Postulates of QM (Liboff chap. 3)

We'll now jump into the formalism, which means spelling out the rules, or basic postulates of QM.

First we recall Born's idea about the interpretation of a particle's wave function $\psi(\vec{r},t)$ [I'm switching notation slightly from P237 to be consistent w/ Liboff.]

Born postulate (sec. 2.8 in Liboff, p.55)

The absolute square of the wave function

$$|\psi(\vec{r},t)|^2$$

represents the probability density for the particle. That is, $|\psi|^2 dx dy dz$ = prob to find particle's position to be w/in volume $dx dy dz$ about point $\vec{r}=(x,y,z)$ at time t.

Recall that the Schrödinger eq'n specifies the wave fn ψ up to an overall (possibly complex) constant. [I.e.; if ψ is sol'n to S.E., so is $A\psi$ where A = const.]

The Born postulate specifies A (up to a complex phase) because the probability of finding the particle <u>somewhere</u> should be equal to 1.

Now on to the postulates of Chapter 3.

Postulate 1: Observables + operators

To any observable A (energy, momentum, position, mass, ang. momentum, no. of particles, ...) there corresponds an operator $\hat{A}$ such that measurement of A yields values a which are eigenvalues of $\hat{A}$. That is, if there is some function φ which satisfies

$$\hat{A}\varphi = a\varphi$$

then measurement of A gives the values a for which this equation is satisfied.

We say the function φ is the eigenfunction of $\hat{A}$ corresponding to the eigenvalue a. Note that different eigenfunctions can correspond to different eigenvalues.

Note: eigenvalues can be continuous or discrete

Comment: Operators are mathematical objects which act on functions, and which may or may not correspond to physical quantities. Some mathematical examples (note names are arbitrary)

$$\hat{D} \equiv \frac{\partial}{\partial x} \qquad \hat{D}\varphi(x) = \frac{\partial \varphi}{\partial x}$$

$\hat{I} \equiv$ identity operator (i.e. leaves φ unchanged): $\hat{I}\varphi = \varphi$

$\hat{Q} \equiv$ integration of φ from $x=0$ to $x=1$: $\hat{Q}\varphi = \int_0^1 \varphi(x)\,dx$

$\hat{\text{Ⓗ}} \equiv$ operator that annihilates φ : $\hat{\text{Ⓗ}}\varphi = 0$

$\hat{B}$ ≡ operator that multiplies by 3 ; $\hat{B}\varphi = 3\varphi$

+ see table 3.1 for other examples.

Physical examples of operators : momentum, energy

Momentum operator $\hat{p}$

$\boxed{\hat{p} = -i\hbar\vec{\nabla}}$, as you know. Its eigenfunctions + eigenvalues satisfy

$$-i\hbar\vec{\nabla}\varphi(\vec{r}) = \vec{p}\,\varphi(\vec{r})$$

or, in 1-dimension (call it x)

$$-i\hbar\frac{\partial\varphi}{\partial x} = p_x\,\varphi(x)$$

sol'n is

$$\varphi(x) = \text{const}\; e^{i p_x x/\hbar} = \text{const}\; e^{ikx}$$

where $p_x = \hbar k$ and since wave no $k = \frac{2\pi}{\lambda}$, this satisfies the deBroglie rel'n $\lambda = h/p$

In 3-dim, the sol'n is

$$\varphi(\vec{r}) = \text{const}\; e^{i\vec{p}\cdot\vec{r}/\hbar} = \text{const}\; e^{i\vec{k}\cdot\vec{r}}$$

and $\vec{k}$ is now a 3-vector

Energy Operator $\hat{H}$

The energy operator is called the Hamiltonian $\hat{H}$.
To get it you take the expression for the energy and substitute $\hat{p}$ for p. I.e.,

$$\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})}$$ energy op.

Then the eigenvalue eq'n is simply the time-indep. Schrödinger eq'n:

$$\hat{H}\varphi(\vec{r}) = E\varphi(\vec{r})$$

Eigenfns + eigenvalues of $\hat{H}$: For simplicity, for now consider a free particle ($V(\vec{r})=0$) in 1-dim:

$$\hat{H}\varphi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\varphi(x)}{\partial x^2} = E\varphi(x)$$

Now note that if we write E in terms of the wave number k, since $E = \frac{p_x^2}{2m}$ for a free particle:

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \frac{2mE}{\hbar^2}$$

+ eq'n becomes

$$\frac{\partial^2\varphi}{\partial x^2} + k^2\varphi = 0$$

We know that the general sol'n to this is

$$\varphi(x) = Ae^{ikx} + Be^{-ikx} \quad (*) \quad \text{with } E = \frac{\hbar^2 k^2}{2m}$$

and our interpretation of k as the wave number with $p = \hbar k$ works.

Comments

- $\hat{H}$ & $\hat{p}$ have common eigenfns (e.g. take $B=0$ in $*$)

  This is not a coincidence, as we will discuss at length later. (As we will see, it happens because the operators $\hat{H}$ & $\hat{p}$ commute with each other.)

- Prob density is uniform. Take $B=0 \Rightarrow |\psi|^2 = |A|^2$

  $\Rightarrow$ equal prob to find particle anywhere.

  Uncertainty in x is $\Delta x = \infty$, which it had better be because the momentum has a definite value, so $\Delta p = 0$

- In 3-dim, Energy eigenfunctions for free particle are

$$\psi(\vec{r}) = A e^{i\vec{k}\cdot\vec{r}} + B e^{-i\vec{k}\cdot\vec{r}}$$

and $E = \dfrac{\hbar^2 |\vec{k}|^2}{2m}$ and $\vec{p} = \hbar\vec{k}$

Postulate 2: Measurement

A measurement of the observable A that gives the value a leaves the system in the state φ_a where $\hat{A}\varphi_a = a\varphi_a$.

Ex: Free part. moving in 1-dim. Measure p_x, + get $p_x = \hbar k$. Then the particle is left in the state $\varphi_k = \text{const}\, e^{ikx}$ + subsequent measurements will give $p_x = \hbar k$

Ex: Position eigenfunction. Suppose you measure the position of free part. in 1-dim + measure $x = x'$.

Post. 1 $\Rightarrow$ $\exists$ a corresponding operator $\hat{x}$

Post. 2 $\Rightarrow$ measuring x + finding x' leaves system in eigen fn of $\hat{x}$ w/ value x'.

Eq'n is $\quad \hat{x}\,\varphi(x) = x'\varphi(x)$

and sol'n is $\quad \varphi(x) = \delta(x - x')$

where $\delta(x-x')$ is the Dirac Delta fn, which we now discuss

Dirac delta function

The Dirac delta function has the properties

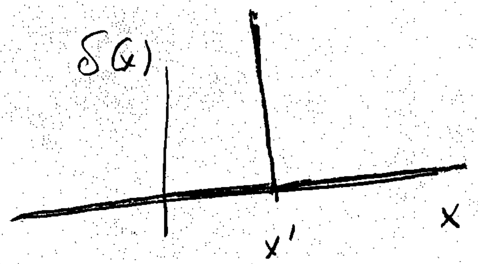
$$\delta(x-x') = \begin{cases} 0 & x \neq x' \\ \infty & x = x' \end{cases}$$

but the ∞ is defined s.t. $\longrightarrow$

$$\int_{-\infty}^{\infty} \delta(x-x')\,dx = 1$$

and
$$\int_{-\infty}^{\infty} f(x)\,\delta(x-x')\,dx = f(x')$$

In words, the δ-fn looks like a probability density that picks out a <u>single</u> value of the variable x. Graphically, it looks like

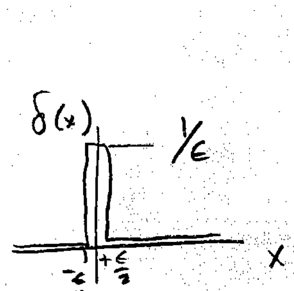


<u>Comments</u>

- Strictly speaking, mathematically this is a distribution, not technically a function, because it's defined in terms of its integration properties.
- If you want to be mathematically correct, you can define the δ-fn as the limit of a more respectable function. There are a number of possibilities; the trick is to keep the normalization straight. Some examples:

$$\delta(x) = \frac{1}{\pi} \lim_{\eta\to\infty} \frac{\sin \eta x}{x}$$

$$\delta(x) = \lim_{\epsilon\to 0} \begin{cases} \frac{1}{\epsilon} & |x| < \frac{\epsilon}{2} \\ 0 & |x| > \frac{\epsilon}{2} \end{cases}$$



$$\delta(x) = \lim_{\epsilon \to 0} \frac{1}{\sqrt{\epsilon\pi}} e^{-x^2/\epsilon}$$

$$\delta(x) = \lim_{\epsilon \to 0} \frac{\epsilon}{\pi} \frac{1}{x^2+\epsilon^2}$$ Lorentzian, or Breit-Wigner

- Another useful representation of the δ-fn is

$$\delta(x-x') = \int \frac{dk}{2\pi} e^{ik(x-x')}$$

$f(x) = \int \frac{dk}{\sqrt{2\pi}} e^{ikx} f(k)$

$f(k) = \int \frac{dx}{\sqrt{2\pi}} e^{-ikx} f(x)$

- And the δ-fn satisfies the following properties:

$x\delta'(x) = -\delta(x)$ see text for how to show these

$\delta(x) = -\delta(-x)$

$\delta(ax) = \frac{1}{a}\delta(x)$

$$\delta[g(x)] = \sum_{x_i} \frac{\delta(x-x_i)}{|g'(x_i)|}$$ where x_i is s.t. $g(x_i)=0$

etc. (see problem 3.6, p. 76 for more properties)

Ex: To prove show $\int$ over test fn give same result both ways:

e.g. $x\delta'(x) = -\delta(x)$

$$\int f(x)\, x\,\delta'(x)\,dx = -\int \frac{d}{dx}[f(x)x]\,\delta(x)\,dx \quad \text{fr/ int. by parts}$$
$$= -\int f(x)\delta(x)\,dx - \underbrace{\int f'(x)\,x\,\delta(x)\,dx}_{=0}$$
$$= -\int f(x)\delta(x)\,dx$$

Postulate 3 Wave function + expectation values

At any time t, system can be described by continuous + differentiable state or wave fn ψ, which contains all info about the state of the system.

(= expectation value)
Avg of any physical observable C is

$$\langle c \rangle = \int \psi^* \hat{c}\, \psi \, d^3r$$

Average means in a large no. N of identical experiments w/ identical initial states $\psi(\vec{r}, 0)$, measure c at time t.

$$\langle c \rangle = \frac{1}{N} \sum_{i=1}^{N} c_i \qquad N \gg 1$$

$$= \sum_c c\, P(c) \rightarrow \int c\, P(c)\, dc$$

(for continuous c)

prob. density

Variance, or mean-squared deviation, in C is given by

$$(\Delta C)^2 \equiv \langle (C - \langle c \rangle)^2 \rangle = \langle c^2 \rangle - \langle c \rangle^2$$

[Smaller variance, more likely to get value close to expectation value in measurement.]

Ex: 1-D. At time t, let particle have wave fn

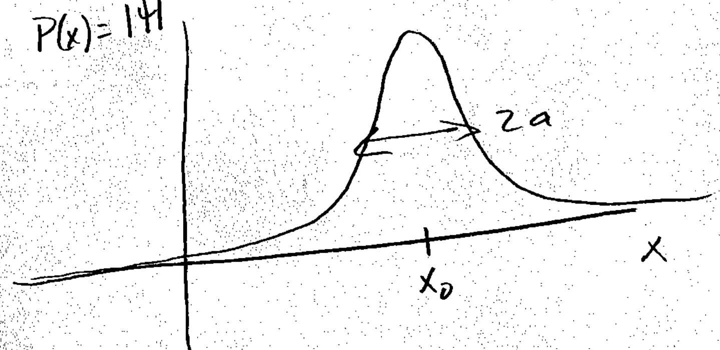
$$\psi = A e^{-(x-x_0)^2/4a^2} e^{\frac{ip_0x}{\hbar}} e^{-i\omega_0 t}$$

where x_0, a, p_0, ω_0 are constants (units: x_0, a = length, p_0 = momentum, ω_0 = frequency)

A is norm const. For simplicity, take it to be real.

Find $\langle x\rangle$, $\Delta x = \sqrt{\Delta x^2}$, $\langle p\rangle$, $\langle \Delta p\rangle$

soln Note
Prob density is $|\psi|^2 = |A|^2 e^{-(x-x_0)^2/2a^2}$ = Gaussian



Now, to get expectation values we need $\langle f\rangle = \int \psi^* f \psi\, dx$ for which we need $|A|^2$ in principle. But instead of evaluating it explicitly, we can save ourselves some work with some cute and relatively straightforward tricks:

Write $$\langle x\rangle = \frac{\int x\, |\psi|^2 dx}{\int |\psi|^2 dx} = \frac{\cancel{|A|^2}\int_{-\infty}^{\infty} dx\, x\, e^{-(x-x_0)^2/2a^2}}{\cancel{|A|^2}\int dx\, e^{-(x-x_0)^2/2a^2}}$$

In the numerator, write $x = (x-x_0) + x_0$. Then

$$\text{Num} = \underbrace{\int_{-\infty}^{\infty} dx\, \cancel{(x-x_0)}\, e^{-(x-x_0)^2/2a^2}}_{=0 \text{ because odd integrand}} + x_0 \int dx\, e^{-(x-x_0)^2/2a}$$

Then $\langle x \rangle = \dfrac{x_0 \int dx\, e^{-(x-x_0)^2/2a^2}}{\int dx\, e^{-(x-x_0)^2/2a^2}}$

$= x_0$

Now $\Delta x = \sqrt{(\Delta x)^2}$

$(\Delta x)^2 = \langle (x-x_0)^2 \rangle$ since $\langle x \rangle = x_0$

$= \dfrac{\cancel{|A|^2} \int dx\, (x-x_0)^2 e^{-(x-x_0)^2/2a^2}}{\cancel{|A|^2} \int dx\, e^{-(x-x_0)^2/2a^2}}$

But note $(x-x_0)^2 e^{-(x-x_0)^2/2a^2} = \dfrac{-\partial}{\partial\left(\frac{1}{2a^2}\right)} e^{-(x-x_0)^2/2a^2}$

$= \dfrac{\dfrac{-\partial}{\partial\left(\frac{1}{2a^2}\right)} \int dx\, e^{-(x-x_0)^2/2a^2}}{\int dx\, e^{-(x-x_0)^2/2a^2}}$

where we took the derivative outside the integral because x and $\frac{1}{2a^2}$ are independent.

Now $\int dx\, e^{-(x-x_0)^2/2a^2} = a\sqrt{2\pi}$

Let $\beta = \frac{1}{2a^2}$ want $\dfrac{\partial}{\partial\beta}\left(a\sqrt{2\pi}\right) = \dfrac{\partial}{\partial\beta}\left(\dfrac{\pi^{1/2}}{\beta^{1/2}}\right)$

$= -\dfrac{1}{2}\dfrac{\pi^{1/2}}{\beta^{3/2}}$

$$\text{So } (\Delta x)^2 = +\frac{1}{2}\frac{\pi^{1/2}\beta^{-3/2}}{\pi^{1/2}\beta^{-1/2}} = \frac{1}{2}\beta^{-2} = \frac{2a^2}{2} = a^2$$

$$\Rightarrow \quad \Delta x = a$$

$\langle p \rangle$: Now we have to take the derivative of ψ before taking $|\psi|^2$, i.e. take

$$\langle p \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{p}\, \psi \, dx}{\int_{-\infty}^{\infty} |\psi|^2 dx} = \frac{\int \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x}\right) dx}{\int |\psi|^2 dx}$$

$$\frac{\partial \psi}{\partial x} = -\frac{2(x-x_0)}{2a^2}\psi + \frac{ip_0}{\hbar}\psi$$

$$\Rightarrow \langle p \rangle = \frac{\frac{i\hbar}{2a^2}\underbrace{\cancel{\int (x-x_0) e^{-(x-x_0)^2/2a^2} dx}}_{0,\ \text{since odd integrand}} + p_0 \int e^{-(x-x_0)^2/2a^2} dx}{\int e^{-(x-x_0)^2/2a^2} dx}$$

$$= p_0$$

Exercise: Find $\langle p^2 \rangle$ + calculate Δp. You get

$$\Delta p = \frac{\hbar}{2a}$$

$$\Rightarrow \quad \Delta p\, \Delta x = \frac{\hbar}{2}$$

This wave fn has the minimum possible uncertainty!

Postulate 4 Time development of wave fn.

Time development of a wave or state function $\Psi(\vec{r},t)$ is determined by the time-dependent Schrödinger eq'n

$$i\hbar \frac{\partial}{\partial t}\Psi(\vec{r},t) = \hat{H}\,\Psi(\vec{r},t)$$

If $\hat{H}$ is indep of time, i.e. if potential depends only on $\vec{r}$, we have $\hat{H} = \hat{H}(\vec{r})$ and we can do the usual separation of variables for the space + time dependence.

write $\Psi(\vec{r},t) = \varphi(\vec{r})\,T(t)$

+ on substitution into S.E. + division by Ψ,

we get $i\hbar \frac{1}{T}\frac{dT}{dt} = \frac{\hat{H}\varphi}{\varphi}$

LHS is fn of t only; RHS fn of $\vec{r}$ only, so for eq'n to be true for any and all $\vec{r}, t$, the two sides must be separately equal to the same constant; call it E.

$$\Rightarrow \hat{H}\varphi(\vec{r}) = E\varphi(\vec{r})$$

(+ since eigenvalues of $\hat{H}$ are energy, we know E = energy)

and $i\hbar \frac{dT}{dt} = ET$

We solve the latter eq'n to get

$$T(t) = \text{const } e^{-iEt/\hbar}$$

Now supposing the eigenvalues of $\hat{H}$ are discrete, we
↳ as in a finite system or one w/ bound states

write $\hat{H}\,\varphi_n = E_n \varphi_n$

where n is an integer and identifies the eigenfn and its corresponding eigenvalue. Then we have for the total wave fn

$$\boxed{\Psi_n(\vec{r},t) = A\,\varphi_n(\vec{r})\,e^{-iE_nt/\hbar}}$$

Let's go back to the 1-D free particle: we know the energies are continuous and we have

$$\hat{H}\varphi_k = E_k \varphi_k$$

$$\varphi_k = A e^{ikx} \quad \& \quad E_k = \frac{\hbar^2 k^2}{2m}$$

So for total wave fn,

$$\Psi_k(x,t) = A e^{i(kx-\omega t)} \qquad \hbar\omega \equiv E_k$$

Now this is a wave propagating in the $+x$ direction — it has the form

$$f(x - vt)$$

Note value of f stays const for $x = vt$. That is, as t increases, x increases so f is moving to right (See illustration p. 83)

For our free particle we can write

$$\psi_k(x,t) = A\, e^{ik(x - \frac{\omega}{k}t)}$$

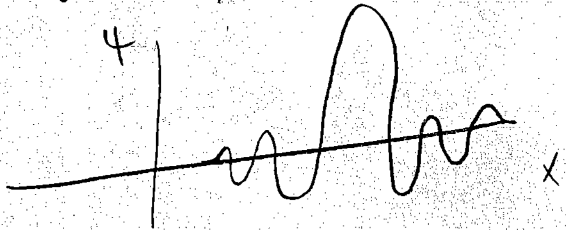
and the speed is

phase velocity $\quad v = \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{p^2}{2m}\frac{1}{p} = \frac{p}{2m} = \frac{1}{2} v_{classical}$

$\Rightarrow$ state fn moves w/ phase velocity = ½ classical vel,

why doesn't this make sense? A plane wave is way too much of an idealization to talk about classical properties like motion of the particle in any detail. (Recall $\Delta p = 0$ and $\Delta x = \infty$, so this particle is by no means localized!)

A better (but more complicated) approx is to describe a free particle is a wave packet, which is a sum of plane waves w/ momenta in a narrow range. Wave fn looks like



and the relevant velocity of the packet is the

group velocity $\quad v_g = \frac{\partial \omega}{\partial k}$

For plane wave, $\quad \omega = \frac{\hbar k^2}{2m} \quad$ so $\quad v_g = \frac{2\hbar k}{2m} = \frac{p}{m}$

= classical velocity, where we use the k of the dominant contribution to the packet

Sol'n to Initial Value Problem in QM

Problem: Given $\Psi(\vec{r},0)$, find $\Psi(\vec{r},t)$

[Aside: We already know the answer if $\Psi(\vec{r},0)$ is in an energy eigenstate: $\Psi(\vec{r},0) = \varphi_n(\vec{r})$

$$\Rightarrow \Psi(\vec{r},t) = e^{-iE_nt/\hbar}\,\varphi_n(\vec{r})$$

Problem here is to find time dependence for general $\Psi(\vec{r},0)$]

Solution: Time dependence is determined by Schr. eq'n.

$$\hat{H}\,\Psi(\vec{r},t) = i\hbar\frac{\partial \Psi(\vec{r},t)}{\partial t} \qquad (*)$$

or $$\frac{\partial \Psi(\vec{r},t)}{\partial t} = \frac{-i}{\hbar}\hat{H}\,\Psi(\vec{r},t)$$

Now if $\hat{H}$ were a constant, we'd immediately see that this integrates to an exponential. In fact that's pretty much what happens here, too.

To see this, assume that $\hat{H}$ is independent of t, and define the operator (which happens to be unitary)

$$\hat{U} \equiv e^{-\frac{it\hat{H}}{\hbar}}$$

As you have seen/will see in the homework, a function f of an operator $\hat{A}$ is also an operator, and →

$f(\hat{A})$ is defined in terms of a power series in $\hat{A}$. In our case, $f \to \hat{U}$ and $\hat{A} \to \hat{H}$, with

$$\hat{U} = e^{-\frac{it\hat{H}}{\hbar}} = 1 - \frac{it\hat{H}}{\hbar} + \frac{1}{2!}\left(\frac{-it\hat{H}}{\hbar}\right)^2 + \cdots$$

Now to work w/ the Schr. eq'n, we actually want

$$\hat{U}^{-1} = e^{it\hat{H}/\hbar}$$

[and note $\hat{U}\hat{U}^{-1} = e^{-it\hat{H}/\hbar} e^{+it\hat{H}/\hbar} = \hat{I}$ = identity operator, i.e. $\hat{U}^{-1}$ really is the inverse of $\hat{U}$. Also $\hat{U}^{-1}\hat{U} = \hat{I}$]

Now multiply Schr. eq'n (*) on left by $\hat{U}^{-1}$ and rearrange:

$$e^{it\hat{H}/\hbar} \frac{\partial \psi(\vec{r},t)}{\partial t} + e^{it\hat{H}/\hbar}\left(\frac{i\hat{H}}{\hbar}\right)\psi(\vec{r},t) = 0$$

which we can rewrite as

$$\frac{\partial}{\partial t}\left[e^{it\hat{H}/\hbar}\psi(\vec{r},t)\right] = 0$$

Now the LHS is easy to integrate from 0 to t:

$$e^{it\hat{H}/\hbar}\psi(\vec{r},t)\Big|_0^t = 0$$

or $\quad e^{it\hat{H}/\hbar}\psi(\vec{r},t) - \psi(\vec{r},0) = 0$

Now it's easy to solve for $\psi(\vec{r},t)$: just multiply (2.18) on the left by $\hat{U} = e^{-it\hat{H}/\hbar}$

$$\Rightarrow \boxed{\psi(\vec{r},t) = e^{-it\hat{H}/\hbar}\psi(\vec{r},0) = \hat{U}\psi(\vec{r},0)}$$

and this is true for <u>any</u> initial state $\psi(\vec{r},0)$, not just eigenstates of $\hat{H}$, for $\hat{H}$ independent of time.

<u>Ex</u> If $\psi(\vec{r},0)$ <u>does</u> happen to be an eigenstate of $\hat{H}$, i.e. $\psi(\vec{r},0) = \varphi_n(\vec{r})$, with $\hat{H}\varphi_n(\vec{r}) = E_n\varphi_n(\vec{r})$, then we have

$$\psi(\vec{r},t) = e^{-it\hat{H}/\hbar} = e^{-iE_nt/\hbar}\varphi_n = e^{-i\omega_n t}\varphi_n$$

where $E_n = \hbar\omega_n$

as shown in HW (prob 3.16)

So our sol'n reduces to what we got fr/ separation of variables.

<u>Comment</u> Why stationary states are called stationary states

Suppose, still, that $\psi(\vec{r},0) = \varphi_n(\vec{r})$. What happens to the expectation value of some arbitrary operator $\hat{A}$ (position, energy, ang. momentum, etc) over time?

<u>t=0</u>: $\langle\hat{A}\rangle_{t=0} = \int\psi^*(\vec{r},0)\,\hat{A}\,\psi(\vec{r},0)\,d^3r = \int\varphi_n^*\,\hat{A}\,\varphi_n\,d^3r$

$t>0$: $\langle \hat{A} \rangle_t = \int \varphi_n^* e^{+i\omega_n t} \hat{A} e^{-i\omega_n t} \varphi_n \, d^3r$

+ assuming $\hat{A}$ not explicit fn of time ($\frac{\partial \hat{A}}{\partial t}=0$),

$= \int \varphi_n^* \hat{A} \varphi_n d^3r$

$= \langle \hat{A} \rangle_{t=0}$

$\Rightarrow$ Expectation values of observables don't change with time when $\psi(\vec{r},0)$ is an eigenstate of the Hamiltonian, hence the name stationary state;

$$\boxed{\langle \hat{A} \rangle_{t>0} = \langle \hat{A} \rangle_{t=0} \quad \text{for stationary state}}$$

Ex Suppose wave fn at $t=0$ is linear combination of eigenfns of $\hat{A}$? How does $\psi(\vec{r},t)$ evolve w/ time?

$\psi(\vec{r},0) = \sum a_n \varphi_n$

$\psi(\vec{r},t) = e^{-it\hat{H}/\hbar} \sum_n a_n \varphi_n = \sum_n a_n e^{-it\hat{H}/\hbar} \varphi_n$

$= \sum_n a_n e^{-iE_n t/\hbar} \varphi_n$

Contributions fr/ each eigenstate evolve separately