POSTULATES OF QM -- *Levine Ch 7.8, Atkins Ch. 5, R&S - Ch 2.*

Much as in thermodynamics, one can establish a set of "laws" which we have called
  "postulates" (since they have <u>non-obvious physical relationship</u>) and then <u>derive all</u>
  <u>QM properties from these</u>
point -- value lies in how well they describe nature
<u>if work</u> → keep them, <u>if fail</u> → devise new theory

Postulate 1.
The state of a system is fully described by the wave function, ψ (r_1, r_2, ... t)
  --where r_1, r_2, ... are positional coordinates of each particle $_{1,2}$ ... and t is time.
  "fully described" ⇒ all that we can know -- is anything we can measure.
  Quality of ψ (r_1, ... t) as a function (Sch. rep.)
      single valued --<u>drawing1</u>
      continuous --<u>drawing2</u>
      integrable square -- $\int \psi * \psi dT = N$
  Since ψ (r_1, ... t) contains all info--could list quantum numbers-"code" values
  $\psi_{abc...}(r_1, r_2 ...t)$ | a,b,c ...> = state   <u>Dirac bra-ket notation</u> < a,b. .| . . | a,b . .>
      # of independent q.n. will reflect the dimensionality of problem
      e.g. 3-D vector fct require 3 indep. fct ⇒ 3 quantum num.
  Interpretation: $\psi_{a,b}^{*}\psi_{a,b}d\tau =$ probability in area $d\tau$
      $$\int \psi_{a,b}^{*}\psi_{a,b}d\tau = \langle a, b|a, b\rangle = 1$$ system is in the state

Postulate 2.
To every physical observable there corresponds a linear, Hermitian operator.
  For any classical observable convert to q.m. operator by:

  these "operate" on wave function: $\begin{cases} const \rightarrow const, \hat{a}\,\bullet \\ position, x \rightarrow posn, \hat{x}\,\bullet \\ fct.pos, f(x) \rightarrow f(x)\,\bullet \\ momentum, px \rightarrow -i\hbar\frac{2}{2x} \end{cases}$

  ex: energy: T = p²/2m , V = V(x), E = (const., conserved system)

  linear: $\hat{G}(c_1\phi_1 + c_2\phi_2) = c_1\hat{G}\phi_1 + c_2\hat{G}\phi_2$
  This is necessary to probe the probe the properties of systems that one in mixed
  states on in state representation by superposition of other wave functions

Hermitian (*Levine 7.2)* -- has to do with observables being real
  quantum measurement has parallel to probability
  $\psi^{*}\psi d\tau \rightarrow$ probability any value $\psi^{*}\hat{\alpha}\psi d\tau \rightarrow$ probability of measured quant

evaluation generally: $\langle \hat{a} \rangle = \int \psi^* \hat{\alpha} \psi d\tau$

to guarantee real need: $<\alpha> = <i|\alpha|i> = <\alpha>^*$

Hermitian more generally: $\int f_j^* \hat{\alpha} f_i d\tau = \int f_j (\alpha f_i)^* d\tau$

in Dirac symbolism $\int f_i^* \alpha f_j d\tau = \langle i|\alpha|j \rangle = \langle j|\alpha|i \rangle^*$. Hermitian

can even compress further as $\alpha_{ij} = <i\,|\alpha|\,j>$ represent a matrix
  these evaluate "probability" of system being in a state defined by f_i and αf_j

Eigen value equations (*Levine 7.3*)   **This is Levine Postulate 4**
for every operator there will be a <u>set</u> of functions that fulfill eigen value equation
  $\alpha f_j = a f_l$ where $\{f_i\}$ are set of eigen functions
  Dirac notation: $\alpha|i> = a_i|i>$ a_i -- eigen value is a constant
This set of functions will completely describe the space upon which the operator can
  operate, so any wave function representing state of system can be expanded as
  linear combination of set: -- or superposition of eigen functions.

$$\psi = \sum_{i=1}^{n} c_i f_i \qquad \{f_i\} \text{ set of eigen functions}$$

since set of f_i, is complete, in Dirac set of $|i>$ is basis for a general vector
  Now effect of operator has changed
  $$\hat{\alpha}\psi = \hat{\alpha}\sum c_i f_i = \sum c_i \alpha f_i = \sum c_i a_i f_i$$
  This is <u>not</u> an eigen value equation relationship since
  $$\sum_i c_i a_i f_i \neq \text{const } \psi$$
  [the mixing of f_i components to make up ψ is now changed]
  or $\alpha\psi = g$ where g is a <u>new</u> <u>function/state</u>
Degenerate eigen fcts: $\hat{\alpha}f = af$ and $\hat{\alpha}g = ag$
  then f and g said to be degenerate (save eigen value)
  but also any linear combination of f and g degenerate:
  $\hat{\alpha}(c_1 f + c_2 g) = c_1 \hat{\alpha}f + c_2 \hat{\alpha}g$
  $\qquad = c_1 af + c_2 ag$
  $\qquad = a(c_1 f + c_2 g)$
  ex. - p orbitals any comb. still a p orbital in absence of magnetic field
  ex: Schroedinger eqn. $\hat{H}\psi = E\psi$, $\hat{H}$ - total energy op., E - const. of motion
  classical H = T + V = $\frac{1}{2}m\upsilon^2 + V(x) = \frac{p^2}{2m} + V(x)$
1-D, single point $\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi_i(x) = E_i\psi_i(x)$ or 3-D $\left(-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right)\psi = E\psi$

Monday -- August 27
So how do we make measurements?
<u>Postulate 3.</u> (Postulate 3′ - Atkins) (deviates a bit from Levine)
  Where a system is in a state characterized by φ and ψ is an eigen function of $\hat{\alpha}$
  which is the operator representation of some observable, with an eigen value of a,

then measurement of that observable on a system will uniquely yield the eigen value a, every time.

$\alpha\psi = a\psi \rightarrow$ if the <u>system is in a state</u> ψ, <u>then every measurement of a yields a</u>

ex. -- easiest example is <u>energy</u>. If a particle has a well-defined (conserved) energy for state ψ_i: $\hat{H}\psi_i = E_i\psi_i$ each measurement yields E_i or $\hat{H}|i\rangle = E_i|i\rangle$

Clearly if molecule in a superposition of states: $\psi = \sum_i c_i\phi_i$ where $\hat{H}\phi_i = E_i\phi_i$

Then measurement of energy would not be well defined -- <u>no eigen value</u>:

$$\hat{H}\psi = \hat{H}\Sigma c_i\phi_i = \sum_i c_i E_i\phi_i \neq (\text{ const}) \psi$$

<u>**Postulate 4.**</u> (Post 3-Atkins, Post 5-Levine)
The result of measurement of any property, whose operator representation is $\hat{\alpha}$, on a system in a state, ψ_N, the average value measure is given by the expectation value

$$\langle\hat{\alpha}\rangle = \int \psi_n^* \hat{\alpha}\psi_n d\tau = \langle n|\hat{\alpha}|n\rangle \quad \text{assuming } \psi_n \text{ normalized or } \langle n|n\rangle = 1$$

if {f_i} = set of eigen functions of α, $\psi_n = \Sigma c_i f_i$

$$\langle\alpha\rangle = \int (\Sigma c_i f_i)^* \hat{\alpha}(\Sigma c_i f_i) d\tau = \int (\Sigma c_i f_i)^* (\Sigma c_i a_i f_i) d\tau = \Sigma c_i^* c_i a_i \quad \text{-- } <i|j> = \delta_{ij} \text{ (}f_i \text{ orthogonal)}$$

or average value corresponding to a distribution over possible eigen values.
Difference from Ψ being in an eigen state $\Psi = f_l$ -- $\langle\alpha\rangle = \int f_i^* \hat{\alpha} f_i d\tau = a_i \int f_i^* f_i d\tau = a_i$

All this easiest in Dirac notation

$$\langle\alpha\rangle = \langle i|\hat{\alpha}|i\rangle \quad = <i|i> a_i = a_i$$

$$\langle\alpha\rangle = \langle\psi|\hat{\alpha}|\psi\rangle = \sum c_i^* c_j a_j \underbrace{\langle i|j\rangle}_{\delta_{ij}} = \sum_i c_i^* c_i a_i \qquad \text{3rd Post}$$

What about time evolution?
<u>**Postulate 5**</u> (Levine 6):
True dependence of a system (development of a state) is described by:

$$-\frac{\hbar}{i}\frac{\partial\psi(x,t)}{\partial} = \hat{H}(x,t)\psi(x,t)$$

$\hat{H}$ is the Hamiltonian, energy operator, which can depend on position and time
<u>If H = H(x)</u>, *i.e.*, is <u>not</u> dependent on time, variables can be separated, $H\Psi = E\Psi$
technique -- if both sides equal a constant--solve independently
let $\Psi(x,t) = \psi(x)\phi(t) +$ divide through by $\Psi(x,t) = \psi(x)\phi(t)$

$$\left(\frac{1}{\phi(t)}\right)[-\hbar/i \frac{\partial}{\partial}\phi(t)] = E \quad : \quad \frac{1}{\psi(x)}\hat{H}\psi(x) = E$$

solve t-depend fct: $\phi(t) = e^{-iEh/\hbar}$ plug in $\Psi(x,t) = \phi(t)\psi(x) = \exp(-iEt/h)\psi(x)$