$$H u_n = E_n u_n, \quad n = 0, 1, \ldots$$

$$\alpha = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$u_n = N_n H_n(\alpha x) e^{-\frac{1}{2}\alpha^2 x^2} \quad \checkmark$$

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{\partial^n}{\partial \xi^n} e^{-\xi^2}$$

$$N_n = \left(\frac{\alpha}{2^n n! \sqrt{\pi}}\right)^{\frac{1}{2}}$$

$$S(\xi, s) = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n \quad \checkmark$$

$$S(\xi, s) = e^{-s^2 + 2s\xi}$$

TRANSITION DIPOLE MOMENTS

$$\langle u_n | \hat{\mu}_x | u_m \rangle$$

$$\hat{\mu}_x = e\hat{x}$$

charge

$$\langle u_n | \hat{x} | u_m \rangle, \quad n, m = 0, 1, \ldots$$

In vibrational spectroscopy (within harmonic approximation),

$$v \to v \pm 1$$

$$(n \to n \pm 1)$$

In particular,

$$\langle u_n | \hat{x} | u_n \rangle = 0,$$

since

$$\int_{-\infty}^{\infty} u_n(x)^* \, x \, \overset{\text{even or odd}}{u_n(x)} \, dx$$

$$= \int_{-\infty}^{\infty} x \, \underbrace{u_n(x)^2}_{\text{even}} \, dx = 0.$$

In general,

$$\langle u_n|\hat{x}|u_m\rangle = \int_{-\infty}^{\infty} \underbrace{u_n^*(x)}_{\text{parity } n} \, \underbrace{x}_{\text{odd}} \, \overset{\text{parity } m}{u_m(x)} \, dx$$

parity of n must differ from parity of m.

Let us calculate

$$\langle u_n|\hat{x}|u_m\rangle .$$

$$\langle u_n|\hat{x}|u_m\rangle = \int_{-\infty}^{\infty} u_n^*(x)\, x\, u_m(x)\, dx$$

$$= N_n N_m \int_{-\infty}^{\infty} H_n(\alpha x) H_m(\alpha x)\, x\, e^{-\alpha^2 x^2} dx$$

$\xi = \alpha x$

$d\xi = \alpha dx$

$$= \frac{N_n N_m}{\alpha^2} \int_{-\infty}^{\infty} H_n(\xi) H_m(\xi)\, \xi\, e^{-\xi^2} d\xi$$

$S(\xi, s)$ $S(\xi, t)$

$$A = \int_{-\infty}^{\infty} S(\xi, s)\, S(\xi, t)\, \xi\, e^{-\xi^2} d\xi$$

$$= \sum_{n,m=0}^{\infty} \frac{s^n t^m}{n!\, m!} \times \int_{-\infty}^{\infty} H_n(\xi) H_m(\xi)\, \xi\, e^{-\xi^2} d\xi$$

$$I_{nm} = \int_{-\infty}^{\infty} H_n(\xi) H_m(\xi)\, \xi\, e^{-\xi^2} d\xi$$

$$\langle u_n | \hat{x} | u_m \rangle = \frac{N_n N_m}{\alpha^2} I_{nm} \checkmark$$

$$A = \sum_{n,m=0}^{\infty} \frac{s^n t^m}{n!\, m!} I_{nm} \checkmark$$

$$A = \int_{-\infty}^{\infty} e^{-s^2 + 2s\xi} e^{-t^2 + 2t\xi} \times \xi e^{-\xi^2} d\xi$$

$$= e^{2st} \int_{-\infty}^{\infty} e^{-(\xi^2 + s^2 + t^2 - 2s\xi - 2t\xi + 2st)} \times \xi\, d\xi$$

$$A = e^{2st} \int_{-\infty}^{\infty} e^{-(\xi - s - t)^2} \xi\, d\xi$$

$$A \overset{z=\xi-s-t}{\underset{dz=d\xi}{=}} e^{2st}\int_{-\infty}^{\infty} e^{-z^2}\left(\cancelto{0}{z}+s+t\right)dz$$

$$= e^{2st}(s+t)\int_{-\infty}^{\infty} e^{-z^2}\,dz$$

$$A = \sqrt{\pi}\, e^{2st}(s+t)$$

$$A = \sqrt{\pi}\,(s+t)\sum_{n=0}^{\infty}\frac{2^n s^n t^n}{n!}$$

$$A = \sqrt{\pi}\left\{\sum_{n=0}^{\infty}\frac{2^n s^{n+1} t^n}{n!} + \sum_{n=0}^{\infty}\frac{2^n s^n t^{n+1}}{n!}\right\}$$

$$= \sum_{n,m=0}^{\infty}\frac{s^n t^m}{n!\,m!} I_{nm}$$

$$I_{nn} = 0$$

The only nonzero contributions are $I_{n,n+1}$ and $I_{n+1,n}$.

$I_{n+1,n}$ (at $s^{n+1}t^{n}$):

$$\frac{I_{n+1,n}}{(n+1)!\,n!} = \sqrt{\pi}\,\frac{2^n}{n!} \quad / \times n!(n+1)!$$

$$I_{n+1,n} = 2^n\sqrt{\pi}\,(n+1)!$$

$I_{n,n+1}$ (at $s^{n}t^{n+1}$):

$$\frac{I_{n,n+1}}{n!\,(n+1)!} = \sqrt{\pi}\,\frac{2^n}{n!} \quad / \, n!(n+1)!$$

$$I_{n,n+1} = 2^n\sqrt{\pi}\,(n+1)!$$

$$I_{n,m} = \begin{cases} 2^n\sqrt{\pi}\,(n+1)!\,, & m = n+1 \\ 0\,, & m \neq n \pm 1 \\ 2^{n-1}\sqrt{\pi}\,n!\,, & m = n-1 \end{cases}$$

$$\langle u_n | \hat{x} | u_m \rangle = \frac{N_n N_m}{\alpha^2} I_{n,m}$$

$$\langle u_n | \hat{x} | u_{n+1} \rangle = \frac{N_n N_{n+1}}{\alpha^2} I_{n,n+1}$$

$$= \frac{1}{\alpha^2} \left(\frac{\alpha}{2^n n! \sqrt{\pi}} \right)^{\frac{1}{2}} \left(\frac{\alpha}{2^{n+1} (n+1)! \sqrt{\pi}} \right)^{\frac{1}{2}}$$

$$\times\, 2^n \sqrt{\pi}\,(n+1)!$$

$$= \frac{1}{\cancel{\alpha^2}} \frac{\cancel{\alpha}\, \cancel{2^n} \cancel{\sqrt{\pi}}\,(n+1)!}{\cancel{2^n} \cancel{\sqrt{\pi}}\,[2n!(n+1)!]^{\frac{1}{2}}}$$

$$= \frac{1}{\alpha}\sqrt{\frac{(n+1)!}{2n!}}$$

$$\langle u_n|\hat{x}|u_{n+1}\rangle = \frac{1}{\alpha}\sqrt{\frac{n+1}{2}} \checkmark$$

Similarly,

$$\langle u_n|\hat{x}|u_{n-1}\rangle = \frac{1}{\alpha}\sqrt{\frac{n}{2}}$$

Ver.: $\langle u_n|\hat{x}|u_{n-1}\rangle = \langle u_{n-1}|\hat{x}|u_n\rangle^*$

$$= \langle u_{n-1}|\hat{x}|u_n\rangle = \frac{1}{\alpha}\sqrt{\frac{n}{2}}$$

$$\langle u_n|\hat{x}|u_m\rangle = \begin{cases} \frac{1}{\alpha}\sqrt{\frac{n+1}{2}}, & m=n+1 \\ 0, & m\neq n\pm 1 \\ \frac{1}{\alpha}\sqrt{\frac{n}{2}}, & m=n-1 \end{cases}$$

$$n \longrightarrow n\pm 1$$

$$(\langle u_n|\hat{x}|u_n\rangle = 0)$$

Comparison with classical mechanics.

Energy levels are quantized, $E_n = \hbar\omega(n+\frac{1}{2})$, $n=0,1,\ldots$. $E_0 > 0$.

$|u_n(x)|^2 \rightarrow$ probability density.

In classical mechanics,

$$P(x) \sim \frac{1}{v}$$

$$x(t) = x_0 \sin(\omega t + \gamma)$$

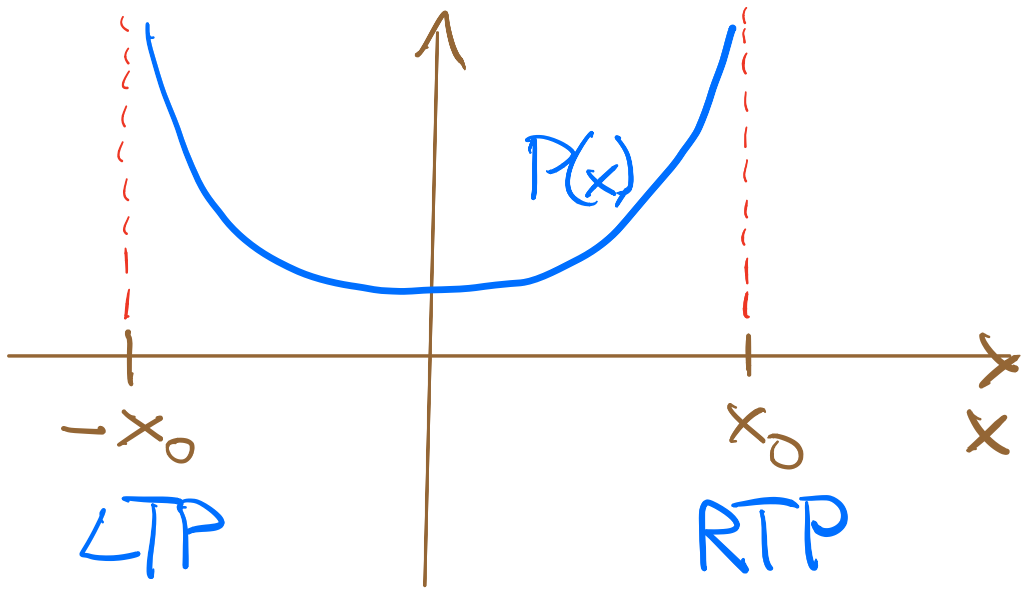
$$v = \dot{x} = x_0 \omega \cos(\omega t + \gamma)$$

$$= x_0 \omega \left[1 - \sin^2(\omega t + \gamma)\right]^{\frac{1}{2}}$$

$$v = \omega \left[x_0^2 - \underbrace{x_0^2 \sin^2(\omega t + \gamma)}_{x(t)^2}\right]^{\frac{1}{2}}$$

$$v \sim (x_0^2 - x^2)^{\frac{1}{2}}$$

$$P(x) \sim (x_0^2 - x^2)^{-\frac{1}{2}}$$



PICTURES OF QUANTUM MECHANICS

Schrödinger's picture

Wave functions (quantum states) depend on time

$$|\varphi_s(t)\rangle ,$$

$$\varphi_s(q_1, \dots, q_f, t)$$

$$\equiv \varphi_s(q, t)$$

$$\equiv \langle q | \varphi_s(t) \rangle$$

$$i\hbar \frac{\partial \varphi_S}{\partial t} = \hat{H}\varphi_S$$

$$\boxed{i\hbar \frac{d}{dt}|\varphi_S(t)\rangle = \hat{H}|\varphi_S(t)\rangle}$$

Observables:

$$\hat{F}_S = F(\hat{q}_S, \hat{p}_S, t) \checkmark$$

$$\langle \varphi_S(t)|\hat{F}_S|\psi_S(t)\rangle \quad \sim dq_1 \ldots dq_f$$

$$= \int_\Gamma \varphi_S^*(q,t)\hat{F}_S\,\psi_S(q,t)\,d\tau$$

Time dependence:

$$\frac{d}{dt}\langle \varphi_S(t)|\hat{F}_S|\psi_S(t)\rangle$$

$$= \left[\frac{d}{dt}\langle \varphi_S(t)|\right]\hat{F}_S|\psi_S(t)\rangle$$

$$+ \langle \varphi_S(t)|\frac{\partial \hat{F}_S}{\partial t}|\psi_S(t)\rangle$$

$$+ \langle \varphi_S(t)|\hat{F}_S\left[\frac{d}{dt}|\psi_S(t)\rangle\right]$$

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

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

$$\frac{d}{dt}\langle \varphi_S(t)| = \left(\frac{1}{i\hbar}\hat{H}|\varphi_S(t)\rangle\right)^{+}$$

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

$$\frac{d}{dt}\langle \varphi_S(t)|\hat{F}_S|\chi_S(t)\rangle$$

$$= -\frac{1}{i\hbar}\langle \varphi_S(t)|\hat{H}\hat{F}_S|\chi_S(t)\rangle$$

$$+ \langle \varphi_S(t)|\frac{\partial \hat{F}_S}{\partial t}|\chi_S(t)\rangle$$

$$+ \frac{1}{i\hbar}\langle \varphi_S(t)|\hat{F}_S\hat{H}|\chi_S(t)\rangle$$

$$\boxed{\begin{aligned}\frac{d}{dt}\langle\varphi_s(t)|\hat{F}_s|\psi_s(t)\rangle &= \langle\varphi_s(t)|\frac{\partial\hat{F}_s}{\partial t}|\psi_s(t)\rangle \\ &+ \frac{1}{i\hbar}\langle\varphi_s(t)|[\hat{F}_s,\hat{H}]|\psi_s(t)\rangle\end{aligned}}$$

Consequences:

the generalization of the Ehrenfest theorems

— $\varphi_s = \psi_s$

$$\frac{d}{dt}\langle\varphi_s(t)|\hat{F}_s|\varphi_s(t)\rangle$$

$$\equiv \frac{d}{dt}\langle\hat{F}_s\rangle_{\varphi_s}$$

$$= \left\langle\frac{\partial\hat{F}_s}{\partial t}\right\rangle_{\varphi_s} + \frac{1}{i\hbar}\langle[\hat{F}_s,\hat{H}]\rangle_{\varphi_s}$$

A QM-al analog of

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\}$$

$$F \longrightarrow \langle \hat{F}_S \rangle$$

$$\{\ ,\ \} \longrightarrow \frac{1}{i\hbar}[\ ,\ ]$$

— If $\dfrac{\partial \hat{F}_S}{\partial t} = 0$ and

$$[\hat{F}_S, \hat{H}] = 0,$$

$$\frac{d}{dt}\langle \varphi_S(t) | \hat{F}_S | \chi_S(t) \rangle = 0,$$

$$\langle \varphi_S(t) | \hat{F}_S | \chi_S(t) \rangle = \text{const.}$$

F is a constant of motion.

(in CM, if $\frac{\partial F}{\partial t}=0$ and $\{F,H\}=0$, then $F=\text{const.}$).

Heisenberg's picture

We will assume that $\frac{\partial \hat{H}}{\partial t}=0$.

In this case, the solutions of the Schrödinger equation have the following form: $t=0$

$$|\varphi_S(t)\rangle = e^{-i\hat{H}t/\hbar}|\varphi_S(0)\rangle$$

$\hat{A}$, $f(\hat{A})$ ← functions of operators

$$f(x) = \sum_n a_n x^n$$

$$x \to \hat{A}$$

$$f(\hat{A}) = \sum_n a_n \hat{A}^n$$

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n \quad \checkmark$$

$$= \mathbb{1} + \hat{A} + \frac{1}{2!}\hat{A}^2 + \dots$$

Properties of $e^{\hat{A}}$:

$$e^{\hat{A}} e^{-\hat{A}} = \mathbb{1} = e^{-\hat{A}} e^{\hat{A}}$$

$$(e^{x} e^{-x} = e^{-x} e^{x} = 1)$$

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} \text{ if } [\hat{A},\hat{B}]=0$$

$$\left(e^{x+y}=e^x e^y\right)$$

$$\left(e^{\hat{A}}\right)^\dagger = e^{\hat{A}^\dagger}$$

Suppose $\hat{A}$ is anti-Hermitian,

$$\hat{A}^\dagger = -\hat{A}.$$

In this case,

$U^\dagger = U^{-1}$

$$e^{\hat{A}} \text{ is unitary.}$$

Proof:

$$\left(e^{\hat{A}}\right)^\dagger = e^{\hat{A}^\dagger} = e^{-\hat{A}} = \left(e^{\hat{A}}\right)^{-1}$$

Consider

$$\hat{A} = -i\hat{H}t/\hbar$$

This $\hat{A}$ is anti-Hermitian,

$$\hat{A}^{\dagger} = i\hat{H}t/\hbar = -\hat{A}.$$

$U(t) = e^{-i\hat{H}t/\hbar}$ is unitary.

$$|\psi_s(t)\rangle = U(t)\,|\psi_s(0)\rangle,$$

where $U(t) = e^{-i\hat{H}t/\hbar}$ is a unitary propagator (time evolution operator).

Unitary operators preserve a norm:

$$\|\psi_s(t)\|^2 = \langle \psi_s(t)|\psi_s(t)\rangle$$

$$= \langle \psi_s(0)|\underbrace{U(t)^\dagger U(t)}_{\Uparrow}|\psi_s(0)\rangle$$

$$= \langle \psi_s(0)|\psi_s(0)\rangle = \|\psi_s(0)\|^2$$

$$\|\psi_s(t)\| = \|\psi_s(0)\| \,!$$

We must now prove that

$$|\psi_s(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi_s(0)\rangle$$

satisfies the Schrödinger eqn.