# One Dimensional Examples 2

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# Time Independent Hamiltonian

$$\hat{H}\psi\left(q_1, q_2, \ldots q_n, t\right) = i\eta \frac{\partial \psi\left(q_1, q_2, \ldots q_n, t\right)}{\partial t}$$

$$\psi\left(q_1, q_2, \ldots q_n, t\right) = \psi\left(q_1, q_2, \ldots q_n\right) Exp\left(-iEt / \eta\right)$$

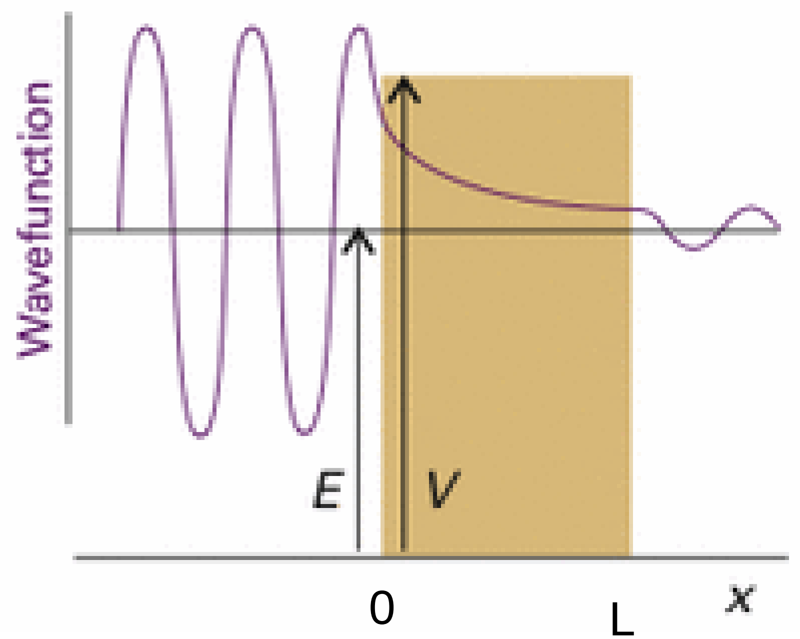
$$\hat{H}\psi\left(q_1, q_2, \ldots q_n\right) = E\psi\left(q_1, q_2, \ldots q_n\right)$$

If the Hamiltonian Operator does not have time dependence then the time dependent problem is transferred to a time independent problem of finding the eigenfunction and eigenvalue of the Hamiltonian operator

# Penetration of Barrier

$$T(E)=\frac{|A''|^2}{|A|^2}=\left[1+\frac{\left(Exp(\kappa L)-Exp(-\kappa L)\right)^2}{16\frac{E}{V}\left(1-\frac{E}{V}\right)}\right]^{-1}$$

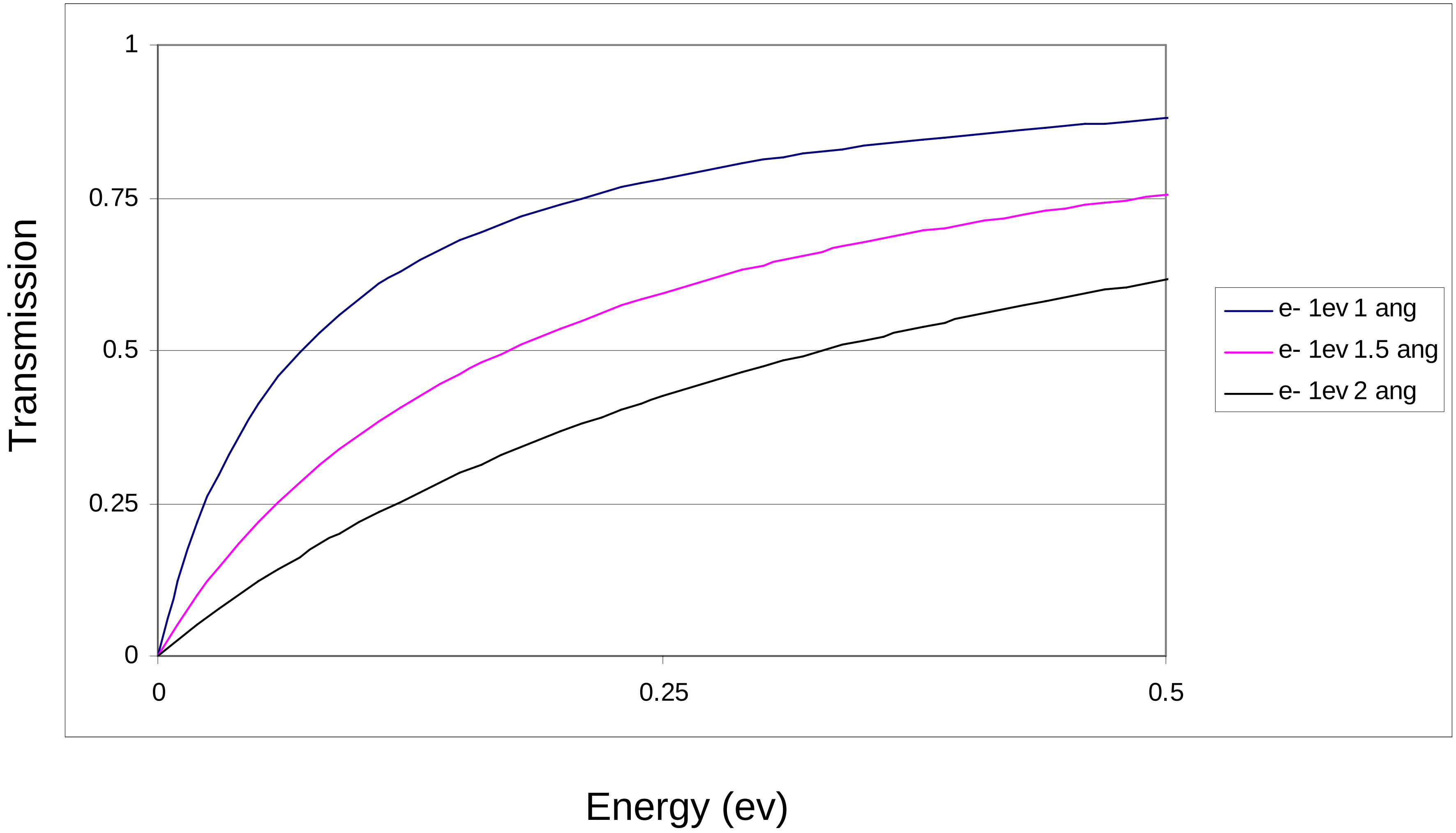
$$\kappa\eta=\sqrt{2m(V-E)}$$



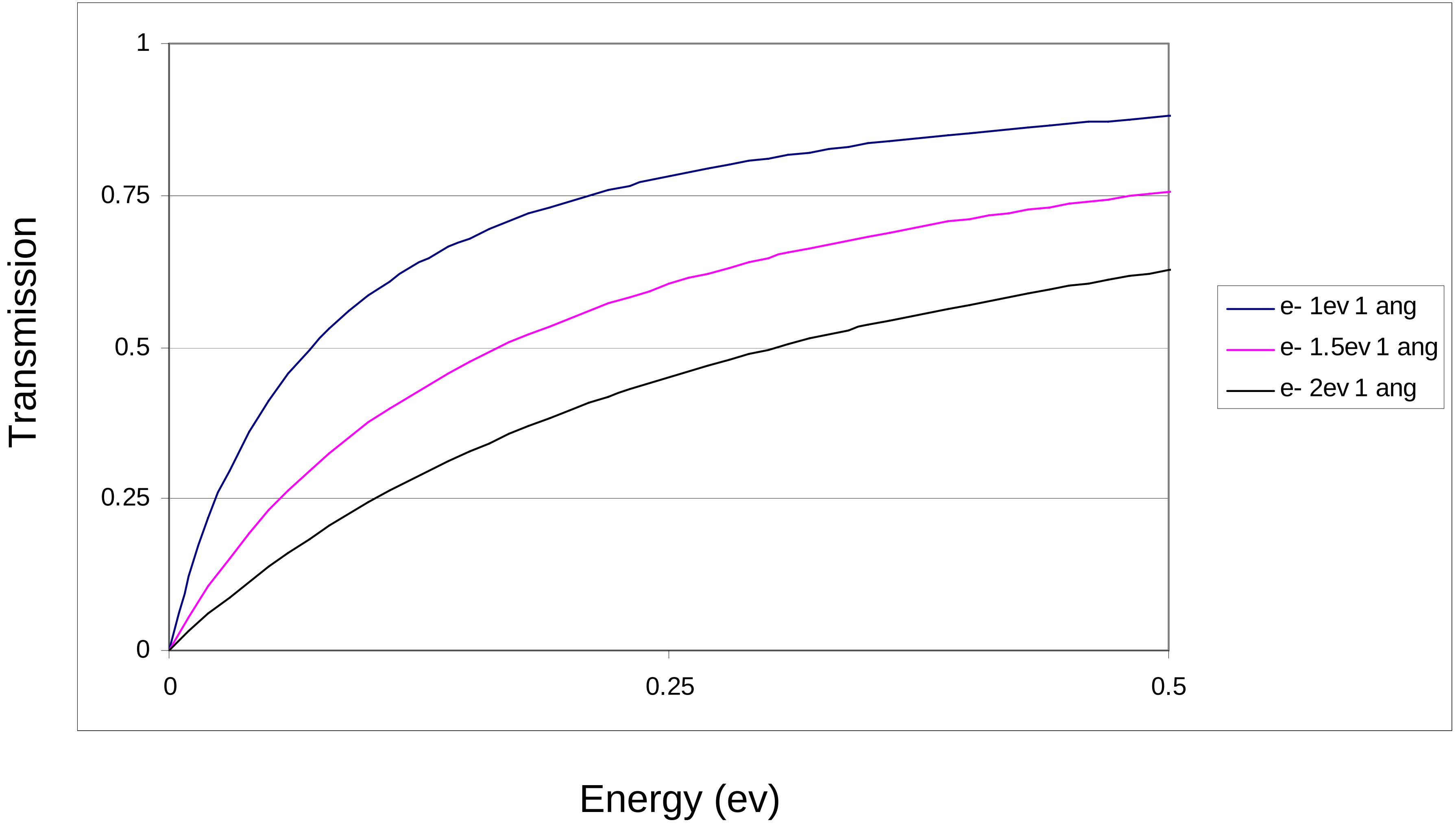

Three parameters we can control
Mass of particle
Barrier Height
Length of Barrier

Try electron with 1 angstrom barrier length with 1 ev barrier

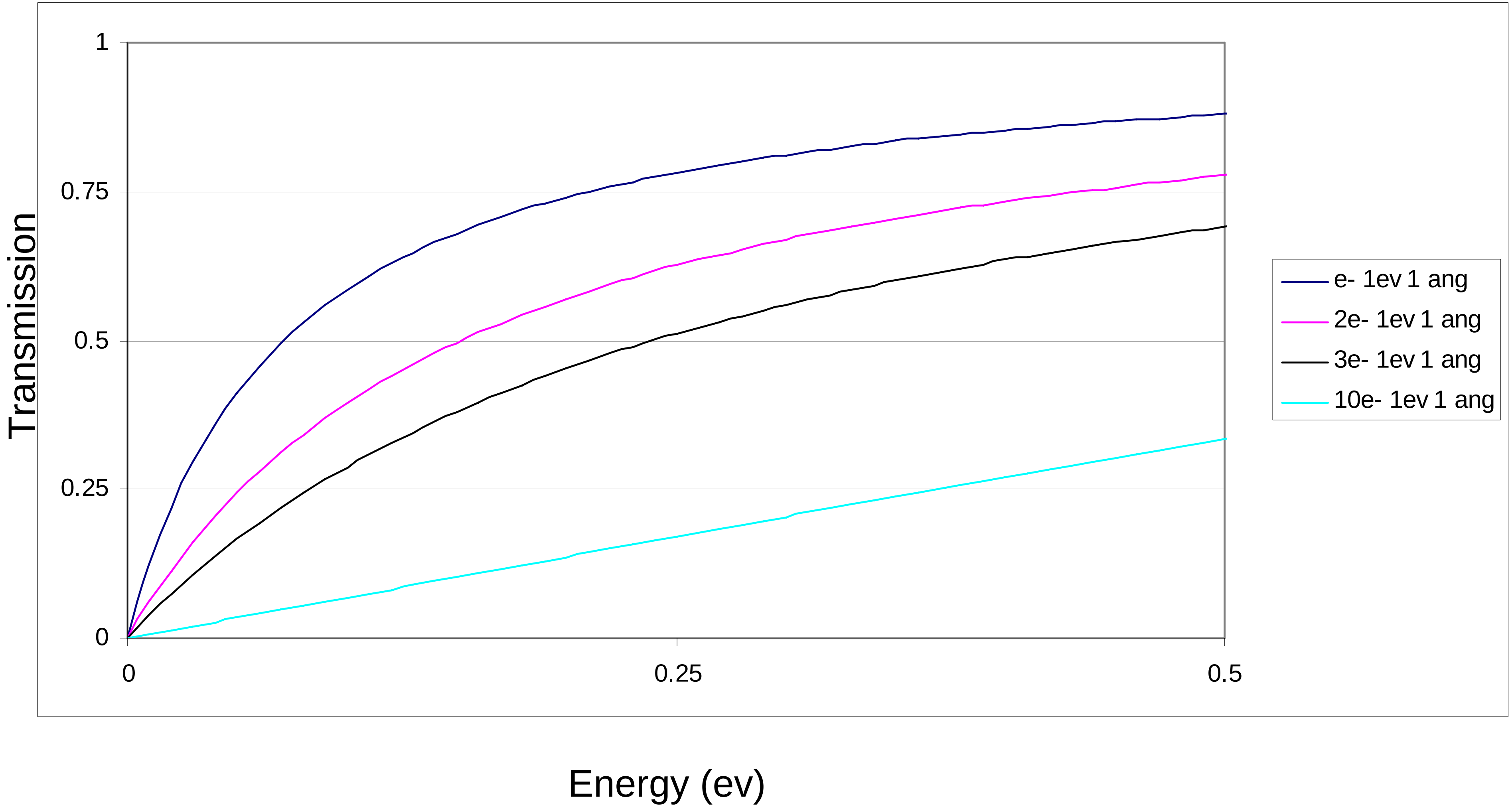
# Barrier Height Dependence



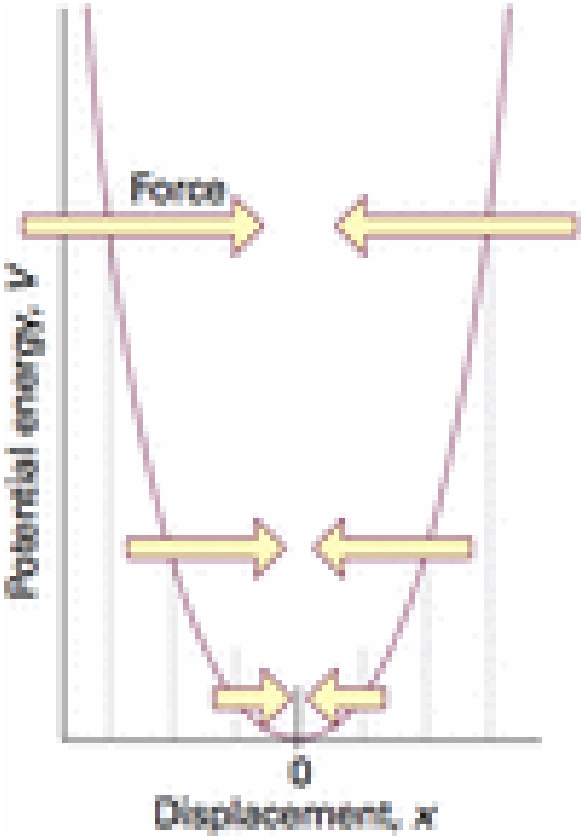
# Length Dependence



# Mass Dependence



# Harmonic Oscillator Classical 1




Restoring force proportional to distance

$$F = m\frac{d^2x}{dt^2} = -kx$$ $k$: force constant

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

We defined $\omega = \sqrt{\frac{k}{m}}$

General Solution is

$$\begin{aligned} x(t) &= AExp(i\omega t) + BExp(-i\omega t) \\ &= C\cos(\omega t) + D\sin(\omega t) \\ &= E\sin(\omega t + \delta) = F\cos(\omega t + \delta') \end{aligned}$$

# Harmonic Oscillator Classical 2

Lets take answer to be

$$x(t) = A\sin(\omega t + \delta)$$

$$p(t) = m\dot{x}(t) = m\omega A\cos(\omega t + \delta)$$

$$F = m\frac{d^2x}{dt^2} = -kx$$

potential $\Rightarrow$ Energy

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

$$E = T + V = \frac{1}{2}m\omega^2 A^2 \cos^2(\omega t + \delta) + \frac{1}{2}m\omega^2 A^2 \sin^2(\omega t + \delta)$$

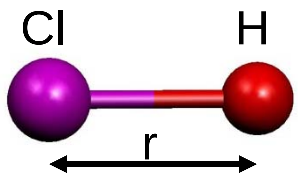
$$= \frac{1}{2}m\omega^2 A^2 = \frac{1}{2}kA^2$$

Energy of oscillator is constant

It determines the maximum displacement

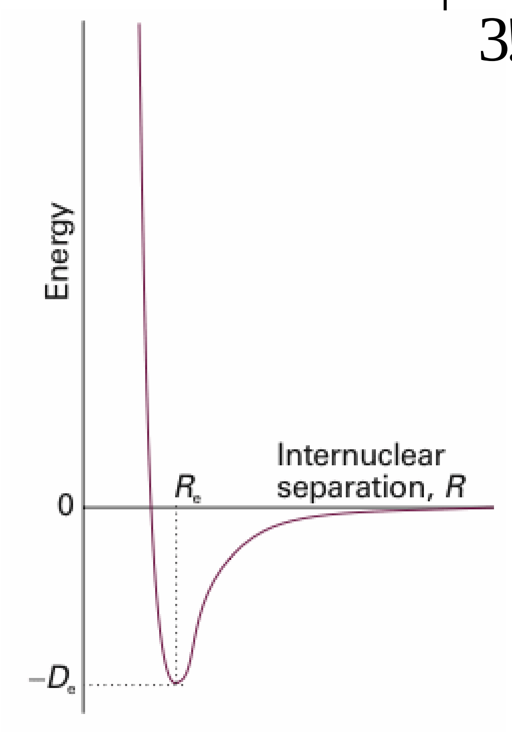
Oscillate with same frequency no matter the total energy

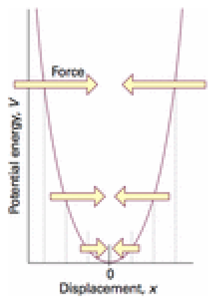
# Taylor's Expansion of Potential Energy




$$\mathrm{V(r)} = V\left(r_{eq}\right) + \left.\frac{dV}{dr}\right|_{r_{eq}}\left(r - r_{eq}\right) + \frac{1}{2}\left.\frac{d^2V}{dr^2}\right|_{r_{eq}}\left(r - r_{eq}\right)^2$$

$$+ \frac{1}{3!}\left.\frac{d^3V}{dr^3}\right|_{r_{eq}}\left(r - r_{eq}\right)^3 + \frac{1}{4!}\left.\frac{d^4V}{dr^4}\right|_{r_{eq}}\left(r - r_{eq}\right)^4 + \ldots..$$




Near the equilibrium bond length the potential energy surface can be approximated using only up to the second derivative

$$\mathrm{V(r)} \approx V\left(r_{eq}\right) + \frac{1}{2}\left.\frac{d^2V}{dr^2}\right|_{r_{eq}}\left(r - r_{eq}\right)^2$$

# Quantum Harmonic Oscillator 1

$$\hat{H}\psi(x) = E\psi(x)$$

$$k = m\omega^2$$

$$\left[-\frac{\eta^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}\right]\psi(x) = E\psi(x)$$

Divide by $\eta\omega$

$$\left[-\frac{\eta}{2m\omega}\frac{d^2}{dx^2} + \frac{m\omega x^2}{2\eta}\right]\psi(x) = \frac{E}{\eta\omega}\psi(x) = \varepsilon\psi(x)$$

Change coordinate so use chain rule for derivative operator

$$y = \sqrt{\frac{m\omega}{\eta}}x$$

$$\frac{d}{dy} = \frac{dx}{dy}\frac{d}{dx} = \sqrt{\frac{\eta}{m\omega}}\frac{d}{dx}$$

$$\frac{d^2}{dy^2} = \frac{d}{dy}\sqrt{\frac{\eta}{m\omega}}\frac{d}{dx} = \frac{\eta}{m\omega}\frac{d^2}{dx^2}$$

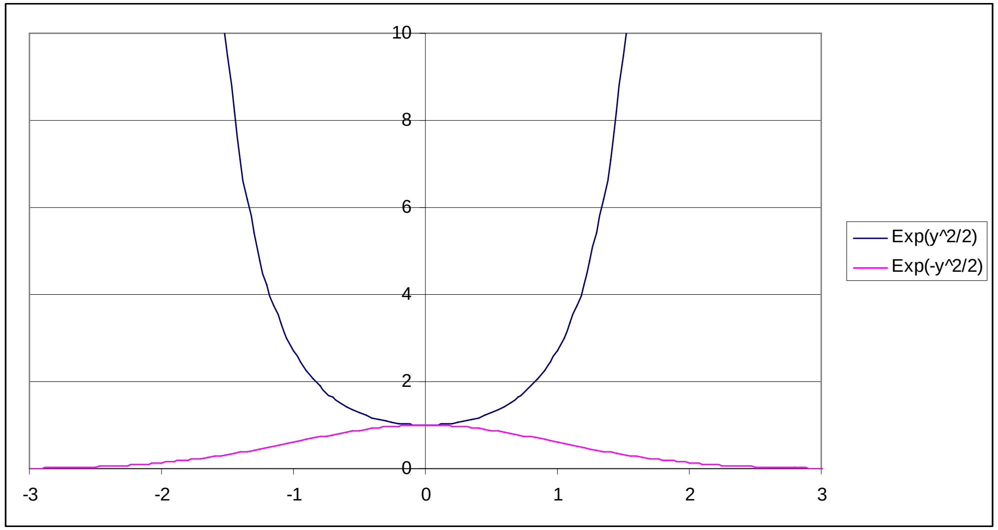
$$\left[-\frac{1}{2}\frac{d^2}{dy^2} + \frac{y^2}{2}\right]\psi(y) = \varepsilon\psi(y)$$

# Quantum Harmonic Oscillator 2

$$\left[-\frac{1}{2}\frac{d^2}{dy^2}+\frac{y^2}{2}\right]\psi(y)=\varepsilon\psi(y)\Rightarrow\frac{d^2\psi(y)}{dy^2}-y^2\psi(y)=-2\varepsilon\psi(y)$$

How to solve this problem? First solve the =0 problem

$$\frac{d^2\psi(y)}{dy^2}-y^2\psi(y)=0 \quad\Rightarrow\quad \frac{d^2\psi(y)}{dy^2}=y^2\psi(y)\rightarrow\psi(y)=\exp\left(\pm\frac{y^2}{2}\right)$$




We need to satisfy

$$\int_{-\infty}^{\infty}\left|\Psi(x)\right|^2 dx=1$$

And V at infinity is large
Wavefunction must decay

We will only keep

$$\psi(y)\approx\exp\left(-\frac{y^2}{2}\right)$$

# Quantum Harmonic Oscillator 3

$$\frac{d^2\psi(y)}{dy^2} - y^2\psi(y) = -2\varepsilon\psi(y)$$

How to solve this problem? First solve the =0 problem

$$\psi(y) \approx \exp\left(-\frac{y^2}{2}\right)$$

Now to solve the real problem

$$\psi(y) = f(y)\exp\left(-\frac{y^2}{2}\right)$$

$$\psi'(y) = f'(y)\exp\left(-\frac{y^2}{2}\right) - yf(y)\exp\left(-\frac{y^2}{2}\right)$$

$$\psi''(y) = f''(y)\exp\left(-\frac{y^2}{2}\right) - 2yf'(y)\exp\left(-\frac{y^2}{2}\right) - f(y)\exp\left(-\frac{y^2}{2}\right) + y^2 f(y)\exp\left(-\frac{y^2}{2}\right)$$

# Quantum Harmonic Oscillator 4

$$\left[f''(y) - f(y) - 2yf'(y) + y^2 f(y) - y^2 f(y)\right]\exp\left(-\frac{y^2}{2}\right) = -2\varepsilon f(y)\exp\left(-\frac{y^2}{2}\right)$$

$$\left[f''(y) - f(y) - 2yf'(y)\right]\exp\left(-\frac{y^2}{2}\right) = -2\varepsilon f(y)\exp\left(-\frac{y^2}{2}\right)$$

$$\left[f''(y) - 2yf'(y) + (2\varepsilon - 1)f(y)\right] = 0$$

If f were described by a polynomial of y

$$f_{n\max}(y) = \sum_{n=0}^{n\max} a_n y^n$$

# Quantum Harmonic Oscillator 5

$$\left[f''(y) - 2yf'(y) + (2\varepsilon - 1)f(y)\right] = 0 \Leftarrow f_{n\max}(y) = \sum_{n=0}^{n\max} a_n y^n$$

$$\sum_{n=2}^{n\max} a_n n(n-1) y^{n-2} - \sum_{n=0}^{n\max} 2a_n n y^n + \sum_{n=0}^{n\max} a_n (2\varepsilon - 1) y^n = 0$$

$$\sum_{n=0}^{n\max} (2\varepsilon - 1 - 2n) a_n y^n + \sum_{m=0}^{m\max = n\max - 2} a_{m+2}(m+2)(m+1) y^m = 0$$

$$\Downarrow$$

$$\sum_{n=0}^{n\max} (2\varepsilon - 1 - 2n) a_n y^n + \sum_{n=0}^{n\max} a_{n+2}(n+2)(n+1) y^n = 0$$

$$(2\varepsilon - 1 - 2n) a_n + (n+2)(n+1) a_{n+2} = 0$$

# Quantum Harmonic Oscillator 6

$$a_{n+2} = \frac{(2n+1-2\varepsilon)a_n}{(n+2)(n+1)}$$

Recursion formula if you define one you can get the next coefficient

Above states that if you define a0 you can define all even coefficients and if you define a1 you define all odd coefficients

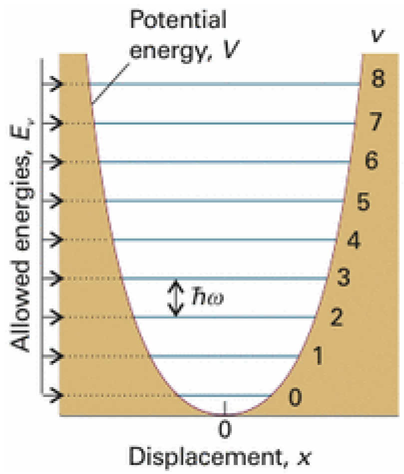
So only can be odd function or even function

The above has to converge since $f_{n\max}(y) = \sum_{n=0}^{n\max} a_n y^n$

so $$a_{n\max+2} = 0 = \frac{(2n\max+1-2\varepsilon)a_{n\max}}{(n\max+2)(n\max+1)}$$

$$(2n\max+1-2\varepsilon) = 0$$

$$\varepsilon = \left(n\max+\frac{1}{2}\right) \rightarrow E = \left(n\max+\frac{1}{2}\right)\eta\omega$$



# Quantum Harmonic Oscillator 7

$$f_{n\max}(y) = \sum_{n=0}^{n\max} a_n y^n \qquad \varepsilon = \left(n\max + \frac{1}{2}\right)$$

$$a_{n+2} = \frac{(2n+1-2\varepsilon)a_n}{(n+2)(n+1)} = \frac{(2n+1-2(n\max+1/2))a_n}{(n+2)(n+1)} = \frac{(2n-2n\max)a_n}{(n+2)(n+1)}$$

For each value of nmax we can define all the coefficients by the above equation, regularly we define $a_{nmax}=2^{nmax}$

$$f_0(y) = 1$$

$$f_1(y) = 2y$$

$$f_2(y) = 4y^2 + ?\,y^0$$

$$f_3(y) = ?$$

$$f_4(y) = ?$$

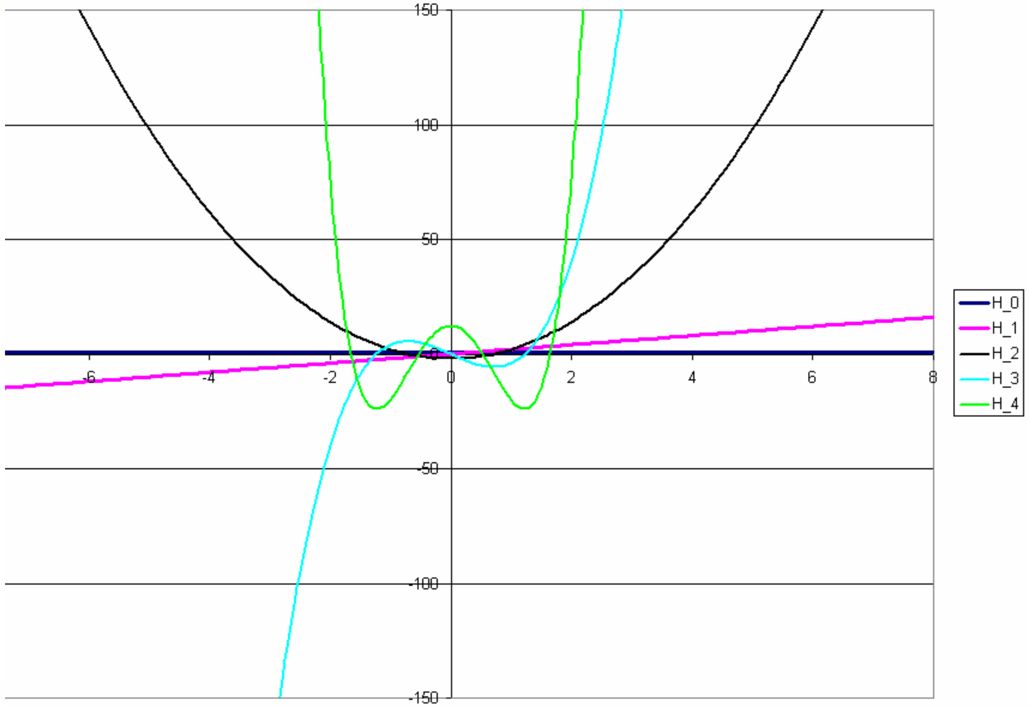
$$a_n = \frac{(n+2)(n+1)}{(2n-2n\max)} a_{n+2}$$

# Hermite Polynomials

What we were calling as *f(y)* have a name called Hermite Polynomials

| $v$ | $H_v(z)$ |
|---|---|
| 0 | $1$ |
| 1 | $2z$ |
| 2 | $4z^2 - 2$ |
| 3 | $8z^3 - 12z$ |
| 4 | $16z^4 - 48z^2 + 12$ |
| 5 | $32z^5 - 160z^3 + 120z$ |
| 6 | $64z^6 - 480z^4 + 720z^2 - 120$ |
| 7 | $128z^7 - 1344z^5 + 3360z^3 - 1680z$ |
| 8 | $256z^8 - 3584z^6 + 13440z^4 - 13440z^2 + 1680$ |

Differential equation: $H_v'' - 2zH_v' + 2vH_v = 0$
Recursion relation: $H_{v+1} = 2zH_v - 2vH_{v-1}$
Orthogonality: $\int_{-\infty}^{\infty} H_v(z)H_{v'}(z)e^{-z^2}\,dz = 0 \quad \text{for } v \neq v'$
Normalization: $\int_{-\infty}^{\infty} H_v(z)^2 e^{-z^2}\,dz = \pi^{1/2}2^v v!$



# Wavefunction

$$\psi(y) = f(y)\exp\left(-\frac{y^2}{2}\right)$$

$$\psi_n(y) = C_n H_n(y)\exp\left(-\frac{y^2}{2}\right) \qquad y = \sqrt{\frac{m\omega}{\eta}}x$$

$$E = \left(n + \frac{1}{2}\right)\eta\omega$$

$C_n$ is the normalization constant to satisfy $\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1$

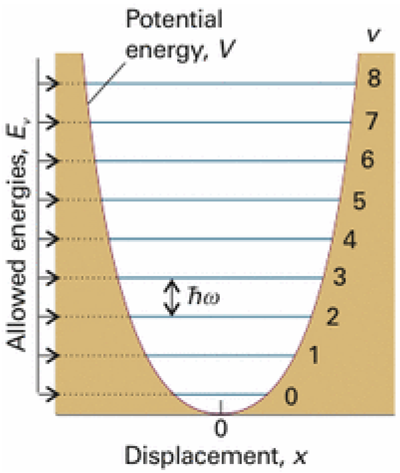
$$\int_{-\infty}^{\infty} H_n^{\ 2}(y)\exp\left(-y^2\right)dy = \sqrt{\pi}\,2^n n!$$

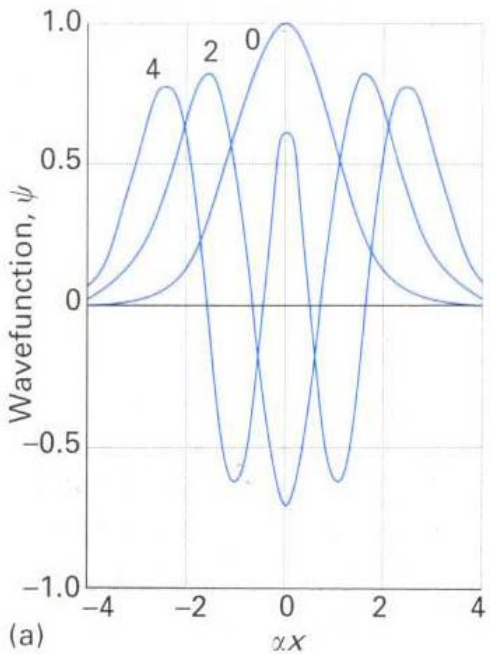
$$C_n = ?$$

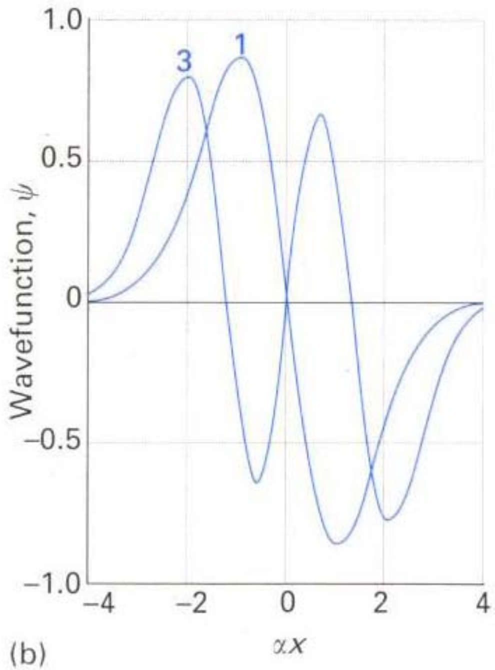
# Wavefunction Nodes

$$\psi_n(x)=\left[\frac{1}{2^n n!}\left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}} H_n(\alpha x)\exp\left(-\frac{\alpha^2x^2}{2}\right) \qquad y=\alpha x=\sqrt{\frac{m\omega}{\hbar}}x$$

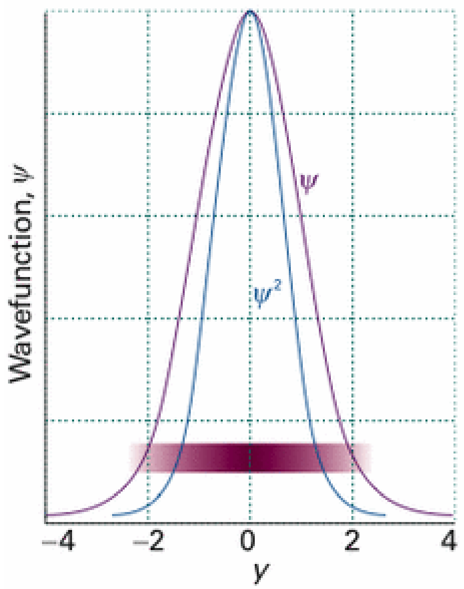
$$E=\left(n+\frac{1}{2}\right)\hbar\omega \qquad n=0,1,2,\ldots$$

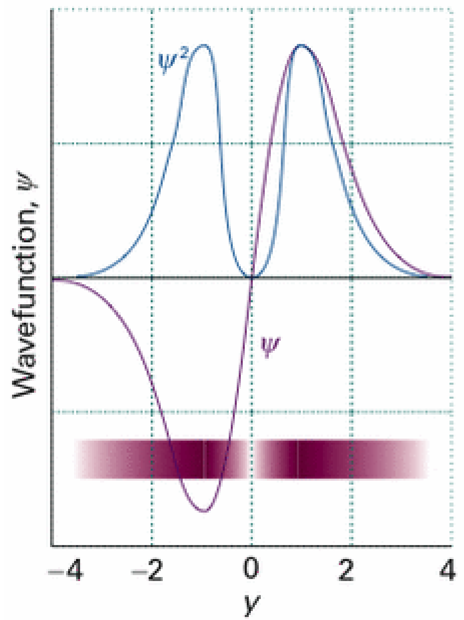


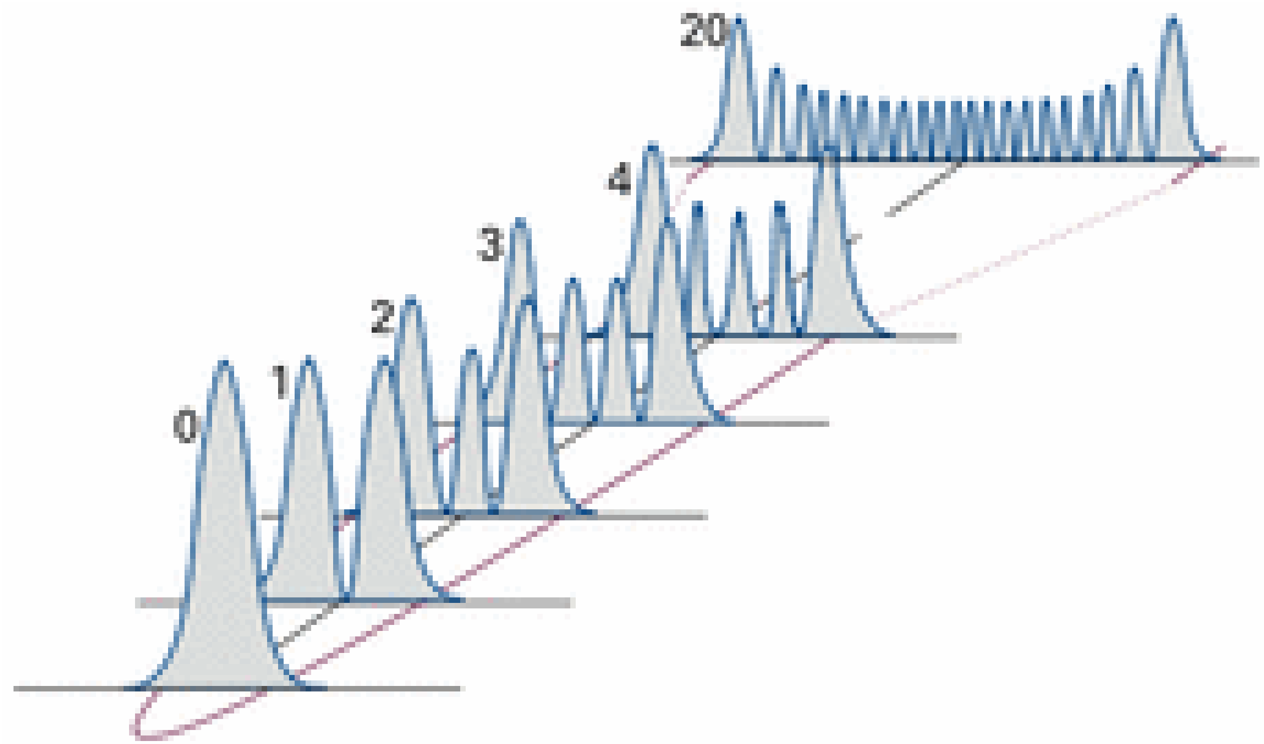



# Probability Distribution

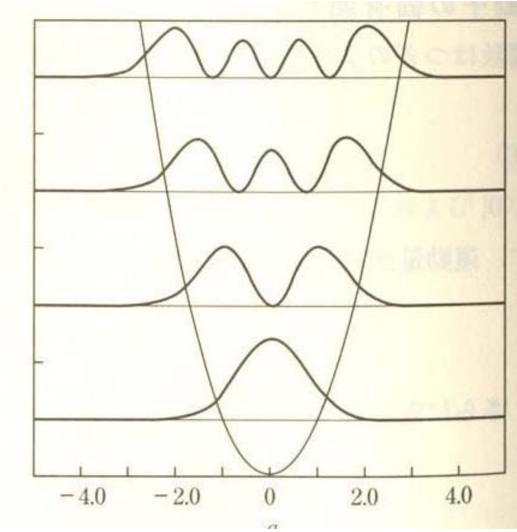



In classical Picture the probability of the harmonic oscillator is higher at the turning points than in the potential minimum. (Kintic energy is small at turning points = particle motion is slow = particle distribution is large at turning points)
This is not the case for quantum harmonic oscillator at low quanta n=1, 2,.. But becomes gradually true at high quanta

# Tunneling 1




As seen from the figure in the left the wavefunction at acertain eigenvalue (energy) has probability outside of the turning points (classical allowed region) this is the tunneling contribution

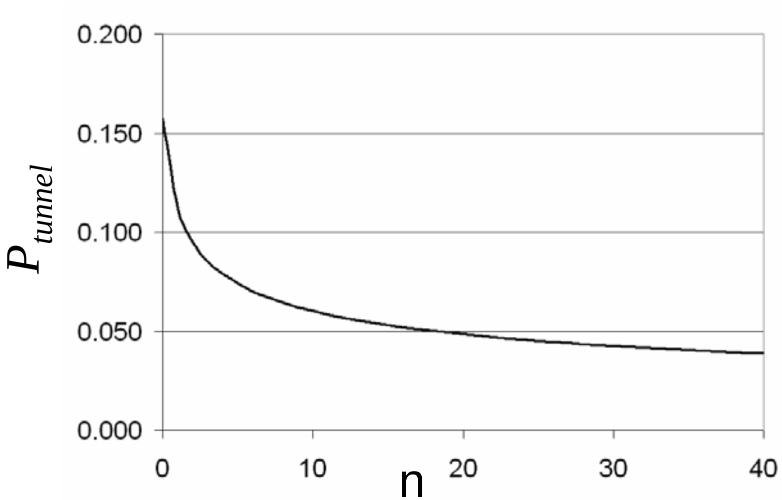
To estimate the tunneling we calculate the probability

$$p_{tunnel} = 2\int_{x_{tp}}^{\infty} \left|\psi_n(x)\right|^2 dx$$

$$x_{tp} = \pm\left(\frac{2E}{k}\right)^{\frac{1}{2}} = \pm\left(\frac{2(n+1/2)\hbar\omega}{k}\right)^{\frac{1}{2}}$$

Table Tunneling Probability

| n | Ptunnel |
|---|---|
| 0 | 0.157 |
| 1 | 0.112 |
| 2 | 0.095 |
| 3 | 0.085 |
| 4 | 0.079 |
| 5 | 0.074 |



# Expectation Values

# H2 and D2 and T2 Vibrations