Application to Vibrational Motion

Schrödinger equations for three basic types of motion: translation, vibration, rotation $\rightarrow$ “quantization”

Vibrational motion

Harmonic oscillator

e.g., diatomic molecule: N_2

Force, $F = -kx$, k: force constant

$$F = -dV/dx \Rightarrow V = 1/2kx^2$$

N_2

Schrödinger equation

$$-(\hbar^2/2m)(d^2\Psi/dx^2) + 1/2kx^2\ \Psi = E\Psi$$

Solution of this equation: (**notebook copies will be provided**)

$\therefore E = (h/2\pi)(2\pi\nu_0)(v + ½) = h\nu_0(n + ½) = \hbar\omega\,(v + ½)$, $v = 0,1,2\ldots.$

$\Delta E = E_{v+1} - E_v = \hbar\omega$ (same ΔE)

if $m\uparrow \Rightarrow \omega \rightarrow 0 \Rightarrow \Delta E \rightarrow 0$: classical mechanics

- zero point energy

$$E_0 = \tfrac{1}{2}\hbar\omega$$

$\Rightarrow$ ~ 3 x 10^{-20} J, 0.2 eV, 15 kJ/mol

$\Rightarrow$ uncertainty of position, momentum $\rightarrow$ kinetic energy

c.f. C.M.: particle can be perfectly still

- particle in a box *vs*. harmonic oscillator

Wavefunction for harmonic oscillator

$\Psi(x) = N \times (\text{polynomial in } x) \times (\text{Gaussian function})$

$\Psi_v(x) = N_v H_v(y) e^{-y^2/2}$, $y = x/\alpha$, $\alpha = (\hbar^2/mk)^{1/4}$

N_v: normalization constant

$H_v(y)$: Hermite polynomial

Gaussian function: $e^{-y^2/2}$

Hermite polynomials, $H_v(y)$

v	$H_v(y)$
0	1
1	2y
2	$4y^2-2$
3	$8y^3-12y$
…..	

$\therefore$ v = 0 (wavefunction for ground state)

$\Rightarrow \Psi_0(x) = N_0 H_0(y) e^{-y2/2} = N_0 e^{-x2/2\alpha2}$

$\Psi_0^{\,2}(x) = N_0^{\,2} e^{-x2/\alpha2}$

lagest at zero displacement (x = 0)

- v = 1 (1^{st} excited state)

$\Rightarrow \Psi_1(x) = N_1 2y\, e^{-y2/2} = (2N_1/\alpha)xe^{-x2/2\alpha 2}$

node at x = 0

maximum probability at $x = \pm\alpha$ ($y = \pm 1$)

Ψ

Ψ^2

f(x) = f(-x): even
f(x) = -f(-x): odd

- oscillator may be found at extensions with V>E that are forbidden by classical mechanics (negative kinetic energy)

$\Rightarrow$ Lowest energy: 8% in classical forbidden region
"tunnel effect" : independent of k, m

$\Rightarrow$v (quantum number) $\uparrow \Rightarrow$ probability $\downarrow$
v $\rightarrow \infty \Rightarrow$ probability $\rightarrow$ 0

- $v = \infty$

$E_k = 0$ at turning point, velocity = 0,

probability: highest

largest amplitudes near the turning points of the classical motion (at $V = E$, kinetic energy = 0)

- expectation values

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예: The potential energy curve for H_2 is close to a harmonic oscillator. The first vibrational transition is at 4000 cm^{-1}.

(a) Calculate the force constant *k* of the hydrogen molecule.

(b) Calculate the vibrational transition energy for D_2 (in cm^{-1}) assume same force constant with H_2.

(c) Calculate the zero point energy of this H_2.