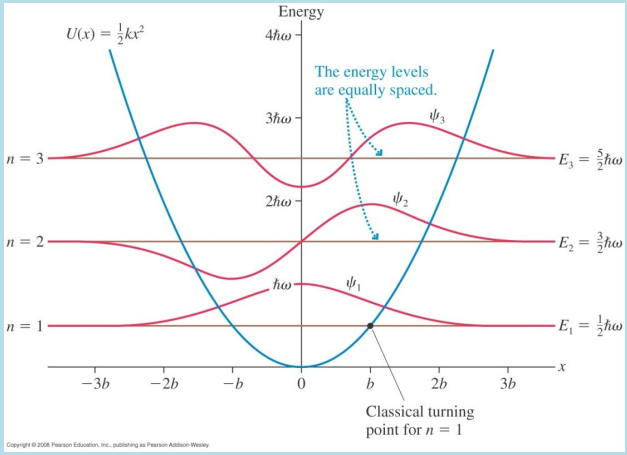
Assume that this translation table work even for an electron under potential $V(x)$!

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

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

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




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

Schrodinger Wave Equation for $\Psi(x,t)$.

Method of separation of variables: Look for separable solutions!

Separable solutions are also called Stationary State in QM.

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

Plug it into Schrodinger Equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad -\frac{\hbar^2}{2m}\phi(t)\frac{d^2\psi}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi}{dt}$$

Note that partial differentiation becomes ordinary differentiation.

Divide both sides by $\psi(x) \cdot \phi(t)$.

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

Now right-hand side is only $t$ related while left-hand side only $x$ related.

But $x, t$ are independent variables. The two formulae are both constants. Call it $E$.

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} \equiv E$$

We find separate ODE for time factor $\phi(t)$ and space factor $\psi(x)$。

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)\right]=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}\equiv E$$

ODE for time factor $\phi(t)$ is first order instead of second order as in classical wave.

$$\frac{d\phi(t)}{dt}=-i\frac{E}{\hbar}\phi(t)$$

The time factor $\phi(t)$ can be determined right away.

$$\phi(t)\sim e^{-i\frac{E}{\hbar}t}=\cos\frac{E}{\hbar}t-i\sin\frac{E}{\hbar}t$$

$\phi(t)$ is complex and hence not classical oscillation. $\sim\cos\omega t$

However, the real part is classical oscillation if we identify $\frac{E}{\hbar}$ as $\omega$.

$E=\hbar\omega$ Constant $E$ is indeed energy of the stationary state.

Time evolution of stationary state wavefunction is simply a Phase factor：$e^{-i\frac{E}{\hbar}t}$.

$$\Psi(x,t)=\psi(x)\cdot e^{-i\frac{E}{\hbar}t}=\psi(x)\cdot e^{-i\omega t}$$

The space part $\psi(x)$ is the initial wavefunction at $t=0$: $\Psi(x,0)=\psi(x)$

With simple time evolution, properties of stationary states are determined by $\psi(x)$.

Separable wavefunction:

$$\Psi(x,t) = \psi(x) \cdot e^{-i\frac{E}{\hbar}t} = \psi(x)e^{-i\omega t}$$

Separable solutions are called stationary states since probability is time independent.

$$P = |\Psi|^2 = \left|\psi_E(x) \cdot e^{-i\frac{E}{\hbar}t}\right|^2 = |\psi_E(x)|^2 \left|e^{-i\frac{E}{\hbar}t}\right|^2 = |\psi_E(x)|^2$$







在定態中，所有對電子的測量結果，都與時間無關！

牛頓力學中，唯一的定態，就是靜止狀態！

但量子力學中，卻有許多定態。

以後更會清楚，一個量子系統的定態決定了此系統的物理性質。

Properties of stationary states are determined by $\psi(x)$.

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)\right]=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}\equiv E$$

$\psi(x)$ corresponds to specific $E$. It is written as $\psi_E(x)$.

$\psi_E(x)$ satisfy the following 2nd order ODE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2}+V(x)\cdot\psi_E(x)=E\cdot\psi_E(x)$$

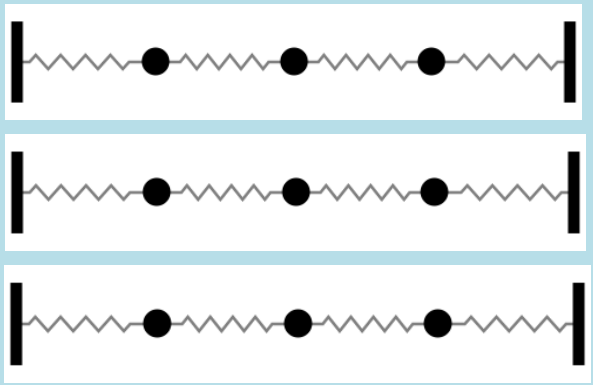
Time-Independent Schrodinger Equation, arguably the most important Eq. in QM.

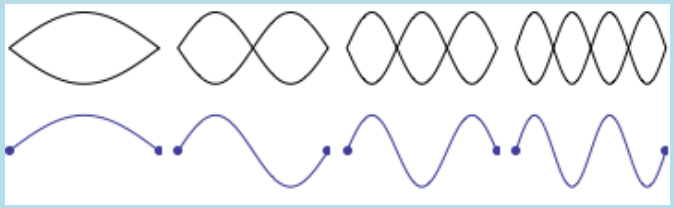
This corresponds to the Eigenfunction Equation in classical wave equation:

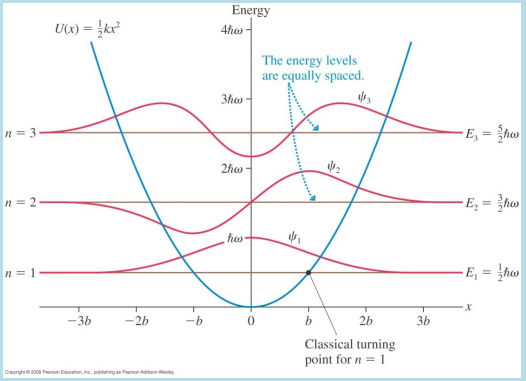
$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_E(x)=E\cdot\psi_E(x) \quad \Longleftrightarrow \quad \frac{d^2X}{dx^2}=\lambda X$$

# Analogy Table

| Coupled Springs | Classical Wave | Electron Wave |
|---|---|---|
| Eigenvector Eq. | Eigenfunction Eq. | Eigenfunction Eq. |
| | | Time-Independent Schrodinger Eq. |
| $-\boldsymbol{A}\cdot\boldsymbol{a}=\lambda\boldsymbol{a}$ | $\frac{d^2X}{dx^2}=\lambda X$ | $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_E=E\cdot\psi_E$ |
| Oscillation Mode | Separable Solution<br>Oscillation Mode | Separable Solution<br>Stationary State |
| $\boldsymbol{a}$ | $X(x)$ | $\psi_E(x)$ |







Let's first try a free electron: $V(x) = 0$

Time-Independent Schrodinger Eq.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E}{dx^2} = E\psi_E$$

To solve it:

$$\frac{d^2\psi_E}{dx^2} = -\frac{2mE}{\hbar^2}\psi_E \equiv -k^2\psi_E \qquad k \equiv \sqrt{\frac{2mE}{\hbar^2}}$$

This is the identical 2nd order ODE for space part $X(x)$ of classical wave:

$$\frac{d^2X}{dx^2} = \lambda X \equiv -k^2X$$

Guessing a solution: $e^{ax}$ $\quad a^2 = -k^2$ $\quad a = \pm ik$

There are two solutions:

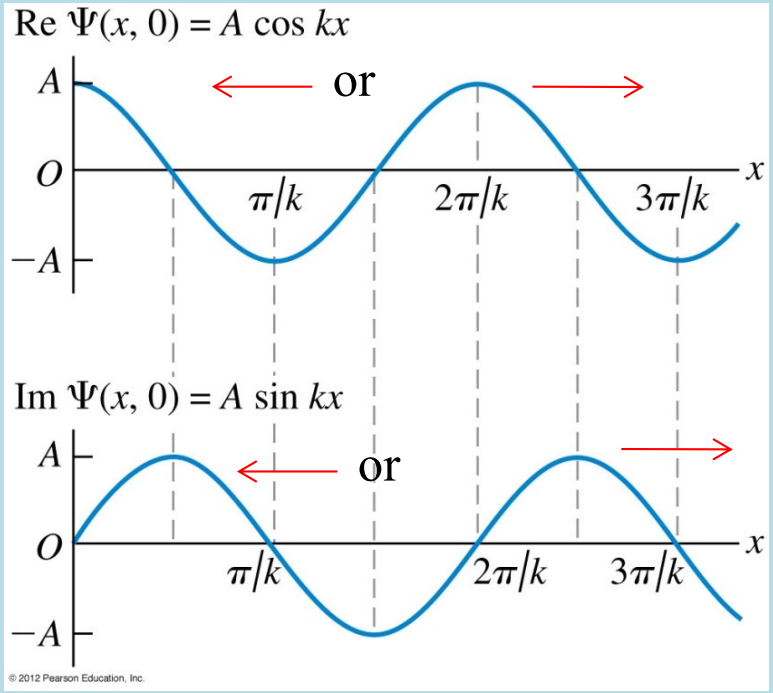
$\psi_E = Ae^{ikx} + Be^{-ikx}$ or equivalently $\sim C\cos kx + D\sin kx$

We recover our original second and correct guess of free electron wave:

$$\Psi(x,t) = \left(Ae^{ikx} + Be^{-ikx}\right) \cdot e^{-i\omega t}$$

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

$$\sim Ae^{ik(x-vt)} + Be^{-ik(x+vt)}$$




They feel like d'Alembert solution

$$\phi(x,t) = f(x-vt) + g(x+vt)$$

But dispersion relation is different

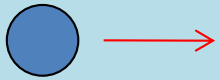
$v = \frac{\omega}{k}$ is no longer a constant.

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



Only phase is propagating. Electron is not moving since it is a stationary state!

This is actually not a free moving electron.

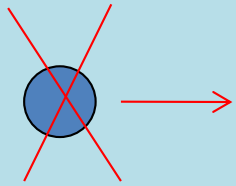


de Broglie's postulation is not correct! Fortunately, Schrodinger Eq. is correct.

$$Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}$$

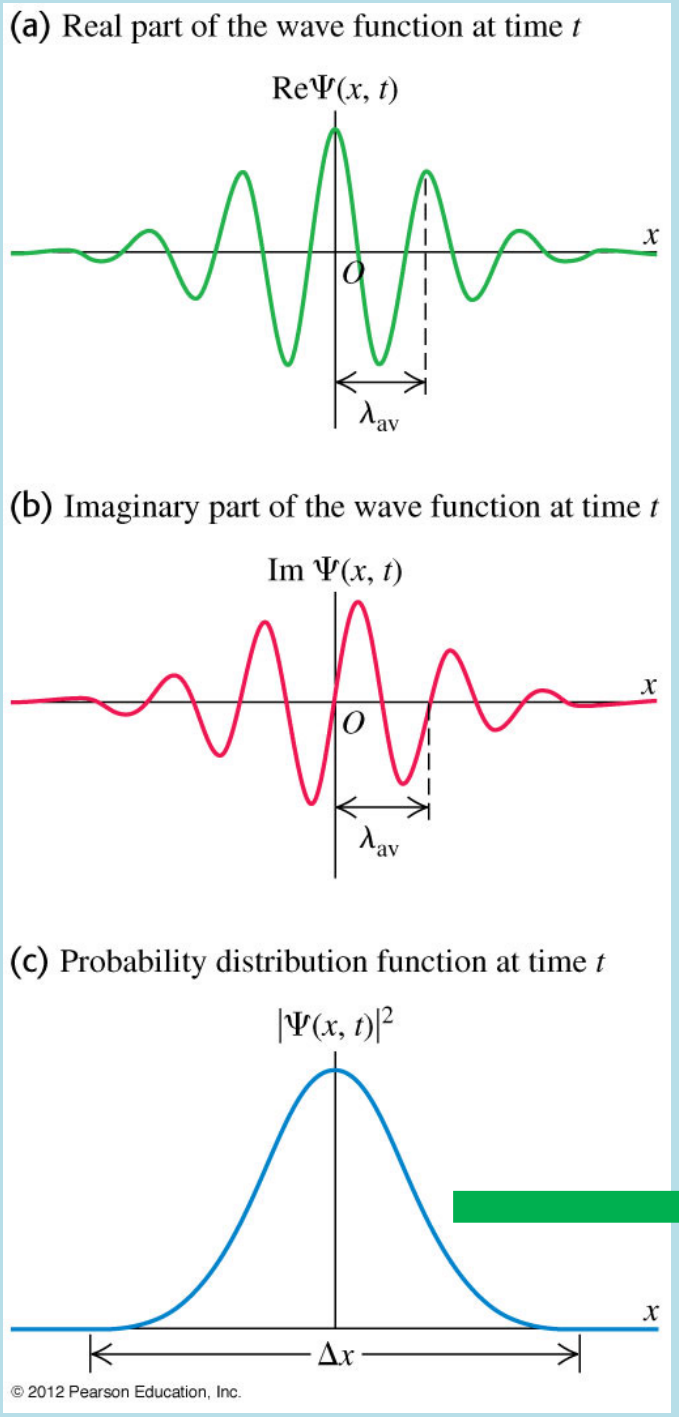
It is an electron wave in free space without boundary!





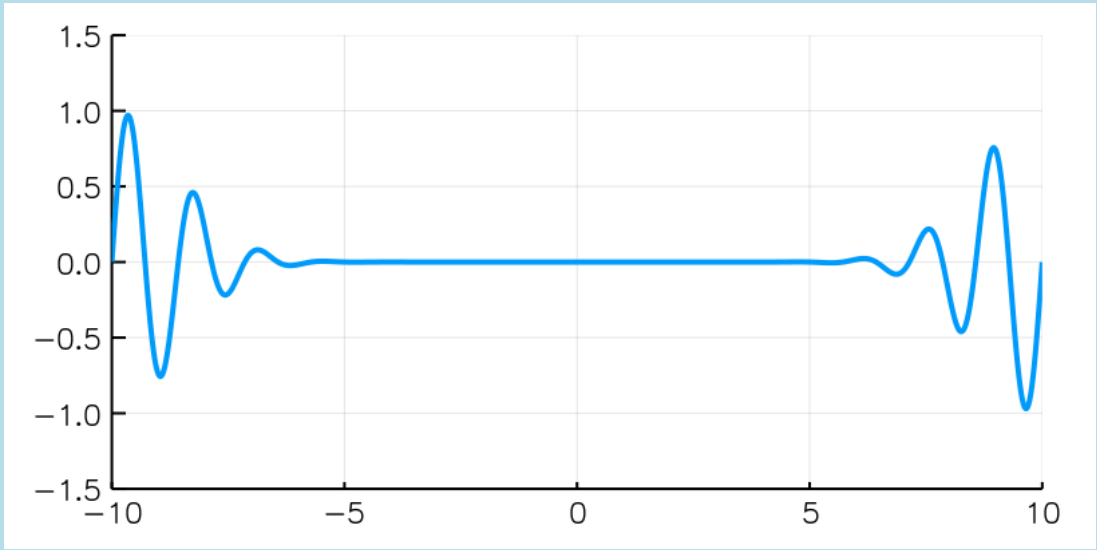
This electron has a certain momentum since wavelength is fixed.

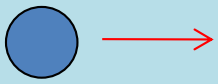
Hence it does not have a certain position due to uncertainty principle.




If you need a particle-like state,

it is wave packet (not a stationary state).



Physics of electron wave is most interesting with boundary or a potential!

We start with two examples:

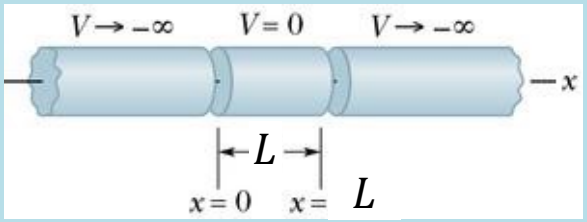
Free electron with boundary, infinite potential well 無限大的位能井

Electron in SHM potential 簡諧運動位能內之電子

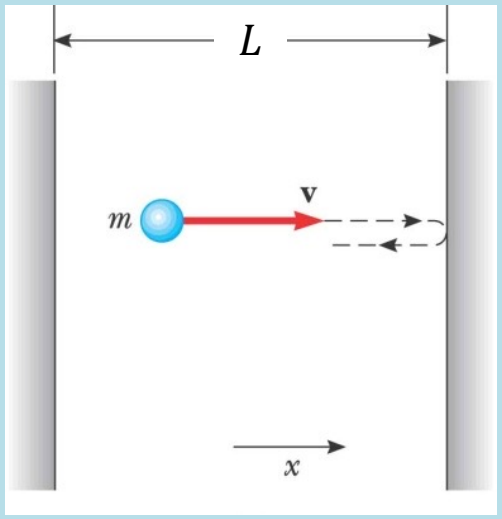


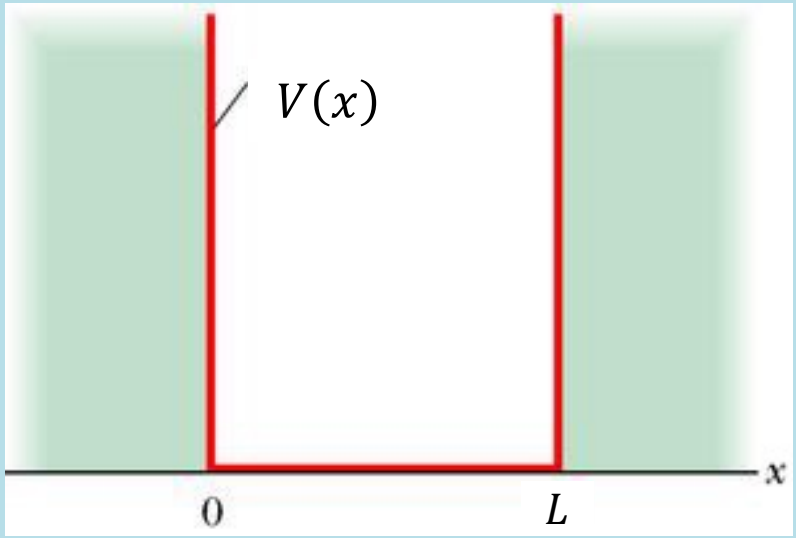
# 無限位能井內的電子定態 Stationary states in infinite potential well

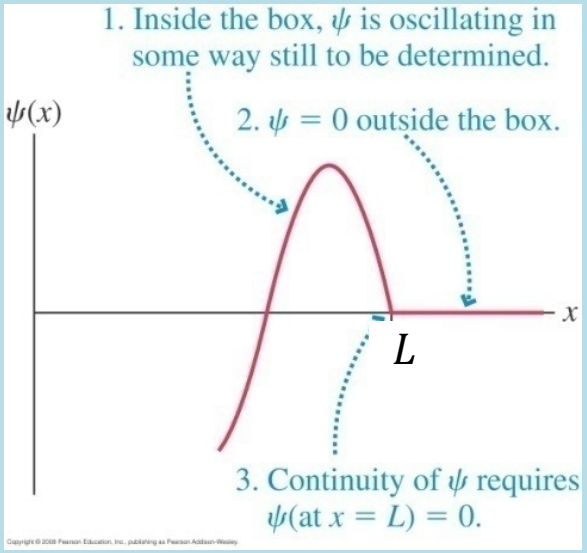
$$V(x) = \infty \quad x < 0$$
$$= 0 \quad 0 < x < L$$
$$= \infty \quad a < x$$




Classically




邊界外的位能是無限大，波函數必須為零，否則位能會是無限大！

邊界內波函數，必須在邊界上與邊界外波函數連續，

因此邊界內波函數在邊界上必須為零。

Boundary condition $\Psi(0,t) = \Psi(L,t) = 0$

金屬中的傳導電子所感受的位能就類似位能井。

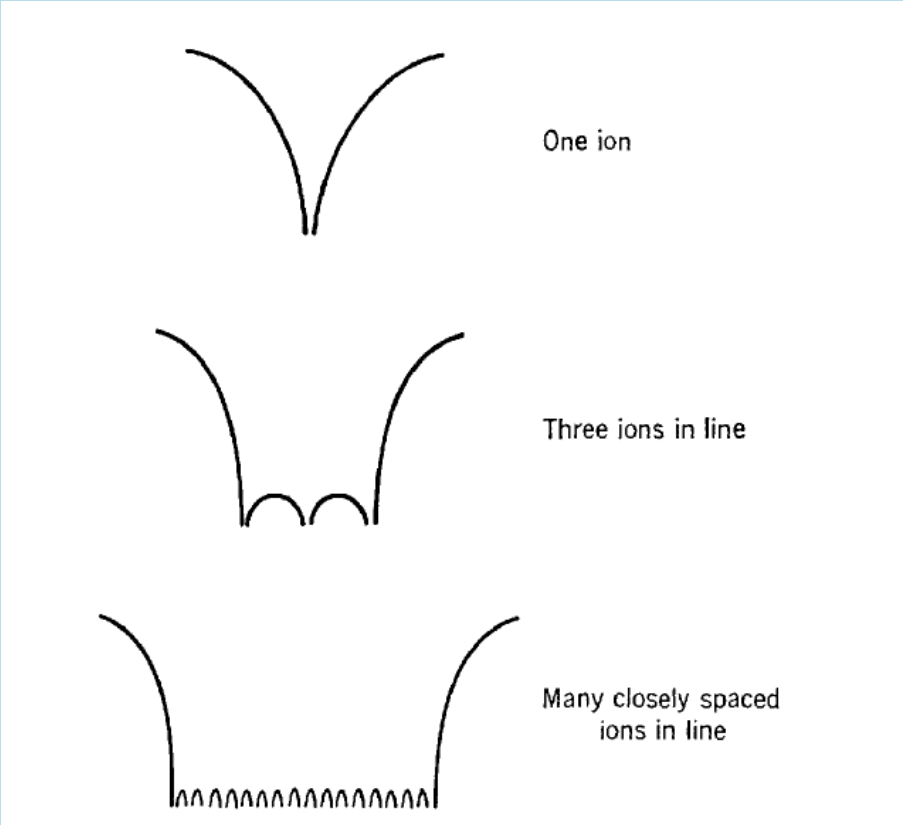
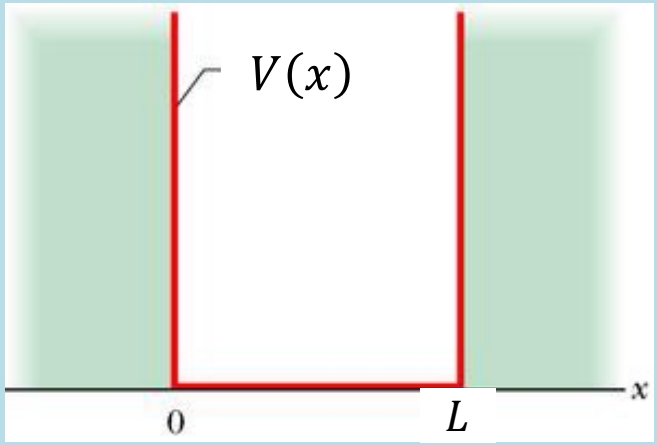



**Figure 6-24** A qualitative indication of how an approximation to a square well potential results from superimposing the potentials acting on a conduction electron in a metal. The potentials are due to the closely spaced positive ions in the metal.




Inside the box, it is free：$V(x) = 0$。

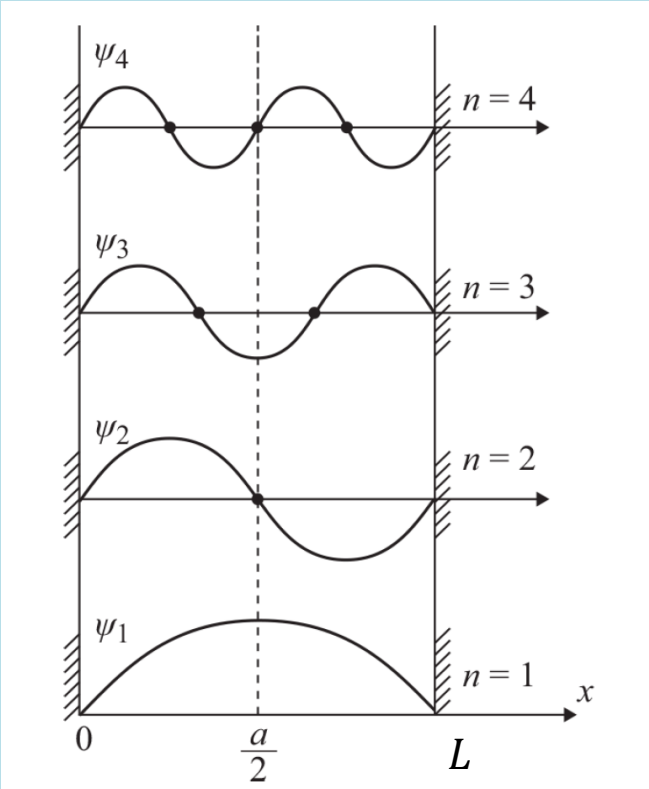
Time-Independent Schrodinger Equation is as in the case of free electron:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \qquad k \equiv \sqrt{\frac{2mE}{\hbar^2}}$$

Boundary condition would be satisfied if:

$$\psi(0) = 0 \qquad \psi(L) = 0$$

This is totally identical problem with $X_i(x)$ in the case of a string with fixed ends.

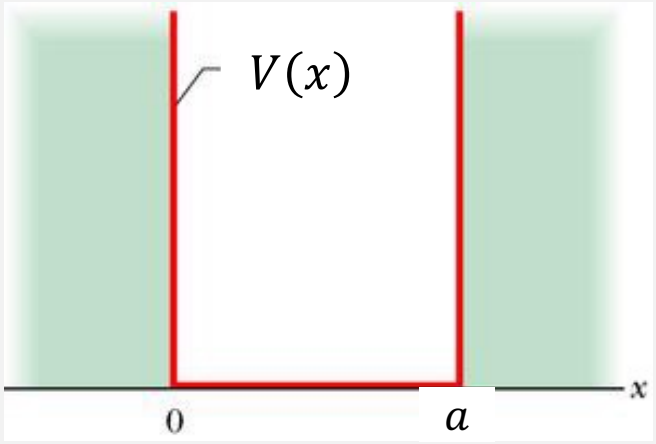



Identical ODE with identical boundary condition yields identical solutions.

$$\psi_n = C \sin(k_n x) = C \sin\left(\frac{n\pi}{L} x\right)$$

Only $k_n = \frac{n\pi}{L}$ and $E_n = \left(\frac{\hbar^2}{2m}\right) k_n^2$ allows a solution $\psi_n$.

# 有邊界之自由電子




$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

$$\psi = Ae^{ikx} + Be^{-ikx}$$

但必須加上邊界條件：

$$\psi(0) = 0 \longrightarrow A + B = 0$$

$$\psi = Ae^{ikx} - Ae^{-ikx} = 2iA\sin kx$$

$$\psi = C\sin kx$$

重新定義常數：$C \equiv 2iA$

$$\psi(a) = 0 \longrightarrow \psi(a) = C\sin ka = 0$$

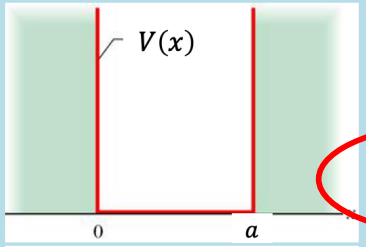
$$\downarrow$$

$$ka = n\pi$$

$n$是自然數。

$$\psi_n = C\sin\left(\frac{n\pi}{a}x\right) \qquad k = \frac{n\pi}{a}$$

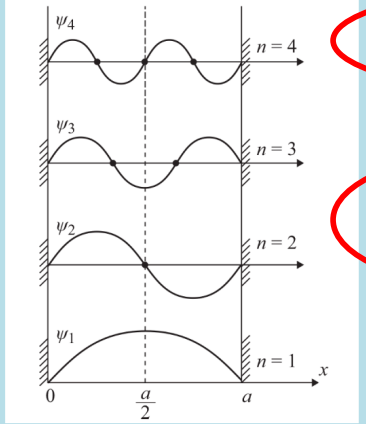
## 有邊界之自由電子




在邊界內，如同自由電子：$V(x)=0$。

$$\frac{d^2\psi}{dx^2}=-\frac{2mE}{\hbar^2}\psi \equiv -k^2\psi \qquad k\equiv\sqrt{\frac{2mE}{\hbar^2}}$$

$$\frac{d^2\psi}{dx^2}=-k^2\psi$$




邊界條件：

$$\psi(0)=0 \qquad \psi(a)=0$$

與弦駐波波函數的空間部分$X_i(x)$滿足一模一樣方程式！

其解自然也是一模一樣！

$$\psi_n = C\sin\left(\frac{n\pi}{a}x\right)$$

注意只有在某些$k=\frac{n\pi}{a}$才有解。

同理只有在對應的$E$才有解。

這是有限空間內薛丁格方程式定態的基本特徵。

$X(x)$滿足標準的二次常微分方程式：

$$\frac{d^2X}{dx^2}=\lambda X$$

我們稱這是算子$\frac{\partial^2}{\partial x^2}$的本徵值方程式！

它的解與$\lambda$是正或負有關：

$$X(x)=\begin{cases} Ae^{\sqrt{\lambda}x}+Be^{-\sqrt{\lambda}x} & \lambda>0 \\ A'\cos\sqrt{-\lambda}x+B'\sin\sqrt{-\lambda}x & \lambda<0 \\ A''x+B'' & \lambda=0 \end{cases}$$

$\lambda$若是正值，$X(x)$是指數函數，$\lambda$若是負值，$X(x)$則是三角函數。

如果考慮邊界條件，只能選$\lambda<0, A'=0$。一般會定義角波數：$k\equiv\sqrt{-\lambda}$

$X(x)=\sin kx$ 自動滿足原點邊界條件 $\phi(0,t)=0$

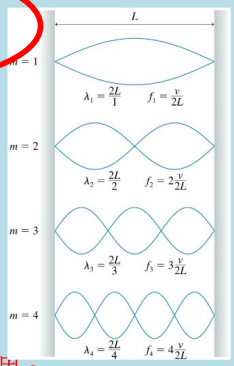
另一端邊界條件就對$k$、也就是$\lambda$有限制：

$X(L,0)\sim\sin(kL)=0$ $\quad k_n=\frac{n\pi}{L}=\sqrt{-\lambda_n}$

$$X_n(x)=\sin\left(\frac{n\pi}{L}x\right) \qquad n=1,2,\cdots\infty \qquad \frac{d^2X_n}{dx^2}=\lambda_n X_n$$

我們稱這些解是算子$\frac{\partial^2}{\partial x^2}$的本徵函數 Eigenfunction！

物理上對應一系列模式(駐波)，離散、可以$n$標定，但有無限多個。

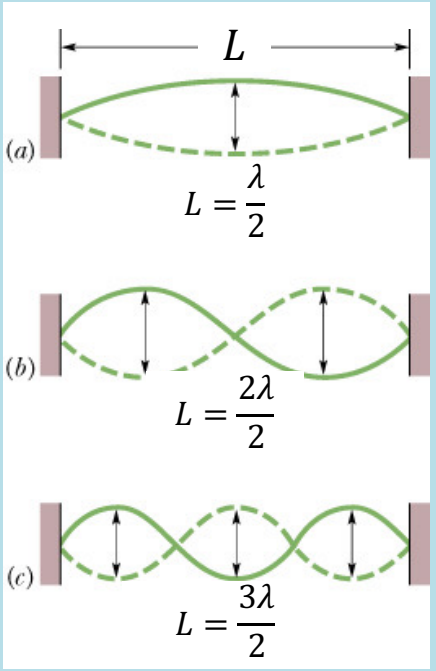


$\psi_n$ is identical to $X_n(x)$ in a string with fixed ends.

Visually, String length equals multiply half wavelength.

$$L = n\frac{\lambda}{2}$$

$$k_n = \frac{2\pi}{\lambda} = \frac{n\pi}{L}$$




$n$ is called quantum number. Give $\psi_n$ a new name $u_n$:

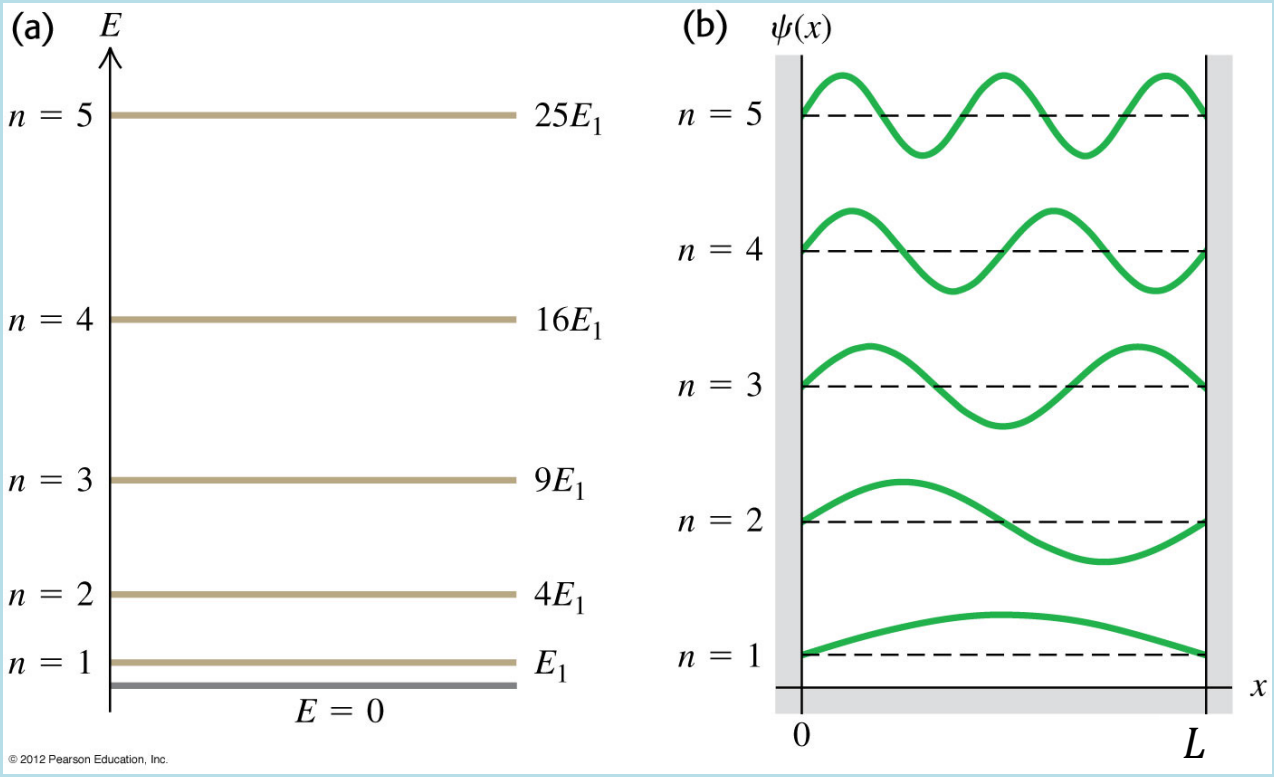
$$\psi_n = u_n(x) = C\sin\left(\frac{n\pi}{L}x\right)$$

Complete wavefunction: $\Psi_n$

$$\Psi_n(x,t) = C\sin\left(\frac{n\pi}{L}x\right)\cdot e^{-i\frac{E_n}{\hbar}t} \quad \Longleftrightarrow \quad y = y_m\left(\sin\frac{n\pi}{a}x\right)\cdot\cos\omega t$$

Real part of electron bound state in infinite well is the same as standing wave.

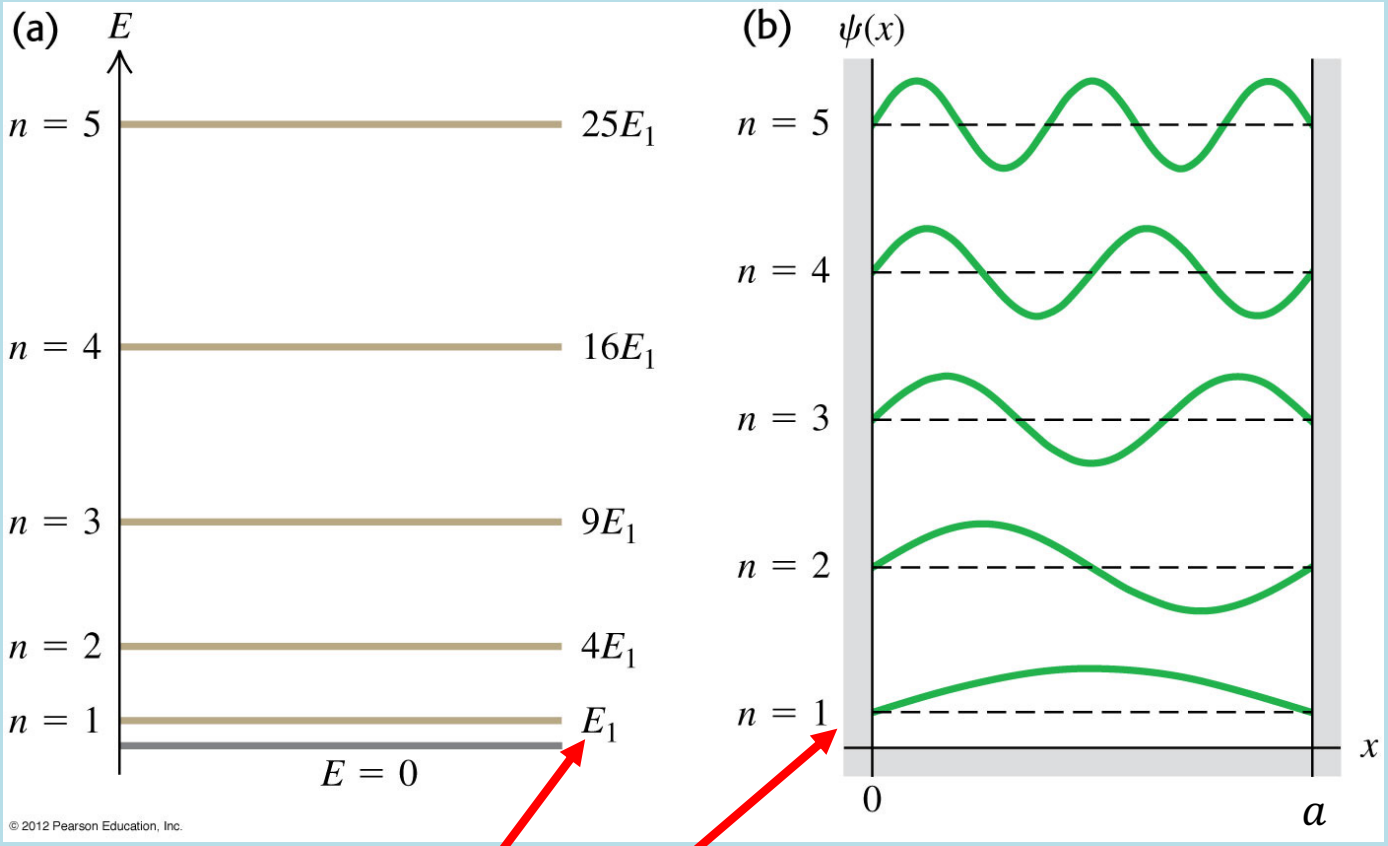
But it also has an imaginary part.




Only $k_n = \frac{n\pi}{L}$ and $E_n = \left(\frac{\hbar^2}{2m}\right) k_n^2$ allows a solution $\psi_n$.

$$E_n = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{a^2}n^2 = \left(\frac{h^2}{8ma^2}\right)n^2$$

This is energy quantization. These quantized energies are eigenvalues!




$$E_1 = \left(\frac{h^2}{8ma^2}\right)$$

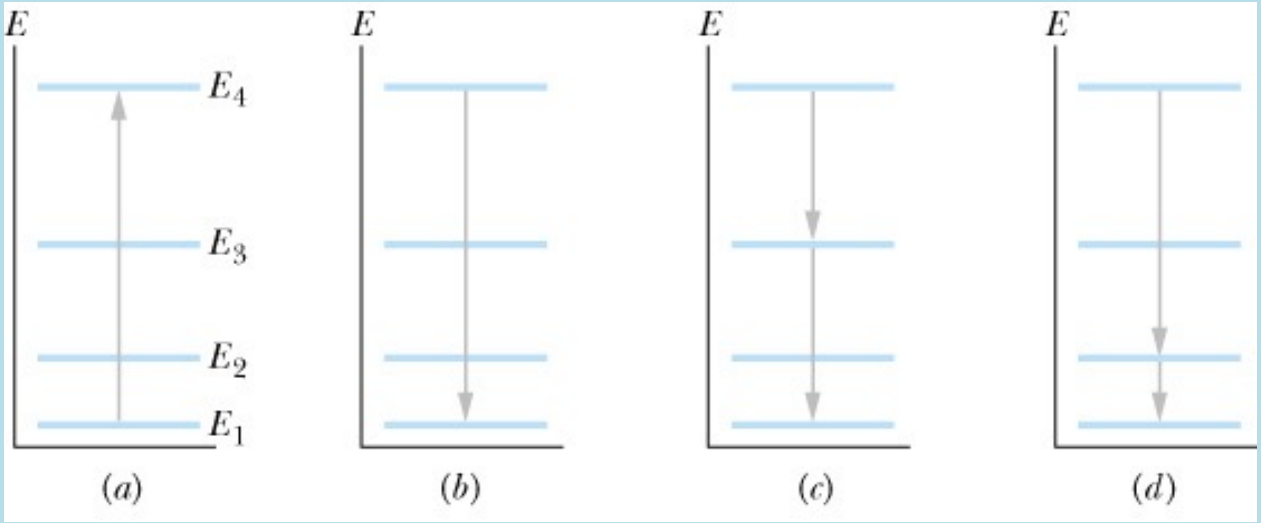
Ground State

注意基態的動量不為零

電子是靜不下來的！

這是測不準原理的結果






電子可以在能階定態之間以放出與吸收光子的方式躍遷。

$$hf = \Delta E$$

Consider an infinite box of unknown width. In transitions between neighboring values of $n$, photons of various energies are emitted. It is found that the largest wavelength of the various photons seen is $450 \times 10^{-9}$ m. Use this information to determine $a$, the width of the infinite box.

到達基態後，電子是穩定的。

基態的存在是量子力學重要的特徵！

總機率必須等於 1

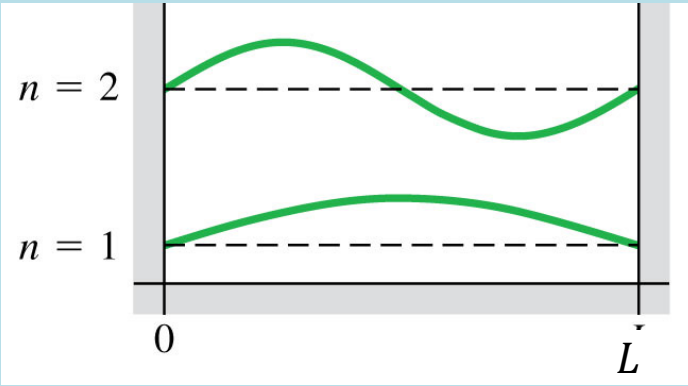
$$\int_0^L |\Psi_n(x,t)|^2 dx = \int_0^L |u_n(x)|^2 dx = 1$$

由歸一化條件可以解出係數 $C$

$$\int_0^L |C|^2 \left[\sin\left(\frac{n\pi}{L}x\right)\right]^2 dx = |C|^2 \int_0^L \left[\frac{1-\cos\left(2\frac{n\pi}{L}x\right)}{2}\right] dx = |C|^2 \frac{L}{2} = 1$$

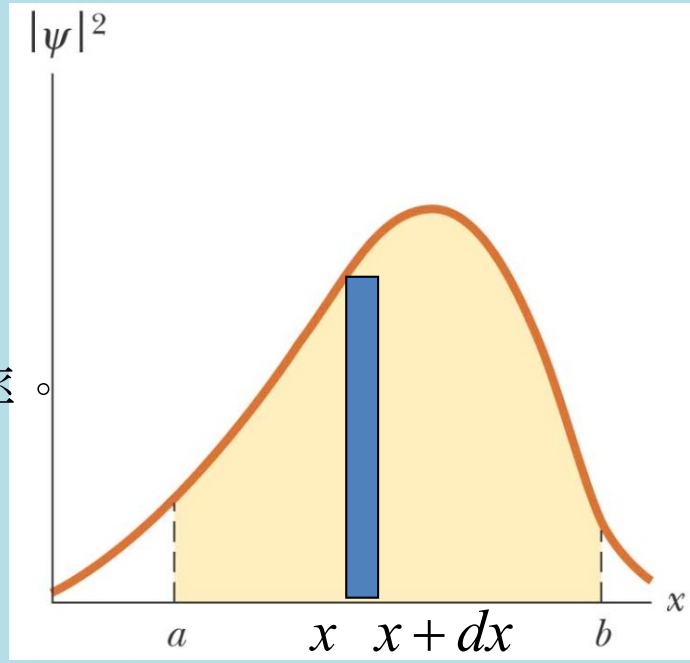
$$|C| = \sqrt{\frac{2}{L}} \qquad u_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

只有$C$的絕對值對物理有影響。所以常就直接取實數。



$$P = |u_n(x)|^2 = \frac{2}{a}\left[\sin\left(\frac{n\pi}{a}x\right)\right]^2$$

$\int_a^b |u_n(x)|^2 \cdot dx$ 在 $a$ 與 $b$ 之間發現該粒子的機率。



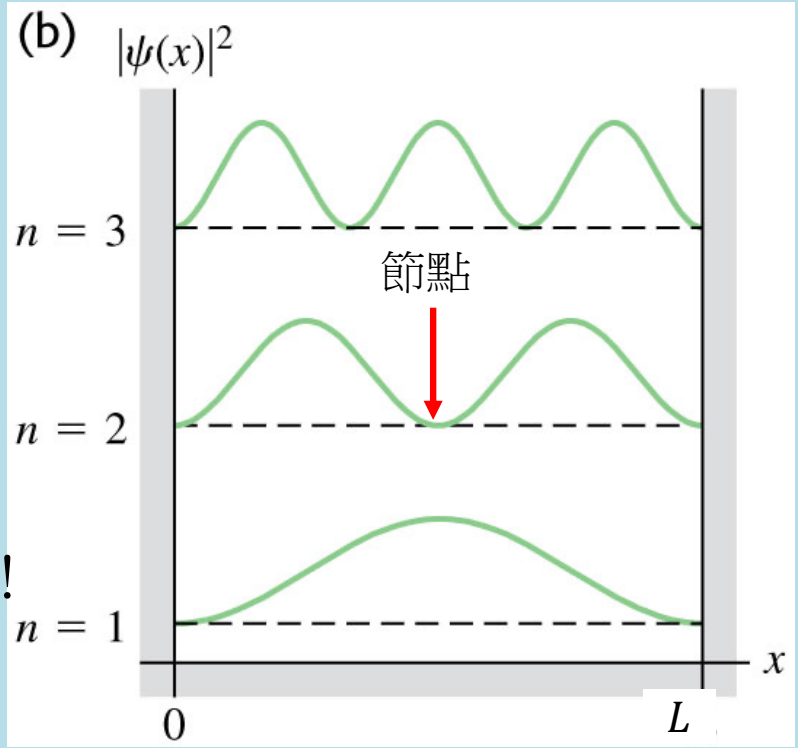

$P\left(\frac{m}{n}a\right) = 0, m < n$ 稱為節點。

在節點處，$P$一直為零，永遠不可能發現該電子！




此電子靜不下來，但在節點卻永遠找不到它！

注意：$n-1$即是節點數目！



We can use these stationary state solutions to construct general solutions.

In coupled spring system, these solutions are separable solutions:

$$\frac{d^2X}{dx^2} = \lambda X$$ We call this eigenfunction equation of $\frac{d^2}{dx^2}$, eigenvalues.

Same for electron in infinite well!

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_E(x)}{dx^2} = E \cdot \psi_E(x)$$

With boundary condition, eigenvalues are countable: $n = 1 \cdots \infty$.

$$u_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \qquad E_n = \left(\frac{h^2}{8mL^2}\right)n^2 \qquad -\frac{\hbar^2}{2m}\frac{d^2u_n}{dx^2} = E_n u_n$$

$\sin\left(\frac{n\pi}{L}x\right)$ of different $n$ ie. eigenfunctions of different eigenvalues are orthogonal.

$$\int_0^L dx \cdot u_n^*(x)u_m(x) = \delta_{mn}$$

Method 0

Are $\sin\left(\frac{n\pi}{L}x\right)$ orthonormal?

If $m \neq n$

$$\int_0^L dx \sin\left(\frac{n\pi}{L}x\right)\sin\left(\frac{m\pi}{L}x\right) = \frac{1}{2}\int_0^L dx\left[\cos\frac{\pi}{L}(m-n)x - \cos\frac{\pi}{L}(m+n)x\right]$$

$$= \frac{L}{2\pi}\left[\frac{1}{m-n}\sin\frac{\pi}{L}(m-n)x + \frac{1}{m+n}\sin\frac{\pi}{L}(m+n)x\right]\Bigg|_0^L = 0$$

Sine functions are periodic.

任一滿足邊界條件$f(0) = f(L) = 0$的函數$f(x)$都可分解為一正弦函數級數：

$$f(x) = \sum_{n=1}^{\infty} a_n \cdot \sin\left(\frac{n\pi}{L}x\right)$$

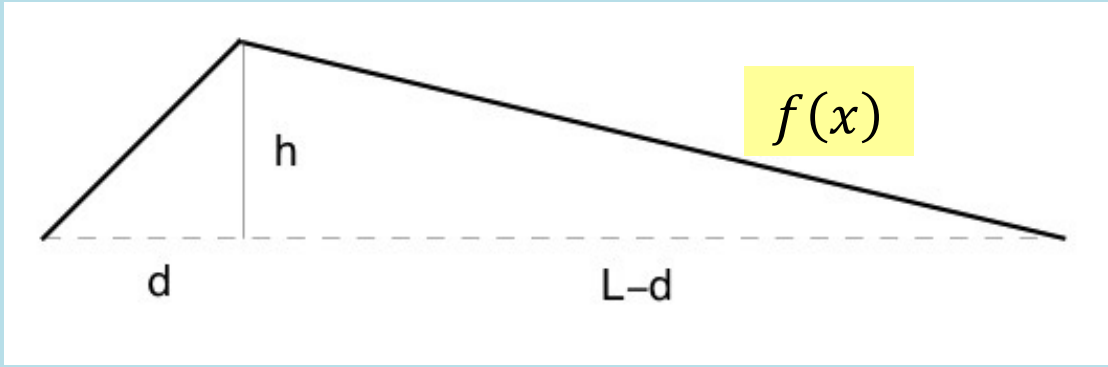
$$a_n = \frac{2}{L}\int_0^L dx \ \sin\left(\frac{n\pi}{L}x\right) f(x)$$

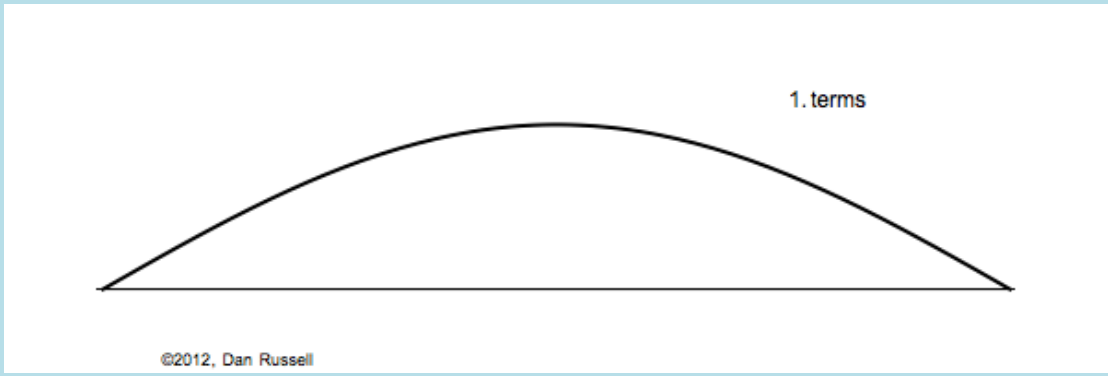
This is a special case of Fourier Series.



Jean-Baptiste Joseph Fourier

1768-1830



正弦函數$u_n$滿足以下定理，

展開定理：任一狀態函數 $\psi$ 可以 $u_n$ 展開。展開讓我們聯想到向量以基底展開：

$$\psi(x) = \sum_{n=0}^{\infty} [c_n \cdot u_n(x)]$$

正交定理：本徵函數彼此正交。這很像一組彼此正交的基底！

$$\int_{-\infty}^{\infty} dx \cdot u_m(x)^* \cdot u_n(x) = \delta_{mn}$$

分量$c_a$可以寫成態函數與本徵函數的空間積分。很像向量與基底的內積投影：

$$c_n = \int_{-\infty}^{\infty} dx \cdot u_n(x)^* \cdot \psi(x)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V(x)\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$ Separation of variables plus Fourier Series

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

Satisfying an ODE, $T(t)$ is a phase factor.

With boundary condition,$\psi(x)$ satisfies an ODE, called eigenvalue equation.

Allowed $\psi_n(x), n=1,\cdots\infty$ would be countable, called eigenfunctions

We found a series of separable solutions: $C\sin\left(\frac{n\pi}{L}x\right)\cdot e^{-i\frac{E_n}{\hbar}t}$

Since wave equation is linear, linear combinations of $\psi_n(x)T_n(t)$ are solutions, too.

$$\Psi(x,t)=\sum_{n=1}^{\infty}A_n\cdot\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)\cdot e^{-i\frac{E_n}{\hbar}t}$$

Any initial condition $u_0(x)$ can be expanded as a linear combination of $X_n(x)$.

$$\Psi(x,0)=u_0(x)=\sum_{n=1}^{\infty}A_n\cdot\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

call it a mixture if you want.

This property of Fourier Series is crucial. We say, it is complete 具有完備性.

各個配料$u_n(x)$依配方$A_n$收集

Find recipe of ingredients.



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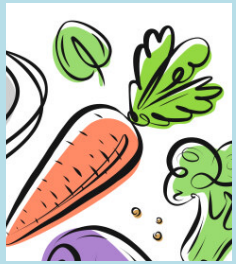

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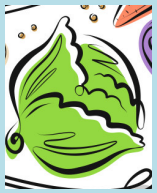

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各個配料分離烹煮$T_n(t) \sim e^{-i\frac{E_n}{\hbar}t}$

最後合體！

Cook and then mix cooked ingredients.





$$\sum_{n=1}^{\infty} A_n \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \cdot e^{-i\frac{E_n}{\hbar}t}$$

這樣的波函數顯然滿足波方程式，又滿足起始條件，就是唯一解。

這一展開式提供對無限大位能井位能下薛丁格波方程式的普遍解法：

將$t = 0$時的波函數，即起始條件，對定態解$u_n$展開如下：

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n u_n(x)$$

根據展開定理，這永遠可以做到！

$t = 0$時此狀態可以視為定態$u_n$的如上疊加，

接著定態隨時間個自演化，位能下薛丁格方程式要求$u_n$乘上$e^{-i\frac{E_n}{\hbar}t}$。

乘完之後依同樣方式疊加，整個波函數也就滿足薛丁格波方程式。

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n u_n(x) e^{-i\frac{E_n}{\hbar}t}$$

很明顯，這個程序不只適用於無限大位能井，原則上適用於任何位能。



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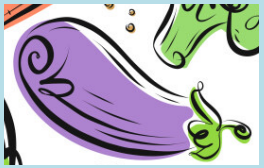

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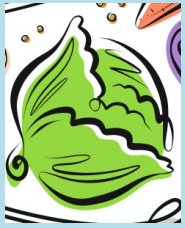

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⋮

各個配料分離烹煮

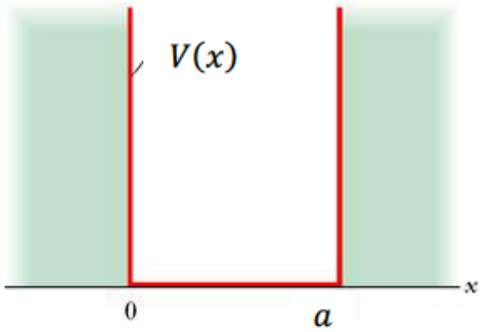




一個量子系統的定態決定了此系統的物理性質。

3. Consider an infinite potential box, with boundaries at $x = 0$ and $x = a$:

$V(x) = \infty, x > a, x < 0$ and $V(x) = 0, 0 < x < a$.




As we have shown in class, in this potential the energy eigenstate can be written as $\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$ with eigenvalues $E_n = \left(\frac{\hbar^2}{2m}\right)\frac{\pi^2}{a^2}n^2$ (you can use the notation $E_n$ to simplify your answers) . Assume the wavefunction of a particle at $t = 0$ (probability already normalized to one) is:

$$\Psi(x,0) = \sqrt{\frac{4}{5}}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\right) + \sqrt{\frac{1}{5}}\left(\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}\right) \quad 0 < x < a,$$

$$= 0 \quad x < 0, x > a$$

A. For a later time $t$, write down the wave function $\psi(x,t)$. There is no need to simplify the answer. (15)

B. At $x = \frac{a}{6}$, calculate the probability density $P\left(\frac{a}{6}, t\right)$ as a function of time $t$.

解答：

A. $t = 0$時此狀態可以視為定態$u_{1,2}$的如上疊加，接著定態隨時間個自演化，位能下薛丁格方程式要求$u_n$乘上$e^{-i\frac{E_n}{\hbar}t}$。乘完之後依同樣方式疊加，整個波函數也就滿足薛丁格波方程式。因此

$$\Psi(x,t) = \sqrt{\frac{4}{5}}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\right)e^{-i\frac{E_1}{\hbar}t} + \sqrt{\frac{1}{5}}\left(\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}\right)e^{-i\frac{E_2}{\hbar}t}。$$

B. $$\Psi\left(\frac{a}{6},t\right) = \sqrt{\frac{4}{5}}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi}{6}\right)e^{-i\frac{E_1}{\hbar}t} + \sqrt{\frac{1}{5}}\left(\sqrt{\frac{2}{a}}\sin\frac{\pi}{3}\right)e^{-i\frac{E_2}{\hbar}t}$$

$$= \sqrt{\frac{2}{5a}}\left(2\frac{1}{2}e^{-i\frac{E_1}{\hbar}t} + \frac{\sqrt{3}}{2}e^{-i\frac{E_1}{\hbar}t}\right)$$

$$P\left(\frac{a}{6},t\right) = \left|\Psi\left(\frac{a}{6},t\right)\right|^2 = \frac{2}{5a}\left|e^{-i\frac{E_1}{\hbar}t} + \frac{\sqrt{3}}{2}e^{-i\frac{E_1}{\hbar}t}\right|^2$$

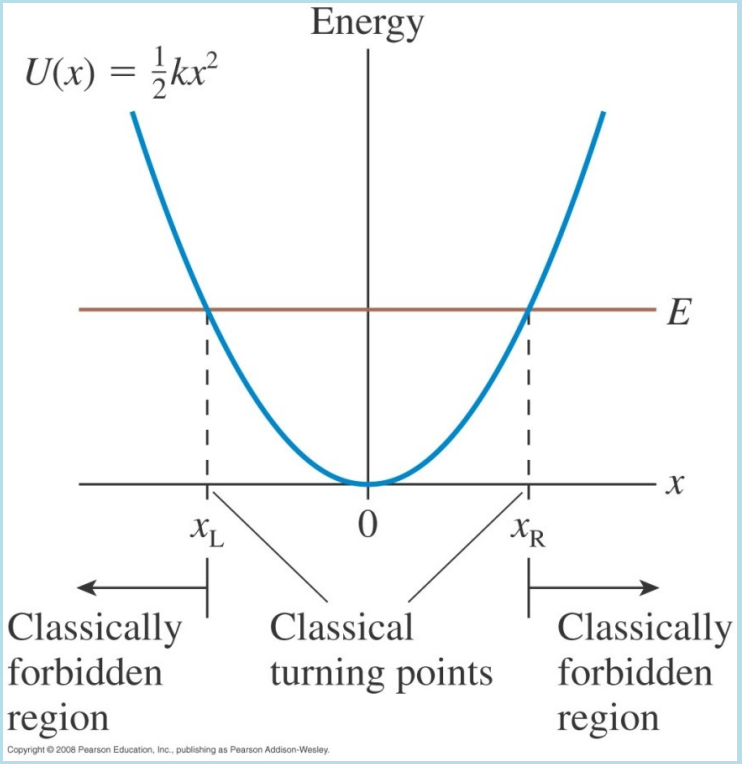
簡諧振盪器、量子彈簧、

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right]\psi(x)=E\psi(x)$$

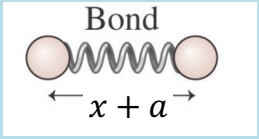
Time-independent Schrodinger Eq.

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=\left(\frac{1}{2}kx^2-E\right)\psi$$

Classically it is a bound state in 1D potential 位能束縛態

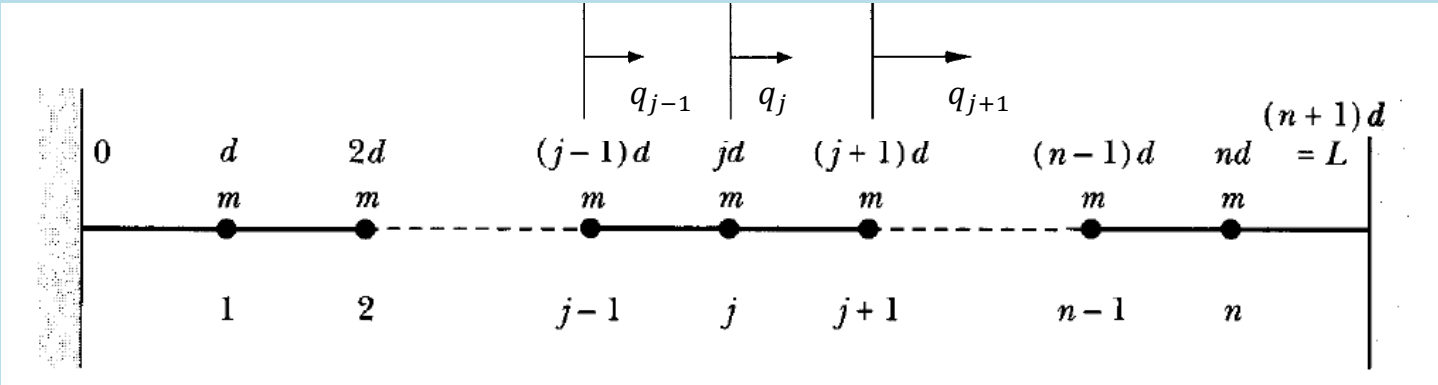


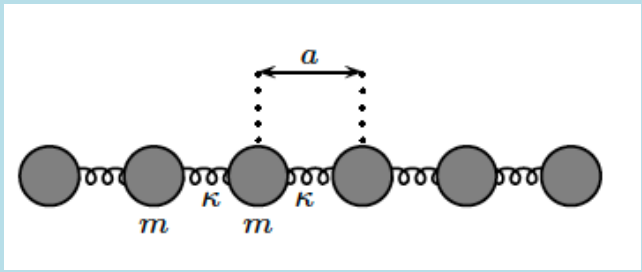

最簡單的量子彈簧就是雙原子分子！



## 12.9 The Loaded String*

固體內原子晶格的振動也是一系列量子彈簧

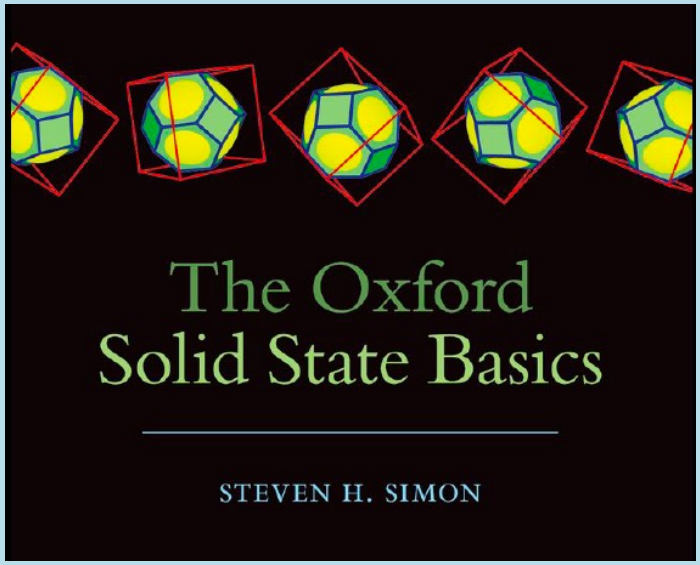



**Vibrations of a One-Dimensional Monatomic Chain**

**9**

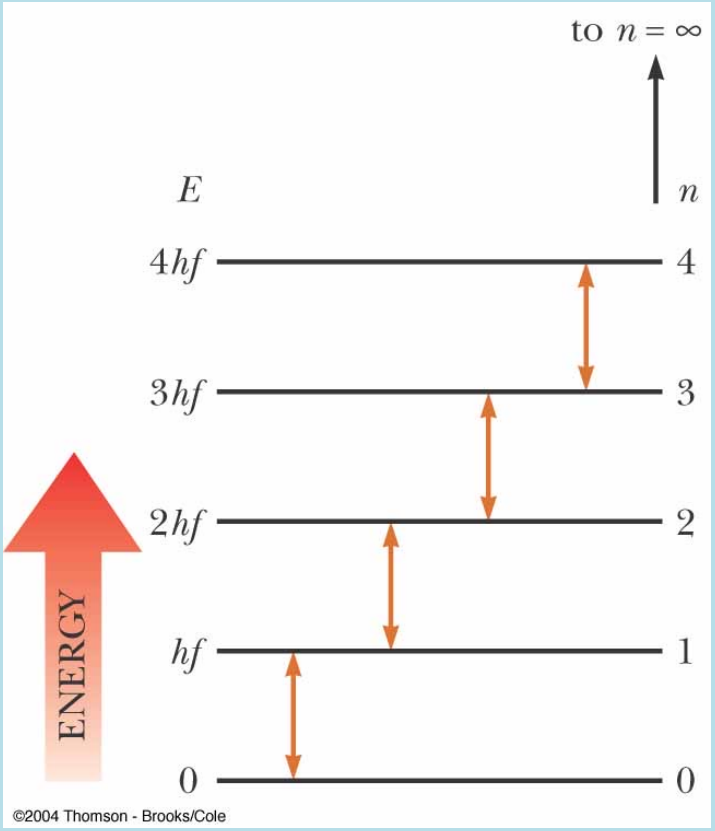
In Chapter 2 we considered the Boltzmann, Einstein, and Debye models of vibrations in solids. In this chapter we will consider a more detailed model of vibration in a solid, first classically, and then quantum-



黑體輻射以及空腔輻射也是一系列的量子彈簧。

如果要解釋黑體輻射，量子彈簧的能量變化必需是能階狀的！

Max Planck 在1900 開啟了量子革命的第一槍！





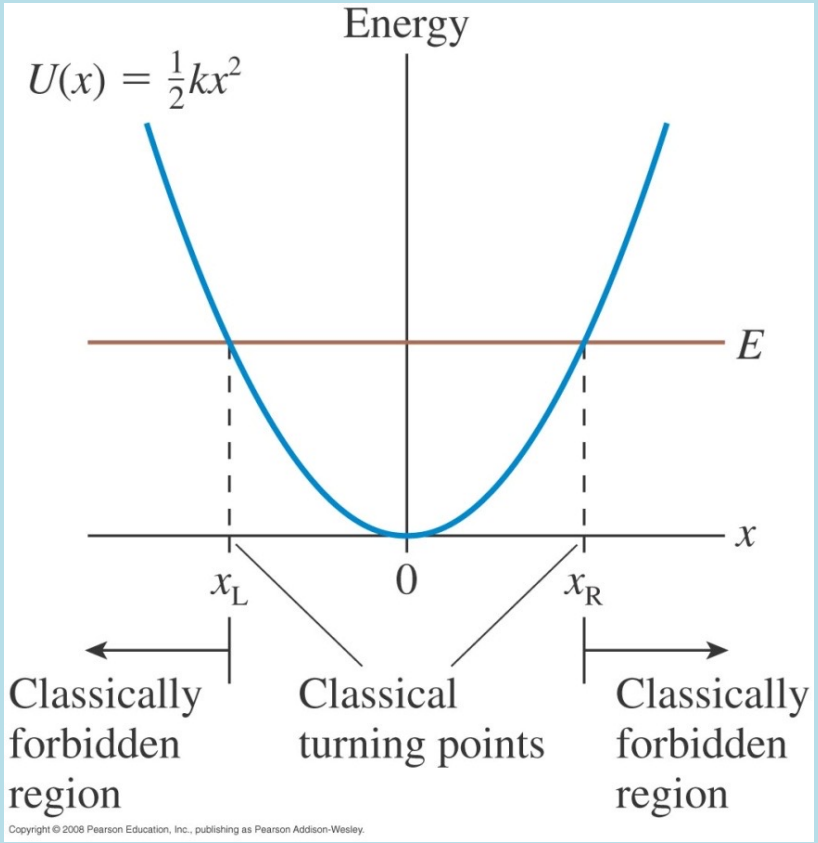

量子彈簧的能量不是連續的，而是固定量子的整數倍（離散型式）

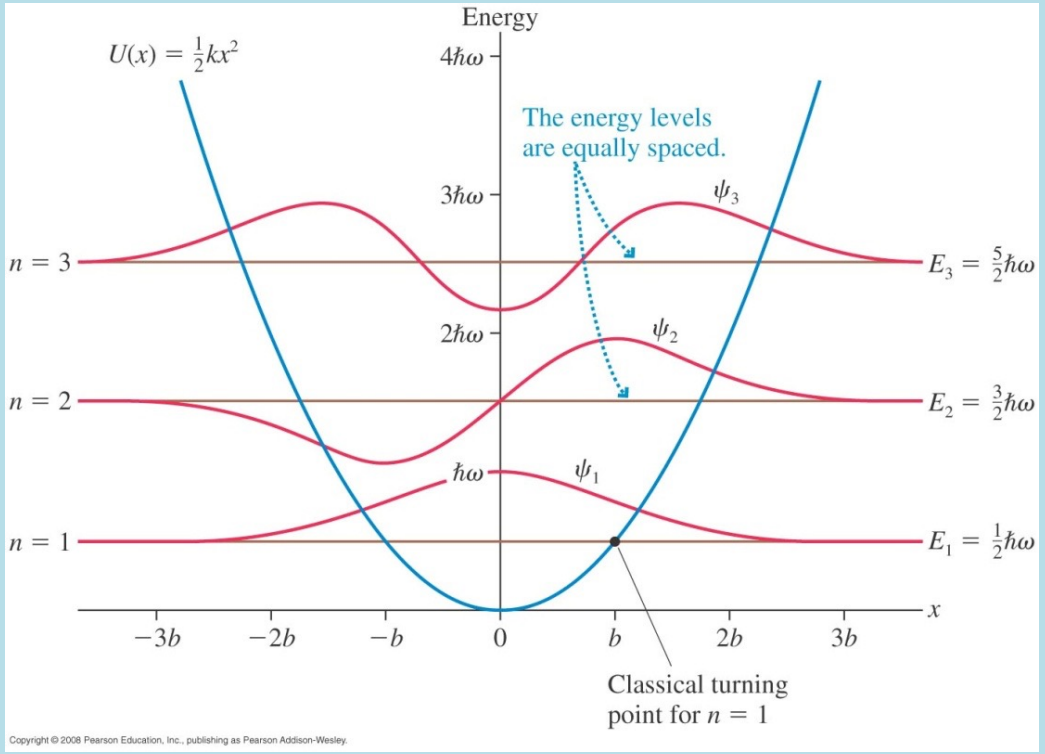
量子(Quantum)的大小與頻率成正比！

$E_n = n \cdot hf$ $h$: Planck Constant $h = 6.625\times10^{-34}\text{J}\cdot s$

# 量子簡諧振盪器Simple Harmonic Oscillator SHO、量子彈簧

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left(\frac{1}{2}kx^2 - E\right)\psi$$




$$E_n = \left(n - \frac{1}{1}\right)\hbar\omega$$

波函數會進入古典禁止區域

能量是量子化的！

1926. № 6.

ANNALEN DER PHYSIK.

VIERTE FOLGE. BAND 79.

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

Quantisation as an eigenvalue problem; by E. Schrödinger*

(Zweite Mitteilung.)[1])

### 1. Der Plancksche Oszillator. Die Entartungsfrage.

Wir behandeln zunächst den eindimensionalen Oszillator. Die Koordinate $q$ sei die Elongation multipliziert mit der Quadratwurzel aus der Masse. Die beiden Formen der kinetischen Energie sind dann

$$T = {}^1/_2\, \dot{q}^2 , \qquad T = {}^1/_2\, p^2 . \tag{20}$$

Die potentielle Energie sei

$$V(q) = 2\pi^2 \nu_0^{\,2} q^2 , \tag{21}$$

wo $\nu_0$ die Eigenfrequenz im Sinne der Mechanik. Dann lautet Gleichung (18) für diesen Fall:

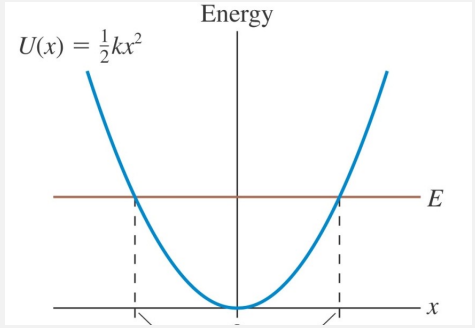
$$\frac{d^2\psi}{dq^2} + \frac{8\pi^2}{h^2}(E - 2\pi^2 \nu_0^{\,2} q^2)\psi = 0 . \tag{22}$$



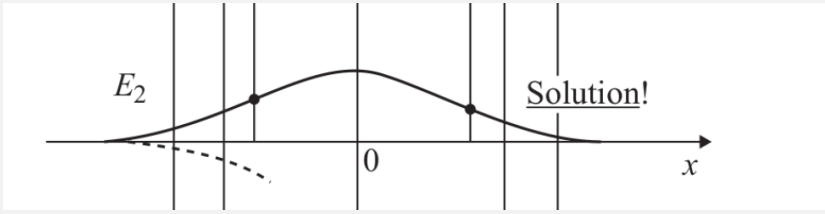

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\cdot\psi(x) = E\cdot\psi(x)$$

先讓我們定性的來猜一下它的定態解。

彈力位能是左右對稱的，對稱點在原點：$x = 0$。




物理結果應該左右對稱，所以，定態方程式的解$\psi$或許也是對稱的？例如：

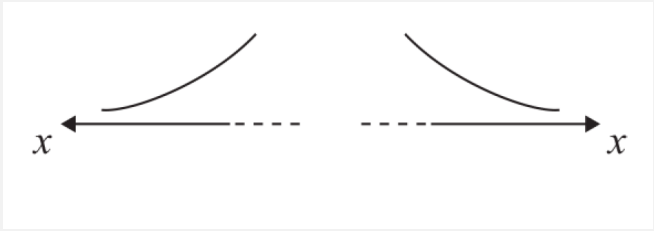



這樣的對稱的解稱為：偶函數。

偶函數在原點的斜率必須為零！斜率在原點才能連續。

在無限限遠處， 可以猜想到，$\psi$及其斜率$\psi'$會漸漸趨近於零。

$x \to \infty, \psi, \psi' \to 0$，在$x \to -\infty$附近，會與$x \to \infty$對稱！如下：

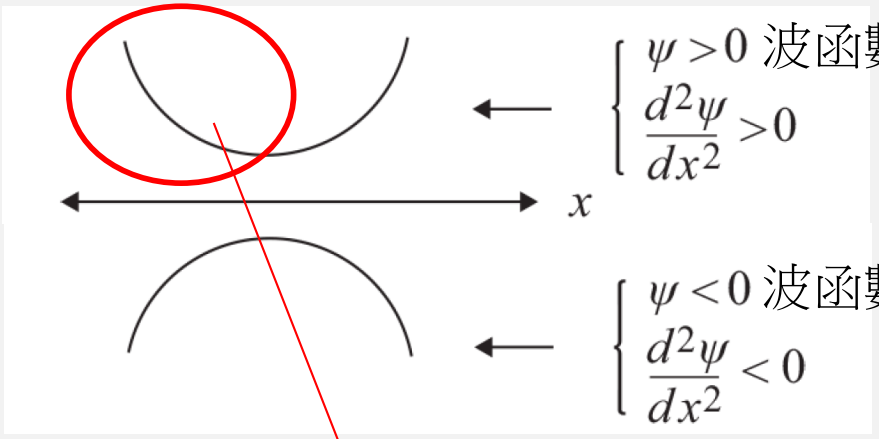


在$x \to \pm\infty$兩者之間，解的變化就由方程式決定，我們也有一些定性的了解：

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

$V(x) - E$的正負號會決定$\frac{\psi''}{\psi}$的正負號！而$\psi''$是斜率的變化！

若$V(x) > E$，這是古典不容許的區域！$\frac{\psi''}{\psi}$為正。




$\psi > 0$ 波函數為正，$\psi''$為正，斜率隨$x$增加而增加！

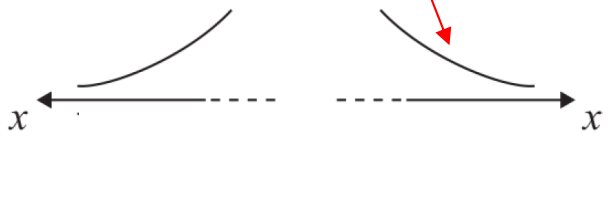
$\frac{d^2\psi}{dx^2} > 0$

$\psi < 0$ 波函數為負，$\psi''$為負，斜率隨$x$增加而減小！

$\frac{d^2\psi}{dx^2} < 0$

通常就說：古典不容許的區域，$x$增加時，波函數會趨離$x$軸而彎曲。

前述$+\infty$處就是這樣的例子： $x$增加時，負的斜率增加，傾斜度減小到零，

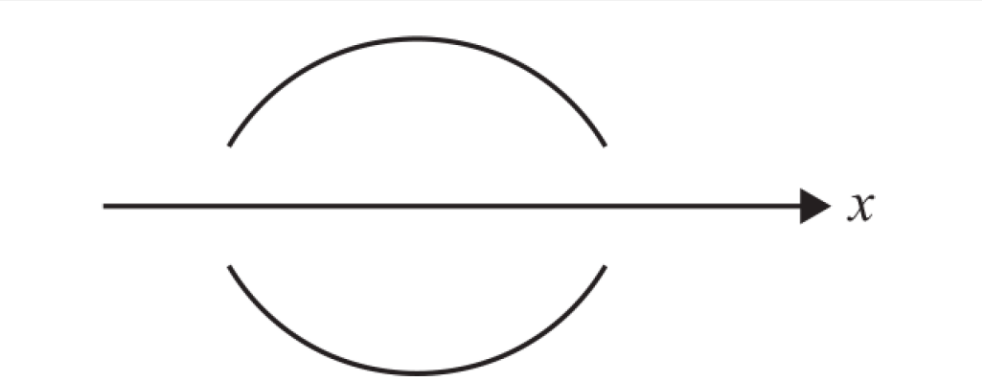



定性上類似指數遞減。

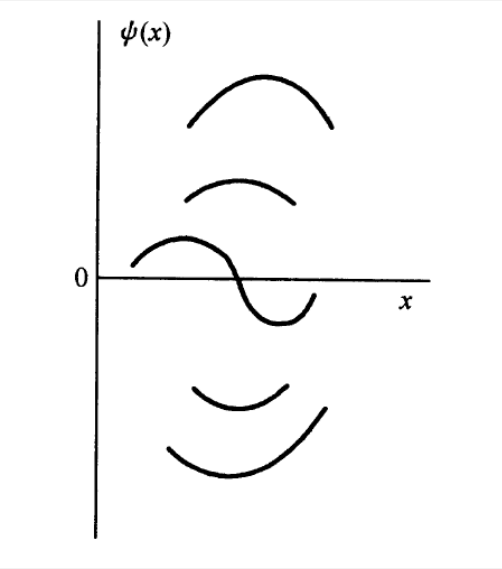
$$\frac{\psi''}{\psi} = \frac{2m}{\hbar^2}[V(x) - E]$$

$V(x) < E$的區域是古典容許的！$\frac{\psi''}{\psi}$為負。

波函數$\psi$為正時，$\psi''$為負，斜率隨$x$增加而減小！




波函數$\psi$為負時，$\psi''$為正，斜率隨$x$增加而增加！




在古典容許的區域，$x$增加時，波函數會趨向$x$軸而彎曲，直到與$x$軸相交。

穿過$x$軸後又會趨向$x$軸彎曲，再一次又穿過$x$軸，典型的情況會來回穿過$x$軸。

結論：在古典不容許的區域，定性上類似指數遞減！

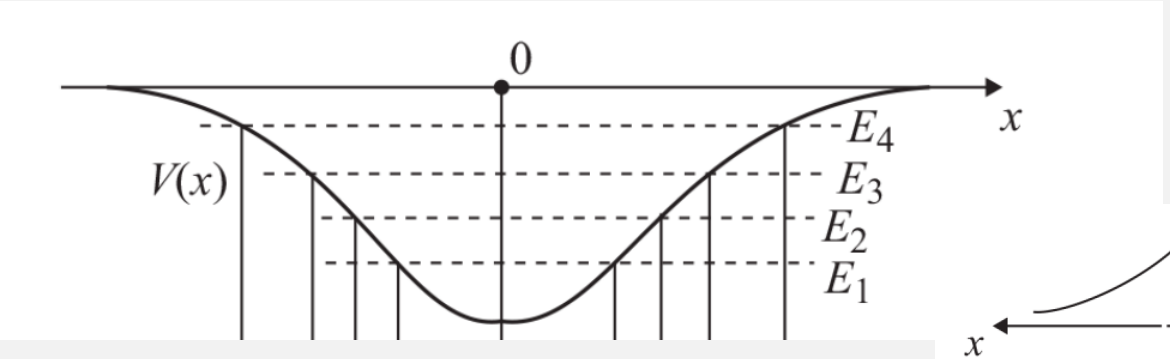
在古典容許的區域，定性上類似來回振盪！

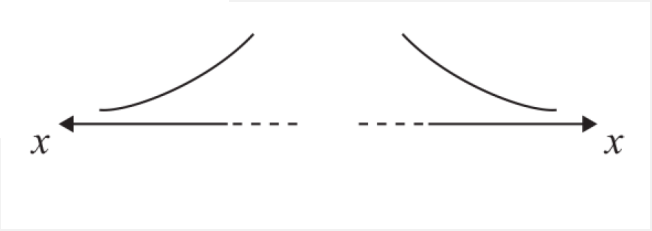
策略：考慮一系列的能量值，大小不同，因此折返點不同。

已知當$x \to \infty$， 波函數解$\psi$及其斜率$\psi'$會趨近於零。

從$x \to \infty$出發向內朝原點前進，以斜率變化$\psi''$的正負，定性得到函數的行為。

而當地$V(x) - E$的正負號，也就是是否為古典容許區域，會決定$\frac{\psi''}{\psi}$的正負號！



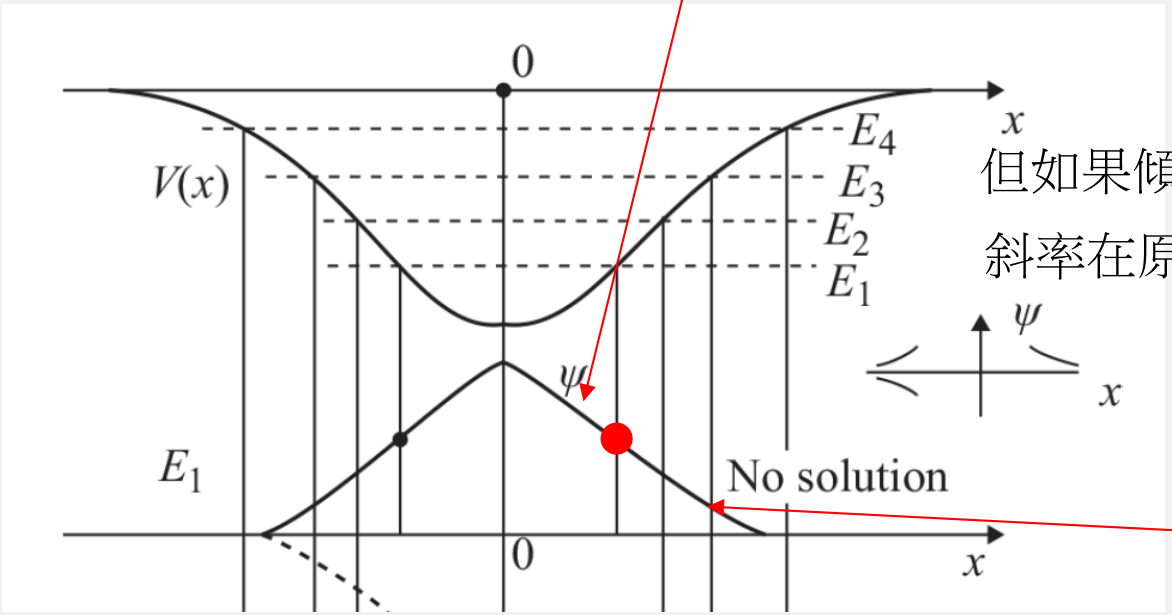



對於$E_1$：



在折返點內，曲線趨向$x$軸彎曲。

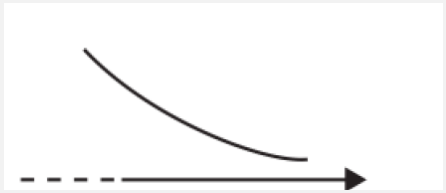
向原點靠近時，傾斜度開始漸漸下降！




但如果傾斜度到達原點，來不及降為零！

斜率在原點就無法連續，此解不成立！

如圖，對於$E_1$，沒有解！



折返點外，從無限遠傾斜度為零，這是古典不容許的區域，$\frac{\psi''}{\psi}$為正。

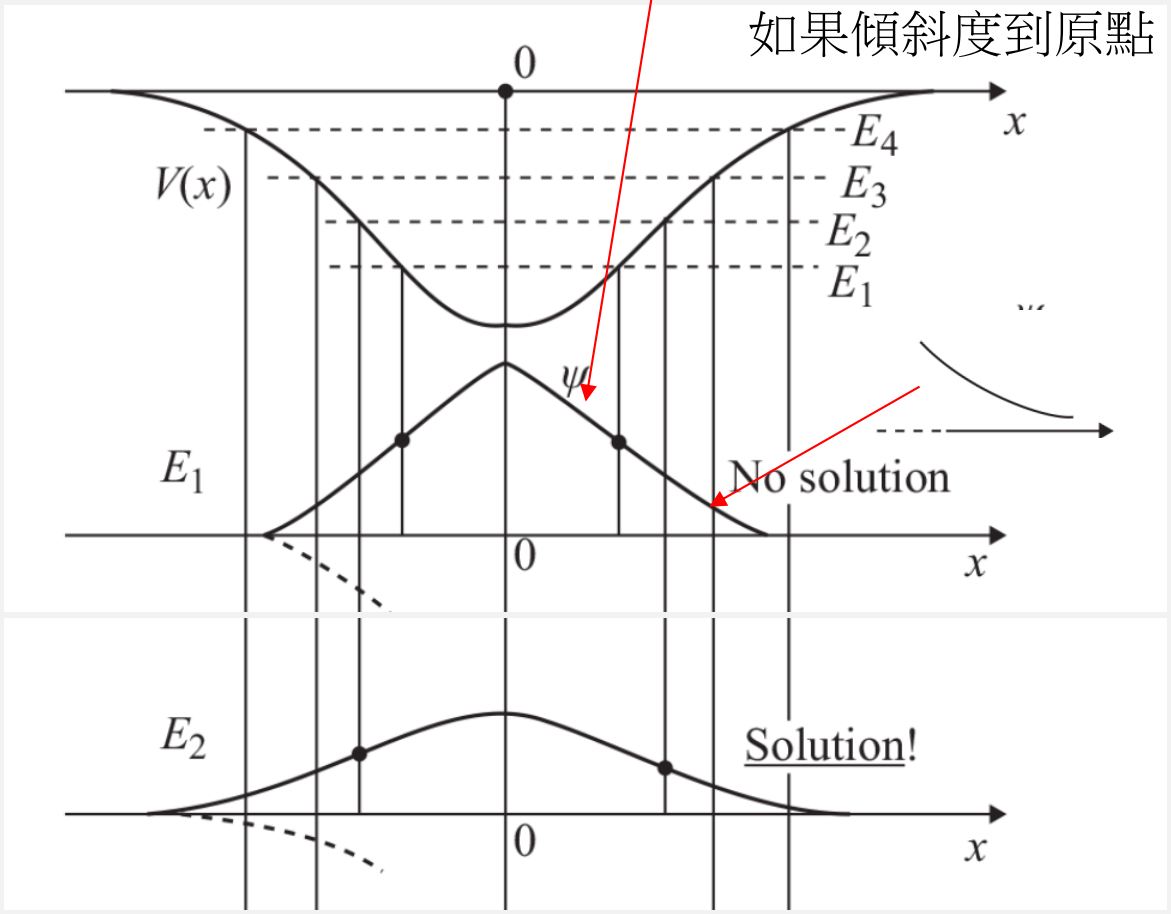
往內走，負的斜率繼續減小。傾斜度增加。



由遠處向原點靠近，傾斜度漸漸增加！

到折返點後，傾斜度又漸漸減小。

如果傾斜度到原點，來不及降為零，解不成立。




對於$E_2$，折返點右移！

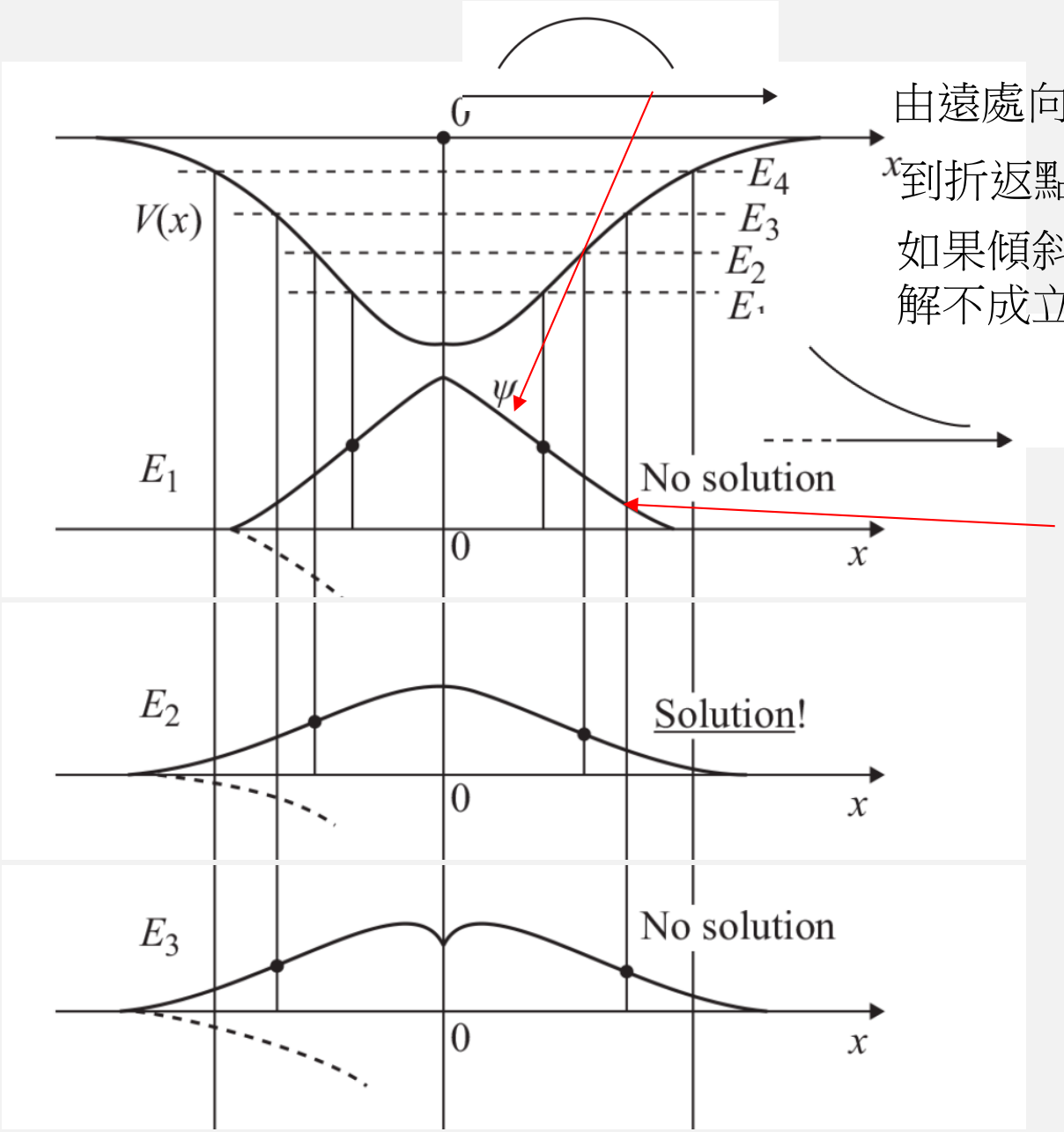
傾斜度有較大間隔下降！

傾斜度在原點恰好降為零！

$E = E_2$，定態方程式有解！

所以條件必須剛好成立，定態方程式才會有解！

能量必須恰好使得傾斜度在∞由零加大，在折返點開始減小，到原點恰好減到零！




由遠處向原點靠近，傾斜度漸漸增加！

到折返點後，傾斜度又漸漸減小。

如果傾斜度到原點，來不及降為零，解不成立。

對於$E_2$，折返點右移！

傾斜度有較大間隔下降！

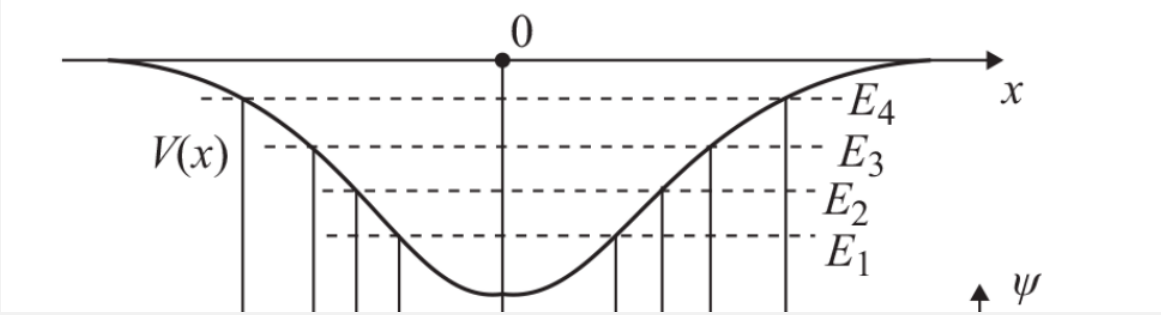
傾斜度在原點恰好降為零！

$E = E_2$，定態方程式有解！

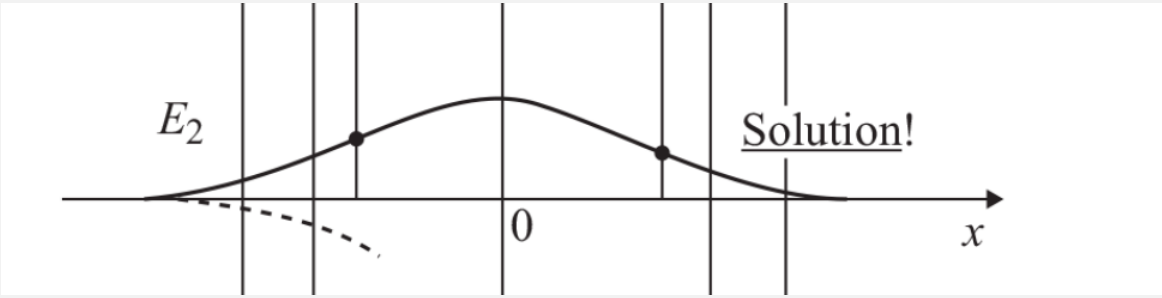
對於大於$E_2$的$E_3$，斜率在原點前變號！但函數不為零，解又不成立了。

在以上的範圍，能量只能是$E_2$，大一點小一點都不行，能量是量子化的。

位能左右對稱，




定態方程式的解是對稱的：偶函數。




偶函數在原點的斜率必須為零！

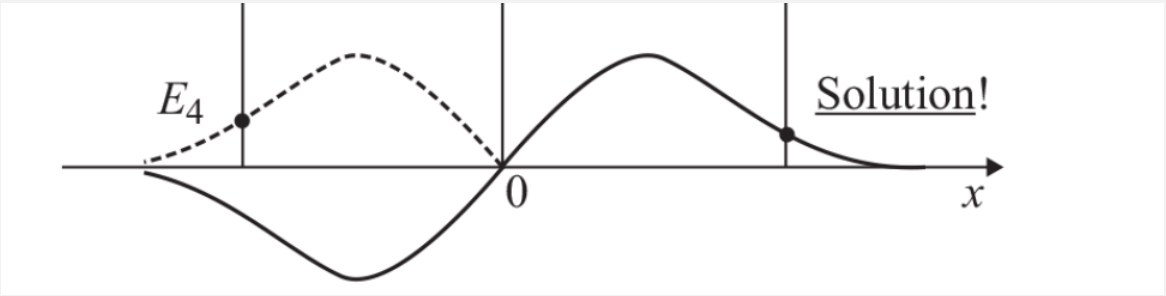
見課本3-6

有較細緻的討論。

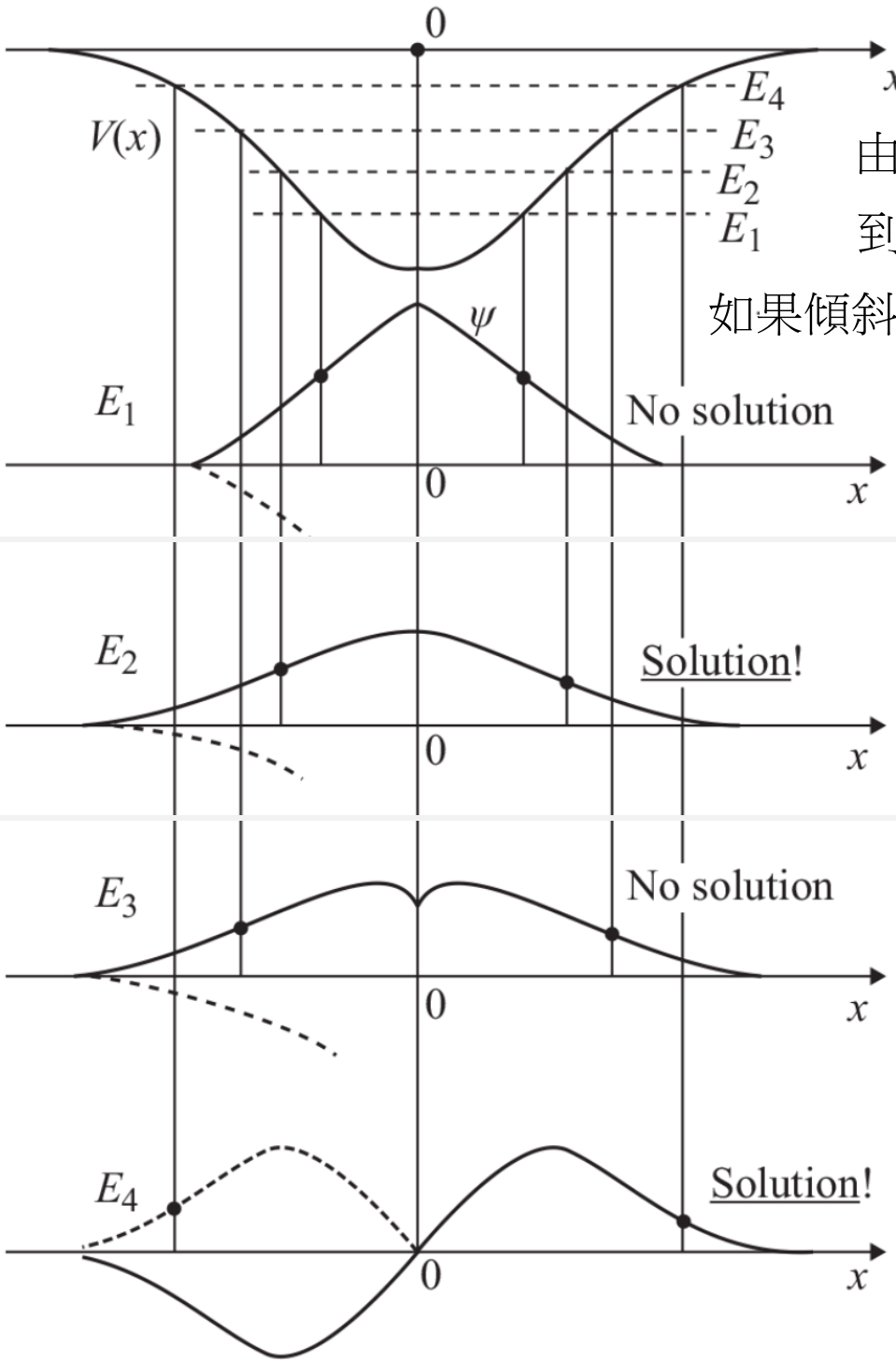
物理應該對稱，但物理是由狀態函數的平方決定，

狀態波函數也可以是反對稱，意思是右邊函數式左邊函數乘−1。

定態方程式的解也可以反對稱的：稱為奇函數，例如：




但注意！如此奇函數在原點的函數值必須為零！




由遠處向原點靠近，傾斜度漸漸增加！

到折返點後，傾斜度又漸漸減小。

如果傾斜度到原點，來不及降為零，解不成立。

對於$E_2$，折返點右移！

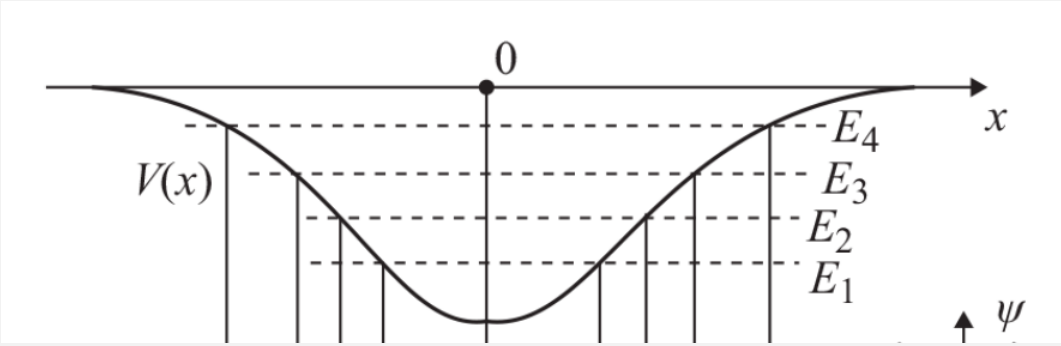
傾斜度有較大間隔下降！

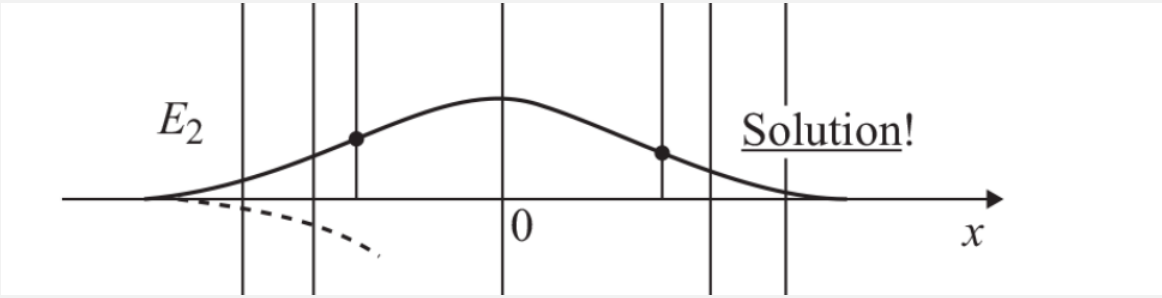
傾斜度在原點恰好降為零！

$E = E_2$，定態方程式有解！

對於大於$E_2$的$E_3$，斜率在原點前變號，但函數不為零！解不成立。

但直到某更大的$E_4$，原點函數值降為零，此解成立。是一奇函數解！

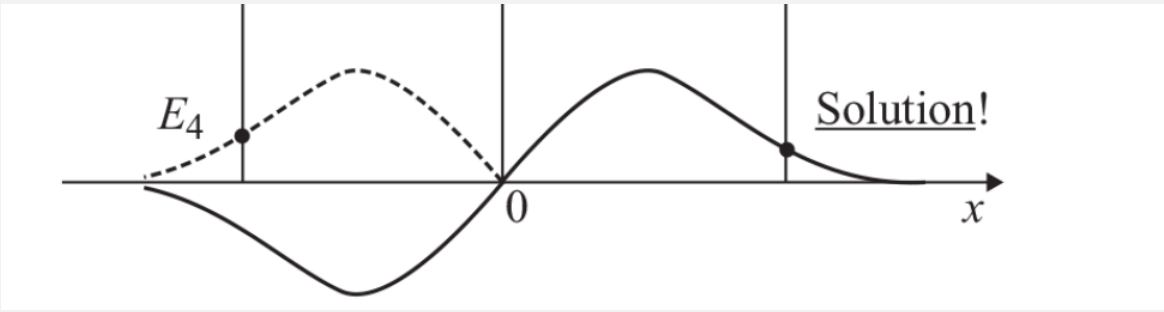



這是偶函數。

所以條件必須剛好成立，定態方程式才會有解！

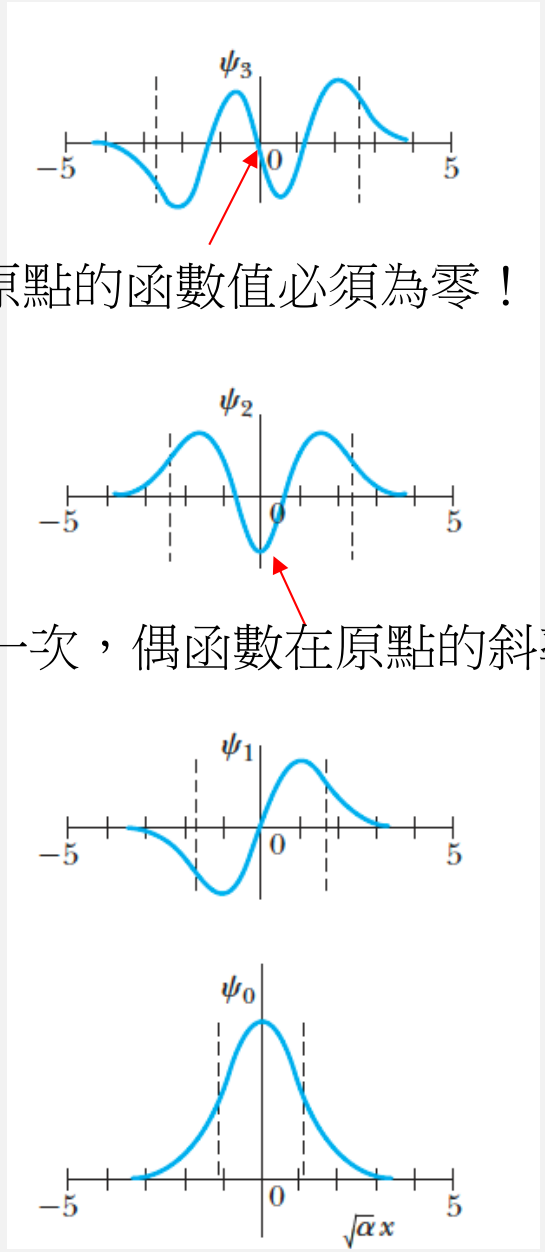
能量必須恰好使得傾斜度在∞由零加大，在折返點開始減小，到原點恰好減到零！



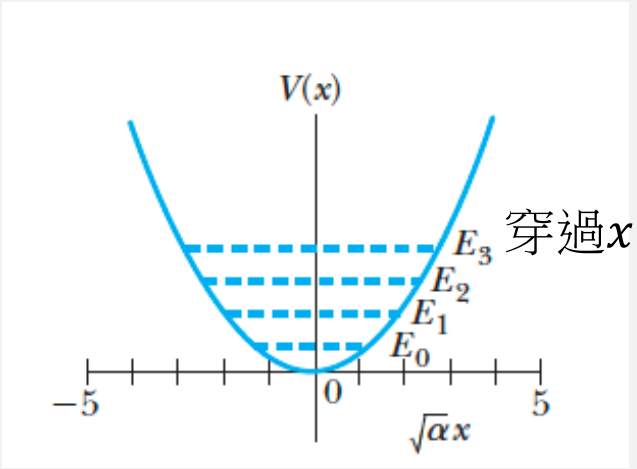

這是奇函數。

能量必須使得傾斜度在∞由零加大，在折返點開始減小直到變號，

函數值開始減小，同時使函數值在原點洽降到零！

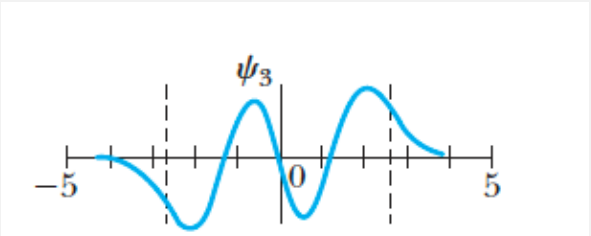



穿過$x$軸一次，奇函數在原點的函數值必須為零！

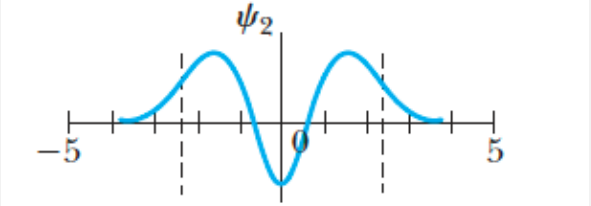



穿過$x$軸一次，偶函數在原點的斜率必須為零！

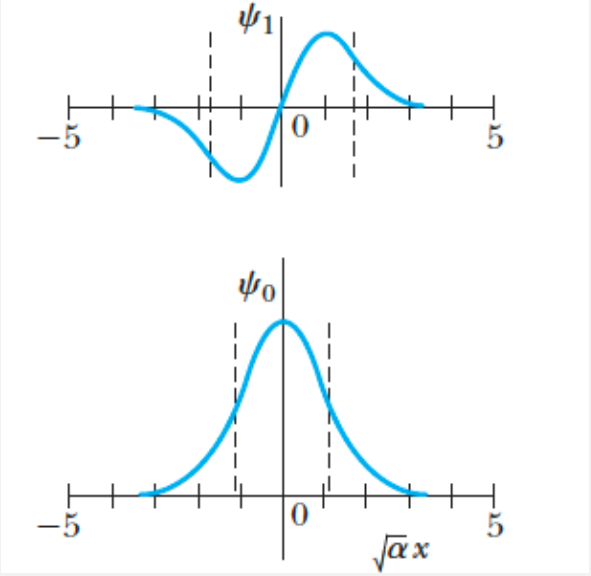
能量再增加，折返點距原點越遠，函數曲線可以來回穿過$x$軸數次，但必須滿足以上條件才是解。



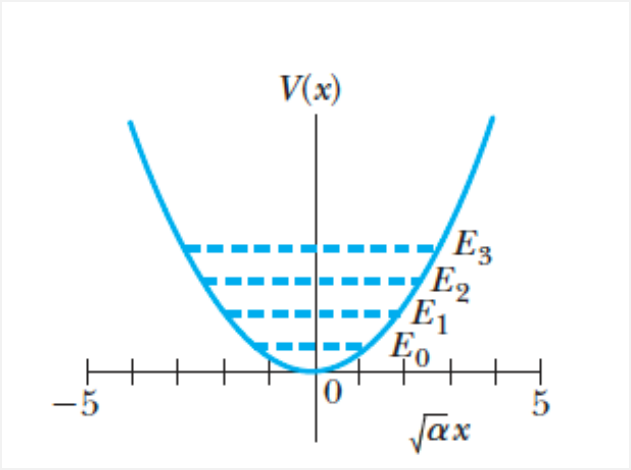

穿過$x$軸一次後使奇函數在原點的函數值為零！ 此能量給出一個解，共穿過$x$軸三次。

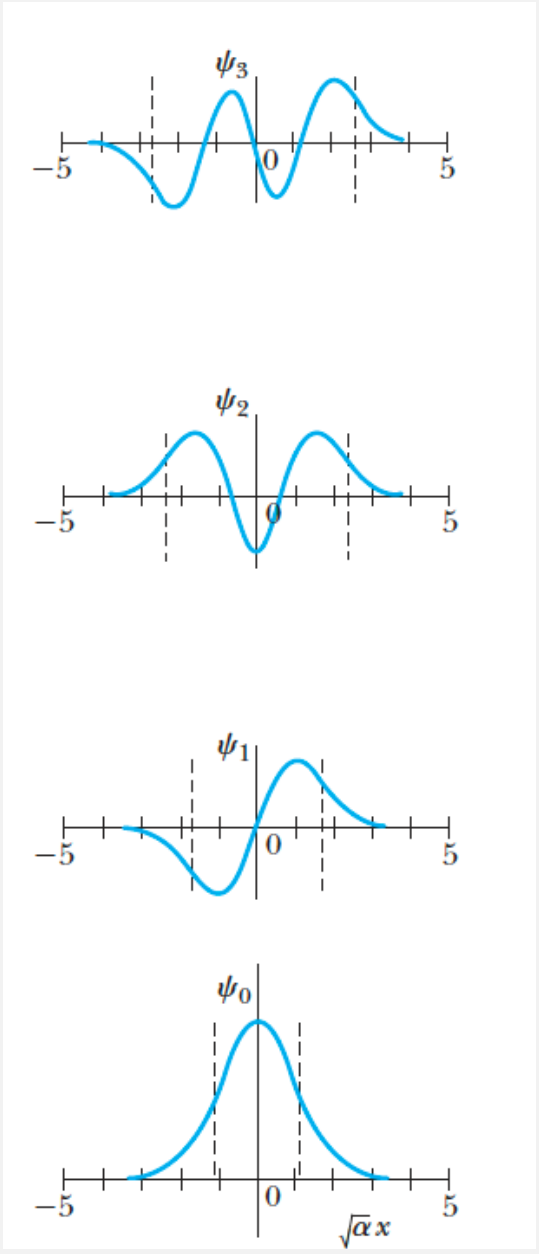


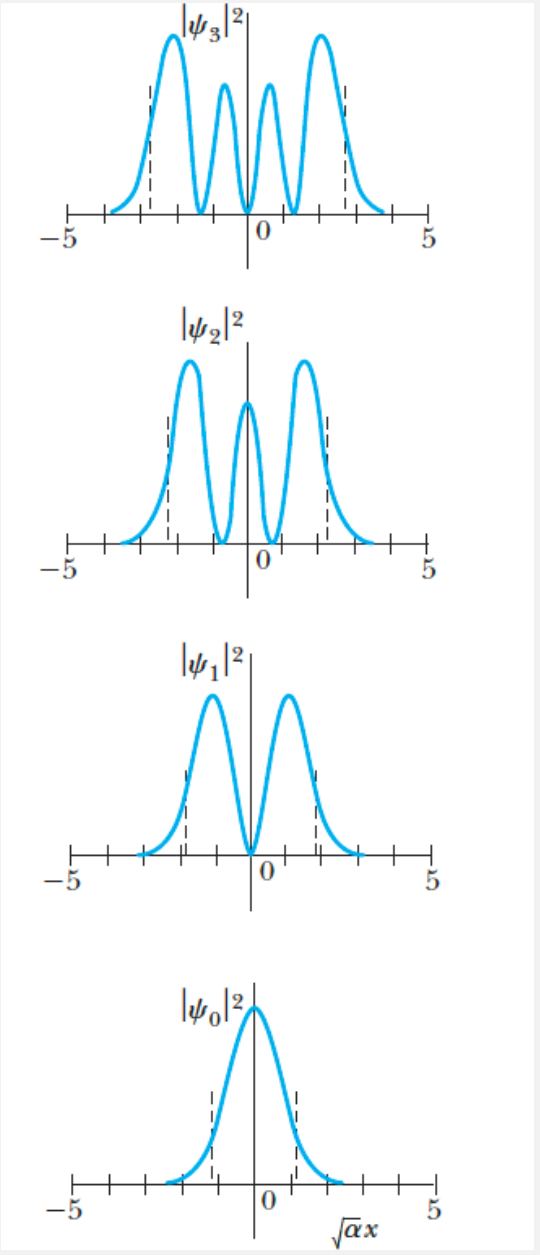

穿過$x$軸一次後使偶函數在原點的斜率為零！此能量給出一個解，共穿過$x$軸二次。




第$n$個能階定態解會有個$n-1$個Node節點。



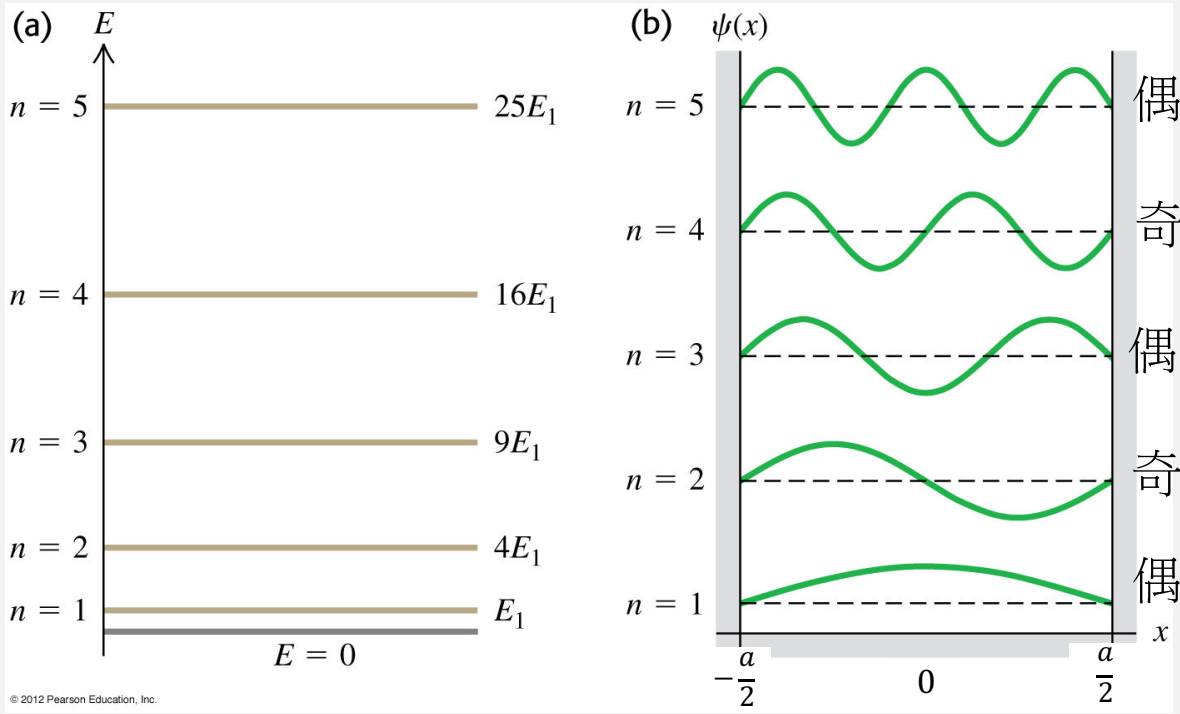



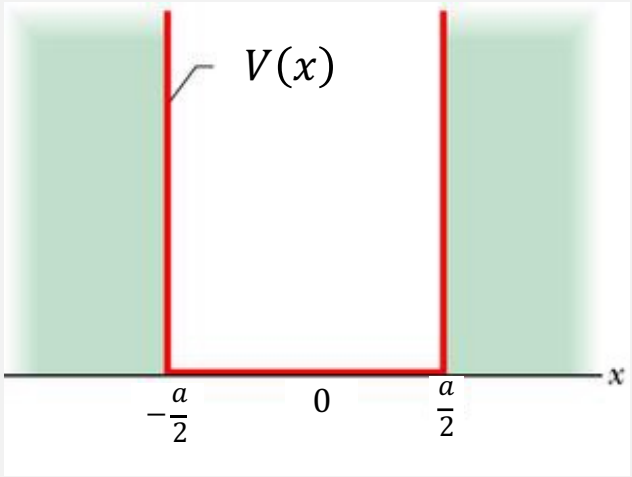




偶函數、奇函數隨能量增加間隔出現！

在無限大位能的問題中，如果將原點置於位能井的中央，

就更能利用本徵函數是奇函數或偶函數的特性。




$$u_n = \sqrt{\frac{2}{a}}\cos\frac{n\pi}{a}x$$

偶函數、奇函數也是間隔分佈！

偶函數在原點的斜率為零， 奇函數在原點的函數值必須為零

第$n$個能階定態解會有個$n-1$個Node節點。

We can do better! Solving the Equation!

1926. № 6.

ANNALEN DER PHYSIK.

VIERTE FOLGE. BAND 79.

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

(Zweite Mitteilung.)[1])

### 1. Der Plancksche Oszillator. Die Entartungsfrage.

Wir behandeln zunächst den eindimensionalen Oszillator. Die Koordinate $q$ sei die Elongation multipliziert mit der Quadratwurzel aus der Masse. Die beiden Formen der kinetischen Energie sind dann

(20) $$\bar{T} = {}^1/_2\, \dot{q}^2 \,, \qquad T = {}^1/_2\, p^2 \,.$$

Die potentielle Energie sei

(21) $$V(q) = 2\pi^2 \nu_0{}^2 q^2 \,,$$

wo $\nu_0$ die Eigenfrequenz im Sinne der Mechanik. Dann lautet Gleichung (18) für diesen Fall:

(22) $$\frac{d^2\psi}{dq^2} + \frac{8\pi^2}{h^2}(E - 2\pi^2 \nu_0{}^2 q^2)\psi = 0 \,.$$




$$\psi(x) \equiv u(x)$$

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left(\frac{1}{2}kx^2 - E\right)\psi \quad \Rightarrow \quad \frac{d^2u}{dx^2} = \frac{m^2\omega^2}{\hbar^2}x^2u - \frac{2mE}{\hbar^2}u \qquad \omega = \sqrt{\frac{k}{m}}$$

$$\frac{d^2u}{dx^2} = \frac{m^2\omega^2}{\hbar^2}x^2u - \frac{2mE}{\hbar^2}u$$ 這些常數很繁雜！

很神奇又自然的：我們可以取任一個較方便的長度單位來解此方程式。

得到解後再換算回原單位！

$\frac{m\omega}{\hbar}$ 單位是長度平方的倒數。 單位是長度。

我們可以選擇長度單位使 $\sqrt{\frac{\hbar}{m\omega}}$ 的數值等於1。 $\sqrt{\frac{\hbar}{m\omega}} = 1$

這等價於引進新的變數$y$，來吸收第一個常數。

$$x = y\sqrt{\frac{\hbar}{m\omega}}$$ 代入 ➡ $$\frac{d^2u}{dx^2} = \frac{m^2\omega^2}{\hbar^2}x^2u - \frac{2mE}{\hbar^2}u$$

$$\left(\frac{m\omega}{\hbar}\right)\frac{d^2u}{dy^2} = \frac{m^2\omega^2}{\hbar^2}\left(\frac{\hbar}{m\omega}\right)y^2u - \frac{2mE}{\hbar^2}u \quad \Rightarrow \quad \frac{d^2u}{dy^2} = y^2u - \frac{2E}{\hbar\omega}u$$

$$\varepsilon \equiv \frac{2E}{\hbar\omega} \quad \Rightarrow \quad \frac{d^2u}{dy^2} = y^2u - \varepsilon u$$

$$\frac{d^2u}{dy^2} = y^2 u - \varepsilon u$$

This is a Homogeneous Linear second order ODE with nontrivial coefficients.

Linear second order ODE 解法

$$u'' + P(x)u' + Q(x)u = f(x)$$

$$P(x) = f(x) = 0$$

$$Q(x) \sim x^2$$

Variation of parameters
Wronskian

Linear ODE

$$u'' + P(x)u' + Q(x)u = f(x)$$

If we find one solution of the homogeneous ODE, we can calculate the general solution.

Complex number 複變函數法

Linear ODE with constant coefficients

$$u'' + a_1 u' + a_0 u = f(x)$$

We can find general solutions using complex number exponential function $e^{\alpha t}$.

級數法 Series

$$\frac{d^2u}{dy^2} - y^2u + \varepsilon u = 0$$ 級數法 Power Series Method of Frobenius



Frobenius 1849-1917

Let's expand the solution as an infinite series 無窮級數:

$$u = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \cdots a_n y^n + \cdots$$

⬇ All derivatives are infinite series.

$$\frac{d^2u}{dy^2} = 0 + 0 + 2a_2 + 6a_3 y + 12a_4 y^2 \cdots n(n-1)a_n y^{n-2} + \cdots$$

$$y^2u = \qquad a_0 y^2 + a_1 y^3 + \cdots a_{n-4} y^{n-2} + \cdots$$

$$\varepsilon u = \qquad \varepsilon a_0 + \varepsilon a_1 y + \varepsilon a_2 y^2 + \varepsilon a_3 y^3 \cdots \varepsilon a_{n-2} y^{n-2} + \cdots$$

⬇ Plug into the ODE and equate the coefficients order by order:

$$2a_2 = \varepsilon a_0 \qquad 6a_3 = \varepsilon a_1$$

$$12a_4 = a_0 + \varepsilon a_2 = a_0\left(1 + \frac{\varepsilon}{2}\right)$$

$$n(n-1)a_n = a_{n-4} + \varepsilon a_{n-2}$$ Recursion遞迴關係

$$a_0 \to a_1 \to a_2 \to a_3 \cdots \to a_n \cdots$$

$$\frac{d^2u}{dy^2} = y^2u - \varepsilon u$$

$$n(n-1)a_n = a_{n-4} + \varepsilon a_{n-2}$$

$$a_0 \to a_1 \to a_2 \to a_3 \cdots \to a_n \cdots$$

$$u = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \cdots a_n y^n + \cdots$$ 此無限級數就是解！

幾乎任何線性微分方程式都可以如此求解！

但這樣的解時常是沒用的！

$$u = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \cdots a_n y^n + \cdots \to \infty, \qquad y \to \infty$$

不可能滿足歸一化條件！

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

需要至少：

$$u \to 0, \qquad y \to \infty$$

薛丁格怎麼解這個方程式？ $\frac{d^2u}{dy^2} = (y^2 - \varepsilon)u$

Sei zur Abkürzung

(23) $$a = \frac{8\pi^2 E}{h^2}, \quad b = \frac{16\pi^4 \nu_0^2}{h^2}$$

also

(22′) $$\frac{d^2\psi}{dq^2} + (a - bq^2)\psi = 0 .$$

Wir führen als unabhängige Variable ein

(24) $$x = q\sqrt[4]{b}$$

und erhalten

(22″) $$\frac{d^2\psi}{dx^2} + \left(\frac{a}{\sqrt{b}} - x^2\right)\psi = 0 .$$

Die Eigenwerte und Eigenfunktionen dieser Gleichung sind *bekannt.*[1]) Die Eigenwerte sind in den hier benützten Zeichen

(25) $$\frac{a}{\sqrt{b}} = 1, 3, 5 \ldots (2n+1) \ldots .$$

Die Eigenfunktionen sind die *Hermiteschen Orthogonalfunktionen*

(26) $$e^{-\frac{x^2}{2}} H_n(x) .$$

他直接知道答案！

$u_0(y) = e^{-\frac{y^2}{2}} \cdot$ (一個特別的多項式)

這是一個指數遞減的高斯分佈函數，乘上一個Hermite多項式！

Method 0

$\frac{d^2u}{dy^2} \sim y^2 u$ 先暫時忘記第三項：

以上顯示：解的微分必須包含 $y \cdot u$。猜想這可以是變數平方的指數函數：

$u \sim e^{-\frac{y^2}{2}}$

$\frac{d}{dy}\left(e^{-\frac{y^2}{2}}\right) = -ye^{-\frac{y^2}{2}}$

$\frac{d^2u}{dy^2} = \frac{d}{dy}\left(-ye^{-\frac{y^2}{2}}\right) = y^2 e^{-\frac{y^2}{2}} - e^{-\frac{y^2}{2}} = y^2 u - u$ $\Leftrightarrow$ $\frac{d^2u}{dy^2} - y^2 u + \varepsilon u = 0$

$e^{-\frac{y^2}{2}}$ 已經是$\varepsilon = 1$時的解了！It could be part of the solution for other $\varepsilon$.

If we guess：

$u(y) = e^{-\frac{y^2}{2}} \cdot h(y)$ with $h(y)$ a finite degree Polynomial 有限次多項式.

$h = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \cdots a_n y^n$

$e^{-\frac{y^2}{2}} y^n \xrightarrow[y \to \infty]{} 0$

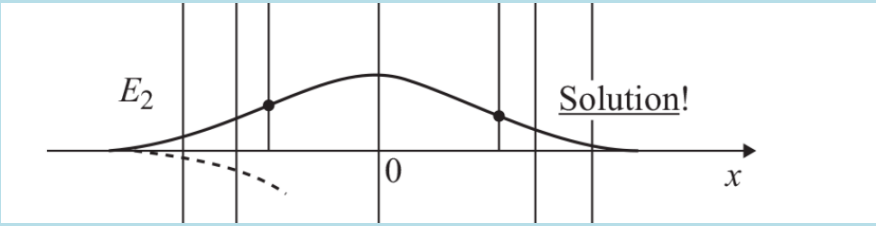
$u \to 0, y \to \infty$ Exponential function falls faster than any finite degree polynomial.

讓我們先感覺一下這個函數$u(y)$的特性：

$$u(y) = e^{-\frac{y^2}{2}} \cdot (\text{多項式} h(y))$$

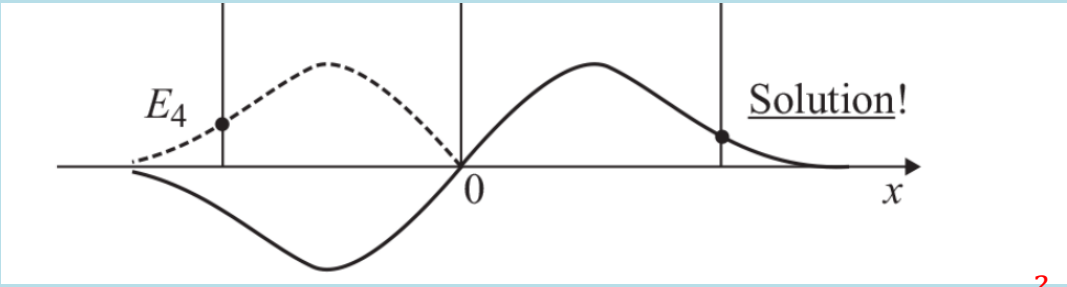
若式中$h(y)$是常數，此函數就是一個高斯分佈：$e^{-\frac{y^2}{2}}$ 。

在∞趨近指數遞減，在原點附近維持緩慢變化：



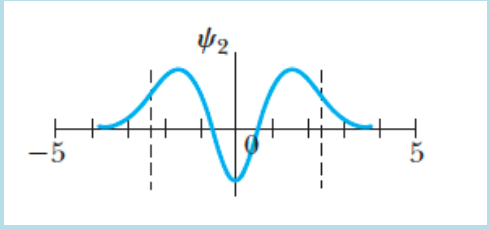

若$h(y)$是一次方$x$，此函數在遠處仍是高斯分佈，在∞趨近指數遞減。

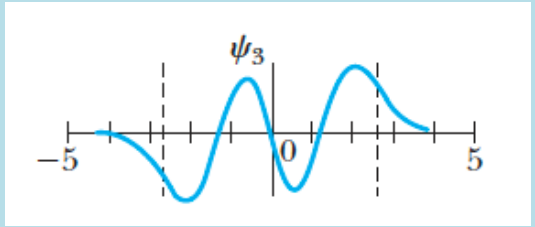
在原點附近高斯分佈變化緩慢，但$h(y) = 0$有一個解，因此會穿過$x$軸一次，




猜想：此解$u(y)$，在趨近∞處由高斯分佈 $e^{-\frac{y^2}{2}}$ 控制，在原點附近則由$h(y)$控制！

該$h(y)$若是$n$次，則會穿過$x$軸$n$次，$n$越大，斜率越大，能量$E$就越大。



Method I

大膽猜想：此解$u(y)$，在趨近∞處由高斯分佈控制，在原點附近則由多項式控制！

我們其實可以直接找到此解$u(y)$在$y$趨近∞時的行為：

在無限遠處 $y \to \infty$，微分方程式的第二項比第三項重要。

$$\frac{d^2u}{dy^2} - y^2u + \varepsilon u = 0 \quad \Rightarrow \quad \frac{d^2u}{dy^2} - y^2u = 0$$

And we know already:

$$\frac{d^2 e^{-\frac{y^2}{2}}}{dy^2} - y^2 e^{-\frac{y^2}{2}} = e^{-\frac{y^2}{2}} \sim 0$$

Therefore, $u$ approaches $e^{-\frac{y^2}{2}}$ at $y \to \infty$ :

$$u(y) \to e^{-\frac{y^2}{2}} \qquad y \to \infty$$

So this separation:

$$u(y) = e^{-\frac{y^2}{2}} \cdot h(y)$$

is to factor out the behaviour $u$ approaches at $y \to \infty$ (asymptotic).

如果這樣設定：

$$u(y) = e^{-\frac{y^2}{2}} \cdot h(y)$$

$$\frac{du}{dy} = e^{-\frac{y^2}{2}} h' - y e^{-\frac{y^2}{2}} h$$

$$\frac{d^2u}{dy^2} = e^{-\frac{y^2}{2}} h'' - 2y e^{-\frac{y^2}{2}} h' + y^2 e^{-\frac{y^2}{2}} h - e^{-\frac{y^2}{2}} h$$

Plug in

$$\frac{d^2u}{dy^2} = y^2 u - \varepsilon u$$

$h(y)$滿足的方程式為：

$$e^{-\frac{y^2}{2}} h'' - 2y e^{-\frac{y^2}{2}} h' + y^2 e^{-\frac{y^2}{2}} h - e^{-\frac{y^2}{2}} h = (y^2 - \varepsilon)\, e^{-\frac{y^2}{2}} h$$

再消掉所有$e^{-\frac{y^2}{2}}$！

$$\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + (\varepsilon - 1)h = 0$$

Hermite Equation



C. Hermite 1822-1901

以上是一個猜測的過程，$h(y)$能不能是有限次多項式，必須直接求解：

$$\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + (\varepsilon - 1)h = 0$$

這個方程式有有限次多項式解嗎？先讓我們假設$h(y)$為$n$次多項式：

$$h(y) = a_n y^n + \cdots$$

代入後先看各項的最高次的貢獻：

$$n(n-1)a_n y^{n-2} - 2na_n y^n + (\varepsilon - 1)a_n y^n$$

第一項的貢獻其實小兩次，在此可以先忽略。第二項與第三項必須抵消。

$$-2na_n y^n + (\varepsilon - 1)a_n y^n = 0$$

簡化後得到一個極漂亮的式子：

$$-2n + (\varepsilon - 1) = 0$$

$n$是多項式解的冪次，$\varepsilon$是該解對應的能量。

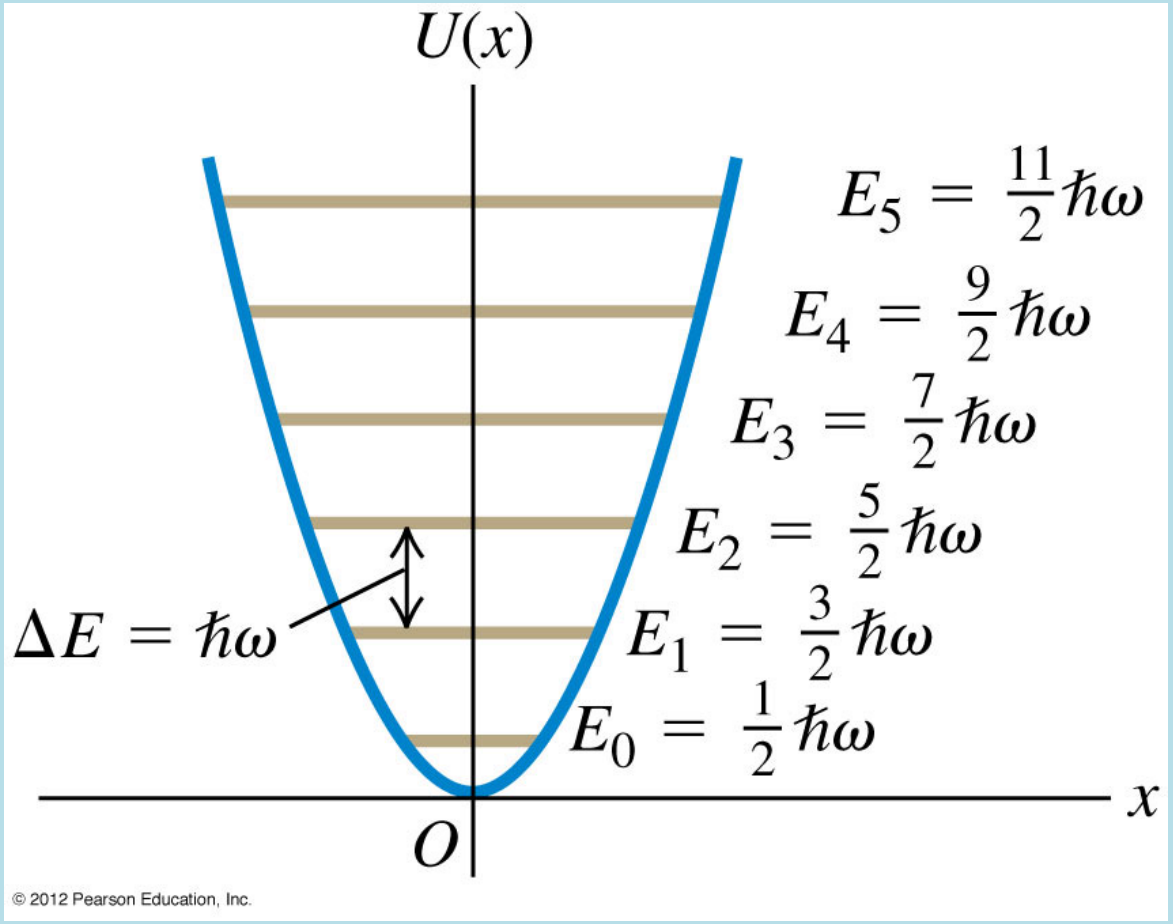
$$\varepsilon = 2n + 1 \equiv \frac{2E}{\hbar\omega}$$

只有當$\varepsilon$為奇整數時，方程式才有限次多項式解！

$$E = \hbar\omega\left(n + \frac{1}{2}\right)$$

能量只有在這些值時，定態方程式才有解！

量子簡諧運動的能量是量子化的！




$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + 2nh = 0$$

$$\varepsilon - 1 \equiv 2n$$

級數法

設$h(y)$為$n$次多項式：

$$h = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \cdots a_n y^n$$

$$\frac{d^2h}{dy^2} = 2a_2 + 6a_3 y + 12a_4 y^2 \cdots + (j+2)(j+1)a_{j+2}y^j + \cdots n(n-1)a_n y^{n-2}$$

$$2y\frac{dh}{dy} = \quad 2a_1 y + 4a_2 y^2 + \cdots j a_j y^j + \cdots + 2na_n y^n$$

$$2nu = 2na_0 + 2na_1 y + 2na_2 y^2 + \cdots 2na_j y^j + \cdots 2na_n y^n$$

Plug into the ODE and equate the coefficients term by term:

$$2a_2 = 2na_0$$

$$6a_3 = (2n+2)a_1$$

$$12a_4 = a_2(2n+4)$$

收集 $y^j$的項，係數必須為零：

$$(j+2)(j+1)a_{j+2} - 2ja_j + 2na_j = 0$$

$$a_{j+2} = \frac{2j-2n}{(j+2)(j+1)}a_j$$

Recursion遞迴關係

事實上奇數項與偶數項的遞迴是分開的：

$a_0 \to a_2 \to a_4 \cdots \to a_n$　　$a_1 \to a_3 \to a_5 \cdots \to a_n$

$$a_{j+2} = \frac{2j-2n}{(j+2)(j+1)} a_j$$ Recursion遞迴關係

若$n$是偶數 $a_0 \to a_2 \to a_4 \cdots \to a_n$

$$a_{n+2} = \frac{2n-2n}{(n+2)(n+1)} a_n = 0$$ 分子為零$a_{n+2} = 0$ 遞迴停止。

其餘奇數次項係數都可設為零，就能得到一個解。

$h = a_0 + a_2 y^2 + \cdots a_n y^n$ 多項式中偶數次項都是偶函數。

若$n$是奇數 $a_1 \to a_3 \to a_5 \cdots \to a_n$ 分子為零$a_{n+2} = 0$ 遞迴停止。

其餘偶數次項係數都可設為零。

$h = a_1 y + a_3 y^3 + \cdots a_n y^n$ 多項式中奇數次項都是奇函數。

這些多項式是Hermite Equation的解，稱為Hermite polynomials。

若$n$不是整數，遞迴不會停止，多項式是無限次，可證明所得的解會發散。

The energy quantization follows the requirement that the recursion of $h(y)$ must terminate. If not, the infinite series will result in a function $u(y)$ that blows up at infinity.

Let us now demonstrate that if the series for $h(u)$ does not terminate, the corresponding $\varphi(u)$ is not an acceptable energy eigenstate. Let us see what the large $u$ behavior of $h(u)$ would be if it does not terminate. For large $j$ the recursion relation (9.2.16) gives

$u(y) \leftrightarrow \varphi(u)$

Notations substitution

$$\frac{a_{j+2}}{a_j} \simeq \frac{2}{j}. \tag{9.2.20}$$

What kind of function of $u$ has coefficients that grow this way? Note that

$$e^{u^2} = \sum_{n=0}^{\infty} \frac{1}{n!}\left(u^2\right)^n = \sum_{j\in \text{ even}} \frac{1}{(j/2)!}u^j. \tag{9.2.21}$$

This series has coefficients $c_j = \frac{1}{(j/2)!}$ for even $j$, and so we see that

$$\frac{c_{j+2}}{c_j} = \frac{(j/2)!}{((j+2)/2)!} = \frac{1}{\frac{j}{2}+1} = \frac{2}{j+2} \simeq \frac{2}{j} \tag{9.2.22}$$

for large $j$. This is just the behavior noted in (9.2.20) for the $h(u)$ coefficients, showing that $h(u) \sim e^{u^2}$ for large $u$. Therefore, if the series for $h(u)$ does not terminate, the wave function behaves like

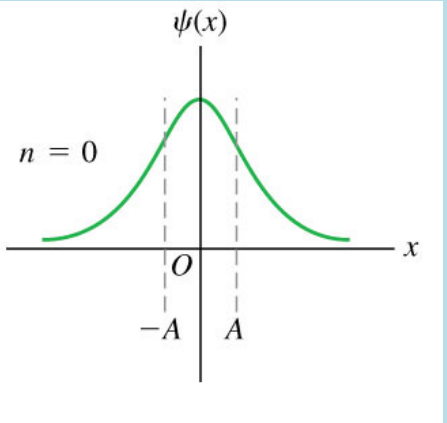
$$\varphi(u) = h(u)e^{-u^2/2} \simeq e^{u^2}e^{-u^2/2} \simeq e^{u^2/2}, \tag{9.2.23}$$

which is in fact the bad solution identified in (9.2.4). This proves that $h(u)$ must be a polynomial, and the recursion relation must terminate for us to get an energy eigenstate!

$u(y) = e^{-\frac{y^2}{2}} \cdot y$的$n$次多項式$h_n$

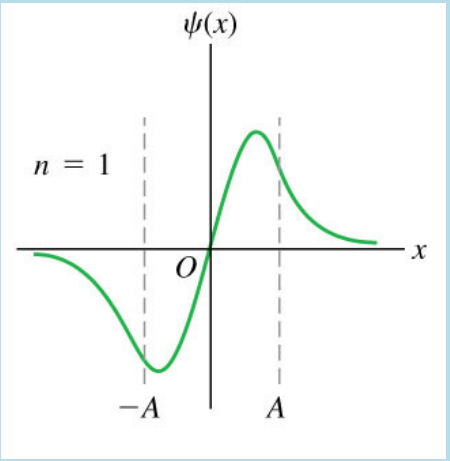
$$h_n(y) = \sum_{j=1}^{n} a_j y^j$$

$$a_{i+2} = \frac{2i - 2n}{(i+2)(i+1)} a_i$$




前三個定態：

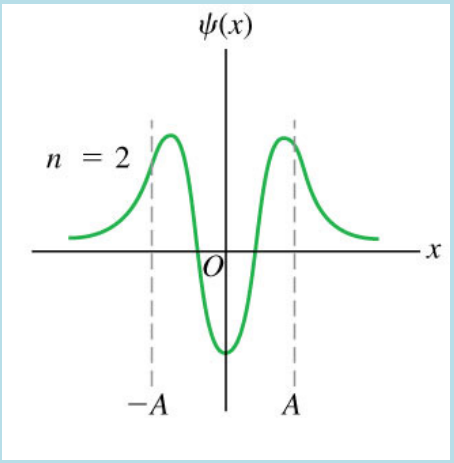
$n = 0$ Ground state $h_0(y) = a_0, \quad u_0(y) = a_0 e^{-\frac{y^2}{2}}$



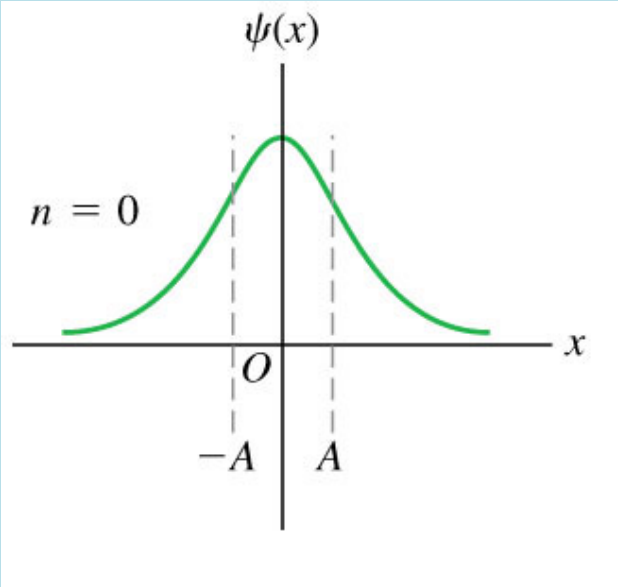

$n = 1$ 1st excited state $h_1(y) = a_1 y, \quad u_1(y) = a_1 y e^{-\frac{y^2}{2}}$

$n = 2$ 2nd excited state $a_2 = \frac{-4}{(2)(1)} a_0$

$h_2(y) = (a_0 - 2a_0 y^2), \quad u_2(y) \sim (a_0 - 2a_0 y^2) e^{-\frac{y^2}{2}}$



Ground state




$$u_0(y) = a_0 e^{-\frac{y^2}{2}}$$

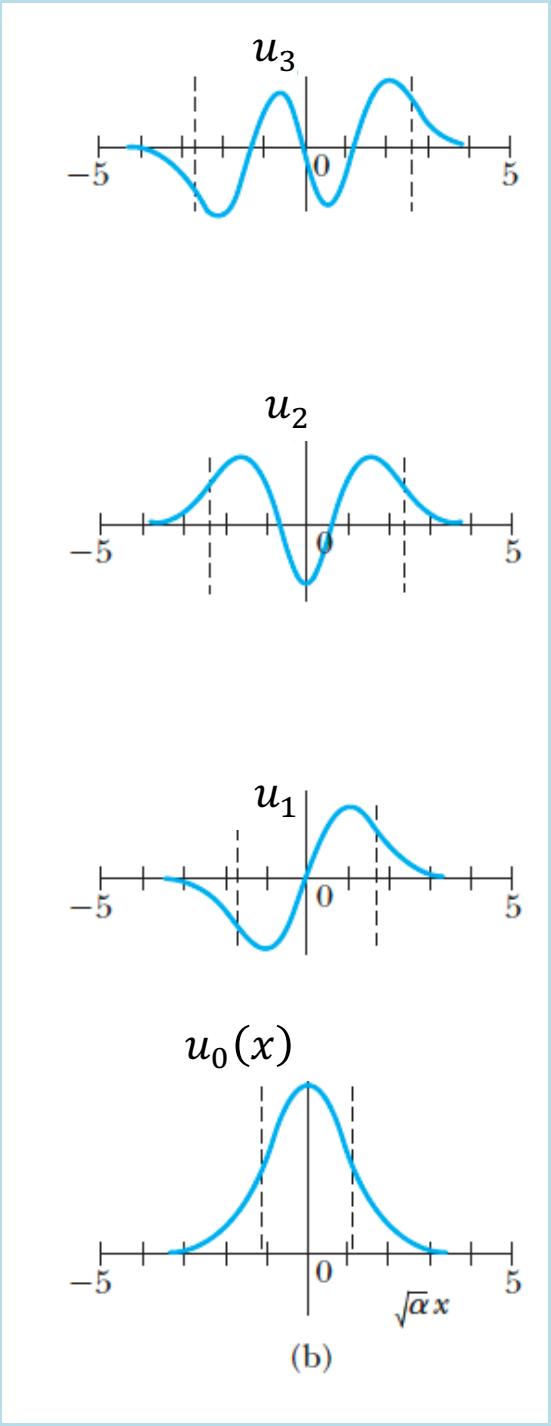
$$x = y\sqrt{\frac{\hbar}{m\omega}}$$

常數則由歸一化條件給定：

$$u_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}$$

$A$是同能量對應古典的折返點！

在折返點外，量子彈簧還有發現電子的機率。

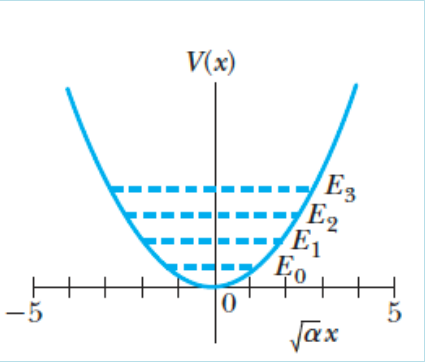



$$u_3(x) \sim \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{3}} \sqrt{\frac{m\omega}{\hbar}} \cdot x \left(2\frac{m\omega}{\hbar}x^2 - 3\right) \cdot e^{-\frac{m\omega x^2}{2\hbar}}$$

$$u_2(x) \sim \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}} \cdot \left(2\frac{m\omega}{\hbar}x^2 - 1\right) \cdot e^{-\frac{m\omega x^2}{2\hbar}}$$

$$u_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}}\, x \cdot e^{-\frac{m\omega x^2}{2\hbar}}$$

$$u_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}$$

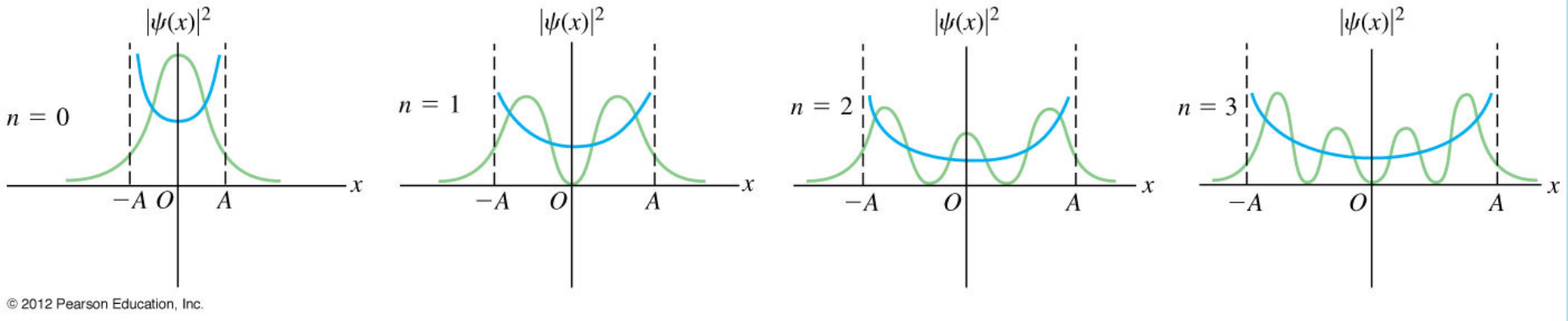



$$u_3(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{3}} (\sqrt{\alpha}x)(2\alpha x^2 - 3) e^{-\alpha x^2/2}$$

$$u_2(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

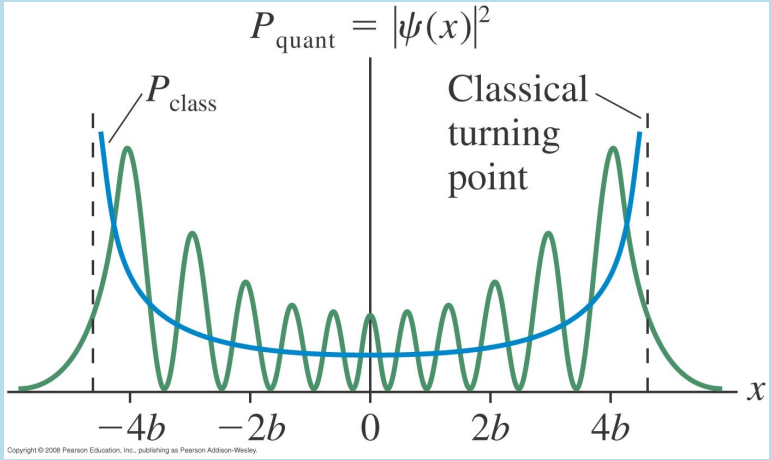
$$u_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha}\, x e^{-\alpha x^2/2}$$

$$u_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad \alpha = \frac{m\omega}{\hbar}$$




綠線是量子機率分佈，藍線是對應古典振動的位置機率，兩端運動慢，出現機率高。

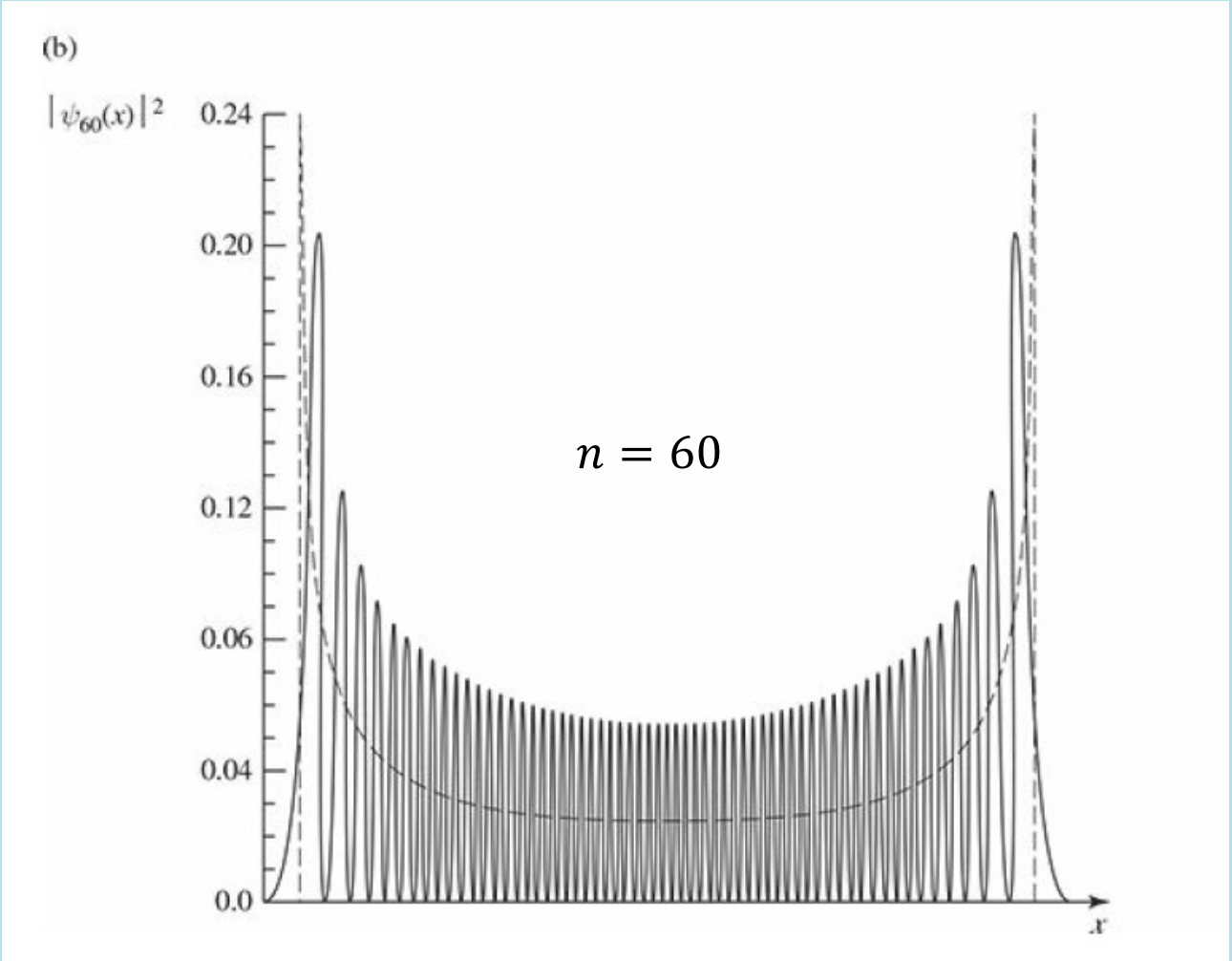
當量子數極小時，量子機率密度與古典運動差別很大！

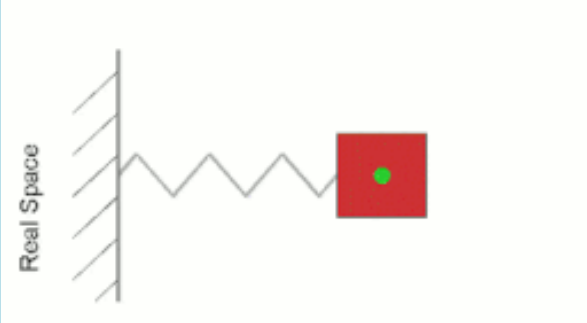



$n = 11$ State

For large $n$, the quantum probability is similar to the classical one.

當量子數極大時，機率密度就類似古典的運動！



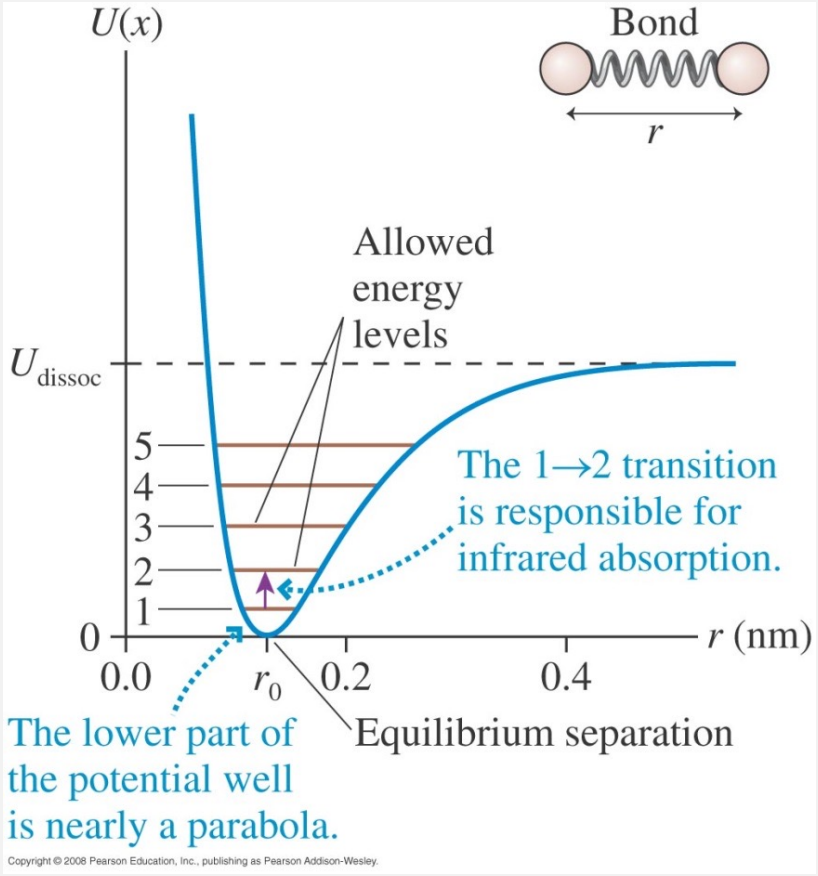



微觀世界有許多彈簧！

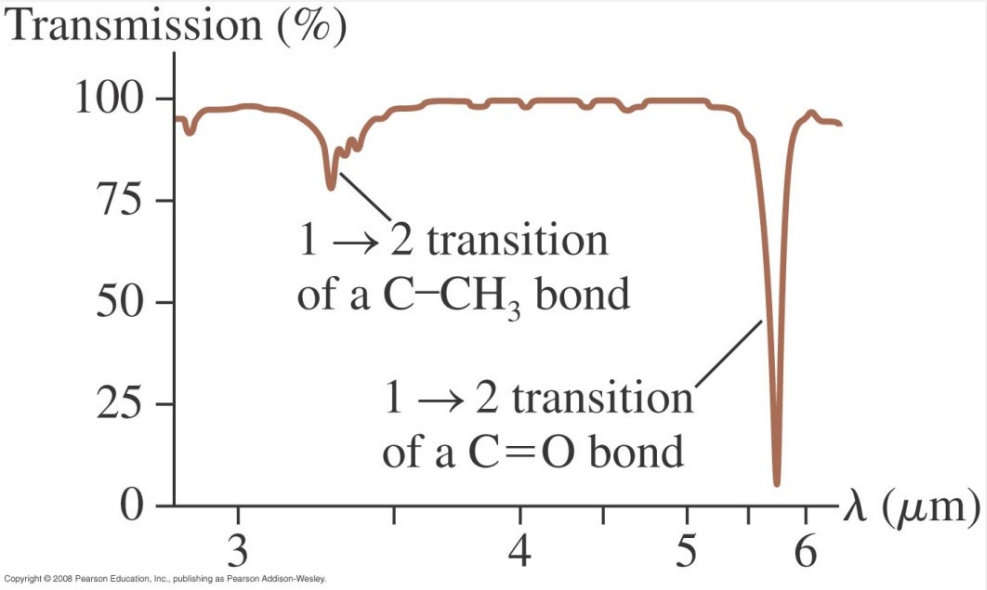
一個力學系統在平衡點附近的小範圍運動，都是簡諧運動！

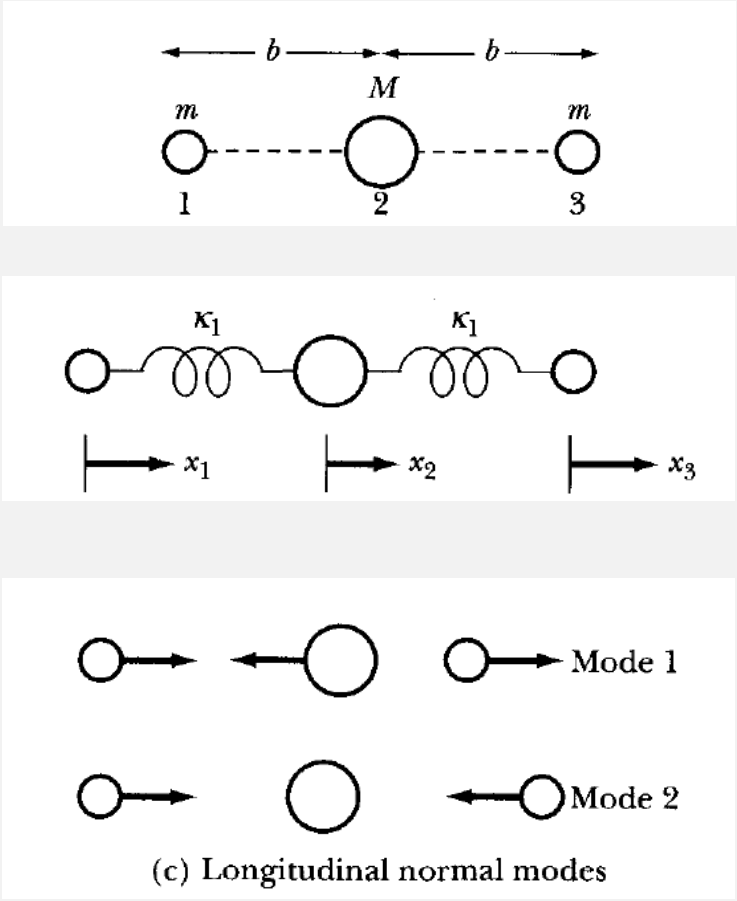


分子的束縛鍵就是一個彈簧！




Molecular Vibration 分子光譜

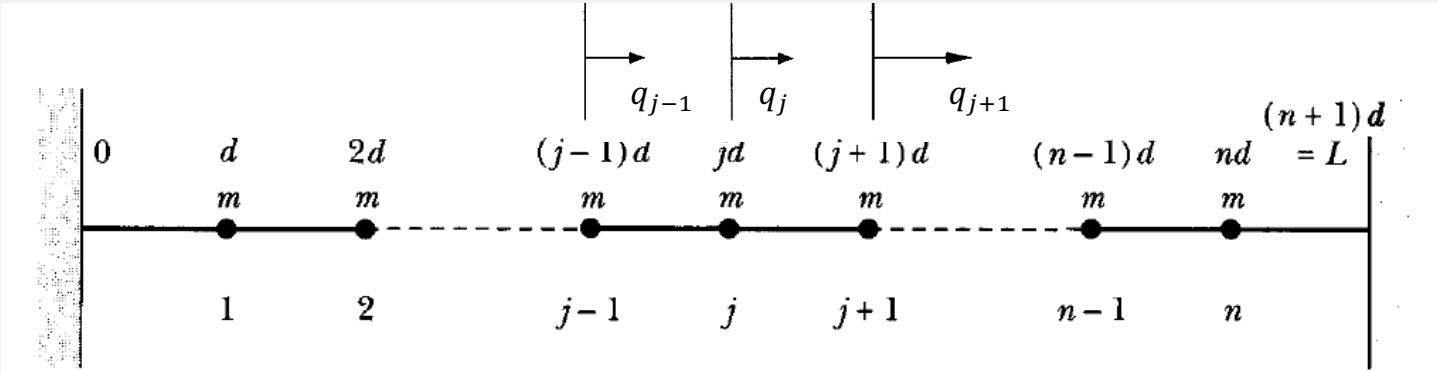




(c) Longitudinal normal modes

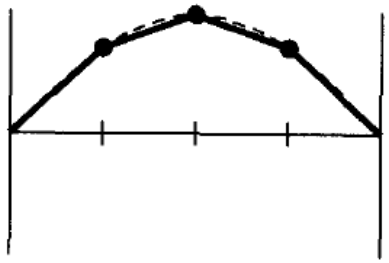
三個原子組成的分子，可以有兩個振盪模式Mode，如同兩條獨立振動的彈簧。

## 12.9 The Loaded String* 原子晶格的振動波

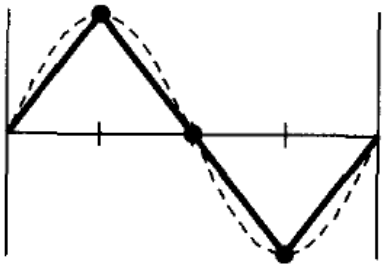



晶格上原子的前後移動，可以改寫成一個一個獨立的振動模式mode。

Summary

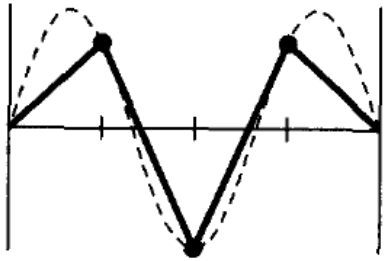


$m = 1$

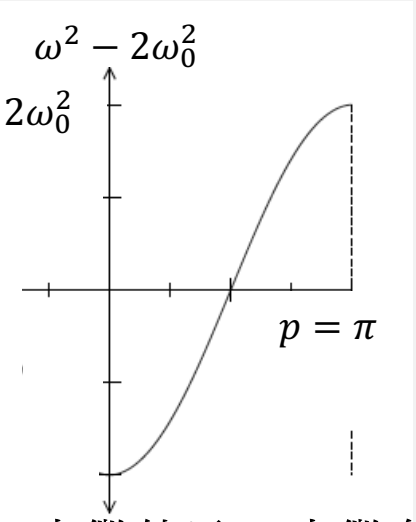


$m = 2$

$n = 3$



$m = 3$




一個自然數$m$對應一本徵值及一本徵向量。

$$p = \frac{m\pi}{N+1} \equiv ka \qquad m = 1,2,3 \cdots N$$

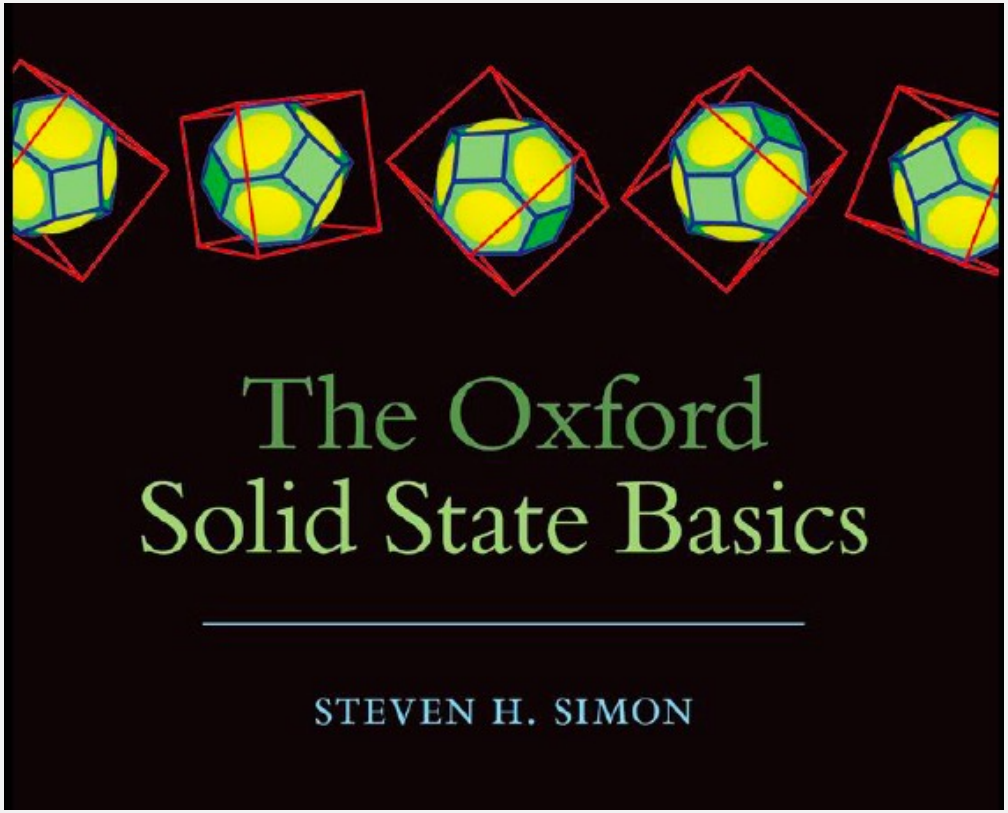
$$\boldsymbol{a}^{(p)} \text{ or } \boldsymbol{a}^{(m)} = \begin{pmatrix} \sin p \\ \vdots \\ \sin(j-1)p \\ \sin jp \\ \sin(j+1)p \\ \vdots \\ \sin Np \end{pmatrix}$$

$$\omega_m^2 = \omega_0^2(2 - 2\cos p)$$

$$\boldsymbol{X} = \boldsymbol{a}^{(m)} C e^{i\omega_m t} \rightarrow \boldsymbol{a}^{(m)} \cdot [A_m \cos \omega_m t]$$

一個自然數$m$對應一個獨立振盪模式(駐波)。

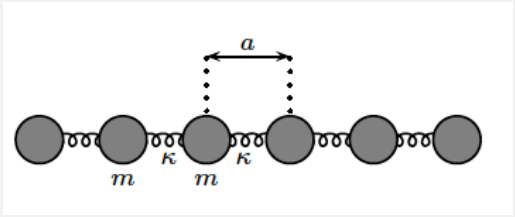
一個模式對應一條彈簧！




# Vibrations of a One-Dimensional Monatomic Chain

9

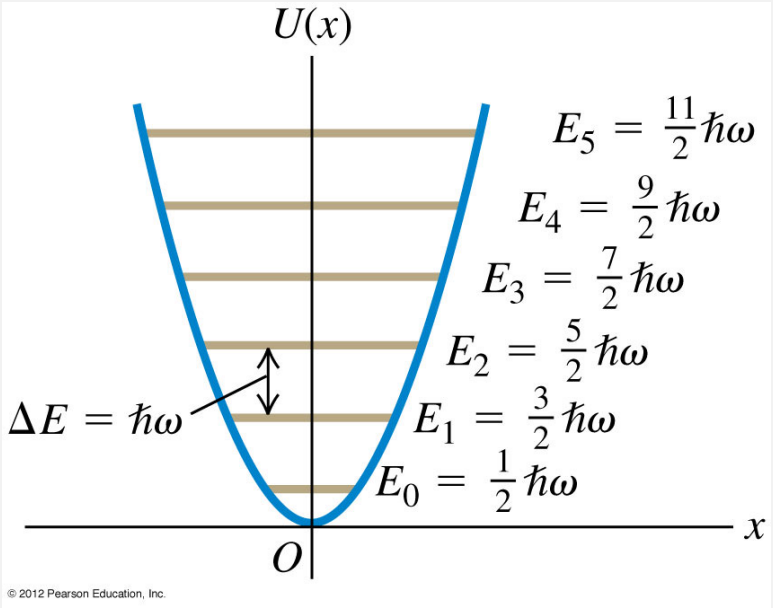
In Chapter 2 we considered the Boltzmann, Einstein, and Debye models of vibrations in solids. In this chapter we will consider a more detailed model of vibration in a solid, first classically, and then quantum-

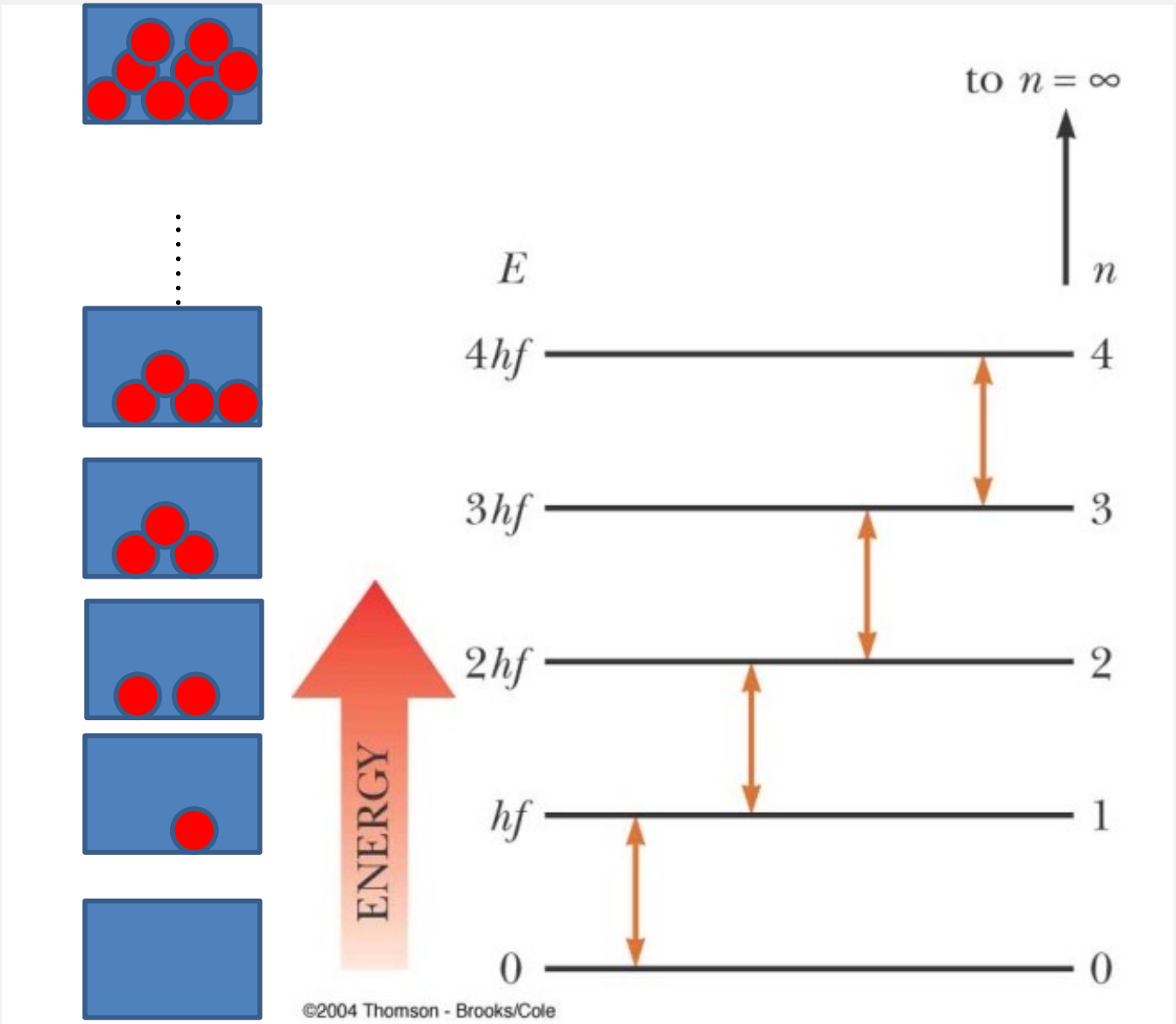





晶體中原子的振動，可以找到一系列$m = 1,2,3 \cdots \infty$，如彈簧的模式。

如同量子彈簧，每一模式的能量皆為量子化。






每一模式的能階像極了在盒子中一個個裝入能量相同的粒子。

量子 ⇨ 粒子　　粒子數 $n = \dfrac{E}{\hbar\omega(k)}$

這就稱為聲子 phonon：量子彈簧的激發態！



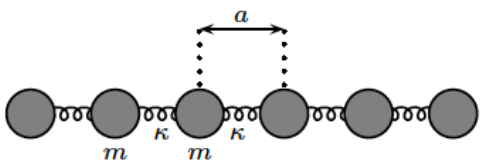



**Fig. 9.1** The one-dimensional monatomic harmonic chain. Each ball has mass $m$ and each spring has spring constant $\kappa$. The lattice constant, or spacing between successive masses at rest, is $a$.

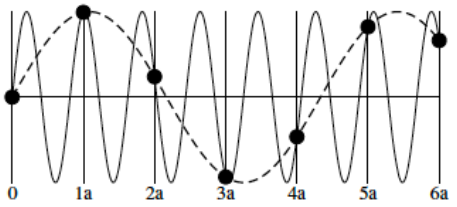
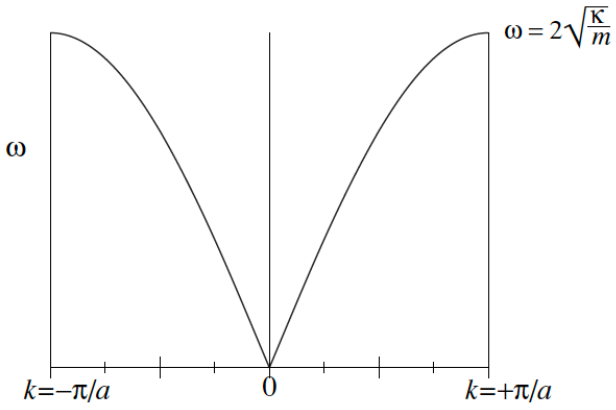



**Fig. 9.3** Aliasing of waves. The dashed curve has wavevector $k$ whereas the solid curve has wavevector $k + 2\pi/a$. These two waves have the same value (solid dots) at the location of the lattice




## 9.3 Quantum Modes: Phonons

We now make a rather important leap from classical to quantum physics.

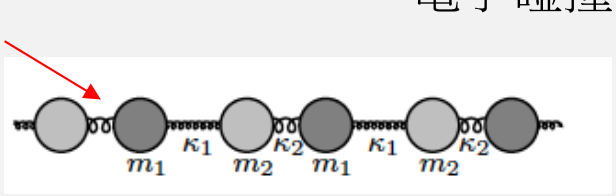
> **Quantum Correspondence:** If a classical harmonic system (i.e., any quadratic Hamiltonian) has a normal oscillation mode at frequency $\omega$ the corresponding quantum system will have eigenstates with energy
>
> $$E_n = \hbar\omega(n + \frac{1}{2}). \qquad (9.7)$$

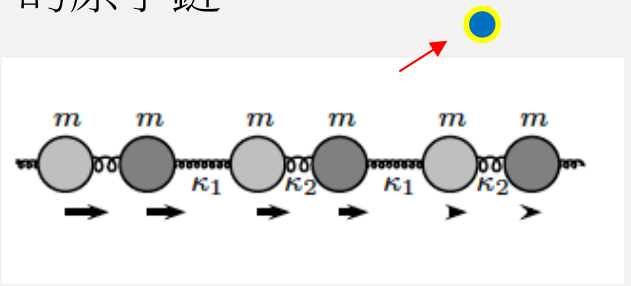
Presumably you know this well in the case of a single harmonic oscillator. The only thing different here is that our harmonic oscillator can be a collective normal mode not just the motion of a single particle. This quantum correspondence principle will be the subject of Exercises 9.1 and 9.7.

**Definition 9.1** *A **phonon** is a discrete quantum of vibration.*[8]

This is entirely analogous to defining a single quantum of light as a photon. As is the case with the photon, we may think of the phonon as actually being a particle, or we can think of the phonon as being a quantized wave.

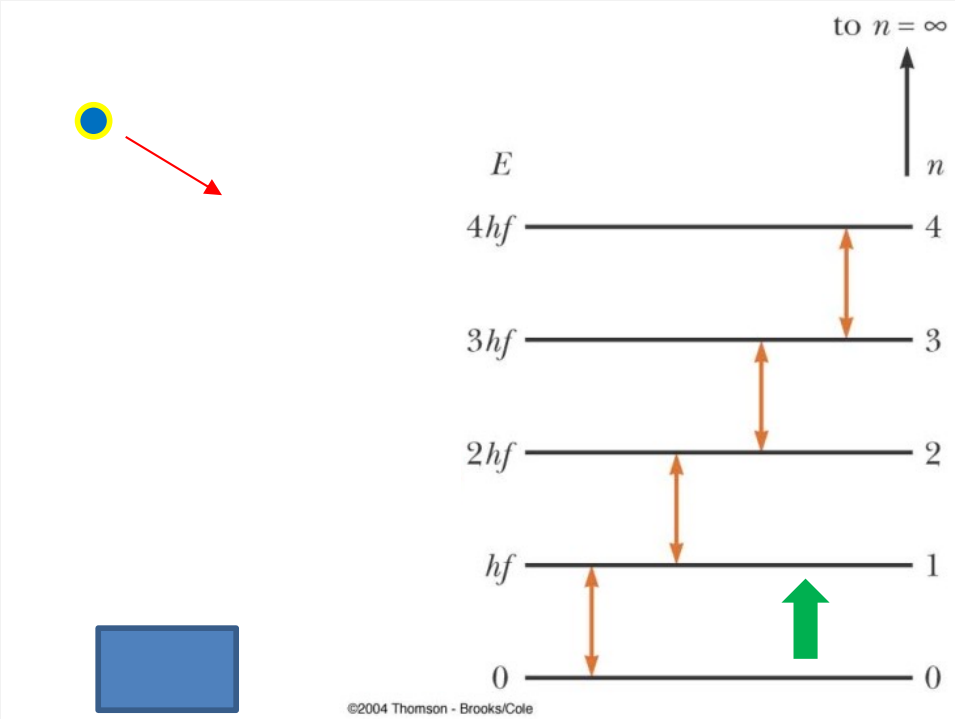
# 電子碰撞晶體中的原子鏈

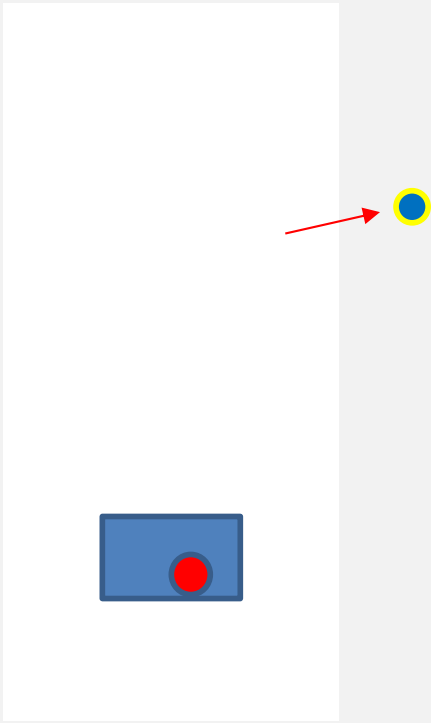



等同

電子碰撞激發某個模式$k$由$n = 1$定態躍遷到$n = 2$定態。



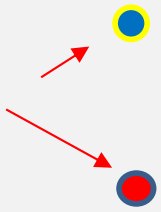



等同

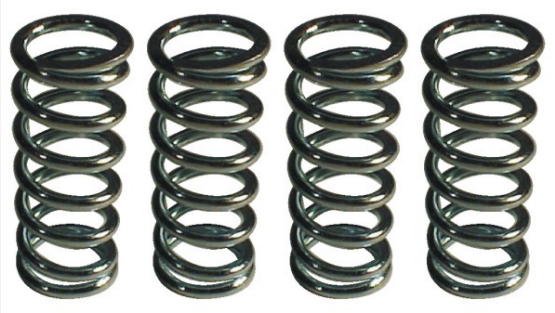
電子移動中放出一個聲子



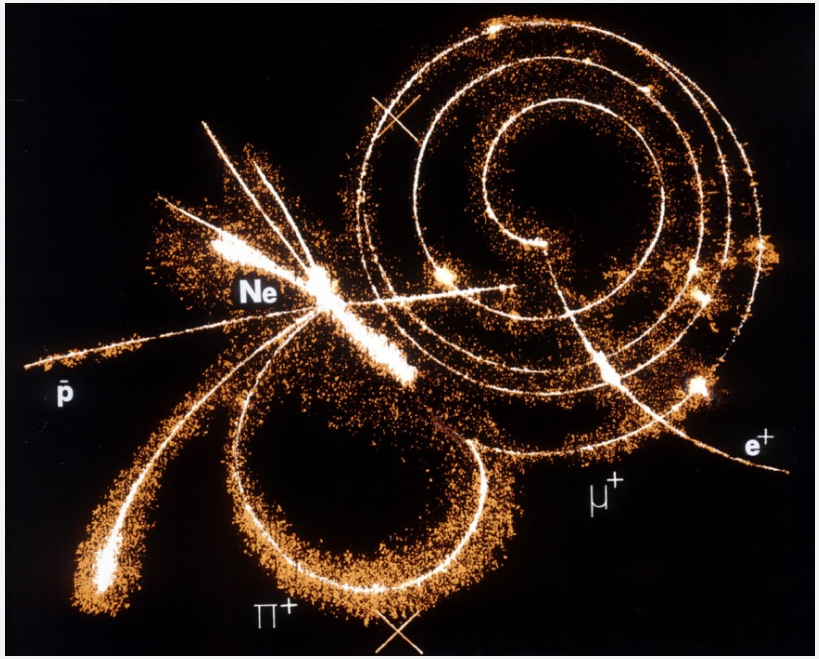
聲子好像一個基本粒子！



量子彈簧不是彈簧，而是可以產生、可以消滅的粒子的系統。







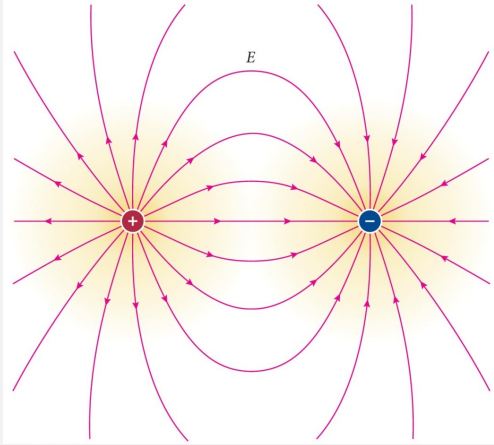
那基本粒子如電子，可不可能看成聲子呢？

基本粒子如電子，可不可能看成是量子彈簧的激發態呢？

當然這時的彈簧就不能是原子的晶格。

但我們早已熟悉、真空中場的擾動，也可看成一個一個的彈簧的組合！

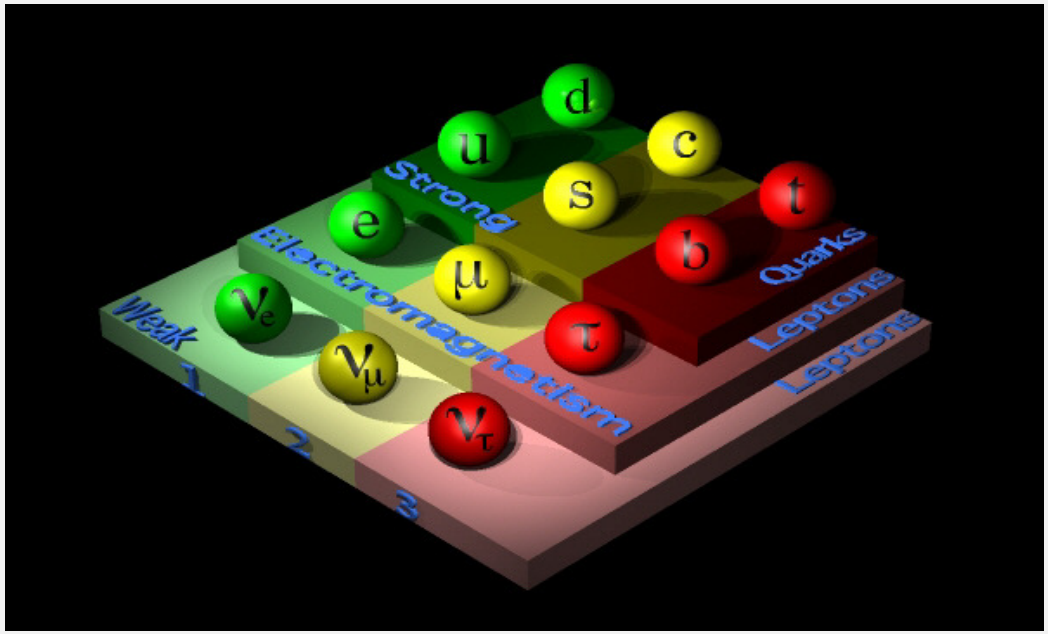







如果場也量子化了，這就稱為量子場，激發態就會是一個個基本粒子。

每一個基本粒子都對應一個量子場




電子 ⟺ 電子場

$u$夸克 $u$夸克場

描述可產生可消滅的粒子的理論：量子場論！

我們的宇宙是由彈簧組成的



以上我們得到的是定態解(時空可分開的解)的狀態函數$u_n$：

如同無限大位能井，SHO的定態狀態函數$u_n$ 也滿足以下重要性質：

展開定理：任一狀態函數$\psi$可以$u_n$作展開。展開聯想到向量以基底展開：

$$\psi(x) = \sum_{n=0}^{\infty} [c_n \cdot u_n(x)]$$

正交定理：本徵函數彼此正交。這很像一組彼此正交的基底！

$$\int_{-\infty}^{\infty} dx \cdot u_m(x)^* \cdot u_n(x) \; = \delta_{mn}$$

$$\psi(x) = \sum_{n=1}^{\infty} c_n u_n(x)$$

代入$\psi$的展開。

分量components $c_n$可以利用$u_n$彼此正交的特性計算出來：

$$\int_{-\infty}^{\infty} dx \cdot u_n^*(x)\psi(x) = \int_{-\infty}^{\infty} dx \cdot u_n^*(x)\left[\sum_{m=1}^{\infty} c_m u_m(x)\right]$$

$$= \sum_{m=1}^{\infty} c_m \int_{-\infty}^{\infty} dx \cdot u_n^*(x)u_m(x) = \sum_{m=1}^{\infty} c_m \delta_{mn} = c_n$$

$$c_n = \int_{-\infty}^{\infty} dx \cdot u_n^*(x)\psi(x) \quad \Longleftrightarrow \quad c_i = \boldsymbol{a}^{(i)T}\begin{pmatrix} x_1(0) \\ x_2(0) \\ x_3(0) \end{pmatrix}$$

分量$c_a$可以寫成態函數與本徵函數的空間積分。很像向量與基底的內積投影：

這一展開式提供對簡諧運動位能下薛丁格波方程式的普遍解法：

將$t=0$時的波函數，即起始條件，對定態解$u_n$展開如下：

$$\Psi(x,0)=\sum_{n=1}^{\infty}c_n u_n(x)$$

根據展開定理，這永遠可以做到！

$t=0$時此狀態可以視為定態$u_n$的如上疊加，

接著定態隨時間個自演化，位能下薛丁格方程式要求$u_n$乘上$e^{-i\frac{E_n}{\hbar}t}$。

乘完之後依同樣方式疊加，

$$\Psi(x,t)=\sum_{n=1}^{\infty}c_n u_n(x)e^{-i\frac{E_n}{\hbar}t}$$

整個波函數是定態解完整波函數的線性疊加組合，滿足線性薛丁格波方程式。

如此，它既滿足波方程式有滿足起始條件，它就是唯一解！

很明顯，這個程序不只適用於無限大位能井，原則上適用於任何位能。

關鍵就是可以證明正交定理與展開定理對任何位能的薛丁格方程式都正確！



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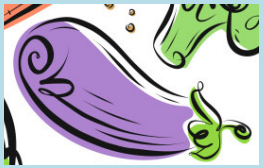

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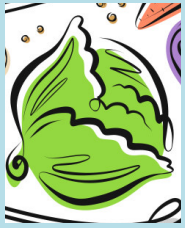

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⋮

各個配料分離烹煮





一個量子系統的定態決定了此系統的物理性質。

若確認任一合邊界條件的函數可以本徵函數分解，我們就能計算其分解係數$a_n$。

但這樣的分解真的是正確的嗎？分解所得的無限級數真的與被分解的函數相等嗎？

數學上相等與否的判準：這些係數組成的$u_n$的線性組合，會趨近被分解的函數。

$$\lim_{N\to\infty}\int_0^L dx\left[\psi(x)-\sum_{n=1}^{N}a_n u_n(x)\right]^2=0$$

兩者差距的平方和(積分)$N\to\infty$時，趨近於零。

這稱為Completeness.完備性，必須嚴格證明的。下學期將說明。