Application to Translational Motion

Reading: Atkins, ch. 9

Schrödinger equations for three basic types of motion: translation, vibration, rotation → "quantization"

1. **Translational motion**

   (1) Free motion

   (2) Particle in a box

   (3) Tunnelling

(1) Free motion

$V = 0$,
$H\Psi = E\Psi$, $H = (\hbar^2/2m)(d^2\Psi/dx^2)$

General solutions, $\Psi_k = Ae^{ikx} + Be^{-ikx}$, $E_k = k^2\hbar^2/2m$
$\Rightarrow H_k\Psi_k = E_k\Psi_k$

- all values of k, all values of the energy are permitted $\rightarrow$ the translational energy of a free particle is not quantized

- e^{ikx} is an eigenfunction of operator p_x with eigenvalue $+k\hbar$: motion toward +x
  e^{-ikx} is an eigenfunction of the operator p_x with eigenvalue $-k\hbar$: motion toward -x
$\Rightarrow |\Psi|^2$ is independent of x

$\rightarrow$ the position of the particle is completely unpredictable
(uncertainty principle, x, p_x do not commute)

(2) Particle in a box in 1-D

- a particle of mass m is confined between two walls at $x = 0$ and $x = L$
- Infinite square wall: $V(x) = 0$ inside the box, infinity at the walls

e.g., a gas phase molecule in 1-D container

π-electrons in a linear conjugated hydrocarbon

Schrödinger equation

i) $0 \le x \le L$, $V(x) = 0$

ii) $x < 0$, $x > L$, $V = \infty$

Boundary conditions

- physically impossible for the particle to be found with an infinite potential energy $\rightarrow$ the wavefunction must be zero ($\Psi = 0$) at $x < 0$, $x > L$

- wavefunction should be continuous

$\Rightarrow \Psi_k(0) = 0$, $\Psi_k(L) = 0$

$x = 0 \Rightarrow \Psi_k(0) = 0 = D = 0$, $\therefore D = 0$

$x = L \Rightarrow \Psi_k(L) = C\, \mathit{sin}\, kL$

if $C = 0$, $\Psi = 0$ for all x: no particle $\rightarrow$ the particle must be somewhere

$\Rightarrow \therefore \sin kL = 0$

$\rightarrow kL = n\pi$, $n = 1,2,3\ldots.$ ($n \neq 0$ since if $n = 0 \rightarrow \Psi = 0$ everywhere)

$\therefore \Psi_n(x) = C\, \mathit{sin}\, (n\pi x/L)$, $n = 1, 2 \ldots.$

- Normalization

$E_n =$

n: “quantum number” (integer, in some case, a half-integer)

- the properties of the solutions

(i) Energy is quantized

$$E_n \propto n^2$$

$\rightarrow$ only certain wavefunctions are acceptable

(ii) ψ vs. n

$\Psi_1(x) = (2/L)^{1/2}$ *sin* $(\pi x/L)$
$\Psi_2(x) = (2/L)^{1/2}$ *sin* $(2\pi x/L)$
……………

$\rightarrow$ same amplitude $(2/L)^{1/2}$, different wavelength

- n$\uparrow \rightarrow \lambda\downarrow$, $E_k = p^2/2m$, $p = h/\lambda$, $\lambda\downarrow$, p$\uparrow$, $E_k\uparrow$
- n$\uparrow \rightarrow \lambda\downarrow \rightarrow E_k\uparrow$
- n$\uparrow \rightarrow$ number of nodes$\uparrow \Rightarrow \Psi_n$ has n-1 nodes

(iii) linear momentum

$\langle p_x \rangle =$

However, each wavefunction is a superposition of momentum eigenfunctions

$\Psi_n = (2/L)^{1/2}\, \mathit{sin}\, (n\pi x/L) = 1/2i\, (2/L)^{1/2}\, (e^{ikx} - e^{-ikx})$

$\Rightarrow$ $+k\hbar$ for half, $-k\hbar$ for half

$\Rightarrow$ equal probability for opposite directions

(iv) $E_{min} \neq 0$

cf) C.M. allow zero energy (stationary particle)

$n \neq 0$, “zero-point energy”

$$E_1 = h^2/8mL^2 \neq 0$$

uncertainty principle: non zero momentum → kinetic energy

curvature in a wavefunction → possession of kinetic energy

(v) $E_{n+1} - E_n = (h^2/8mL^2)(2n + 1)$

$L\uparrow \quad \Delta E \rightarrow 0$:

not quantized for complete free particles

(vi) probability

$\Psi^2(x) = (2/L)\, sin^2\, (n\pi x/L)$

low n $\rightarrow$ nonuniformity

n $\rightarrow \infty$, uniform $\Rightarrow$ classical mechanics

(independent of position)

"correspondence principle"

(vii) orthogonality

$\int \Psi_n{}^* \Psi_{n'} d\tau = 0, n' \neq n$: orthogonal

wavefunctions corresponding to different energies are orthogonal

ex. Ψ_1 Ψ_3

$\langle n | n' \rangle = 0$ ($n' \neq n$): Dirac bracket notation

$\langle n |$ "bra" $\Rightarrow \Psi_n{}^*$, $| n' \rangle$ "ket" $\Rightarrow \Psi$

normalized, $\langle n | n \rangle = 1$

$\langle n | n' \rangle = \delta_{nn'}$: kronecker delta, $n = n' \Rightarrow 1$

$n \neq n' \Rightarrow 0$

Orthogonality: important in Q.M.: eliminate a large number of integrals $\rightarrow$ central role in the theory of chemical bonding and spectroscopy e.g.) model of 1-D particle in a box: π electrons in linear conjugated hydrocarbons

(3) Particle in a box in 2-D

partial differential equations $\rightarrow$
separation of variables techniques:
divide equation into two or more
ordinary differential equations

$E = E_X + E_Y$

3-D: same, additional term, n_3 & L_3

- Degeneracy

ket $|n_1\ n_2>$

if $L_1 = L_2 = L$ (square)

$\Psi_{n1,n2}(x, y) = (2/L)\ \mathit{sin}\ (n_1\pi x/L)\ \mathit{sin}\ (n_2\pi y/L)$

$E_{n1,n2} = (n_1^2 + n_2^2)\ (h^2/8mL^2)$

if $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$

$\Psi_{1,2}(x, y) = (2/L)\ \mathit{sin}\ (\pi x/L)\ \mathit{sin}\ (2\pi y/L)$, $E_{1,2} = 5h^2/8mL^2$

$\Psi_{2,1}(x, y) = (2/L)\ \mathit{sin}\ (2\pi x/L)\ \mathit{sin}\ (\pi y/L)$, $E_{1,2} = 5h^2/8mL^2$

$\Rightarrow$ Different wavefunctions, same energy $\Rightarrow$ "degeneracy"

energy level $5h^2/8mL^2$ is doubly degenerate

$|1\ 2>$ and $|2\ 1>$ are degenerate

degeneracy: many examples in atoms, symmetry properties

3-D: same, additional term, n_3 & L_3

(4) Tunnelling

- if the potential energy of a particle does not rise to infinite in the wall & $E < V \rightarrow \Psi$ does not decay abruptly to zero
- if the walls are thin $\rightarrow \Psi$ oscillate inside the box & on the other side of the wall outside the box $\rightarrow$ particle is found on the outside of a container: leakage by penetration through classically forbidden zones "tunnelling"

cf) C.M.: insufficient energy to escape

(I) $x < 0$, $V = 0$,

(II) $0 \le x \le L$, $E < L \rightarrow$

(III) $X > 0$, $V = 0$

In region III, no reflected wave, $B' = 0$

Conditions

at x = 0 and x = L, must be continuous

1. $\Psi_I(0) = \Psi_{II}(0)$, $\Psi_{II}(L) = \Psi_{III}(L)$

slope (1st derivatives) must also be continuous

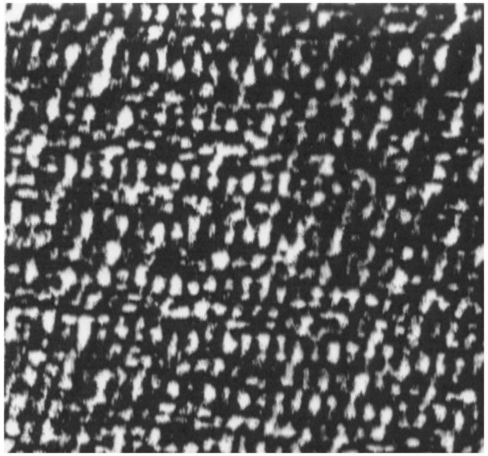
2. $\Psi'_I(0) = \Psi'_{II}(0)$, $\Psi'_{II}(L) = \Psi'_{III}(L)$

Transmission probability: probability that the particle passes the barrier enhanced reflection (antitunnelling)

- high, wide barrier $\kappa L >> 1$

$\Rightarrow$ T decrease exponentially with thickness of the barrier, with $m^{1/2}$

$\Rightarrow$ low mass particle $\rightarrow$ high tunnelling *tunnelling is important for electron



e.g) proton transfer reaction
STM (scanning tunnelling microscopy)