In QM, we examine behavior of Particles subject to <u>conservative forces</u>, which can be described by a potential: $F = -\frac{dV}{dx}$

Called conservative because sum of kinetic + potential energies are conserved

$$E = K + V = \text{const}$$

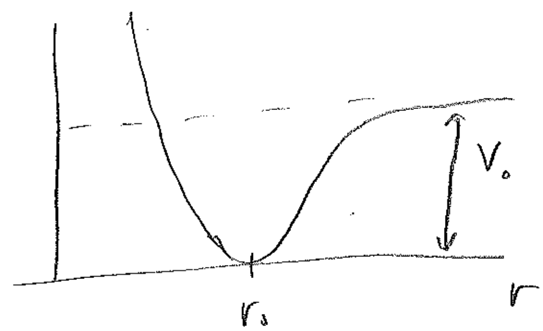
$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

Diatomic molecules: H_2, O_2 [discussion in French]

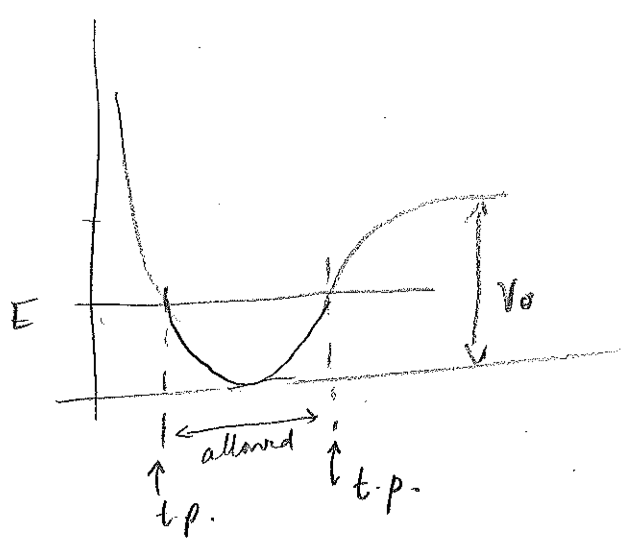
Let r = separation between atoms

Let r_0 = equilibrium separation (bond length)

Let $V(r)$ = interatomic potential energy



[At $r=r_0$, $V = \min$, $F = -\frac{dV}{dr} = 0$.
If $r<r_0$, $V\uparrow$, $F>0$, atoms push back
If $r>r_0$, $V\uparrow$, $F<0$, atoms pull together]

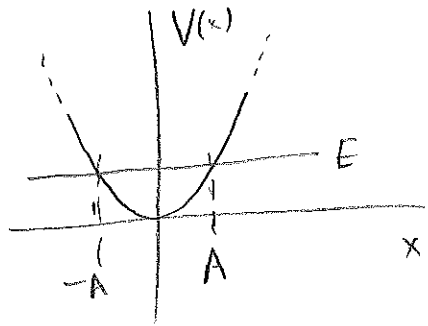


If $E<V_0$, atoms oscillate btw. t.p.

If $E>V_0$, bond breaks.

Near $r=r_0$, potential is approx. quadratic: $V(r) \approx \frac{1}{2}k_s(r-r_0)^2$

For convenience, define $x = r - r_0$, so $x = 0$ is minimum



$V(x) = \frac{1}{2} k_s x^2$

$F = -\frac{dV}{dr} = -k_s x$ (Hooke's law)

behaves like harmonic oscillator

$E = K + \frac{1}{2} k_s x^2$

Let $x = \pm A$ be turning points (where $K = 0$)

$\Rightarrow E = \frac{1}{2} k_s A^2$

Newton's 2nd law $F = ma$

Classically, motion described by

$m \frac{d^2 x}{dt^2} = -k_s x$ where $\omega^2 = \frac{k_s}{m}$

Solution $x = A \cos(\omega t + \phi)$
(simple harmonic motion)

$\therefore$ we can write $V(x) = \frac{1}{2} m\omega^2 x^2$ and $E = \frac{1}{2} m\omega^2 A^2$.

Quantum mechanically, can't describe particle as moving along a well-defined trajectory.

We'll discover that

① E is quantized

② $E = \hbar\omega (n + \frac{1}{2})$ $n = 0, 1, 2, \ldots$

③ $E_{min} = \frac{1}{2}\hbar\omega$ "zero point energy"
↳ not 0.

④ particle can be found w/ small probability in forbidden region.

Quantum harmonic oscillator

t.i.S.e for particle in a potential $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + \frac{1}{2}m\omega^2x^2u = Eu$$

[Just as it is useful to write integrals in terms of dimensionless variables, so too w/ differential eqns.]

Find combinations of constants $m, \hbar, \omega$ w/ units of energy & length.

$\hbar\omega$ has units of energy, so ratio $\frac{E}{\hbar\omega}$ is dimensionless

Define $\mathcal{E} = \frac{E}{\hbar\omega}$ (dimensionless energy)

Divide eqn by $\hbar\omega$:

$$-\frac{\hbar}{2m\omega}\frac{d^2u}{dx^2} + \frac{1}{2}\underbrace{\frac{m\omega}{\hbar}}x^2u = \mathcal{E}u$$

$$\left[\frac{kg\cdot s^{-1}\cdot m^2}{m\cdot\left(\frac{kg\cdot m}{s}\right)}\right]$$

Observe that $\frac{m\omega}{\hbar}x^2$ is dimensionless

Define $y = \sqrt{\frac{m\omega}{\hbar}}\,x$ (dimensionless position)

Observe $\frac{d}{dx} = \frac{dy}{dx}\frac{d}{dy} = \sqrt{\frac{m\omega}{\hbar}}\frac{d}{dy} \Rightarrow \frac{d^2}{dx^2} = \frac{m\omega}{\hbar}\frac{d^2}{dy^2}$

$$-\frac{1}{2}\frac{d^2u}{dy^2} + \frac{1}{2}y^2u = \mathcal{E}u$$

$$\left(-\frac{d^2}{dy^2} + y^2\right) u = 2\epsilon u$$

Let $\hat{D} = \frac{d}{dy}$

$$(-\hat{D}^2 + y^2) u = 2\epsilon u$$

Algebraically $(-D^2 + y^2) = (-D + y)(D + y)$
but this doesn't quite work for operators

Consider $(-\hat{D} + y)(\hat{D} + y) u$

$$= -\hat{D}^2 u + y\hat{D} u - \underbrace{\hat{D}(yu)}_{u + y\hat{D}u} + y^2 u$$

$$= \underbrace{(-D^2 + y^2) u}_{2\epsilon u} - u$$

$$= (2\epsilon - 1) u$$

$\therefore$ $\frac{1}{2}(-\hat{D} + y)(\hat{D} + y) = (\epsilon - \frac{1}{2}) u$

Define

$$\hat{a} = \frac{1}{\sqrt{2}}(\hat{D} + y)$$

$$\hat{a}^+ = \frac{1}{\sqrt{2}}(-\hat{D} + y)$$

$$\lambda = \epsilon - \frac{1}{2}$$

Then $\boxed{\hat{a}^+ \hat{a} u = \lambda u}$ ← eigenvalue equation for operator $\hat{a}^+\hat{a}$

Spoiler: we will discover that eigenvalues λ are all non-negative integers
ie $\lambda = 0, 1, 2, \ldots$

[Try a simpler equation]

Let u_0 be a function that obeys

$$\hat{a} u_0 = 0$$

$$\left(\frac{d}{dy} + y\right) u_0 = 0$$

$$\frac{du_0}{dy} = -y u_0$$

$$\frac{du_0}{u_0} = -y\,dy$$

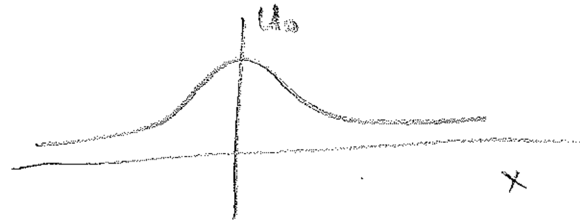
$$\ln u_0 = -\frac{1}{2} y^2 + \text{const}$$

$$u_0 = B e^{-\frac{y^2}{2}} = B e^{-\frac{m\omega}{2\hbar} x^2}$$

[use B, because A = turning pts]

gaussian function

[normalize it later]



Now $\hat{a} u_0 = 0 \Rightarrow \hat{a}^\dagger \hat{a} u_0 = 0 = 0 \cdot u_0$

so u_0 obeys t.i.s.e. w/ $\lambda = 0$ & $\therefore E_0 = \frac{1}{2}\hbar\omega$

u_0 has no nodes so this will be the lowest possible energy (ground state)

[observe $E_0 > 0$ like particle in a box]

[Recall: already met this in a problem]

We now construct all the other eigenfunctions through induction.

Suppose u_n obeys the t.i.S.e. for $\lambda = n$, i.e. $E_n = \hbar\omega(n+\frac{1}{2})$

$a^\dagger a\, u_n = n u_n$ and is normalized: $\int_{-\infty}^{\infty} u_n^* u_n \, dx = 1$

[we have one such solution, viz. u_0]

Claim: $a^\dagger u_n$ obeys the t.i.S.e. for $\lambda = n+1$,
and therefore is proportional to u_{n+1}

(use exercise)

Proof: $a^\dagger a\,(a^\dagger u_n) = a^\dagger (a a^\dagger) u_n = a^\dagger (a^\dagger a + 1) u_n$

$$= a^\dagger (\underbrace{a^\dagger a u_n}_{n u_n}) + a^\dagger u_n = (n+1)\, a^\dagger u_n$$

QED

Thus $u_{n+1} \propto a^\dagger u_n$

!! Still need to normalize u_{n+1}. Let $u_{n+1} = c\, a^\dagger u_n$

$$1 = \int u_{n+1}^* u_{n+1} \, dx = |c|^2 \int (a^\dagger u_n)^* (a^\dagger u_n)\, dx$$

IBP (explain) $\longrightarrow$ $= |c|^2 \int u_n^* \, a a^\dagger u_n \, dx = |c|^2 \int u_n^* \,(a^\dagger a + 1)\, u_n$

$$= |c|^2 \int u_n^* (n+1) u_n \, dx = |c|^2 (n+1) \underbrace{\int u_n^* u_n \, dx}_{1}$$

$$\Rightarrow |c|^2 = \frac{1}{\sqrt{n+1}}$$

$$\boxed{u_{n+1} = \frac{1}{\sqrt{n+1}}\, a^\dagger u_n}$$

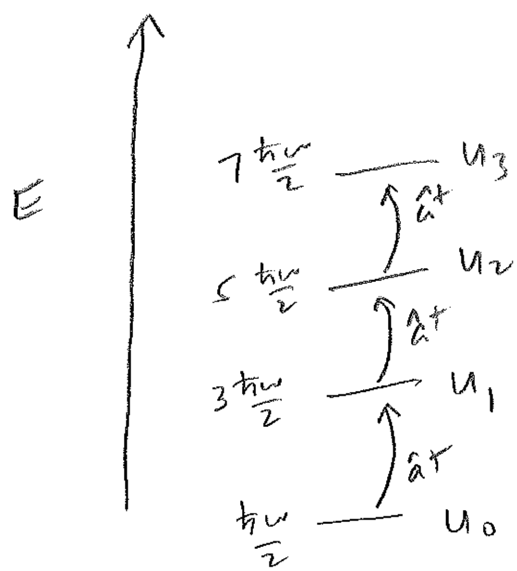
$$u_n = \frac{1}{\sqrt{n}}\,\hat{a}^{+} u_{n-1}$$

$$= \frac{1}{\sqrt{n}}\,\hat{a}^{+}\,\frac{1}{\sqrt{n-1}}\,\hat{a}^{+}\,u_{n-2}$$

$$= \frac{1}{\sqrt{n(n-1)(n-2)\cdots}}\,\underbrace{\hat{a}^{+}\,\hat{a}^{+}\cdots\hat{a}^{+}}_{n \text{ times}}\,u_0$$

$$= \frac{1}{\sqrt{n!}}\left(\hat{a}^{+}\right)^{n} u_0$$

$$= \frac{1}{\sqrt{n!\,2^n}}\left(-\frac{d}{dy} + y\right)^{n} B\,e^{-\frac{1}{2}y^2}$$



$\hat{a}^{+}$ is a raising operator because it raises the eigenvalue λ by 1 and the energy by $\hbar\omega$

Normalize $u_0 = B\, e^{-\frac{1}{2}y^2}$

$$1 = \int_{-\infty}^{\infty} dx\, |u_0|^2 = |B|^2 \int_{-\infty}^{\infty} dx\, e^{-y^2} = |B|^2 \sqrt{\frac{\hbar}{m\omega}} \int_{-\infty}^{\infty} dy\, e^{-y^2}$$

$$y = \sqrt{\frac{m\omega}{\hbar}}\, x \Rightarrow dx = \sqrt{\frac{\hbar}{m\omega}}\, dy$$

$$I = \int_{-\infty}^{\infty} dy\, e^{-y^2}$$ not solvable w/ elementary functions (Numerical integration $\Rightarrow$ 1.77...)

Trick: $I^2 = \int_{-\infty}^{\infty} dy\, e^{-y^2} \int_{-\infty}^{\infty} dx\, e^{-x^2}$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\, dy\, e^{-(x^2+y^2)}$$ ($\rightarrow$ polar)

$$= \int_0^{2\pi} d\theta \int_0^{\infty} r\, dr\, e^{-r^2}$$

$$= \pi \int_0^{\infty} 2r\, dr\, e^{-r^2}$$ $u = r^2$, $du = 2r\,dr$

$$= \pi \int_0^{\infty} du\, e^{-u}$$

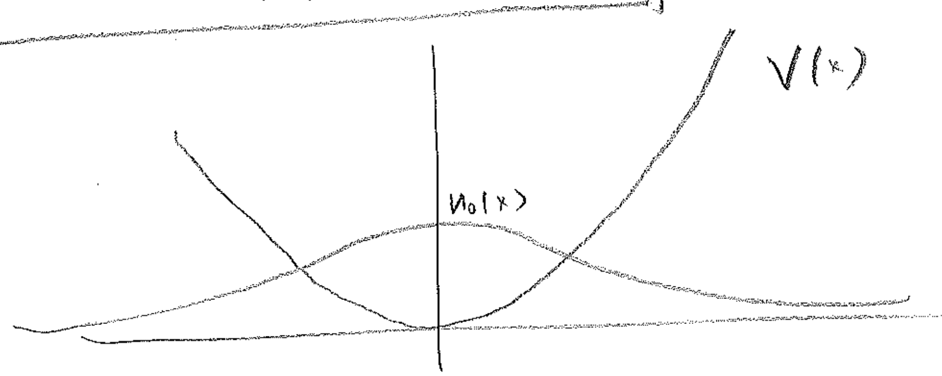
$$= \pi \left[-e^{-u}\right]\Big|_0^{\infty}$$

$$= \pi$$

$$\Rightarrow I = \sqrt{\pi}$$

$$1 = |B|^2 \sqrt{\frac{\hbar\pi}{m\omega}} \Rightarrow B = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$$

$$\boxed{u_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\left(\frac{m\omega}{2\hbar}\right)x^2}}$$



Exercise.

for hmc osc

t.i.S.e. is $\hat{a}^{+}\hat{a}\, u = \lambda u$, where $E = \hbar\omega(\lambda + \frac{1}{2})$

Suppose u_n obeys t.i.S.e w/ $\lambda = n$

(a) Show that $\hat{a} u_n$ obey t.i.S.e w/ $\lambda = n-1$

i.e. w/ energy lower than u_n

$\hat{a}$ = lowering operator

(b) why can't you use this approach on the gnd state eigenfn u_0 to obtain a solution w/ energy $< E_0 = \frac{1}{2}\hbar\omega$?

Exercise

check that the eigenfunction $u_1(x)$ of the first excited state of the harmonic oscillator is normalized!

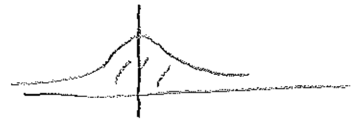
$$y = \sqrt{\frac{m\omega}{\hbar}}\, x$$

$$\int |u_1|^2 dx = \sqrt{\frac{\hbar}{m\omega}} \int |u_1|^2 dy$$

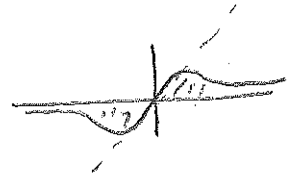
$$= \sqrt{\frac{\hbar}{m\omega}} \sqrt{\frac{m\omega}{\pi\hbar}}\, 2 \underbrace{\int y^2 e^{-y^2} dy}_{\frac{\sqrt{\pi}}{2}} = 1$$

other integrals

$$\int_{-\infty}^{\infty} dy \; e^{-y^2} = \sqrt{\pi}$$



$$\int_{-\infty}^{\infty} dy \; y\, e^{-y^2} = 0$$



(antisymmetric, odd)

$$\int_{-\infty}^{\infty} dy \; y^2 e^{-y^2} = \; ?$$

Let $y = \sqrt{\alpha}\, u$

$dy = \sqrt{\alpha}\, du$

$$\int dy\, e^{-y^2} = \sqrt{\alpha} \int du\, e^{-\alpha u^2} = \sqrt{\pi}$$

$$\int du\, e^{-\alpha u^2} = \sqrt{\frac{\pi}{\alpha}}$$

Let $f(\alpha) = \int du\, e^{-\alpha u^2}$, $\qquad g(\alpha) = \sqrt{\frac{\pi}{\alpha}}$

$$f(\alpha) = g(\alpha)$$

$$\Rightarrow \frac{df}{d\alpha} = \frac{dg}{d\alpha}$$

$$\frac{df}{d\alpha} = \frac{d}{d\alpha} \int du\, e^{-\alpha u^2} = \int du \, \frac{d}{d\alpha} e^{-\alpha u^2} = \int du\, (-u^2) e^{-\alpha u^2}$$

$$\frac{dg}{d\alpha} = -\frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}$$

$$\Rightarrow \int du\, u^2 e^{-\alpha u^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^3}}$$

Take another $\frac{d}{d\alpha}$ to get $\int du\, u^4 e^{-\alpha u^2}$ $\qquad \left[\frac{3}{4}\sqrt{\pi} \right]$

Any even power $\qquad \left[\frac{(n-1)!!}{2^{n/2}} \sqrt{\pi} \right]$

Odd powers $\Rightarrow \int du\, u^{odd} e^{-\alpha u^2} = 0$

(review)

t.i.S.e for harmonic osc. can be written as an eigenvalue eqn:

$$\hat{a}^+ \hat{a}\, u = \lambda u$$

This eqn has allowed eigenvalues $\lambda = n$ where $n = 0, 1, 2, \ldots$

$$\hat{a}^+ \hat{a}\, u_n = n u_n \quad \Rightarrow E_n = \hbar\omega\left(n + \tfrac{1}{2}\right)$$

Ground state eigenfunction u_0 obeys $\hat{a}\, u_0 = 0$ and has form

$$u_0 = B e^{-\frac{1}{2}y^2} \quad \text{where} \quad B = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$$

If u_n has eigenvalue n, then $\hat{a}^+ u_n$ has eigenvalue $n+1$

so $\hat{a}^+$ is a raising operator

$$u_n = \frac{1}{\sqrt{n!}}\left(\hat{a}^+\right)^n u_0$$

$$= \frac{B}{\sqrt{n!\,2^n}}\left(-\frac{d}{dy} + y\right)^n e^{-\frac{1}{2}y^2}$$

$$u_n = \frac{B}{\sqrt{n!\,2^n}}\, e^{-\frac{1}{2}y^2} \underbrace{e^{\frac{1}{2}y^2}\left(-\frac{d}{dy}+y\right)^n e^{\frac{1}{2}y^2}}$$

This is a polynomial of order n
called $H_n(y)$, Hermite polynomial

[explain why polynomial]

$$\Rightarrow \boxed{\begin{array}{l} u_n = \dfrac{1}{\sqrt{n!\,2^n}}\left(\dfrac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} H_n(y)\, e^{-\frac{1}{2}y^2} \\ \epsilon_n = \hbar\omega\left(n+\frac{1}{2}\right) \end{array}}$$

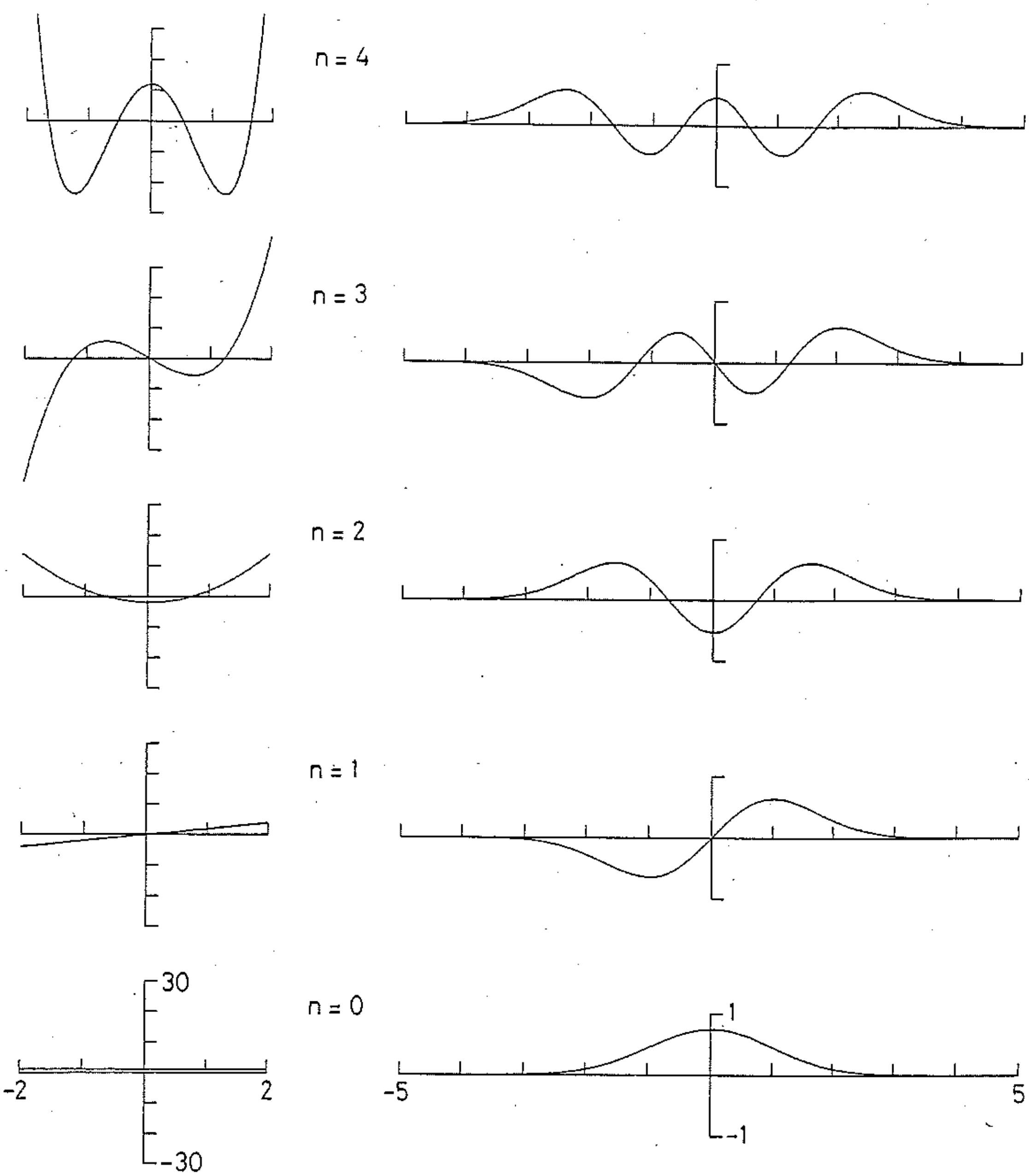
→ see plots
- # node = n
- equal spacing
- t.p. = pt of inflection

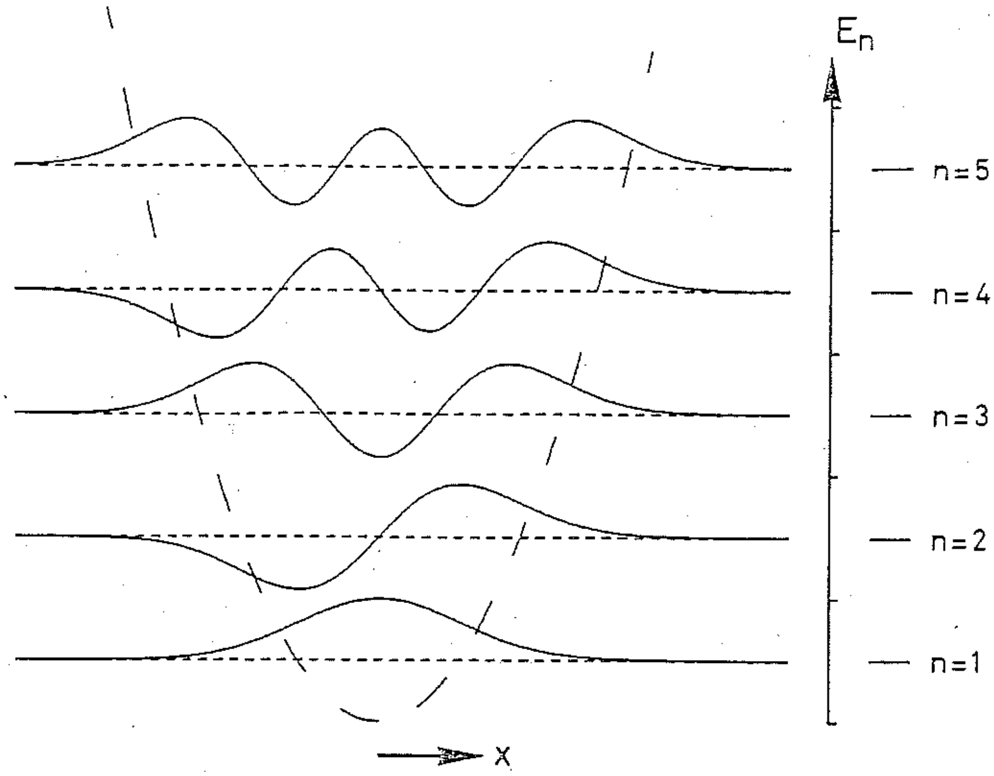
n	H_n
0	1
1	$2y$
2	$4y^2-2$

$$e^{\frac{1}{2}y^2}\left(-\frac{d}{dy}+y\right)e^{-\frac{1}{2}y^2} = e^{\frac{1}{2}y^2}(y+y)e^{-\frac{1}{2}y^2}$$

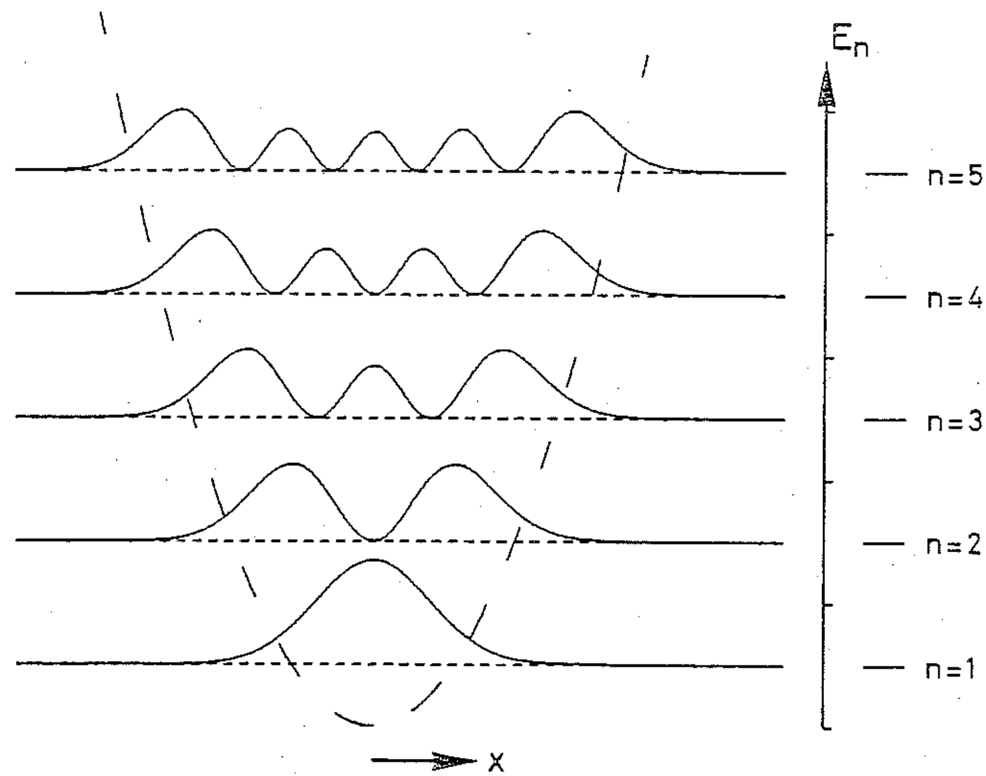
$$e^{\frac{1}{2}y^2}\underbrace{\left(-\frac{d}{dy}+y\right)\left(2ye^{-\frac{1}{2}y^2}\right)}$$

$$(\underbrace{-2-(2y)(-y)+y(2y)}_{4y^2-2})\,e^{-\frac{1}{2}y^2}$$


n = 4
n = 3
n = 2
n = 1
n = 0
30
-30
-2
2
-5
5
1
-1

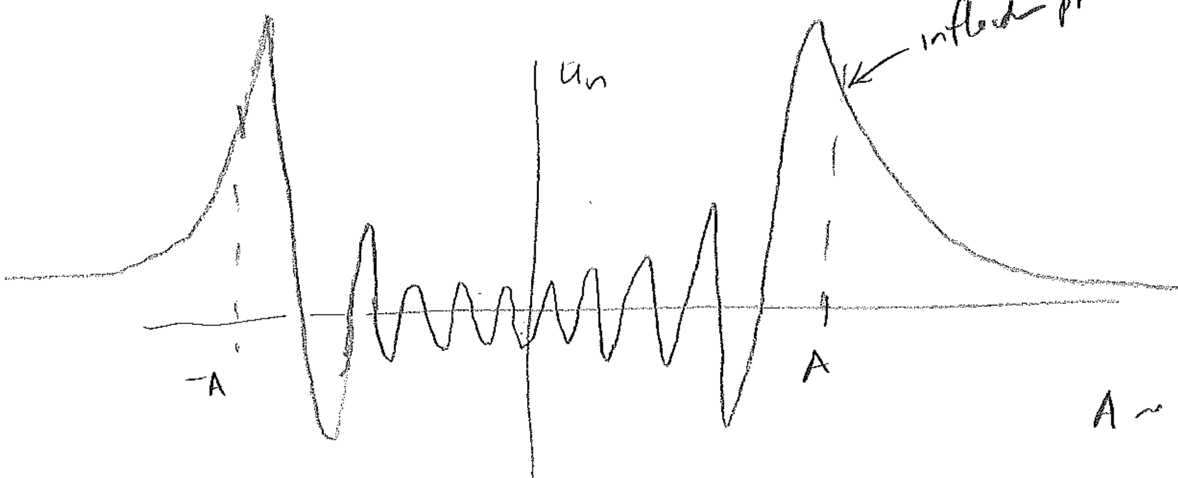


E_n
n = 5
n = 4
n = 3
n = 2
n = 1
x



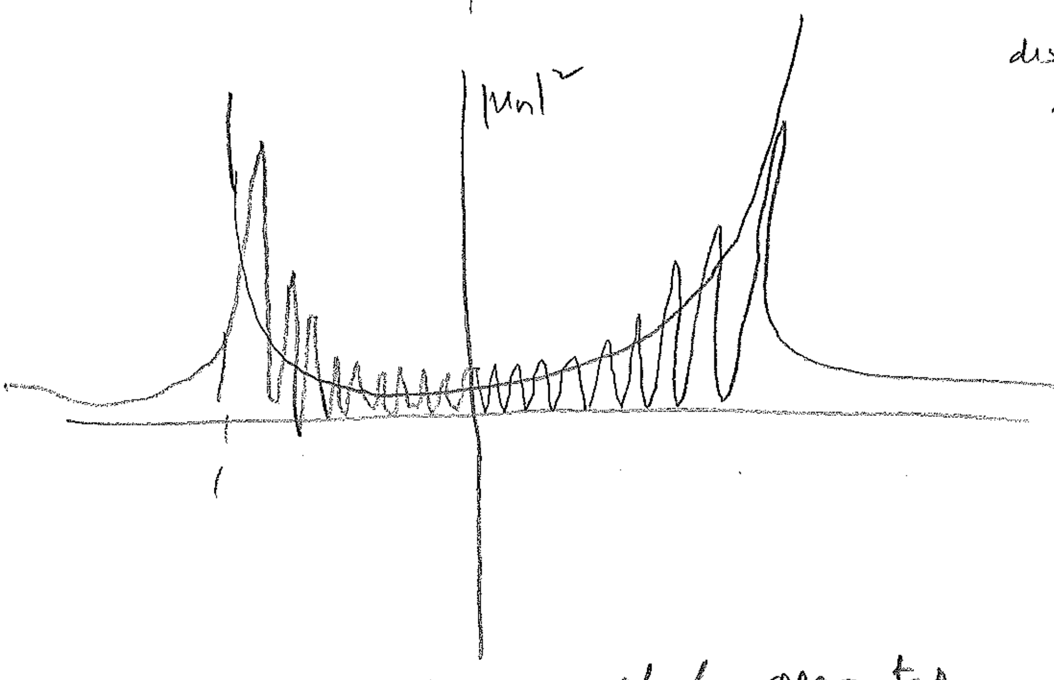
E_n
n = 5
n = 4
n = 3
n = 2
n = 1
x

large n → classical physics (correspondence principle)



$A \sim \sqrt{\frac{2\hbar}{m\omega}}\sqrt{n}$

distance between nodes
$\sim \frac{1}{\sqrt{n}}$



Classically particle moves slowly near t.p.