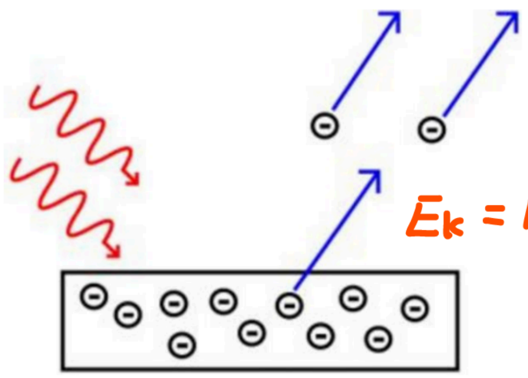
量子力学基本概念

Wave-Particle Duality

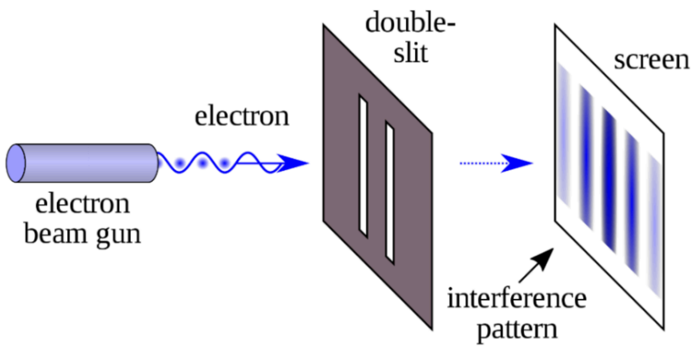
Photoelectric effect



$E_k = h\nu - \phi$

Double-slit experiment

双缝实验，电子→电子有波动特性



- The energy of ejected electrons did *not* depend on the intensity of the incoming light, but instead on its *frequency*.
  射出的电子的能量并不取决于入射光的强度，而是取决于其频率。

High frequency light-> High energy electrons
High intensity light-> More ejected electrons

- The electrons passing through the two slits to interfere, producing bright and dark bands on the screen — a result that would not be expected for classical particles.

Matter Wave

- All matter can exhibit wave-like behavior, proposed by Louis de Broglie（德布罗意）in 1924.

- De Broglie equations:

$$\boxed{p = \frac{h}{\lambda} = \hbar k}$$

p: momentum
λ: wavelength
k=2π/ *λ*: wave vector

$$\boxed{E = h\nu = \hbar\omega}$$

Planck constant: $h = 6.63 \times 10^{-34} J.s$

Also referred to as the Planck-Einstein relation（普朗克–爱因斯坦关系式）

Reduced Planck constant: $\hbar = h / 2\pi = 1.05 \times 10^{-34} J.s$

约化普朗克常数

Heisenberg Uncertainty Principle

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约化普朗克常数

Wave Function

- **Wave function *ψ*(x, t)**: a complex-valued（复值） probability amplitude, which is a mathematical description of the quantum state of an isolated quantum system.

  复值概率振幅，是孤立量子系统量子态的数学描述。

- Physical meaning: $|\Psi(x,t)|^2$ is the probability density function, with $|\Psi(x,t)|^2 dx$ describing the probability to find the particle between *x* and *x*+dx at time *t*.

- Normalization: $\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1$

- Other representation: $|\Psi(p,t)|^2$ $|\Psi(x,y,z,t)|^2$

  $|\Psi(r,\theta,\phi,t)|^2$ $|\Psi(\vec{r}_1, \vec{r}_2 ... \vec{r}_N, t)|^2$

Schrödinger Equation

一维位置基时变薛定谔方程：

➢ Time-dependent Schrödinger Equation in position basis in 1D:

$$j\hbar\frac{\partial\Psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\cdot\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)$$ 本质上是一个公理！！！

V(x): time-independent potential function 势场分布，不随时间变化
m: particle mass
$j=\sqrt{-1}$

求解：

令 $\Psi(x,t)=\psi(x)\Phi(t)$

则薛定谔方程化为： $j\hbar\cdot\psi(x)\Phi'(t)=-\frac{\hbar^2}{2m}\cdot\psi''(x)\Phi(t)+V(x)\psi(x)\Phi(t)$

$$j\hbar\frac{\Phi'(t)}{\Phi(t)}=-\frac{\hbar^2}{2m}\cdot\frac{\psi''(x)}{\psi(x)}+V(x)$$

时间的函数恒等于空间的常数，则必然都恒等于一个常量。可以证明，这个常量就是粒子总能量E

$$\Longrightarrow j\hbar\frac{\Phi'(t)}{\Phi(t)}=E\longrightarrow\Phi(t)=e^{-j\frac{E}{\hbar}t}=e^{-j\omega t}\qquad ①$$

$$\Longrightarrow \psi''(x)+\frac{2m}{\hbar^2}[E-V(x)]\psi(x)=0\qquad ②$$

(1) 考虑自由空间中的电子(势场V(x)处处为零)

$$\Longrightarrow \psi''(x)+\frac{2mE}{\hbar^2}\psi(x)=0\longrightarrow r^2+\frac{2mE}{\hbar^2}=0\qquad r=\pm j\sqrt{\frac{2mE}{\hbar^2}}=\pm j\sqrt{\frac{p^2}{\hbar^2}}=\pm jk$$

通解：

① 行波解 $\psi(x)=C_1e^{jkx}+C_2e^{-jkx}$

$$\Psi(x,t)=C_1e^{j(-\omega t+kx)}+C_2e^{j(-\omega t-kx)}$$

② 驻波解 $\psi(x)=C_1'\cos kx+C_2'\sin kx$

(2) 考虑无限深势阱，见下

0 ~ L内，仍有V(x)=0，则： $\psi(x)=C_1\cos kx+C_2\sin kx$

边界条件： $\psi(x=0)=0,\ \psi(x=L)=0\longrightarrow C_1=0,\ kL=n\pi,\ k=\frac{n\pi}{L}$

归一化： $\int_0^L|\psi(x)|^2dx=1\longrightarrow C_2=\sqrt{\frac{2}{L}}$

故

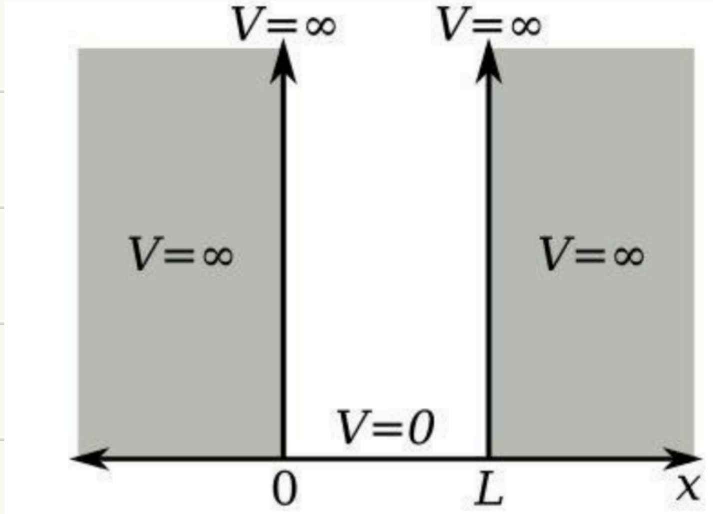
Infinite Potential Well

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \qquad n = 1, 2, 3, \cdots$$

$$E = \frac{n^2 \hbar^2 \pi^2}{2mL^2}$$

能量本征值

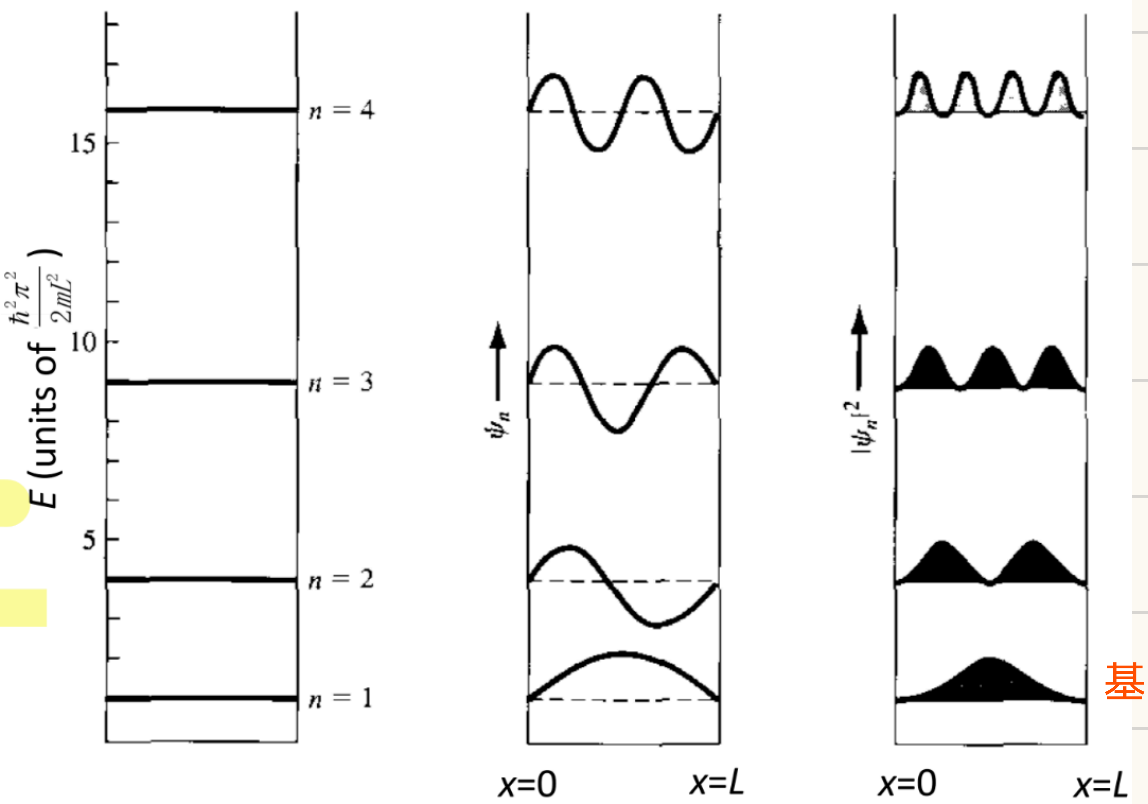
eigen energy



能量是量子化的

- The energy is quantized!
- As the energy increases, the probability of finding the particle at any given value of x becomes more uniform.

均匀



基态

Solving the Bound State Problem

(1) Infinte Potential Well

束缚态边界问题，能量不可连续

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \qquad E = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \qquad n = 1, 2, 3, \cdots$$

(2) Step Potential（台阶势）Function

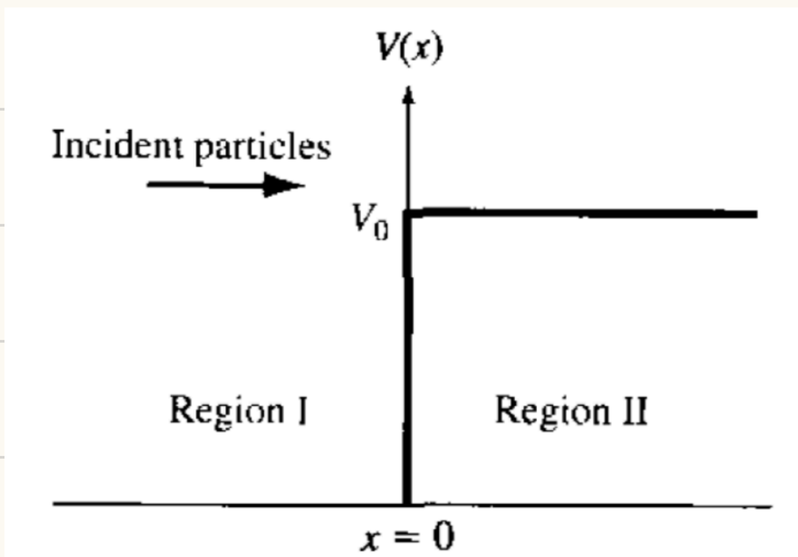
非束缚态边界问题，能量可连续

$(V_0 > E)$

Region I $\quad V(x) = 0$

$$\psi''(x) + \frac{2mE}{\hbar^2} \psi(x) = 0$$

$$\psi_1(x) = A_1 e^{jk_1 x} + B_1 e^{-jk_1 x} \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$



Region II $\quad V(x) = V_0 > E$

$$\psi''(x) - \frac{2m(V_0 - E)}{\hbar^2} \psi(x) = 0$$

$$\psi_2(x) = A_2 e^{-k_2 x} + B_2 e^{k_2 x} \qquad k_2 = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$$

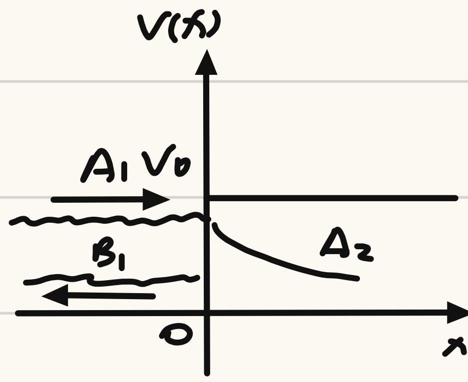
边界条件:

波函数有界: $B_2 = 0$

边界条件: $\psi_1(0) = \psi_2(0) \longrightarrow A_1 + B_1 = A_2$

$$\frac{\partial \psi_1(x)}{\partial (x)}\Big|_{x=0} = \frac{\partial \psi_2(x)}{\partial x}\Big|_{x=0} \longrightarrow jk_1 A_1 - jk_1 B_1 = -k_2 A_2$$

$$\longrightarrow \begin{cases} B_1 = \dfrac{-(k_2^2 + 2jk_1k_2 - k_1^2)}{k_1^2 + k_2^2} A_1 \\[2ex] A_2 = \dfrac{2k_1(k_1 - jk_2)A_1}{k_1^2 + k_2^2} \end{cases}$$



Define a reflection coefficient R and transmission coefficient T:

$$R = \frac{v_r \cdot B_1 \cdot B_1^*}{v_i \cdot A_1 \cdot A_1^*} \qquad T = \frac{v_t \cdot A_2 \cdot A_2^*}{v_i \cdot A_1 \cdot A_1^*}$$

$= 1$ $\qquad > 0 \qquad R + T \neq 1$

理解：反射系数与透射系数之和大于1

因为可能确实有粒子透射进入x>0的区域，但是随着势垒向无穷远处延伸，粒子最终无法达到无穷远，最终都会被反射回来

然而，当势垒并不向无穷远处延伸，而是有有限的宽度时，这个时候我们就要考虑能够穿透这堵墙的粒子，即要考虑穿透率。这就是下面的方势垒问题。

(3) Square Potential Barrier

非束缚态边界问题，能量可连续

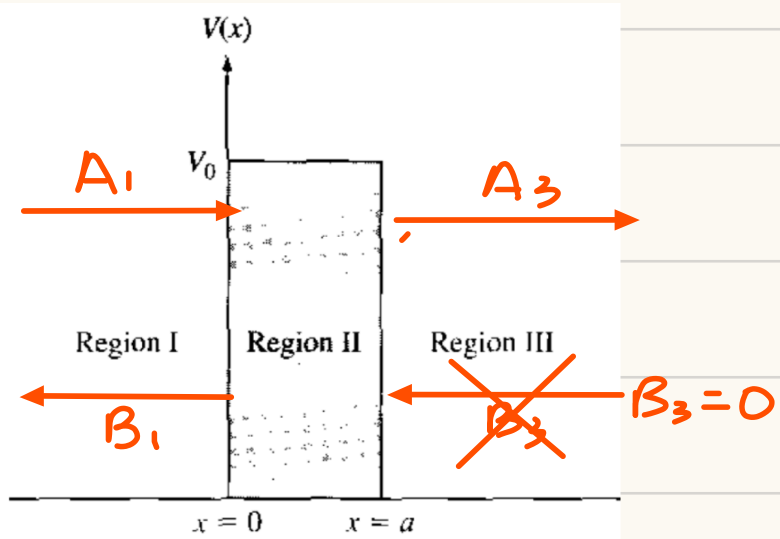
In Region I and III:

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \qquad k_1 = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi_1(x) = A_1 e^{jk_1 x} + B_1 e^{-jk_1 x}$$

$$\psi_3(x) = A_3 e^{jk_1 x} + B_3 e^{-jk_1 x}$$

No reflectance in Region III -> $B_3 = 0$



In Region II:

$$\frac{\partial^2 \psi(x)}{\partial x^2} - \frac{2m(V_0 - E)}{\hbar^2}\psi(x) = 0 \qquad k_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

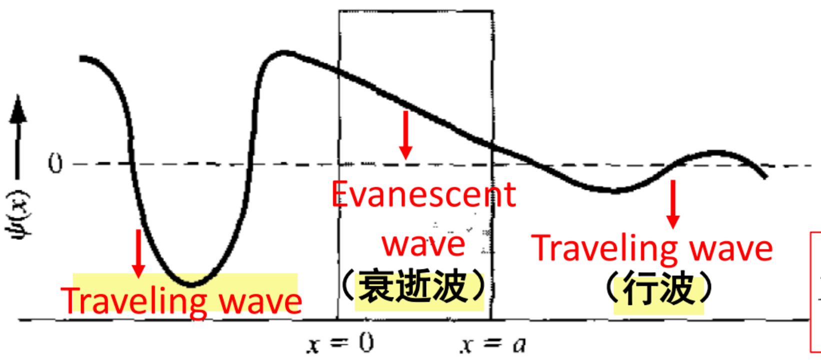
$$\psi_2(x) = A_2 e^{k_2 x} + B_2 e^{-k_2 x}$$

边界条件:

$$\psi_1(0) = \psi_2(0), \quad \left.\frac{\partial \psi_1(x)}{\partial x}\right|_{x=0} = \left.\frac{\partial \psi_2(x)}{\partial x}\right|_{x=0}$$

$$\psi_2(a) = \psi_3(a), \quad \left.\frac{\partial \psi_2(x)}{\partial x}\right|_{x=a} = \left.\frac{\partial \psi_3(x)}{\partial x}\right|_{x=a}$$

- Parameters to be determined: A_1, B_1, A_2, B_2, A_3



Wave functions through the potential barrier

Transmission coefficient

$$\boxed{T = \frac{v_t \cdot A_3 \cdot A_3^*}{v_i \cdot A_1 \cdot A_1^*} = \frac{A_3 \cdot A_3^*}{A_1 \cdot A_1^*}}$$

I，III都是自由空间vt=vi

$$\boxed{T \approx 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)e^{-2k_2 a} \text{ if } E << V_0}$$

认为E<V0时，近似得到T: $T \approx 16\frac{E}{V_0}\left(1-\frac{E}{V_0}\right)e^{-2k_2 a}$ $\quad k_2 = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$

$\xrightarrow{\frac{E}{V_0}}$

$V_0\uparrow \quad k_2\downarrow$

$V_0\uparrow \quad$ 抛$\downarrow$

案例：量子隧穿

Consider an electron with an energy of 2 eV impinging on a potential barrier with $V_0 =$ 20 eV and a width of 3 Å. $1\,\text{Å} = 0.1\,\text{nm} = 10^{-10}\,\text{m}$

$$\boxed{T \approx 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)e^{-2K_2 a}}$$

The factor K_2 is

$$K_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2(9.11 \times 10^{-31})(20 - 2)(1.6 \times 10^{-19})}{(1.054 \times 10^{-34})^2}}$$

or

$$K_2 = 2.17 \times 10^{10}\ \text{m}^{-1}$$

Then

$$T = 16(0.1)(1 - 0.1)\exp[-2(2.17 \times 10^{10})(3 \times 10^{-10})]$$

and finally

$$T = 3.17 \times 10^{-6}$$

The tunneling probability may appear to be a small value, but the value is not zero.

Electron in the hydrogen atom

Bohr's Model for Isolated Hydrogen Atom

Classical Bohr theory: The nucleus is a heavy, positively charged proton and the electron is a light, negatively charged particle, which is revolving around the nucleus.

波尔的氢原子模型依旧采用经典的方法

库仑力提供向心力: $\frac{q^2}{4\pi\varepsilon_0 r^2} = m\frac{v^2}{r}$

系统总能量: $E_t = E_k + E_p = \frac{1}{2}mv^2 - \frac{q^2}{4\pi\varepsilon_0 r} = -\frac{1}{2}\times\frac{q^2}{4\pi\varepsilon_0 r}$

玻尔假设角动量是量子化的: $L = r\times mv = n\hbar \quad n=1,2,3,\cdots$

因此: $E_n = -\frac{m_0 q^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2}$

$m_0 = 9.1\times10^{-31}\ kg$: 电子质量

$q = 1.6\times10^{-19}\ C$: 元电荷

$\varepsilon_0 = 8.85\times10^{-12} F\cdot m^{-1}$ 真空电容率

能解释氢原子谱线，但有问题！无法解释谱线中的精细结构，并且只能解释氢原子

因为是用的方法还是经典力学的方法。需要回到薛定谔方程求解

Calculation using Quantum Mechanics Technique

Time-independent Schrödinger Equation in 3D:

$$\nabla^2\psi(r,\theta,\varphi) + \frac{2m_0(E-V(r))}{\hbar^2}\psi(r,\theta,\varphi) = 0$$

采用球坐标表示，这样势场函数只与极径有关

拉普拉斯算符展开:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{2m_0(E-V(r))}{\hbar^2} = 0$$

Using the separation-of-variables technique, assume:

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

薛定谔方程化为:

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Phi}\cdot\frac{\partial^2\Phi}{\partial\varphi^2} + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + r^2\sin^2\theta\frac{2m_0(E-V)}{\hbar^2} = 0$$

The second term is only a function of ϕ , let:

$$\frac{1}{\Phi}\cdot\frac{\partial^2\Phi}{\partial\varphi^2}=-m^2 \quad m=0,1,2,\cdots \qquad \text{m: quantum number}$$

We can further separate the variables θ and r with quantum numbers l and n :

n = 1, 2, 3,…, principal quantum number 主量子数，描述电子绕核运动的能量或电子的能级

l = n-1, n-2, …, 0，azimuthal quantum number 角量子数 描述电子绕核运动轨迹(电子云)的形状

|m| = l, l-1, …, 0，magnetic quantum number 磁量子数 描述电子云方向或电子的磁矩

根据求解得到:

$$E_n=-\frac{m_0 q^4}{(4\pi\varepsilon_0)^2\,2\hbar^2 n^2} \quad n=1,2,3,\cdots$$

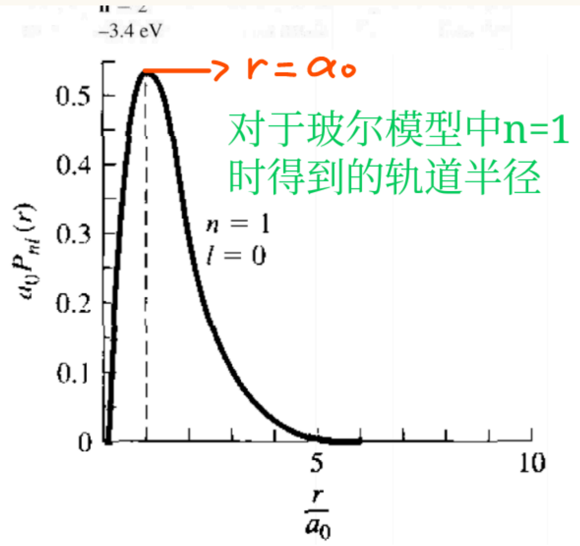
与玻尔模型得到的结果相同

For lowest energy level, the wave function is:

$$\boxed{\Psi_{100}=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}}$$

Bohr radius: $a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_0e^2}=0.529\text{Å}$

（玻尔半径）



The electron energy is discrete → Energy band(能带)