

Harmonic Oscillator – Levine Ch 4/Atkins 3.5/R&S 5.1/Dykstra 2.2

Talked about potential wells and finite ones now well with sloping sides:

$V = (1/2) kx^2$ so $V =$ only at $x =$, since $V(x)$ is finite expect:

a. $\psi(x)$ penetrate walls but then damp to zero on both sides (finite)

b. in between walls $\psi(x)$ must be nonzero for some x ,

so $\psi(x)$ must have curvature $\rightarrow T > 0 \rightarrow$ zero point E

c. solutions must oscillate with # nodes increasing with increasing E

d. as k inc \rightarrow V and T inc \rightarrow zero point E will increase

as k decrease \rightarrow $\psi(x)$ becomes continuum state ($V \sim$ const., flat)

e. as v n(q.n.) increase \rightarrow nodes inc \rightarrow T inc \rightarrow V inc, results in more time at turning points, contrast to particle in box, more like classic harmonic oscillator.

[Insert Graph](#)

Solution—can read about details in text (Levine 4.2)

$$\Rightarrow H\Psi(x) = (T + V) \Psi(x) = [-(\hbar^2/2m) d^2/dx^2 + kx^2/2] \Psi(x) = E \Psi(x)$$

$$-(\hbar^2/2m) [d^2/dx^2 + \alpha^2 x^2] \psi(x) = E \psi(x) \text{ where } \alpha^2 = mk/\hbar^2$$

$$[d^2/dx^2 + (2mE/\hbar^2 - \alpha^2 x^2)] \psi(x) = 0 \text{ again recall } \hbar = h/2\pi$$

Recall that solutions $\psi(x)$ must damp to zero as x increase (pass barrier)

One way to do this is multiply oscillating function by $\exp(-x^2/2)$

form $e^{-\alpha x}$ would damp, but need x^2 for $\pm x$ sym. (even) ($c = \alpha/2$ arbitrary)

If $\psi(x) = e^{-x^2/2} f(x)$ then second derivative above reduces to: $[d^2/dx^2] \Psi(x) = \exp(-x^2/2) [(\alpha^2 x^2) f(x) + 2(-\alpha x) f(x) (df/dx) - f(x) + (d^2 f/dx^2)]$

Now could eliminate $\exp(-x^2/2)$ from Schroedinger Eqn since in each term:

$$(\alpha x^2) f(x) + 2(-\alpha x) f(x) [df/dx] - \alpha f(x) + [d^2 f/dx^2] + (2mE/\hbar^2 - \alpha^2 x^2) f(x) = 0$$

Results in 2nd order eqn: $[d^2 f/dx^2] - 2(\alpha x) f(x) [df/dx] + (2mE/\hbar^2 - \alpha) f(x) = 0$

This can be solved with a power series solution: $f(x) = \sum c_n x^n$

Solution has parity $\psi(x) = e^{-\alpha x^2/2} [c_0 + c_1 x + c_2 x^2 + c_3 x^3 + \dots]$

As it must, $[H, \psi] = 0$ since $V = (1/2) kx^2 \rightarrow$ even

Oscillation will develop from the relative signs of c's for powers of x

Solution known as Hermite polynomials to this form differential eqn

$$\Psi_v(x) = N_v \exp(-\alpha x^2/2) H_v(x) = N_v \exp(-y^2/2) H_v(y) \quad \text{--where } y = \alpha^{1/2} x$$

$$H_0(y) = 1 \qquad H_4(y) = 16y^4 - 48y^2 + 12 \qquad \text{even}$$

$$H_1(y) = 2y \qquad H_5(y) = 32y^5 - 160y^3 + 120y \qquad \text{odd}$$

$$H_2(y) = 4y^2 - 2 \qquad H_6(y) = 64y^6 - 480y^4 + 720y^2 - 120 \qquad \text{even}$$

$$H_3(y) = 8y^3 - 12y \qquad H_7(y) = 128y^7 - 1344y^5 + 3360y^3 - 1680y \qquad \text{odd}$$

[INSERT GRAPH](#)

See term oscillate in sign—causes oscillation of $\Psi_v(x)$

$v = 0$ just exponential decay from 1 at $x=0$

$v = 1$ odd, $\Psi = 0$ at $x = 0$ then inc + and - and damp with opposite sign curvature

$v = 2$ even - $\Psi = -2$ at $x = 0$, then curve positive ($E > V$), but as x inc. $4y^2 > |-2|$

so Ψ becomes (+), opposite curvature then needed for decay--**oscillation**

[INSERT GRAPH](#)

As v inc amplitude grows when $E \sim V$ (i.e. $T \sim 0$) called turning point, classically,

in q.m. this is due to higher powers increasing faster than lower ones.

Solving the equation: $E_v = (v+1/2)h\nu \rightarrow \nu = (1/2) \sqrt{k/m}$ or $\nu = 2\pi \nu$ m/h

[INSERT GRAPH](#)

So see steady, uniform increase of E with v

With $\Delta E = E_{v+1} - E_v = h\nu$, where ν is the frequency of the oscillator

$v=0 \rightarrow E_0 = h\nu/2$ - zero point energy, continually oscillating

or $T \rightarrow 0$ so $\langle p^2 \rangle > 0$ so need $\langle x^2 \rangle > 0$ which fits the uncertainty principle

Balls on springs or pendulums are nice, but can we use this for **chemistry**?

Harmonic Oscillator is a good model for vibration of molecules

[INSERT GRAPH](#)

Potential energy, diatomic: $U(R) = \langle H_{el}(R) \rangle + V_{nn}(R)$ where V_{nn} nuclear repulse

Electrons hold atoms together nuclei repell (+ $\leftarrow \rightarrow$ +) keep atoms from collapse

At long distance this approaches Energy of 2 atoms- arbitrary zero

At short distance, repulsion dominate - $U_{eq} \rightarrow$ lowest energy at R_{eq}

Approximate bottom of well as parabola $U(R) \sim (1/2)k(\Delta R)^2$ where $R = R - R_{eq}$

“harmonic approximation” -- (note power series expansion):

$$U(\mathbf{R}) = U(\mathbf{R}_e) + \left. \frac{dU}{d\mathbf{R}} \right|_{\mathbf{R}_e} (\mathbf{R} - \mathbf{R}_e) + \frac{1}{2} \left. \frac{d^2U}{d\mathbf{R}^2} \right|_{\mathbf{R}_e} (\mathbf{R} - \mathbf{R}_e)^2 + \dots$$

First term const, second zero at minimum, so the third term is lowest order non-zero, non-constant term gives rise to harmonic motion

Higher terms eg. $\left. \frac{d^3U}{d\mathbf{R}^3} \right|_{\mathbf{R}_e} (\mathbf{R} - \mathbf{R}_e)^3$ etc -- Anharmonic corrections

Kinetic energy must be modified since vibration is relative motion

not interested in translation so reduce coordinates to $\mathbf{q} = \mathbf{R} - \mathbf{R}_e$ 1-D

And mass term modifies to: $\mu = (\mathbf{m}_1\mathbf{m}_2/\mathbf{m}_1+\mathbf{m}_2)$ -- which is reduced mass

$$\mathbf{H}_{\text{vib}} \Psi_v(\mathbf{q}) = \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{d\mathbf{q}^2} + k\mathbf{q}^2/2 \right] \Psi_v(\mathbf{q}) = \mathbf{E} \Psi_v(\mathbf{q})$$

Solution just as before $E_0(v + 1/2)\hbar$

extent $U(\mathbf{R}) \sim k\mathbf{q}^2/2$ get even spacing of levels $E = \hbar \omega$, where ω = freq vib

If differ from this, get anharmonic correction, $E < \hbar \omega$, spacings collapse

This happens at top of potential where curve bends to allow dissociation

IR spectroscopy (handwaving insight only - details Chem 543)

electric field of light leads to a resonant oscillator when $\omega_{\text{light}} = \omega_{\text{vib}}$

if molecule has a change ($d\mu/d\mathbf{q} \neq 0$) in electric dipole moment (μ)

classically this causes molecule to have larger amplitude

– in q.m. this leads to a change in quantum number, v , and energy E_v

Harmonic oscillator: $\Delta v = \pm 1 = v - v'$ **only** + \rightarrow absorption, - \rightarrow emission

$$\Delta E = (v + 1/2)\hbar\omega - (v' + 1/2)\hbar\omega = \hbar\omega \text{ -- all allowed transitions overlap}$$

IR spectrum $v = 0 \rightarrow v' = 1$ (fundamental) yields the frequency of vibration for dipolar oscillator -- frequency vary like $\sqrt{k/\mu}$

-- strong bonds higher freq C-C $\sim 1000 \text{ cm}^{-1}$, C=C $\sim 1600 \text{ cm}^{-1}$, C \equiv C $\sim 2200 \text{ cm}^{-1}$

-- higher mass lower freq HCl $\sim 2800 \text{ cm}^{-1}$, DCl $\sim 2000 \text{ cm}^{-1}$

*Also responsible for kinetic isotope effects: deuterate a position and if H-motion involved in reaction coordinate, the rate will decrease due to difference in zero point energy of ground and excited (transition) state [INSERT GRAPH](#)

*Also affect thermodynamics: Boltzmann $N_i/N_j = g_i/g_j \exp[-(E_i-E_j)/kT]$
this gives the relative population (N_i/N_j) of $E_i + E_i$ energy levels, so changing (eg. lowering) frequency changes (increases) population of (higher quantum number) E- levels and increases entropy (corresponds to the # states populated)