Appendix 1

Basics of Quantum Mechanics
(量子力学基础)

Objectives

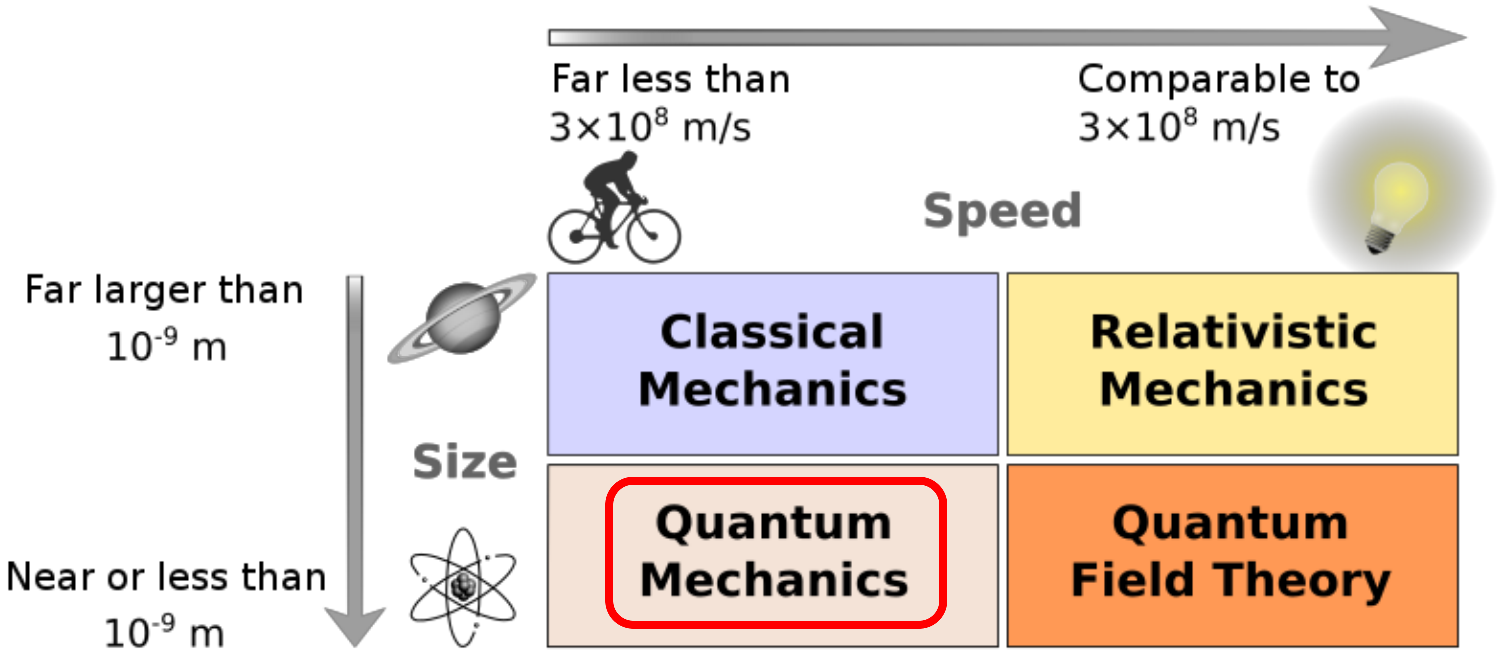
- What is Quantum Mechanics?
- Five Postulates of Quantum Mechanics (量子力学的五个基本假定)
- Commutation and Uncertainty Principle (对易与不确定性原理)

What is Quantum Mechanics?

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Quantum Mechanics (量子力学)

❖ Quantum mechanics is a **fundamental theory** in physics that describes nature at the small distance and energy scales of **atoms and subatomic particles** (原子与亚原子粒子).



Appendix 1: Basics of Quantum Mechanics (量子力学基础)

- Quantum Mechanics (量子力学)

The 5th Solvay Conference, Brussels, 1927

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➢ Quantum Mechanics (量子力学)

❖ The physicists contribute the most to the foundation of quantum mechanics:

Max Planck
普朗克
(1858-1947)
German

1918

Albert Einstein
爱因斯坦
(1879-1955)
German

1921

Niels Bohr
玻尔
(1885-1962)
Danish

1922

Louis de Broglie
德布洛意
(1892-1987)
French

1929

Werner Heisenberg
海森堡
(1901-1976)
German

1932

Erwin Schrödinger
薛定谔
(1887-1961)
Austrian

1933

Paul Dirac
狄拉克
(1902-1984)
English

1933

Wolfgang Pauli
泡利
(1900-1958)
Austrian

1945

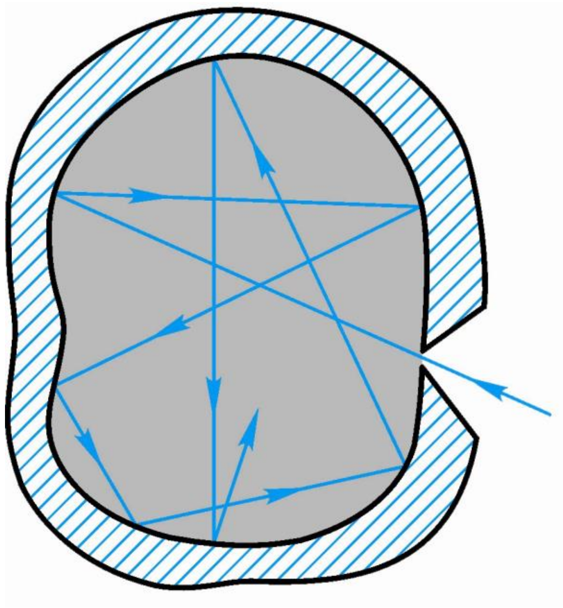
Max Born
玻恩
(1882-1970)
German

1954

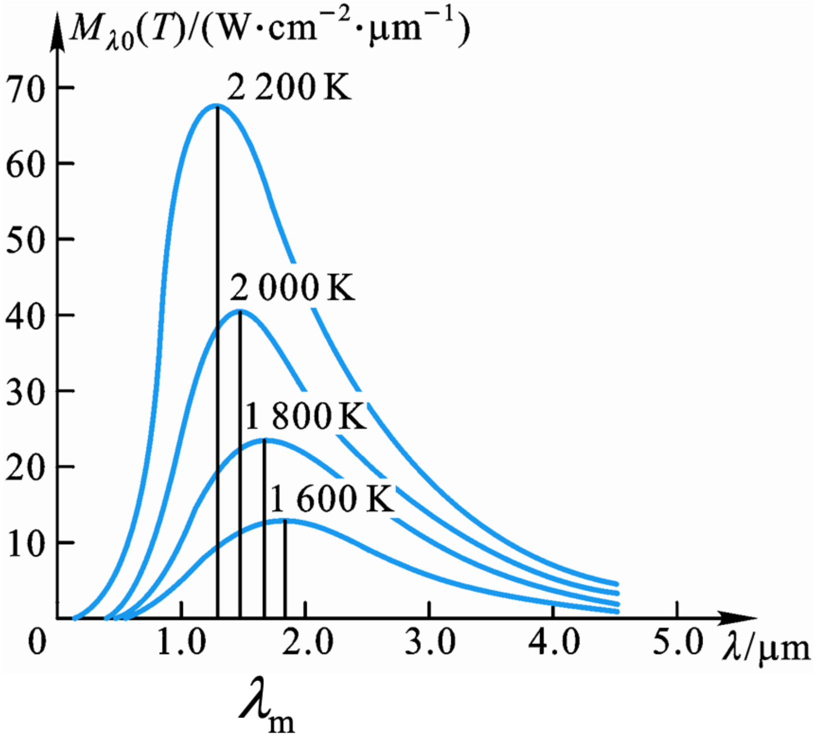
Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Early-Stage Quantum Theories (早期量子理论)**

❖ **Planck's hypothesis of energy quanta** in 1900 (普朗克能量子假设):



A model of black body (黑体模型)



Black-body radiation (黑体辐射)

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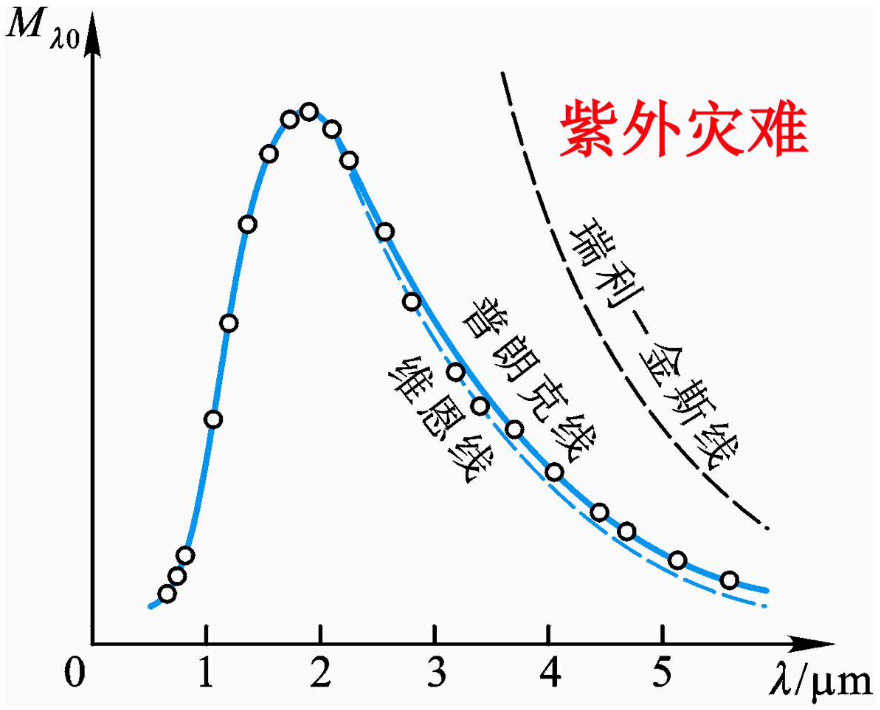
Wien Theory (维恩理论):

$$M_\lambda(T) = C_1\lambda^{-5}\mathrm{e}^{-\frac{C_2}{\lambda T}}$$

Rayleigh-Jeans Theory (瑞利-金斯理论):

$$M_\lambda(T) = C_3\lambda^{-4}T$$



Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Early-Stage Quantum Theories (早期量子理论)

❖ **Planck's hypothesis of energy quanta** in 1900 (普朗克能量子假设):

Planck Theory (普朗克理论):

$$M_{\lambda 0}(T) = 2\pi hc^2\lambda^{-5}\frac{1}{e^{\frac{hc}{\lambda kT}}-1} \qquad M_{\nu 0}(T) = \frac{2\pi h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}}-1}$$

Planck's Constant (普朗克常数): $h = 6.6260693\times 10^{-34}\,\mathrm{J\cdot s}$

Energy quanta (能量子) for black-body radiation or absorption:

$$\varepsilon = h\nu$$

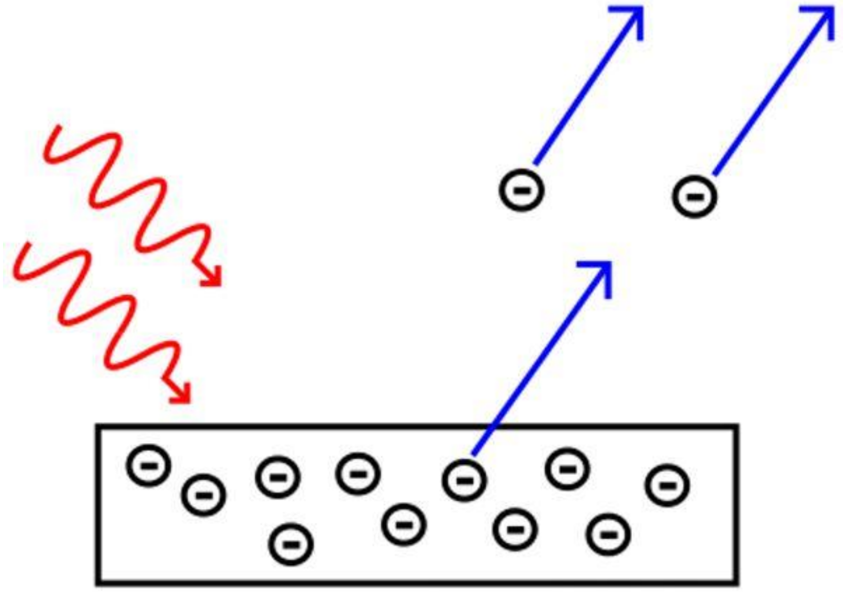
Max Planck
普朗克 (1858-1947)

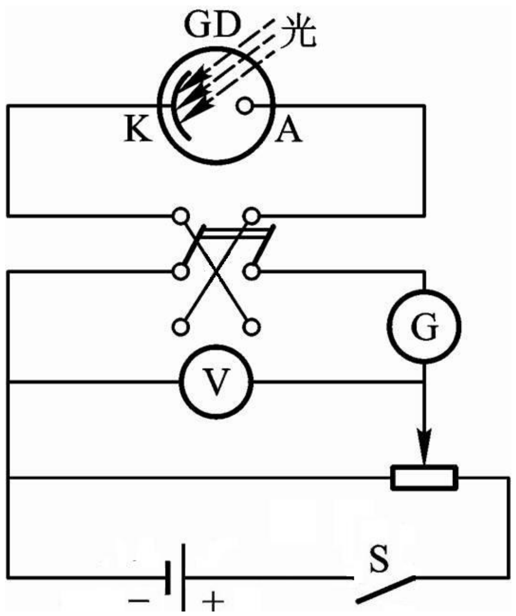
 1918

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Early-Stage Quantum Theories (早期量子理论)**

❖ **Einstein's photon theory** in 1905 (爱因斯坦光子理论):

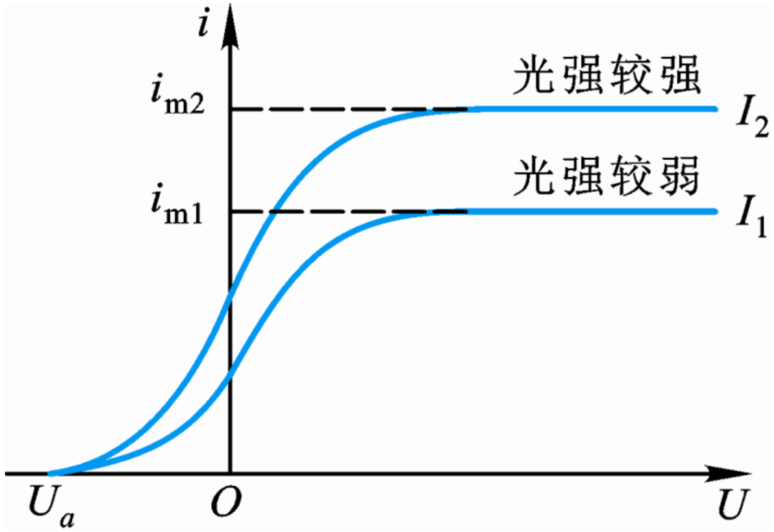


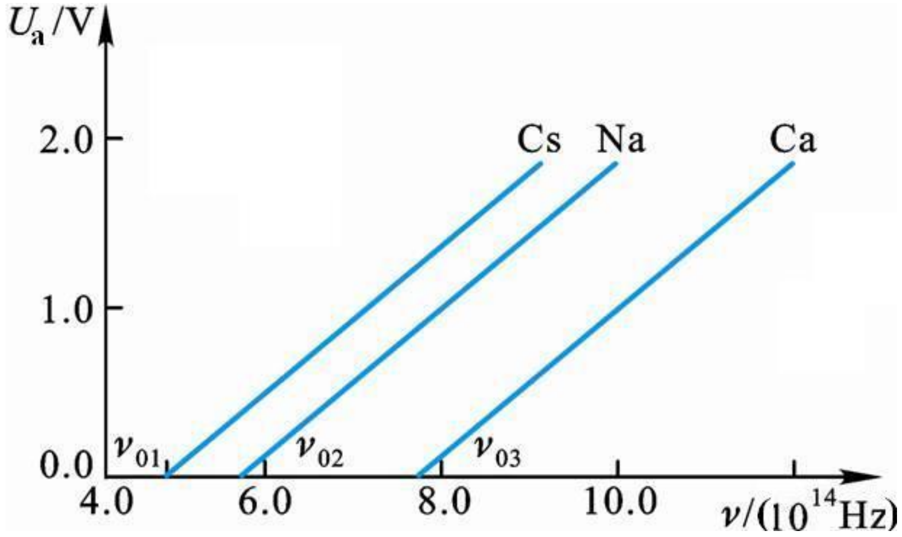


Photoelectric Effect (光电效应)

➢ Early-Stage Quantum Theories (早期量子理论)

❖ **Einstein's photon theory** in 1905 (爱因斯坦光子理论):





The Characteristics of Photoelectric Effect

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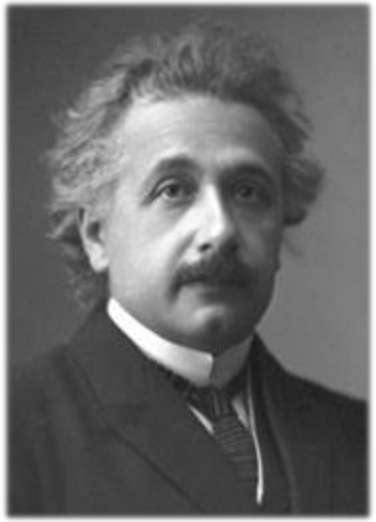
➢ Early-Stage Quantum Theories (早期量子理论)

❖ **Einstein's photon theory** in 1905 (爱因斯坦光子理论):

Photon Energy: $\varepsilon = h\nu$



Albert Einstein
爱因斯坦 (1879-1955)

1921

Photoelectric Equation:

$$h\nu = \frac{1}{2}mv_{\mathrm{m}}^{2} + A = eU_{\mathrm{a}} + A$$

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Early-Stage Quantum Theories (早期量子理论)

❖ **Bohr's theory of hydrogen atom** in 1913 (玻尔氢原子理论):

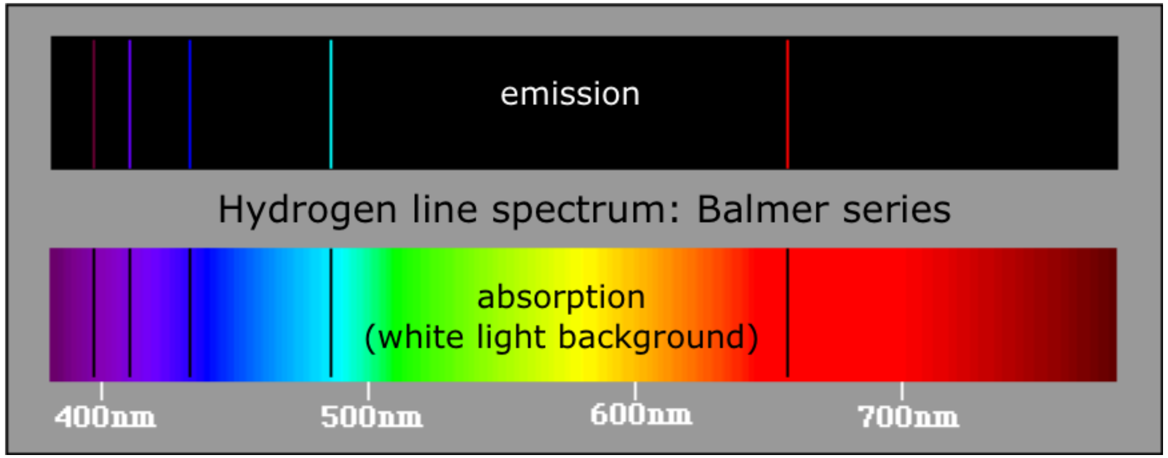
Rydberg Formula (里德伯公式):

$$\tilde{\nu} = R\left(\frac{1}{k^2} - \frac{1}{n^2}\right) \qquad \tilde{\nu} = \frac{1}{\lambda}$$

$$n>k \quad (n=k+1,\ k+2,\ \cdots)$$

Rydberg Constant (里德伯常数):

$$R = 1.096776 \times 10^7\,\mathrm{m}^{-1}$$



Balmer Series (巴耳末系) of Hydrogen Spectrum (k=2)

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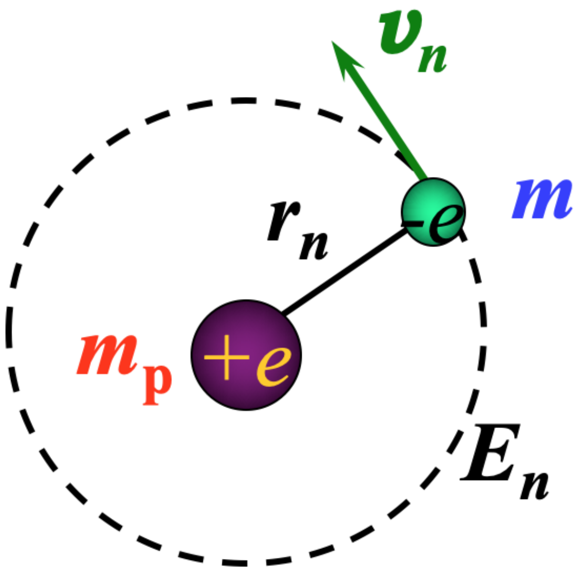
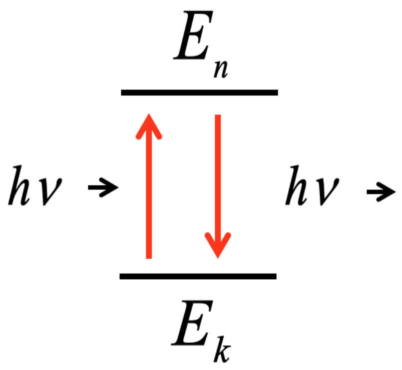


Stationary State (定态)

$$h\nu_{kn} = \left| E_k - E_n \right|$$



Frequency Condition (频率条件)

$$L = mv_n r_n = n\frac{h}{2\pi} = n\hbar$$

$$n = 1，2，3，\cdots$$

Quantization Condition (量子化条件)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

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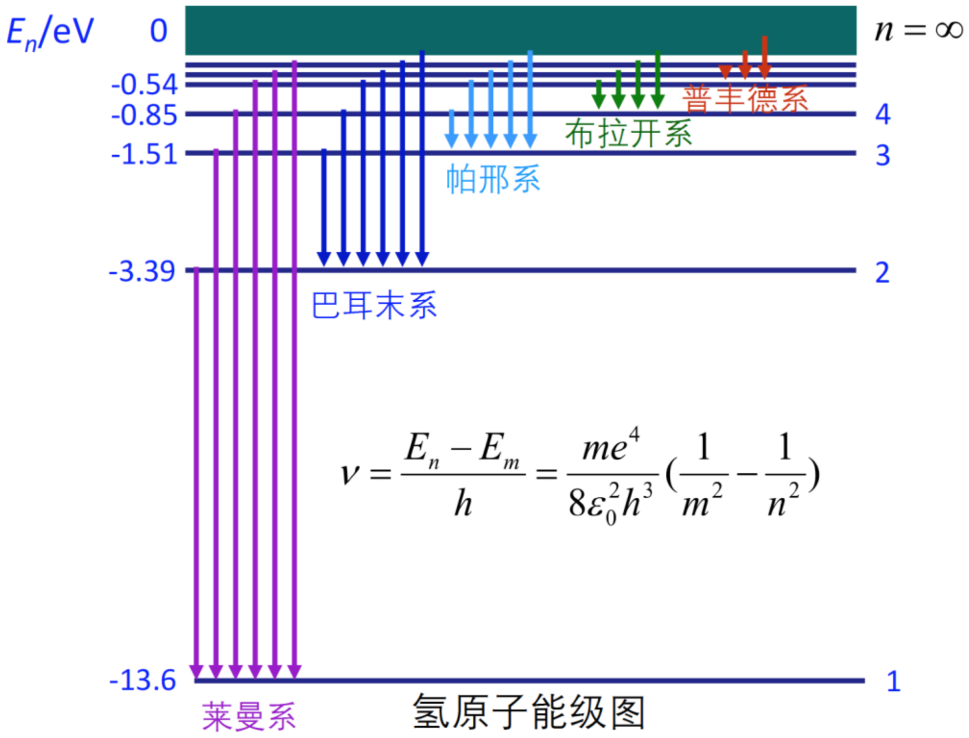


$$\nu = \frac{E_n - E_m}{h} = \frac{me^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

氢原子能级图

Niels Bohr
玻尔 (1885-1962)

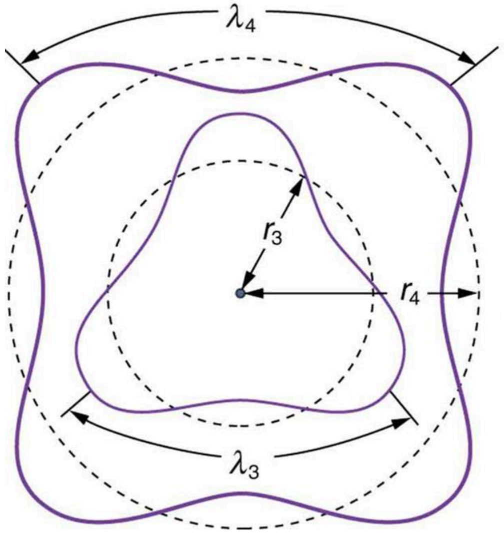
 1922

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Matter Wave (物质波)**

❖ **de Broglie's theory of matter wave** in 1924 (德布洛意物质波理论):

All matter can exhibit wave-like behavior, called **matter wave** or **de Broglie wave (德布洛意波).**



Matter Wave of Electron

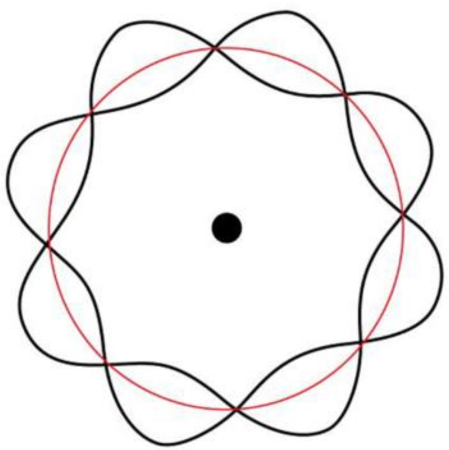
Louis de Broglie
德布洛意 (1892-1987)


1929

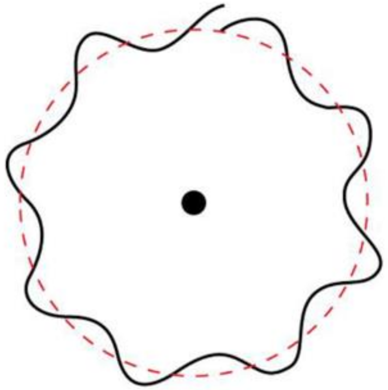
Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Matter Wave (物质波)**

❖ **de Broglie's theory of matter wave** in 1924 (德布洛意物质波理论):



Standing Wave
(allowed)



Non-Standing Wave
(not allowed)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Matter Wave (物质波)

❖ Wave-particle duality (波粒二象性):

The “**wave**” nature of a matter is described by its frequency $\boldsymbol{\nu}$ and wavelength $\boldsymbol{\lambda}$;

The “**particle**” nature of a matter is described by its energy $\boldsymbol{E}$ and momentum $\boldsymbol{p}$.

They are connected by the **de Broglie relations (德布洛意关系)**:

$$\boldsymbol{\nu} = \frac{\boldsymbol{E}}{\boldsymbol{h}} \qquad \boldsymbol{\lambda} = \frac{\boldsymbol{h}}{\boldsymbol{p}} \qquad \text{or} \qquad \boldsymbol{E} = \hbar\boldsymbol{\omega} \qquad \boldsymbol{p} = \hbar\boldsymbol{k}$$

$\boldsymbol{h}$: Planck constant (普朗克常数)

$\hbar = \frac{\boldsymbol{h}}{2\boldsymbol{\pi}}$: Reduced Planck constant (约化普朗克常数)

$\boldsymbol{\omega} = 2\boldsymbol{\pi\nu}$: Angular frequency (角频率)

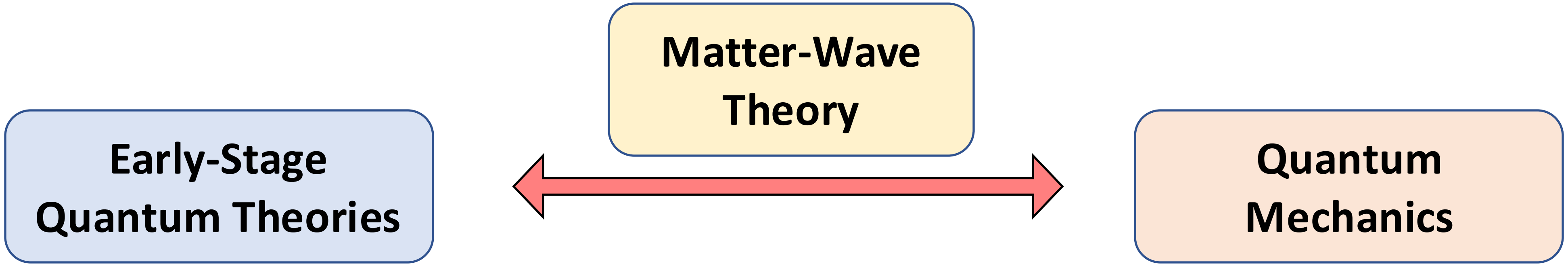
$\boldsymbol{k} = \frac{2\boldsymbol{\pi}}{\boldsymbol{\lambda}}$: Wavenumber (波数)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Matter Wave (物质波)

❖ The importance of matter-wave theory:

The matter-wave theory **bridges the gap** between the **early-stage quantum theories** and **quantum mechanics**!



Five Postulates of Quantum Mechanics

(量子力学的五个基本假定)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

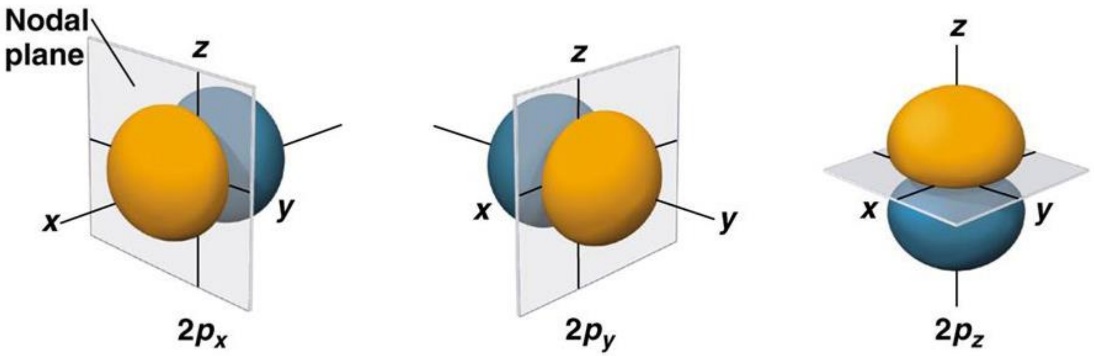
- **Five Postulates of Quantum Mechanics (量子力学的五个基本假定)**

  - **Wave Functions (波函数)**
  - **Operators of Observables (力学量算符)**
  - **Superposition Principle (态叠加原理)**
  - **Schrodinger Equation (薛定谔方程)**
  - **Identical Particles (全同粒子)**

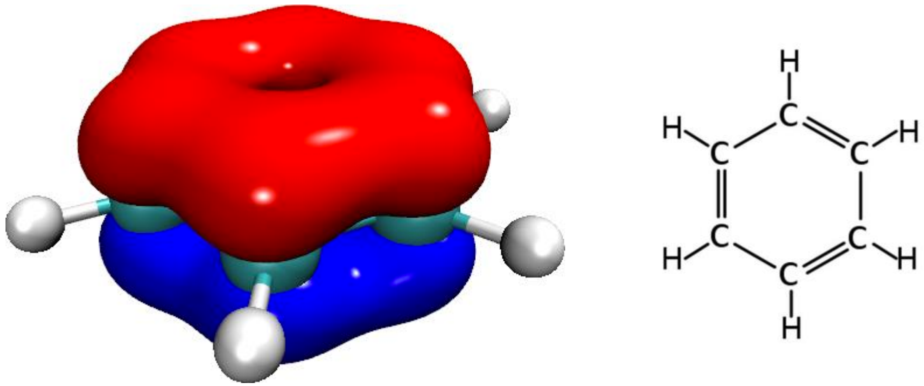
Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-1: Wave Function (基本假定一: 波函数)

❖ **Wave function** $\boldsymbol{\psi(r,t)}$ represents a mathematical description of the **quantum state (量子态)** of a quantum system (e.g., particles).



The wave functions of the 2p atomic orbitals of a hydrogen atom.



The wave function of a molecular orbital of a benzene molecule.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-1: Wave Function (基本假定一: 波函数)

❖ The physical meaning of wave function $\boldsymbol{\psi}(\boldsymbol{r},\boldsymbol{t})$ is that it represents a complex-valued **probability amplitude (概率幅)**.

$$\int_{-\infty}^{+\infty} |\boldsymbol{\psi}(\boldsymbol{r},\boldsymbol{t})|^2 \boldsymbol{dr} = \mathbf{1}$$

Normalization of wave function (波函数的归一化):

The **probability** of finding the particle in the whole real space is 1.

Max Born
玻恩 (1882-1970)

 1954

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

- **Five Postulates of Quantum Mechanics (量子力学的五个基本假定)**

  - Wave Functions (波函数)
  - **Operators of Observables (力学量算符)**
  - Superposition Principle (态叠加原理)
  - Schrodinger Equation (薛定谔方程)
  - Identical Particles (全同粒子)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-2: Operators of Observables (基本假定二: 力学量算符)

❖ An **operator** $\hat{O}$ corresponds to an **operation** to a wave function (quantum state):

$$\hat{O}\psi = \psi'$$

Linear operator (线性算符):

$$\hat{O}(c_1\psi_1 + c_2\psi_2) = c_1\hat{O}\psi_1 + c_2\hat{O}\psi_2$$

Here, c_1 and c_2 are arbitrary complex coefficients.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-2: Operators of Observables (基本假定二: 力学量算符)

❖ **Eigenvalues** and **eigenfunctions** of an operator **(算符的本征值与本征函数):**

If an operator $\hat{\boldsymbol{O}}$ satisfies: $\hat{\boldsymbol{O}}\boldsymbol{\psi} = \boldsymbol{O}\boldsymbol{\psi}$ ($\boldsymbol{O}$ is a number),

$\boldsymbol{O}$ is called an **eigenvalue** (本征值) of the operator $\hat{\boldsymbol{O}}$ on wave function $\boldsymbol{\psi}$;

$\boldsymbol{\psi}$ is accordingly called an **eigenfunction** (本征函数) of the operator $\hat{\boldsymbol{O}}$.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-2: Operators of Observables (基本假定二: 力学量算符)

❖ Hermitian operators (厄米算符):

A Hermitian operator is defined as an operator with its **conjugate transpose (共轭转置)** equal to itself:

$$\hat{O}^{+} = \hat{O}$$

or

$$\left(\hat{O}\psi, \varphi\right) = \left(\psi, \hat{O}\,\varphi\right) \qquad \left(\psi, \hat{O}\varphi\right) = \int \psi^{*}\hat{O}\varphi d\tau$$

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-2: Operators of Observables (基本假定二: 力学量算符)

❖ Hermitian operators (厄米算符):

The **eigenvalues** of an Hermitian operator are **real numbers (实数).**

$$\hat{O}\psi_n = O_n\psi_n$$

The **eigenfunctions** of an Hermitian operator are **orthogonal (正交)** to each other.

$$(\psi_n, \psi_m) = 0 \qquad n \neq m$$

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-2: Operators of Observables (基本假定二: 力学量算符)

❖ Observables (力学量):

An **observable** is a physical quantity that can be measured, such as position $\boldsymbol{r}$, momentum $\boldsymbol{p}$, angular momentum $\boldsymbol{l}$, kinetic energy $\boldsymbol{T}$, potential energy $\boldsymbol{V}$, Hamiltonian $\boldsymbol{H}$…

An observable corresponds to a **linear Hermitian operator (线性厄米算符).**

$$\boldsymbol{r} \to \hat{\boldsymbol{r}} = \boldsymbol{r} \qquad \boldsymbol{p} \to \hat{\boldsymbol{p}} = -i\hbar\nabla \qquad \boldsymbol{l} \to \hat{\boldsymbol{l}} = \boldsymbol{r} \times \hat{\boldsymbol{p}}$$

$$\boldsymbol{T} \to \hat{\boldsymbol{T}} = -\frac{\hbar^2}{2m}\nabla^2 \qquad \boldsymbol{V} \to \hat{\boldsymbol{V}} = \boldsymbol{V} \qquad \boldsymbol{H} \to \hat{\boldsymbol{H}} = \hat{\boldsymbol{T}} + \boldsymbol{V}$$

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-2: Operators of Observables (基本假定二: 力学量算符)

❖ Hamiltonian (哈密顿量):

Hamiltonian is an operator corresponding to the **total energy** of a quantum system, which is expressed as the sum of operators corresponding to the **kinetic energy** (动能) and **potential energy** (势能):

$$\boldsymbol{\hat{H}} = \boldsymbol{\hat{T}} + \boldsymbol{\hat{V}}$$

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \qquad \hat{V} = \hat{V}(r,t)$$

Here, m is the mass of the particle and $\hat{p} = -i\hbar\nabla$ is the momentum operator.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Five Postulates of Quantum Mechanics (量子力学的五个基本假定)**

- ❑ Wave Functions (波函数)
- ❑ Operators of Observables (力学量算符)
- ❑ **Superposition Principle (态叠加原理)**
- ❑ Schrodinger Equation (薛定谔方程)
- ❑ Identical Particles (全同粒子)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-3: Superposition Principle (基本假定三: 态叠加原理)

- The **superposition principle** states that any quantum state can be represented as a **superposition of two or more other distinct states**:

$$\boldsymbol{\psi = \alpha_1\psi_1 + \alpha_2\psi_2 + \cdots + \alpha_n\psi_n}$$

Here, $\boldsymbol{\alpha_n}$ denotes **complex coefficients**.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-3: Superposition Principle (基本假定三: 态叠加原理)

❖ If a quantum state $\boldsymbol{\psi}$ is represented as a superposition of the eigenstates $\boldsymbol{\phi_i}$ of an observable $\widehat{\boldsymbol{O}}$, the average value of $\widehat{\boldsymbol{O}}$ on state $\boldsymbol{\psi}$ is:

$$\langle \widehat{\boldsymbol{O}} \rangle = \langle \boldsymbol{\psi} | \widehat{\boldsymbol{O}} | \boldsymbol{\psi} \rangle = \sum_{\boldsymbol{i}} |\boldsymbol{c_i}|^2 \boldsymbol{O_i}$$

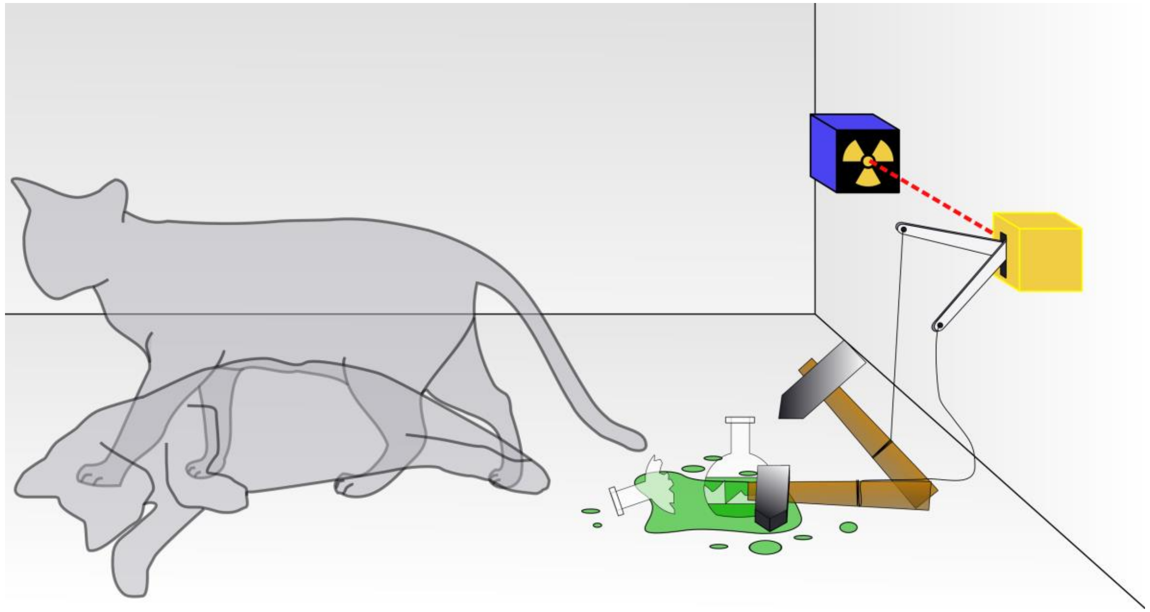
$$\psi = \sum_i c_i \phi_i \qquad\qquad \hat{O}\psi_n = O_n \psi_n$$

Here, $|\boldsymbol{c_i}|^2$ denotes the probability of the observable with eigenvalue $\boldsymbol{O_i}$.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-3: Superposition Principle (基本假定三: 态叠加原理)

❖ Schrodinger's Cat (薛定谔的猫):



Schrodinger's cat represents a **thought experiment (思想实验)** proposed by Schrodinger in 1935 to doubt the **Copenhagen interpretation of quantum superposition**.

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Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-4: Schrodinger Equation (基本假定四: 薛定谔方程)

❖ **Schrodinger equation** represents the **equation of motion (运动方程)** of a quantum system, proposed by Schrodinger in 1926:

$$i\hbar\frac{\partial}{\partial t}\boldsymbol{\psi}(\boldsymbol{r},\boldsymbol{t}) = \hat{\boldsymbol{H}}\boldsymbol{\psi}(\boldsymbol{r},\boldsymbol{t})$$

$\hat{\boldsymbol{H}}$ denotes the **Hamiltonian** of the quantum system.

Erwin Schrödinger
薛定谔 (1887-1961)

 1933

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-4: Schrodinger Equation (基本假定四: 薛定谔方程)

❖ **Time-independent Schrodinger equation (定态薛定谔方程):**

$$\hat{\boldsymbol{H}}\boldsymbol{\psi}(\boldsymbol{r}) = \boldsymbol{E}\boldsymbol{\psi}(\boldsymbol{r})$$

Here, $\boldsymbol{E}$ is a constant equal to the **total energy** of the system at state $\boldsymbol{\psi}(\boldsymbol{r})$.

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Five Postulates of Quantum Mechanics (量子力学的五个基本假定)**

❑ Wave Functions (波函数)

❑ Operators of Observables (力学量算符)

❑ Superposition Principle (态叠加原理)

❑ Schrodinger Equation (薛定谔方程)

❑ **Identical Particles (全同粒子)**

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-5: Identical Particles (基本假定五: 全同粒子)

❖ **Identical particles** (indistinguishable particles) are particles that cannot be distinguished from one another.

❖ There are two distinct categories of identical particles:

Identical Particles

- **Bosons** (玻色子): With integer spin ($s = 0, \hbar, 2\hbar, 3\hbar, \ldots$)
- **Fermions** (费米子): With half integer spin ($s = \frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{5}{2}\hbar, \ldots$)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

❑ Postulate-5: Identical Particles (基本假定五: 全同粒子)

❖ **Bosons**: Wave function with **exchange symmetry (交换对称性)**

$$\psi(q_1, \cdots, \boldsymbol{q_i}, \cdots, \boldsymbol{q_j}, \cdots q_N) = \psi(q_1, \cdots, \boldsymbol{q_j}, \cdots, \boldsymbol{q_i}, \cdots q_N)$$

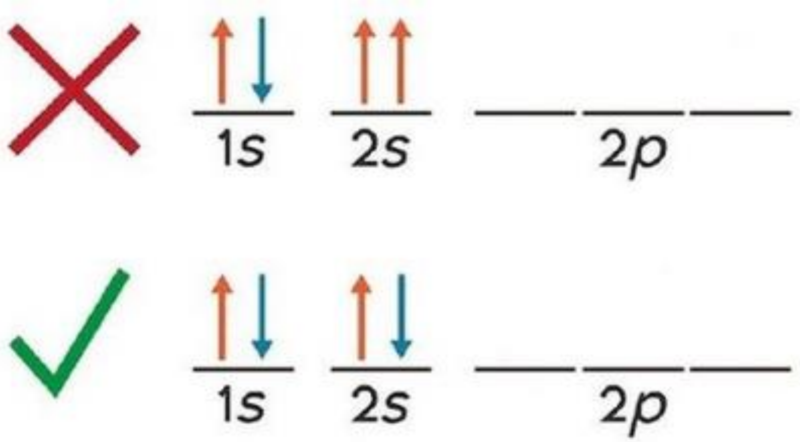
❖ **Fermions**: Wave function with **exchange antisymmetry (交换反对称性)**

$$\psi(q_1, \cdots, \boldsymbol{q_i}, \cdots, \boldsymbol{q_j}, \cdots q_N) = -\psi(q_1, \cdots, \boldsymbol{q_j}, \cdots, \boldsymbol{q_i}, \cdots q_N)$$

❑ Postulate-5: Identical Particles (基本假定五: 全同粒子)

❖ Pauli Exclusion Principle (泡利不相容原理):

Pauli proved in 1925 that two or more electrons (more generally, **identical Fermions**) cannot occupy simultaneously the same quantum state.



Example: It is impossible for two electrons of a poly-electron atom to have the same values of the 4 quantum numbers.

Wolfgang Pauli
泡利 (1900-1958)


1945

Commutation and Uncertainty Principle

（对易与不确定性原理）

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Commutation Relation (对易关系)

❖ For two operators $\hat{A}$ and $\hat{B}$, a **commutator (对易式)** is defined as:

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

- If $[\hat{A}, \hat{B}] = 0$, operators $\hat{A}$ and $\hat{B}$ are **commuting** (对易的).
- If $[\hat{A}, \hat{B}] \neq 0$, operators $\hat{A}$ and $\hat{B}$ are **non-commuting** (非对易的).

e.g., $[x, \hat{p}_x] = i\hbar$ $[y, \hat{p}_y] = i\hbar$ $[z, \hat{p}_z] = i\hbar$

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Complete Set of Commuting Observables (对易力学量完全集)**

❖ A CSCO is a set of **commuting operators** (e.g., $\hat{A}_1, \hat{A}_2, \hat{A}_3 \ldots$) whose eigenvalues completely specify the state of a quantum system.

$$\text{e.g., } \hat{H}, \hat{L}^2, \hat{L}_z \text{ and } \hat{S}_z$$

❖ Any state $\boldsymbol{\psi}$ of the quantum system can be expanded by the common eigenfunctions (e.g., ψ_n) of the CSCO.

$$\boldsymbol{\psi} = \sum_{\boldsymbol{n}} a_n \psi_n$$

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ Uncertainty Principle (不确定性原理)

❖ Heisenberg proposed in 1927 that the more precisely the position ($\boldsymbol{x}$) of a particle is determined, the less precisely its momentum ($\boldsymbol{p_x}$) can be known, and *vice versa*.

$$\boldsymbol{\sigma_x \sigma_{p_x}} \geq \frac{\hbar}{\mathbf{2}}$$

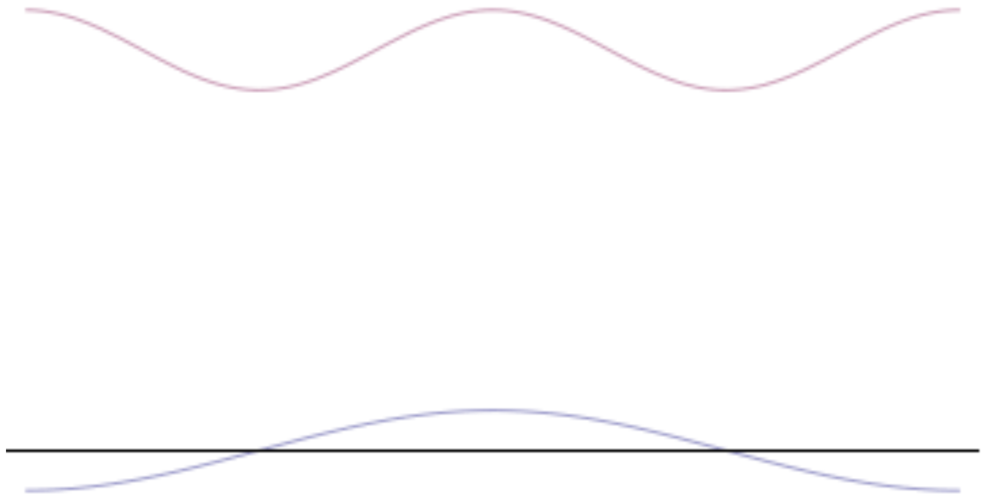
$$\boldsymbol{\sigma_A} = \sqrt{\langle \boldsymbol{\hat{A}}^2 \rangle - \langle \boldsymbol{\hat{A}} \rangle^{\mathbf{2}}} \qquad \langle \boldsymbol{\hat{A}} \rangle = (\psi, \hat{A}\psi)$$

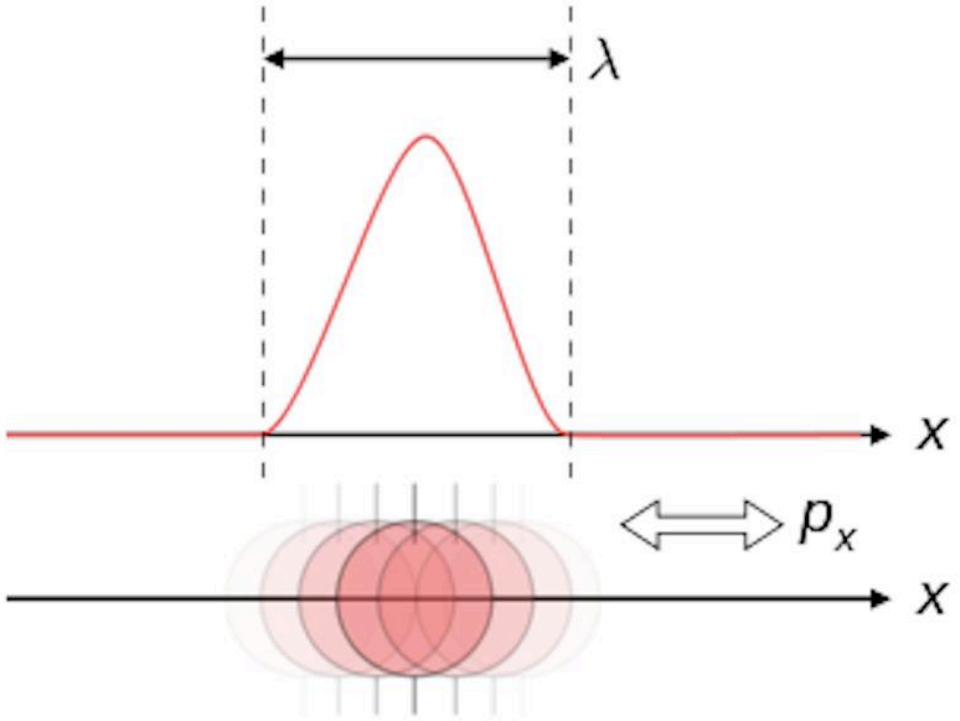
Werner Heisenberg
海森堡 (1901-1976)

 1932

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Uncertainty Principle (不确定性原理)**





Summary (总结)

Appendix 1: Basics of Quantum Mechanics (量子力学基础)

➢ **Summary (总结)**

❖ **A brief introduction to quantum mechanics;**

❖ **Five postulates of quantum mechanics:**

1) Wave functions

2) Operators of observables

3) Superposition principle

4) Schrodinger equation

5) Identical particles

❖ **Commutation and uncertainty principle.**