Goal

1. Wave functions of electrons and their probabilistic interpretation
2. Schrödinger equation.
3. Framework of quantum mechanics.

Scenario

✓ Bohr theory of atom : account for many aspects of atomic phenomena.
However, has sever limitations
i.e., can explain only hydrogen, one-electron ions (He^+, Li^+)
✓ Why certain spectral lines are more intense than others?
= Why certain transitions b/w energy levels have greater probabilities of occurrence than others?
✓ Why many spectral lines consist of several separate lines whose wave lengths differ slightly?

✓ Bohr theory : one of the seminal achievements
However, a more general approach to atomic phenomena is required.

✓ Birth of quantum mechanics : 1925 ~ 1926.
Erwin Schrödinger, Werner Heisenberg, Max Born, Paul Dirac ...

✓ Quantum mechanics makes it possible to understand a vast body of data ("a large part of physics and the whole of chemistry", Dirac).

✓ Classical mechanics is an approximation of quantum mechanics.
What are described.
Classical : future trajectory of a particle is completely determined by its initial position and momentum.
Quantum : the initial state of a particle cannot be established with sufficient accuracy due to the uncertainty principle.
Probabilities vs. Asserting (Determinism)

e.g.
The radius of the electron's orbit in a ground state of H.
5.3×10^{-11} m : most probable radius
cf. In classical mechanics, the exact value.

- Wave function

ψ : Already introduced quantity for wave nature of a moving body
⇒ Solution of Schrödinger eq.
$\psi(x, y, z, t)$. ↔ Amplitude. (Classical phicture)
ψ itself has no physical interpretation
$\psi^*\psi \, dx dy dz = |\psi|^2 dv$: Probability of finding a particle in dv.
(Quantum picture)
cf. Photoelectric effect
Light intensity : $|\psi|^2$ ⇒ # of photo-electrons

Normalization : $\int |\psi|^2 dv = 1$.

1. ψ : continuous and single-valued.
2. $\partial\psi/\partial x, \partial\psi/\partial y, \partial\psi/\partial z$: continuous and single-valued. } momentum P : continuous and single-valued.
3. ($\int |\psi|^2 dv = 1$ (finite) $\psi \to 0$ $(x, y, z, \to \pm\infty)$)

Related to momentum P.

- Schrödinger's wave equation

Classical wave equation + de Broglie wave

$$\frac{\partial^2 W}{\partial x^2} + \frac{\partial^2 W}{\partial y^2} + \frac{\partial^2 W}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2 W}{\partial t^2} \quad — ①$$

$$W(x,y,z,t) = w(x,y,z)e^{-i\omega t} = w(x,y,z)e^{-2\pi i\nu t} \cdots ☆$$

$v = \nu\lambda$

$$\Rightarrow \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} = -\left(\frac{2\pi}{\lambda}\right)^2 w = -\left(\frac{\omega}{v}\right)^2 w \quad \frac{\partial W}{\partial t} = -i\omega W \quad — ②$$

Consider a particle with the mass m is moving at the speed v.

From de Broglie's relation,

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2m(E-V)}}$$

V: Potential energy

$E-V$: Kinetic energy.

Replacing $w(x,y,z) \rightarrow \psi(x,y,z)$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = \underset{\hbar\omega}{E}\psi \quad \hbar = \frac{h}{2\pi} \quad — ③$$

For a single freq.

(Time-independent) Stationary state

$$☆ \rightarrow \Psi(x,y,z,t) = \psi(x,y,z)e^{-2\pi i\nu t} = \psi(x,y,z)e^{-i\omega t}$$

To derive an equation that represents de Broglie waves that vary with time.

$\omega \rightarrow -\omega$, ① : No change ③ : The sign changes

$\Rightarrow$ We cannot go back to ①

$$\frac{\partial\Psi}{\partial t} = -i\omega\Psi \quad \Rightarrow \quad \hbar\frac{\partial\Psi}{\partial t} = -i\hbar\omega\Psi$$

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

(Time-dependent)

By another way,

$$\Psi = Ae^{i(kr-\omega t)} = Ae^{2\pi i(\frac{r}{\lambda}-\nu t)}$$

A particle moving freely in the $+r$ direction.

$$E = h\nu = \hbar\omega = 2\pi\hbar\nu \quad , \quad \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

$$\Rightarrow \quad \Psi = Ae^{\frac{i}{\hbar}(pr-Et)}$$

An unristructed particle of total energy E and momentum p moving in the $+r$ direction.

To obtain the fundamental differential equation for Ψ.

$$\frac{\partial\Psi}{\partial r} = \frac{ip}{\hbar}\Psi \quad \Rightarrow \quad \frac{\partial^2\Psi}{\partial r^2} = -\frac{p^2}{\hbar^2}\Psi$$

$$\Rightarrow \quad p^2\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial r^2}$$

$$\frac{\partial\Psi}{\partial t} = -\frac{iE}{\hbar}\Psi \quad \Rightarrow \quad E\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$$

$$E = \frac{p^2}{2m} + V$$

$$\Rightarrow \quad E\Psi = \frac{1}{2m}p^2\Psi + V\Psi$$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial r^2} + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

- Linearity and sperposition.

If Ψ_1 and Ψ_2 are two solutions for Schrödinger's eq.

$$\Psi = a\Psi_1 + b\Psi_2 \quad \text{is also a solution.}$$

$$P_1 = |\Psi_1|^2 \quad , \quad P_2 = |\Psi_2|^2$$

$$P = (\Psi_1+\Psi_2)^*(\Psi_1+\Psi_2) = |(\Psi_1+\Psi_2)|^2$$

$$= P_1 + P_2 + \underbrace{\Psi_1^*\Psi_2}_{} + \underbrace{\Psi_1\Psi_2^*}_{} \quad \text{Interference.}$$

✓ Explain the double slit experiment!

- Expectation values

How to extract information from a wave function?

Schrödinger eq. $\Rightarrow$ Ψ all information of a particle
in the form of probabilities (not specific numbers)

$$\langle x \rangle = \bar{x} = \frac{N_1 x_1 + N_2 x_2 + \cdots + N_n x_n}{N_1 + N_2 + \cdots + N_n} = \frac{\Sigma N_i x_i}{\Sigma N_i}$$

$$= \frac{N_1}{\Sigma N_i} x_1 + \frac{N_2}{\Sigma N_i} x_2 + \cdots + \frac{N_n}{\Sigma N_i} x_n$$

$$= P_1 x_1 + P_2 x_2 + \cdots + P_n x_n$$

When we deal with a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i

$$P_i = |\Psi_i|^2 dx$$

$$\Rightarrow \quad \langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}$$

if Ψ is a normalized function.

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi|^2 dx$$

For other physical quantity

$$\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\Psi|^2 dx$$

$\langle p \rangle$, $\langle E \rangle$ cannot be calculated this way

$$\Delta x \Delta p \geq \hbar/2, \quad \Delta E \Delta t \geq \hbar/2$$

$\Rightarrow$ Another way to find expectation values.

$\Rightarrow$ Operators

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

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi^* \hat{E} \psi \, dx = \int_{-\infty}^{\infty} \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, dx = i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial t} dx$$

- Operators

One of the mathematical formulation of quantum mechanics.

Operator : functions over a space of physical state to another.

ex.)

$$\frac{d}{dx}(ax^2+bx+c) = 2ax+b$$

Difine an operator : $\hat{A}$

Properties of operators

(i) $\hat{A}(c_1 f_1 + c_2 f_2) = c_1 \hat{A} f_1 + c_2 \hat{A} f_2$

(ii) $(\hat{A}+\hat{B})f = \hat{A}f + \hat{B}f$. Distribution law cf. Association law

$(\hat{A}\hat{B})f = \hat{A}(\hat{B}f)$

$\hat{A}\hat{B} \neq \hat{B}\hat{A}$ (Generally)

ex.)

$$\hat{x}\left(\frac{d}{dx}\right)(ax^2+bx+c) \neq \left(\frac{d}{dx}\right)\hat{x}(ax^2+bx+c). \qquad \hat{x} \equiv x \times$$

times.

When $\hat{A}\hat{B} = \hat{B}\hat{A}$ (commutable).

$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$.

(iii). $\int f_1^* \hat{A} f_2 \, dv = \int f_2 \hat{A}^\dagger f_1^* \Rightarrow \hat{A}$: Hermitean operator

$$f_1^* \hat{A} f_2 \longrightarrow f_2^* \hat{A} f_1 \longrightarrow (f_2^* \hat{A} f_1)^* \longrightarrow f_2 \hat{A}^\dagger f_1^*$$

Free particle wave function : $\Psi = A e^{-\frac{i}{\hbar}(Et - Px)}$

$$\frac{\partial \Psi}{\partial x} = \frac{i}{\hbar} P \Psi \longrightarrow P\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi = -i\hbar\frac{\partial}{\partial x}\Psi.$$

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E \Psi \longrightarrow E\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

$$\int \psi_1^* \hat{P}_x \psi_2 \, dv = -i\hbar \int \psi_1^* \frac{\partial}{\partial x}\psi_2 \, dx\,dy\,dz$$

$\psi \to 0 \quad (x \to \pm\infty)$

$$= -i\hbar \left\{ \int \psi_1^* \psi_2 \, dy\,dz \Big|_{x=-\infty}^{x=\infty} - \int \psi_2 \frac{\partial}{\partial x}\psi_1^* \, dx\,dy\,dz \right\}$$

$$= \int \psi_2 \left(i\hbar\frac{\partial}{\partial x}\right)\psi_1^* \, dx\,dy\,dz = \int \psi_2 \hat{P}_x^\dagger \psi_1 \, dv$$

$\hat{P}_x$: Hermitean

$\hat{x} \equiv x \times$: Hermitean.

- Reconsidering the uncertainty principle (Fluctuations of two physical quantities)

$\langle(\Delta x)^2\rangle = \langle(x-\langle x\rangle)^2\rangle = \langle x^2\rangle - \langle x\rangle^2 \qquad \Delta x \equiv x - \langle x\rangle$

$= \langle x^2 - 2x\langle x\rangle + \langle x\rangle^2\rangle$ Variance

$\Delta A \equiv \hat{A} - \langle\hat{A}\rangle \,, \quad \Delta B \equiv \hat{B} - \langle\hat{B}\rangle$ } Hermitian

Purpose : $[\hat{A},\hat{B}] \neq 0$ How and what is $\{\langle(\Delta A)^2\rangle, \langle(\Delta B)^2\rangle\}$?

$[\hat{A},\hat{B}] = i\hat{C}$

Introduce $\hat{D} \equiv t\Delta\hat{A} - i\Delta\hat{B}$ (t: arbitrary const.)

$\langle\hat{D}^\dagger\hat{D}\rangle = \langle(t\Delta\hat{A} + i\Delta\hat{B})(t\Delta\hat{A} - i\Delta\hat{B})\rangle$

$= t^2\langle(\Delta\hat{A})^2\rangle + t\langle\hat{C}\rangle + \langle(\Delta B)^2\rangle$

$\langle(t\Delta\hat{A} + i\Delta\hat{B})(t\Delta\hat{A} - i\Delta\hat{B})\rangle$

$= t^2\langle(\Delta A)^2\rangle + it\langle(\hat{B}-\langle\hat{B}\rangle)(\hat{A}-\langle\hat{A}\rangle)\rangle - it\langle(\hat{A}-\langle\hat{A}\rangle)(\hat{B}-\langle\hat{B}\rangle)\rangle + \langle(\Delta B)^2\rangle$

$= t^2\langle(\Delta A)^2\rangle + it(\langle\hat{B}\hat{A}\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle + \langle\hat{B}\rangle\langle\hat{A}\rangle)$

$- it(\langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle) + \langle(\Delta B)^2\rangle$

$= t^2\langle(\Delta A)^2\rangle + it(\langle\hat{B}\hat{A}\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle) - it(\langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle) + \langle(\Delta B)^2\rangle$

$= t^2\langle(\Delta A)^2\rangle + it(\langle\hat{B}\hat{A}\rangle - \langle\hat{A}\hat{B}\rangle) + \langle(\Delta B)^2\rangle$

Generally, $\langle\hat{D}^\dagger\hat{D}\rangle = \langle\psi|\hat{D}^\dagger\hat{D}|\psi\rangle = \|\hat{D}|\psi\rangle\|^2 \geq 0$

$$\Rightarrow \langle(\Delta\hat{A})^2\rangle\left\{\left(t + \frac{\langle\hat{C}\rangle}{2\langle(\Delta\hat{A})^2\rangle}\right)^2 - \frac{\langle\hat{C}\rangle^2 - 4\langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle}{4\langle(\Delta\hat{A})^2\rangle}\right\} \geq 0$$

$$\Rightarrow \left(t + \frac{\langle\hat{C}\rangle}{2\langle(\Delta\hat{A})^2\rangle}\right)^2 \geq \frac{\langle\hat{C}\rangle^2 - 4\langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle}{4\langle(\Delta\hat{A})^2\rangle}$$

This inequality holds for any t.

$$\Rightarrow \frac{\langle\hat{C}\rangle^2 - 4\langle(\Delta\hat{A})^2\rangle\langle(\Delta B)^2\rangle}{4\langle(\Delta\hat{A})^2\rangle} \leq 0$$

$$\Rightarrow \langle\hat{C}\rangle^2 - 4\langle(\Delta\hat{A})\rangle\langle(\Delta\hat{B})\rangle \leq 0 \quad \Rightarrow \langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle \geq \frac{\langle\hat{C}\rangle^2}{4}$$

Meaning

if $\hat{C} \neq 0$ i.e., $[\hat{A},\hat{B}] \neq 0 \Rightarrow \Delta\hat{A}, \Delta\hat{B} \neq 0$

Uncertainty (Fluctuations) of the physical quantity $\hat{A}$, $\hat{B}$
under the commutation relation $[\hat{A}, \hat{B}] = i\hat{C}$

$$\langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle \geq \frac{\langle\hat{C}\rangle^2}{4}. \quad \text{or,} \quad \Delta A\,\Delta B \geq \frac{\langle\hat{C}\rangle}{2}.$$

$[x, p_x] = i\hbar$

$$\Rightarrow \quad \Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}.$$