PHY 301

Quantum Mechanics

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2021-2022

Contents

1 Introduction

Quantum: quantities can vary by discrete amounts.

Mechanics: study of motion.

1.1 Franklin's Oil-Drop Experiment

Spilled a spoonful (2 ml) of oil on the surface of a lake and extended to about 2000 m^2, but not more. This experiment shows the **existent** and **size** of atoms.

$$V = Sh$$

$$h = \frac{V}{S} \sim \frac{2 \times 10^{-6}}{2 \times 10^{3}} \text{ m} \sim 10^{-9} \text{ m}$$

Atomic and molecular scales are **nanometric**

1.2 From Classical Mechanics to Quantum Mechanics

In classical mechanics, position is a function of time. **Deterministic**.

In quantum mechanics, the position of a particle is a random variable. **Probabilistic**.

2 Wave Function

2.1 Definition in 1-D space

Definition 2.1 (Wave Function)**.** *For a small particle living in a* ***one-dimensional space****, the wave function* Ψ *is a complex-valued function of space and time:*

$$\Psi : \mathbf{R} \times \mathbf{R} \to \mathbb{C}$$

$$(x, t) \mapsto \Psi(x, t) \in \mathbf{C}$$

Remark 2.1. $|\Psi(x,t)|^2$ *is the p.d.f. of finding the particle in position* x *at time* t*.*

Remark 2.2. $\int_a^b |\Psi(x,t)|^2 dx$ *is the c.d.f of finding the particle between position* $[a, b]$ *at time* t*.*

Remark 2.3. *Integration is over* ***space****,* t *is a* ***parameter****.*

2.2 Mean and variance of the position

These two statistics are expressed as integrals over the entire space. They are **deterministic functions of time**. Given wave function Ψ, then we have:

$$\langle x\rangle(t) = \int_{-\infty}^{+\infty} x|\Psi(x,t)|^2 dx$$
$$\langle Var(x)\rangle(t) = \int_{-\infty}^{+\infty} (x - \langle x\rangle(t))^2|\Psi(x,t)|^2 dx$$
$$[\Psi] = \frac{1}{\sqrt{L}}$$

2.3 Example: probability density of position for classical object

...

3 The Schrödinger equation

One dimension's Schrödinger equation for wave wave function Ψ ($x \in \mathbf{R}$ is a space coordinate, t is time, V is a **real-valued potential**) is

$$\boxed{i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\Psi(x,t)} \tag{1}$$

Complex conjugate form is

$$\boxed{-i\hbar \frac{\partial \Psi^*}{\partial t}(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi^*(x,t) + V(x)\Psi^*(x,t)} \tag{2}$$

Planck constant $\hbar$ is

$$\hbar = \frac{h}{2\pi} \simeq 1.05 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$$

Assumption 3.1. *Ψ and all its derivatives are smooth and go to zero when $|x|$ goes to infinity, faster than any negative power of x.*

3.1 Normalization

Due to its definition, the wave function has to be normalized at all time. That is, for all t, we have

$$\boxed{\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)dx = 1} \tag{3}$$

Remark 3.1. *Not all solutions of the Schrödinger equation are wave function.*

Theorem 3.1. *A normalized wave function stays normalized.*

Proof. For a normalized wave function at time $t = 0$:

$$\int_{-\infty}^{\infty} \Psi^*(x,0)\Psi(x,0)dx = 1$$

consider $t > 0$:

$$\begin{aligned}
&\frac{d}{dt}\left(\int_{-\infty}^{\infty}\Psi^*(x,t)\Psi(x,t)dx\right)\\
&=\int_{-\infty}^{+\infty}\frac{\partial\Psi^*(x,t)}{\partial t}\Psi(x,t)dx+\int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial t}dx\\
&=\frac{1}{i\hbar}\int_{-\infty}^{+\infty}\left(+\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*(x,t)}{\partial x^2}-V(x)\Psi^*(x,t)\right)\Psi(x,t)dx+\\
&\frac{1}{i\hbar}\int_{-\infty}^{+\infty}\Psi^*(x,t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)\right)dx\\
&=\frac{\hbar}{2mi}\left(\left[\Psi\frac{\partial}{\partial x}\Psi^*\right]_{-\infty}^{+\infty}-\int\frac{\partial}{\partial x}\Psi^*\frac{\partial}{\partial x}\Psi dx\right.\\
&\left.-\left[\Psi^*\frac{\partial}{\partial x}\Psi\right]_{-\infty}^{+\infty}+\int\frac{\partial}{\partial x}\Psi\frac{\partial}{\partial x}\Psi^*dx\right)\\
&=0
\end{aligned}$$

by Assumption 3.1. Hence, Ψ is normalized at all time. □

3.2 Linear momentum

We can not know actual position of a particle, hence we use the expectation of position $\langle x\rangle(t)$ instead.

$$\boxed{\langle x\rangle(t)=\int_{-\infty}^{+\infty}\Psi^*(x,t)x\Psi(x,t)dx} \tag{4}$$

the velocity of a particle is

$$\boxed{\langle V\rangle=\frac{d\langle x\rangle}{dt}} \tag{5}$$

the average linear momentum is

$$\boxed{\langle p\rangle=\int_{-\infty}^{+\infty}\Psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x,t)dx} \tag{6}$$

Proof.

$$
\begin{aligned}
\langle p \rangle &= m\frac{d\langle x \rangle}{dt} \\
&= m\int_{-\infty}^{\infty} \frac{d\Psi^*(x,t)}{dt}x\Psi + \Psi^*(x,t)x\frac{d\Psi(x,t)}{dt}dx \\
&= \frac{m}{i\hbar}\int_{-\infty}^{\infty} (\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*(x,t)}{\partial x^2} - V(x)\Psi^*(x,t))x\Psi(x,t) + (-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t))x\Psi^*(x,t)dx \\
&= \frac{\hbar}{2i}\int_{-\infty}^{\infty} \frac{\partial^2\Psi^*(x,t)}{\partial x^2}x\Psi(x,t) - \frac{\partial^2\Psi(x,t)}{\partial x^2}x\Psi^*(x,t)dx \\
&= \frac{\hbar}{2i}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}(\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \frac{\partial\Psi(x,t)}{\partial x}\Psi^*(x,t))dx \\
&= \frac{\hbar}{2i}([x(\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \frac{\partial\Psi(x,t)}{\partial x}\Psi^*(x,t))]_{-\infty}^{+\infty} - \int_{-\infty}^{\infty} \frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \frac{\partial\Psi(x,t)}{\partial x}\Psi^*(x,t)dx) \\
&= \frac{\hbar}{i}\int_{-\infty}^{\infty} \frac{\partial\Psi(x,t)}{\partial x}\Psi^*(x,t)dx \\
&= \int_{-\infty}^{\infty} \Psi^*(x,t)(-i\hbar\frac{\partial}{\partial x})\Psi(x,t)dx
\end{aligned}
$$

□

3.3 From the Schrödinger equation to the Newton law

Ehrenfest's theorem

$$\frac{d\langle p \rangle}{dt} = -\langle V'(x) \rangle \tag{7}$$

$\boxed{\textit{obey classical laws?}}$

Proof. ... □

3.4 Correspondence principle

$\boxed{\hbar \textit{ to } 0?}$

Energy = kinetic energy + potential energy

Position operator ...

Linear-momentum operator ...

Hamiltonian operator ...

3.5 Separable solutions: time-independent solutions

Consider one kind of solutions of Schrödinger equation in the form:

$$\Psi(x,t) := \psi(x)\phi(t)$$

the Schrödinger equation becomes:

$$i\hbar\psi(x)\phi'(t) = -\frac{\hbar^2}{2m}\psi''(x)\phi(t) + V(x)\psi(x)\phi(t) \tag{8}$$

$$i\hbar\frac{\phi'(t)}{\phi(t)} = -\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} + V(x) \tag{9}$$

Eq.9 is satisfied for all values of the independent variables x and t, hence there exists a **constant number** E that Eq.9 $= E$ for both sides. We have

$$i\hbar\frac{\phi'(t)}{\phi(t)} = E \tag{10}$$

$$-\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} + V(x) = E \tag{11}$$

Time-dependent factor Eq.10

$$\phi'(t) = \frac{E\phi(t)}{i\hbar}$$

$$\phi(t) = \phi(0)e^{\frac{E}{i\hbar}t} \tag{12}$$

Space-dependent factor Eq.11

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x)$$

$$\hat{H}\psi(x) = E\psi(x) \tag{13}$$

Eq.13 is called the ***time-independent Schrödinger equation***.

There are reasons about why introduce time-independent Schrödinger equation: 1. 2.

Remark 3.2. *E is a constant number.*

Remark 3.3. *E is a real number.*

Remark 3.4. $\exp(-\frac{iEt}{\hbar})^* = \exp(\frac{iEt}{\hbar})$ *when $E \in R$*

Proof. ... □

Remark 3.5. *$E \geq min(V(x))$*

Proof. ... □

3.6 Example: the infinite square well

Suppose

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a \\ \infty, & \text{otherwise} \end{cases}$$

then $\psi(x) = 0$ when $x \notin [0, a]$. When $x \in [0, a]$, we have time-independent Schrödinger $\psi(x)$ satisfied

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} &= E\psi \\ \frac{d^2\psi}{dx^2} &= -k^2\psi \end{aligned} \tag{14}$$

where

$$\boxed{k \equiv \frac{\sqrt{2mE}}{\hbar}} \tag{15}$$

Eq.14 is the classical simple harmonic oscillator equation with general solution

$$\psi(x) = A\sin kx + B\cos kx \tag{16}$$

where A and B are constant.

Continuity of $\psi(x)$ requires boundary condition

$$\psi(0) = \psi(a) = 0$$

by $\psi(0) = 0$, we have $B = 0$, $\psi(x) = A\sin kx$

by $\psi(a) = 0$,, we have trivial (non-normalizable) solution $A = 0$ or $\sin kx = 0$,

$ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \ldots$, $k \leq 0$ is useless. Hence the distinct solutions are

$$k_n = \frac{n\pi}{a}, \qquad \text{with } n = 1, 2, 3, \ldots$$

According to Eq.15, the corresponding values of E is

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

To find A, we normalize $\Psi(x,t)$

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$
$$\int_{-\infty}^{\infty} \psi(x)^2 dx = 1$$
$$\int_{-\infty}^{\infty} |A|^2 sin^2(kx) dx = 1$$
$$|A|^2 = \frac{2}{a}$$
$$A = \sqrt{\frac{2}{a}}$$

Finally, we have solutions of time-independent Schrödinger Eq.13

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

with corresponding energy

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Consequence I if the wave function at $t = 0$ is a normalized eigenfunction $\psi(x)$ (ie. $n = 1$), we integrate the Schrödinger equation by introducing a phase factor, we have

$$\Psi(x,t) = \exp(-\frac{iEt}{\hbar})\psi(x), \forall x, \forall t.$$

$|\Psi(x,t)^|2$ and then $\langle x \rangle$ are independent on time t. The wave function is stationary.

Consequence II If the wave function at $t = 0$ is a sum of eigenfunction $\psi(x)$ with $c_n \in \mathbb{C}$, we integrate the Schrödinger equation by introducing phase factors, we have

$$\Psi(x,t) = A \exp -\frac{iE_1t}{\hbar}\psi_1(x) + B \exp -\frac{iE_2t}{\hbar}\psi_2(x), A \in \mathbb{C}, \forall x, \forall t$$

if $E_1 \neq E_2$, then $|\Psi(x,t)|^2$ and then $\langle x \rangle$ are dependent on time t. The wave function is a periodic function of time.

3.7 The free particle: time-dependent solutions

When $V(x) = 0$, we have

$$i\hbar\frac{\phi'(t)}{\phi(t)} = E$$
$$-\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} = E$$

by Eq.10, Eq.11. let $k \equiv \frac{\sqrt{2mE}}{\hbar} > 0$, we get general solution

$$\Psi(x,t) = Ae^{ik\left(x - \frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x + \frac{\hbar k}{2m}t\right)}$$

let $k \equiv \pm\frac{\sqrt{2mE}}{\hbar}$ the solution becomes

$$\Psi_k(x,t) = Ae^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} \tag{17}$$

Eq.17 has a space period λ and a time period T.

Eq.17 is not normalizable.

4 de Broglie Waves

$E < V_0$ and $\hat{H}\psi = E\psi$. V is constant on three pieces of R with function

$$V(x) = \begin{cases} -V_0 & \text{for } -a \le x \le a \\ 0 & \text{for } |x| > a \end{cases}$$

The solutions of the time-independent Schrödinger equation is

$$\psi(x) = \begin{cases} e^{ikx} + Ae^{-ikx} & \text{for } x < -a \\ Be^{iqx} + Ce^{-iqx} & \text{for } -a < x \le a \\ De^{ikx} & \text{for } x > a \end{cases}$$

When $x < 0$,

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$
$$\psi(x) = 1$$

when $0 < x <= a$,

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}(V_0 - E)\psi(x) \tag{18}$$
$$\frac{d^2\psi(x)}{dx^2} = \mathcal{K}^2\psi(x) \tag{19}$$
$$\psi(x) = B \tag{20}$$

as

$$\boxed{\mathcal{K} = \frac{\sqrt{2m(V_0 - E)}}{\hbar}, \mathcal{K} > 0} \tag{21}$$

when $x > a$,

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$
$$\psi(x) = A\sin(kx) + iB\cos(kx)$$

WAVE PERIOD