Why do you need to know this material?

You should know how experimental results motivated the development of quantum theory, which underlies all descriptions of the structure of atoms and molecules and pervades the whole of spectroscopy and chemistry in general.

What is the key idea?

Experimental evidence led to the conclusions that energy cannot be continuouly varied and that the classical concepts of a ‘particle and a ‘wave’ blend together when applied to light, atoms and molecules.

What do you need to know already?

You should be familiar with the basic principles of classical mechanics, which are reviewed in next.

Quantum Theory : Introduction & Principles

- Classical mechanics (古典力學) :

對巨觀的粒子可以：(1)施以作用力後精確地預測該粒子的運動軌跡 (2)可以提供粒子任何的能量 使其達所預期的能量激(動)發狀態 (excited state).。

問題來了!

- 然而在19世紀末，科學家發現古典力學無法運用於微觀的粒子(如:原子、分子、電子、質子…等等)，他們發現實驗結果推翻了古典力學所認定的觀念，例如：粒子不一定具有arbitrary energy，且粒子性與波動性混雜在一起而無法精確描述其運動軌跡；此時引發科學家更進一步研究而發展出quantum mechanics（量子力學)。

The failures of classical physics

- (a) Black-body radiation

  金屬球加熱放光,太陽(受熱)放光

  An object capable of emitting and absorbing all wavelengths of radiation uniformly.

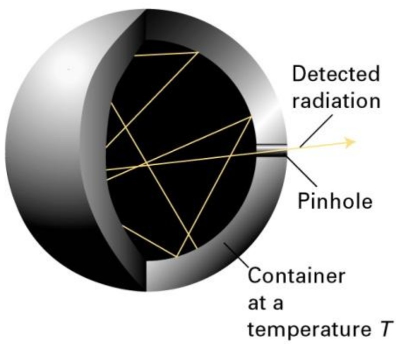
- A good approximation to a black body is a pinhole in an energy container maintained at a constant temperature, because any radiation leaking out of the hole has been absorbed and reemitted inside so many times that it has come to thermal equilibrium with the walls.

Figure 7.6 **Blackbody radiation**

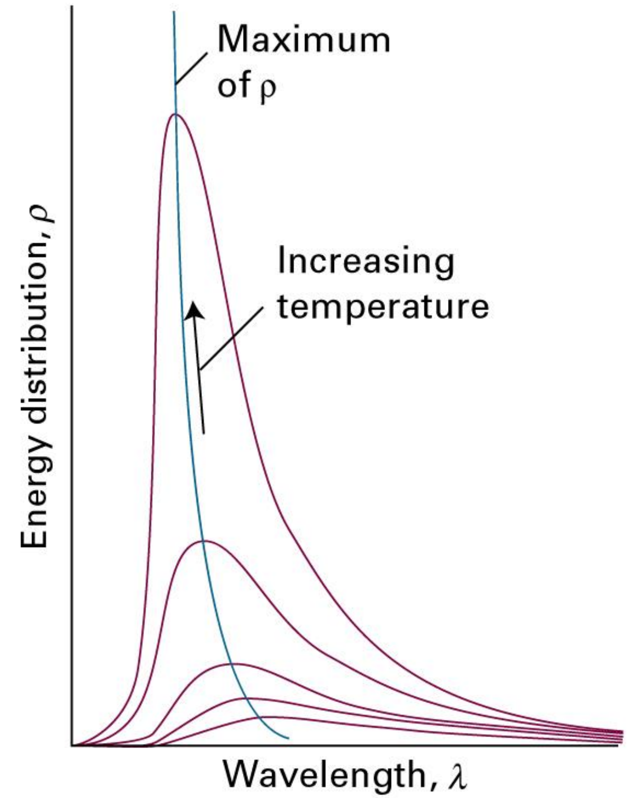
Smoldering coal

Electric heating element

Lightbulb filament



Spectrum →



Black-body radiation
(內部空心之熱金屬球體)

由以上實驗結果，做波長$_{max}$位置與溫度間的關係分析，得Wien displacement law：

$$T\lambda_{max} = \tfrac{1}{5} C_2, \qquad \text{where } C_2 = 1.44\ cmK$$ (稱2nd radiation const.)

由C_2值可以預測在1000K 時， $\lambda_{max} \approx 2900$ nm

- 另一特徵是：該radiation total energy density，ε (單位體積電磁波能量，E/V) 隨溫度升高而成一個關係存在，稱Stefan-Boltzman law. $\varepsilon = aT^4$
- 另外一種表示稱為 excitance $M = \sigma T^4, \quad \sigma = 5.67 \times 10^{-8}\, Wm^{-2}K^{-4}$
- *M*為單位面積所發射出來的能量(the power emitted by a region of surface divided by the area of surface)亦即為亮度(brightness of the emission)其亦與ε成比例；σ 稱Stefan-Boltzman const。由該關係可以預測1 cm^2 的black-body at 1000 K可以發射出大約6W的電磁波。

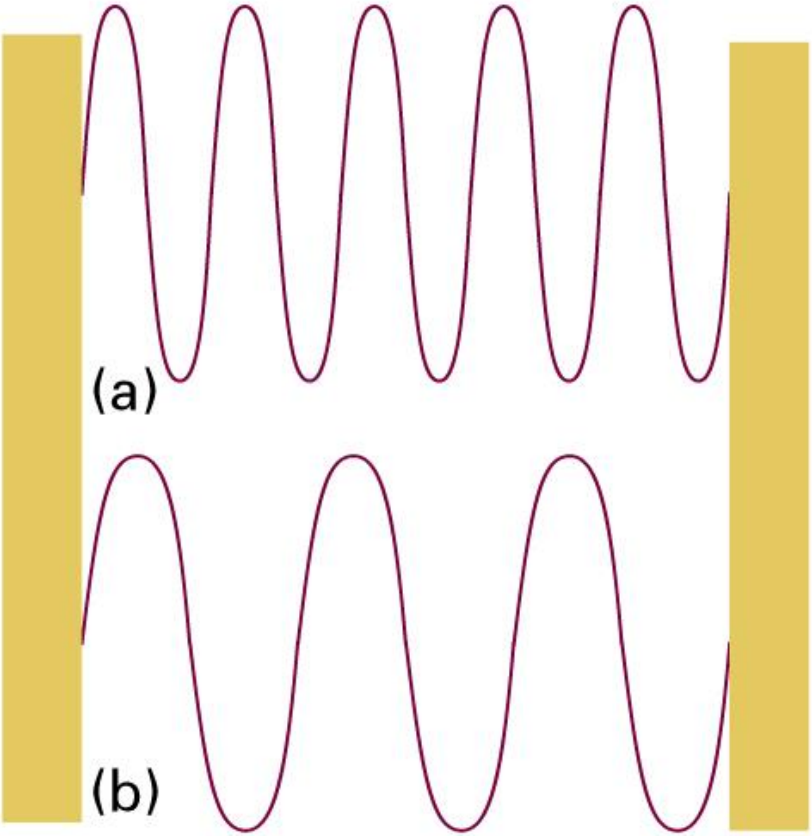
以古典力學觀點要來解釋black-body radiation所分析的結果

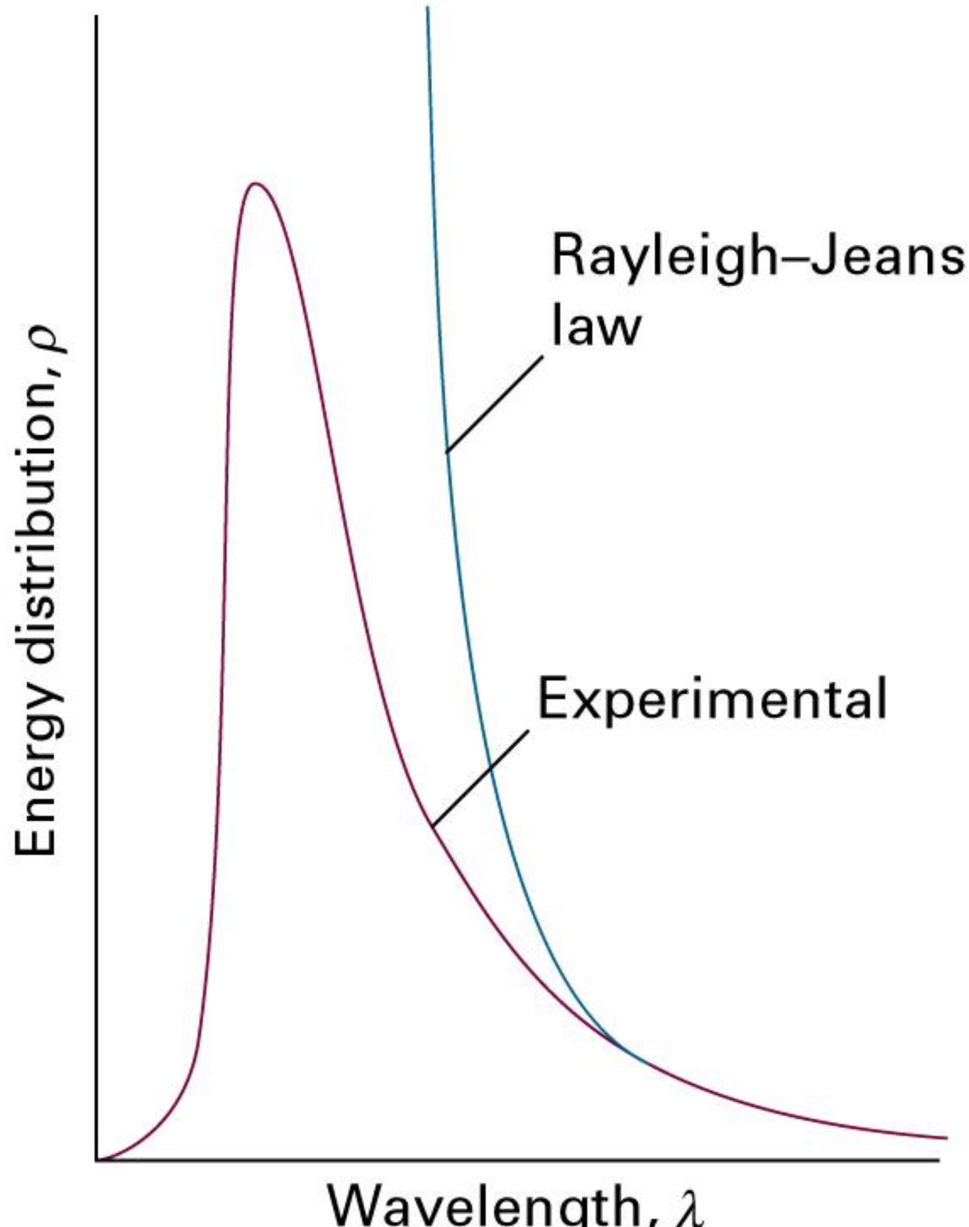
- Rayleigh假設該黑體是由可產生各種可能頻率的振動子(oscillators)的集合，當某一頻率的振動子被激發時，就產生該頻率，由equipartition理論可以推導出 Rayleigh-Jeans law：$d\varepsilon = \rho d\lambda$

$$\rho = \frac{8\pi kT}{\lambda^4}$$

k：Boltzmann const
某波長的energy density

該關係只能解釋實驗結果中長波長的部份，對短波長的部份則失敗，因為其預測 $\rho \to \infty \quad at \quad \lambda \to 0$ ，物理上給其一個名詞叫UV catastrophe，說明即使是冷物體亦會發光，此與事實不符。


(a)
(b)


Rayleigh–Jeans law
Experimental
Energy distribution, ρ
Wavelength, λ

The Planck distribution

- 德國科學家Max Planck發現可以解釋黑體輻射的實驗結果，如果他假設：the energy of each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily.
- 這種假設下，推論如下結果…

令

$\mathrm{E} = nh\nu,\quad n = 0,1,2,\ldots$ (表示振動子能量僅具discrete values)

$$d\varepsilon = \rho d\lambda\ ,\ \rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right)$$

該式子與實驗結果的分布圖完全吻合，其中 $h = 6.62608 \times 10^{-34} Js$

at $\lambda \to 0,\ \rho \to 0,\ \because e^{hc/\lambda kT} \to \infty$

At $\lambda \to \infty,\ e^{hc/\lambda kT} - 1 = \left(1 + \frac{hc}{\lambda kT} + \cdots\right) - 1 \approx \frac{hc}{\lambda kT},\quad \therefore \rho \approx \frac{8\pi kT}{\lambda^4}$

(與Rayleigh-Jeans同)

Planck distribution 亦可解釋Stefan-Boltzman and Wien Laws

$$\varepsilon = \int_0^\infty \rho d\lambda = aT^4 \quad \therefore a = \frac{4\sigma}{c},\ \sigma = \frac{2\pi^5 k^4}{15C^2h^3} = 5.6704 \times 10^{-8}\,\mathrm{Wm^{-2}K^{-4}}$$ (與前同)

同理 Wien Law， $T\lambda_{max} = \frac{1}{5}C_2$，由at λ_{max}, $\frac{d\rho}{d\lambda} = 0$ 代入

得 $T\lambda_{max} = \frac{hc}{5k},\quad \therefore C_2 = \frac{hc}{k} = 1.439\,\mathrm{cmK},$ 與前Wien 分析結果同.

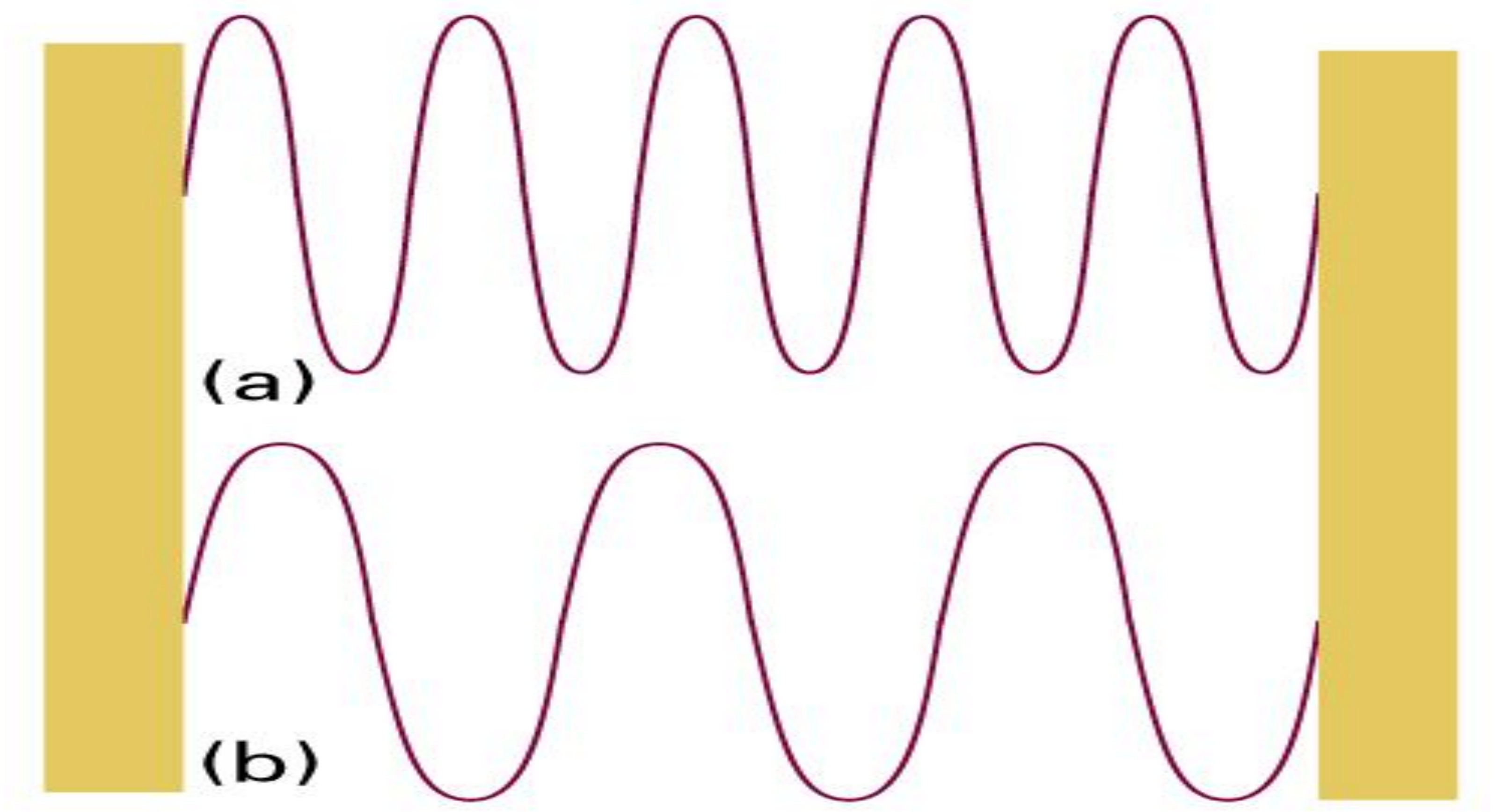
Derivation of Rayleigh –Jeans formula for black-body radiation

設有一邊長為L之正立方黑體,其內壁為金屬,而在其壁上之電子因加速運動會產生電磁波,在此封閉之黑體內,來回振蕩而不互相干涉消滅的條件是:內須以駐波的形式存在。又因金屬表面的電場必須為零,所以其符合boundary condition, that is, at x=0 or L, ε=0

Standing wave,

$$2L = n\lambda, \Rightarrow n = \frac{2L}{\lambda}, \Rightarrow n = 1,2,3,\ldots\ldots$$

Standing waves



http://www.youtube.com/watch?v=X8qZO6g_X5Q

其中每一allowed λ,對應著不同的 n,代表電磁波的能態(state)。所以有多少不同的 n 值,就代表有多少種存在的能態,因此我們可以在此黑體空間中對 n 作積分,

$$n_x = \frac{2L}{\lambda_x}, n_y = \frac{2L}{\lambda_y}, n_z = \frac{2L}{\lambda_z}$$

For a vector N(λ) in 3-dimension,以 n_x, n_y, n_z,為axises, 其與三軸的夾角分別為α, β, γ, then

$$n_x = \frac{2L}{\lambda}\cos\alpha, n_y = \frac{2L}{\lambda}\cos\beta, n_z = \frac{2L}{\lambda}\cos\gamma$$

and

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

N(λ)代表空間中任意方向之state的數量

$$n_x{}^2 + n_y{}^2 + n_z{}^2 = \frac{4L^2}{\lambda^2}$$

$$N(\lambda) = \sqrt{n_x{}^2 + n_y{}^2 + n_z{}^2} = \frac{2L}{\lambda}$$

若將N(λ)設為空間中的向量,並令為R,則在R→R+dR的球殼體積為

$$dV(R) = 4\pi R^2 dR$$

然而因為n_x,n_y,n_z皆為正整數,所以只考慮該體積的1/8為符合實際討論的條件

$$\therefore dV(R) = \frac{1}{8}(4\pi R^2 dR) = \frac{\pi}{2} R^2 dR, R = \frac{2L}{\lambda}$$

$$c = \lambda\upsilon, \therefore R(\upsilon) = \frac{2L\upsilon}{c}, dR(\upsilon) = \frac{2L}{c} d\upsilon$$

$$dV(R) = \frac{\pi}{2}(\frac{2L\upsilon}{c})^2 \frac{2L}{c} d\upsilon = \frac{\pi}{2}(\frac{2L}{c})^3 \upsilon^2 d\upsilon = N(\upsilon)d\upsilon$$

其中 dV(R)代表殼層厚度(dv)中 各種不同波長或state 的總數N(v)dv

然而考慮電磁波有兩個偏極方向所以上式應再乘上2,

$$N(\upsilon)d\upsilon = 2\times\frac{\pi}{2}(\frac{2L}{c})^3\upsilon^2 d\upsilon$$

除以體積L^3,則代表空腔中的 能態 in $\upsilon \to \upsilon + d\upsilon$

單位体積中的光子總數為

$$\eta = \frac{8\pi\upsilon^2}{c^3}d\upsilon = \text{density of state}$$

依據 equipartition 定律,每個 光子的平均能量為 kT,(因為在空腔中來回振蕩多次,光子能量與器壁達成熱平衡)

光子能量為E的機率與 $e^{-E/kT}$ 成正比(Boltzmann distribution)

所以每個光子的平均能量為

$$\frac{\int e^{-E/kT}EdE}{\int e^{-E/kT}dE} = kT$$

所以可以量測的energy flux

(單位体積單位時間在該頻率範圍的能量 $\rho(\upsilon)d\upsilon$)

$$\rho(\upsilon)d\upsilon = \eta \times kT = (\frac{8\pi\upsilon^2}{c^3}) \times kTd\upsilon$$

$$= -\frac{8\pi kT}{\lambda^2 c}\frac{c}{\lambda^2}d\lambda = -\frac{8\pi kT}{\lambda^4}d\lambda = -\rho(\lambda)d\lambda$$

$$\therefore \rho(\lambda)d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda$$

得證Rayleigh Jeans blackbody radiation formula

Planck's formula of black-body radiation

- Planck 提出能量是不連續的大膽假設,即ε=nhv, n=0, 1, 2, 3,.....亦即每個光子的能量只存在 hv, 2hv, 3hv,..
- 依據此假設,計算每個光子的平均能量:從積分變成summation

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} \varepsilon\, p(\varepsilon)}{\sum_{n=0}^{\infty} p(\varepsilon)}$$

P(ε)代表能量是ε時的機率函數,依據Boltzmann distribution

$$p(\varepsilon) = e^{-\varepsilon/kT} = e^{-nh\nu/kT}$$

代入

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} \varepsilon\, p(\varepsilon)}{\sum_{n=0}^{\infty} p(\varepsilon)} = \frac{\sum_{n=0}^{\infty} nh\nu e^{\frac{-nh\nu}{kT}}}{\sum_{n=0}^{\infty} e^{\frac{-nh\nu}{kT}}} = \frac{kT\sum_{n=0}^{\infty} n\alpha e^{-n\alpha}}{\sum_{n=0}^{\infty} e^{-n\alpha}}$$

$$\alpha = \frac{h\nu}{kT}$$

then

$$\because d\ln x = \frac{1}{x}dx,\ \therefore d\ln\sum_{n=0}^{\infty}e^{-n\alpha} = \frac{1}{\sum_{n=0}^{\infty}e^{-n\alpha}}d\sum_{n=0}^{\infty}e^{-n\alpha}$$

$$= \frac{\sum_{n=0}^{\infty}de^{-n\alpha}}{\sum_{n=0}^{\infty}e^{-n\alpha}} = \frac{\sum_{n=0}^{\infty}-ne^{-n\alpha}d\alpha}{\sum_{n=0}^{\infty}e^{-n\alpha}}$$

$$\therefore \frac{d}{d\alpha}\ln\sum_{n=0}^{\infty}e^{-n\alpha} = \frac{\sum_{n=0}^{\infty}-ne^{-n\alpha}}{\sum_{n=0}^{\infty}e^{-n\alpha}}$$

$$\therefore -h\nu\frac{d}{d\alpha}\ln\sum_{n=0}^{\infty}e^{-n\alpha} = \frac{\sum_{n=0}^{\infty}nh\nu e^{-n\alpha}}{\sum_{n=0}^{\infty}e^{-n\alpha}} = \bar{\varepsilon} \quad (\alpha = \frac{h\nu}{kT})$$

$$\sum_{n=0}^{\infty} e^{-n\alpha} = (1-e^{-\alpha})^{-1}$$

$$\because \sum_{n=0}^{\infty} e^{-n\alpha} = (e^{-\alpha})^0 + (e^{-\alpha})^1 + (e^{-\alpha})^2 + (e^{-\alpha})^3 + ...$$

$$= 1 + x + x^2 + x^3 + ... = \frac{1}{1-x} \quad (x<1)$$

$$\bar{\varepsilon} = -h\nu \frac{d}{d\alpha} \ln \sum_{n=0}^{\infty} e^{-n\alpha} = -h\nu \frac{d}{d\alpha} \ln(1-e^{-\alpha})^{-1}$$

$$= \frac{-h\nu}{(1-e^{-\alpha})^{-1}} d(1-e^{-\alpha})^{-1} = \frac{-h\nu}{(1-e^{-\alpha})^{-1}} (-1)(1-e^{-\alpha})^{-2} e^{-\alpha}$$

$$= \frac{h\nu}{(1-e^{-\alpha})} e^{-\alpha} = \frac{h\nu}{(e^{\alpha}-1)} = \frac{h\nu}{(e^{\frac{h\nu}{kT}}-1)}$$

將所得的光子平均能量乘上 頻率處在v→v+dv的光子數目即為實驗所能測量的單位時間單位体積的energy flux, ρ(v)d v ,

$$\rho(\nu)d\nu = (\frac{8\pi\nu^2}{c^3})(\frac{h\nu}{e^{h\nu/kT}-1})d\nu$$

$$or,$$

$$\rho(\lambda)d\lambda = -\rho(\nu)d\nu = (\frac{-8\pi hc}{\lambda^3}\times\frac{-1}{\lambda^2})(\frac{1}{e^{hc/\lambda kT}-1})d\lambda$$

$$= \frac{8\pi hc}{\lambda^5}(\frac{1}{e^{hc/\lambda kT}-1})d\lambda$$

$$(\text{where}, \nu = c/\lambda,\ d\nu = -\frac{c}{\lambda^2}d\lambda)$$

由所算出的Planck function,可以對λ微分設等於零求出$\lambda_{max}T$ 的表示法,對照實驗值可求出Planck constant $h = 6.626*10^{-34}$ (J*s)。當時的科學家認為Planck's assumption (quantization) was considered as impressive numerical work, 很多還是認為古典力學理論還是正確的,只是某些計算可能還須做一些處理,就會得到相同結果,而不需要去做 quantization assumption!

(b) Photo-electric Effect

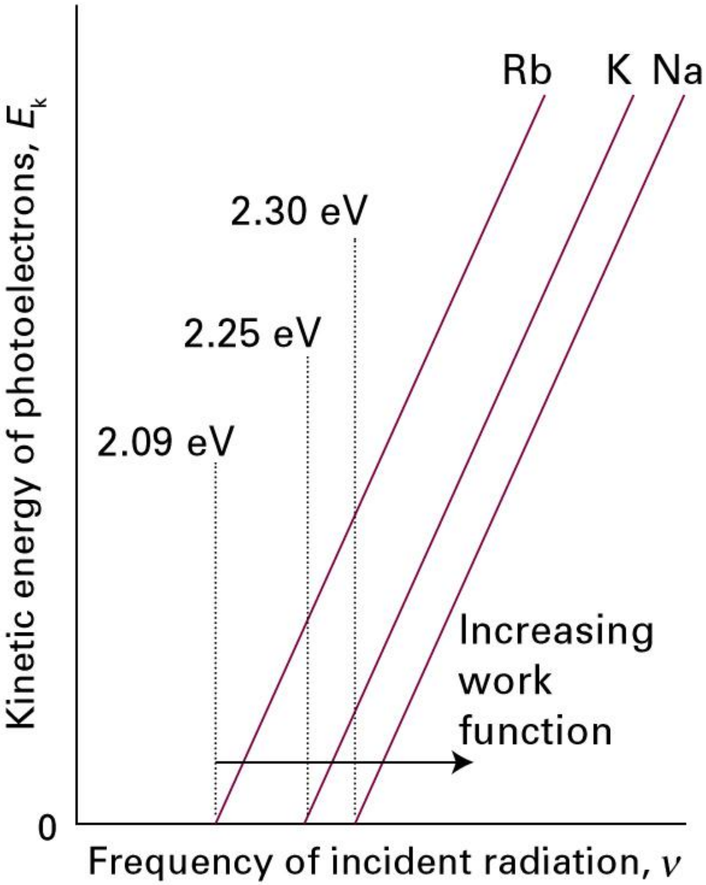
Force on electron of metal is suppose to be proportional to the strength of electromagnetic field of light,

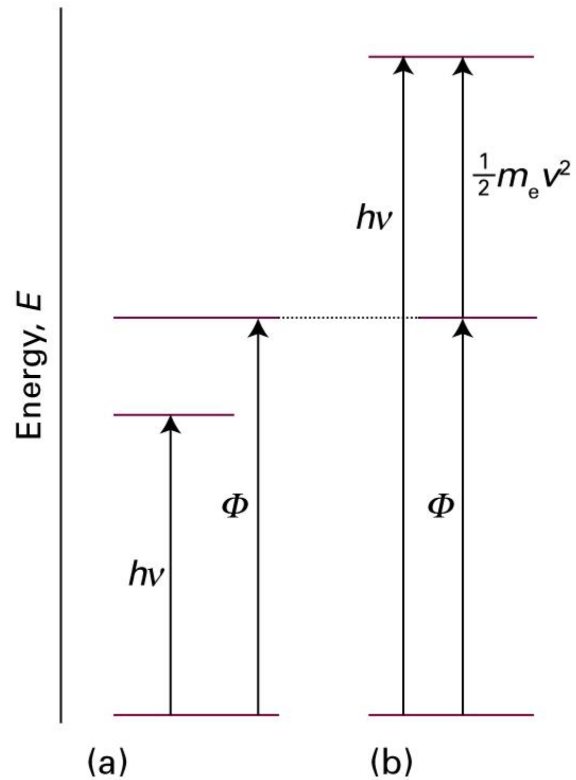
$$\vec{F} = e\vec{E} + e\vec{v}_e \times \vec{B}$$

However, the result from Einstein experiment he found that

1. Kinetic energy of electron 與光照的強度無關
2. 有threshold effect (no ejection for light frequency $v < v_0$)
3. 光電子產生無任何時間延遲

Eienstein 取用Planck假設,E=hv,並將光子視為粒子就可以很合理的來解釋實驗結果,並由實驗數據推算出 $h=6.625\times10^{-34}$Js



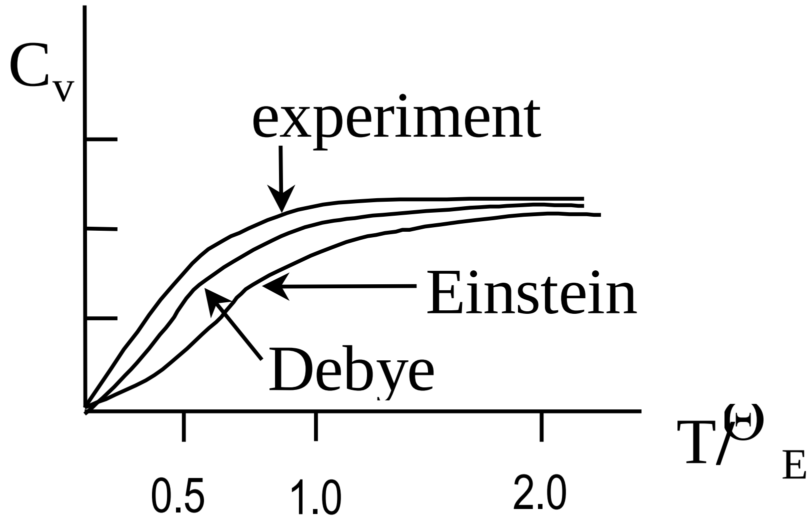


(c) Heat Capacities

- Dulong and Petit 做了很多單原子固體heat capacity ($C_V = \left(\frac{\partial U}{\partial T}\right)_V$)的測量，發現其值接近於6 cal/mol•K or 25 J/mol•K (與原子種類無關)。該結果可以用古典理論來解釋：因為每一原子受熱在固體結構中振動能每一方向為1RT(由equipartition theory)，三個方向為3RT ……

$\therefore\ C_V = 3R \approx 6\,cal/mol \bullet K$ 沒有問題；但後來發現在低溫時，C_V隨溫度下降而減少，當 $T \to 0, C_V \to 0$

實驗結果如下圖



古典理論是假設每一個原子振動頻率是連續的；因此對低溫時C_v < 3R 無法解釋。

Einstein引用Planck的discrete energy value的假設，認為每一原子皆具單一振動頻率(v)，當溫度高時，大多數原子皆可被激發而振動，所以接近3R, 但低溫時，多數原子無法被激發振動，且所可能具有的能量為

$$E = nh\nu, \quad n = 0, 1, 2, \ldots$$

依此推導出 $U_m = \frac{3N_A h\nu}{e^{h\nu/kT} - 1}$， 對T微分

得

$$C_{V,m} = 3Rf^2 , \qquad \underline{f = \frac{\Theta_E}{T}\left(\frac{e^{\Theta_E/2T}}{e^{\Theta_E/T} - 1}\right)}$$ 稱為Einstein formula

$\Theta_E = h\nu / k$ 稱為Einstein temperature 與 ν 成正比關係。高頻表示高溫。

當溫度很高時，

$$T >> \Theta_E , \quad f = \frac{\Theta_E}{T}\left[\frac{1 + \frac{\Theta_E}{2T} + \cdots}{\left(1 + \frac{\Theta_E}{T} + \cdots\right) - 1}\right] \approx 1$$

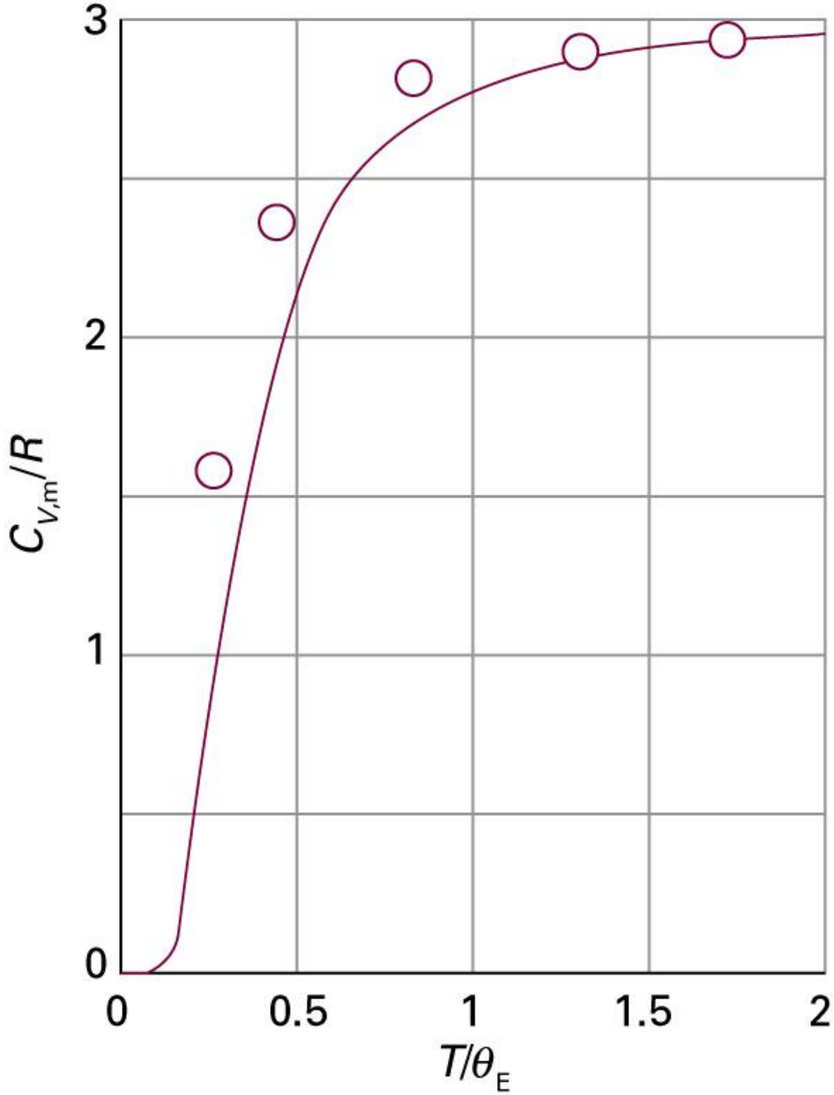
$\therefore$ at high T， $C_{\nu,m} = 3R$

當溫度很低時

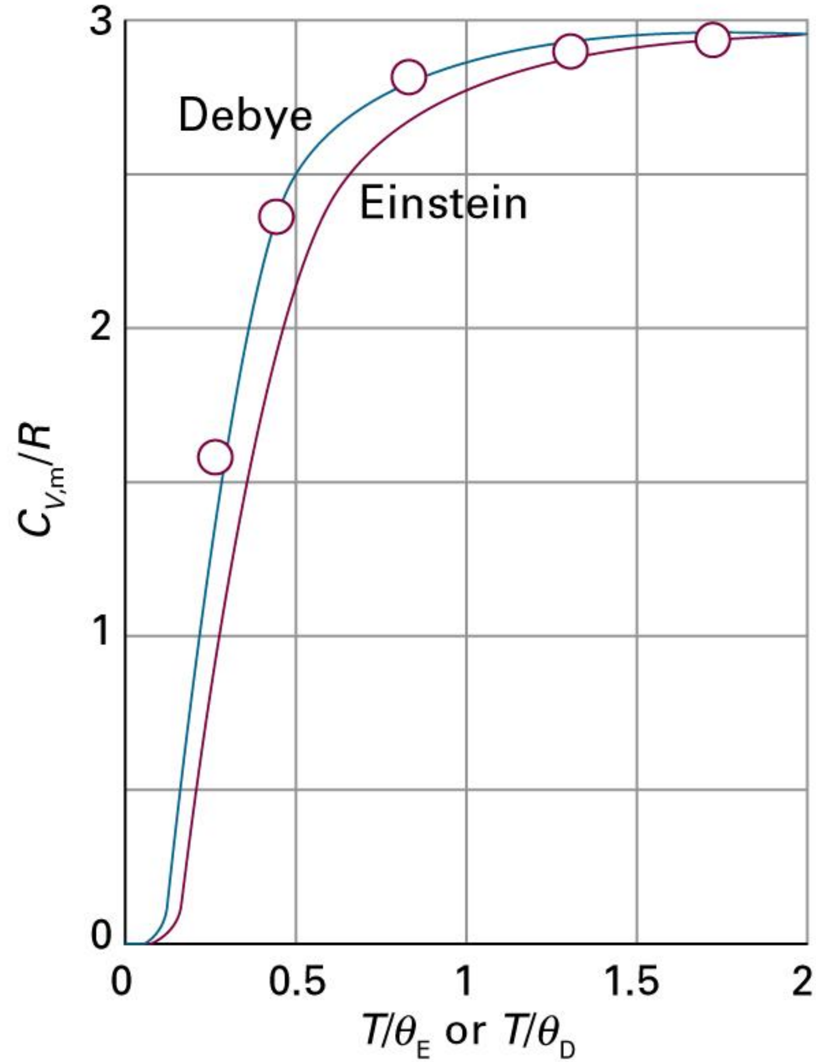
$$T << \Theta_E , \quad f \approx \frac{\Theta_E}{T}\left(\frac{e^{\Theta_E/2T}}{e^{\Theta_E/T}}\right) = \frac{\Theta_E}{T} \cdot e^{-\Theta_E/2T}$$

$\therefore$ 當

$$T \rightarrow 0, \; f \rightarrow 0, \quad C_{\nu,m} \rightarrow 0$$



3
2
1
0
0
0.5
1
1.5
2
$C_{V,m}/R$
T/θ_E



3
2
1
0
0
0.5
1
1.5
2
Debye
Einstein
$C_{V,m}/R$
T/θ_E or T/θ_D

Einstein 所預測結果與實驗值曲線很類似，但其值皆較低，主要原因是Einstein 假設晶體中的每一原子皆以相同頻率振動，但事實上 they oscillate over a range of frequencies from zero up to a maximum value, ν_D， 如果將所有可能存在的頻率考慮進去，則得Debye formula:

$$C_{\mathrm{V,m}} = 3Rf \ , \ \ f = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \ \ , \ \Theta_D = \frac{h\nu_D}{k} \ \ ,$$

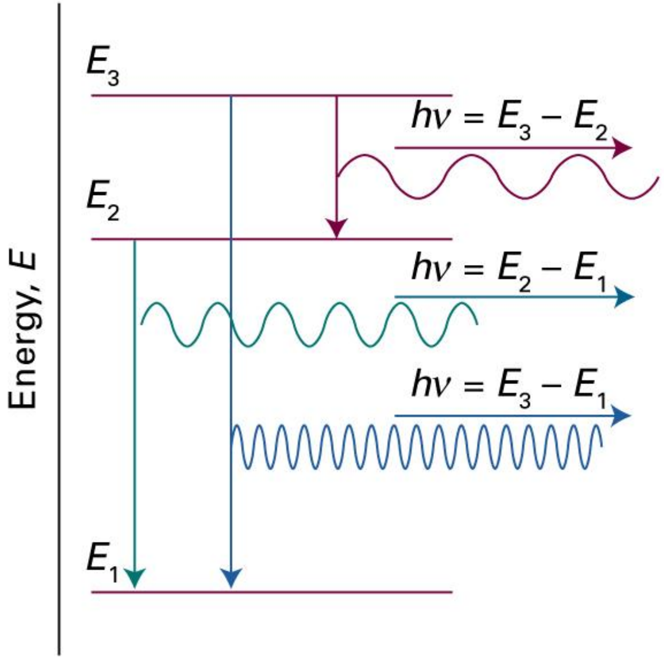
.

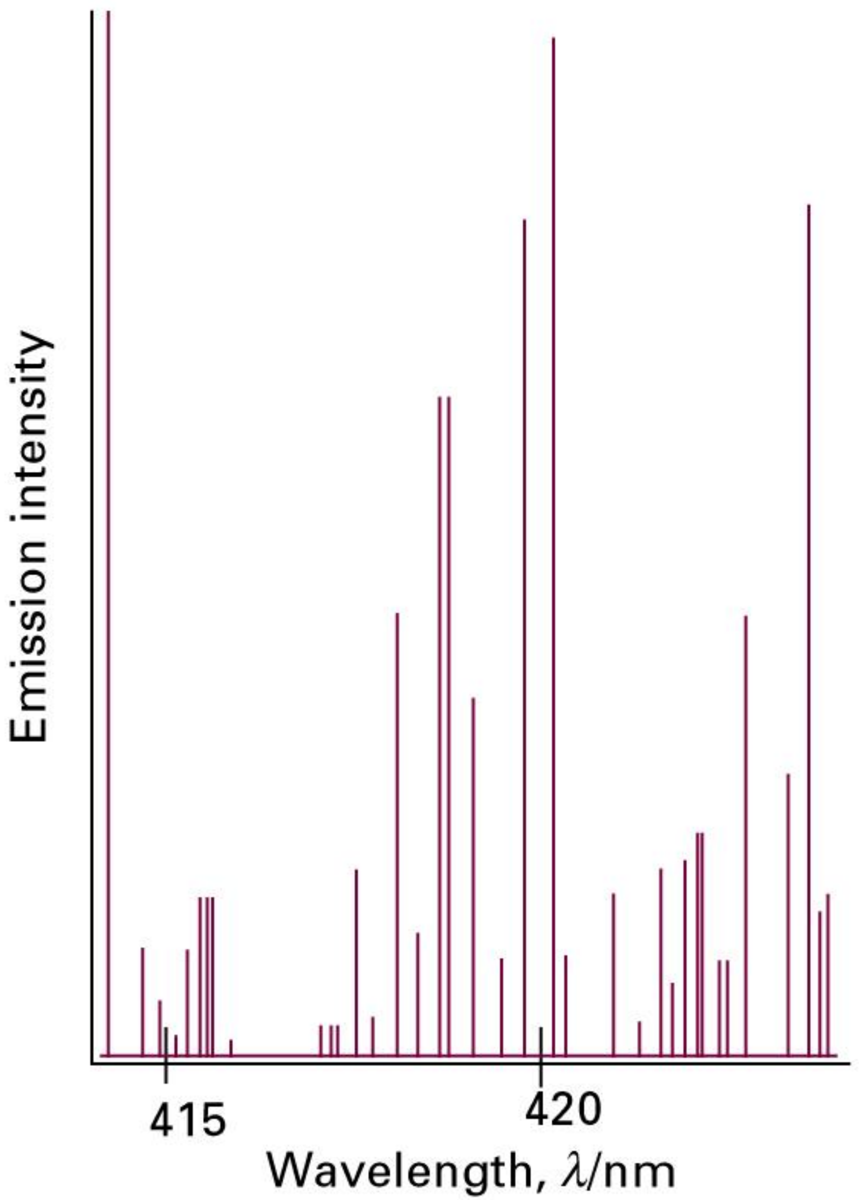
稱Debye temperature

其結果與實驗值就很吻合了，說明了 thermal properties of solids 在低溫亦須引用量子化的觀念才是恰當的。

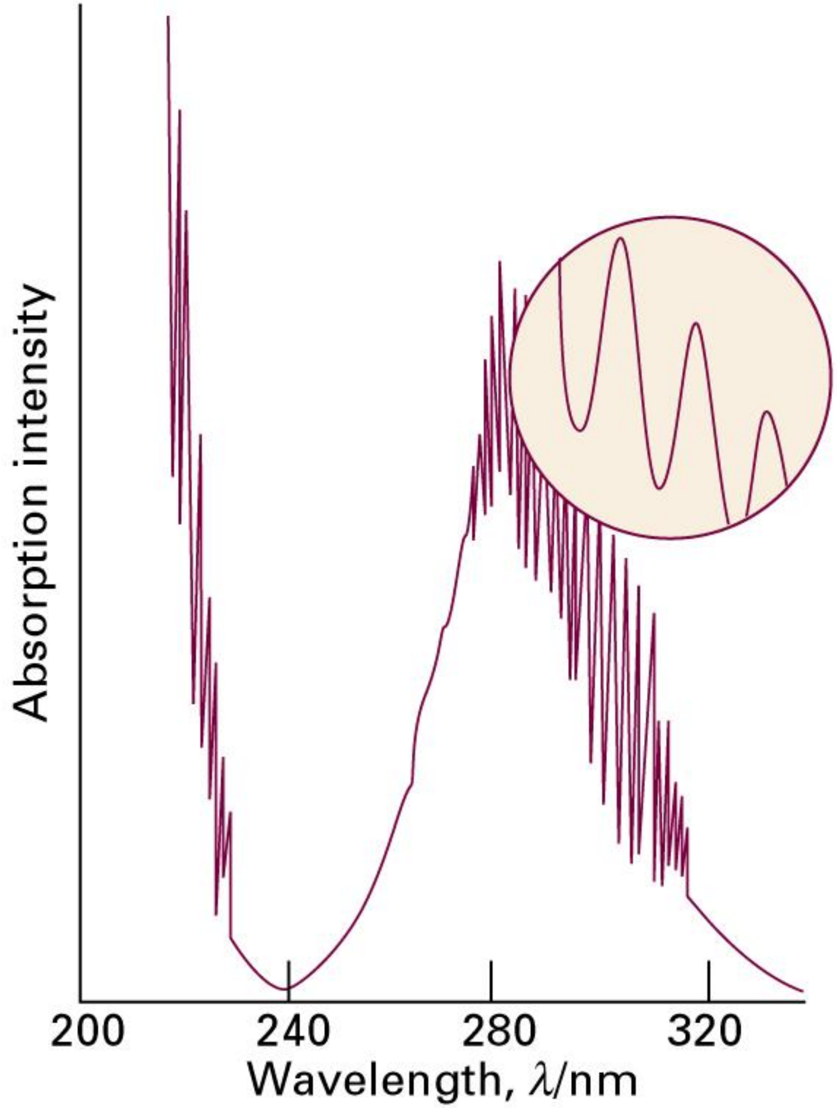
(d) Atomic and molecular spectra

- The most compelling evidence for the quantization of energy comes from the observation of the frequencies of radiation absorbed or emitted by atoms and molecules.





Emission intensity
415
420
Wavelength, λ/nm



Absorption intensity
200
240
280
320
Wavelength, λ/nm

Figure 7.8

The line spectra of several elements.

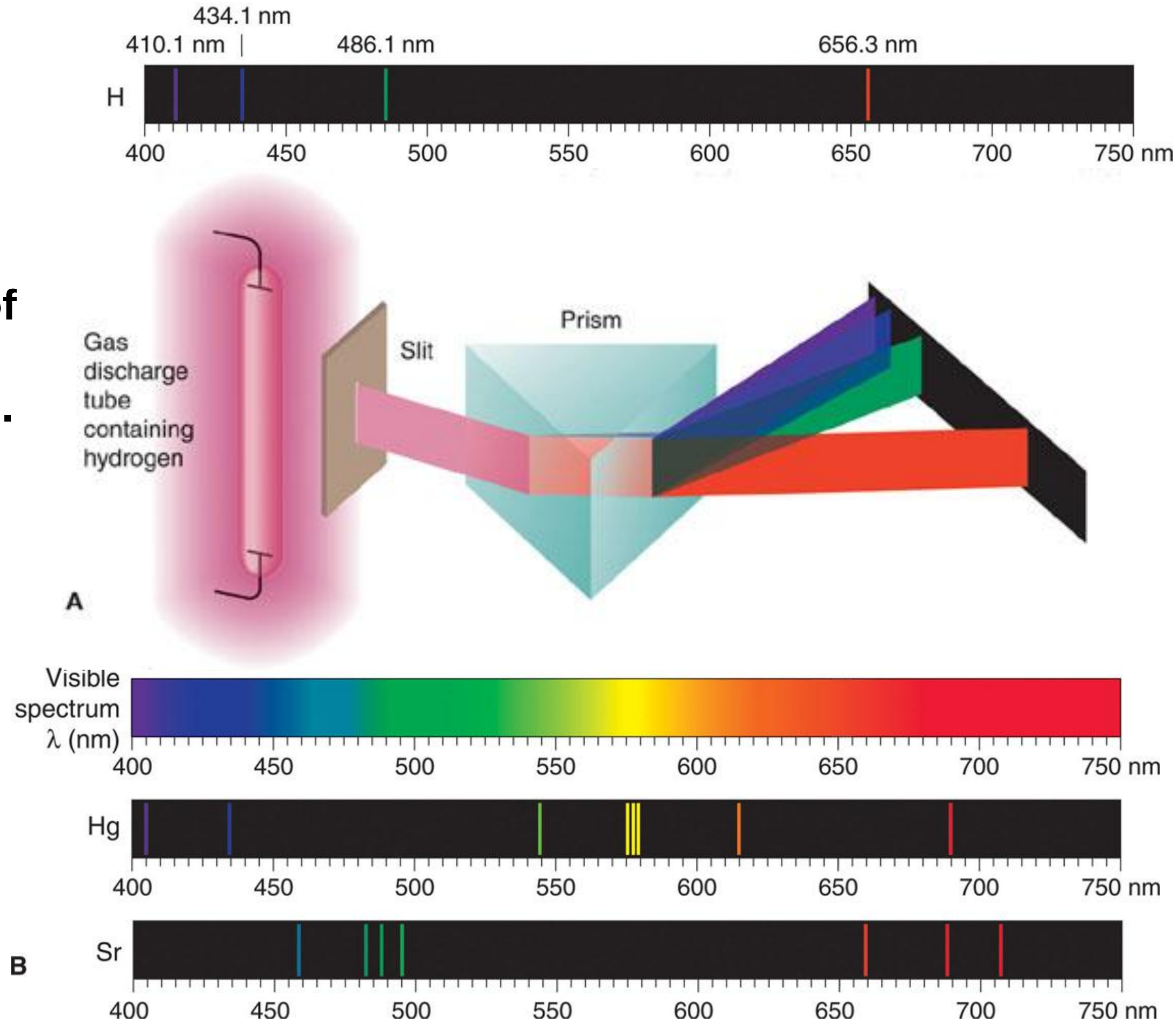
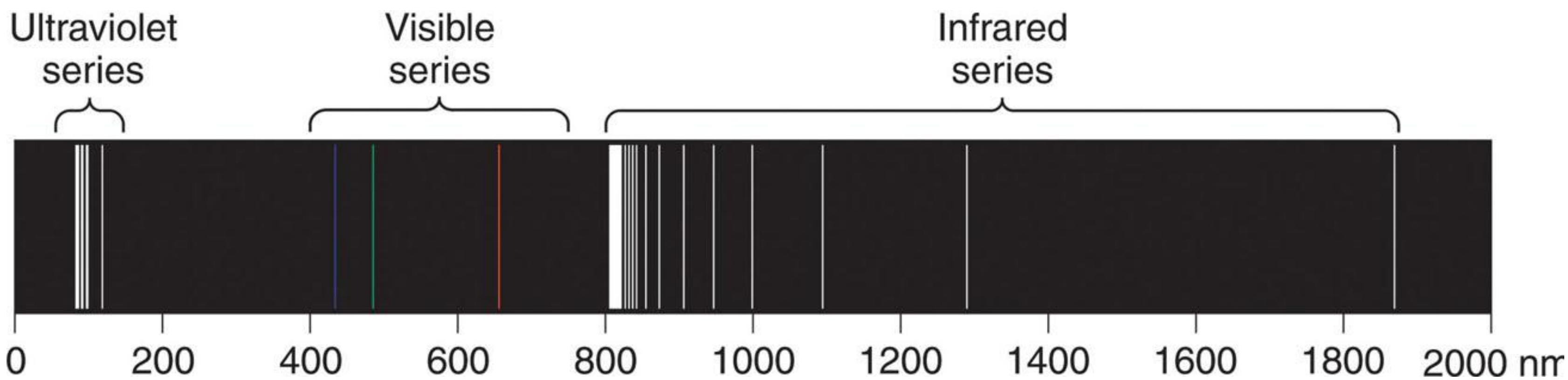


Figure 7.9 **Three series of spectral lines of atomic hydrogen.**



Rydberg equation $$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

R is the Rydberg constant = 1.096776x10^{7} m^{-1}

for the visible series, $n_1 = 2$ and $n_2 = 3, 4, 5, ...$

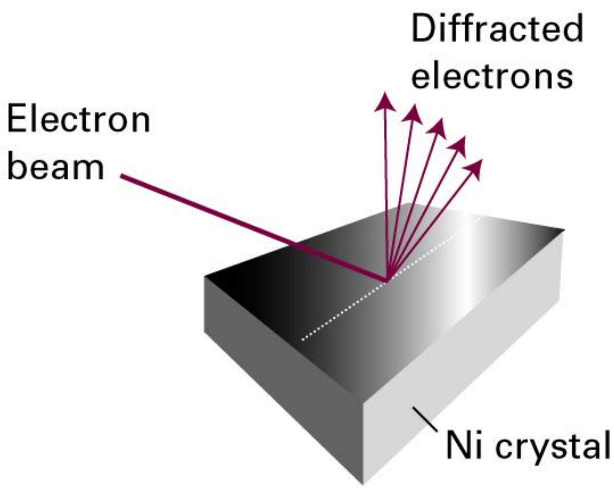
Wave-particle Duality

1.波動性:最大的特色是兩波相遇時會產生 interference(有很明顯的干涉條紋)

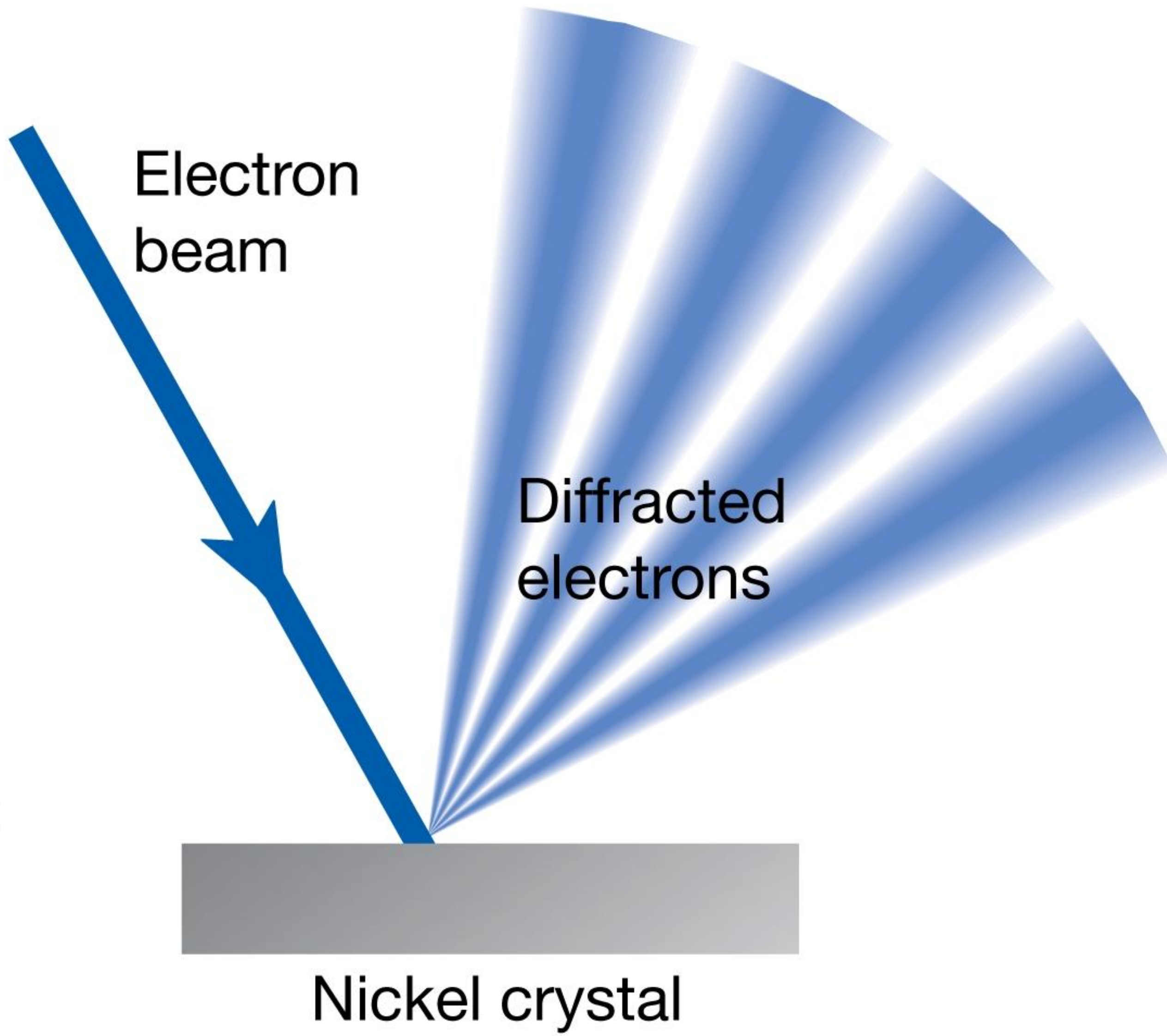
2.粒子性最大特色是具有動量,動能。

J.J Thomson因為發現電子是粒子(求出其質/荷(m/e)比值,而得諾貝爾獎

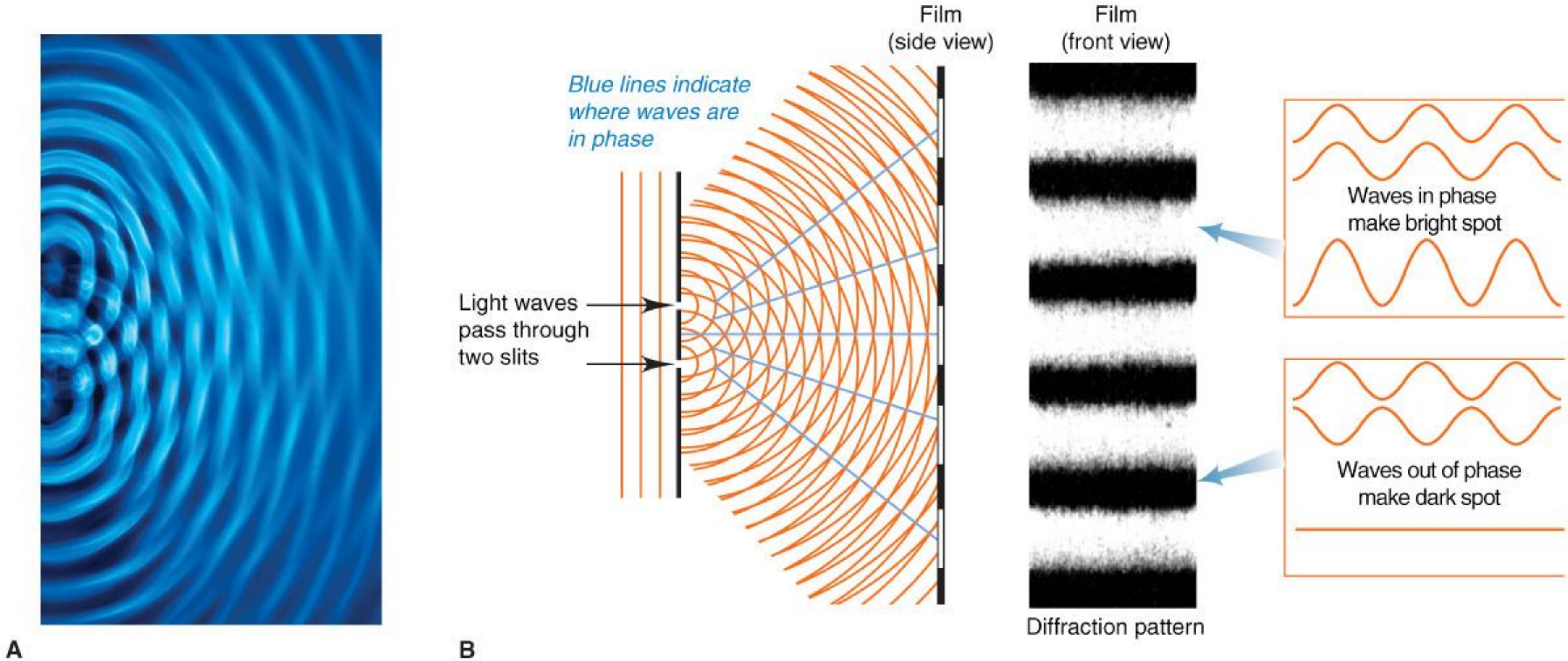
很有意思的是其兒子G.P. Thomson証明電子具波動性(電子經過狹縫孔洞產生干涉條紋)亦得諾貝爾獎



Diffracted
electrons
Electron
beam
Ni crystal



Electron
beam
Diffracted
electrons
Nickel crystal



Film
(side view)
Film
(front view)
Blue lines indicate
where waves are
in phase
Light waves
pass through
two slits
Waves in phase
make bright spot
Waves out of phase
make dark spot
Diffraction pattern
A
B

The dynamics of microscopic system.

- 量子力學接受wave-particle duality of matter，認為粒子並非只走直線，而是像波動般往整個空間分布…
- the wave that in quantum mechanics replaces the classical concept of trajectory is called a wavefN, Ψ(psi).

Quantum Mechanics (量子力學)

- In quantum mechanics, all the dynamic properties of a system are contained in the *wavefunction*, which is obtained by solving the Schrödinger equation.

Why do you need to know this material?

Quantum theory provides the essential foundation for understanding of the properties of electrons in atoms and molecules.

What is the key idea?

All the dynamical properties of a system are contained in the wavefunction, which is obtained by solving the Schrodinger equation.

What do you need to know already?

You need to be aware of the shortcomings of classical physics that drove the development of quantum theory.

The Schrödinger equation.

- 1926年，Austrian physicist , Erwin Schrödinger proposed an equation for finding the wavefɴ of any system. The time-independent Schrödinger equation for a particle of mass (m) moving in one dimension with energy (E) is

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

常簡寫為

$$\hat{\mathrm{H}}\Psi=E\Psi\text{，}\quad \text{其中 } \hat{H}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\quad \text{稱Hamiltonian operator.}$$

若為二度空間的系統 …

$$\Psi = \Psi(x, y)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x, y)$$

- 若為三度空間的系統 …

$$\Psi = \Psi(x, y, z)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

簡寫成 $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

若以polar coordinate (極座標)表示，則

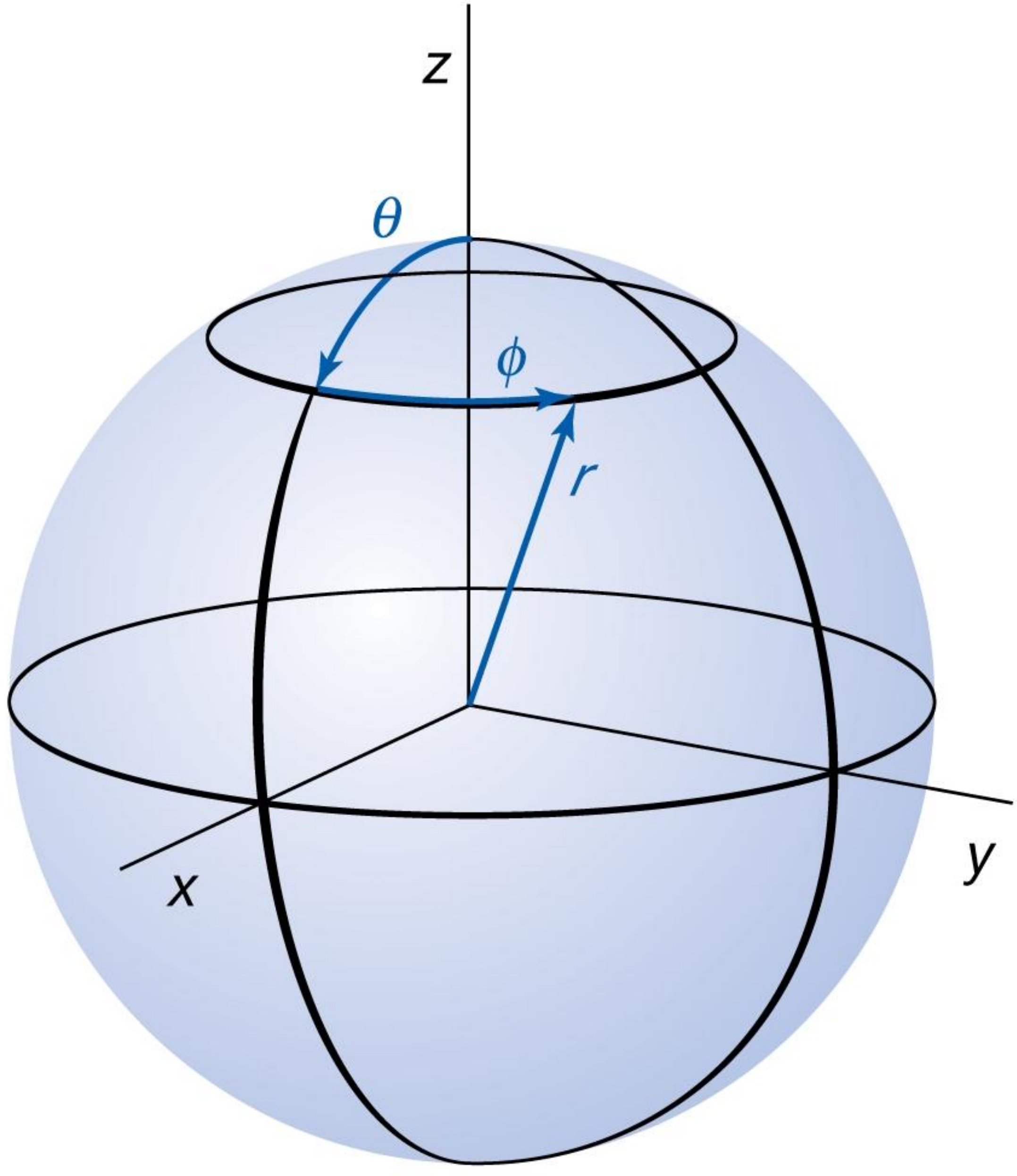
$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

- 而

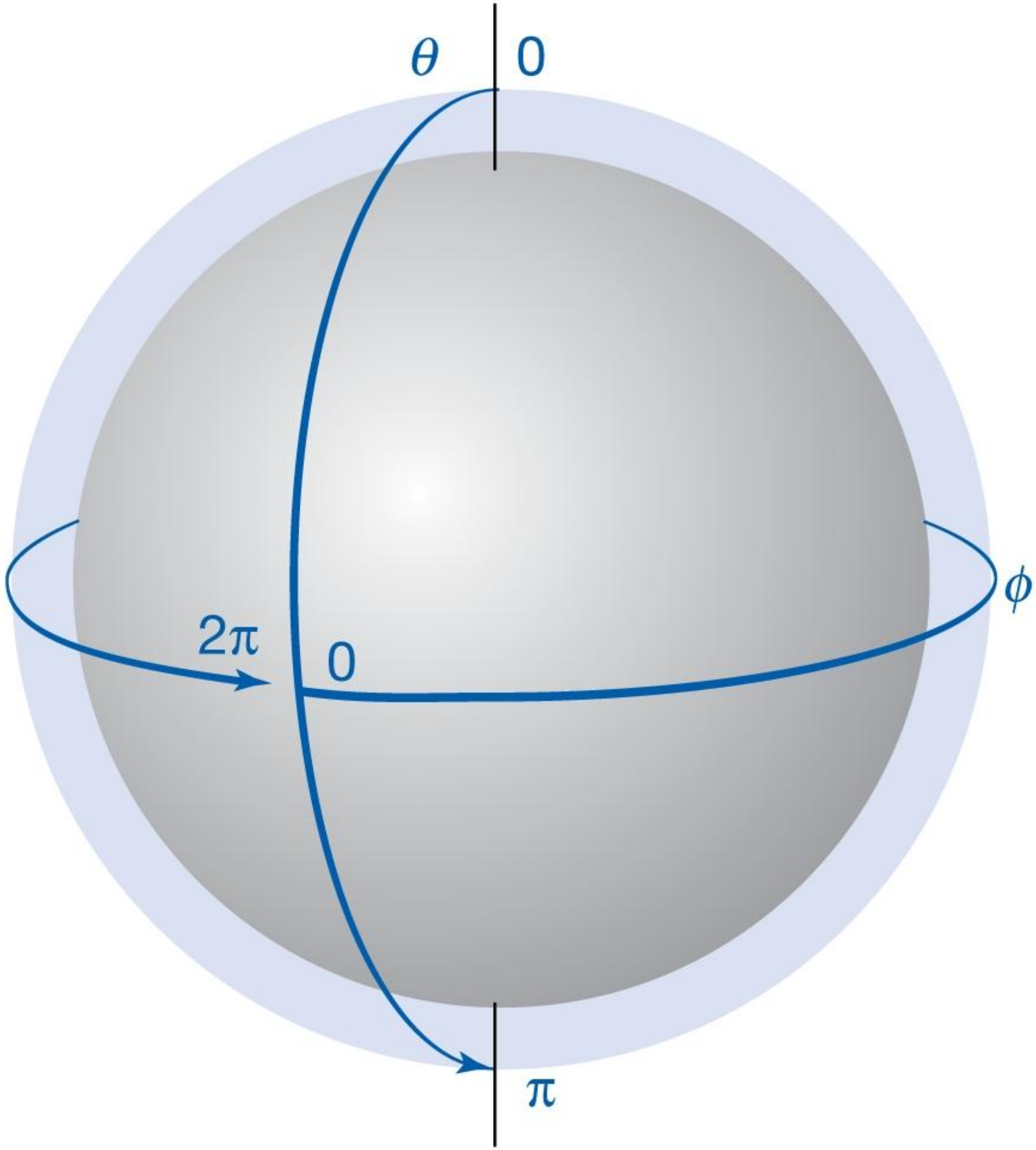
$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \quad \cdots\cdots \quad \text{(angular part)}$$

Time-dependent Schrödinger equation

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$



z
θ
φ
r
x
y



θ
0
ϕ
2π
0
π

Schrödinger equation 實際上是與de Broglie的物質波相吻合的，證明：

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

- 該微分方程的通解 (if V(x) 為const.)：

$$\Psi(x) = e^{ikx} = \cos kx + i\sin kx$$

其中

$$k = \left[\frac{2m(E-V)}{\hbar^2}\right]^{\frac{1}{2}}$$ ，而 $\cos kx$ 與一般 $\cos\frac{2\pi}{\lambda}x$ 相似

$$\therefore k = \frac{2\pi}{\lambda} = \left[\frac{2m(E-V)}{\hbar^2}\right]^{\frac{1}{2}} \quad ,\text{而}\ E - V = E_k \qquad (\text{動能})$$

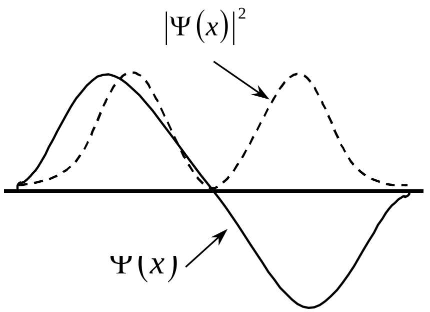
$$\therefore k = \frac{\sqrt{2mE_k}}{\hbar} \quad or \quad E_k = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m},$$

$$\Rightarrow p = \hbar k = \hbar \frac{2\pi}{\lambda} = \frac{h}{\lambda} \cdots \therefore \lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E-V)}}$$

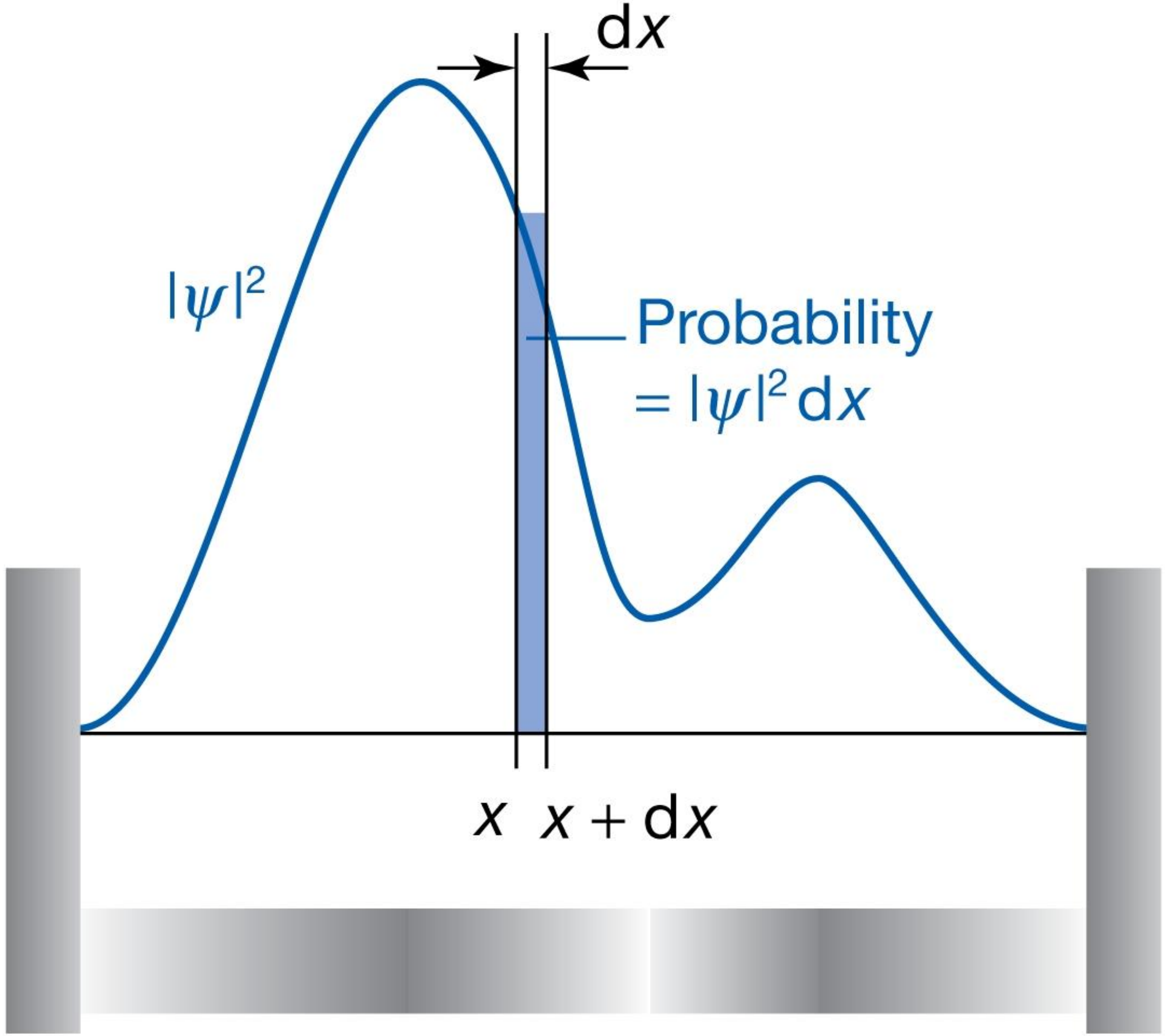
此與de Broglie理論相符

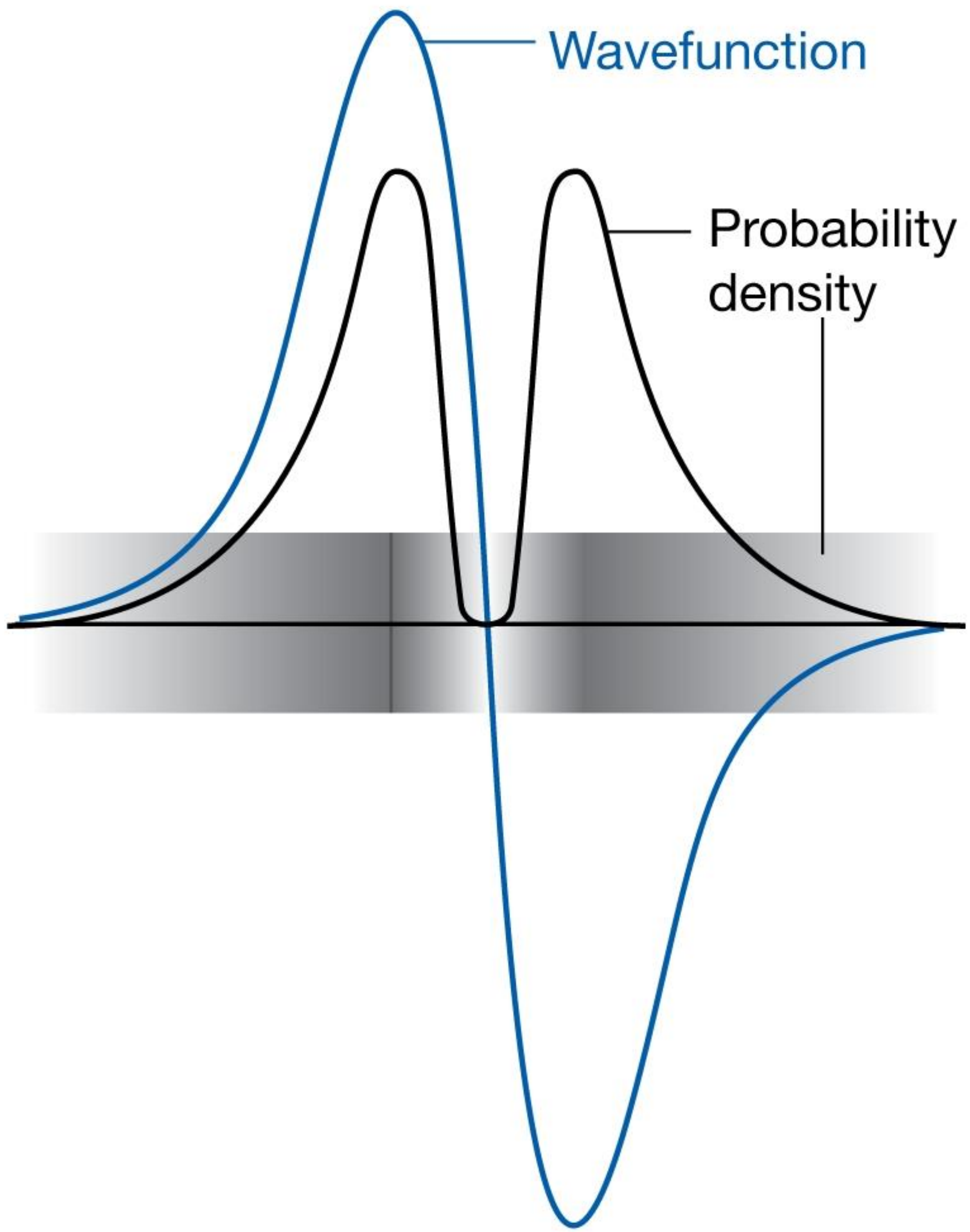
The Born interpretation of the wavefN.

- Max Born 以光波動理論的觀點(電磁波在某區域的振幅的平方是代表電磁波在該區域的強度)來解釋wavefN所代表的意思；因此以wavefN的平方來表示粒子在該區域出現的機率大小，其值(考慮可能是複數)與粒子在該區域出現的機率成正比例。



- ∴.If the wavefN of a particle has the value at some point x , the probability of finding the particle between x and x+dx is proportional to $|\Psi(x)|^2dx$, while
- $|\Psi(x)|^2$ is proportional to probability density.


dx
|ψ|²
Probability
= |ψ|² dx
x x + dx



Wavefunction
Probability density

Normalization

- 波函數，乘上任何的常數N 所得之結果 NΨ仍會是 Schrödinger equation 的解，如此一來可以使我們找到一常數N，使NΨ 的平方 $|N\Psi|^2$ 可normalize而等於Born所解釋的概率(本來是與機率成正比)。∴在整個空間中粒子出現的機率總和為1，因此波函數乘上N之後其平方積分和應為1，即令

$$N^2\int\Psi^*\Psi d\tau = 1，求出N$$

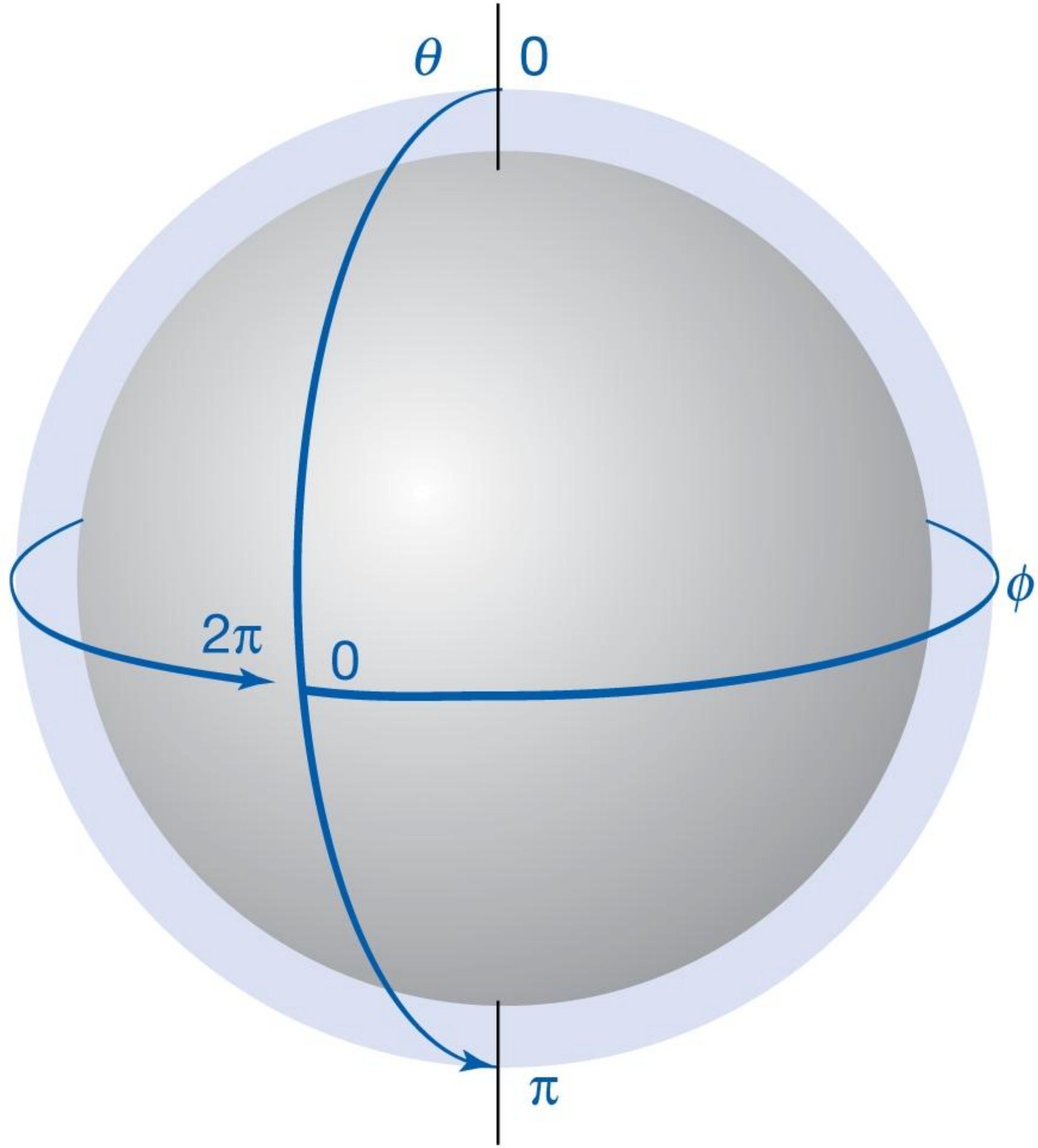
- 所得的波函數，就稱為已被normalized，而N就稱為 normalization factor。

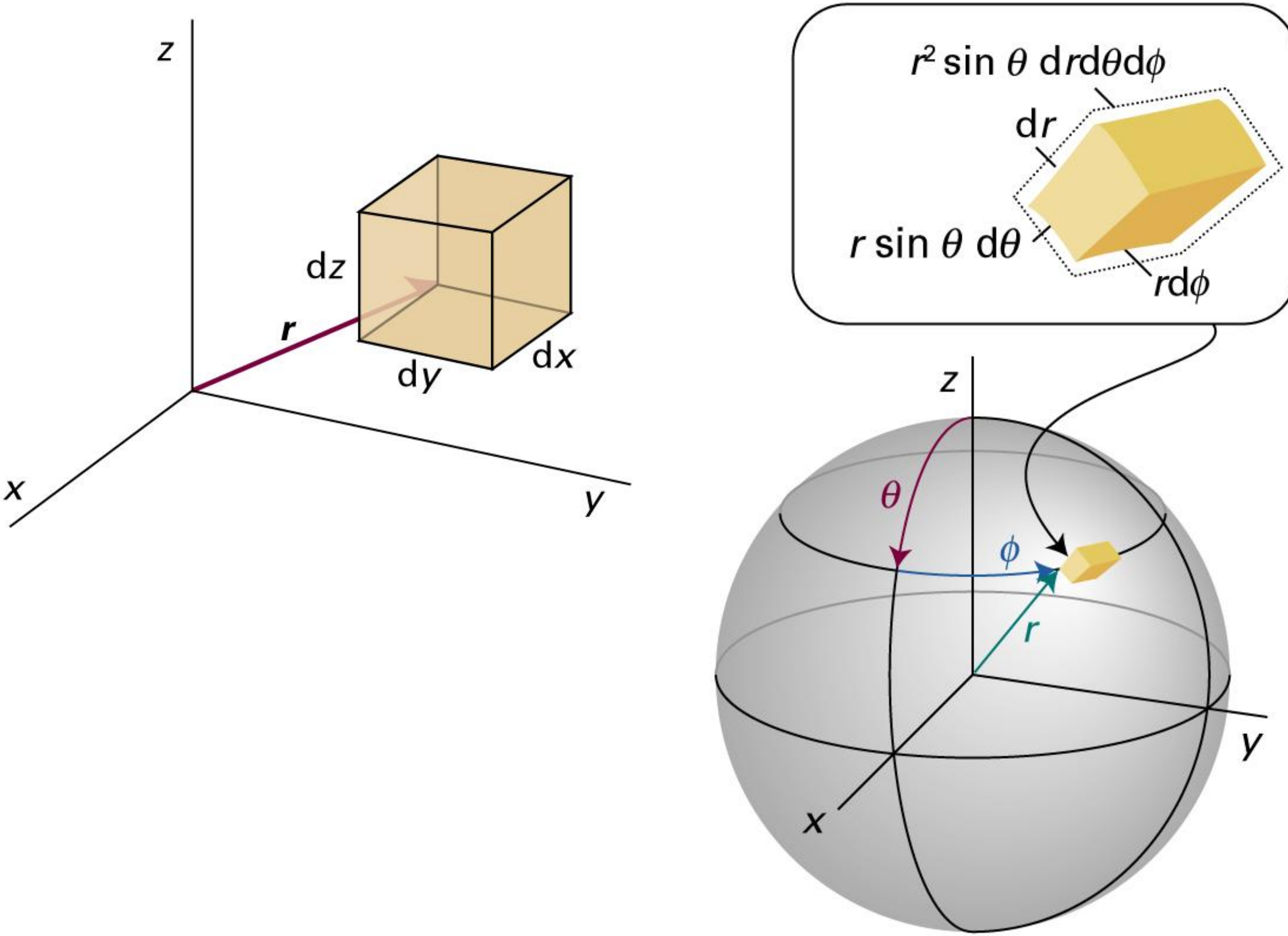
- 若為polar coordinate system , 則

$$d\tau = r^2 \sin\theta\, dr\, d\theta\, d\phi, \quad 其中 \quad \theta = 0 \sim \pi$$

$$\phi = 0 \sim 2\pi$$

$$r = 0 \sim \infty$$


θ
0
ϕ
2π
0
π



z
dz
r
dy
dx
x
y
r² sin θ drdθdϕ
dr
r sin θ dθ
rdϕ
z
θ
ϕ
r
x
y

- 在三度空間中

則以 $\left|\Psi(x,y,z)\right|^2 d\tau$ 表示之，其中 $d\tau = dxdydz$

或是 $\left|\Psi(r)\right|^2 d\tau$ 表示，其中 $d\tau = r^2 \sin\theta\, dr\, d\theta\, d\phi$

e.g. 氫原子電子在基態時的wavefN, $\Psi(r) = e^{-r/a_0}$ 則其：(a)在原子核周圍1.0 pm^3找到電子的相對概率，(b)在距核為1a_0的周圍1.0 pm^3找到電子的相對概率為何?

(a) $\left|\Psi(r)\right|^2 d\tau = e^{-2r/a_0} d\tau = e^{-0} \cdot (1.0\, pm^3) = 1.0\, pm^3$

(b) $\left|\Psi(r)\right|^2 d\tau = e^{-2r/a_0} d\tau = e^{-2} \cdot (1.0\, pm^3) = 0.14 \times 1.0\, pm^3$

7.1：1

- 上題若改為 He^{+} 核，其groundstate wave fN為 $\psi(r)=e^{-2r/a_0}$ ，同樣的問題，此時其解為何 ？

- e.g. 在前面氫原子的系統中， $\Psi = e^{-r/a_0}$ ，並未 normalized ,所以其 $|\Psi(r)|^2 d\tau$ 只是相對機率大小，若欲求絕對機率，則須將 Ψ normalize , 令其為 $\mathrm{N}\Psi$

…

$$\Rightarrow \mathrm{N}^2 \int \Psi^* \Psi d\tau = N^2 \int \Psi^* \Psi r^2 dr \sin\theta \, d\theta \, d\phi = N^2 \left(\int_0^\infty r^2 \cdot e^{-2r/a_0} dr \right) \left(\int_0^\pi \sin\theta \, d\theta \right) \left(\int_0^{2\pi} d\phi \right)$$

$$= N^2 \left(\frac{1}{4} a_0^{\ 3} \times 2 \times 2\pi \right) = \pi a_0^{\ 3} \mathrm{N}^2 = 1$$

$$\therefore \quad N = \left(\frac{1}{\pi a_0^{\ 3}} \right)^{1/2}$$

$\therefore$ 經過normalized的wavef$_N$，為 $\Psi = \left(\frac{1}{\pi a_0^{\ 3}} \right)^{1/2} \cdot e^{-r/a_0}$

- 可以以此fN 求在某一個特定r，電子出現的絕對概率，即為 $|\Psi(r)|^2 d\tau$ ，所以在上題中，若

$$a_0 = 52.9\,pm,\quad \Psi(r) = \left(\frac{1}{\pi a_0{}^3}\right)^{1/2} \cdot e^{-r/a_0}$$ ，則：

(a) 的解為 $$\left\{\left[\frac{1}{\pi\cdot(52.9\,pm)^3}\right]^{1/2}\right\}^2 \cdot e^{-0} \cdot (1.0\,pm)^3 = 2.2\times10^{-6}$$

(b) 的解為 $$\left\{\left[\frac{1}{\pi\cdot(52.9\,pm)^3}\right]^{1/2}\right\}^2 \cdot e^{-2} \cdot (1.0\,pm)^3 = 2.9\times10^{-7}$$

USEFUL INTEGRALS :

Ⅰ. $$\int x^n e^{ax} dx = \left(x^n e^{ax} / a\right) - \left(n / a\right) \int x^{n-1} e^{ax} dx$$

Ⅱ. $$\int_0^\infty x^n e^{-ax} dx = \left(n! / a^{n+1}\right) = \Gamma_{n+1}\left(a\right) \quad , n > -1, a > 0$$

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\sqrt{\pi/a}$$

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$$

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\pi/a^3}$$

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

SUMMARY:

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot \cdots \cdot(2n-1)}{2^{n+1}}\sqrt{\frac{\pi}{a^{2n+1}}}$$

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

Ⅲ.

$$\int_1^{\infty} e^{-ax} dx = \frac{e^{-a}}{a}$$

$$\int_1^{\infty} x e^{-ax} dx = \left(\frac{e^{-a}}{a^2}\right)(1+a)$$

$$\int_1^{\infty} x^2 e^{-ax} dx = \left(\frac{2e^{-a}}{a^3}\right)\left(1+a+a^2/2\right)$$

SUMMARY:

$$\int_1^{\infty} x^n e^{-ax} dx = \left(\frac{n!\,e^{-a}}{a^{n+1}}\right)\sum_{k=0}^{n} a^k \big/ k! \equiv A_n(a)$$

IV. $$\int_0^1 e^{-ax}dx = \left(\frac{1}{a}\right)\left(1 - e^{-a}\right)$$

$$\int_0^1 xe^{-ax}dx = \left(\frac{1}{a^2}\right)\left[1 - e^{-a}\left(1 + a\right)\right]$$

$$\int_0^1 x^2 e^{-ax}dx = \left(\frac{2}{a^3}\right)\left[1 - e^{-a}\left(1 + a + a^2/2\right)\right]$$

V. $$\int_y^\infty x^n e^{-ax}dx = \left(\frac{n!e^{-ay}}{a^{n+1}}\right)\sum_{k=0}^{n}(ay)^k/k!$$

VI. $$\int_{-1}^{+1} e^{-ax}dx = \left(\frac{1}{a}\right)\left(e^{a} - e^{-a}\right)$$

$$\int_{-1}^{+1} xe^{-ax}dx = \left(\frac{1}{a^{2}}\right)\left[e^{a} - e^{-a} - a\left(e^{a} + e^{-a}\right)\right]$$

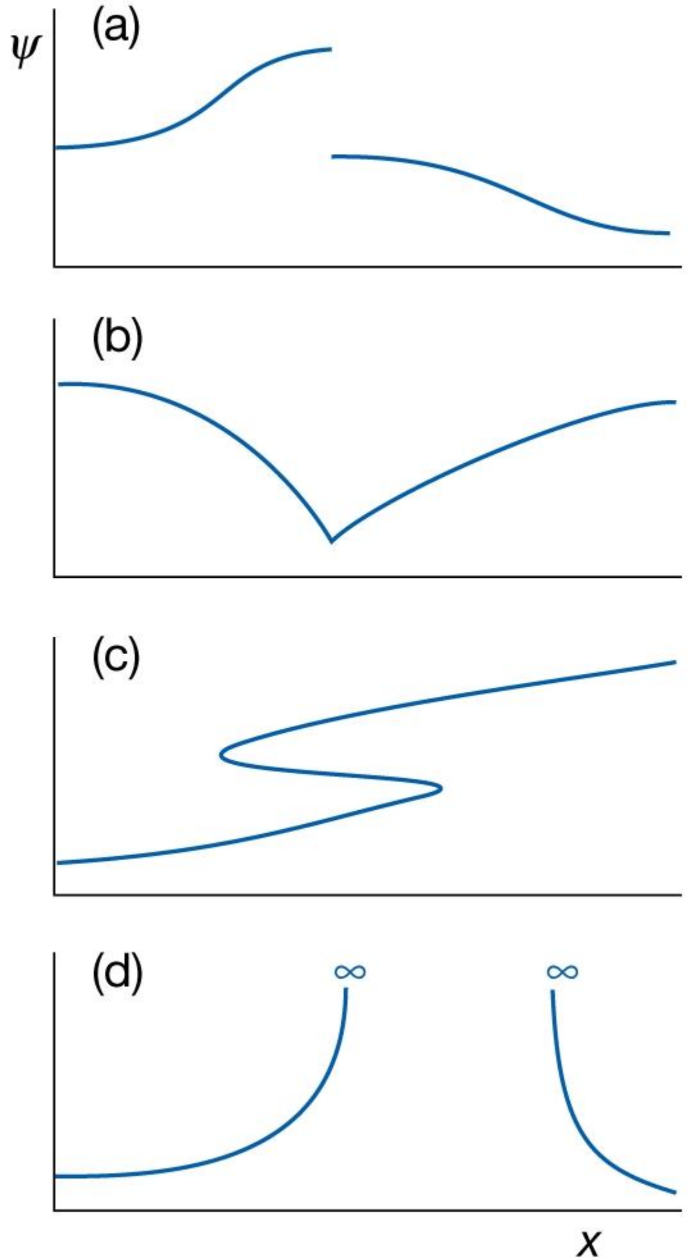
$$\int_{-1}^{+1} x^{n}e^{-ax}dx = (-1)^{n+1}\left[A_n(-a) - A_n(a)\right]$$

SUMMARY:

$$\int_{-1}^{+1} x^{n}dx = \begin{cases} 0, & n = 1, 3, 5, \ldots \\ 2/(n+1), & n = 0, 2, 4, \ldots \end{cases}$$

- 為使波函數的解釋有意義(即Born的解釋)，Schrödinger equation 中有不少的解必須去除，因此所得解的波函數必須具備下列條件：

(1) $\Psi(r)$ 必須finite everywhere , $\Psi(r)$ 不能等於 ∞
(2) $\Psi(r)$ 必須continuous ,$\Psi'(r)$ 也必須continuous
(3) $\Psi(r)$ 必須single-valued
(4) $\Psi(r)$ can not be zero everywhere


ψ
(a)
(b)
(c)
(d)
∞
∞
x

The principles of quantum theory

Why do you need to know this material?

The wavefunction is the central feature in quantum mechanics, so you need to know how to extract dynamical information from it. The procedures described here allow you to predict the results of measurements of observables.

What is the key idea?

The wavefunction is obtained by solving the Schrodinger equation, and the dynamical information it contains is extracted by determining the eigenvalues of hermitian operators.

What do you need to know already?

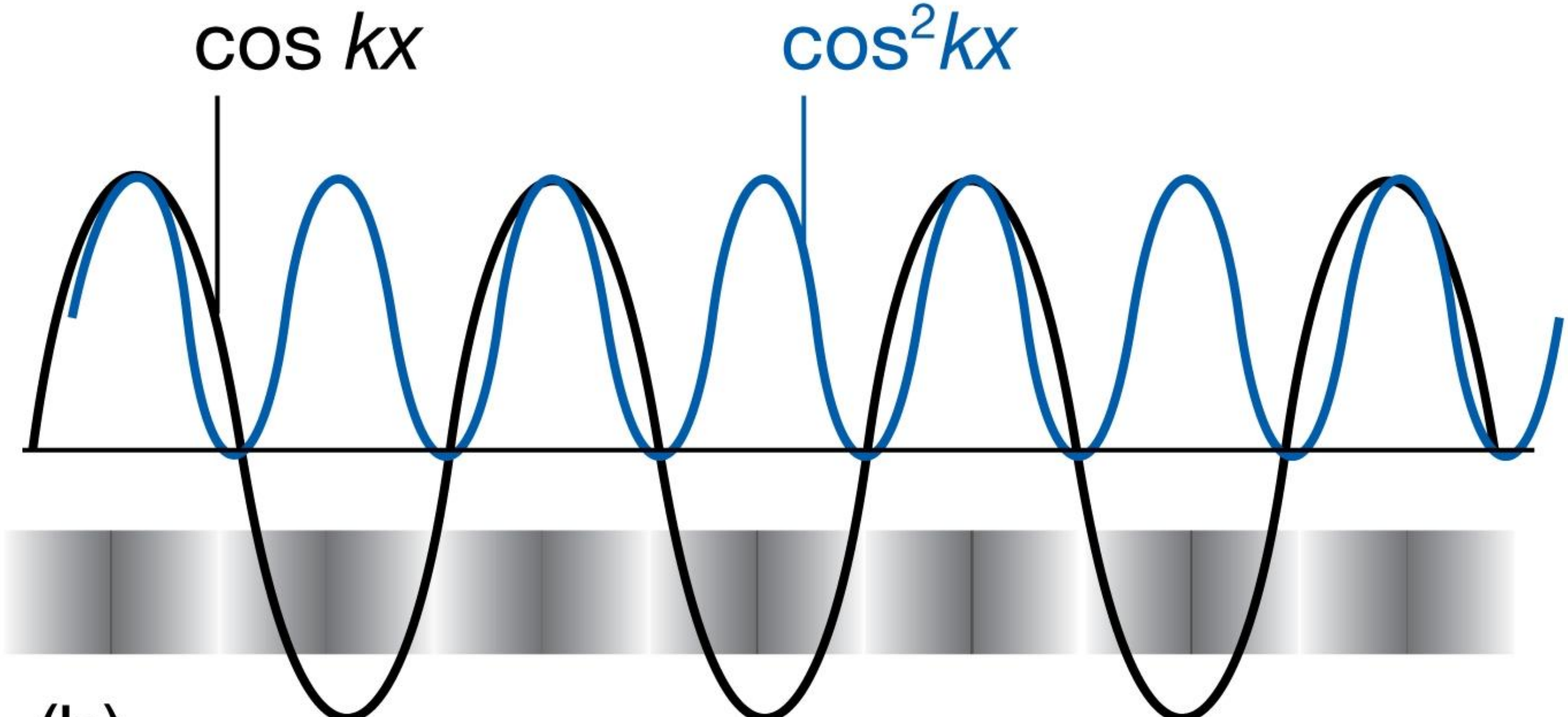
You need to know that the state of a system is fully described by a wavefunction. You also need to be familiar with elementary integration and manipulation of complex functions.

The information in a wavefN

- 一般而言，波函數是含蓋所有dynamical properties (如位置、動量、能量…)的訊息，然而這些訊息如何得到？

(a) Probability density

- Probability density, N $|\Psi|^2$, 表示運動粒子在某指定區域範圍內出現的機率密度，其與波函數的平方成正比例。
- Probability, N$|\Psi|^2$dx, 則表示運動粒子在某指定區域範圍內出現的機率



(b)

(b) **Eigenvalues and eigenfNs**

(operator)(fN)=(constant factor)(same fN) eg. $\hat{\Omega}\Psi=\omega\Psi$

具此形式的equation，稱eigenvalue equation，其中 $\hat{\Omega}$ 稱為eigen operator , Ψ 就是該operator 的eigenfN , ω 稱該 eigenfN的eigenvalue.

e.g. 證明 e^{ax} 為 $\frac{d}{dx}$ 的eigenfN ; e^{ax^2}又如何？

$$\frac{d}{dx}e^{ax}=a\cdot e^{ax}\quad \therefore e^{ax}\text{是為}\frac{d}{dx}\text{的}eigenf_N\text{，}eigenvalue\text{為}a\,.$$

而$\frac{d}{dx}e^{ax^2}=e^{ax^2}\cdot 2ax=2a\cdot xe^{ax^2}$ … 並非eigenvalue equation

一般常見的 是eigenoperator $\hat{\Omega}$ 皆代表著observables，亦即 measurable properties of a system , 例如：動量、能量、electric dipole moment、位置、…等，其相對應的 eigenvalues就代表著該observable的測量值，例如：系統的粒子可以存在於多種不同狀態，每一種狀態皆有不同的動量(or能量)，可以用實驗方法將其測量出來。

在量子力學上這種關係就成了eigenvalue equation , 其中的 Ψ 就代表系統粒子所處的某一種狀態，$\hat{P}$(or $\hat{H}$)就代表該動量(or總能量)，是一種 measurable physical property或是稱為observable，以operator方式表示之，而ω即為系統粒子在該狀態下所測量到的動量或是總能量。

(c) **Operator.**

Observable 通常以operator 的形式表之，主要是由兩種operator推演出來的：

$$\underset{(位置)}{\hat{x}} = x\cdot \quad , \quad \underset{(動量)}{\hat{p}_x} = \frac{\hbar}{i}\frac{d}{dx} \quad , \quad \hat{E}_k = ?$$

operator 一定是operate 在另一個fN上，

e.g. $\hat{P}_x = \frac{\hbar}{i}\frac{d}{dx}$, 令$\Psi_+ = Ae^{ikx}$,

則 $\hat{P}_x \Psi_+ = \frac{\hbar}{i}\frac{d}{dx}(Ae^{ikx}) = \frac{\hbar}{i}\cdot ik \cdot Ae^{ikx} = k\hbar\left(Ae^{ikx}\right)$

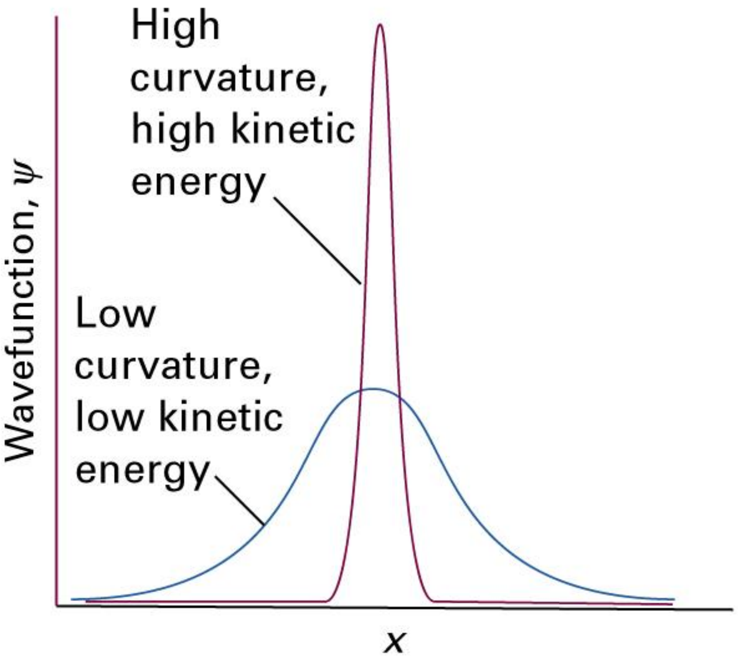
$\therefore$ $k\hbar$ 為eigenvalue，代表該系統粒子具有動量值為 $k\hbar$

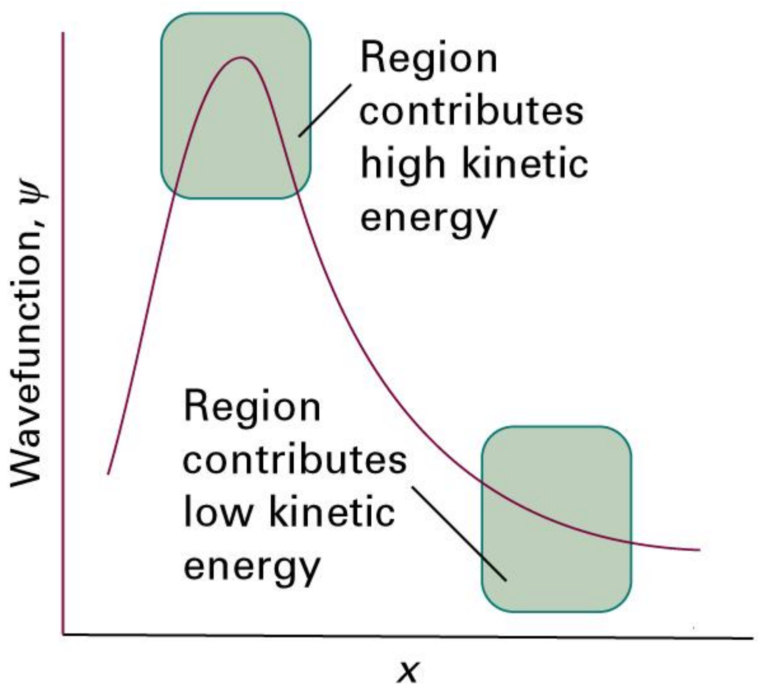
另一wavefN $\Psi_- = Be^{-ikx}$ $\hat{P}_x \Psi_- = \frac{\hbar}{i}\frac{d}{dx}(Be^{-ikx}) = \frac{\hbar}{i}\cdot(-ik)\cdot Be^{-ikx} = -k\hbar\left(Be^{-ikx}\right)$

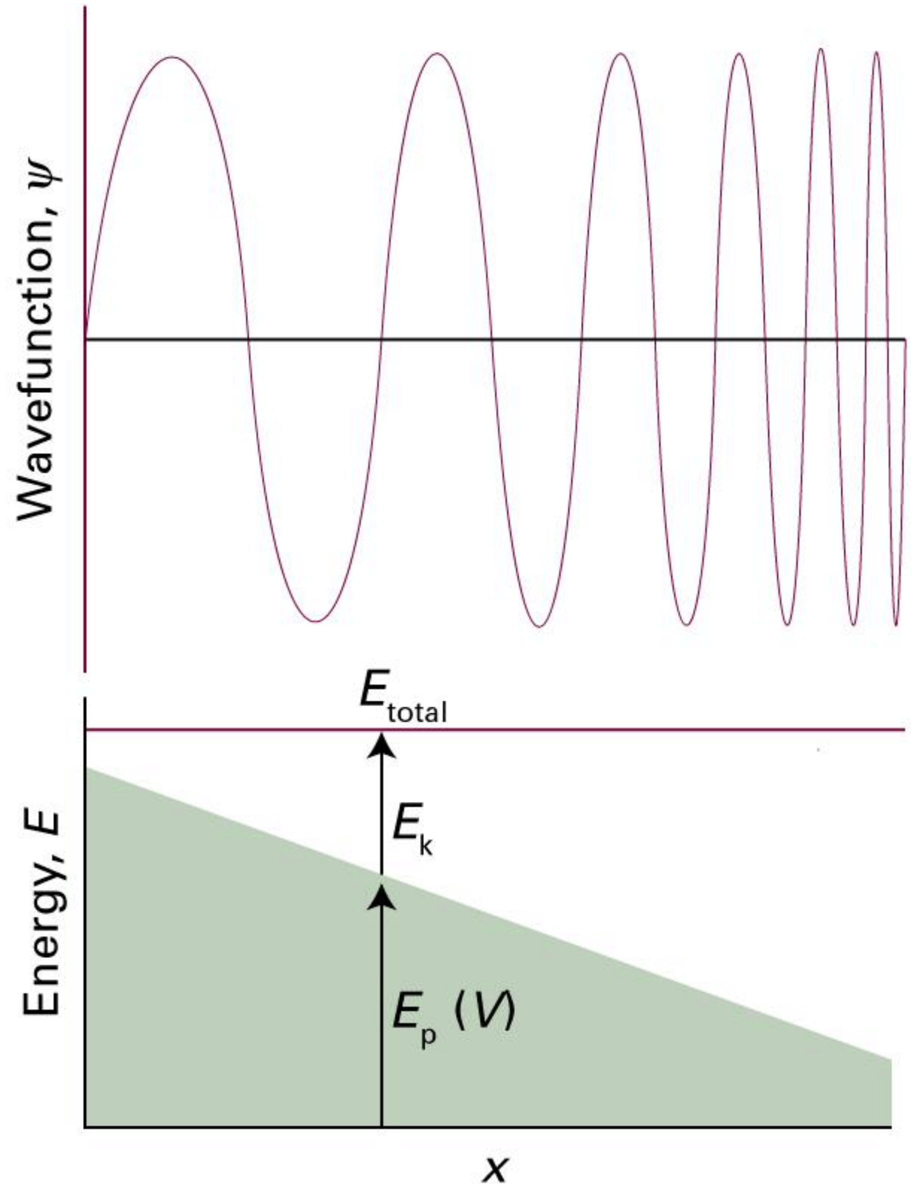
$\therefore -k\hbar$ 為另一eigenvalue，代表該系統粒子具有另一動量值為 $-k\hbar$，可知粒子往 +x 方向，具 $+k\hbar$ 動量，往 -x方向，具 $-k\hbar$ 動量。

$$\hat{E}_k = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

而所被operate的wavefN，二次導數與曲率(curvature)有關，$\therefore$ 曲率越大區域，代表越大的E_k值。


High curvature, high kinetic energy
Low curvature, low kinetic energy
Wavefunction, ψ
x


Region contributes high kinetic energy
Region contributes low kinetic energy
Wavefunction, ψ
x


Wavefunction, ψ
E_total
E_k
E_p (V)
Energy, E
x

(d) **Expectation value**

若上題中，

$$\Psi = 2A\cos kx$$

則

$$\hat{P}_x\Psi = \frac{\hbar}{i}\frac{d}{dx}(2A\cos kx) = \frac{\hbar}{i}\cdot(-k)\cdot 2A\sin kx$$ … 並非eigenvalue equation.

where is the eigenvalue ?
what is the momentum of the system ?

此時只能用平均值(或稱為期望值, expectation value)來表示

e.g. 試計算the average value of an electron from the nucleus in the hydrogen atom in its state of lowest energy 其中 wavefN

$$\Psi = \left(\frac{1}{\pi a_0^{\,3}}\right)^{1/2} e^{-r/a_0}$$

已經normalized ，a_0 為Bohr radius

$$\langle r \rangle = \int \Psi^* \hat{r} \Psi d\tau = \frac{1}{\pi a_0^{\,3}} \int e^{\frac{-r}{a_0}}\, r\, e^{\frac{-r}{a_0}} r^2 \sin\theta\, dr\, d\theta\, d\phi$$

(該波函數不為r operator的eigenfN,直接積分)

$$= \frac{1}{\pi a_0^{\,3}} \int_0^{\infty} r^3\, e^{\frac{-2r}{a_0}} dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$= \frac{1}{\pi a_0^{\,3}} \cdot \frac{3! a_0^{\,4}}{2^4} \cdot 2 \cdot 2\pi = \frac{3}{2} a_0$$

～表示該wavefN並非$\hat{r}$的eigenf N

那mean kinetic energy，$\langle E_k \rangle = ?$

$$\langle E_k \rangle = \int \Psi^* E_k \Psi d\tau = \frac{1}{\pi {a_0}^3} \int e^{\frac{-r}{a_0}} \frac{-\hbar^2}{2m} \nabla^2 e^{\frac{-r}{a_0}} r^2 \sin\theta \, dr \, d\theta \, d\phi \quad \ldots \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

$$\therefore \nabla^2 \cdot e^{\frac{-r}{a_0}} = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 \right) \cdot e^{\frac{-r}{a_0}} = \frac{\partial^2}{\partial r^2}\left(e^{\frac{-r}{a_0}} \right) + \frac{2}{r}\frac{\partial}{\partial r}\left(e^{\frac{-r}{a_0}} \right) + \frac{1}{r^2}\Lambda^2 \left(e^{\frac{-r}{a_0}} \right)$$

$$= \frac{1}{{a_0}^2} e^{\frac{-r}{a_0}} + \frac{2}{r}\left(\frac{-1}{a_0} \right) e^{\frac{-r}{a_0}} = \left(\frac{1}{{a_0}^2} - \frac{2}{r a_0} \right) \cdot e^{\frac{-r}{a_0}} \quad \text{代回}$$

$$\therefore \text{上式} \langle E_k \rangle = \frac{-\hbar^2}{2m\pi {a_0}^3} \int e^{\frac{-r}{a_0}} \left(\frac{1}{{a_0}^2} - \frac{2}{r a_0} \right) e^{\frac{-r}{a_0}} \cdot r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{-\hbar^2}{2m\pi {a_0}^3} \left[\frac{1}{{a_0}^2} \int_0^\infty e^{\frac{-2r}{a_0}} r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi - \frac{2}{a_0} \int_0^\infty e^{\frac{-2r}{a_0}} r dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \right]$$

$$= \frac{-\hbar^2}{2m\pi {a_0}^3} \left[\frac{1}{{a_0}^2} \cdot \frac{2!}{(2/a_0)^3} (4\pi) - \frac{2}{a_0} \cdot \frac{1!}{(2/a_0)^2} \cdot (4\pi) \right]$$

$$= \frac{\hbar^2}{2m{a_0}^2} = \frac{h^2}{8m\pi^2 {a_0}^2}$$

(此即ground state hydrogen atom電子的平均動能)

(e) Superposition

一般fN，can be expanded in terms of all the eigenfNs of an operator , so called complete set of fNs.

$$\Psi = c_1\varphi_1 + c_2\varphi_2 + \cdots = \sum_{k=1} c_k\varphi_k$$ (稱superposition)

其中 c_k 為常數，而 $\varphi_1, \varphi_2, \ldots, \varphi_k, \cdots$ 為某一operator的eigenfNs.

令此operator以 $\hat{\Omega}$ 表之… 則 $\left\langle \hat{\Omega} \right\rangle = \dfrac{\int \Psi^* \hat{\Omega} \Psi d\tau}{\int \Psi^* \Psi d\tau}$ ~

稱為該wavefN(or state)Ψ的expectation value(平均值)

e.g. 在前題中，$\Psi = 2A\cos kx = Ae^{ikx} + Ae^{-ikx} = c_1\varphi_1 + c_2\varphi_2$ ，

其中 $c_1 = c_2 = 1$

$\varphi_1 = Ae^{ikx}$ $\varphi_2 = Ae^{-ikx}$ 皆為 $\hat{P}_x$ 的eigenfN

$$\therefore \left\langle \hat{P}_x \right\rangle = \frac{\int \Psi^* \hat{P}_x \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\int (\varphi_1 + \varphi_2)^* \hat{P}_x (\varphi_1 + \varphi_2) dx}{\int (\varphi_1 + \varphi_2)^* (\varphi_1 + \varphi_2) dx}$$

分子部份

$$\int (\varphi_1 + \varphi_2)^* \hat{P}_x (\varphi_1 + \varphi_2) dx = \int \varphi_1{}^* \hat{P}_x \varphi_1 dx + \int \varphi_1{}^* \hat{P}_x \varphi_2 dx + \int \varphi_2{}^* \hat{P}_x \varphi_1 dx + \int \varphi_2{}^* \hat{P}_x \varphi_2 dx$$

$$= A^2 \left[(k\hbar) \int \varphi_1{}^* \varphi_1 dx + (-k\hbar) \int \varphi_1{}^* \varphi_2 dx + (k\hbar) \int \varphi_2{}^* \varphi_1 dx + (-k\hbar) \int \varphi_2{}^* \varphi_2 dx \right]$$

$$= A^2 ((k\hbar) + 0 + 0 - (-k\hbar)) = 0$$

分母部份

$$\int (\varphi_1 + \varphi_2)^* (\varphi_1 + \varphi_2) dx = \int \varphi_1{}^* \varphi_1 dx + \int \varphi_1{}^* \varphi_2 dx + \int \varphi_2{}^* \varphi_1 dx + \int \varphi_2{}^* \varphi_2 dx$$

$$= A^2 (1 + 0 + 0 + 1) = 2A^2$$

$$\therefore \quad \left\langle \hat{P}_x \right\rangle = \frac{0}{2A^2} = 0$$ ~得知平均值為0 .

其所表示好意思是粒子動量有一半的機率是+kh/2π(向右),另一半是-kh/2 π(向左)所以平均值為零。

因此對於operator operate在一非eigenfN (or非eigen state)，無法得到任何eigenvalue，就可以得到expectation value .<$\hat{\Omega}$>=？
但若該fN以eigenfN的superposition方式來展開表示時，其expectation value 就可以以下表示:

補充：

$$\left\langle \hat{\Omega} \right\rangle = \int \Psi^* \hat{\Omega} \Psi d\tau \quad \ldots \text{if } \Psi \text{ is normalized}$$

if Ψ is an eigenfN of $\hat{\Omega}$, 且eigenvalue 為 ω

則 $\left\langle \hat{\Omega} \right\rangle = \int \Psi^* \hat{\Omega} \Psi d\tau = \omega \int \Psi^* \Psi d\tau = \omega$

if Ψ is not an eigenfN of $\hat{\Omega}$, but a linear combination of $\hat{\Omega}$

的一組 eigenfN $\{\phi_1, \phi_2, \phi_3, \ldots\}$

則 $\langle\Omega\rangle = |c_1|^2\omega_1 + |c_2|^2\omega_2 + |c_3|^2\omega_3 + \cdots\cdots$

其中 $\omega_1, \omega_2, \omega_3, \cdots\cdots$ 為 $\varphi_1, \varphi_2, \varphi_3, \cdots\cdots$ 對應於 $\hat{\Omega}$ 的 *eigenvalues*

而 $c_1, c_2, c_3, \cdots\cdots$ 為 $\Psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + \cdots\cdots$ *linear combination* 的係數

（假設Ψ已經normalized 了）

則 $|c_1|^2 + |c_2|^2 + |c_3|^2 + \cdots\cdots = 1$，令 $\Psi = c_1\varphi_1 + c_2\varphi_2$，$\underline{c_n = \int \varphi_n \Psi d\tau}$

證明：

$$\langle\hat{\Omega}\rangle = \int (c_1\varphi_1 + c_2\varphi_2)^* \hat{\Omega} (c_1\varphi_1 + c_2\varphi_2) d\tau = \int (c_1\varphi_1 + c_2\varphi_2)^* (c_1\omega_1\varphi_1 + c_2\omega_2\varphi_2) d\tau$$

$$= c_1^* c_1 \omega_1 \int \varphi_1^* \varphi_1 d\tau + c_2^* c_2 \omega_2 \int \varphi_2^* \varphi_2 d\tau + c_1^* c_2 \omega_2 \int \varphi_1^* \varphi_2 d\tau + c_2^* c_1 \omega_1 \int \varphi_2^* \varphi_1 d\tau$$

$$= |c_1|^2 \omega_1 + |c_2|^2 \omega_2$$

($|c_1|^2, |c_2|^2$ 則視為weighted by the probability of measurement)

其中 $\int \varphi_1^* \varphi_1 d\tau = 1$ ， $\int \varphi_2^* \varphi_2 d\tau = 1$ （因為已經 normalized了）

而 $\int \varphi_1^* \varphi_2 d\tau = 0$ ， $\int \varphi_2^* \varphi_1 d\tau = 0$ (互為orthogonal)

(g) **Hermitian operators**

$$\text{Hermiticity: } \int \psi_i^* \hat{\Omega} \psi_j \, dx = \left\{ \int \psi_j^* \hat{\Omega} \psi_i \, dx \right\}^*$$

Ex: x

$$\int_{-\infty}^{\infty} \psi_i^* x \psi_j \, dx = \int_{-\infty}^{\infty} \psi_j x \psi_i^* \, dx = \left\{ \int_{-\infty}^{\infty} \psi_j^* x \psi_i \, dx \right\}^*$$

Ex: p_x

$$\int_{-\infty}^{\infty} \psi_i^* \hat{p}_x \psi_j \mathrm{d}x = \left\{ \int_{-\infty}^{\infty} \psi_j^* \hat{p}_x \psi_i \mathrm{d}x \right\}^*$$

$$\int_{-\infty}^{\infty} \psi_i^* \hat{p}_x \psi_j \mathrm{d}x = \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \psi_i^* \frac{\mathrm{d}\psi_j}{\mathrm{d}x} \mathrm{d}x$$

$$= \frac{\hbar}{\mathrm{i}} \psi_i^* \psi_j \Big|_{-\infty}^{\infty} - \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \psi_j \frac{\mathrm{d}\psi_i^*}{\mathrm{d}x} \mathrm{d}x$$

$$\int_{-\infty}^{\infty} \psi_i^* \hat{p}_x \psi_j \mathrm{d}x = -\frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \psi_j \frac{\mathrm{d}\psi_i^*}{\mathrm{d}x} \mathrm{d}x = \left\{ \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \psi_j^* \frac{\mathrm{d}\psi_i}{\mathrm{d}x} \mathrm{d}x \right\}^*$$

$$= \left\{ \int_{-\infty}^{\infty} \psi_j^* \hat{p}_x \psi_i \mathrm{d}x \right\}^*$$

Hermitian operators

a. eigenvalues are real
b. eigenvectors are orthogonal

Orthogonality: $\int \psi_i^* \psi_j \, d\tau = 0$

$$\int \psi^* \hat{\Omega} \psi \, d\tau = \int \psi^* \omega \psi \, d\tau = \omega \int \psi^* \psi \, d\tau = \omega$$

$$\omega^* = \left\{ \int \psi^* \hat{\Omega} \psi \, d\tau \right\}^* = \int \psi^* \hat{\Omega} \psi \, d\tau = \omega$$

Hermitian operators

Justification 9.2 *The orthogonality of wavefunctions*

Suppose we have two wavefunctions ψ_n and ψ_m corresponding to two different energies E_n and E_m, respectively. Then we can write

$$\hat{H}\psi_n = E_n\psi_n \qquad \hat{H}\psi_m = E_m\psi_m$$

Now multiply the first of these two Schrödinger equations by ψ_m^* and the second by ψ_n^* and integrate over all space:

$$\int \psi_m^* \hat{H}\psi_n \mathrm{d}\tau = E_n \int \psi_m^* \psi_n \mathrm{d}\tau \qquad \int \psi_n^* \hat{H}\psi_m \mathrm{d}\tau = E_m \int \psi_n^* \psi_m \mathrm{d}\tau$$

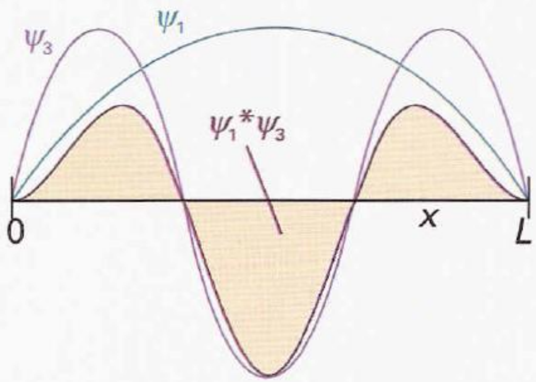
Next, noting that the energies themselves are real, form the complex conjugate of the second expression (for the state m) and subtract it from the first expression (for the state n):

$$\int \psi_m^* \hat{H}\psi_n \mathrm{d}\tau - \left(\int \psi_n^* \hat{H}\psi_m \mathrm{d}\tau\right)^* = E_n \int \psi_m^* \psi_n \mathrm{d}\tau - E_m \int \psi_n \psi_m^* \mathrm{d}\tau$$

By the hermiticity of the hamiltonian (Section 8.5c), the two terms on the left are equal, so they cancel and we are left with

$$0 = (E_n - E_m)\int \psi_m^* \psi_n \mathrm{d}\tau$$

However, the two energies are different; therefore the integral on the right must be zero, which confirms that two wavefunctions belonging to different energies are orthogonal.



The uncertainty principle

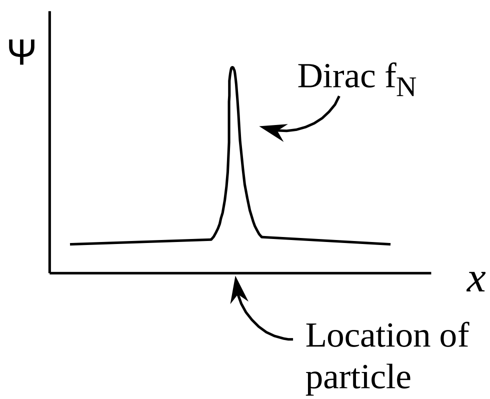
如前例子 若$\Psi(x) = Ae^{-ikx}$, $\hat{P}_x \Psi(x) = \frac{\hbar}{i}\frac{d}{dx} Ae^{-ikx} = -k\hbar Ae^{-ikx}$

可以得知該粒子的動量為 $-k\hbar$，但卻無法預知粒子的位置；

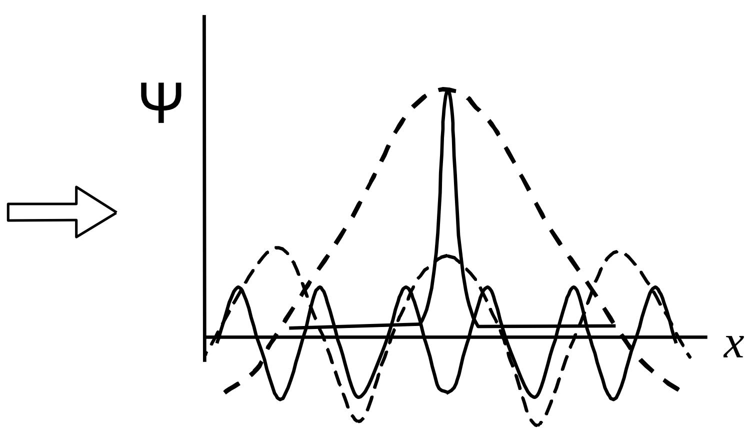
若 $\Psi(x)$ 寫成 $A\cos kx$ or $A\sin kx$ 的形式，雖然可以精確

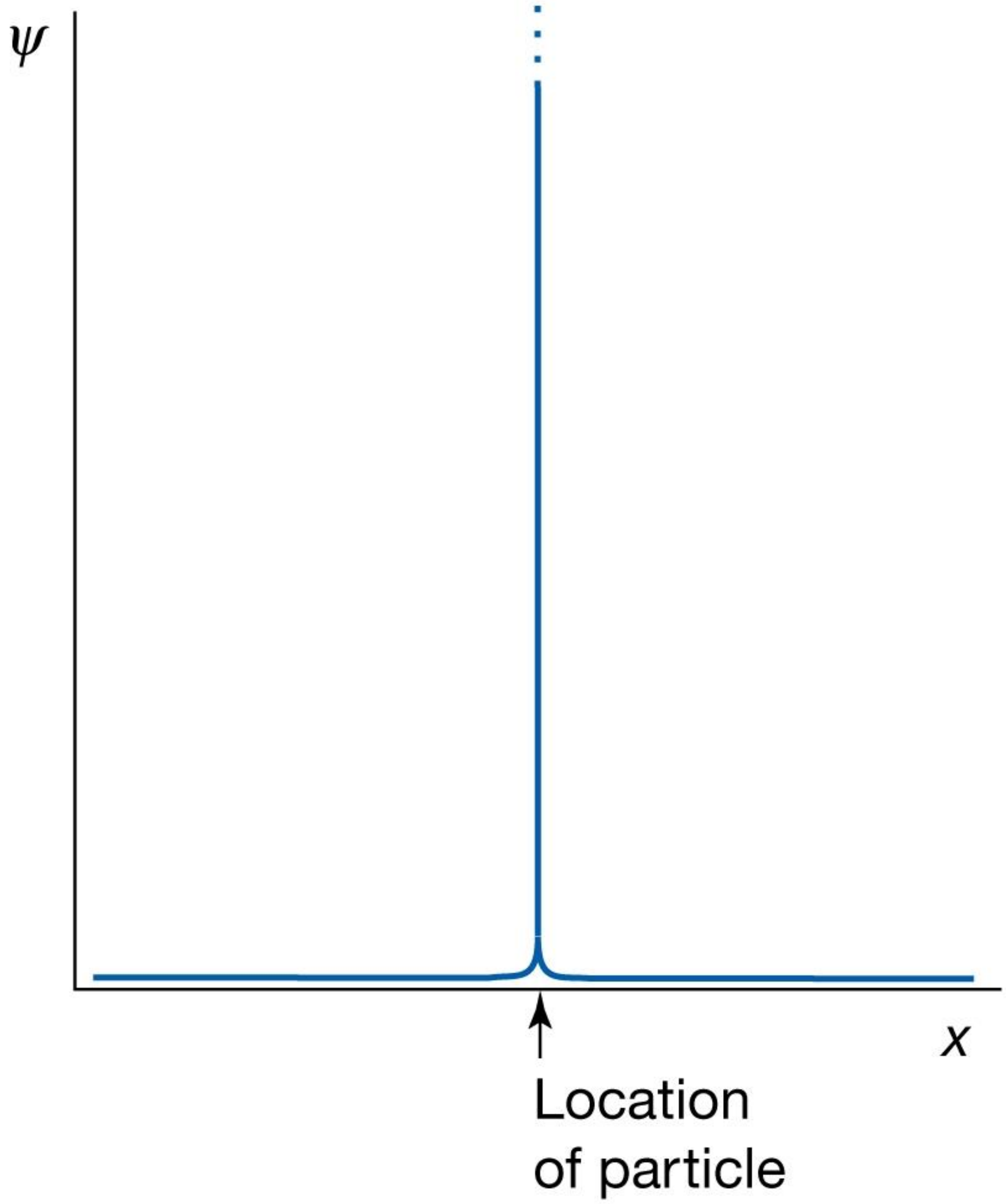
知道粒子的位置，然而動量卻不知，why？

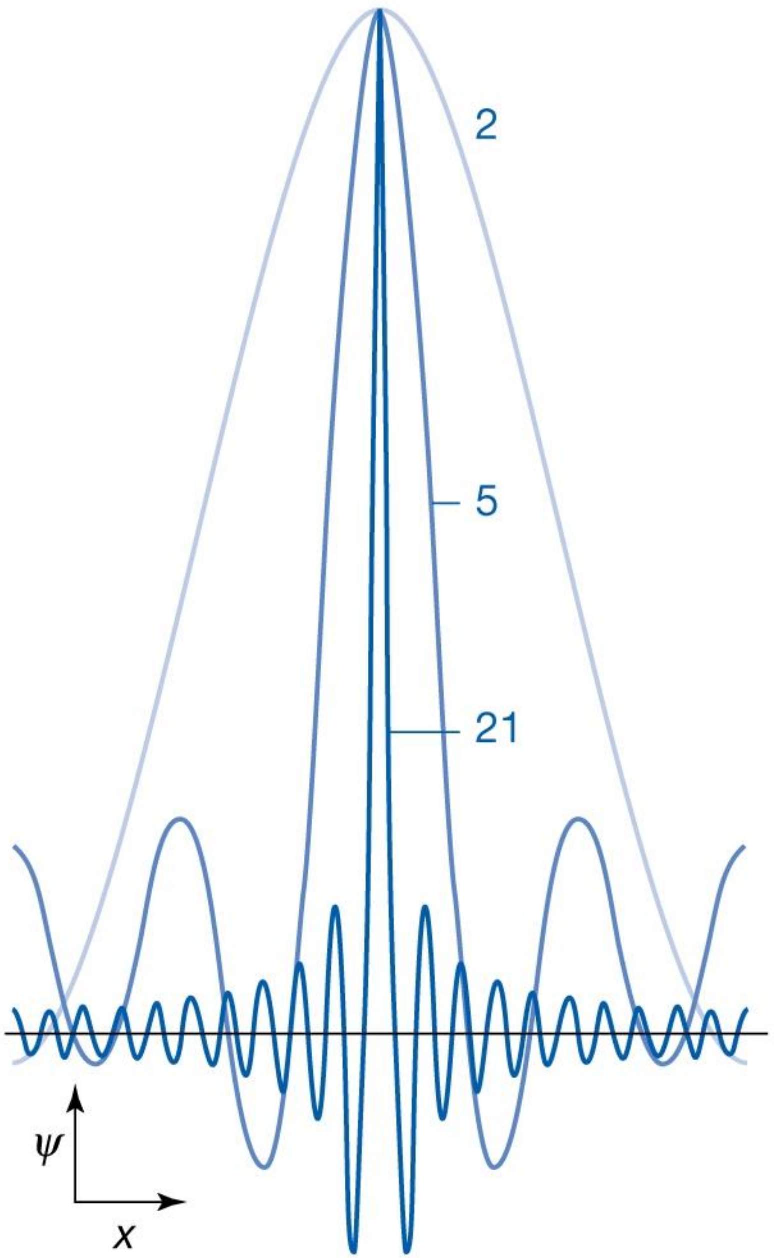
如此，it is impossible to specify simultaneously , with arbitrary precision , both the momentum and its position of a particle . ~ 此稱為 Heisenberg uncertainty principle .



是由許多的 linear combination 而成，但每一個 f_N 有一定的動量，因此真正的能量卻不知道。




ψ
x
Location
of particle



2
5
21
ψ
x

而 $\Delta P\cdot\Delta x \ge \frac{1}{2}\hbar$，由於 $\frac{1}{2}\hbar$ 是一個很小的量，所以在巨觀的系統下是不易察覺該principle的存在的，但在微觀之下，其影響就很明顯，這也說明了為什麼對微觀粒子的運動軌跡，無法精確描述的原因。

The commutator of position and momentum

Complementary Observables

若兩個observables所對應的operator為 $\hat{A}$ & $\hat{B}$，且 $[\hat{A},\hat{B}]$ 定義為 $[\hat{A},\hat{B}]=\hat{A}\hat{B}-\hat{B}\hat{A}$, 又若 $[\hat{A},\hat{B}]\neq 0$，則稱 $\hat{A}$ and $\hat{B}$ are not commute, 而互為complementary operators (observables).若 $[\hat{A},\hat{B}]=0$，則稱 $\hat{A}$ and $\hat{B}$ 互相commute… 若互相commute 則 $\Delta A\cdot\Delta B=0$ 若 $[\hat{A},\hat{B}]\neq 0$ 則 $\Delta A\cdot\Delta B \ge \frac{1}{2}\left|\left\langle [\hat{A},\hat{B}] \right\rangle\right|$

補充： The commutator of position and momentum

由 Heisenberg uncertainty principle (1) 求 $[\hat{x}, \hat{P}_X] = ?$

(2)證明 $\Delta P \cdot \Delta x \geq \frac{1}{2}\hbar$

(1)

$$\left[\hat{x}, \hat{P}_x\right]\Psi(x) = \left(\hat{x}\hat{P}_x - \hat{P}_x\hat{x}\right)\Psi(x) = \hat{x}\frac{\hbar}{i}\frac{d}{dx}\Psi(x) - \hat{P}_x \cdot x \cdot \Psi(x)$$

$$= x\frac{\hbar}{i}\frac{d}{dx}\Psi(x) - \left(\frac{\hbar}{i}\frac{d}{dx}\right) \cdot x \cdot \Psi(x) = \frac{\hbar}{i}x\frac{d}{dx}\Psi(x) - \frac{\hbar}{i} \cdot \left[\Psi(x) + x\frac{d\Psi(x)}{dx}\right]$$

$$= -\frac{\hbar}{i}\Psi(x)$$

$\therefore \quad \left[\hat{x}, \hat{P}_x\right] = -\frac{\hbar}{i} \neq 0$ …… 那$\left[\hat{x}, \hat{P}_y\right]$又如何呢？

(2)

由 Heisenberg uncertainty principle

$$\Delta P_x \cdot \Delta x \geq \frac{1}{2}\left|\left\langle \left[\hat{x}, \hat{P}_x\right] \right\rangle\right| = \frac{1}{2}\left|\left\langle -\frac{\hbar}{i} \right\rangle\right| = \frac{1}{2}\left|-\frac{\hbar}{i}\right| = \frac{1}{2}\hbar$$

$$\therefore \quad \Delta P_x \cdot \Delta x \geq \frac{1}{2}\hbar$$

一般定義某一測量值的mean square deviation：

$$< P_x{}^2 > - < P_x >^2$$

root mean square deviation： $\left\{\left\langle P_x{}^2 \right\rangle - \left\langle P_x \right\rangle^2\right\}^{\frac{1}{2}} = \Delta P_x$

同理~ $\Delta x = \left\{\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2\right\}^{\frac{1}{2}}$