INTRODUCTION TO

QUANTUM MECHANICS

THIRD EDITION

DAVID J. GRIFFITHS

DARRELL F. SCHROETER

1.1 The Schrödinger Equation

Imagine a particle of mass m, constrained to move along the x axis, subject to some specified force $F(x,t)$ (Figure 1.1). The program of *classical* mechanics is to determine the position of the particle at any given time: $x(t)$. Once we know that, we can figure out the velocity ($v = dx/dt$), the momentum ($p = mv$), the kinetic energy $\left(T = (1/2)mv^2\right)$, or any other dynamical variable of interest. And how do we go about determining $x(t)$? We apply Newton's second law: $F = ma$. (For *conservative* systems—the only kind we shall consider, and, fortunately, the only kind that *occur* at the microscopic level—the force can be expressed as the derivative of a potential energy function,[1] $F = -\partial V/\partial x$, and Newton's law reads $m\, d^2x/dt^2 = -\partial V/\partial x$.) This, together with appropriate initial conditions (typically the position and velocity at $t = 0$), determines $x(t)$.

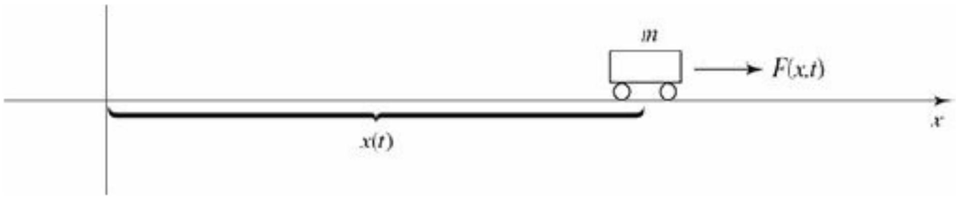


Figure 1.1: A "particle" constrained to move in one dimension under the influence of a specified force.

Quantum mechanics approaches this same problem quite differently. In this case what we're looking for is the particle's **wave function**, $\Psi(x,t)$, and we get it by solving the **Schrödinger equation**:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi. \tag{1.1}$$

Here i is the square root of -1, and $\hbar$ is Planck's constant—or rather, his *original* constant (h) divided by 2π:

$$\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34}\ \text{J s}. \tag{1.2}$$

The Schrödinger equation plays a role logically analogous to Newton's second law: Given suitable initial conditions (typically, $\Psi(x,0)$), the Schrödinger equation determines $\Psi(x,t)$ for all future time, just as, in classical mechanics, Newton's law determines $x(t)$ for all future time.[2]

電子的真面目

波的強度等於若觀察時在該處發現此粒子的機率！

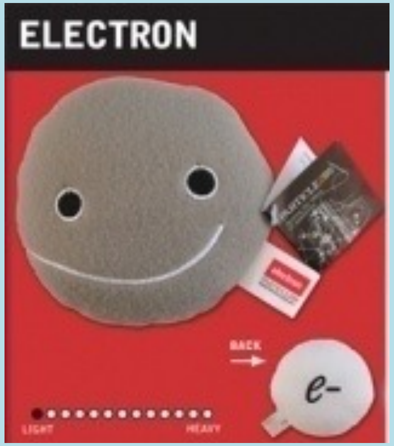
未觀察時，狀態的變化以波方程式來計算。

觀察時電荷及位置總是顆粒狀

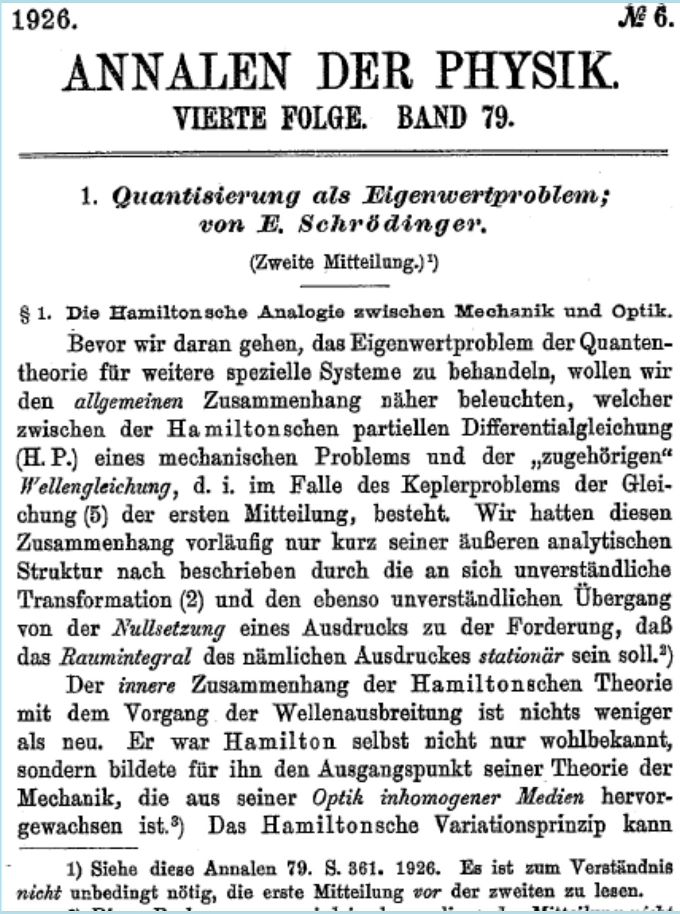
由波函數來描述的粒子

（而不是位置函數）

讓我們從一維的電子波開始研究！



A total of five papers in 1926



1926. № 6.

ANNALEN DER PHYSIK.
VIERTE FOLGE. BAND 79.

1. *Quantisierung als Eigenwertproblem;*
von E. Schrödinger.

(Zweite Mitteilung.)[1]

§ 1. **Die Hamiltonsche Analogie zwischen Mechanik und Optik.**

Bevor wir daran gehen, das Eigenwertproblem der Quantentheorie für weitere spezielle Systeme zu behandeln, wollen wir den *allgemeinen* Zusammenhang näher beleuchten, welcher zwischen der Hamiltonschen partiellen Differentialgleichung (H. P.) eines mechanischen Problems und der „zugehörigen" *Wellengleichung*, d. i. im Falle des Keplerproblems der Gleichung (5) der ersten Mitteilung, besteht. Wir hatten diesen Zusammenhang vorläufig nur kurz seiner äußeren analytischen Struktur nach beschrieben durch die an sich unverständliche Transformation (2) und den ebenso unverständlichen Übergang von der *Nullsetzung* eines Ausdrucks zu der Forderung, daß das *Raumintegral* des nämlichen Ausdruckes *stationär* sein soll.[2]

Der *innere* Zusammenhang der Hamiltonschen Theorie mit dem Vorgang der Wellenausbreitung ist nichts weniger als neu. Er war Hamilton selbst nicht nur wohlbekannt, sondern bildete für ihn den Ausgangspunkt seiner Theorie der Mechanik, die aus seiner *Optik inhomogener Medien* hervorgewachsen ist.[3] Das Hamiltonsche Variationsprinzip kann

1) Siehe diese Annalen 79. S. 361. 1926. Es ist zum Verständnis *nicht* unbedingt nötig, die erste Mitteilung *vor* der zweiten zu lesen.

無法如其他的波方程式由介質的性質推導！

根據少數的線索，猜出物質波的波動方程式。

Ψ

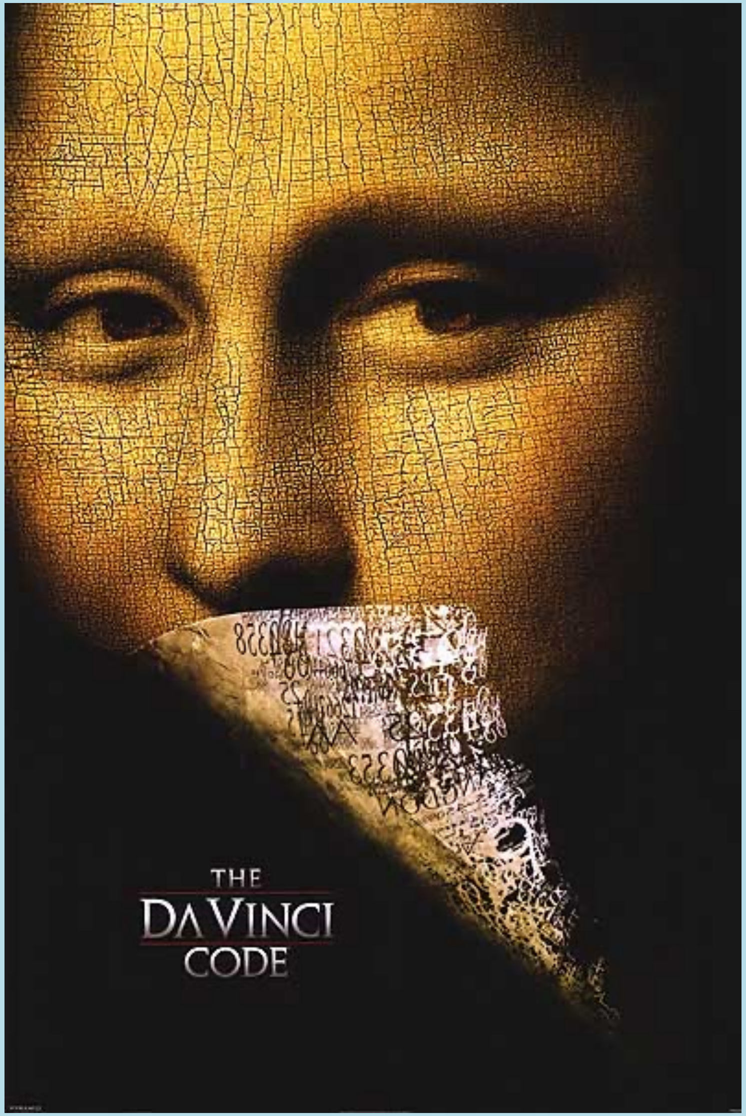
With reference to the origin of the Schrödinger equation, the American Nobel laureate Richard Feynman noted:

> Where did we get that [Schrödinger's equation] from? Nowhere. It is not possible to derive from anything you know. It came out of the mind of Schrödinger, invented in his struggle to find an understanding of the experimental observation of the real world (Feynman *et al.*, 1965, chapter 16, p. 12).

For an historian, this answer is unsatisfying. What exactly was the knowledge on which the Schrödinger equation was based? If it were just some contemporary experimental findings that it describes, how come then that this equation serves to this day in accounting for ever new phenomena that could not have been known to Schrödinger? And what was going on in Schrödinger's mind, on which intellectual resources did he draw to formulate his consequential equations?

Abbildung 2. Tombstone of Annemarie and Erwin Schrödinger (1887–1961) with the Schrödinger equation $i\hbar\dot{\psi} = H\psi$ in modern notation. Photo by C. Joas, 2008.

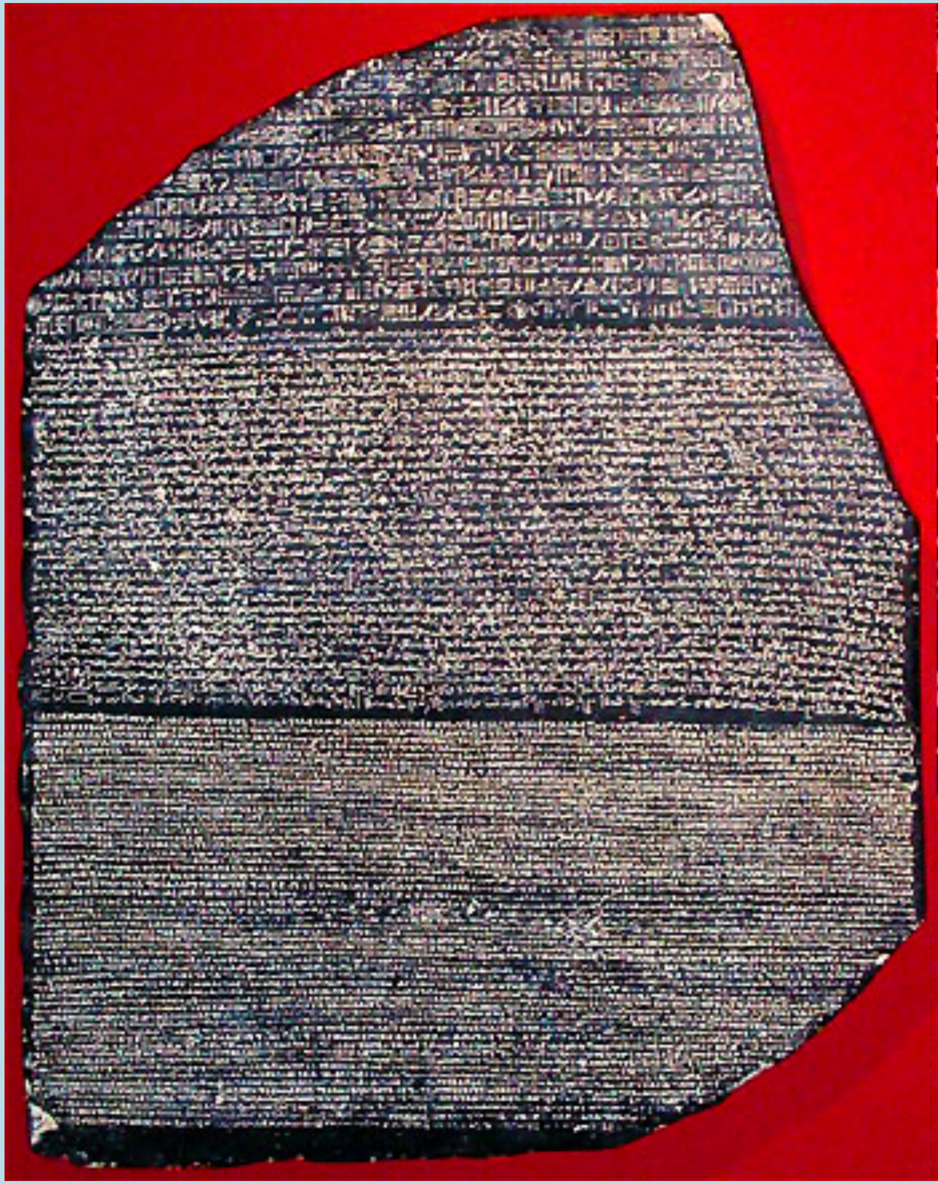
找物質波的波方程式如同解讀一個密碼



解碼，如果如一個古老的失傳的語言，有對照表就非常有用

Rosetta Stone

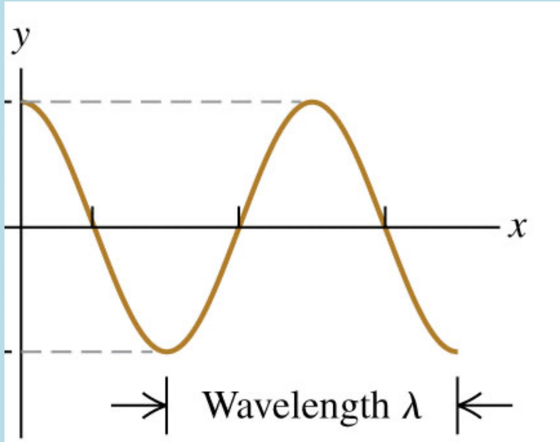
It was created in 196 BC, discovered by the French in 1799 at Rosetta



找尋波方程式時可以用的線索：

德布羅意的猜想：一個不受力、動量固定的自由粒子對應於波長固定的正弦波。

牛頓第一運動定律！



波函數

粒子與波的翻譯表

$$\Psi = A[\cos(kx - \omega t)]$$

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

$$E = hf$$

$$p = \frac{h}{\lambda}$$

$$E = \hbar\omega$$

$$p = \hbar k$$

$$\frac{\hbar^2}{2m}k^2 = \hbar\omega$$

尋找一個波方程式可以得到這個關係。

$\Psi = A[\cos(kx - \omega t)]$ 但這個波函數用在電子波會有問題！

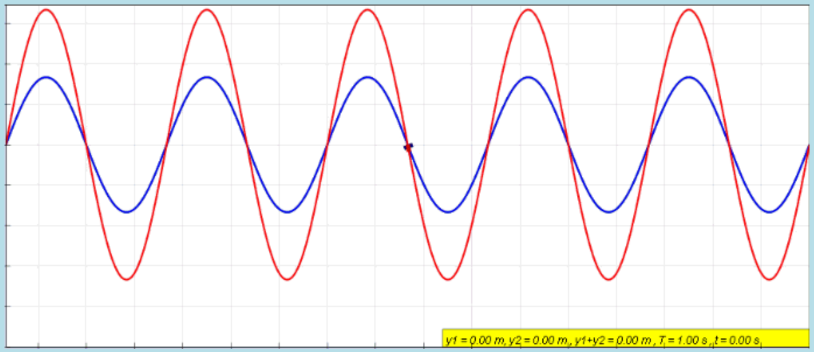
Starting from (1), we build a superposition in which the particle has an equal probability of being found moving in the $+x$ and the $-x$ directions. Such a state must exist, and we build it by adding two waves of type (1):

$$\Psi(x, t) = \cos(kx - \omega t) + \cos(kx + \omega t) = 2\cos kx \cos \omega t. \qquad (3.1.3)$$

This choice is no good; it also vanishes identically when $\omega t = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots$.

疊加後就是傳統的駐波，駐波會在特定時間波函數全為零！

但電子不能有任何時間不見了！



正弦波還有另一個寫法：虛數的指數函數，這會不會是電子波正確的寫法呢？

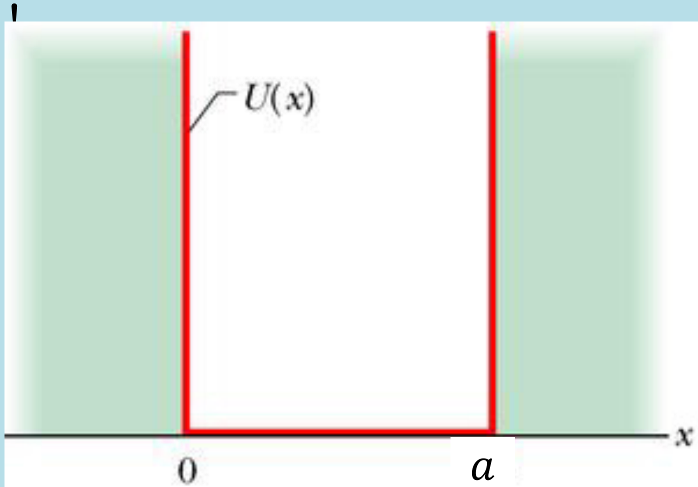
$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

(iii) Let's try a similar superposition of exponentials from (3), with both having the same time dependence:

$$\begin{aligned}\Psi(x,t) &= e^{i(kx-\omega t)} + e^{i(-kx-\omega t)} \\ &= (e^{ikx} + e^{-ikx})\, e^{-i\omega t} \\ &= 2\cos kx\, e^{-i\omega t}.\end{aligned} \tag{3.1.4}$$

This wave function meets our criteria! It is never zero for all values of x because $e^{-i\omega t}$ is never zero.

相似的疊加，不會有全部為零的片刻！可能可以！



虛數的指數函數可能是電子波正確的寫法，先看看這個寫法在一般的波怎麼用：

一般的波，滿足如下的波方程式：

$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2}$$

這個虛數的指數函數有實數部與虛數部，分別是同相的餘弦波與正弦波！

$$\Psi = A[\cos(kx-\omega t) + i\sin(kx-\omega t)]$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

虛數或複數的指數函數具有非常簡單的微分特性：

$$\frac{d^n}{dx^n}e^{ix} = (i)^n \cdot e^{ix}$$

$$\frac{d^n}{dx^n}e^{\alpha x} = (\alpha)^n \cdot e^{\alpha x}$$

雖然明明知道一般波函數是實數不是複數，但複數的指數函數很方便計算，

我們可以先將以虛數的指數函數寫成的解代入波方程式，找到$k-\omega$的關係。

最後再加上波函數必須為實數的條件。

$$e^{i\theta} \equiv \cos\theta + i\sin\theta$$

Euler's Formula　　虛數的指數函數

Carl Friedrich Gauss (1777–1855)

$$\frac{d}{d\theta} e^{i\theta} = -\sin\theta + i\cos\theta = ie^{i\theta}$$

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

正好是我們期待指數函數必須滿足的微分關係。

$$\frac{d^n}{dx^n} e^{i\alpha x} = (i\alpha)^n \cdot e^{i\alpha x}$$

$$e^{i\alpha} \cdot e^{i\beta} = (\cos\alpha + i\sin\alpha) \cdot (\cos\beta + i\sin\beta) =$$

$$(\cos\alpha\cos\beta - \sin\alpha\sin\beta) + i(\sin\alpha\cos\beta + \cos\alpha\sin\beta) =$$

$$\cos(\alpha+\beta) + i\sin(\alpha+\beta) = e^{i(\alpha+\beta)}$$

正好是我們期待指數函數必須滿足的乘積關係。

此定義滿足指數函數所有重要性質！

虛數或複數的指數函數具有非常簡單的微分特性：

$$\frac{d^n}{dx^n}e^{\alpha x} = (\alpha)^n \cdot e^{\alpha x}$$

α是任意複數常數。

$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

$$\frac{\partial^n \Psi}{\partial x^n} = (ik)^n \cdot \Psi$$

$$\frac{\partial^n \Psi}{\partial t^n} = (-i\omega)^n \cdot \Psi$$

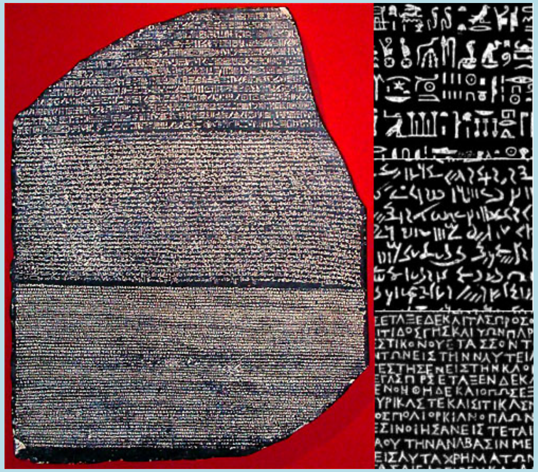
將此波函數代入，可以確定它的確是波方程式的解，只要：

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2} \longrightarrow -k^2\Psi = -\frac{1}{v^2}\omega^2\Psi$$

k,ω滿足色散關係！ $$k^2 = \frac{1}{v^2}\omega^2$$ Dispersion Relation

波方程式給出了色散關係！

或者說從色散關係就能倒回去得到波方程式！



最後再加上波函數必須為實數的條件。這很容易：

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2}$$

方程式的實數部

方程式的虛數部

$$\mathrm{Re}\frac{\partial^2 \Psi}{\partial x^2} = \mathrm{Re}\frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2}$$

$$\frac{\partial^2 \mathrm{Re}\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \mathrm{Re}\Psi}{\partial t^2}$$

$$\frac{\partial^2 \mathrm{Im}\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \mathrm{Im}\Psi}{\partial t^2}$$

複數解的實數部與虛數部都滿足波方程式！

複數解的實數部與虛數部彼此獨立的！

實數部與虛數部都是解。

$$\mathrm{Re}\Psi(x,t) = \mathrm{Re}\, e^{i(kx-\omega t)} = \cos(kx-\omega t)$$

現在把同樣辦法用在電子波：

對電子波而言，色散關係如下：

對於自由電子，已知：$\frac{p^2}{2m} = E$ $\xrightarrow[p = \hbar k]{E = \hbar\omega}$ $\frac{\hbar^2}{2m}k^2 = \hbar\omega$

如果模仿前述的波方程式，在色散關係乘一個自由電子波函數：$\Psi = Ae^{i(kx-\omega t)}$

$$\frac{\hbar^2}{2m}k^2\Psi = \hbar\omega\Psi$$

已知，對這一個波函數取時空微分就分別得到k, ω：

$$\frac{\partial^n\Psi}{\partial x^n} = (ik)^n \cdot \Psi$$

$$\frac{\partial^n\Psi}{\partial t^n} = (-i\omega)^n \cdot \Psi$$

由色散關係，自然猜出可以得出此關係的波方程式如下：

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

Schrodinger Wave Equation

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

方程式的實數部

方程式的虛數部

$$-\frac{\hbar^2}{2m}\frac{\partial^2\mathrm{Re}\Psi}{\partial x^2}=-\hbar\frac{\partial\mathrm{Im}\Psi}{\partial t}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\mathrm{Im}\Psi}{\partial x^2}=\hbar\frac{\partial\mathrm{Re}\Psi}{\partial t}$$

現在解的實數部與虛數部是糾纏在一起的！

解的實數部與虛數部不是彼此獨立的！

所以我已經不能要求這個電子波函數是實數了！

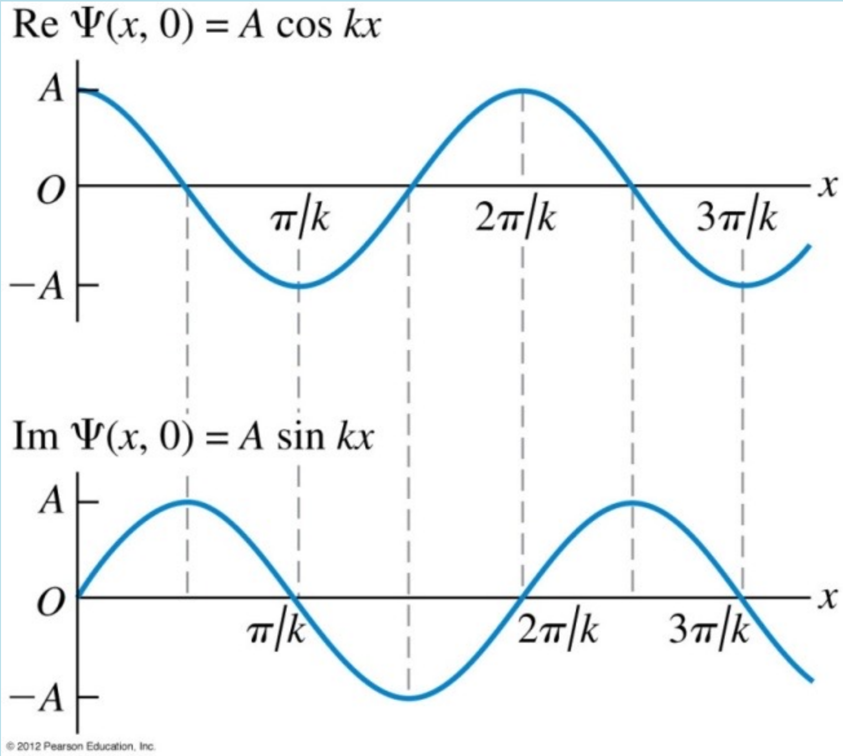
假戲真作！弄假成真。

電子波函數真的是複數！它的實數部與虛數部都有意義，且糾纏在一起。

自由電子波複數的波函數：

$$\Psi = Ae^{i(kx-\omega t)} = A[\cos(kx-\omega t) + i\sin(kx-\omega t)]$$

$$\frac{\hbar^2}{2m}k^2 = \hbar\omega$$



滿足此Schrodinger Wave Equation

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

請注意：在上述的推導，以下的對應關係扮演重要角色：

$$\frac{\partial^n \Psi}{\partial x^n} = (ik)^n \cdot \Psi \quad \longrightarrow \quad \frac{\partial}{\partial x} \leftrightarrow ik$$

$$\frac{\partial^n \Psi}{\partial t^n} = (-i\omega)^n \cdot \Psi \quad \longrightarrow \quad \frac{\partial}{\partial t} \leftrightarrow -i\omega$$

這暗示我們：在量子翻譯表中，時間微分翻譯為ω，位置微分翻譯為k。

左手邊的運算作用於自由電子波函數時，與右手邊的數乘該波函數一樣。

我們又已經知道：ω翻譯為E，k翻譯為p 。

因此，終極翻譯表，直接由粒子圖像翻譯為波函數的運算！

$$\frac{\partial}{\partial x} \leftrightarrow ik$$

$$\frac{\partial}{\partial t} \leftrightarrow -i\omega$$

$$p = \hbar k$$

$$E = \hbar\omega$$

$$-i\hbar\frac{\partial}{\partial x} \leftrightarrow p$$

$$i\hbar\frac{\partial}{\partial t} \leftrightarrow E$$

動量翻譯為空間微分運算。

能量翻譯為時間微分運算。

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

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

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

運算得運算於某個東西之上。

這東西自然是波函數Ψ。

Schrodinger Wave Equation

粒子 → 波動

將波函數的運算動作取名，定義為一個個算子Operator！

$$-i\hbar\frac{\partial}{\partial x}\equiv\hat{p}$$

$$i\hbar\frac{\partial}{\partial t}\equiv\hat{H}$$

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

動量就是空間微分運算

能量就是時間微分運算

大膽地猜，所有物理量都對應到一個算子！

$$\frac{p^2}{2m}=E \quad\Longrightarrow\quad \frac{\hat{p}^2}{2m}=\hat{H}$$

若有古典對應，$\hat{H}$就採取古典一樣的形式，

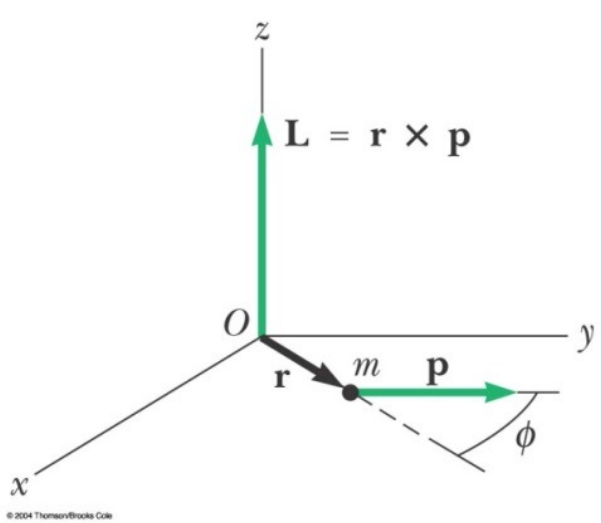
古典　　　　量子

角動量算子

$$\vec{L} = \vec{r}\times\vec{p}$$

$$L_z = xp_y - yp_x$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$



$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

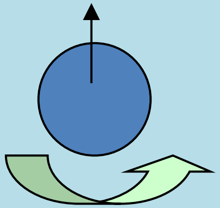
$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

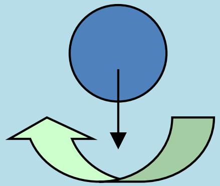
$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

所有物理量都對應到一個運算的算子！例如電子自旋的情況，

電子自旋的狀態只有兩個，

狀態 $|\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ $|\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}$



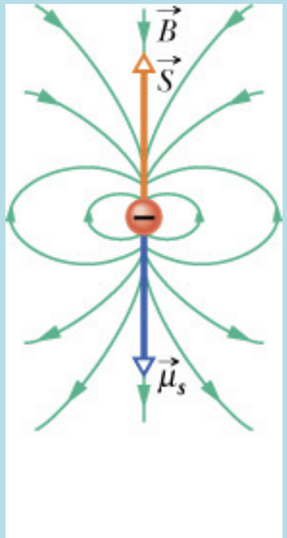


或是兩者的疊加狀態，因此組成一二維線性空間。 $c_1|\uparrow\rangle + c_2|\downarrow\rangle = \begin{pmatrix}c_1\\c_2\end{pmatrix}$

線性空間上運算就是線性變換，而線性變換等價於矩陣。

自旋角動量，大膽猜想在此二維線性空間上，就表示為2×2矩陣：

$$\hat{S}_x = \frac{1}{2}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} \quad \hat{S}_y = \frac{1}{2}\begin{pmatrix}0 & -i\\i & 0\end{pmatrix} \quad \hat{S}_z = \frac{1}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$



在電磁學中，能量等於磁偶極矩與磁場的內積，

注意磁偶極矩與電子角動量成正比，若選磁場方向為z：

$$U = -\vec{\mu}\cdot\vec{B} = \frac{e}{m}\vec{S}\cdot\vec{B} \quad \Rightarrow \quad \hat{H} = \frac{e}{m}\vec{S}\cdot\vec{B} = \frac{eB_z}{m}\hat{S}_z$$

在電子自旋的情況，能量算子$\hat{H}$就正比於沿磁場方向的自旋算子$\hat{S}_z$ 。

當電子不是自由粒子，而是受到一個位能的影響，假設翻譯表還是可以用！

此時動量與能量的關係要修改為：然後代入翻譯表：

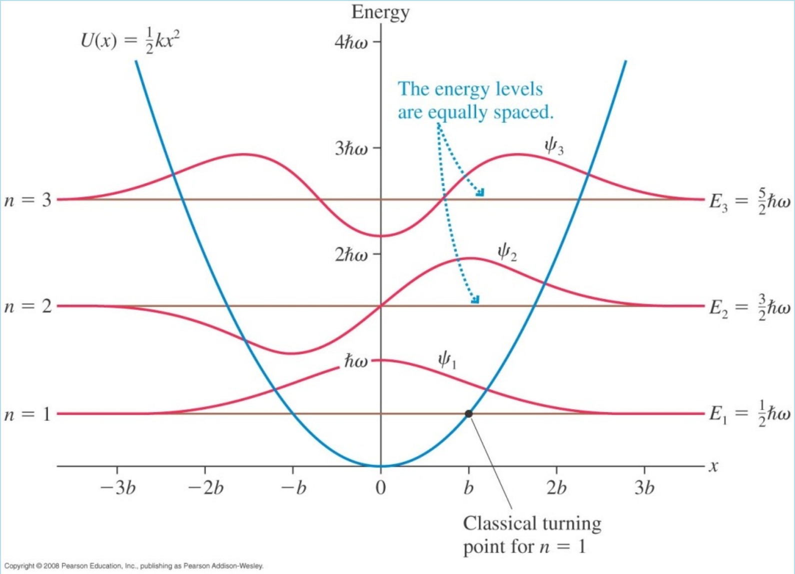
$$\frac{p^2}{2m} + V = E$$

$$-i\hbar\frac{\partial}{\partial x} \leftrightarrow p$$

$$i\hbar\frac{\partial}{\partial t} \leftrightarrow E$$

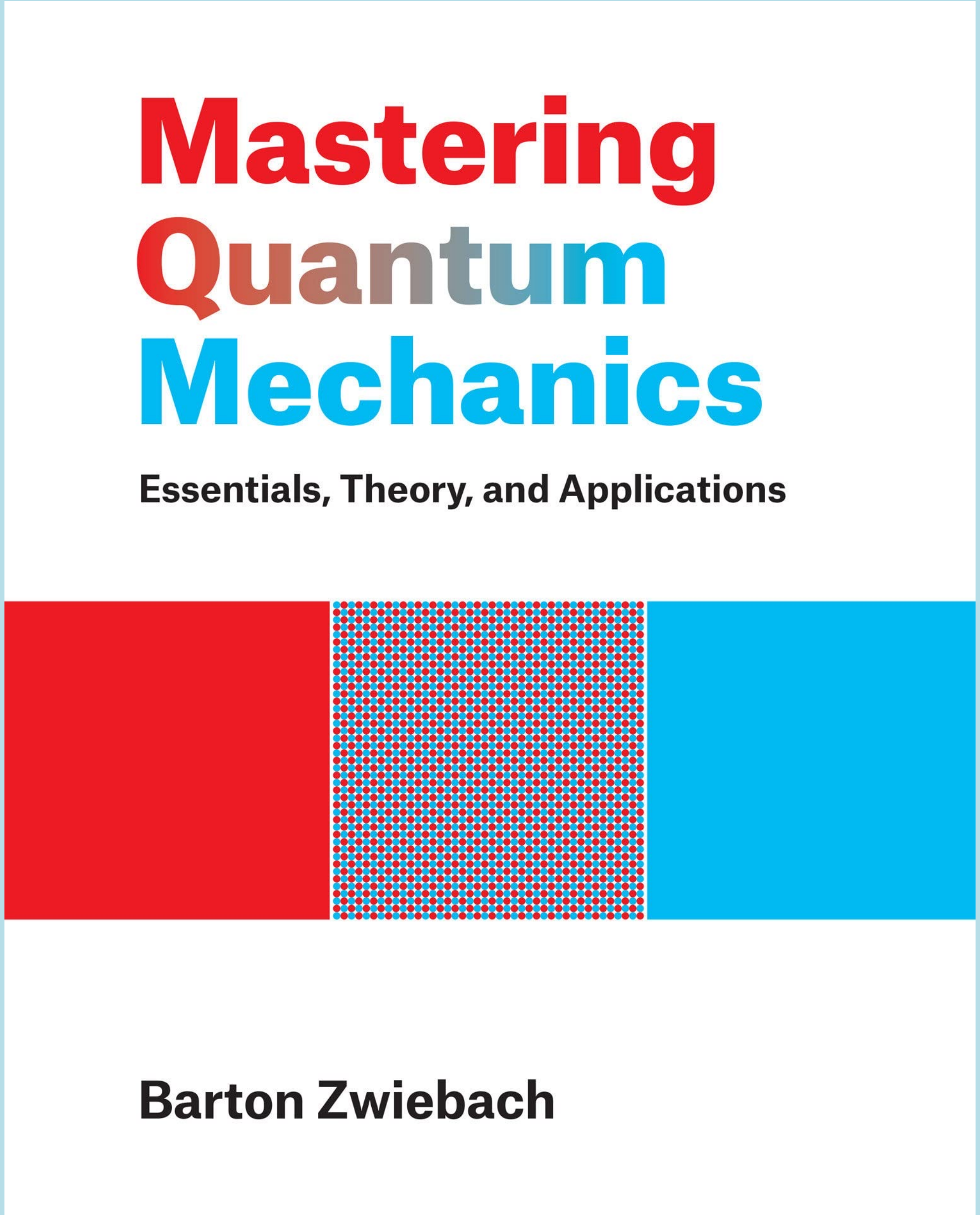
電子波波方程式

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



Schrodinger Wave Equation 以上大致是一個猜出來的過程。

此方程式的正確性是在薛丁格以它計算出氫原子能階，才算確立。


Mastering
Quantum
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Essentials, Theory, and Applications
Barton Zwiebach

$\hbar\omega$ and $p = \hbar k$. Let's assume our wave is propagating in the $+\,x$ direction. All the following are examples of waves that could be candidat[illegible]article wave function:

1. $\sin(kx - \omega t)$,

2. $\cos(kx - \omega t)$,
3. $e^{i(kx-\omega t)} = e^{ikx}e^{-i\omega t}$ (fixed time dependence $\propto e^{-i\omega t}$),
4. $e^{-i(kx-\omega t)} = e^{-ikx}e^{i\omega t}$ (fixed time dependence $\propto e^{+i\omega t}$).

The third and fourth options use time dependences with opposite signs. We will use superposition to decide which of these four candidates is the right one. Let's take them one by one:

(i) Starting from (1), we build a superposition in which the particle has an equal probability of being found moving in the $+\,x$ and the $-\,x$ directions. Such a state must exist, and we build it by adding two waves of type (1):

$$\Psi(x,t) = \sin(kx - \omega t) + \sin(kx + \omega t). \tag{3.1.1}$$

Expanding the trigonometric functions, this can be simplified to

$$\Psi(x,t) = 2\sin kx \cos\omega t. \tag{3.1.2}$$

But this result is not sensible. The wave function vanishes identically for all x at the special times $\omega t = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \ldots$. A wave function that is zero all over space at some particular time cannot represent a particle. Thus, (1) is not a good candidate.

(iii) Let's try a similar superposition of exponentials from (3), with both having the same time dependence:

$$\begin{aligned} \Psi(x,t) &= e^{i(kx-\omega t)} + e^{i(-kx-\omega t)} \\ &= (e^{ikx} + e^{-ikx})\, e^{-i\omega t} \\ &= 2\cos kx\, e^{-i\omega t}. \end{aligned} \tag{3.1.4}$$

This wave function meets our criteria! It is never zero for all values of x because $e^{-i\omega t}$ is never zero.

$$\boxed{\text{free-particle wave function:} \quad \Psi(x,t) = e^{i(kx-\omega t)},} \tag{3.1.7}$$

The wave function Ψ_p represents a state of definite momentum. We now look for an *operator* that extracts the value of the momentum from the wave function. The operator, to be called the *momentum operator*, must involve a derivative with respect to x, as this would bring down a factor of k from the exponential. More precisely, we can see that

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_p(x,t) = \frac{\hbar}{i}(ik)\Psi_p(x,t) = \hbar k\Psi_p(x,t) = p\,\Psi_p(x,t), \tag{3.2.3}$$

where the p factor in the last right-hand side is in fact the momentum of the state. We thus identify the operator $\frac{\hbar}{i}\frac{\partial}{\partial x}$ as the *momentum operator* $\hat{p}$:

$$\boxed{\hat{p} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}.} \tag{3.2.4}$$

We have verified that acting on the wave function $\Psi_p(x, t)$ describing a particle of momentum p, the operator $\hat{p}$ gives precisely the number p times the wave function:

$$\hat{p}\,\Psi_p = p\,\Psi_p. \tag{3.2.5}$$

Begin with the product of the energy times the wave function Ψ_p:

$$E\,\Psi_p = \frac{p^2}{2m}\Psi_p = \frac{p}{2m}\,(p\Psi_p) = \frac{p}{2m}\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_p, \tag{3.2.7}$$

where we used equation (3.2.5) to write $p\Psi_p$ as the momentum operator acting on Ψ_p. Since the remaining p on the last expression is a constant, we can move it across the derivative until it is close to the wave function, at which point we replace it by the momentum operator:

$$E\,\Psi_p = \frac{1}{2m}\,\frac{\hbar}{i}\,\frac{\partial}{\partial x}\,(p\Psi_p) = \frac{1}{2m}\,\frac{\hbar}{i}\,\frac{\partial}{\partial x}\Big(\frac{\hbar}{i}\,\frac{\partial}{\partial x}\,\Psi_p\Big). \tag{3.2.8}$$

This can be written as

$$E\,\Psi_p = \frac{1}{2m}\hat{p}\,\hat{p}\,\Psi_p = \frac{\hat{p}^2}{2m}\,\Psi_p, \tag{3.2.9}$$

which suggests the following definition of the *energy operator* $\hat{E}$:

$$\hat{E} \equiv \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \tag{3.2.10}$$

Indeed, with this definition, (3.2.9) shows that

$$\hat{E}\,\Psi_p = E\,\Psi_p, \tag{3.2.11}$$

as befits the energy operator. The state Ψ_p is a state of definite energy E, the eigenvalue of the energy operator.

Let us now find a differential equation for which our de Broglie wave function is a solution. First, we note that a suitable time derivative also extracts the energy eigenvalue from Ψ_p. Using (3.2.1), we find that

$$i\hbar\frac{\partial}{\partial t}\Psi_p(x,t) = i\hbar(-i\omega)\Psi_p(x,t) = \hbar\omega\,\Psi_p(x,t) = E\,\Psi_p(x,t). \tag{3.2.12}$$

We can now replace the final right-hand side $E\Psi_p$ by $\hat{E}\,\Psi_p$, giving us a differential equation satisfied by Ψ_p:

$$i\hbar\,\frac{\partial}{\partial t}\Psi_p(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_p(x,t). \tag{3.2.13}$$

Since the momentum p appears only in the wave function, we are inspired by this differential equation to think of it more generally as an equation for general wave functions $\Psi(x, t)$ of a free particle:

$$\boxed{i\hbar\,\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t).} \tag{3.2.14}$$

This inspired guess is the **free-particle Schrödinger equation**. Schematically, using the

Screenshot

Note that the Schrödinger equation admits solutions that are more general than the de Broglie wave function for a particle of definite momentum and energy. This often happens in physics. Limited evidence leads to some equation that happens to contain much more physics than the unsuspecting inventor ever imagined. Since the equation we wrote is linear, any superposition of plane wave solutions with different values of k is a solution. Take, for example,

$$\Psi(x,t) = a_1\, e^{i(k_1 x - \omega_1 t)} + a_2\, e^{i(k_2 x - \omega_2 t)}, \tag{3.2.18}$$

where a_1 and a_2 are arbitrary complex numbers, and $k_1 \neq k_2$. This is a solution provided the pairs (k_1, ω_1) and (k_2, ω_2) each satisfy (3.2.17). While each summand is a state of definite momentum, the total solution is not a state of definite momentum. Indeed,

and the right-hand side cannot be written as a number times $\Psi(x, t)$. The full state is not a state of definite energy either. The general solution of the free Schrödinger equation is the most general superposition of plane waves:

$$\Psi(x,t) = \int_{-\infty}^{\infty} dk\, \Phi(k)\, e^{i(kx - \omega(k)t)}, \tag{3.2.20}$$

where $\Phi(k)$ is an *arbitrary* function of k that controls the superposition, and we have written $\omega(k)$ to emphasize that ω is a function of the momentum, as in (3.2.17). The momentum eigenstate plane waves Ψ_p are not localized in space; they are nowhere vanishing. General superpositions, as in the above expression, can be made to represent localized solutions by choosing a suitable $\Phi(k)$. In that case they are said to describe *wave packets*.

We now have the tools to evolve in time any initial state of a free particle: given the initial wave function $\Psi(x, 0)$ at time zero, we can obtain $\Psi(x, t)$. (This is a preview of a more detailed discussion to come in section 4.3.) Indeed, if we know $\Psi(x, 0)$, we can write:

$$\Psi(x,0) = \int_{-\infty}^{\infty} dk\, \Phi(k)\, e^{ikx}, \tag{3.2.22}$$

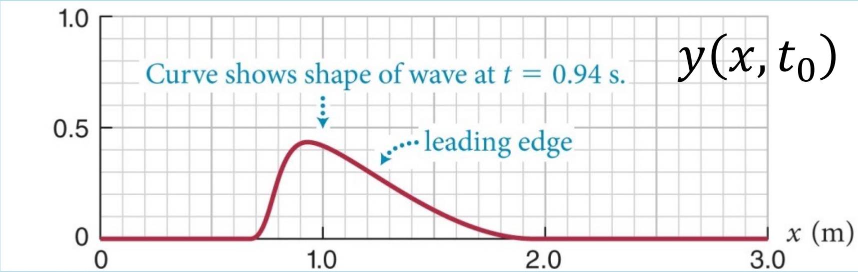
where $\Phi(k)$ is, by definition, the Fourier transform of $\Psi(x, 0)$. The Fourier transform $\Phi(k)$ can be calculated in terms of $\Psi(x, 0)$. Once we know $\Phi(k)$, the time evolution simply requires the replacement

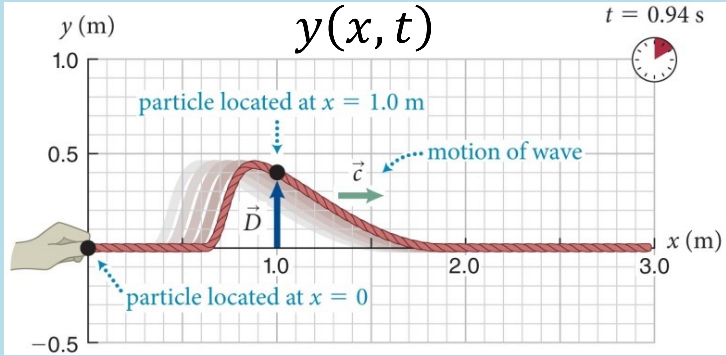
$$e^{ikx} \rightarrow e^{ikx} e^{-i\omega(k)t} \tag{3.2.23}$$

in the above integrand so that the answer for the time evolved $\Psi(x, t)$ is in fact given by (3.2.20).

波函數$\Psi(x,t)$與時間變數的關聯，與空間變數的關聯可以分開來看。

固定$t=t_0$，$\Psi(x,t)\rightarrow\Psi(x,t_0)$，波函數成為一個$x$的單變數函數。





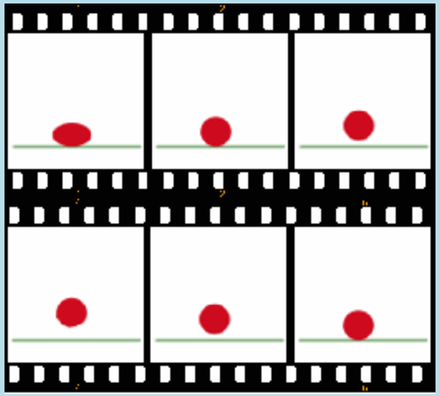
在古典波$y(x,t_0)$就是$t=t_0$時的瞬間波形。

在電子波，$\Psi(x,t_0)$就描述電子在$t=t_0$時的狀態，可稱為瞬間波函數。

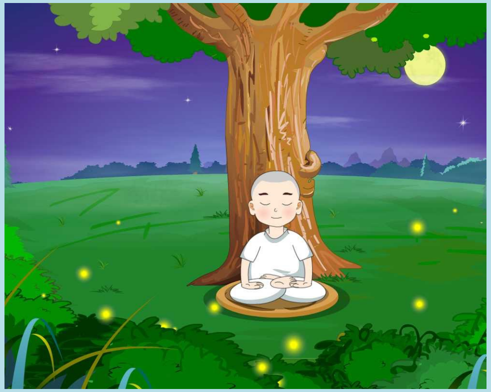
例如$\Psi(x,0)$就描述電子在$t=0$時的瞬間波函數，也就是起始條件。

如同古典波，接下來波型隨時間的演化，就由波方程式決定，

電子波隨時間的演化$\Psi(x,t)$就由薛丁格方程式決定。



注意自由電子波有一特徵與一般波完全迥異：



$$\Psi = Ae^{i(kx-\omega t)} = \left(Ae^{ikx}\right)\cdot e^{-i\omega t}$$

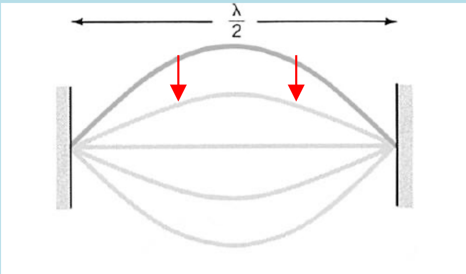
波函數的時間部分與空間部分可以分離separable。

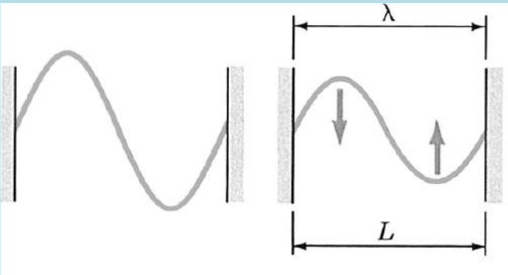
$$\Psi(x,t) = \psi(x)\cdot\phi(t)$$

Ae^{ikx}是時間為零時的瞬間波函數$\Psi(x,0)$，$e^{-i\omega t}$是未來的演化evolution。

不同位置x的起始條件與未來t的演化可分離，

表示不同位置x的波是用同樣方式、一起變化的。



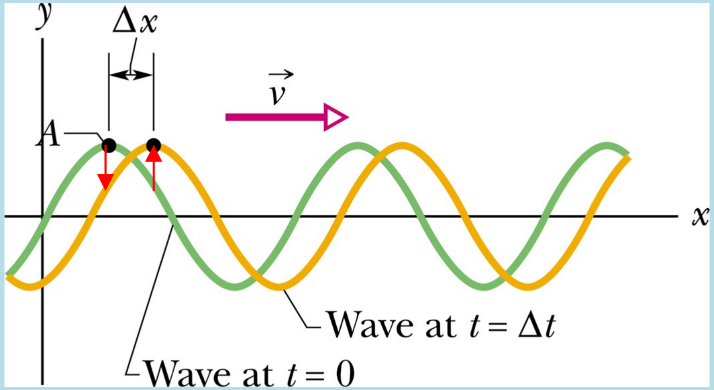


這個特徵比較接近駐波

$$A\cdot\sin kx\cdot\cos\omega t$$

一般行進波波函數是無法分離的！

$$A\cos(kx-\omega t)$$



這樣可以分離的量子波函數，稱為定態。它可測量的量都與時間無關。

Schrodinger Wave Equation

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

給定起始條件，未來的波函數原則上可以完全被決定，沒有不確定性！

但複數波函數不是可以測量的物理量。

實驗顯示：波強度正比於以電子束進行實驗得到的分布，應可觀測。

因此波強度對單次實驗雖然無法預測，但能預測機率。

波強度可以以波函數的絕對值平方$|\Psi(x,t)|^2$計算。

$$I = |\Psi(x,t)|^2 = \Psi^*(x,t)\cdot\Psi(x,t)$$

波函數的機率解釋

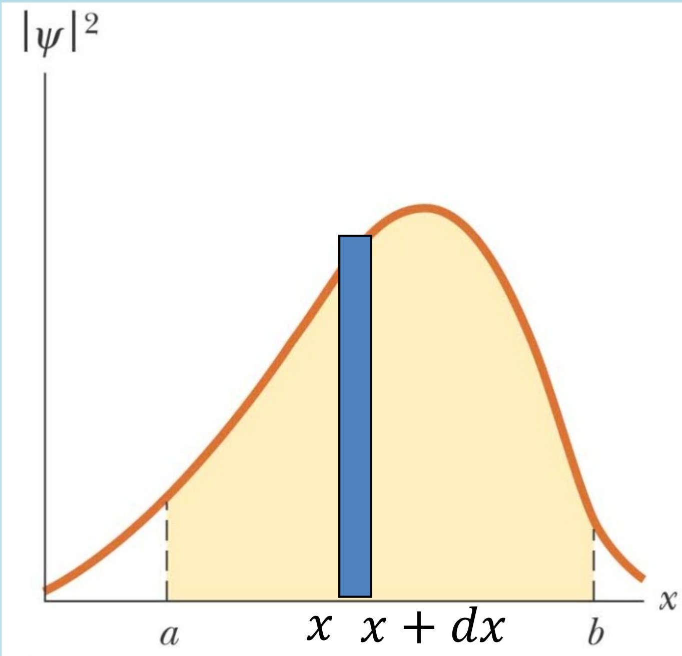
x是連續變數，所以機率大小是以機率密度表示！

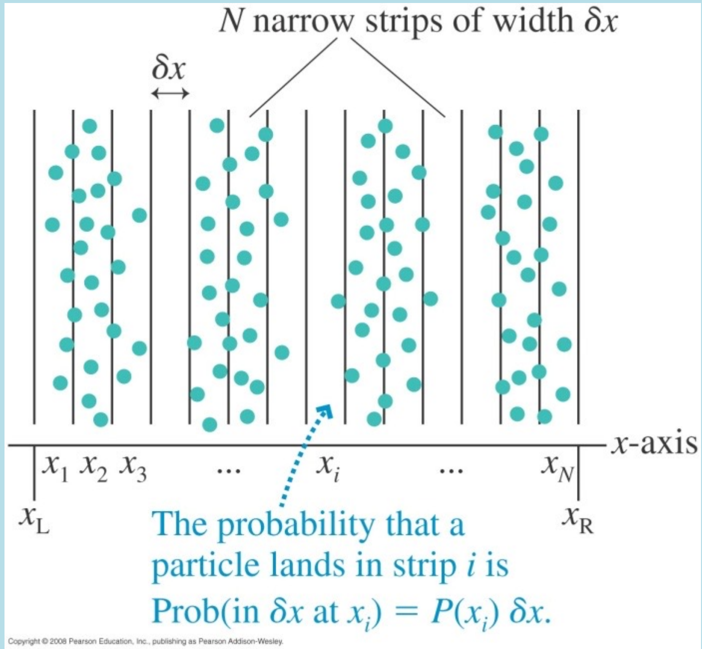
時間為t的瞬間在x與$x+dx$之間發現該粒子的機率，可以寫成：

（意思就是位置在x附近，不準度大約是dx）

$$P(x,t)\cdot dx = |\Psi(x,t)|^2\cdot dx = \Psi^*(x,t)\cdot\Psi(x,t)\cdot dx$$

此瞬間t的波函數絕對值平方$|\Psi(x,t)|^2$就是此瞬間的機率密度$P(x)$。





有時會以點的數目來表示機率大小！

$$\int_a^b |\Psi(x,t)|^2\cdot dx$$

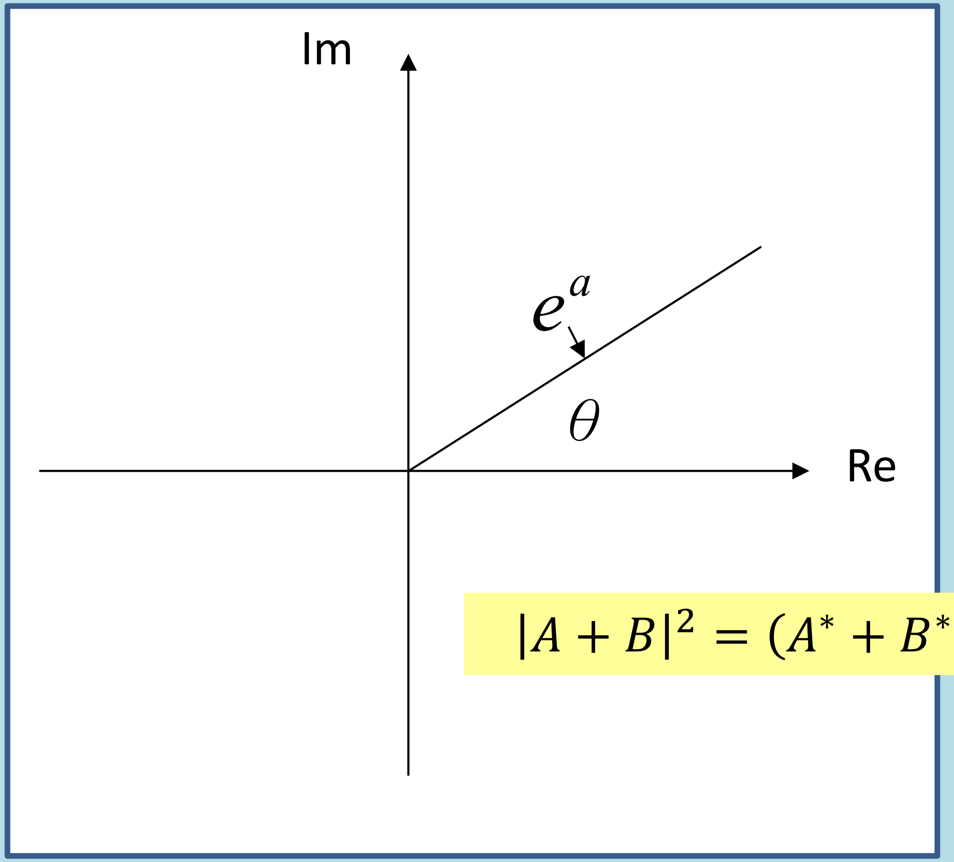
將機率密度積分，可以得在a與b之間發現該粒子的機率。

我們可以更進一步定義複數$\alpha = a + i\theta$的指數函數：

$$e^{\alpha} = e^{a+i\theta} = e^{a}e^{i\theta} = e^{a}(\cos\theta + i\sin\theta)$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

在複數平面上表示，a 決定絕對值，θ 決定幅角



$$\left|e^{i\theta}\right| = 1$$

$$\left|e^{a+i\theta}\right| = e^{a}$$

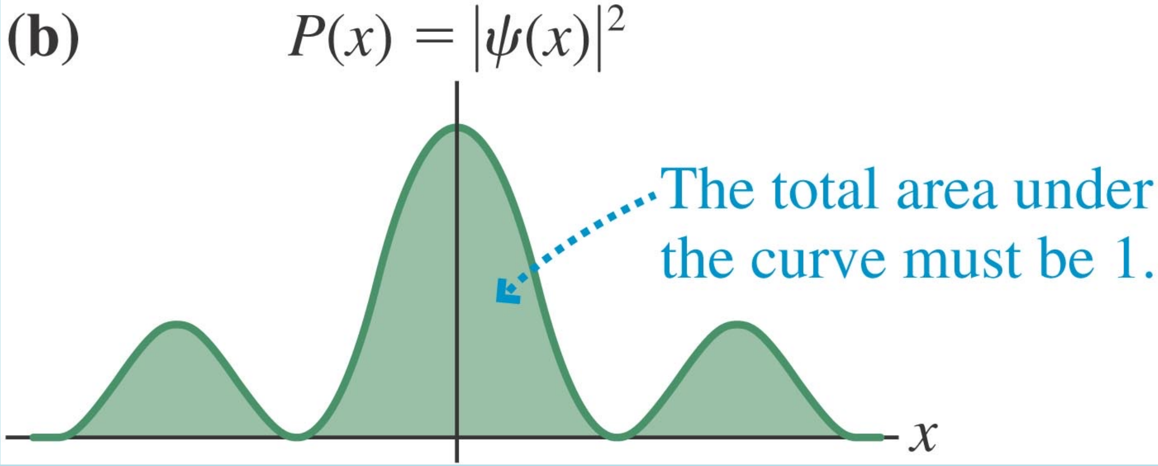
$$|mn| = |m| \cdot |n|$$

$$|A+B|^2 = (A^* + B^*)(A+B) = |A|^2 + |B|^2 + A^*B + B^*A$$

$$\frac{d^n}{dx^n}e^{\alpha x} = (\alpha)^n \cdot e^{\alpha x}$$

所以，複數的指數函數，所有的微分都與自己成正比！

發現該粒子的總機率必需等於 1。



$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \cdot dx = 1$$

機率密度的總積分必需等於 1。

歸一化條件 Normalization Condition

這個是電子波函數在薛丁格方程式以外必須滿足的額外的條件。

光子或會衰變生成的粒子就不滿足此條件。

但總機率是不是會隨時間變化？

計算機率密度的時變率：

$$\frac{\partial}{\partial t}|\Psi(x,t)|^2 = \frac{\partial}{\partial t}[\Psi^*(x,t)\cdot\Psi(x,t)] = \frac{\partial \Psi^*}{\partial t}\cdot\Psi + \Psi^*\cdot\frac{\partial \Psi}{\partial t}$$

薛丁格方程式給出波函數的時變率：

$$\frac{\partial \Psi}{\partial t} = i\frac{\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2} - \frac{i}{\hbar}V(x)\Psi \qquad \frac{\partial \Psi^*}{\partial t} = -i\frac{\hbar}{2m}\frac{\partial^2\Psi^*}{\partial x^2} + \frac{i}{\hbar}V(x)\Psi^*$$

代入前式，有位能的第二項會消掉：

$$\frac{\partial}{\partial t}P(x,t) = -i\frac{\hbar}{2m}\left(\frac{\partial^2\Psi^*}{\partial x^2}\cdot\Psi - \Psi^*\cdot\frac{\partial^2\Psi}{\partial x^2}\right) = -i\frac{\hbar}{2m}\frac{\partial}{\partial x}\left(\frac{\partial\Psi^*}{\partial x}\cdot\Psi - \Psi^*\cdot\frac{\partial\Psi}{\partial x}\right) \equiv \frac{\partial}{\partial x}j(x,t)$$

機率密度的時變率等於一個量的空間微分，這與電荷守恆式一樣。

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}j(x,t) \qquad \frac{\partial}{\partial t}Q + \vec{\nabla}\cdot\vec{j} = 0$$

$$j(x,t) = -i\frac{\hbar}{2m}\left(\frac{\partial\Psi^*}{\partial x}\cdot\Psi - \Psi^*\cdot\frac{\partial\Psi}{\partial x}\right)$$

Probability Current

取機率密度時變率的全空間積分，右手邊會出現j在$\pm\infty$的差，此處Ψ應為零。

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} dx\cdot P(x,t) = \int_{-\infty}^{\infty} dx\cdot\frac{\partial}{\partial x}j(x,t) = 0$$

因此總機率守恆。

假設某時間時，瞬間波函數可以寫成：$Ae^{-\mu|x|}$

考慮其歸一化條件，並計算機率密度。

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 $2/\alpha$.

Strategy This wave function is sketched in Figure 6.1. We will use Equation (6.8) to normalize Ψ. Then we will find the probability by using the limits in the integration of Equation (6.7).

Solution If we insert the wave function into Equation (6.8), we have

$$\int_{-\infty}^{\infty} A^2 e^{-2\alpha|x|}\, dx = 1$$

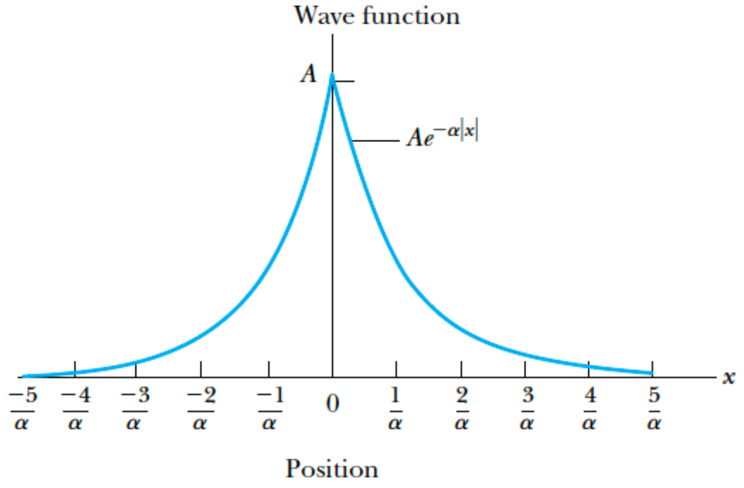


Figure 6.1 The wave function $Ae^{-\alpha|x|}$ is plotted as a function of x. Note that the wave function is symmetric about $x = 0$.

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Solution If we insert the wave function into Equation (6.8), we have

$$\int_{-\infty}^{\infty} A^2 e^{-2\alpha|x|}\, dx = 1$$

Because the wave function is symmetric about $x = 0$, we can integrate from 0 to ∞, multiply by 2, and drop the absolute value signs on $|x|$.

$$2\int_0^{\infty} A^2 e^{-2\alpha x}\, dx = 1 = \frac{2A^2}{-2\alpha} e^{-2\alpha x}\Big|_0^{\infty}$$

$$1 = \frac{-A^2}{\alpha}(0 - 1) = \frac{A^2}{\alpha}$$

The coefficient $A = \sqrt{\alpha}$, and the normalized wave function Ψ is

$$\Psi = \sqrt{\alpha}\, e^{-\alpha|x|}$$

We use Equation (6.7) to find the probability of the particle being between 0 and $1/\alpha$, where we again drop the absolute signs on $|x|$ because x is positive.

$$P = \int_0^{1/\alpha} \alpha e^{-2\alpha x}\, dx$$

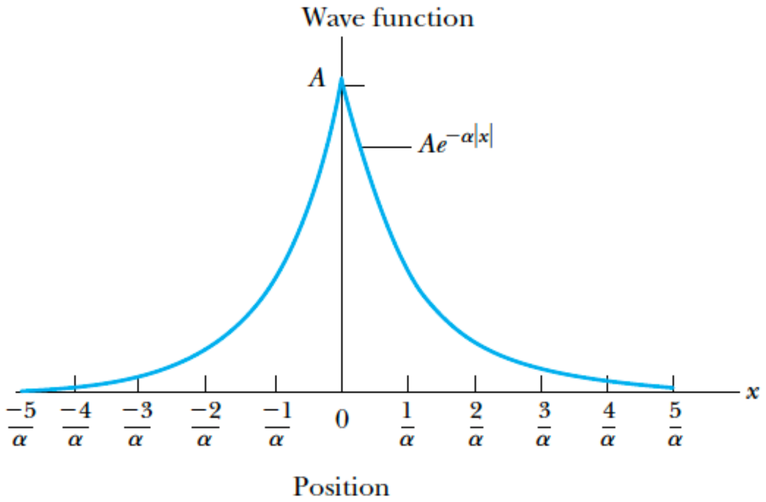


Figure 6.1 The wave function $Ae^{-\alpha|x|}$ is plotted as a function of x. Note that the wave function is symmetric about $x = 0$.

The integration is similar to the previous one.

$$P = \frac{\alpha}{-2\alpha} e^{-2\alpha x}\Big|_0^{1/\alpha} = -\frac{1}{2}(e^{-2} - 1) \approx 0.432$$

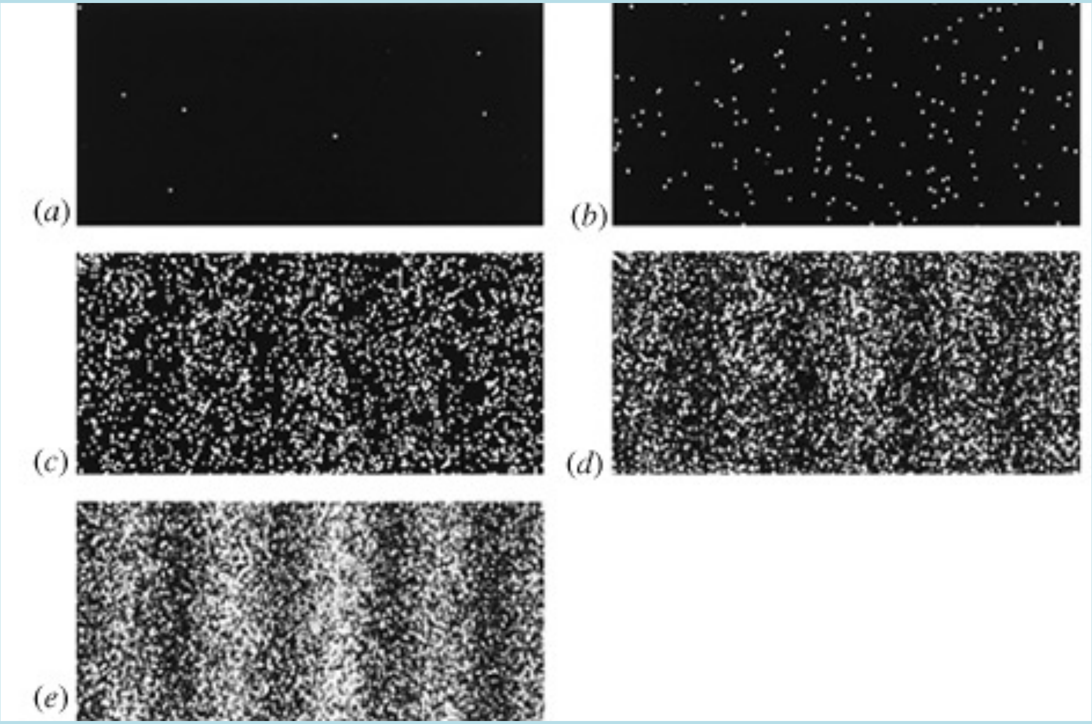
The probability of the particle being between $1/\alpha$ and $2/\alpha$ is

$$P = \int_{1/\alpha}^{2/\alpha} \alpha e^{-2\alpha x}\, dx$$

$$P = \frac{\alpha}{-2\alpha} e^{-2\alpha x}\Big|_{1/\alpha}^{2/\alpha} = -\frac{1}{2}(e^{-4} - e^{-2}) \approx 0.059$$

We conclude that the particle is much more likely to be between 0 and $1/\alpha$ than between $1/\alpha$ and $2/\alpha$. This is to be expected, given the shape of the wave function shown in Figure 6.1.

自由電子波波函數及其機率解釋能計算雙狹縫干涉的粒子分佈嗎？



$$\Psi = \Psi_1 + \Psi_2 = Ae^{i(kx_1-\omega t)} + Ae^{i(kx_2-\omega t)}$$

x_1, x_2 是狹縫1,2距觀測點的距離！

觀測點的機率密度：

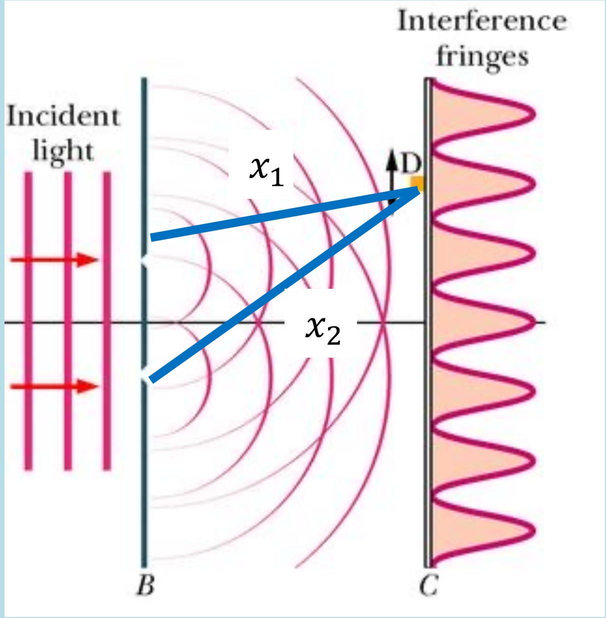
$$|\Psi_1 + \Psi_2|^2 = (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2) = |\Psi_1|^2 + |\Psi_2|^2 + \Psi_2^*\Psi_1 + \Psi_1^*\Psi_2$$

$$= P_1 + P_2 + 2\mathrm{Re}\,\Psi_1^*\Psi_2 = 2|A|^2 + 2\mathrm{Re}\,\Psi_1^*\Psi_2 \qquad 2\text{-}16$$

$\mathrm{Re}\,\Psi_1^*\Psi_2$ 就是干涉的結果！

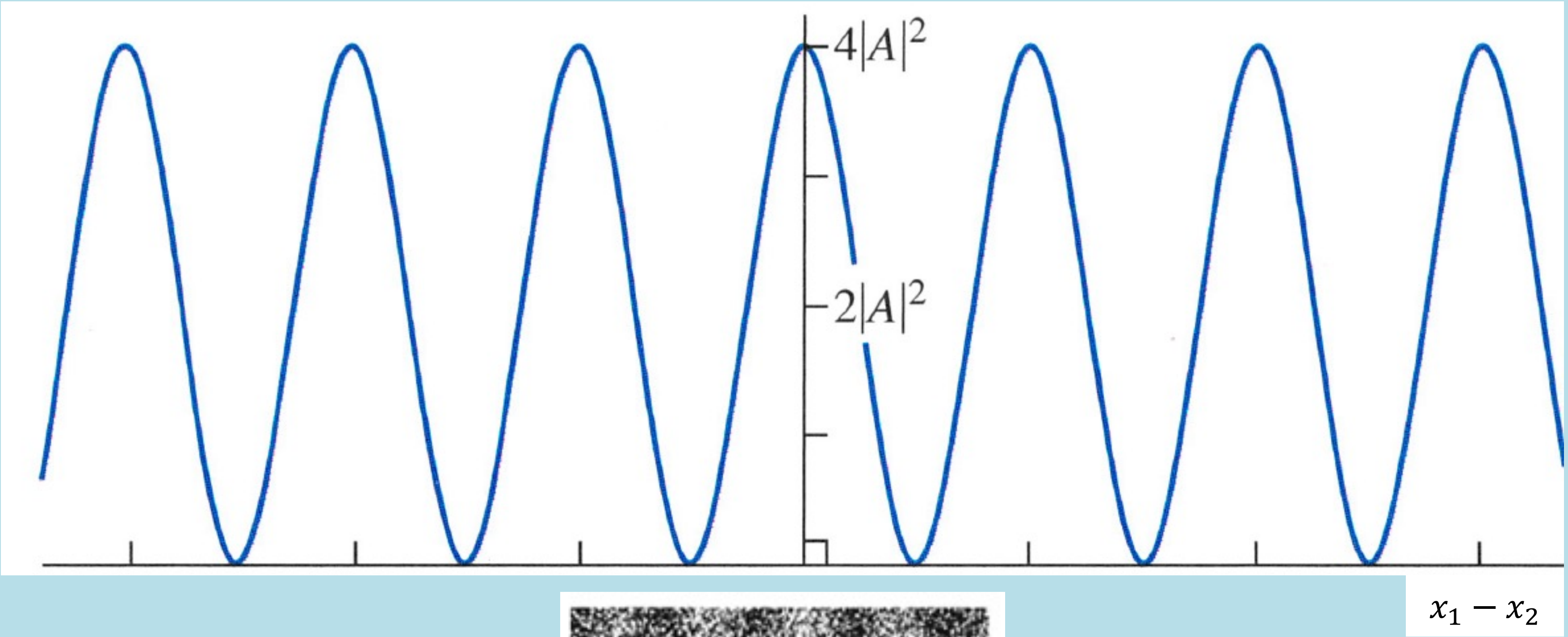
$$\mathrm{Re}\,\Psi_1^*\Psi_2 = \mathrm{Re}\left[A^*e^{-i(kx_1-\omega t)} \cdot Ae^{i(kx_2-\omega t)}\right] = |A|^2\mathrm{Re}\left[e^{-ik(x_1-x_2)}\right] = |A|^2\cos k(x_1 - x_2)$$

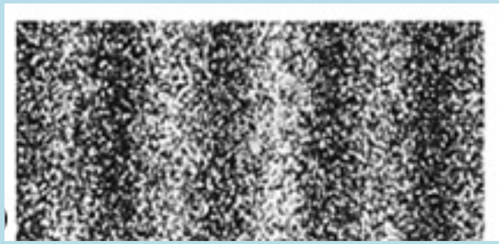
$$|\Psi_1 + \Psi_2|^2 = 2|A|^2[1 + \cos k(x_1 - x_2)]$$



$$|\Psi_1+\Psi_2|^2 = 2|A|^2[1+\cos k(x_1-x_2)] = 4|A|^2\left(\cos\frac{k(x_1-x_2)}{2}\right)^2$$

與一般雙狹縫干涉完全一致！





$\Psi = Ae^{i(kx-\omega t)}$

$$\frac{\hbar^2}{2m}k^2 = \hbar\omega$$

通常會說這是單一方向傳播的電子波，波長確定，動量確定。

但這一單一方向傳播電子波機率密度為一常數。

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \cdot dx \ = \infty$$

$P = |\Psi(x,t)|^2 = |A|^2$ 這個解根本不滿足Normalization Condition.

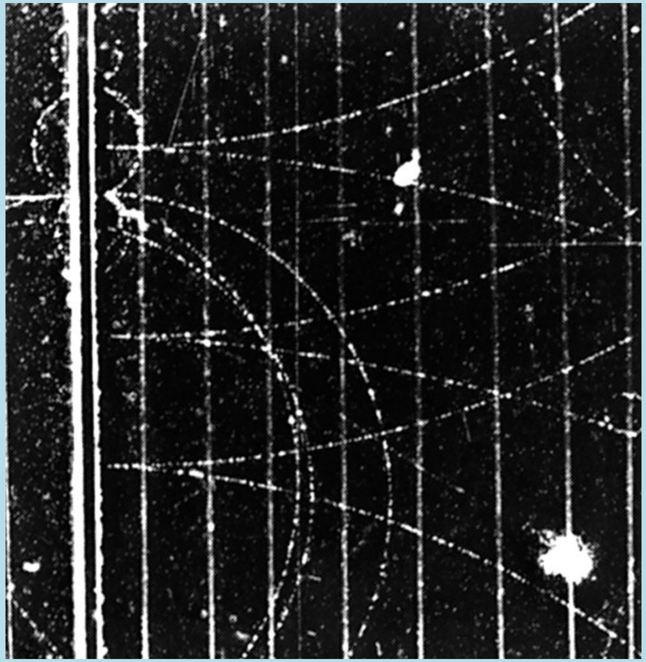
動量完全確定，位置完全不確定，（這是波狀的態的波函數）。

因為沒有任何位置資訊，不能稱它為沿+*x*方向運動的電子，

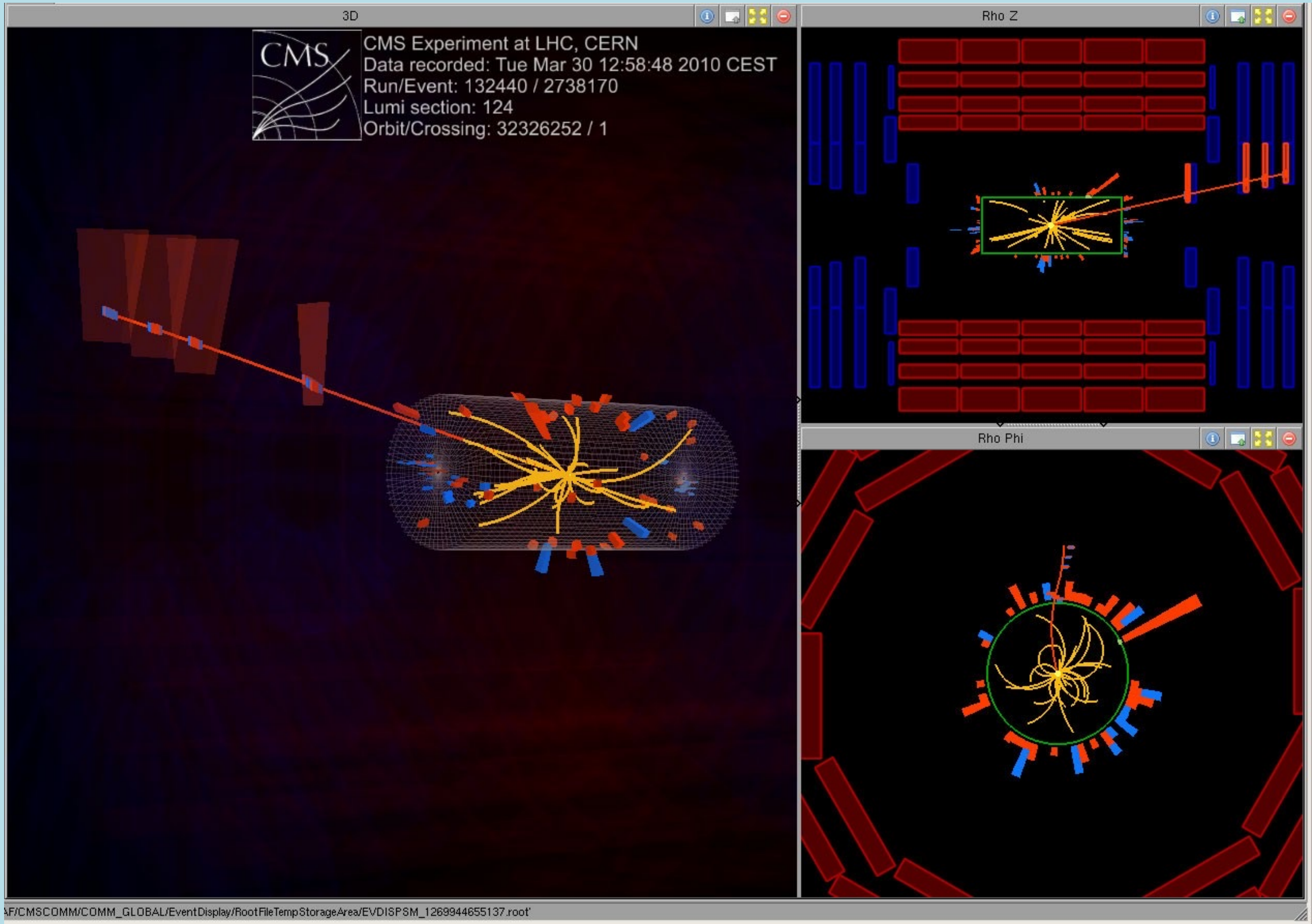
它只是擁有+*x*方向的動量，但並沒有任何實質東西的位置在改變。

在傳播與運動的是波函數的相位及波形，但那不是可觀察的物理量。

位置完全不確定，完全的全球化。



我們觀察到的粒子總是得有一些地方特色：區域性！

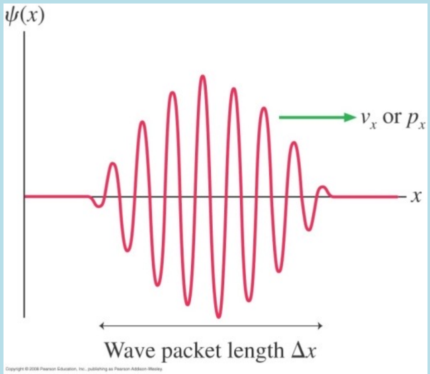


波函數$e^{i(kx-\omega t)}$並不能描述圖中一個個自由運動的粒子。

$e^{i(kx-\omega t)}$雖然不是一顆觀察到的自由電子的狀態，但具有確定的動量。

$e^{i(kx-\omega t)}$是動量的本徵態Eigenstate，在自由空間中是定態Stationary State。

而且$e^{i(kx-\omega t)}$可以作為材料，建造出比較像觀察到的自由電子的狀態：波包。



波包如粒子具有一些區域性，而這區域性又會如自由粒子般運動。

波包也滿足薛丁格方程式。