] + \left[\hat{\pi},\hat{V}\right] = 0 + 0 \qquad V = \text{even}$$

ex. 1 let V = +1 $\infty > x > 1$, $-\infty < x < -1$

V = -1 1 > x > -1

this is even, $\psi_i \rightarrow$ has definite parity, is eigen fct of parity operator

These concepts are central to applications of group theory and symmetry to molecular q.m. problems and spectroscopy.

Test: $[\pi, V]f = \pi(Vf) - V(\pi f) = V(-x)f(-x) - V(x)f(-x)$

= 0 if V even ≠ 0 if V odd or mixed parity

Probability amplitudes and superposition of states (*Levine 7.6*)

recall make a measurement on some <u>normalized</u> state 4

$$\langle\alpha\rangle = \langle\psi|\hat{\alpha}|\psi\rangle = \sum_i \sum_i c_i c_j \langle i|\alpha|j\rangle = \sum\sum c_i * c_j a_j \langle i\,|\,j\rangle = \sum_j |c_j|^2 a_j$$

$$\langle\alpha\rangle = \sum_i p_i a_i$$

so measurement is some weighted coverage over several eigen values of α

p_i is $|c_i|^2$ or probability of measuring each a_i

Thm 8 -- Measurement of property corresponding to $\hat{\alpha}$ in ψ has a probability of a_i equal to $|c_i|^2$ where c_i is expansion coeff:

$$\psi = \sum c_i g_i \text{ and } \hat{\alpha} g_i = a_i g_i$$

[If ai degenerate, probability is sum of $|c_i|^2$ for degenerate a_i]

recall: $c_i = \langle i|\psi\rangle$ --called the probability amplitude (Levine)

Thm 9 Probaliity of observing a_i (for $\alpha|i\rangle = a_i|i\rangle$) if a_i is non-degenerate is $|\langle i|\psi\rangle|^2$ for state ψ -- thus more similar g_i and ψ, the more similar will be $\langle\alpha\rangle$ and a_i

Friday--September 1

Time evolution of expectation value: (Atkins, Ch 5.5)