Ch 6

Quantum Mechanics

- Schrödinger equation
- Operators, expectation values
- Particle in a box
- Finite potential well potential
- Simple harmonic oscillator
- Barrier and tunneling

The uncertainty and probabilistic nature of quantum mechanics might be overstated in pop science. In fact, quantum mechanical calculations give some of the most accurate predictions human can made about nature. Some history of Schrödinger wave equation (Schrödinger: life and thought, by Moore)

- Nov 1925, Schrödinger gave a seminar on de Broglie's work. One audience (Debye) suggested that there should be a wave equation.
- Schrödinger first tried to treat everything relativistically but failed.
 During the Christmas of 1925, he considered non-relativistic case and got the time-independent Schrödinger eq.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

He then obtained the correct energy spectrum for the hydrogen atom, and studied the spectrum of SHO, the Stark effect, the absorption and emission of radiation by an atom, all within 6 months of his discovery. This indicates that the equation could be right.

• The radiation problem led him to write down the time-dependent Schrödinger eq. +2

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

• Start from the simplest case: free particle (with plane wave)

$$\Psi_{\vec{p}}(\vec{r},t) \sim \exp\left[i\frac{\vec{p}\cdot\vec{r}}{\hbar} - i\frac{E(\vec{p})t}{\hbar}\right]$$

• What's the differential eq. that it satisfies?

Space derivative Time derivative $i\hbar \frac{\partial}{\partial t} \Psi_{\vec{p}}(\vec{r},t) = \vec{p} \Psi_{\vec{p}}(\vec{r},t)$ $i\hbar \frac{\partial}{\partial t} \Psi_{\vec{p}}(\vec{r},t) = E(\vec{p}) \Psi_{\vec{p}}(\vec{r},t)$

It is known that $E(\vec{p}) = \frac{|\vec{p}|^2}{2m}$

Replace the **p** in E by $-i\hbar \nabla$

$$i\hbar \frac{\partial}{\partial t} \Psi_{\vec{p}}(\vec{r},t) = E(-i\hbar \nabla) \Psi_{\vec{p}}(\vec{r},t)$$

• Suppose that this works also for a bounded particle with

 $E(\vec{r}, \vec{p}) = \frac{|\vec{p}|^2}{2m} + V(\vec{r})$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$
 So far, this is just a guess

• Time-dependent Schrödinger equation (1926)

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

• Time-independent Schrödinger equation

If the potential is static, then use separation of variables:

 $\Psi(\vec{r},t) = \psi(\vec{r})f(t)$

$$= \begin{cases} i\hbar \frac{df}{dt} = Ef \\ -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E\psi \end{cases}$$

$$\Psi(\vec{r},t) = \psi(\vec{r})e^{-i/\hbar t}$$

$$\Psi^*\Psi = |\psi(\vec{r})|^2$$

Probability distribution is independent of time (called stationary state)

- Ex 6.2: Show that $Ae^{i(kx-\omega t)}$ satisfies the time-dependent Schrödinger wave equation. (We just showed this.)
- Ex 6.3:

Determine whether $\Psi(x, t) = A \sin(kx - \omega t)$ is an acceptable solution to the time-dependent Schrödinger wave equation.

Solution

$$\frac{\partial \Psi}{\partial t} = -\omega A \cos(kx - \omega t)$$
$$\frac{\partial \Psi}{\partial x} = kA \cos(kx - \omega t)$$
$$-i\hbar\omega \cos(kx - \omega t) = \left(\frac{\hbar^2 k^2}{2m} + V\right)\Psi$$
$$= \left(\frac{\hbar^2 k^2}{2m} + V\right)A \sin(kx - \omega t)$$

- The *i* in quantum mechanics
 - The wave function Ψ(*r*,*t*) is in general a complex function.
 So it cannot be directly measured.
 - Also, $\Psi(\vec{r}, t)$ and $e^{i\alpha}\Psi(\vec{r}, t)$, where α is a real constant, represent the same state

Normalization of wave function

Ex 6.4: Consider a wave packet formed by using the wave function $Ae^{-\alpha|x|}$, where A is a constant to be determined by normalization. Normalize this wave function and find the probabilities of the particle being between 0 and $1/\alpha$, and between $1/\alpha$ and $2/\alpha$.



In quantum mechanics, physical observables, such as position, momentum, energy... etc are represented by (Hermitian) operators.
Relations between classical variables remain the same, such as E = p²/2m + V, L = r × p ... etc

Differential Operators $\hat{A}: f \to f' = \hat{A}f$

- Momentum operator $\underline{1-\dim}$ $\hat{p} \equiv \frac{\hbar}{i} \frac{d}{dx}$ $\hat{p}: \psi \to \psi' = \hat{p}\psi = \frac{\hbar}{i} \frac{d}{dx}\psi$ $\underline{3-\dim}$ $\hat{\vec{p}} = \frac{\hbar}{i} \nabla$
- Hamiltonian operator

哈密頓算符
$$\widehat{H} = \frac{\widehat{p}^2}{2m} + V(\overrightarrow{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\overrightarrow{r})$$

• Angular momentum operator

$$\hat{\vec{L}} = \vec{r} \times \hat{\vec{p}} = \frac{\hbar}{i}\vec{r} \times \nabla$$

Note: Not all classical variables have corresponding operators.

For example, angle θ , time *t* do not have corresponding operators.

3. Quantisierung als Eigenwertproblem; von E. Schrödinger.

(Erste Mitteilung.)

Quantization as an eigenvalue problem

• Eigenvalue equation

(Operator)(function) = number × (same function)



Boundary condition

In order to normalize the wave functions, they must approach zero as *r* approaches infinity. This requires the eigenenergies to be discrete. Bohr's assumption of stationary states is thus a natural result of mathematics.

• Expectation value

$$\langle x \rangle = \int dx \, x |\psi(x,t)|^{2}$$
 optional

$$\langle \hat{p} \rangle = \int dx \psi^{*}(x) \hat{p} \psi(x)$$

$$= \int dx \psi^{*}(x) \frac{\hbar}{i} \frac{d}{dx} \psi(x)$$

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int dx \psi(x) e^{-ikx}$$

$$\psi(k) = \int dk \, \hbar k |\psi(k)|^{2}$$

$$\langle F(x,\hat{p}) \rangle = \int dx \psi^*(x) F\left(x,\frac{\hbar}{i}\frac{d}{dx}\right) \psi(x)$$
$$\langle \widehat{H} \rangle = \int dx \psi^*(x) \widehat{H} \psi(x)$$

. .

 $\left\langle \widehat{\vec{L}} \right\rangle = \int dx \psi^*(x) \widehat{\vec{L}} \psi(x)$

對易關係

• Commutation relation (Heisenberg, Born etc)

對易子 Commutator of operators A,B:
$$\begin{bmatrix} \hat{A}, \hat{B} \end{bmatrix} \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

交換子 $[x, \hat{p}] \equiv x\hat{p} - \hat{p}x = i\hbar \neq 0$

$$\Delta A \Delta B \ge \left| \frac{1}{2i} \left\langle [\hat{A}, \hat{B}] \right\rangle \right|$$

e.g.,
$$\Delta x \Delta p \ge \frac{\hbar}{2}$$

- Two physical operators that commute with each other can both be measured accurately without interference. They are called compatible observables. 相容觀測量
- Compatible observables can share the same eigenstates, called simultaneous eigenstates 共同本徵態

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Some properties of wave function



Atkins, Physical Chemistry

Fig. 8.24 The wavefunction must satisfy stringent conditions for it to be acceptable. (a) Unacceptable because it is not continuous; (b) unacceptable because its slope is discontinuous; (c) unacceptable because it is not single-valued; (d) unacceptable because it is infinite over a finite region.

Note: There are exceptions to rule (b) when V is *infinite*.

Case 1: A "particle" in an empty box (infinite potential well)

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+0\right]\psi(x) = E\psi(x)$$

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$



eigenstates $\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$

eigenenergy

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2}$$
 (n = 1, 2, 3, ...)

Quantization of energy (due to BC)

normalization

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

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$$

Wave functions



Energy levels



Figure 3.11 Energy levels of an electron confined to a box 0.1 nm wide.

Ex 6.8:

Determine the expectation values for x, x^2 , p, and p^2 of a particle in an infinite square well for the first excited state.

Solution

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

$$\langle x^2 \rangle_{n=2} = \frac{2}{L} \int_0^L x^2 \sin^2 \left(\frac{2\pi x}{L}\right) dx = 0.32L^2$$

$$\langle p \rangle_{n=2} = (-i\hbar) \frac{2}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \left[\frac{d}{dx} \sin\left(\frac{2\pi x}{L}\right)\right] dx = 0$$
$$\langle p^2 \rangle_{n=2} = \frac{2}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{2\pi x}{L}\right) dx = \frac{4\pi^2 \hbar^2}{L^2}$$

$$E_2 = \frac{4\pi^2 \hbar^2}{2mL^2} = \frac{\langle p^2 \rangle_{n=2}}{2m}$$

3-dim box

Ex 6.10:

Consider a free particle inside a box with lengths L_1 , L_2 , and L_3 along the *x*, *y*, and *z* axes, respectively, as shown in Figure 6.6. The particle is constrained to be inside the box. Find the wave functions and energies. Then find the ground-state energy and wave function and the energy of the first excited state for a cube of sides *L*.

Solution
$$-\frac{\hbar^2}{2m}\nabla^2 \psi = E\psi$$

 $\Rightarrow \psi(x, y, z) = A \sin(k_1 x) \sin(k_2 y) \sin(k_3 z)$
 $\frac{\hbar^2}{2m} (k_1^2 + k_2^2 + k_3^2) \psi = E\psi$
 $\Rightarrow E = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)$

For the *cubical* box, with $L_1 = L_2 = L_3 = L$.

$$E_{\rm gs} = \frac{3\pi^2\hbar^2}{2mL^2} \qquad \psi_{\rm gs} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$
$$E_{\rm 1st} = \frac{\pi^2\hbar^2}{2mL^2}(2^2 + 1^2 + 1^2) = \frac{3\pi^2\hbar^2}{mL^2}$$

Case 2: A particle in a finite potential well

$$V(x) = \begin{cases} V_0 & x \le 0 & \text{region I} \\ 0 & 0 < x < L & \text{region II} \\ V_0 & x \ge L & \text{region III} \end{cases} \xrightarrow{Region I} Region II Region III$$
Region II $\frac{d^2\psi}{dx^2} = -k^2\psi$, where $k = \sqrt{(2mE)/\hbar^2}$
Region I, III $\frac{d^2\psi}{dx^2} = \alpha^2\psi$, where $\alpha = \sqrt{(2m(V_0 - E))/\hbar^2}$
 $\psi_{I}(x) = Ae^{\alpha x} \quad \text{region II, } x < 0$
 $\psi_{III}(x) = Be^{-\alpha x} \quad \text{region III, } x > L$
 $\psi_{II} = Ce^{ikx} + De^{-ikx} \quad \text{region II, } 0 < x < L$

The boundary condition (BC) requires that

$$\psi_{I} = \psi_{II}, d\psi_{I} / dx = d\psi_{II} / dx \text{ at } x = 0 \text{ and}$$

 $\psi_{II} = \psi_{III}, d\psi_{II} / dx = d\psi_{III} / dx \text{ at } x = L$
These determine the relations between A,B,C,D



- Note that the wave function is nonzero outside of the box.
- The penetration depth is the distance outside the potential well where the probability significantly decreases.

$$\delta x \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

Case 3:



To avoid divergence, we need

$$\left(\frac{\beta}{\alpha} - 1\right) = 2n, n = 0, 1, 2, \dots$$
$$\beta = (2n + 1)\alpha$$
Eigenenergies $E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad \omega = \sqrt{\frac{k}{m}}$

The Solutions of Hermit diff eq are Hermit polynomials

 Table 5.2
 Some Hermite Polynomials
 Hermite (physicists') Polynomials 50 H_n(y) En n 40 α_n 30 $\frac{1}{2}h\nu$ 0 1 1 2y = 3 $4y^{2} - 2 = 5$ $8y^{3} - 12y = 7$ $16y^{4} - 48y^{2} + 12 = 9$ $32y^{5} - 160y^{3} + 120y = 11$ 20 $\frac{3}{2}h\nu$ 1 $\frac{\frac{5}{2}h\nu}{\frac{7}{2}h\nu}$ $\frac{\frac{9}{2}h\nu}{\frac{9}{2}h\nu}$ 2 3 4 10 H_n (x) 0 -10 $\frac{11}{2}h\nu$ 5 n = 0-20 n = 1 n = 2 -30 n = 3 Eigenstates $\Psi_n = H_n(\overline{x})e^{-\alpha x^2/2}$ n = 4-40 n = 5 -2 -1 0 2 1 3 Х

Normalized wave functions



- Ground state is a Gaussian function
- Note that the number of nodal points is 0,1,2,... n.
- More wiggling costs more energy

Energy levels of SHO



- *E*₀=0: the particle stays at the bottom, and not moving.
 This would violate the uncertainty relation.
- This concept emerged around 1913 (Einstein and O. Stern). Debye, also noted that the zero-point energy of the atoms of a crystal lattice would cause a reduction in the intensity of the X-ray diffraction even as the temperature approached absolute zero. (wiki)
- In 1916 Nernst proposed that empty space was filled with zero-point electromagnetic radiation. (wiki)

Ex 6.12: Normalize the ground state wave function ψ_0 for the simple harmonic oscillator and find the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$.

Solution

$$\psi_0(x) = Ae^{-\alpha x^2/2}$$

$$\int_{-\infty}^{\infty} \psi_0^*(x)\psi_0(x) \, dx = 1 \quad \Longrightarrow \quad A = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_0^*(x)x\psi_0(x) \, dx$$

$$= \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} xe^{-\alpha x^2} \, dx = 0$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_0^*(x)x^2\psi_0(x) \, dx = \frac{1}{2\alpha} = \frac{\hbar}{2m\omega}$$



Reflection and Transmission of wave



• The probability of the particles being reflected *R* or transmitted *T* is

$$R = \frac{|\psi_{I}(\text{reflected})|^{2}}{|\psi_{I}(\text{incident})|^{2}} = \frac{B^{*}B}{A^{*}A}$$
$$T = \frac{|\psi_{III}(\text{transmitted})|^{2}}{|\psi_{I}(\text{incident})|^{2}} = \frac{F^{*}F}{A^{*}A}$$
Set A=1, wish to determine B, F (need to know C,D)
$$R + T = 1$$

Let's consider the $E < V_0$ case. Find calculate T.

From the B.C., we need to match ψ and $\frac{d\psi}{dx}$ at x=0, L



Analogy with Wave Optics *Frustrated* total internal reflection



Ex 6.16: Consider a particle of kinetic energy *K* approaching the step function of Figure 6.17 from the left, where the potential barrier steps from 0 to V_0 at x = 0. Find the penetration distance Δx , where the probability of the particle penetrating into the barrier drops to 1/e. Calculate the penetration distance for a 5-eV electron approaching a step barrier of 10 eV.



Alpha decay as an example of tunneling (Gamow 1928)



Q: Many nuclei heavier than lead are natural emitters of alpha particles, but their emission rates vary over a factor of 10¹³, whereas their energies tend to range only from 4 to 8 MeV. Why?

- Inside the nucleus, an alpha particle feels the strong, short-range attractive nuclear force.
 Outside it feels a repulsive Coulomb force.
- The nuclear force potential is approximately by a square well.
- The potential barrier (26.4 MeV for Po-212) at the nuclear radius is several times greater than the energy of an alpha particle (8.78 MeV).
- According to quantum mechanics, however, the alpha particle can "tunnel" through the barrier.
 Hence this is observed as radioactive decay.
 (this is a probabilistic process)

Scanning tunneling microscope (STM)

Binning and Rohrer (1981)





Surface of Si (111)

The tunneling current decays quickly with the tip-surface distance.

Ex 6.17:

Consider the α -particle emission from a ²³⁸U nucleus, which emits a 4.2-MeV α particle. We represent the potentials as shown in Figure 6.19. The α particle is contained inside the nuclear radius of $r_N \approx 7 \times 10^{-15}$ m. Find the barrier height and the distance the α particle must tunnel and use a square-top potential to calculate the tunneling probability.



 $\kappa L = 140.$

$$T = 16 \left(\frac{4.2 \text{ MeV}}{38 \text{ MeV}} \right) \left(1 - \frac{4.2 \text{ MeV}}{38 \text{ MeV}} \right) e^{-280}$$
$$= 1.6e^{-280} = 4 \times 10^{-121}$$

A better estimate gives

$$T = 1.5 \times 10^{-41}$$
$$K = \frac{1}{2} mv^2$$
$$v = \sqrt{\frac{2K}{m}} = \sqrt{\frac{2(4.2 \text{ MeV})}{3727 \text{ MeV}/c^2}} = 0.047c = 1.4 \times 10^7 \text{ m/s}$$

The diameter of the nucleus is about 1.4×10^{-14} m, so it takes the α particle $(1.4 \times 10^{-14} \text{ m})/(1.4 \times 10^7 \text{ m/s}) \approx 10^{-21}$ s to cross. The α particle must make many traverses back and forth across the nucleus before it can escape. According to our probability calculation it must make about 10^{41} attempts, so we estimate the α particle may tunnel through in about 10^{20} s. The half-life of a ²³⁸U nucleus is 4.5×10^9 y or about 10^{17} s. Our rough estimate does not seem all that bad. Case 5: Hydrogen atom (next chapter)