

CHAPTER 5

量子力學

Quantum Mechanics

5.1 量子力學 Quantum Mechanics

波耳氫原子理論應用上的限制:

— 只能應用於氫原子與其它單電子離子, 如 He^+ 與 Li^{2+} --
甚至不能使用在 He 原子.

Ex: 習題(4.)34, 35

— 無法解釋:

- 某些光譜線強度較大(能階躍遷機率較大).
- 某些特別光譜是由幾個波長接近卻又分開的光譜線組成.

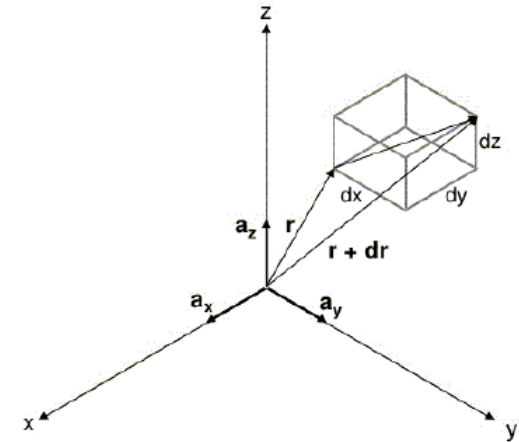
⇒ 量子力學的產生

物質波的波函數

物質波可用波函數 $\Psi(x,y,z,t)$ 來描述

波函數的強度 $|\Psi(x,y,z,t)|^2$ 的物理意義

波函數與其共軛複數的乘積

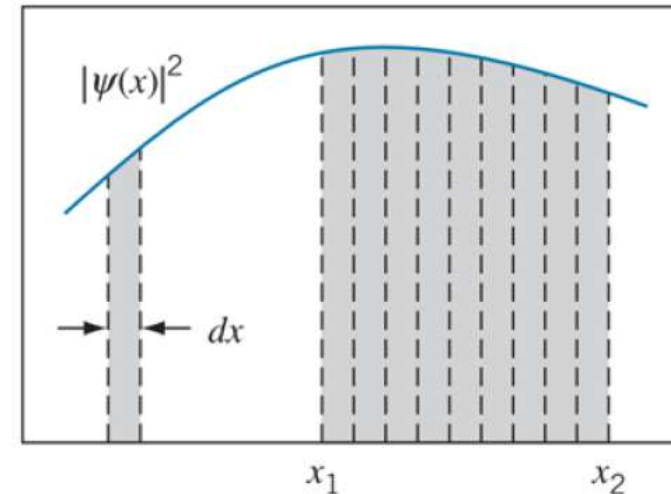


- t 時刻，出現在空間 (x,y,z) 點附近單位體積內的粒子數與總粒子數之比
- t 時刻，粒子出現在空間 (x,y,z) 點附近單位體積內的機率
- t 時刻，粒子在空間的機率密度分布
(1926 年Max Born)

- 機率 $P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 dx$

- 歸一化(Normalization)

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$$



- 良好的波函數(Well-Behaved Wave Functions)

1. Ψ 於任何地方都是連續且為單一值。

2. $\partial \Psi / \partial x$, $\partial \Psi / \partial y$, $\partial \Psi / \partial z$ 於任何地方都是連續且為單一值。

二次微分不發散！

3. Ψ 可被 歸一化，也就是說當 $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$, $z \rightarrow \pm\infty$ 時， Ψ 趨近於 0，積分值

$\int |\Psi|^2 dV$ 於整個空間時為有限常數。

5.4 線性與疊加

Linearity and Superposition

$$|\Psi|^2 = |\Psi_1 + \Psi_2|^2 = \Psi_1^* \Psi_1 + \Psi_2^* \Psi_2 + \Psi_1^* \Psi_2 + \Psi_1 \Psi_2^*$$

干涉項！

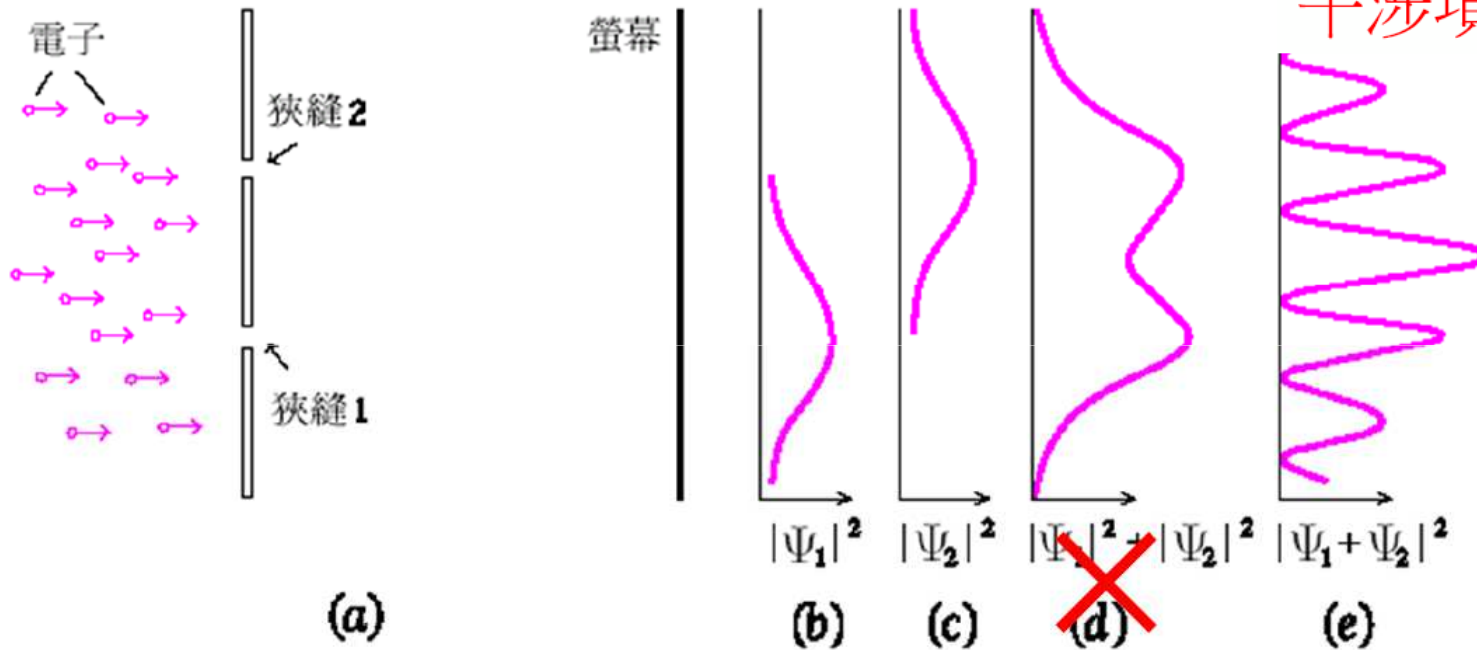


圖5.2 (a) 雙狹縫實驗的安排。(b) 只有狹縫 1 開啟時螢幕上的電子強度。(c) 只有狹縫 2 開啟時螢幕上的電子強度。(d) 將 (b) 與 (c) 強度相加的結果。(e) 開啟狹縫 1 及狹縫 2 實際上螢幕的強度。波函數 Ψ_1 和 Ψ_2 相加 ($\Psi = \Psi_1 + \Psi_2$) 可得到螢幕上的結果，而不是 $|\Psi_1|^2$ 與 $|\Psi_2|^2$ 相加。

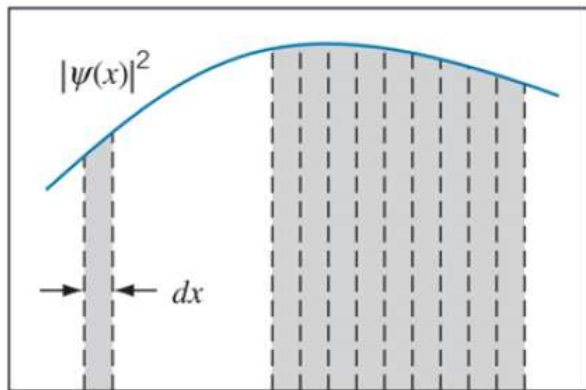
5.5 期望值 Expectation Values

如何由波函數中擷取資訊。

為了更清楚地說明這個過程，我們先回答一個稍微有點不同的問題：一群在 x 軸上分布的相同粒子平均位置 $\bar{x}$ 在哪裡？如果在 x_1 有 N_1 個粒子、 x_2 有 N_2 個粒子……依此類推，平均位置就會是在整群粒子分布的重心上，所以

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\sum N_i x_i}{\sum N_i} \quad (5.16)$$

當我們處理單一粒子時，我們必須將在 x_i 位置的粒子數 N_i 替換為該粒子在 x_i 附近的 dx 範圍內出現的機率 P_i 。這個機率為



$$P_i = |\Psi_i|^2 dx \quad \Rightarrow \quad \langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}$$

對於已歸一化的 (normalized) 波函數

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}$$

位置的期望值 $\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi|^2 dx$

對任一物理量，只要是由波函數 Ψ 描述的粒子的位置函數，如位能 $U(x)$ ，其期望值均可以下式求得

期望值 $\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\Psi|^2 dx$

但是動量的期望值? (由測不準原理的限制，不存在 $p(x)$!)

動量的期望值 $\langle p \rangle$ 無法由此法算得，因為根據測不準原理沒有這樣的函數 $p(x)$ 存在。如果給定 x ，則 $\Delta x = 0$ ，因為 $\Delta x \Delta p \geq \hbar/2$ 而無法找到對應的 p 。同樣的問題也會發生在能量的期望值 $\langle E \rangle$ ，因為 $\Delta E \Delta t \geq \hbar/2$ 同樣意味著若我們在確定的時間 t 時，不可能算出函數 $E(t)$ 。5.6 節我們會看到如何決定 $\langle p \rangle$ 和 $\langle E \rangle$ 。

5.2 波動方程式 The Wave Equation

它可以有許多種類的解答，包含了複數型式

波動方程式
$$\frac{\partial^2 f}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 f}{\partial t^2} \quad (5.3)$$

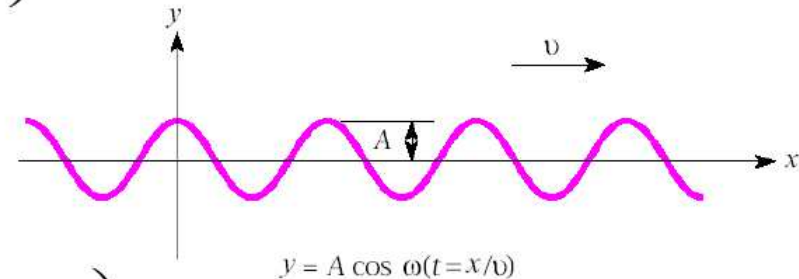
此式為描述一變動量 f 沿 x 軸以速度 v 傳播之波，其解的形式為

$$f = F\left(t \pm \frac{x}{v}\right) \quad (5.4)$$

e.g. 往 $+x$ 方向移動的波

$$f = Ae^{-i\omega(t-x/v)} \quad (5.5)$$

$$f = A \cos \omega\left(t - \frac{x}{v}\right) - iA \sin \omega\left(t - \frac{x}{v}\right) \quad (5.6)$$



5.3 薛丁格方程式：時間相依型

Schrödinger's Equation: Time-Dependent Form

描述物質波運動的方程式是什麼？

Erwin Schrödinger



阿哈！就是薛丁格方程
(Schrödinger's equation)

假設一個自由粒子在+x軸方向移動，對應之波函數為

$$\Psi = Ae^{-i\omega(t-x/v)} \quad \text{or} \quad \Psi = Ae^{-2\pi i(\nu t - x/\lambda)}$$

自由粒子 $\Psi = Ae^{-(i/\hbar)(Et - px)} \quad (5.9)$

$$E = h\nu = 2\pi\hbar\nu \quad \text{且} \quad \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

$$\text{對 } x \text{ 偏微} \quad p^2\Psi = -\hbar^2 \frac{\partial^2\Psi}{\partial x^2} \quad \text{對 } t \text{ 偏微} \quad E\Psi = -\frac{\hbar}{i} \frac{\partial\Psi}{\partial t}$$

當粒子速度遠小於光速時， $E = \frac{p^2}{2m} + U$

$$\Rightarrow E\Psi = \frac{p^2\Psi}{2m} + U\Psi$$

對於自由粒子，位能 U 為常數

一維的時間相依 Schrödinger 方程式 $i\hbar \frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2\Psi}{\partial x^2} + U\Psi$

一維自由粒子的 Schrödinger 方程式 $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi$

三維自由粒子的 Schrödinger 方程式 $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U\Psi$

當粒子受到隨空間且隨時間而變的位能 $U = U(x, y, z, t)$ 的作用時，我們仍假設上述結論亦適用！

亦即，一般情況下

三維的時間相依 Schrödinger 方程式為

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U(x, y, z, t)\Psi$$

- Schrödinger 方程式的有效性
 - 由於 Schrödinger 方程式準確的預測出所有（非相對論的）實驗結果，上述假設應為真。

5.6 運算子 Operators

我們還有另一個計算 $\langle p \rangle$ 和 $\langle E \rangle$ 方法的線索。將自由粒子的波函數 $\Psi = Ae^{-(i/\hbar)(Et - px)}$ 對 x 還有 t 微分。我們發現

$$\left\{ \begin{array}{l} \frac{\partial \Psi}{\partial x} = \frac{i}{\hbar} p \Psi \\ \frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E \Psi \end{array} \right.$$

也可以寫成另一個型式

$$\left\{ \begin{array}{l} p \Psi = \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi \\ E \Psi = i \hbar \frac{\partial}{\partial t} \Psi \end{array} \right. \quad \begin{array}{l} (5.21) \\ (5.22) \end{array}$$

明顯地，動態 p 感覺上可以與微分運算符號 $(\hbar/i)\partial/\partial x$ 對應，而動態 E 同樣地對應到微分運算子 $i\hbar\partial/\partial t$ 。

通常在運算子上會加上一個小符號，如 $\hat{p}$ 是對應到動量 p 的運算子， $\hat{E}$ 是對應到總能量 E 的運算子。從式 (5.21) 和 (5.22) 可得這些運算子

動量運算子	{	$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$	(5.23)
總能量運算子		$\hat{E} = i\hbar \frac{\partial}{\partial t}$	(5.24)

雖然我們只證明式 (5.23), (5.24) 可應用於自由粒子，它們實際上是一個通用的公式，就如同薛丁格方程式一般。

動量運算子

總能量運算子

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

所以我們可以得到

動能運算子

$$\hat{KE} = \frac{\hat{p}^2}{2m} = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (5.26)$$

式 (5.25) 因此寫成

$$\hat{E} = \hat{KE} + \hat{U}$$

$$i\hbar \frac{\partial}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U \quad (5.27)$$

現在讓我們把式 (5.27) 兩邊同乘以 Ψ

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

這就是薛丁格方程式。式 (5.23), (5.24) 所做的假設等同於薛丁格方程式的假設。

Hamiltonian 運算子 $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U$

一維的時間相依 Schrödinger 方程式

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi \quad \longleftrightarrow \quad i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

運算子與期望值

因為 p 與 E 在方程式裡可用對應的運算子來代替。我們可以用運算子來求 p 和 E 的期望值。因此 p 的期望值為

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi dx = \int_{-\infty}^{\infty} \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx \quad (5.28)$$

E 的期望值為

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{E} \Psi dx = \int_{-\infty}^{\infty} \Psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \Psi dx = i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial t} dx \quad (5.29)$$

式 (5.28), (5.29) 都可以帶入任何可接受的波函數 $\Psi(x, t)$ 中。

任意物理系統的可觀測值 G 可以用一適合的量子力學運算子 $\hat{G}$ 來表示。為了得到此運算子，我們可以將 G 用 x 和 p 來表示，再將 p 以 $(\hbar/i)\partial/\partial x$ 代入。若某系統的波函數為 Ψ 為已知，則 $G(x, p)$ 的期望值為

運算子的期望值

$$\langle G(x, t) \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{G} \Psi dx \quad (5.30)$$

運用這個方法，任一系統所有在測不準原理允許下的資訊都可以從波函數 Ψ 求得。

Table 5.1 Operators Associated with Various Observable Quantities

Quantity	Operator
Position, x	x
Linear momentum, p	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
Potential energy, $U(x)$	$U(x)$
Kinetic energy, $KE = \frac{p^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Total energy, E	$i\hbar \frac{\partial}{\partial t}$
Total energy (Hamiltonian form), H	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$

Example 5.2

A particle limited to the x axis has the wave function $\Psi = ax$ between $x = 0$ and $x = 1$; $\Psi = 0$ elsewhere. (a) Find the probability that the particle can be found between $x = 0.45$ and $x = 0.55$. (b) Find the expectation value $\langle x \rangle$ of the particle's position.

Solution

(a) The probability is

$$\int_{x_1}^{x_2} |\Psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251a^2$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x |\Psi|^2 dx = a^2 \int_0^1 x^3 dx = a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

5.7 薛丁格方程式：穩態型式

Schrödinger's Equation: Steady-State Form

若位能 U 與時間無關，則可將波函數分為兩部分：（分離變數法）

$$\Psi = \psi e^{-(iE/\hbar)t}$$

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

空間相關項： $\psi(x)$ 時間相關項： $\exp(-i E t / \hbar)$

代入時間相依型的薛丁格方程式，我們可以發現

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} e^{-(iE/\hbar)t} \frac{\partial^2 \psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

將等式兩邊都有的指數項消掉可以得到

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$$

一維穩態 Schrödinger 方程式

$$\text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0$$

一維穩態 Schrödinger 方程式

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$$

$$\text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0$$

三維穩態 Schrödinger 方程式

$$E\psi = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi$$

$$\text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0$$

運算子和本徵函數、特徵值

本徵值方程式 $\hat{G}\psi_n = G_n\psi_n$

G_n ：本徵值 (eigenvalue)

ψ_n ：本徵函數 (eigenfunction)

能量本徵值及能量本徵函數

穩態Schrödinger 方程式 $\hat{H}\psi_n = E_n\psi_n$

Hamiltonian 運算子 $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U$

對於氫原子 (見Chap.6) $E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots$

Example 5.3

An eigenfunction of the operator d^2/dx^2 is $\psi = e^{2x}$. Find the corresponding eigenvalue.

Solution

Here $\hat{G} = d^2/dx^2$, so

$$\hat{G}\psi = \frac{d^2}{dx^2}(e^{2x}) = \frac{d}{dx} \left[\frac{d}{dx}(e^{2x}) \right] = \frac{d}{dx}(2e^{2x}) = 4e^{2x}$$

But $e^{2x} = \psi$, so

$$\hat{G}\psi = 4\psi$$

From Eq. (5.34) we see that the eigenvalue G here is just $G = 4$.

5.8 箱子中的粒子 Particle in a Box

一維無限深位能井 $V_0 (U_0) \rightarrow \infty$

微觀粒子被局限於某區域中，並在該區域內可以自由運動的問題

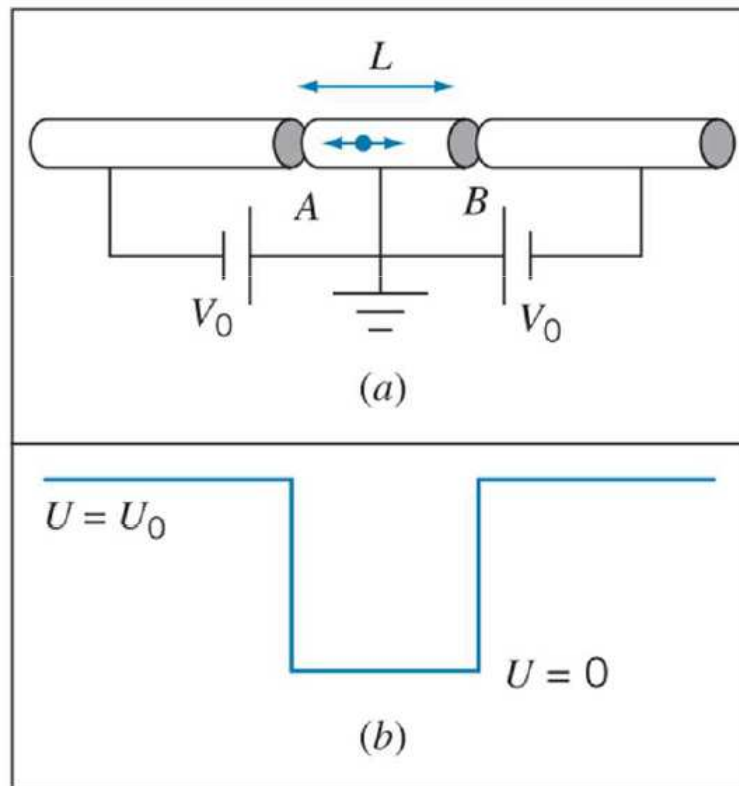
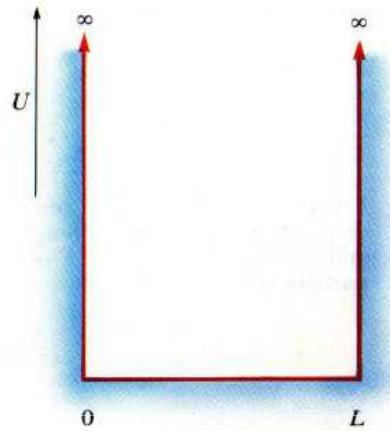
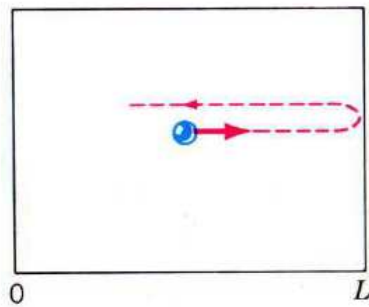


FIGURE 5.6

(a) Apparatus for confining an electron to the center region of length L .

(b) The potential energy of an electron in this apparatus.

無限深位能井



$$U = \begin{cases} 0 & 0 < x < L \\ \infty & x \leq 0 \text{ or } x \geq L \end{cases}$$

$$\Rightarrow \Psi(x) = 0, \quad \text{for } x < 0 \text{ or } x > L$$

∴ 波函數必須是連續函數

$$\therefore \Psi(x) = 0 \text{ at } x = 0 \text{ and } x = L \quad \Rightarrow \text{駐波！}$$

當 $0 < x < L$ $U(x) = 0$ $\boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0}$

$$\Rightarrow \frac{\partial^2 \Psi}{\partial x^2} = -\frac{2m}{\hbar^2} E \Psi = -k^2 \Psi \quad \boxed{E \equiv \frac{\hbar^2 k^2}{2m}}$$

$$\Rightarrow \Psi(x) = A \sin(kx) + B \cos(kx)$$

$$\because \Psi(0) = 0 \Rightarrow B = 0$$

$$\because \Psi(L) = 0 \Rightarrow kL = n\pi \quad n = 1, 2, 3 \dots$$

駐波條件！

$$\Rightarrow \Psi(x) = A \sin\left(\frac{n\pi}{L} x\right) \quad E_n = \left(\frac{h^2}{8mL^2}\right) n^2$$

電子被限制於其中，因此其能量呈現量子化！

$$\boxed{E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{h}{\lambda}\right)^2 = \frac{1}{2m} \left(\frac{h}{(2L/n)}\right)^2}$$

Two-Dimensional **Infinite** Potential Energy Well

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} \right) + U(x, y) \psi(x, y) = E \psi(x, y)$$

$$U(x, y) = 0 \quad 0 \leq x \leq L; 0 \leq y \leq L$$
$$= \infty \quad \text{otherwise}$$

$$\psi(x, y) = A' \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L}$$

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2) = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2)$$

$$\leftrightarrow E = \frac{1}{2m} (\hbar^2 k_x^2 + \hbar^2 k_y^2)$$

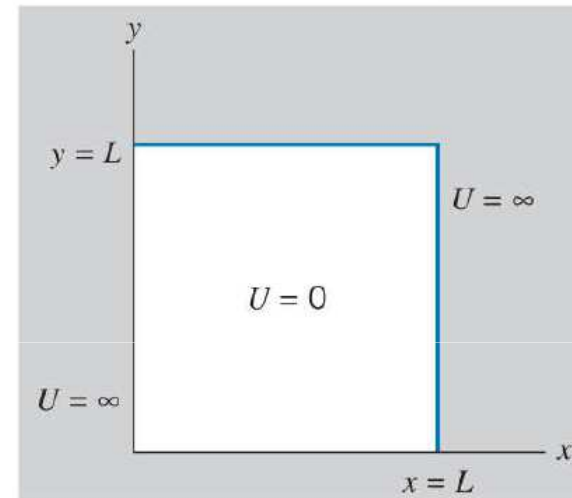


FIGURE 5.15 A particle moves freely in the **two-dimensional** region $0 < x < L$, $0 < y < L$, but encounters **infinite** barriers beyond that region.

Example 5.4

Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box (Fig. 5.6). Classically we would expect the particle to be in this region 10 percent of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state. From Eqs. (5.2) and (5.46) the probability of finding the particle between x_1 and x_2 when it is in the n th state is

$$\begin{aligned} P_{x_1, x_2} &= \int_{x_1}^{x_2} |\psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx \\ &= \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2} \end{aligned}$$

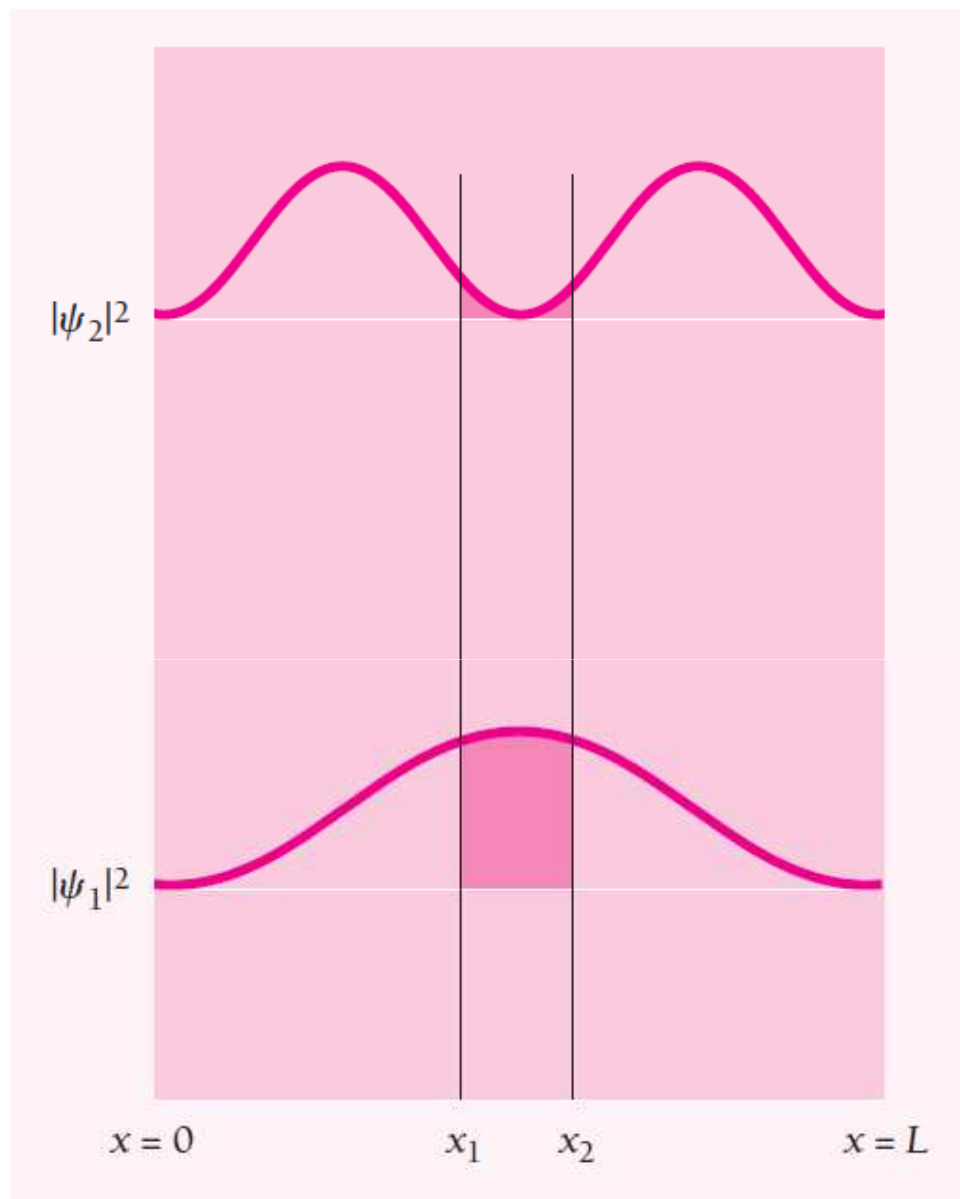
Here $x_1 = 0.45L$ and $x_2 = 0.55L$. For the ground state, which corresponds to $n = 1$, we have

$$P_{x_1, x_2} = 0.198 = 19.8 \text{ percent}$$

This is about twice the classical probability. For the first excited state, which corresponds to $n = 2$, we have

$$P_{x_1, x_2} = 0.0065 = 0.65 \text{ percent}$$

This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.



$$P_{x_1, x_2} = \int_{x_1}^{x_2} |\psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx$$

$$= \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2}$$

Example 5.5

Find the expectation value $\langle x \rangle$ of the position of a particle trapped in a box L wide.

Solution

From Eqs. (5.19) and (5.46) we have

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} x |\psi|^2 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2} \right]_0^L\end{aligned}$$

Since $\sin n\pi = 0$, $\cos 2n\pi = 1$, and $\cos 0 = 1$, for all the values of n the expectation value of x is

$$\langle x \rangle = \frac{2}{L} \left(\frac{L^2}{4} \right) = \frac{L}{2}$$

This result means that the average position of the particle is the middle of the box in all quantum states. There is no conflict with the fact that $|\psi|^2 = 0$ at $L/2$ in the $n = 2, 4, 6, \dots$ states because $\langle x \rangle$ is an *average*, not a probability, and it reflects the symmetry of $|\psi|^2$ about the middle of the box.

$$\psi^* = \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

$$\frac{d\psi}{dx} = \sqrt{\frac{2}{L}} \frac{n\pi}{L} \cos \frac{n\pi x}{L}$$

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi dx = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi dx$$

$$= \frac{\hbar}{i} \frac{2}{L} \frac{n\pi}{L} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} dx$$

$$\int \sin ax \cos ax dx = \frac{1}{2a} \sin^2 ax$$

$$\langle p \rangle = \frac{\hbar}{iL} \left[\sin^2 \frac{n\pi x}{L} \right]_0^L = 0$$

$$\sin^2 0 = \sin^2 n\pi = 0$$

$$E = p^2/2m,$$

$$p_n = \pm \sqrt{2mE_n} = \pm \frac{n\pi\hbar}{L}$$

$$p_{av} = \frac{(+n\pi\hbar/L) + (-n\pi\hbar/L)}{2} = 0$$

$$\hat{p}\psi_n = p_n\psi_n$$

$$\frac{\hbar}{i} \frac{d}{dx} \left(\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \right) = \frac{\hbar}{i} \frac{n\pi}{L} \sqrt{\frac{2}{L}} \cos \frac{n\pi x}{L}$$

$$\neq p_n\psi_n$$

We can see at once that the energy eigenfunctions are not also momentum eigenfunctions

To find the correct momentum eigenfunctions, we note that

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{1}{2i}e^{i\theta} - \frac{1}{2i}e^{-i\theta}$$

$$\frac{d}{dx} e^{in\pi x/L}$$

$$\psi_n^+ = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{in\pi x/L}$$

$$\hat{p}\psi_n^+ = p_n^+ \psi_n^+$$

$$\frac{\hbar}{i} \frac{d}{dx} \psi_n^+ = \frac{\hbar}{i} \frac{1}{2i} \sqrt{\frac{2}{L}} \frac{in\pi}{L} e^{in\pi x/L} = \frac{n\pi\hbar}{L} \psi_n^+ = p_n^+ \psi_n^+$$

$$\psi_n^- = \frac{1}{2i} \sqrt{\frac{2}{L}} e^{-in\pi x/L}$$

$$p_n^+ = +\frac{n\pi\hbar}{L}$$

$$p_n^- = -\frac{n\pi\hbar}{L}$$

$$\psi(x,y) = A' \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L}$$

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2) = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2)$$

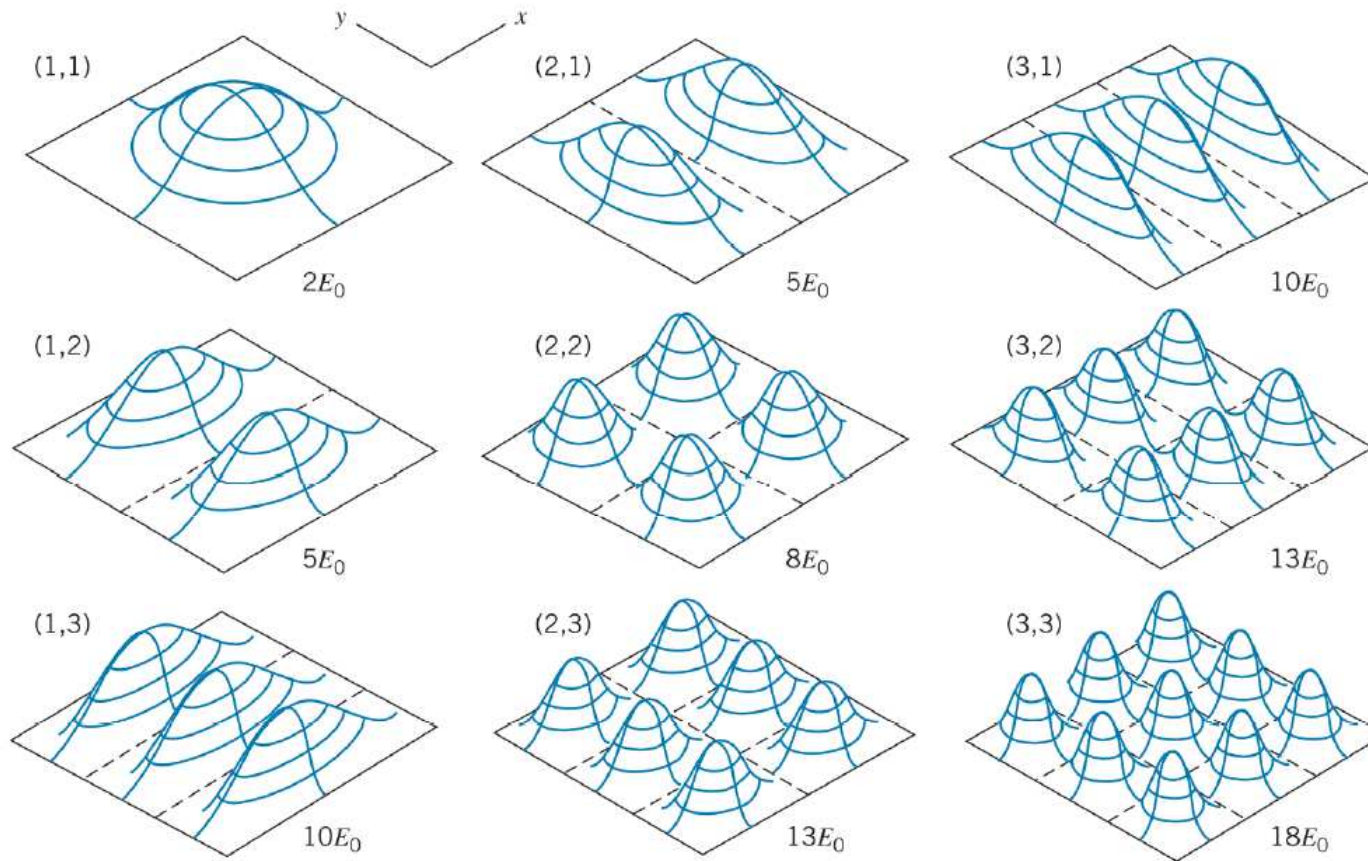
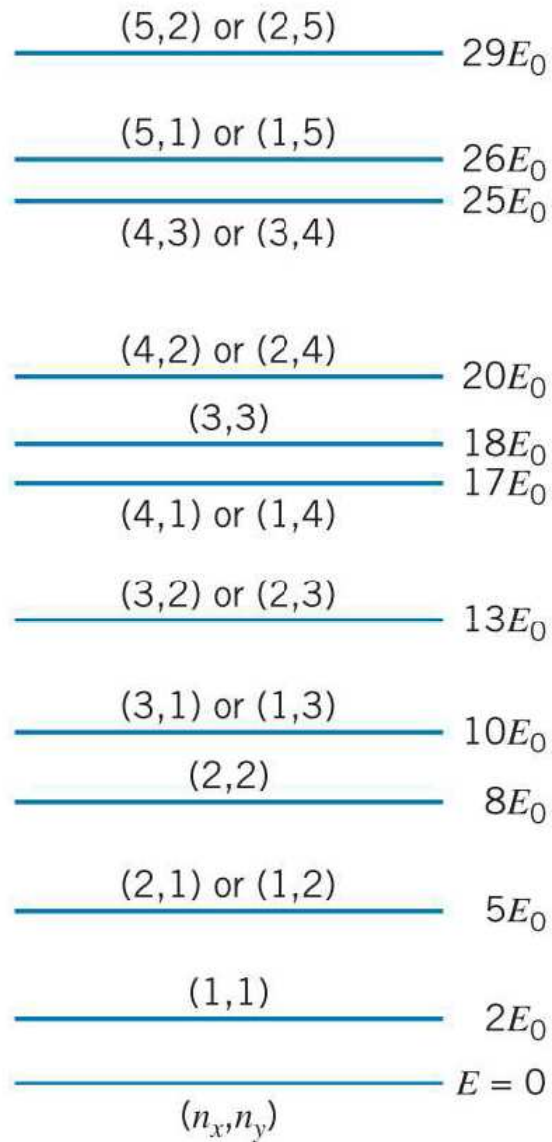


FIGURE 5.17 The **probability density** for some of the lower energy levels of a particle confined to the infinite two-dimensional potential energy well. The individual plots are labeled with the **quantum numbers** (n_x, n_y) and with the value of the **energy** E .



$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2) = \frac{h^2}{8mL^2} (n_x^2 + n_y^2)$$

FIGURE 5.16 The lower permitted energy levels of a particle confined to an infinite two-dimensional potential energy well.

簡併度 (degeneracy) 可大於 1 !

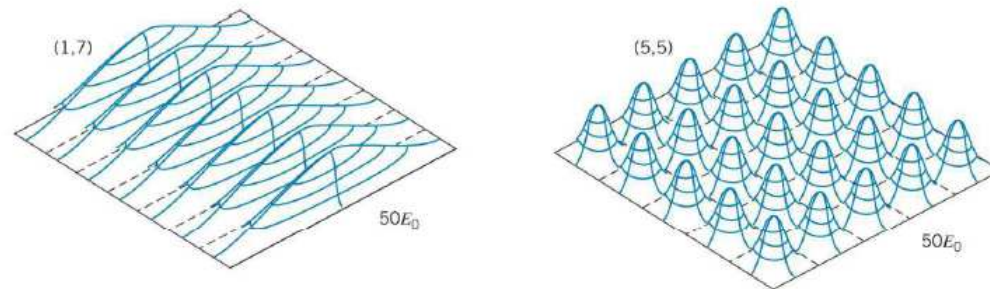


FIGURE 5.19 Two very different probability densities with exactly the **same** energy.

5.9 有限位能井 Finite Potential Well

一維有限深位能井 $V_0 (U_0) < \infty$

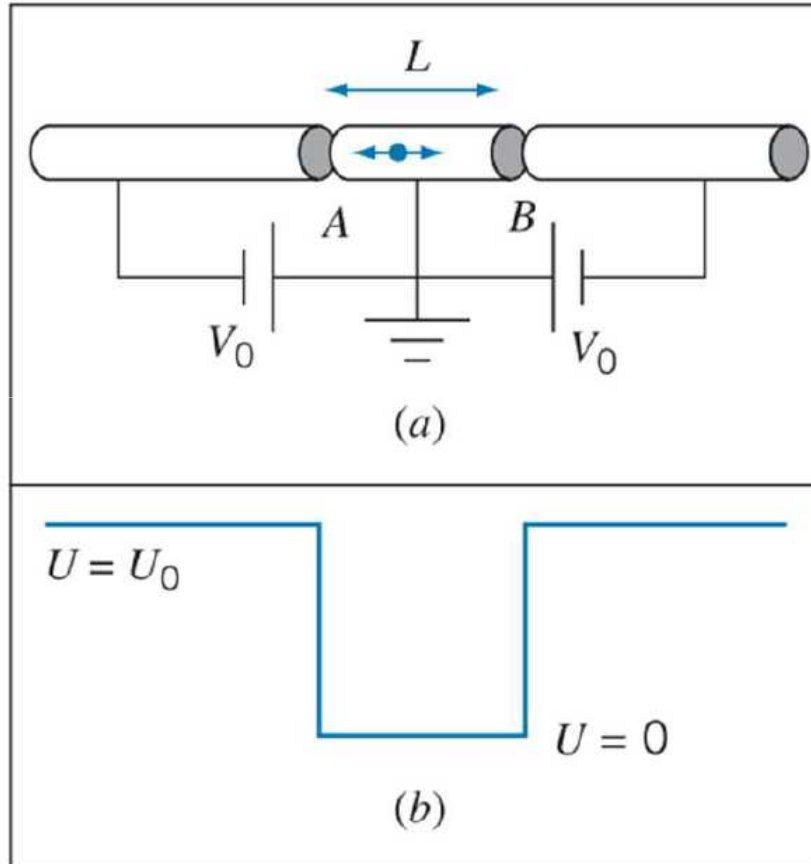


FIGURE 5.6

(a) Apparatus for confining an electron to the center region of length L .

(b) The potential energy of an electron in this apparatus.

圖 5.7 描繪出一個方形的電位井，高度為 U ，寬度為 L ，其中有一個粒子的能量 E 小於 U 。根據古典力學的說法，當粒子撞擊至井的邊緣時，它會彈回來而不可能到達第 I 區及第 III 區。而量子力學認為，粒子會前後跳動沒錯，但是縱使現在 $E < U$ ，它仍有某種程度的機率可穿隧到 I, III 區。

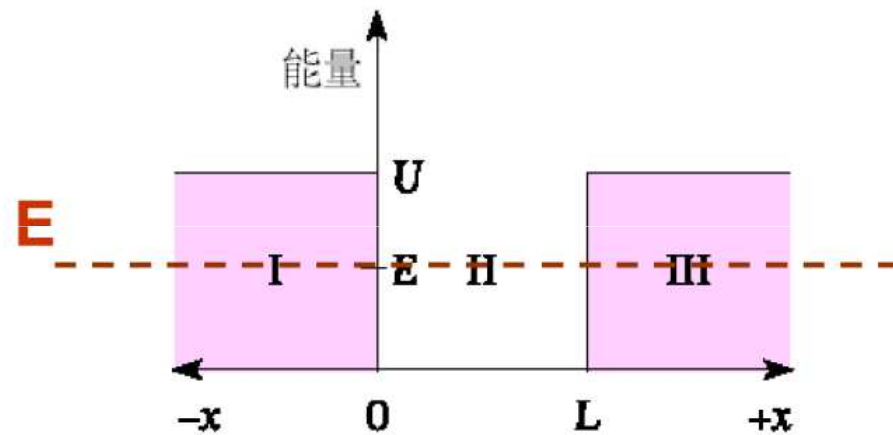


圖5.7 一個有限能障的方形電位井。能量 E 的粒子束縛在其中，能障的高度 U 大於 E 。
(potential barrier)

當 $x < 0$ 或 $x > L$ ， $U - E > 0$ ，

穩態 Schrödinger 方程式可寫為

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \quad a = \frac{\sqrt{2m(U-E)}}{\hbar}$$

$$\Rightarrow \begin{aligned} \psi_{\text{I}} &= Ce^{ax} + De^{-ax} & x < 0 \\ \psi_{\text{III}} &= Fe^{ax} + Ge^{-ax} & x > L \end{aligned}$$

$\therefore \psi_{\text{I}}$ 和 ψ_{III} 必須為有限值

$\therefore D = 0$ 且 $F = 0$

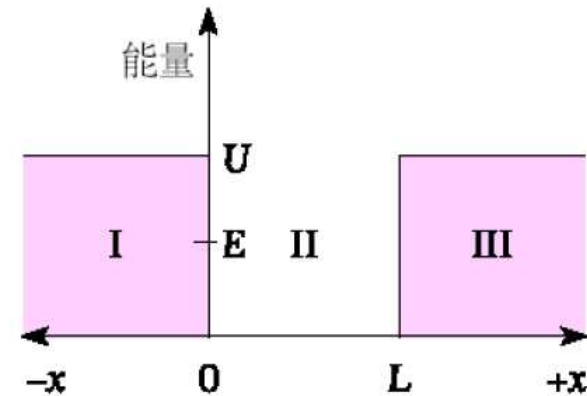
$$\Rightarrow \psi_{\text{I}} = Ce^{ax} \quad \text{且} \quad \psi_{\text{III}} = Ge^{-ax}$$

當 $0 < x < L$ ， $U = 0$ ，穩態 Schrödinger 方程式可寫為

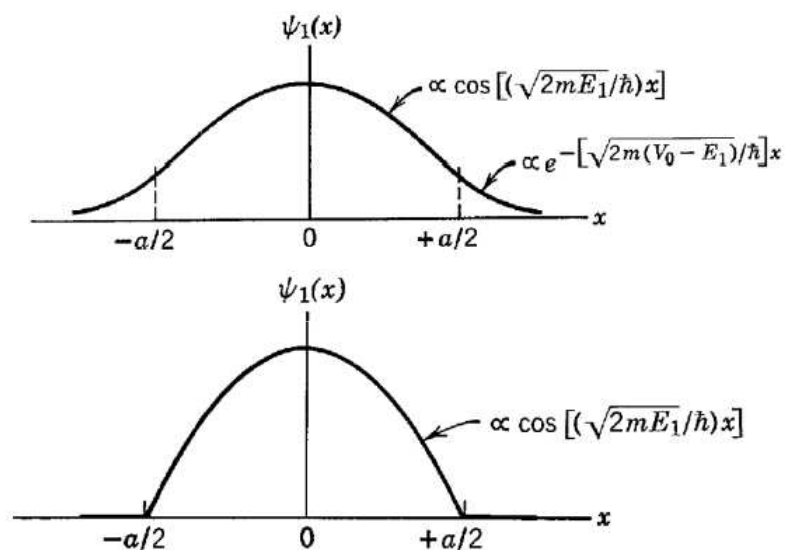
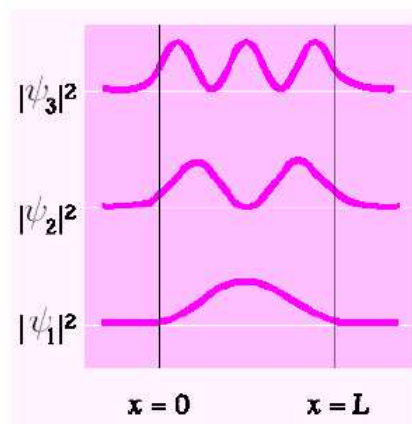
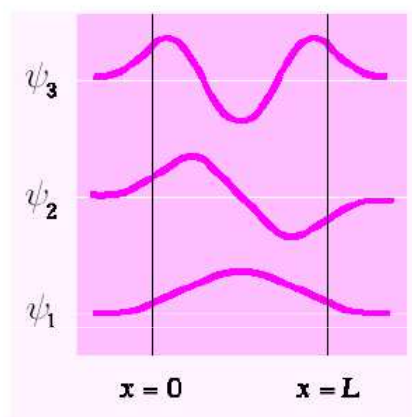
$$\frac{d^2\psi_{\text{II}}}{dx^2} + \frac{2m}{\hbar^2}E\psi_{\text{II}} = 0$$

$$\Rightarrow \psi_{\text{II}} = A \sin \frac{\sqrt{2mE}}{\hbar}x + B \cos \frac{\sqrt{2mE}}{\hbar}x$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$



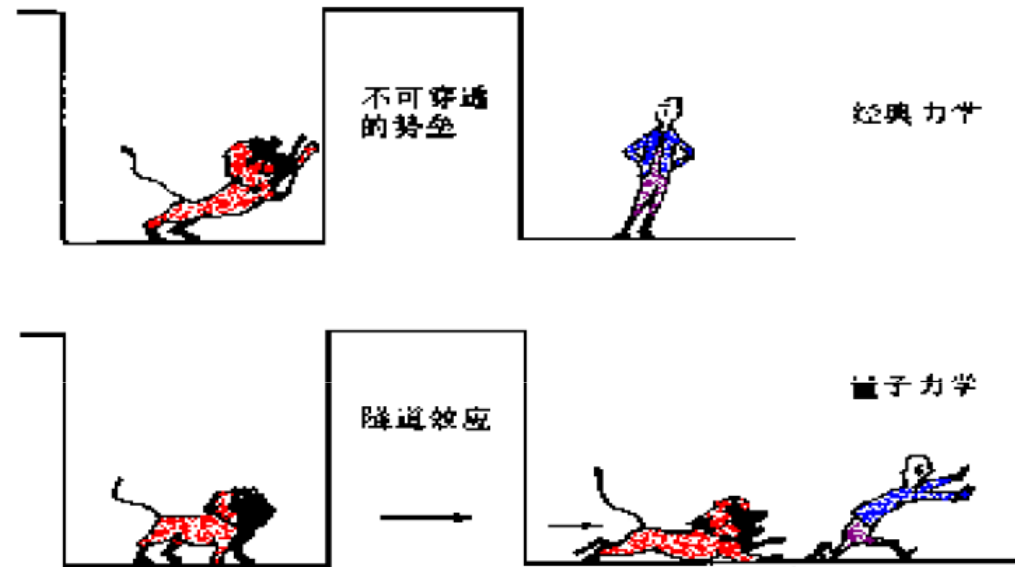
對任一解來說， ψ 和 $d\psi/dx$ 都必須在 $x=0$ 和 $x=L$ 處連續：波函數不管在能障內或外的邊界處不但要有同樣的值，還要有相同的斜率，才能互相完美的匹配。當這些邊界條件考慮進去時，結果確實與具有特定能量 E_n 的粒子發生的情況相吻合。完整的波函數和它們的機率密度如圖 5.8。



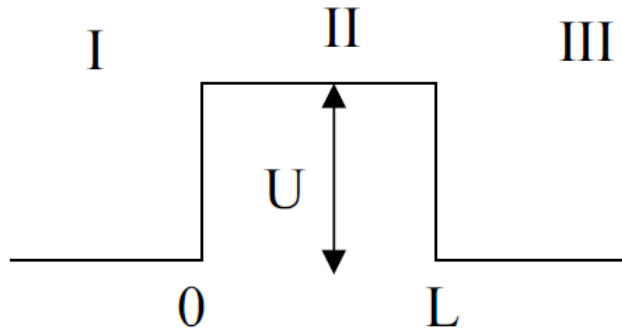
- 在位能阱外，粒子依然有存在機率。
- 與無窮大位能障壁情形相比， λ_n 波長較長，因此對應的 E_n 較低。

5.10 穿隧效應 Tunnel Effect

- 粒子能穿透比動能更高的能障（potential barrier）的現象稱為穿隧效應。



- 穿隧效應在古典概念下是無法理解的，它是微觀粒子具有波動性的表現！



(assume $0 < E < U$)

In region I :

$$\psi_{\text{I}} = Ae^{ik_1x} + Be^{-ik_1x}$$

In region II :

$$\psi_{\text{II}} = Ce^{-k_2x} + De^{k_2x}$$

In region III :

$$\psi_{\text{III}} = Fe^{ik_1x} + Ge^{-ik_1x}$$

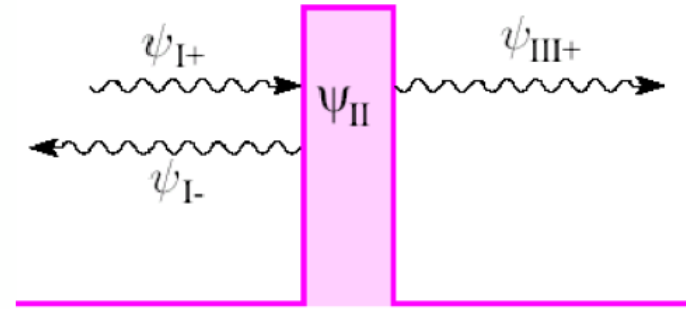
$$\frac{d^2\psi_{\text{I,III}}}{dx^2} + \frac{2m}{\hbar^2} E \psi_{\text{I,III}} = 0$$

$$\frac{d^2\psi_{\text{II}}}{dx^2} + \frac{2m}{\hbar^2} (E - U) \psi_{\text{II}} = 0$$

$$k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda}$$

$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar}$$

$$k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda}$$



入射波 $\psi_{I+} = Ae^{ik_1x}$

反射波 $\psi_{I-} = Be^{-ik_1x} \Rightarrow \psi_I = \psi_{I+} + \psi_{I-}$

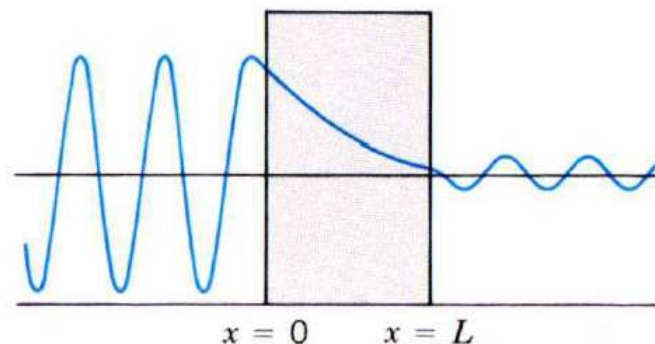
穿透波 $\psi_{III+} = Fe^{ik_1x} \Rightarrow \psi_{III} = \psi_{III+} = Fe^{ik_1x}$

穿隧機率
$$T = \frac{|\psi_{III}|^2 v_{III+}}{|\psi_{I+}|^2 v_{I+}} = \frac{FF^* v_{III+}}{AA^* v_{I+}}$$

v_{I+} 、 v_{III+} 分別為 I 、 III 處波的群速度

⇒ 穿隧機率 $T \approx \exp(-2k_2L)$

$$k_2 = \sqrt{\frac{2m(U-E)}{\hbar^2}}$$



這正是在能障區域波幅衰減因子 $\exp(-k_2L)$ 的平方！

⇒ 只有在一定的條件下，穿隧效應才較顯著！

例如，當 $U-E = 1 \text{ MeV}$ 時，一個 α 粒子穿過一個寬度為 $L \sim 10^{-14} \text{ m}$ 的能障，其穿隧機率為 $T \sim 10^{-4}$ ；但若 $L \sim 10^{-13} \text{ m}$ ，則 $T \sim 10^{-38}$ 。

由此可見，對於宏觀物體，穿隧效應在實際上已經沒有意義了，量子概念過渡到了古典概念。

任意形狀的能障 $U(x)$ 的透射係數

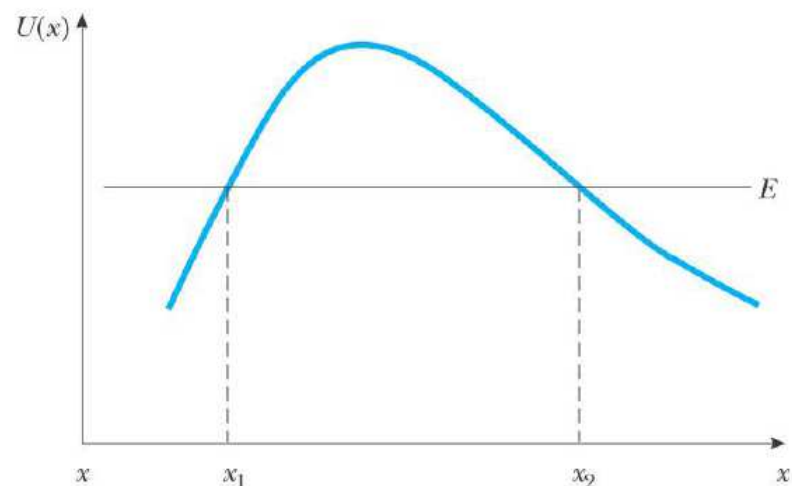
把能障 $U(x)$ 用一系列矩形能障來近似，總的透射係數就等於各個矩形能障透射係數的乘積。
對每個矩形能障適用上述近似公式，因此

$$T \approx T_1 T_2 T_3 \cdots$$

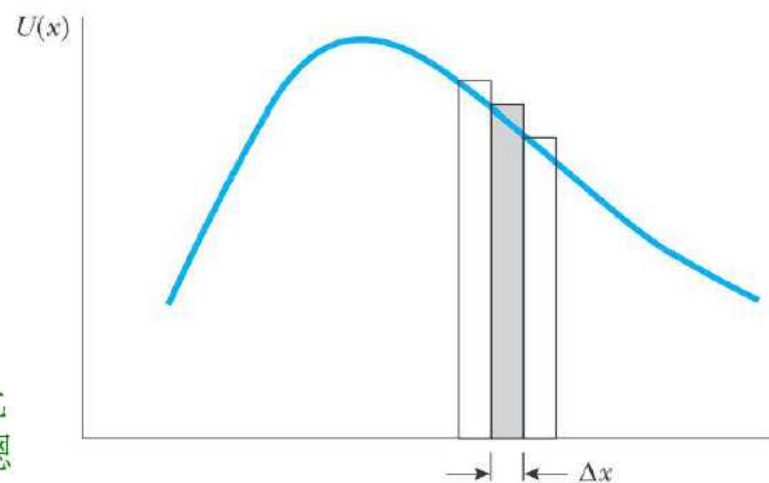
$$\approx \exp\left(-2 \sum \frac{\sqrt{2m[U(x) - E]} \Delta x}{\hbar}\right)$$

$$\approx \exp\left(-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m[U(x) - E]} dx\right)$$

這個公式近似適用的條件，是能障 $U(x)$ 的變化比較平緩，能障區域比粒子能量高得多，而總透射係數很小， $T \ll 1$ 。



(a)



(b)

Example 5.6

Electrons with energies of 1.0 eV and 2.0 eV are incident on a barrier 10.0 eV high and 0.50 nm wide. (a) Find their respective transmission probabilities. (b) How are these affected if the barrier is doubled in width?

Solution

(a) For the 1.0-eV electrons

$$\begin{aligned}k_2 &= \frac{\sqrt{2m(U - E)}}{\hbar} \\&= \frac{\sqrt{(2)(9.1 \times 10^{-31} \text{ kg})[(10.0 - 1.0) \text{ eV}](1.6 \times 10^{-19} \text{ J/eV})}}{1.054 \times 10^{-34} \text{ J} \cdot \text{s}} \\&= 1.6 \times 10^{10} \text{ m}^{-1}\end{aligned}$$

Since $L = 0.50 \text{ nm} = 5.0 \times 10^{-10} \text{ m}$, $2k_2L = (2)(1.6 \times 10^{10} \text{ m}^{-1})(5.0 \times 10^{-10} \text{ m}) = 16$, and the approximate transmission probability is

$$T_1 = e^{-2k_2L} = e^{-16} = 1.1 \times 10^{-7}$$

One 1.0-eV electron out of 8.9 million can tunnel through the 10-eV barrier on the average. For the 2.0-eV electrons a similar calculation gives $T_2 = 2.4 \times 10^{-7}$. These electrons are over twice as likely to tunnel through the barrier.

(b) If the barrier is doubled in width to 1.0 nm, the transmission probabilities become

$$T'_1 = 1.3 \times 10^{-14} \quad T'_2 = 5.1 \times 10^{-14}$$

Evidently T is more sensitive to the width of the barrier than to the particle energy here.

5.11 諧振子 Harmonic Oscillator

簡諧運動(simple harmonic motion)是其中的一個特例，作用在質量 m 粒子的回復力 F 是線性的；也就是說 F 正比於粒子離開平衡點的位移 x ，但是作用於相反的方向。因此

虎克定律

$$F = -kx$$

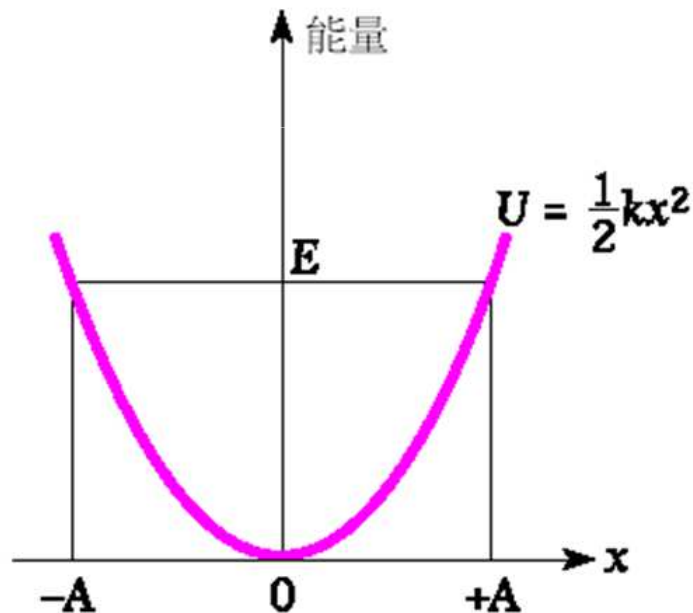


圖5.10 諧振子的位能正比於 x^2 ，其中 x 是離開平衡位置的位移。移動的振幅 A 決定於振子的總能量 E ，在古典理論中可為任意值。

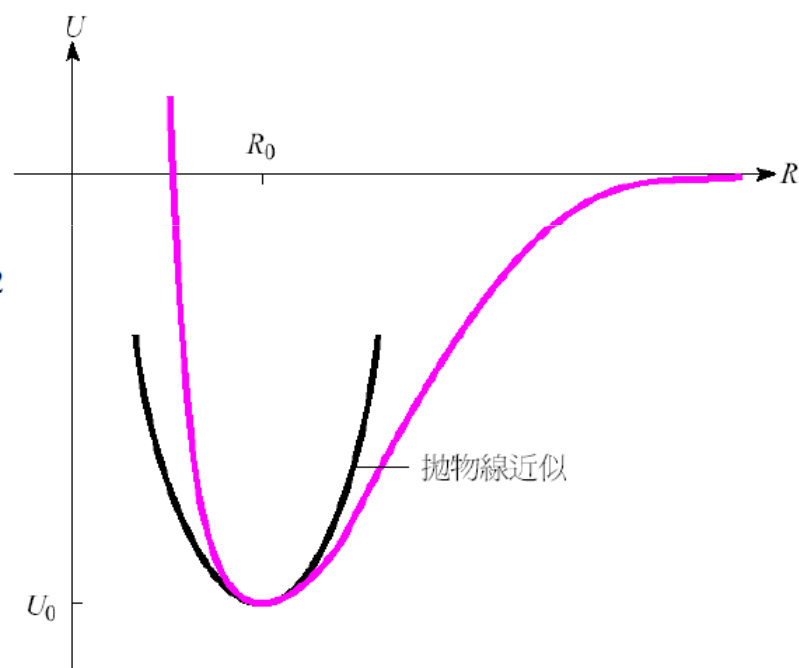
任何在平衡點附近做微小振動的系統，其行為都等同於簡諧振子。

$$F(x) = F_{x=0} + \left(\frac{dF}{dx}\right)_{x=0} x + \frac{1}{2} \left(\frac{d^2F}{dx^2}\right)_{x=0} x^2 + \frac{1}{3!} \left(\frac{d^3F}{dx^3}\right)_{x=0} x^3 + \dots$$

在平衡點， $F_{x=0} = 0$ 。在 x 很小的情況下，高次項可忽略，因此

$$F(x) \approx \left(\frac{dF}{dx}\right)_{x=0} x = -kx$$

$$U(x) = -\int_0^x F(x) dx = k \int_0^x x dx = \frac{1}{2} kx^2$$



THE SIMPLE HARMONIC OSCILLATOR

$$U = \frac{1}{2}kx^2 \quad \longrightarrow \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$$

The wave function must **fall to zero** for both $x \rightarrow +\infty$ and $x \rightarrow -\infty$. The simplest function that satisfies these conditions, which turns out to be the correct ground state wave function, is $\psi(x) = Ae^{-ax^2}$

Check:

$$\frac{d\psi}{dx} = -2ax(Ae^{-ax^2})$$

$$\frac{d^2\psi}{dx^2} = -2a(Ae^{-ax^2}) - 2ax(-2ax)Ae^{-ax^2} = (-2a + 4a^2x^2)Ae^{-ax^2}$$

$$\Rightarrow \frac{\hbar^2 a}{m} - \frac{2a^2 \hbar^2}{m} x^2 + \frac{1}{2} k x^2 = E$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \quad \text{for } \psi(x) = Ae^{-ax^2}$$

$$\Rightarrow \frac{\hbar^2 a}{m} - \frac{2a^2\hbar^2}{m}x^2 + \frac{1}{2}kx^2 = E$$

$$\Rightarrow -\frac{2a^2\hbar^2}{m} + \frac{1}{2}k = 0 \quad \text{and} \quad \frac{\hbar^2 a}{m} = E$$

$$\Rightarrow a = \frac{\sqrt{km}}{2\hbar} \quad \text{and} \quad E = \frac{1}{2}\hbar\sqrt{k/m}$$

$$\Rightarrow \boxed{E = \frac{1}{2}h\nu} \quad \text{with} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$\psi(x) = \left(\frac{m\omega_0}{\hbar\pi}\right)^{1/4} e^{-(\sqrt{km}/2\hbar)x^2}$$

(A 的值可由歸一化條件求得)

The general solution is of the form $\psi_n(x) = Af_n(x)e^{-ax^2}$ where $f_n(x)$ is a polynomial in which the highest power of x is x^n . The corresponding energies are

諧振子的能階 $E_n = (n + \frac{1}{2})h\nu \quad n = 0, 1, 2, 3, \dots$

零點能量 $E_0 = \frac{1}{2}h\nu$

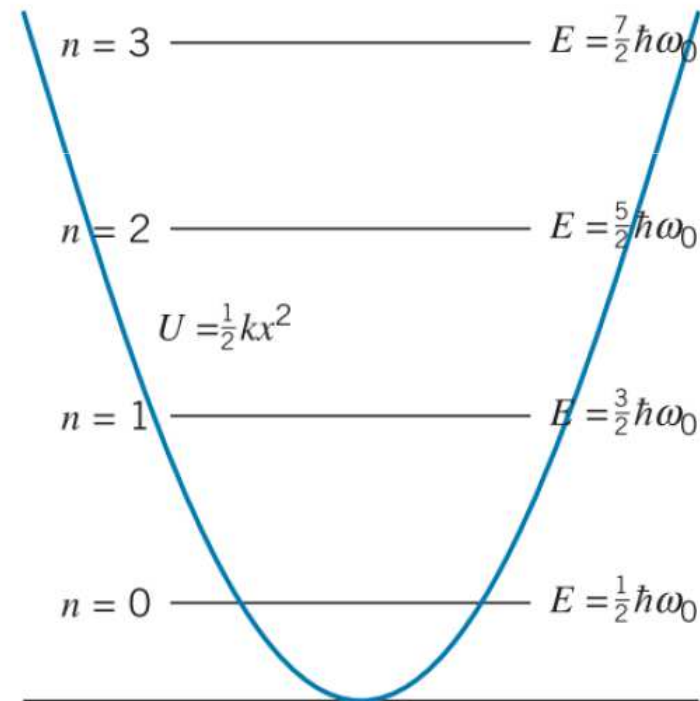


FIGURE 5.21 Energy levels of the simple harmonic oscillator. Note that the levels have equal spacing.

The general solution is of the form $\psi_n(x) = Af_n(x)e^{-ax^2}$
 where $f_n(x)$ is a polynomial in which the highest power of x is x^n .

諧振子波函數

$$\psi_n = \left(\frac{2m\nu}{\hbar}\right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2} \quad y = \left(\frac{1}{\hbar} \sqrt{km}\right)^{1/2} x = \sqrt{\frac{2\pi m\nu}{\hbar}} x$$

其中 $H_n(y)$ 為 Hermite polynomial

表5.2 前六個Hermite多項式

n	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}h\nu$
1	$2y$	3	$\frac{3}{2}h\nu$
2	$4y^2 - 2$	5	$\frac{5}{2}h\nu$
3	$8y^3 - 12y$	7	$\frac{7}{2}h\nu$
4	$16y^4 - 48y^2 + 12$	9	$\frac{9}{2}h\nu$
5	$32y^5 - 160y^3 + 120y$	11	$\frac{11}{2}h\nu$

比較相同能量下古典與量子力學諧振子機率密度的結果是非常有趣且具有啟發性的。圖 5.13 上方的曲線是古典諧振子的機率密度。而粒子出現在運動端點的機率 P 為最大，因為粒子在此運動最慢，而在平衡點位置 ($x=0$) 機率最小，因為它快速地運動。

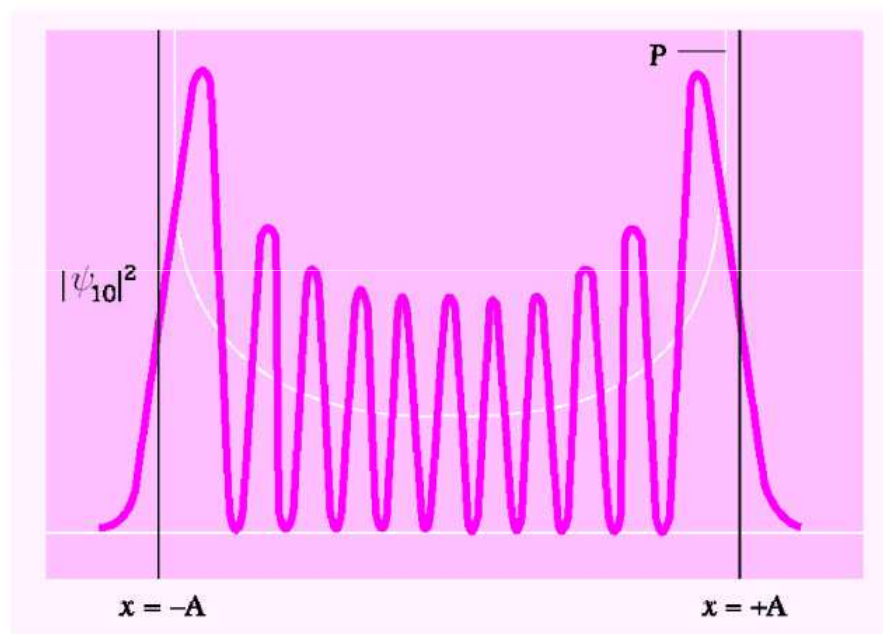
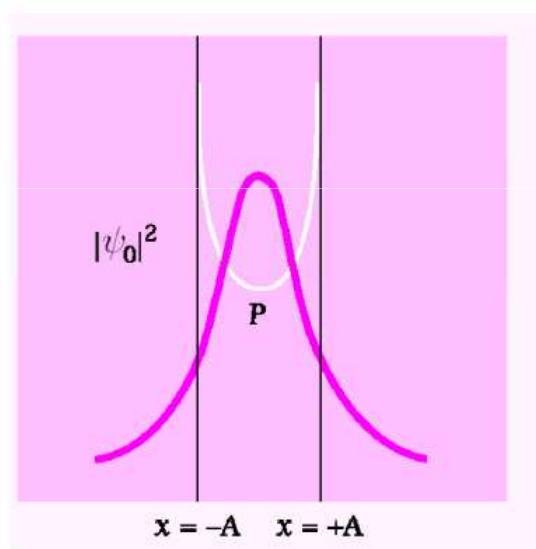


圖5.13 量子力學諧振子 $n=0$ 和 $n=10$ 狀態的機率密度。相同能量古典諧振子的機率密度以白色線表示。 $n=10$ 狀態下， $x=0$ 時波長最短， $x=-A$ 時最長。

Example 5.7

Find the expectation value $\langle x \rangle$ for the first two states of a harmonic oscillator.

Solution

The general formula for $\langle x \rangle$ is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx$$

In calculations such as this it is easier to begin with y in place of x and afterward use Eq. (5.67) to change to x . From Eq. (5.72) and Table 5.2,

$$\psi_0 = \left(\frac{2m\nu}{\hbar} \right)^{1/4} e^{-y^2/2}$$

$$\psi_1 = \left(\frac{2m\nu}{\hbar} \right)^{1/4} \left(\frac{1}{2} \right)^{1/2} (2y) e^{-y^2/2}$$

The values of $\langle x \rangle$ for $n = 0$ and $n = 1$ will respectively be proportional to the integrals

$$n = 0: \int_{-\infty}^{\infty} y |\psi_0|^2 dy = \int_{-\infty}^{\infty} y e^{-y^2} dy = - \left[\frac{1}{2} e^{-y^2} \right]_{-\infty}^{\infty} = 0$$

$$n = 1: \int_{-\infty}^{\infty} y |\psi_1|^2 dy = \int_{-\infty}^{\infty} y^3 e^{-y^2} dy = - \left[\left(\frac{1}{4} + \frac{y^2}{2} \right) e^{-y^2} \right]_{-\infty}^{\infty} = 0$$

The expectation value $\langle x \rangle$ is therefore 0 in both cases. In fact, $\langle x \rangle = 0$ for *all* states of a harmonic oscillator, which could be predicted since $x = 0$ is the equilibrium position of the oscillator where its potential energy is a minimum.