Chapter 1 - The Wave Function

This class is about learning how to deal with non relativistic quantum mechanics. We will start with one dimension but get to 3D and more than one particle.

Classical mechanics: $\frac{dP(t)}{dt} = F(x(t),t)$ Newton's Eq

$\frac{dx(t)}{dt} = \frac{P(t)}{m} = v(t)$ Calculus

$P(t)$ = the momentum of the particle at time t

$x(t)$ = the position of the particle at time t

m = the mass of the particle

$F(x(t),t)$ = the force on the particle when it is at x at time t

$v(t)$ = the velocity of the particle = $P(t)/m$

For conservative forces, there is a relation between the force and the potential energy.

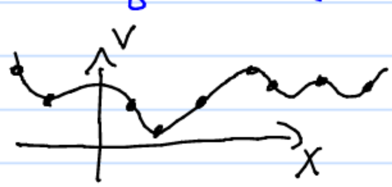
$V(x(t),t)$ = particle's potential energy when it is at x at time t

$$F(x(t),t) = -\frac{\partial V(x,t)}{\partial x}$$

Note the partial derivative. Don't forget - sign

Examples: $V(x(t),t) = \frac{1}{2} m\omega^2 x^2(t)$ $\quad F(x(t),t) = -m\omega^2 x(t)$

$V(x(t),t) = -E\,q\,x(t)\cos(\Omega t)$ $\quad F(x(t),t) = E\,q\cos(\Omega t)$

Qualitative question  Direction of F at different x

The Schrodinger Eq. is only good for non relatistic systems.

The motion of nuclei inside molecules $\frac{10^{-10} m}{10^{-15} s} \sim 10^5 m/s \ll c$
or longer

1 keV electron $E = 10^3 V \; 1.6 \times 10^{-19} C = 1.6 \times 10^{-16} J$

$V = (2 \times 1.6 \times 10^{-16} J / 9.11 \times 10^{-31} kg)^{1/2} = 1.9 \times 10^7 m/s \sim c/16$

Typical relativistic correction $(v/c)^2$ is less than 1% for examples

Schrodinger's Eq $\quad i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t)$

Very important: x does not depend on t !!!

$\hbar$ = h-bar = $\frac{\text{Planck's const}}{2\pi} = \frac{6.626 \times 10^{-34} Js}{2\pi}$
$= 1.054572 \times 10^{-34} Js$

I will expect you to know Sch. Eq., h, $\hbar$, mass of electron and proton, charge of electron and proton, ...

Sch. Eq. has $\Psi(x,t)$ = complex

Reminder $\quad z = a + ib \quad\quad Y = c + id \quad\quad a,b,c,d$ real

$Yz = (c+id)(a+ib) = ac - bd + i(bc + ad)$

$z^* z = (a-ib)(a+ib) = a^2 + b^2 + i(ab - ab) = a^2 + b^2$

$z = Re^{i\theta} \quad\quad z^* = Re^{-i\theta} \quad\quad R = |z| = \sqrt{z^* z} = \sqrt{a^2+b^2}$

$\tan\theta = b/a$

"Statistical interpretation" Probability for finding particle between $x=a$ and $x=b$ at time t

$$P_{ab}(t) \equiv \int_a^b |\Psi(x,t)|^2 \, dx$$

The $|\Psi(x,t)|^2$ must have units of probability/length

Probability Density $\rho(x,t) \equiv |\Psi(x,t)|^2$

This interpretation is supported by continuity equation.

For any density and related current $\frac{\partial \rho(x,t)}{\partial t} + \frac{\partial J_x(x,t)}{\partial x} = 0$

This is a conservation equation. To show, integrate from $x=a$ to b

$$\underbrace{\frac{d P_{ab}(t)}{dt}}_{\text{rate of prob change}} + \underbrace{J_x(b,t)}_{\text{current out at } b} - \underbrace{J_x(a,t)}_{\text{current in at } a} = 0$$

Figure out definition of $J_x(x,t)$

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t} \Psi^* \Psi = \frac{\partial \Psi^*}{\partial t} \Psi + \Psi^* \frac{\partial \Psi}{\partial t}$$

$$= \left(-\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*\right) \Psi + \Psi^* \left(\frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi\right)$$

$$= \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi\right]$$

$$= \frac{\partial}{\partial x} \left(-\frac{\hbar}{2im} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi\right]\right)$$

Define $J_x(x,t) = \frac{\hbar}{i2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi\right)$

How to show $J_x(x,t)$ is real? $J_x^* = J_x$?

The probability for finding the particle anywhere should always be 1.

$$\int_{-\infty}^{\infty} \rho(x,t)\, dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

To show a constant $\frac{d}{dt}\int_{-\infty}^{\infty} \rho(x,t)\, dx = \int_{-\infty}^{\infty} \frac{\partial \rho(x,t)}{\partial t} dx$

$$= -\int_{-\infty}^{\infty} \frac{\partial J_x(x,t)}{\partial x} dx = -J_x(\infty,t) + J_x(-\infty,t) = 0$$

The Sch. Eq. is linear in $\Psi(x,t)$. This means if Ψ is a solution $C\Psi$ is also solution. If your original choice isn't normalized properly, then multiply by C.

Math detour into probability (frequentist version!)

Suppose a quantity Q takes distinct values $Q(j)$ (age in years, number of rocks in head, number of toes, ...)

$N(j)$ = number of objects where $Q = Q(j)$

$N = \sum_{j=min}^{max} N(j)$ = total number of objects

$P(j) = \frac{N(j)}{N}$ = probability an object has $Q = Q(j)$

The average of some function of Q is

$$\langle f(Q) \rangle = \sum_{j=min}^{max} f(Q(j))\, P(j)$$

Some of the more important averages are the average (or mean), the variance, and the standard deviation.

Average $\langle Q \rangle = \sum_j Q(j) P(j)$

Variance $\langle (Q - \langle Q \rangle)^2 \rangle = \sum_j [Q(j) - \langle Q \rangle]^2 P(j) \equiv \sigma_Q^2$

Neat relationship $\sigma_Q^2 = \langle [Q - \langle Q \rangle]^2 = \langle Q^2 - 2Q\langle Q \rangle + \langle Q \rangle^2 \rangle$

$$= \langle Q^2 \rangle - 2\langle Q \rangle^2 + \langle Q \rangle^2$$
$$= \langle Q^2 \rangle - \langle Q \rangle^2$$

Standard deviation $\sigma_Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}$

Since $\sigma_Q^2 \geq 0$ $\quad \langle Q^2 \rangle \geq \langle Q \rangle^2$ <u>always</u>

How to deal with a continuous variable? Discretize like Newton's calculus, then go to continuous limit.

Probability to be between Q and $Q + dQ$ $= \rho(Q)\,dQ$

Normalization $\int_{-\infty}^{\infty} \rho(Q)\,dQ = 1$

Average $\langle Q \rangle = \int_{-\infty}^{\infty} Q\,\rho(Q)\,dQ$

Variance $\sigma_Q^2 = \langle [Q - \langle Q \rangle]^2 \rangle = \int_{-\infty}^{\infty} (Q - \langle Q \rangle)^2 \rho(Q)\,dQ$

$$= \langle Q^2 \rangle - \langle Q \rangle^2 = \int_{-\infty}^{\infty} Q^2 \rho(Q)\,dQ - \langle Q \rangle^2$$

By convention in quantum mechanics, $\langle Q \rangle$ is called the <u>expectation value</u>.

Expectation value of x: $\langle x\rangle(t) = \int_{-\infty}^{\infty} x\, \Psi^*(x,t)\, \Psi(x,t)\, dx$

How to find the expectation value of the velocity?

Define $\langle v\rangle(t) \equiv \frac{d\langle x\rangle(t)}{dt} = \int_{-\infty}^{\infty} x \left[\frac{\partial}{\partial t} \rho(x,t)\right] dx$

$$= -\int_{-\infty}^{\infty} x\, \frac{\partial J_x(x,t)}{\partial x}\, dx \underset{\substack{\text{integrate}\\ \text{by parts}}}{=} \int_{-\infty}^{\infty} J_x(x,t)\, dx$$

This should make perfect sense because J_x is the current density.

Simplify a bit more

$$\langle v\rangle(t) = \frac{\hbar}{2im} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi\, dx \underset{\substack{\text{integrate}\\ \text{by parts}}}{=} \frac{\hbar}{im} \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\partial \Psi(x,t)}{\partial x}\, dx$$

In quantum mechanics easier to work with momentum

$$\langle p\rangle(t) = m\,\langle v\rangle(t) = \int_{-\infty}^{\infty} \Psi^*(x,t) \left[\frac{\hbar}{i}\frac{\partial}{\partial x} \Psi(x,t)\right] dx$$

For a general quantity that depends on x and p

$$\langle Q(x,p)\rangle(t) = \int_{-\infty}^{\infty} \Psi^*(x,t) \left[Q\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi(x,t)\right] dx$$

Example $\langle T\rangle(t) = \left\langle \frac{p^2}{2m}\right\rangle(t) = \int_{-\infty} \Psi^*(x,t)\, \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2}\, dx$

Very deep principle, x and p are operators

One possible representation x and $\frac{\hbar}{i}\frac{\partial}{\partial x}$

Is $\langle xp \rangle(t) = \langle px \rangle(t)$? No!

$$\langle px \rangle(t) = \int_{-\infty}^{\infty} \Psi^*(x,t) \left[\frac{\hbar}{i} \frac{\partial}{\partial x} \left(x \Psi(x,t) \right) \right] dx$$

$$= \int_{-\infty}^{\infty} \Psi^*(x,t) \left[\frac{\hbar}{i} \Psi(x,t) + x \frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x} \right] dx$$

$$= \frac{\hbar}{i} + \langle xp \rangle(t)$$

Final topic is uncertainty principle. Because $\Psi(x,t)$ is a wave, you can't simultaneously define the position and wavelength.

de Broglie formula $p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} = \hbar k$

Uncertainty in the wavelength means momentum is not certain.

Uncertainty principle $\sigma_x \sigma_p \geq \hbar/2$

Some examples worked out.

(1) Suppose $\Psi(x,t) = \psi(x) e^{i\varphi(t)}$ where $\psi(x)$ is a real function. Compute $\langle p \rangle(t)$

$$\langle p \rangle(t) = \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial x} dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi(x) e^{-i\varphi(t)} \frac{d\psi(x)}{dx} e^{i\varphi(t)} dx$$

$$= \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi(x) \frac{d\psi(x)}{dx} dx = \frac{\hbar}{2i} \int_{-\infty}^{\infty} \frac{d}{dx} \left(\psi^2(x) \right) dx$$

$$= \frac{\hbar}{2i} \psi^2(x) \Big|_{-\infty}^{\infty} = 0$$

(2) Is $\langle p^2\rangle(t) \geq 0$?

$$\langle p^2\rangle(t) = -\hbar^2 \int_{-\infty}^{\infty} \Psi^*(x,t)\, \frac{\partial^2 \Psi(x,t)}{\partial x^2}\, dx$$

$$= \hbar^2 \int_{-\infty}^{\infty} \frac{\partial \Psi^*(x,t)}{\partial x} \frac{\partial \Psi(x,t)}{\partial x}\, dx \qquad \text{integrate by parts}$$

$$= \int_{-\infty}^{\infty} \left| \hbar \frac{\partial \Psi(x,t)}{\partial x} \right|^2 dx \geq 0 \checkmark$$

(3) At $t=0$ $\Psi(x,0) = A e^{-\alpha(x-x_0)^2 + i\beta x}$. Compute A, $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, $\langle p^2\rangle$ at $t=0$ (α and β are real).

Very useful integrals $\int_{-\infty}^{\infty} e^{-ax^2+bx+c}\, dx = \sqrt{\frac{\pi}{a}}\, e^c e^{b^2/4a}$

$\int_{-\infty}^{\infty} x e^{-ax^2} dx = 0$ $\qquad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a^3}} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$

Get A from the normalization relation

$$\int_{-\infty}^{\infty} |\Psi(x,0)|^2 dx = A^2 \int_{-\infty}^{\infty} e^{-\alpha(x-x_0)^2 - i\beta x}\, e^{-\alpha(x-x_0)^2 + i\beta x}\, dx$$

$$= A^2 \int_{-\infty}^{\infty} e^{-2\alpha(x-x_0)^2} dx = A^2 \sqrt{\frac{\pi}{2\alpha}} = 1 \implies A = \left(\frac{2\alpha}{\pi}\right)^{1/4}$$

Now do $\langle x\rangle$

$$\langle x\rangle = A^2 \int_{-\infty}^{\infty} x\, e^{-2\alpha(x-x_0)^2} dx = A^2 \int_{-\infty}^{\infty} (x - x_0 + x_0)\, e^{-2\alpha(x-x_0)^2} dx$$

$$= x_0$$

Now do $\langle x^2\rangle$

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

$$= A^2 \int_{-\infty}^{\infty} (x-x_0)^2 e^{-2\alpha(x-x_0)^2} dx + x_0^2 = \frac{1}{4\alpha} + x_0^2$$

The α can be related to the standard deviation

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{4\alpha} + x_0^2 - x_0^2 \quad \Rightarrow \quad \alpha = \frac{1}{4\sigma_x^2}$$

Now do $\langle p \rangle$

$$\langle p \rangle = \frac{\hbar}{i} A^2 \int_{-\infty}^{\infty} e^{-\alpha(x-x_0)^2 - i\beta x} \frac{\partial}{\partial x}\left(e^{-\alpha(x-x_0)^2 + i\beta x}\right) dx$$

$$= \frac{\hbar}{i} A^2 \int_{-\infty}^{\infty} e^{-\alpha(x-x_0)^2 - i\beta x} \left(-2\alpha(x-x_0) + i\beta\right) e^{-\alpha(x-x_0)^2 + i\beta x} dx$$

$$= \frac{\hbar}{i} \langle -2\alpha(x-x_0) + i\beta \rangle = \hbar\beta \qquad \Rightarrow \beta = \frac{\langle p \rangle}{\hbar}$$

Now do the $\langle p^2 \rangle$

$$\langle p^2 \rangle = \hbar^2 \int \left| \frac{\partial \Psi}{\partial x} \right|^2 dx = \hbar^2 \langle [-2\alpha(x-x_0) - i\beta][(-2\alpha(x-x_0) + i\beta] \rangle$$

$$= \hbar^2 \langle 4\alpha^2 (x-x_0)^2 + \beta^2 \rangle = \hbar^2 \left(\frac{4\alpha^2}{4\alpha}\right) + \hbar^2\beta^2$$

Now do the $\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$

$$\sigma_p^2 = \hbar^2\alpha + \hbar^2\beta^2 - (\hbar\beta)^2 = \hbar^2\alpha$$

Check the Heisenberg uncertainty relation

$$\sigma_x \sigma_p = \frac{1}{2\sqrt{\alpha}} \hbar\sqrt{\alpha} = \hbar/2 \geq \hbar/2 \checkmark$$

Epilogue: Griffiths has a very mid 20^{th} century attitude to Q.M. (analogous to late 19^{th} century attitude to E&M) The Sch. Eq. has been verified to incredible precission. There is no wave function collapse. All 3 choices in Sec 1.2 are wrong.