Quantum Mechanics

Jilin U. Center for Theoretical Physics
Takumi Kuwahara (桑原 拓巳)

2. Wave Mechanics, Matrix Mechanics, and their equivalence

2.1 Wave Mechanics

Wave

Nature contains various "waves"

- Sound wave
- Water (gravity) wave (fluid dynamics)
- Electromagnetic wave (Light/Maxwell theory)
- Gravitational wave (Gravity/General relativity)

Any kinds of wave satisfy "wave equation"

$$\frac{1}{v^2}\frac{\partial^2}{\partial t^2}\psi(\boldsymbol{x},t) - \nabla^2\psi(\boldsymbol{x},t) = 0$$

$$\psi(\boldsymbol{x},t) = Ae^{i\boldsymbol{k}\cdot\boldsymbol{x} - i\omega t}$$

de Broglie Wave

Any particles have also wave properties (wave-particle duality)

Louis de Broglie

Characteristic properties of matter and wave

matter

- momentum: $\boldsymbol{p}$
- energy: E

wave

- wave number: $\boldsymbol{k}$
- frequency: $\nu = \omega/2\pi$

de Broglie's idea:

a particle of any mass is associated with wave

matter wave properties

$$\boldsymbol{k} = \boldsymbol{p}/\hbar$$

$$\omega = E/\hbar$$

Schrödinger Equation

Inspired by de Broglie's consideration:

Matter also has properties describing as wave

Erwin Schrödinger

Wave function: $\Psi(\boldsymbol{x}, t) = Ae^{i\boldsymbol{k}\cdot\boldsymbol{x} - i\omega t}$

This wave function satisfies:

$$-i\hbar\nabla\Psi(\boldsymbol{x}, t) = \boldsymbol{p}\Psi(\boldsymbol{x}, t)$$

$$i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{x}, t) = E\Psi(\boldsymbol{x}, t)$$

$$\boldsymbol{p} = \hbar\boldsymbol{k}$$

$$E = \hbar\omega$$

Time-independent Schrödinger Equation

A free particle: a definite energy E does not change

$$\Psi(\boldsymbol{x}, t) = e^{-iEt/\hbar}\psi(\boldsymbol{x})$$

and a relation between energy and momentum:

$$E = \frac{\boldsymbol{p}^2}{2m}$$

dispersion relation for matter wave

$$\omega = \omega(k)$$

Schrödinger Equation for free particle (time independent)

$$E\psi(\boldsymbol{x}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{x})$$

Generalization

Schrödinger equation under a potential $V(\vec{x})$

$$E = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x}) \qquad E\psi(\boldsymbol{x}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\psi(\boldsymbol{x})$$

N-particle system: such as atomic system

Hamiltonian: $$H = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i} + V(\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N)$$

$$E\psi(\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N) = \left[\sum_i -\frac{\hbar^2}{2m_i}\nabla_i^2 + V(\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N)\right]\psi(\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N)$$

Application

Hydrogen atom: detail in a few lectures later

Coulomb potential $$V(\boldsymbol{x}) = -\frac{e^2}{4\pi r}$$

The wave function for electron exists only for specific energies

Energy for wave function: $$E_n = -\frac{e^4 m_e}{32\pi^2 n^2 \hbar^2}$$

with integer $n = 1,2,\cdots$

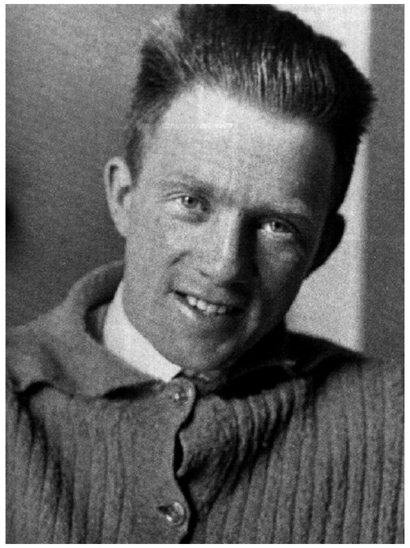
No solutions any other energies

2.2 Matrix Mechanics

Heisenberg's idea

"A physical theory should not concern what can never be observed"

even if it can be imagined classically

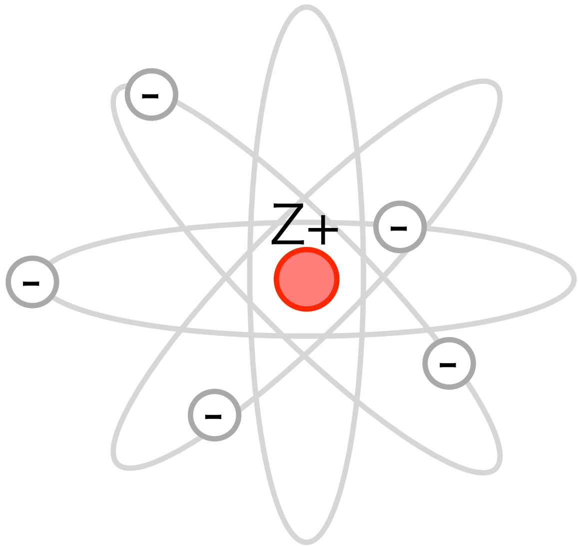


Werner Heisenberg

Atomic spectra

Never observed: Electron orbits in atoms

Observation: Frequencies of spectrum lines, and their radiation power



"classical" image of electron orbits

Radiation Power

Radiation power in classical electrodynamics (**Heaviside-Lorentz unit**)

$$P = \frac{e^2}{3\pi c^3} |\ddot{\boldsymbol{x}}|^2$$

This formula should give the power emitted in radiative transition from $E_m \to E_n$

Replace classical orbits with complex amplitude for this transition

$$\boldsymbol{x} \to [\boldsymbol{x}]_{nm} \propto e^{-i\omega_{nm}t}, \quad \omega_{nm} \equiv \frac{1}{\hbar}(E_m - E_n)$$

related with the frequencies of radiation (observables)

Radiation Power

Rate of emitting photon carrying energy $\hbar\omega_{nm}$

spontaneous emission $$A_m^n \equiv \frac{P(m \to n)}{\hbar\omega_{nm}} = \frac{e^2}{3\pi c^3 \hbar}\omega_{nm}^3 \left| [\boldsymbol{x}]_{nm} \right|^2$$

Absorption rate (using Einstein relation)

$$B_n^m = B_m^n = \frac{\pi c^3}{2\hbar\omega_{nm}^3} A_m^n = \frac{e^2}{6\hbar^2} \left| [\boldsymbol{x}]_{nm} \right|^2$$

to define kinematics for B_n^m, we extend the definition $[\boldsymbol{x}]_{nm}$ to $E_n > E_m$

$$[\boldsymbol{x}]_{nm} = [\boldsymbol{x}]_{mn}^* \propto e^{-i\omega_{nm}t}$$

Harmonic Oscillator

Let's consider the 1dim harmonic oscillation for atomic spectra

Classical equation of motion

$$\frac{m_e}{2}\dot{x}^2 + \frac{m_e\omega_0^2}{2}x^2 = E$$

For atomic orbital motions, Heisenberg used

1). **Heisenberg's assumption**

$$\frac{m_e}{2}[\dot{x}^2]_{nm} + \frac{m_e\omega_0^2}{2}[x^2]_{nm} = \begin{cases} E_n & (n = m) \\ 0 & (n \neq m) \end{cases}$$

2). **Condition at high frequency** (Derived by W. Kuhn)

$$\sum_m B_n^m(E_m - E_n) = \frac{e^2}{4m_e}$$

High-frequency emission is same as
high energy scattering with free electron

Harmonic Oscillator

$$B_n^m = \frac{e^2}{6\hbar^2} |[\boldsymbol{x}]_{nm}|^2$$

$$E_m - E_n = \hbar\omega_{nm}$$

Combine with relations above

$$\sum_m B_n^m (E_m - E_n) = \frac{e^2}{6\hbar} \sum_m \omega_{nm} |[\boldsymbol{x}]_{nm}|^2 = \frac{e^2}{4m_e}$$

Heisenberg's quantum condition (in 3dim: average in 3 directions)

$$\hbar = \frac{2m_e}{3} \sum_m \omega_{nm} |[\boldsymbol{x}]_{nm}|^2$$

Heisenberg's quantum condition (in 1dim)

$$\hbar = 2m_e \sum_m \omega_{nm} |[x]_{nm}|^2$$

Harmonic Oscillator

Exact solutions of equation of motion

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \qquad\qquad \hbar = 2m_e \sum_m \omega_{nm} |\,[x]_{nm}|^2$$

Complex amplitudes

$$[x]_{n,n+1} = e^{-i\omega_0 t}\sqrt{\frac{(n+1)\hbar}{2m_e\omega_0}}\,, \qquad [x]_{n,m} = 0 \qquad (n - m \neq \pm 1)$$

More generally, Heisenberg considered the anharmonic oscillation

$$\frac{m_e}{2}\dot{x}^2 + \frac{m_e\omega_0^2}{2}x^2 + \frac{\lambda}{3}x^3 = E$$

to realize not only nearest levels,

but also multiple emission lines: $[x]_{12}\,, [x]_{13}\,, \cdots, [x]_{23}\,, \cdots$

Matrix Mechanics

Max Born realized:

Heisenberg's calculation were just special cases of matrix multiplications

$$[x^2]_{nm} = \sum_k [x]_{nk}[x]_{km}\,,$$

$$[x^3]_{nm} = \sum_{k,l} [x]_{nk}[x]_{kl}[x]_{lm}\,,$$

$$[\dot{x}^2]_{nm} = \sum_k [\dot{x}]_{nk}[\dot{x}]_{km} = \sum_k \omega_{nk}\omega_{mk}[x]_{nk}[x]_{km}\,,$$

Max Born

Matrix mechanics

= Mechanics with a generalization of $x \in \mathbb{R} \to [x] \in M$

Uncertainty Principle

Matrix for momentum

$$[p]_{nm} = m_e[\dot{x}]_{nm} = -im_e\omega_{nm}[x]_{nm}$$

Then, we can find the non-commutative property

$$[px]_{nn} = -im_e\sum_m \omega_{nm}|[x]_{mn}|^2,$$

$$[xp]_{nn} = im_e\sum_m \omega_{nm}|[x]_{mn}|^2,$$

$$\hbar = 2m_e\sum_m \omega_{nm}|[x]_{nm}|^2$$

The result is

$$[xp - px]_{nn} = 2im_e\sum_m \omega_{nm}|[x]_{mn}|^2 = i\hbar,$$

This is well-known **uncertainty principle**

2.3 Equivalence between wave mechanics and matrix mechanics

Property of Wave function

Wave function is an element of L^2 function space

to define the finite inner products.

$\psi : \mathbb{R}^n \to \mathbb{C}$ square integrable

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx < \infty$$

Inner products

$$(g, f) \equiv \int_{\mathbb{R}^n} g^*(x) f(x)$$

An Hermitian operator A satisfies

$$(g, Af) = \int_{\mathbb{R}^n} g^* (Af) = \int_{\mathbb{R}^n} (Ag)^* f = (Ag, f)$$

Hamiltonian as an Hermitian operator

Hamiltonian is an **Hermitian** operator

$$\int_{\mathbb{R}^n} \psi_m^* (H\psi_n) = \int_{\mathbb{R}^n} (H\psi_m)^* \psi_n \qquad H = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})$$

proof: potential part is trivial (as far as real function)
kinetic term is proven by integral by part

Energy and wave function

$$E_n \int_{\mathbb{R}^n} \psi_m^* \psi_n = E_m^* \int_{\mathbb{R}^n} \psi_m^* \psi_n \quad \Rightarrow \quad E_n = E_n^* \text{ i.e. } E_n \in \mathbb{R} \text{ for } m = n$$

$$\int_{\mathbb{R}^n} \psi_m^* \psi_n = 0 \quad \text{for } m \neq n$$

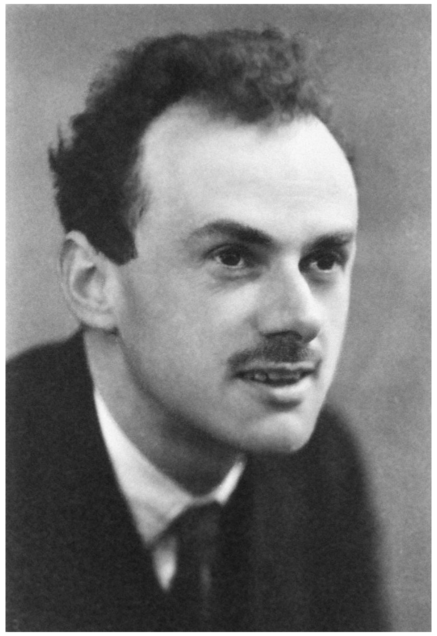
(* we call as eigen-energy and eigen-state, detail later)

We can take the normalization for wave function

$$\int_{\mathbb{R}^n} \psi_m^* \psi_n = \delta_{n,m}$$

Reformulate Matrix Mechanics

We can reconstruct the matrix mechanics
in terms of wave functions, elements of L^2 function space



Paul Dirac

Matrix element for an operator A

$$[A]_{mn} = \int_{\mathbb{R}^n} \psi_m^* \, [A\psi_n]$$

In particular, the momentum/position operators

$$[\boldsymbol{X}\psi_n] \equiv \boldsymbol{x}\psi_n(\boldsymbol{x})$$
$$[\boldsymbol{P}\psi_n] \equiv -i\hbar\nabla\psi_n(\boldsymbol{x})$$

Using time-dependent wave function, we naturally get:

$$[A]_{mn} \propto e^{-\frac{i}{\hbar}(E_n - E_m)t}$$

Cont'd

A product of operations

$$\int_{\mathbb{R}^n} \psi_m^* \left[B[A\psi_n]\right] = \sum_k [B]_{mk}[A]_{kn}$$

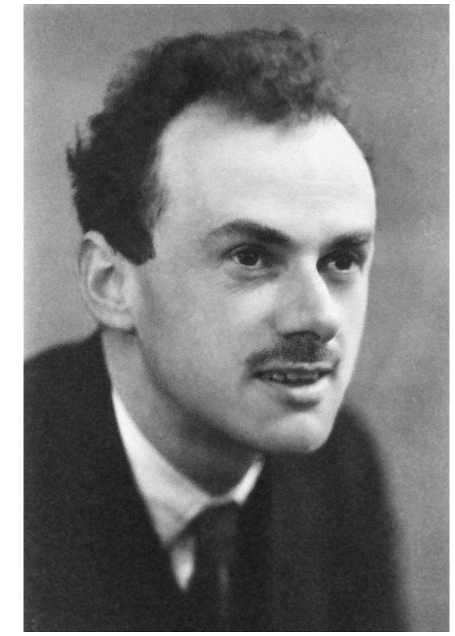
expected from the matrix manipulation

Uncertainty principle (1dim)

$$\int dx\, \psi_m^* \left[[P, X]\psi_n\right] = i\hbar\delta_{m,n}$$

Exercises) prove these relations

On the Theory of Quantum Mechanics



Paul Dirac

Abstract formulation of QM: P. A. M. Dirac (1926)

Equivalence of
- Schrödinger's Wave mechanics
- Heisenberg's Matrix mechanics

Different mechanics are different representations of QM

- Wave Mechanics → position representation
- Matrix Mechanics → energy-state representation

Mathematical formulation: J. von Neumann (1927)

John von Neumann

Rigorous formulation in Mathematics

A physical state is described by an abstract vector
in a specific vector space

Hilbert space

Complete set and transformation theory

Two representations rely on different vector spaces

	Matrix Mechanics	Wave Mechanics
vector space	ℓ^2 vector space $\ell^2 = \left\{ (c_1, c_2, \cdots) \,\middle|\, \sum_{n=1}^{\infty} \lvert c_n \rvert^2 < \infty \right\}$	L^2 function space $L^2 = \left\{ \psi : \mathbb{R}^n \to \mathbb{C} \,\middle|\, \int_{\mathbb{R}^n} \lvert \psi \rvert^2 < \infty \right\}$
complet set representations	$\psi = \sum_n c_n \phi_n$ $c_n \equiv \langle \phi_n, \psi \rangle\,, \quad \phi_n \in \ell^2$	$\psi = \int da\, c_a \phi_a(x)$ or $\psi = \sum_a c_a \phi_a(x)$ $c_a \equiv \int dy\, \phi_a^*(y) \psi(y)\,, \quad \phi_a \in L^2$

* any vectors are expanded as a linear combination of complete set

$\{\phi_n\}$ and $\{\phi_a\}$ above

Summary Table

	Matrix Mech.	Wave Mech.	Abstract formulation Dirac/von Neumann
Basis	vectors $\{\phi_n\}_{n=1}^{\infty}$ energy states	wave function ψ position reps	state vectors
Operation	(infinite) Matrix	operator: $A : L^2 \to L^2$	operator: $A : \mathscr{H} \to \mathscr{H}$
Math. Basic	ℓ^2 vector space	L^2 function space	Hilbert space $\mathscr{H}$

2.4 Probabilistic Interpretation

Meaning of wave function

Max Born

Let us focus on wave function:

What the physical meaning of wave function?

- ✘ particles are spread out in space
- ❍ a probability density to find a particle around $\boldsymbol{x} \sim \boldsymbol{x} + d\boldsymbol{x}$ (M. Born) at time t

$$dP(t) = |\Psi(\boldsymbol{x}, t)|^2 d^3\boldsymbol{x}$$

with proper normalization $$\int |\Psi(\boldsymbol{x}, t)|^2 d^3\boldsymbol{x} = 1$$

it is possible for the L^2 function space

and total probability is conserved in time

$$i\hbar \frac{dP(t)}{dt} = i\hbar \frac{d}{dt} \int |\Psi(\boldsymbol{x}, t)|^2 d^3\boldsymbol{x}$$

$$= \int \left\{ \Psi^*(\boldsymbol{x}, t)[H\Psi](\boldsymbol{x}, t) - [H\Psi]^*(\boldsymbol{x}, t)\Psi(\boldsymbol{x}, t) \right\} = 0$$

Properties

i) Expectation values

$$\langle A \rangle = \int \Psi^*(\boldsymbol{x}, t)[A\Psi](\boldsymbol{x}, t) d^3\boldsymbol{x}$$

ii) Operators representing observables to be Hermitian

their expectation values are observable = real quantities

$$\langle A \rangle^* = \left[\int \Psi^*(\boldsymbol{x}, t)[A\Psi](\boldsymbol{x}, t) d^3\boldsymbol{x} \right]^*$$

$$= \int \Psi^*(\boldsymbol{x}, t)[A\Psi](\boldsymbol{x}, t) d^3\boldsymbol{x} = \langle A \rangle$$

Exercise) show the equality by the definition of the Hermitian operator

$$\int_{\mathbb{R}^n} g^* (Af) = \int_{\mathbb{R}^n} (Ag)^* f$$

Eigenfunctions and Eigenvalues

When a state Ψ has a real value a for an Hermitian operator A

$$\langle (A-a)^2 \rangle = \int \Psi^*(\boldsymbol{x},t)[(A-a)^2\Psi](\boldsymbol{x},t)d^3\boldsymbol{x} = 0$$

Exercise) show this equality

The equation holds $[A\Psi](\boldsymbol{x},t) = a\Psi(\boldsymbol{x},t)$

we call $\Psi(\boldsymbol{x},t)$ is **eigenfunction/eigenstate** of A

a is **eigenvalue** of A

time-independent Schrödinger equation: $[H\psi](\boldsymbol{x}) = E\psi(\boldsymbol{x})$

time-independent wave function is eigenstate of Hamiltonian H
and energy is eigenvalue of Hamiltonian H (or simply eigen-energy)

Ehrenfest theorem

Classical relations of expectation values

$$\frac{d}{dt}\langle \boldsymbol{X} \rangle = \frac{1}{i\hbar}\int d^3x \Psi^*(\boldsymbol{x}, t)[\boldsymbol{X}, H]\Psi(\boldsymbol{x}, t) = \frac{1}{m}\langle \boldsymbol{P} \rangle$$

$$\frac{d}{dt}\langle \boldsymbol{P} \rangle = \frac{1}{i\hbar}\int d^3x \Psi^*(\boldsymbol{x}, t)[\boldsymbol{P}, H]\Psi(\boldsymbol{x}, t) = -\langle \nabla V(\boldsymbol{X}) \rangle$$

Exercise) show these equalities

Similar to classical equations of motion

* generally not quite same: because $\langle V(\boldsymbol{X}) \rangle \neq V(\langle \boldsymbol{X} \rangle)$ in general

Uncertainty principle and Simultaneous eigenfunctions

Wave function cannot be the eigenfunctions of both position and momentum

if $\begin{cases} X_i \Psi(\boldsymbol{x}, t) = x_i \Psi(\boldsymbol{x}, t) \\ P_i \Psi(\boldsymbol{x}, t) = p_i \Psi(\boldsymbol{x}, t) \end{cases}$ $\quad [X_i, P_j]\Psi(\boldsymbol{x}, t) = (x_i p_j - p_j x_i)\Psi(\boldsymbol{x}, t) = 0$

contradict with $[X_i, P_j] = i\hbar\delta_{ij}$ from wave mechanics

Commutator: $[A, B] \equiv AB - BA$

Wave function can be the **simultaneous eigenfunction** for A and B

only when A and B are commuted $[A, B] = AB - BA = 0$

A generalization of probabilistic interpretation

We can consider wave function not energy eigenstate (as abstract formulation by Dirac)

$$\psi(\boldsymbol{x}) = \sum_n c_n \psi_n(\boldsymbol{x})$$

Normalization: $$\int d^3x \, |\psi(\boldsymbol{x})|^2 = 1 \quad \Rightarrow \quad \sum_n |c_n|^2 = 1$$

Eigenvalue of any function of Hamiltonian

$$\langle f(H) \rangle_\psi = \int d^3x \psi^*(\boldsymbol{x})[f(H)\psi](\boldsymbol{x}) = \sum_n |c_n|^2 f(E_n)$$

Exercise) show this equation

Summary

- Two different formulation of Quantum Mechanics
  - ✓ Wave Mechanics (Schrödinger)
  - ✓ Matrix Mechanics (Heisenberg)
- Same mechanics with different representation (Dirac)

- Probabilistic interpretation of Wave function (position representation of states)

Next Lecture

- Blackboard Lecture
- General Principle of Quantum Mechanics
  - Hilbert space and States
  - Continuum States
  - Observables