In particular

$$|\psi(t)\rangle = \sum_n \psi_n(t)|n\rangle,$$

$$\psi_n(t) - \langle n|\psi(t)\rangle$$

and the Schrödinger equation becomes in the energy representation

$$i\hbar \frac{\partial}{\partial t}\psi_n(t) = E_n \psi_n(t)$$

thus

$$\psi_n(t) = e^{-\frac{i}{\hbar}E_n(t-t_0)}\psi_n(t_0).$$

That's

$\langle n|H = E_n\langle n|$ in the energy basis.

As we did for Wave Mechanics, we can investigate the consequences of the postulates and hence shed light on their physical content.

4.5) Consequences and Physical Interpretation of the Postulates

1) $|\psi(t)\rangle$ obeys the Schrödinger equation, a linear, homogeneous equation. Thus the principle of superposition applies (i.e. $|\psi\rangle$ belong to a vector space $\mathcal{H}$). In particular if $|\psi_1(t_0)\rangle + \lambda|\psi_2(t_0)\rangle$ is a solution to Schrödinger's equation at t_0, then at t $|\psi_1(t)\rangle + \lambda|\psi_2(t)\rangle$ is a solution to Schrödinger's equation. Hence $|\psi(t)\rangle$ depends linearly on $|\psi(t_0)\rangle$ that is the <u>time evolution operator</u>

$U(t,t_0)$ is a linear operator which relates $|\psi(t)\rangle$ to $|\psi(t_0)\rangle$ uniquely (since Schrödinger eq. is 1st order in t) and is independent of which state $|\psi\rangle$ is being discussed. Thus for any state $|\psi\rangle$ (linearity)

$$|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle.$$

Since $H(t)$ is Hermitian, probability is conserved.

$$\frac{d}{dt}\langle\phi(t)|\psi(t)\rangle = \left(\frac{d}{dt}\langle\phi(t)|\right)|\psi(t)\rangle + \langle\phi(t)|\left(\frac{d}{dt}|\psi(t)\rangle\right)$$

but $\frac{d}{dt}|\psi(t)\rangle = \frac{1}{i\hbar} H(t)|\psi(t)\rangle$

and, taking the Hermitian conjugate,

$$\frac{d}{dt}\langle\psi(t)| = \left(\frac{1}{i\hbar}\right)^* \langle\psi(t)|H^\dagger(t)$$

$$= -\frac{1}{i\hbar}\langle\psi(t)|H(t)$$

(for arbitrary state $|x\rangle$

$$\left(\frac{d}{dt}\langle\psi(t)|\right)|x\rangle = \left(\langle x|\frac{d}{dt}|\psi(t)\rangle\right)^*$$

$$= \left(\langle x|\frac{1}{i\hbar}H(t)|\psi(t)\rangle\right)^*$$

$$= -\frac{1}{i\hbar}\langle x|H(t)|\psi(t)\rangle^*$$

$$= -\frac{1}{i\hbar}\langle\psi(t)|\underbrace{H^\dagger(t)}_{=H(t)}|x\rangle$$

)

So

$$\frac{d}{dt}\langle\phi(t)|\psi(t)\rangle = -\frac{1}{i\hbar}\langle\phi(t)|H(t)|\psi(t)\rangle$$

$$+\frac{1}{i\hbar}\langle\phi(t)|H(t)|\psi(t)\rangle$$

$$\Rightarrow \quad \frac{d}{dt}\langle \phi(t) | \psi(t) \rangle = 0 .$$

Thus

$$\langle \phi(t) | \psi(t) \rangle = \langle \phi(t_0) | \psi(t_0) \rangle$$

is independent of time.

Hence time evolution does not modify the global probability of finding a particle in space

$$\langle \psi(t) | \psi(t) \rangle = \int d^3r \, |\psi(\vec{r},t)|^2 = \text{constant independent of time}$$

hence $|\psi(\vec{r},t)|^2$ is interpreted as a probability density.

Further, since $|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle$ and $|\phi(t)\rangle = U(t,t_0)|\phi(t_0)\rangle$ we find

$$\langle \phi(t) | \psi(t) \rangle = \langle \phi(t_0) | U^\dagger(t,t_0)\, U(t,t_0) | \psi(t_0) \rangle$$

$$= \langle \phi(t_0) | \mathbb{1} | \psi(t_0) \rangle$$

$$\Rightarrow U^\dagger(t,t_0)\, U(t,t_0) = \mathbb{1}$$

$\Rightarrow$ $U^{-1}(t,t_0) = U^{\dagger}(t,t_0)$ so $U(t,t_0)$ is unitary.

2) The mean value or <u>expectation value</u> of an observable Ω of the system in state $|\psi(t)\rangle$ is

$$\langle A\rangle(t) = \langle\psi(t)|A|\psi(t)\rangle$$

$$= \int d^3r\, d^3r' \langle\psi(t)|\vec{r}\rangle\langle\vec{r}|A|\vec{r}'\rangle\langle\vec{r}'|\psi(t)\rangle$$

$$= \int d^3r\, d^3r'\, \psi^*(\vec{r},t)\langle\vec{r}|A|\vec{r}'\rangle\psi(\vec{r}',t)$$

Now suppose $A = A(\vec{R},\vec{P};t)$; then

$$\langle\vec{r}|A(\vec{R},\vec{P};t)|\vec{r}'\rangle = A(\vec{r},\tfrac{\hbar}{i}\vec{\nabla}_{\vec{r}};t)\,\delta^3(\vec{r}-\vec{r}')$$

So

$$\langle A\rangle(t) = \int d^3r\, \psi^*(\vec{r},t)\, A(\vec{r},\tfrac{\hbar}{i}\vec{\nabla}_{\vec{r}};t)\,\psi(\vec{r},t)$$

as we had in wave mechanics.

From the abstract expression, we find

$$\frac{d}{dt}\langle A\rangle(t) = \Big(\underbrace{\frac{d}{dt}\langle \psi(t)|}_{-\frac{1}{i\hbar}\langle\psi(t)|H(t)}\Big) A|\psi(t)\rangle + \langle\psi(t)|A\Big(\underbrace{\frac{d}{dt}|\psi(t)\rangle}_{=\frac{1}{i\hbar}H(t)|\psi(t)\rangle}\Big)$$

$$+ \langle\psi(t)|\underbrace{\frac{\partial A}{\partial t}}_{\text{if } A \text{ has explicit time dependence}}|\psi(t)\rangle$$

$$= \frac{i}{\hbar}\langle\psi(t)|[H(t),A]|\psi(t)\rangle + \langle\psi(t)|\frac{\partial A}{\partial t}|\psi(t)\rangle .$$

That is Ehrenfest's Theorem

$$\boxed{\frac{d}{dt}\langle A\rangle(t) = \frac{i}{\hbar}\langle[H(t),A]\rangle + \langle\frac{\partial A}{\partial t}\rangle .}$$

For $\vec{R}$ and $\vec{P}$ and $H = \frac{1}{2m}\vec{P}^2 + V(\vec{R})$

we find
$$\frac{d}{dt}\langle\vec{R}\rangle = \frac{i}{\hbar}\langle[H,\vec{R}]\rangle = \frac{i}{\hbar}\langle[\tfrac{\vec{P}^2}{2m},\vec{R}]\rangle$$
$$\frac{d}{dt}\langle\vec{P}\rangle = \frac{i}{\hbar}\langle[H,\vec{P}]\rangle = \frac{i}{\hbar}\langle[V(\vec{R}),\vec{P}]\rangle$$

But

$$\left[\frac{\vec{P}^2}{2m}, \vec{R}\right] = \frac{-i\hbar}{m}\vec{P}$$

$$\left[V(\vec{R}), \vec{P}\right] = i\hbar \vec{\nabla}_{\vec{R}} V(\vec{R}) \,.$$

Hence

$$\frac{d}{dt}\langle \vec{R} \rangle = \frac{1}{m}\langle \vec{P} \rangle$$

$$\frac{d}{dt}\langle \vec{P} \rangle = \langle -\vec{\nabla}_{\vec{R}} V(\vec{R}) \rangle \,,$$

(Newton's Law is obtained for highly localized states)

---

3) Heisenberg's Uncertainty Principle

$A = A^\dagger$; $B = B^\dagger$; Define the Root mean square deviations

$$\Delta A \equiv \sqrt{\langle (A - \langle A \rangle)^2 \rangle} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

$$\Delta B \equiv \sqrt{\langle (B - \langle B \rangle)^2 \rangle} = \sqrt{\langle B^2 \rangle - \langle B \rangle^2} \,,$$

then

$$\Delta A \cdot \Delta B \geq \frac{1}{2} \left| \langle [A, B] \rangle \right| \,.$$

Proof: $\lambda \in \mathbb{R}$; Define

$$F(\lambda) \equiv \langle (A - \langle A\rangle - i\lambda(B - \langle B\rangle)) \times$$

$$\times (A - \langle A\rangle + i\lambda(B - \langle B\rangle))\rangle$$

$$= (\Delta A)^2 + i\lambda \langle [A - \langle A\rangle, B - \langle B\rangle]\rangle$$

$$+ \lambda^2 (\Delta B)^2$$

$$\boxed{F(\lambda) = (\Delta A)^2 + i\lambda\langle [A,B]\rangle + \lambda^2 (\Delta B)^2}$$

But $F(\lambda) \geq 0$ for all λ, since

$$F(\lambda) = \langle D^\dagger D\rangle = \langle \psi | D^\dagger D | \psi\rangle$$

$$= \langle \phi | \phi \rangle \geq 0 \text{ where}$$

$$|\phi\rangle \equiv D|\psi\rangle \text{ and } \langle\phi| = \langle\psi|D^\dagger$$

with $D = A - \langle A\rangle + i\lambda(B - \langle B\rangle)$.

Now $\left.\dfrac{dF}{d\lambda}\right|_{\lambda=\lambda_{min}} = 0 = i\langle [A,B]\rangle + 2\lambda_{min}(\Delta B)^2$

$$\Rightarrow \lambda_{min} = \frac{-i}{2}\frac{\langle [A,B]\rangle}{(\Delta B)^2}$$

This is a minimum since

$$\frac{d^2F}{d\lambda^2} = 2(\Delta B)^2 > 0$$

and $\lambda_{min} = \lambda_{min}^* =$ real as required.

Thus

$$F(\lambda_{min}) \geq 0,$$

$$F(\lambda_{min}) = (\Delta A)^2 + \frac{1}{2}\left(\frac{\langle[A,B]\rangle}{\Delta B}\right)^2 - \frac{1}{4}\left(\frac{\langle[A,B]\rangle}{(\Delta B)}\right)^2$$

$\Rightarrow$

$$\boxed{\Delta A \cdot \Delta B \geq \frac{1}{2}|\langle[A,B]\rangle|}$$

For

$$A = X$$
$$B = P$$

we find $[X,P] = i\hbar$, so $|\langle[X,P]\rangle| = \hbar$

$$\Rightarrow \quad \Delta X\, \Delta P \geq \frac{\hbar}{2}.$$

4) Conservative Systems and Stationary States

We have already touched upon this on pages -356- to -358-.

Suppose H is independent of time, for example $H = \frac{1}{2m}\vec{P}^2 + V(\vec{R})$, then the Schrödinger equation becomes

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = H\,|\psi(t)\rangle .$$

This can be solved, given the state at time t_0, $|\psi(t_0)\rangle$, the state at time t, $|\psi(t)\rangle$, is

$$|\psi(t)\rangle = e^{-iH(t-t_0)/\hbar}\,|\psi(t_0)\rangle$$

i.e. i) $|\psi(t_0)\rangle = e^{0}\,|\psi(t_0)\rangle = |\psi(t_0)\rangle$ as needed

and ii) $i\hbar \frac{d}{dt}|\psi(t)\rangle = i\hbar\left(\frac{d}{dt}e^{-iH(t-t_0)/\hbar}\right)|\psi(t_0)\rangle$

since $[H,H]=0$, $$= H\,e^{-iH(t-t_0)/\hbar}\,|\psi(t_0)\rangle$$

$$= H\,|\psi(t)\rangle$$ as required.

This gives the time evolution operator as

$$U(t,t_0) = e^{-iH(t-t_0)/\hbar}$$

with $U^{-1}(t,t_0) = U^{\dagger}(t,t_0) = e^{+iH(t-t_0)/\hbar} = U(t_0,t)$.

Since $H = H^{\dagger}$, the eigenvalues, the energy, are real and the eigenstates form a basis for $\mathcal{H}$. Since H is independent of time both the eigenvalues E_n and eigenstates, $|n\rangle$ of H are time independent (here we let $\{E_n\}$ be a set of discrete eigenvalues)

$$H|n\rangle = E_n|n\rangle.$$

The eigenstates are chosen to be orthonormal

$$\langle m|n\rangle = \delta_{mn}$$

and they are complete by postulate 3

$$\mathbb{1} = \sum_n{}' |n\rangle\langle n|$$

Any state at time t_0, $|\psi(t_0)\rangle$, can be expanded in terms of $\{|n\rangle\}$,

$$|\psi(t_0)\rangle = \sum_n' \psi_n(t_0)\,|n\rangle$$

with $\quad \langle n|\psi(t_0)\rangle = \psi_n(t_0)$.

The state at time t is given by

$$|\psi(t)\rangle = U(t,t_0)\,|\psi(t_0)\rangle$$
$$= \sum_n' \psi_n(t_0)\,U(t,t_0)|n\rangle$$

but

$$U(t,t_0)|n\rangle = e^{-iH(t-t_0)/\hbar}\,|n\rangle$$
$$= e^{-iE_n(t-t_0)/\hbar}\,|n\rangle$$

So

$$\boxed{|\psi(t)\rangle = \sum_n' \psi_n(t_0)\,e^{-iE_n(t-t_0)/\hbar}\,|n\rangle}$$

In particular if $|\psi(t)\rangle$ itself is an eigenstate of H with energy E_n, say, then

$$|\psi(t)\rangle = e^{-iE_n(t-t_0)/\hbar}\,|\psi(t_0)\rangle,$$

only one phase appears (for example E_n can have a degeneracy so $|\psi(t_0)\rangle = \sum_\alpha' \psi_\alpha(t_0)\,|n,\alpha\rangle$

where $\{\alpha\}$ labels the other eigenvalues of the operators in the CSCO that commute with H (like $\vec{L}^2, L_z \to \{l, m\}$ in the central potential case)). Since $|\psi(t)\rangle$ and $|\psi(t_0)\rangle$ differ by an overall phase, by postulate I, they represent the same state of the system, there is no observable consequence of the phase. Hence the physical properties of an eigenstate of (time independent) H do not vary in time. For this reason, they are called <u>stationary states</u>. Clearly

$$\langle \psi(t) | A | \psi(t) \rangle = \langle \psi(t_0) | A | \psi(t_0) \rangle$$

and hence, for A time independent, is itself time independent.

Furthermore, when an observable has no explicit time dependence

$$\frac{\partial A}{\partial t} = 0,$$

and also commutes with H itself,

$[A,H]=0$, it is a

<u>constant of motion</u>.

From Ehrenfest's theorem

1) $\frac{d}{dt}\langle A\rangle = 0$

2) Since $[H,A]=0$, the common eigenvectors $\{|n,a\rangle\}$ form a time independent basis. Thus we have

$$H|n,a\rangle = E_n|n,a\rangle$$

$$A|n,a\rangle = a|n,a\rangle$$

with $\langle m,a'|n,a\rangle = \delta_{mn}\delta_{aa'}$

and $\mathbb{1} = \sum_n\!\!\!\!\!\!\int \; \sum_a\!\!\!\!\!\!\int \; |n,a\rangle\langle n,a|$.

Hence any vector has an expansion in terms of $\{|n,a\rangle\}$

$$|\psi(t_0)\rangle = \sum_n{}' \sum_a{}' \psi_{na}(t_0)\,|n,a\rangle$$

and
$$|\psi(t)\rangle = U(t,t_0)\,|\psi(t_0)\rangle$$

$$= \sum_n{}' e^{-iE_n(t-t_0)/\hbar} \times$$

$$\times \left(\sum_a{}' \psi_{na}(t_0)\,|n,a\rangle\right)$$

By Postulate 3: spectral decomposition, the probability, $P(n,a;t_0)$, of measuring <u>a when observing A</u> <u>and</u> <u>E_n when observing H</u> at time t_0 for the system in state $|\psi(t_0)\rangle$ is

$$P(n,a;t_0) = |\psi_{na}(t_0)|^2.$$

At time t, this probability is

$$P(n,a;t) = |\psi_{na}(t)|^2.$$

But

$$\psi_{na}(t) = \langle n,a|\psi(t)\rangle$$
$$= e^{-iE_n(t-t_0)/\hbar}\,\psi_{na}(t_0)$$

from the expansion of $|\psi(t)\rangle$ above.

Thus

$$P(n,a;t_0) = P(n,a;t),$$

the probability is time independent.

Similarly, the probability of measuring a when observing A for the system in state $|\psi(t)\rangle$ is

$$P(a;t) = \sum_n{}' |\psi_{na}(t)|^2 = \sum_n{}' P(n,a;t)$$

$$= \sum_n{}' |\psi_{na}(t_0)|^2 = P(a;t_0);$$

also time independent.