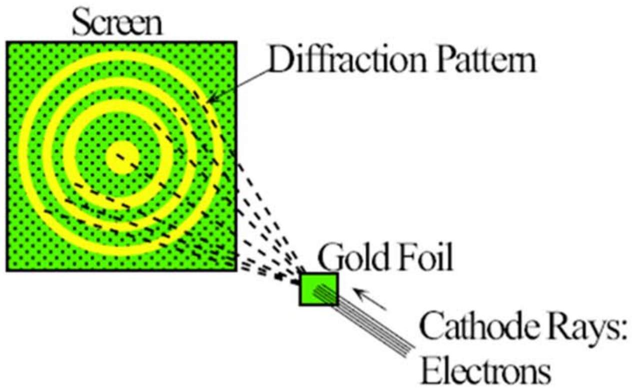
Chapter 5. Matter Waves

Matter waves

- We were able to derive the wave equations for waves in a string or for electromagnetic waves from a knowledge of the medium in which the waves propagate.

- We construct a formal equation that will meet very general requirements that matter often exhibits wave-like properties, such as electron diffraction.



letters to nature

Wave–particle duality of C_{60} molecules

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- How can we construct the wave equation for matter waves?

Matter waves

- The desired solution may have the form like

$$\Psi = Ae^{i(kx-\omega t)} \tag{1}$$

- The features the matter wave equation should include are the energy *E* and the momentum *p*, which are common between the "particle" and the "wave".

	E	p
particle	$(\frac{p^2}{2m}) + V$	mv
wave	$\hbar\omega$	$\hbar \mathrm{k}$

- If we assume that the matter wave equation has the harmonic solutions as the above, then

$$\frac{\partial \Psi}{\partial t} = -i\omega\Psi \quad \Rightarrow \quad E = \hbar\omega = \frac{i\hbar}{\Psi}\frac{\partial \Psi}{\partial t} \tag{2}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2\Psi \quad \Rightarrow \quad p^2 = -\frac{\hbar^2}{\Psi}\frac{\partial^2 \Psi}{\partial x^2} \tag{3}$$

Schrödinger time dependent wave equation

- Since the energy of a particle is given by

$$E = (p^2 / 2m) + V,$$

a reasonable choice of a wave equation is

$$\frac{i\hbar}{\Psi}\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2}\cdot\frac{1}{\Psi} + V$$

$$i.e. \quad \boxed{i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi} \qquad (4)$$

- The above equation is the <u>Schrödinger time-dependent wave equation</u>.
- The equation must be used if we want to describe processes related to dynamic transition, such as in optical absorption and carrier relaxation.

Schrödinger time-independent wave equation

- If we are not concerned with the dynamic changes of energy state, but concerned with the question of what energy states are allowed in the presence of a particular potential energy $V(x, y, z)$, so called stationary states of the system, the states can be expressed as

$$\Psi(x, y, z, t) = \psi(x, y, z)e^{-i\omega t} \tag{5}$$

$i.e.$ The dependence of Ψ on the coordinates can be separated from the dependence of Ψ on time.

- Substitution of the equation (5) into (4) leads to

$$\hbar\omega\psi = E\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi \text{ for 1−D}$$

$$\text{or } \boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + [V(x) - \mathrm{E}]\,\psi(x) = 0} \text{ for 1−D} \tag{6}$$

$$\text{or } \boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + [V(x, y, z) - \mathrm{E}]\,\psi = 0} \text{ for 3−D} \tag{7}$$

Time−independent Schrödinger equation

Schrödinger time-independent wave equation

- Procedure for solving the wave equation

  i.e. obtaining a set of ψ_i with corresponding allowed energy values E_i

1. Obtain the general solution $\psi(x)$ for the particular V of interest.
2. Retain only mathematically well behaved solution, i.e.

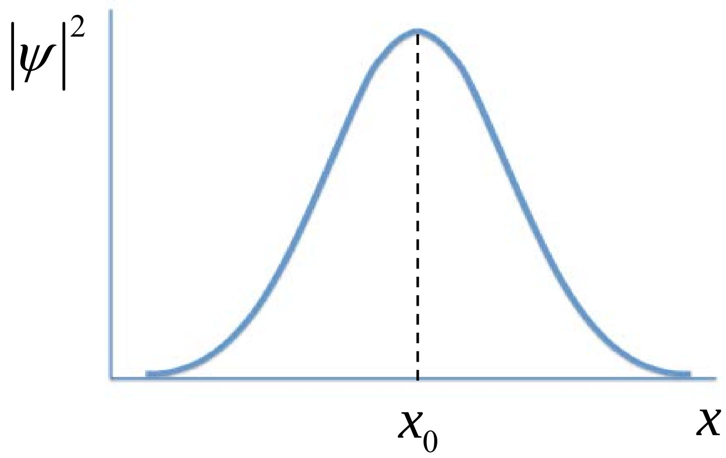
$$\left.\begin{array}{l}\text{single valued}\\ \text{not zero}\\ \text{continous}\\ \text{continous derivatives}\\ \text{finite}\\ \text{square integrable}\end{array}\right\}\quad \text{may limit } E_n$$

3. Apply boundary conditions.

   $\rightarrow$ may limit E_n

$\psi(x)$

- What is $\psi(x)$?
- Physical significance of $\psi(x)$ can be associated at least with the real quantity $\psi\psi^*$.
- Suppose that a plot of $\psi\psi^* = |\psi|^2$ *vs* x representing a "particle" has the dependence on *x* shown in the below figure.



$\psi(x)$

- Two interpretations of $|\psi|^2\, dxdydz$.

① The probability of finding the particle between x and $x+dx$ or within $dxdydz$ of (x, y, z).

<“Where is the particle likely to be”>

② Represent the density function for the “particle”

– e.g., $-q|\psi|^2$ represents a spatial distribution of charge corresponding to a single electron.

– collapse to a specific location during measurement with a probability ∝ density function

– The probability of measuring a particular point is proportional to the magnitude of the density function $|\psi|^2$ at that point.

<Particle does not have a position>

$\psi(x)$

- Since in either interpretation, $|\psi|^2$ is a probability, it must be "square integrable".

$$\iiint |\psi|^2 \, dxdydz = \text{constant}$$

- When the wave function is multiplied by an appropriate constant *A* such that

$$A^2 \iiint |\psi|^2 \, dxdydz = 1$$

- The wave function is said to be normalized, and *A* is called the normalization constant.
- A normalized wave function satisfies

$$\iiint |\psi|^2 \, dxdydz = 1 \qquad (8)$$

$\psi(x)$

- To be used as a probability, the wave function must be normalized.

$$e.g. \int_{-\infty}^{\infty} -q|\psi|^2\, dx = -q \qquad (9)$$

- In spherical coordinates

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta \; dr d\theta d\phi = 1 \qquad (10)$$

- Three important systems allow exact solutions.

① $V = 0$ for $0 \leq x \leq L$, A free electron model of a confined electron

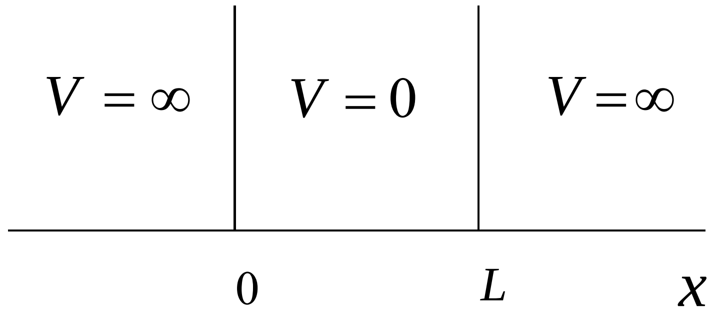
② $V = \frac{1}{2}gx^2$, Linear harmonic oscillator (F=-gx)

③ $V = \frac{Zq^2}{4\pi\varepsilon_0\varepsilon_r r}$, Hydrogenic atom ($Z$=1, hydrogen)

Free electron model of a confined electron

"Particle in a box"

1-D case



- The Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - \mathrm{E}\psi(x) = 0 \quad (11)$$

- The solution of the above equation has the form.

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (12)$$

- Substitution eq. 12 into eq. 11 results in

$$E = \frac{\hbar^2 k^2}{2m}, \quad 0 \le x \le L$$

$V = \infty$ for $x < 0,\ x > L$

$\psi_{outside} = 0$

$\psi \neq 0$ for $0 < x < L$

Free electron model of a confined electron

- B.C's

① $\psi = 0$ at $x = 0$ and L

$$\rightarrow\ k = \frac{n\pi}{L}, \quad \frac{n\lambda}{2} = L$$

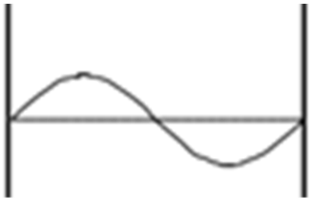
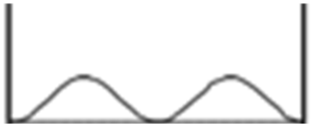
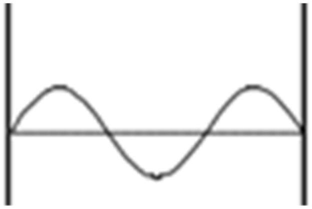
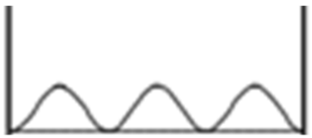
$$\psi_n = C_n \sin\frac{n\pi x}{L}$$

② $\int_0^L \psi^* \psi\, dx = 1 \ \rightarrow\ C_n = \left(\frac{2}{L}\right)^{1/2}$

$$\therefore \psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

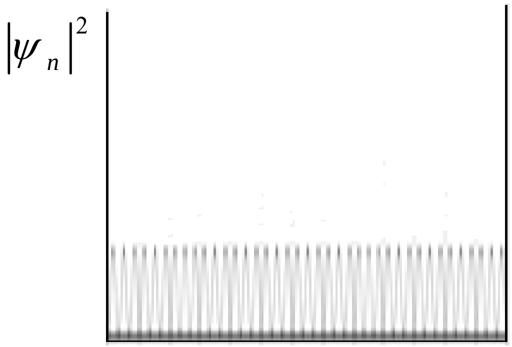
Free electron model of a confined electron

n	E_n	ψ_n	ψ_n	$\lvert\psi_n\rvert^2$
1	$\frac{\hbar^2\pi^2}{2mL^2}$ ground state	$\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}$		
2	$4\frac{\hbar^2\pi^2}{2mL^2}$	$\left(\frac{2}{L}\right)^{1/2}\sin\frac{2\pi x}{L}$		
3	$9\frac{\hbar^2\pi^2}{2mL^2}$	$\left(\frac{2}{L}\right)^{1/2}\sin\frac{3\pi x}{L}$		

- Number of nodes in $\psi = (n-1)$
- More nodes correspond to the higher energy.

Free electron model of a confined electron

- For large n



$$E_1 = 3.8\times10^{-15} L^{-2}\ \text{eV}$$

(L in centimeters)

Classical	Wave
① Equal probability of finding particle anywhere (for any E) = $1/L$	Probability is function of x and varies with E
② Continuous $E \geq 0$ allowed	Discrete E_n allowed

③ As $n \to \infty$, wave picture reduces to classical picture.
"correspondence principle"

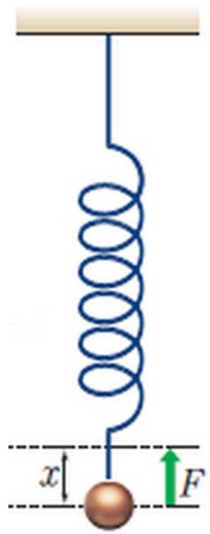
Linear harmonic oscillator

:Consists of a particle moving under a restoring force proportional to the displacement.

$$F = -gx$$

$$V = -\int F dx = \frac{1}{2} g x^2$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (\frac{1}{2} g x^2 - E)\psi = 0$$



- solution :

$\psi(x) = f(x) e^{-\frac{\gamma x^2}{2}}$ when $\gamma^2 = \frac{mg}{\hbar^2}$

$f(x)$: p olynomial that terminate after a finite number of terms to keep $\psi(x)$ finite and normalizable

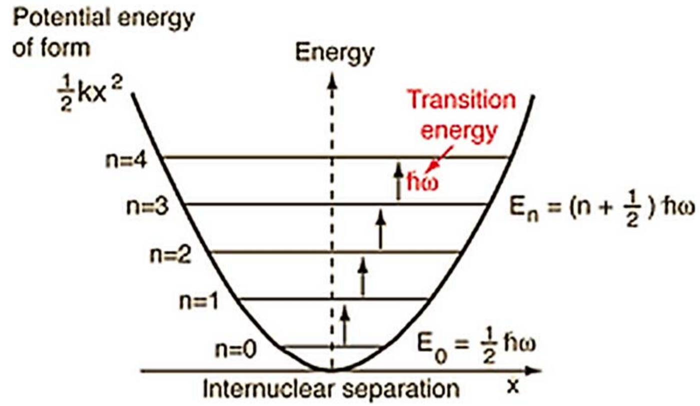
$$\psi_n = H_n\,(\sqrt{\gamma} x) e^{-\frac{\gamma x^2}{2}}$$

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$$

Linear harmonic oscillator

From termination condition :

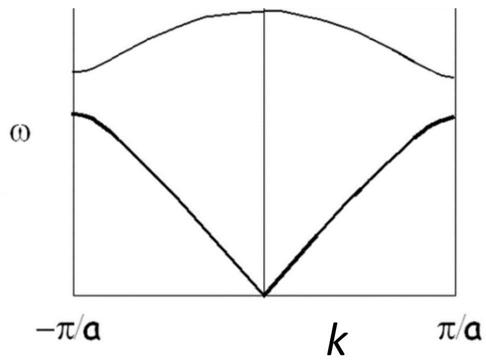
$$E_n = (n + \frac{1}{2})\hbar\omega \qquad \omega = 2\pi\sqrt{\frac{g}{m}}$$



- Applications

  ① Vibration of atoms in a crystal can be represented by a collection of oscillators representing lattice waves.

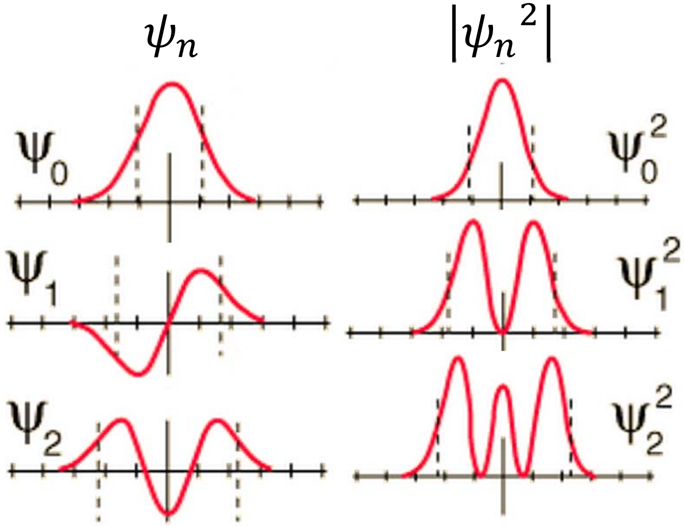
  $\longrightarrow$ phonon $\quad \hbar\omega_{\text{phonon}}$



Linear harmonic oscillator

② Collection of charge oscillators generates electromagnetic radiation → photon $\hbar\omega_{\text{photon}}$

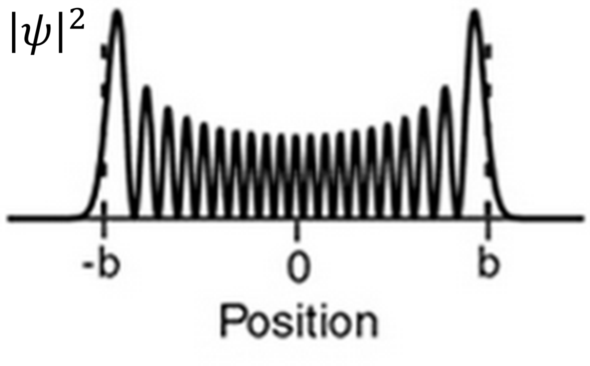
n	ψ_n	E_n
0	$A_0 e^{-\frac{\gamma x^2}{2}}$	$\frac{1}{2}\hbar\omega$
1	$A_1 \gamma^{\frac{1}{2}} x e^{-\frac{\gamma x^2}{2}}$	$\frac{3}{2}\hbar\omega$
2	$A_2\{2\gamma x^2 - 1\} e^{-\frac{\gamma x^2}{2}}$	$\frac{5}{2}\hbar\omega$



Linear harmonic oscillator

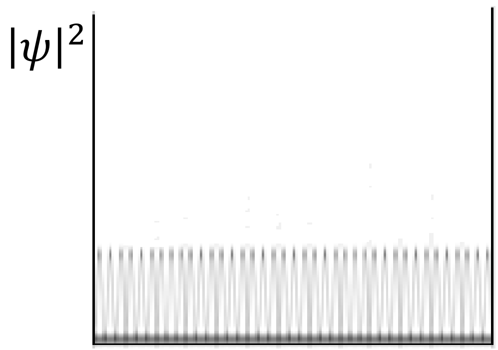
- Classically, mid point has lowest probability, side point has largest probability.
  → not the case in quantized oscillator.

-For large *n*



[Linear harmonic oscillator]

Max. probability at the classical "turn around" points, at the "ends" of the oscillation.



[Particle in a box]

Constant probability