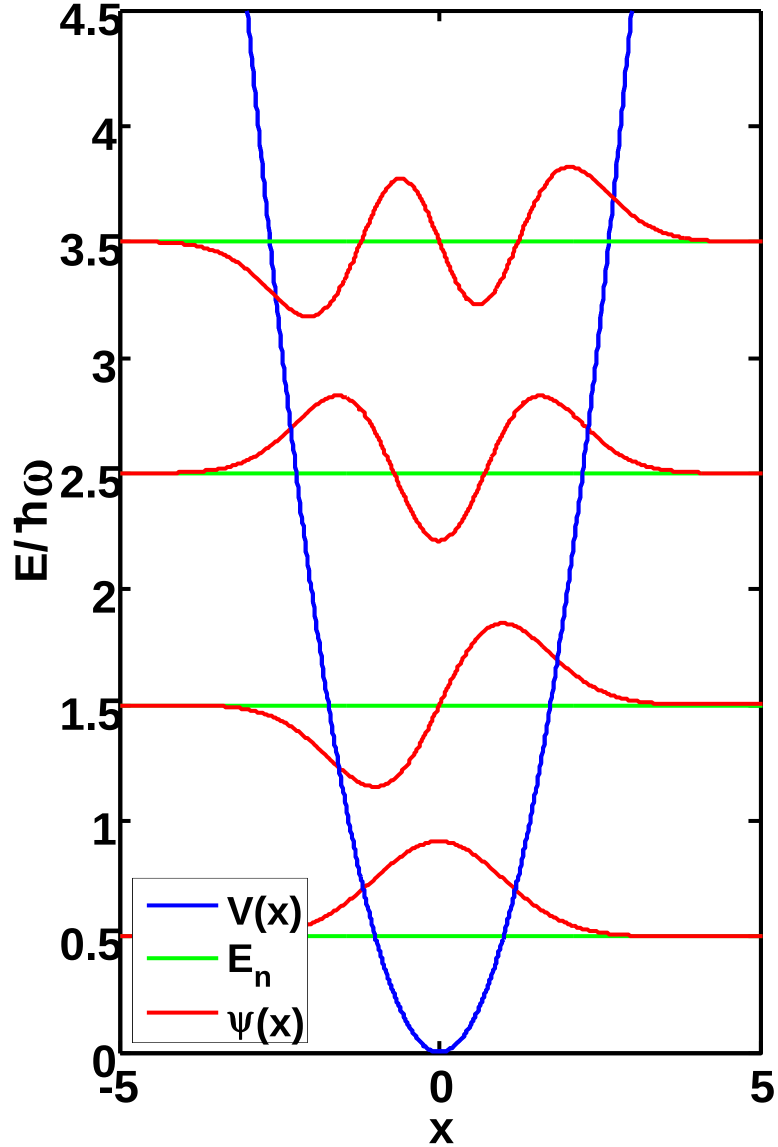
Lecture 20: 03/04/09

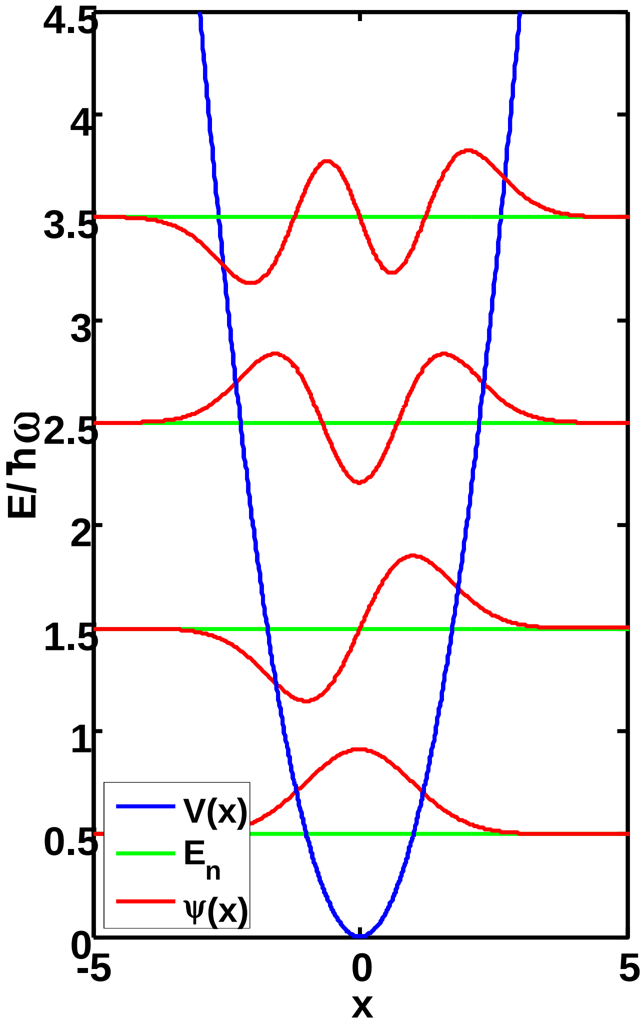
- simple harmonic oscillator $V(x) = \frac{1}{2} c x^2$:
  - End result

- **Numerical solution of Schrödinger's Equation**



Recap:

$II_{2,5}$ The simple harmonic oscillator potential $V(x)=1/2cx^2$:



Potential: $V(x) = \frac{1}{2} c x^2 = \frac{1}{2} m \omega^2 x^2$

- Introduce: $\xi = \sqrt{\frac{m\omega}{\hbar}}\, x \qquad K = \frac{E}{\frac{1}{2}\hbar\omega}$

$\Rightarrow$ S.E.: $\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\,\psi(\xi)$

$\psi(\xi) = \sum_{j=0}^{\infty} a_j \xi^j e^{-\xi^2/2}$ solves S.E.

with $a_{j+2} = \frac{2j+1-K}{(j+2)(j+1)}\, a_j$

But: need to terminate power series to make $\psi(\xi)$ normalizable!

$\Rightarrow \quad E_n = (n + \frac{1}{2})\hbar\omega \qquad n = 0, 1, 2 \ldots$

$\Rightarrow \quad a_{j+2} = \frac{2(j-n)}{(j+2)(j+1)}\, a_j$

- Solve in 4 steps:

1) Quantitative $\psi(x)$

2) Consider large x i.e large ξ

3) Solve at all x i.e all ξ

4) Make sure $\psi(\xi)$ can be normalized

$\Rightarrow$ require $\psi(\xi) \xrightarrow[\xi \to \pm\infty]{} 0$ $\Rightarrow$ quantized allowed energy E_n

- **End result:**

$$\psi_n(x) = H_n(\xi)\, e^{-\xi^2/2} = \sum_{j=0}^{n} a_j \xi^j e^{-\xi^2/2}$$

recursion formula:
(with $K_n = 2n+1$

$$a_{j+2} = \frac{2(j-n)}{(j+2)(j+1)} a_j$$

$\Rightarrow$ for <u>even</u> wave functions: $n = 0, 2, 4, \ldots$

start $a_0 \neq 0$, $a_1 = 0$

$\Rightarrow H_0(\xi) = a_0 \quad \Rightarrow \psi_0 = a_0 e^{-\xi^2/2}$

$\Rightarrow H_2(\xi) = a_0(1 - 2\xi^2) \Rightarrow \psi_2 = a_0(1 - 2\xi^2) e^{-\xi^2/2}$

$\Rightarrow$ for <u>odd</u> wave functions: $n = 1, 3, 5, \ldots$

$\Rightarrow H_1(\xi) = a_1 \xi \quad \Rightarrow \psi_1 = a_1 \xi e^{-\xi^2/2}$ ...

start with $a_1 \neq 0$, $a_0 = 0$

n = # of nodes	E_n	$\psi_n(\xi)$	Hermite polynomial $H_n(\xi)$
ground state → 0	$\frac{1}{2}\hbar\omega$	$a_0 e^{-\xi^2/2}$	1
1	$\frac{3}{2}\hbar\omega$	$a_1 \xi e^{-\xi^2/2}$	2ξ
2	$\frac{5}{2}\hbar\omega$	$a_0(1-2\xi^2)e^{-\xi^2/2}$	$4\xi^2-2$
3	$\frac{7}{2}\hbar\omega$	$a_1(\xi-\frac{2}{3}\xi^3)e^{-\xi^2/2}$	$8\xi^3-12\xi$ ↖ coefficient of highest power of ξ is 2^n

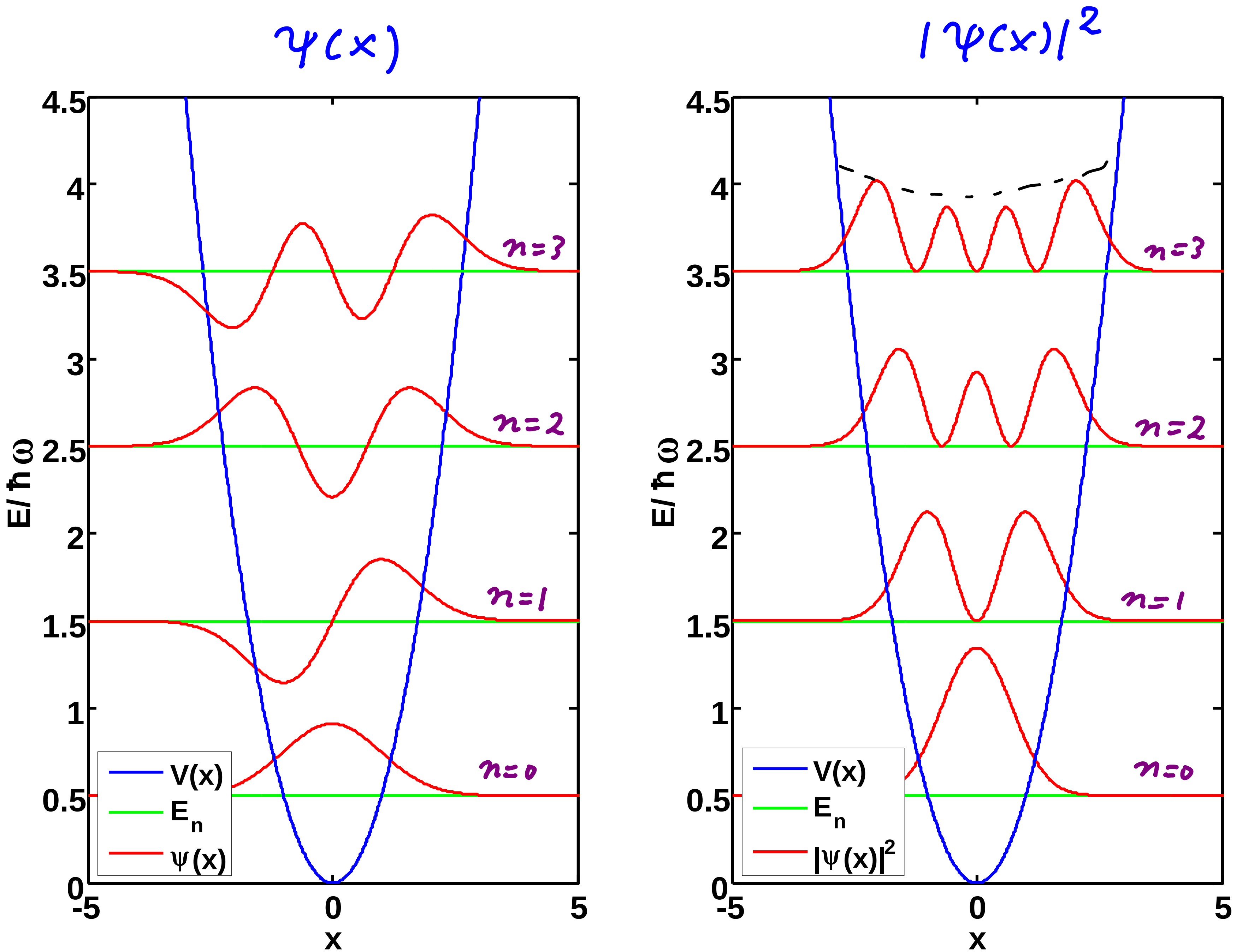
⇒ normalized stationary state wave function for $V=\frac{1}{2}cx^2$

$$\psi_n(\xi) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \qquad \omega = \sqrt{\frac{c}{m}}$$

$n = 0, 1, 2, 3, \ldots$

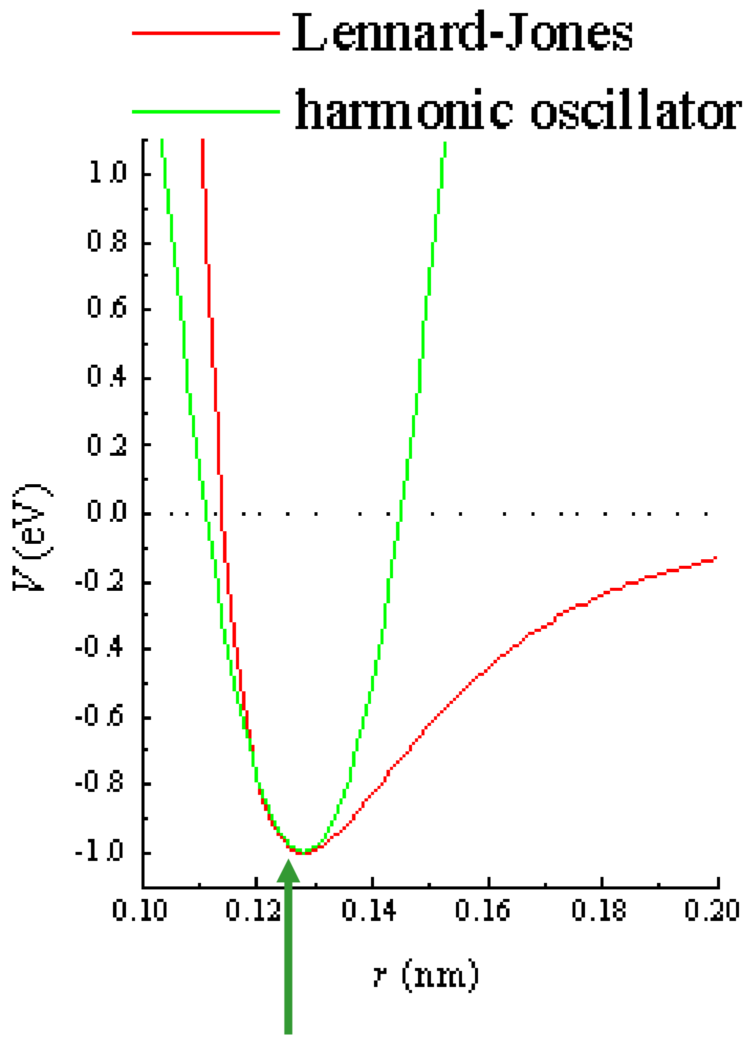
$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega$$

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

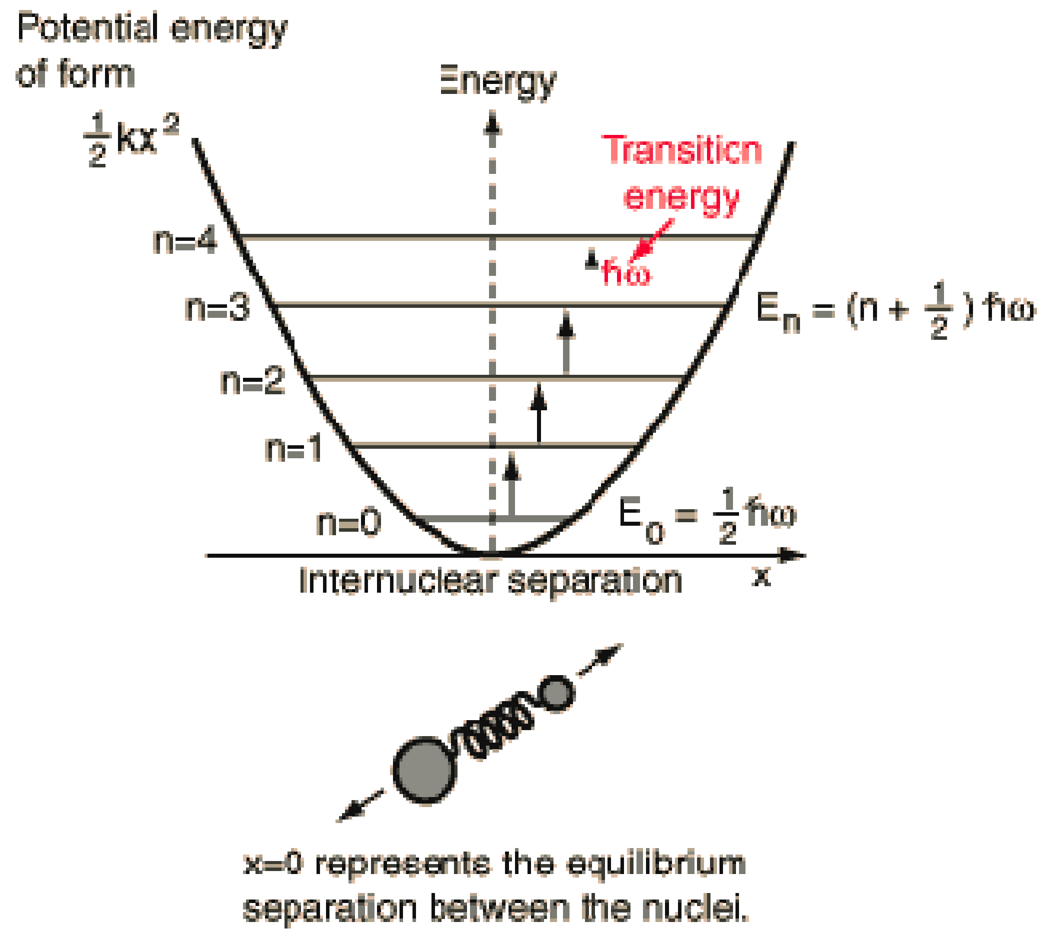


ψ(x)
|ψ(x)|²
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
E/ħω
-5
0
5
x
n=3
n=2
n=1
n=0
V(x)
E_n
ψ(x)
|ψ(x)|²

Atomic molecule vibration



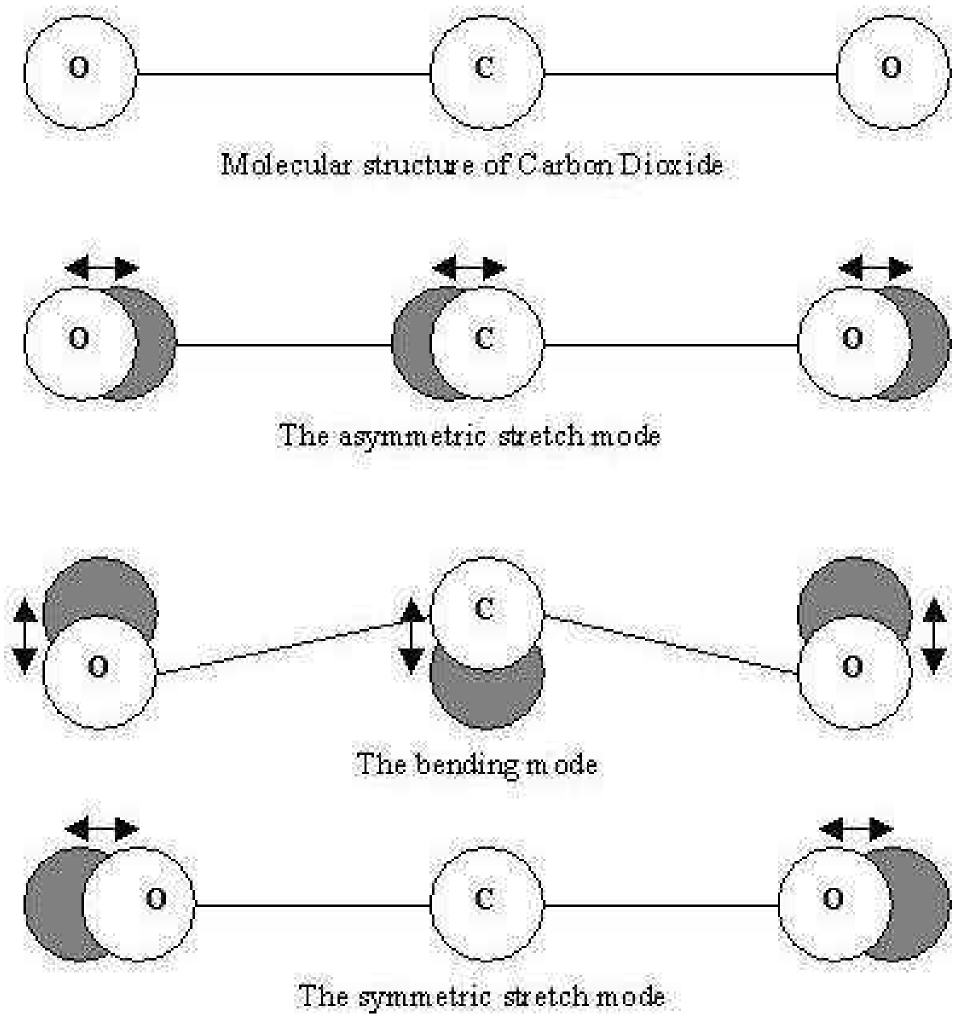
Near equilibrium: simple harmonic

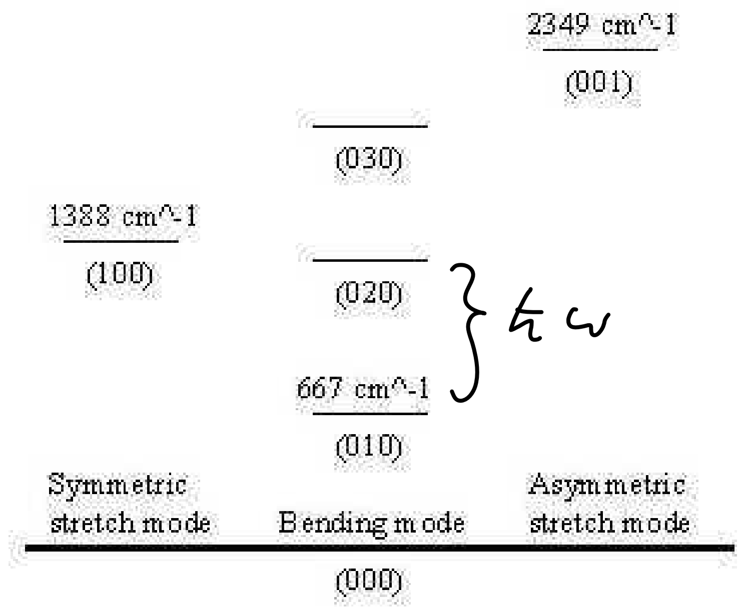


reduced mass, μ

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad E_n = (n + \frac{1}{2})\hbar\omega$$

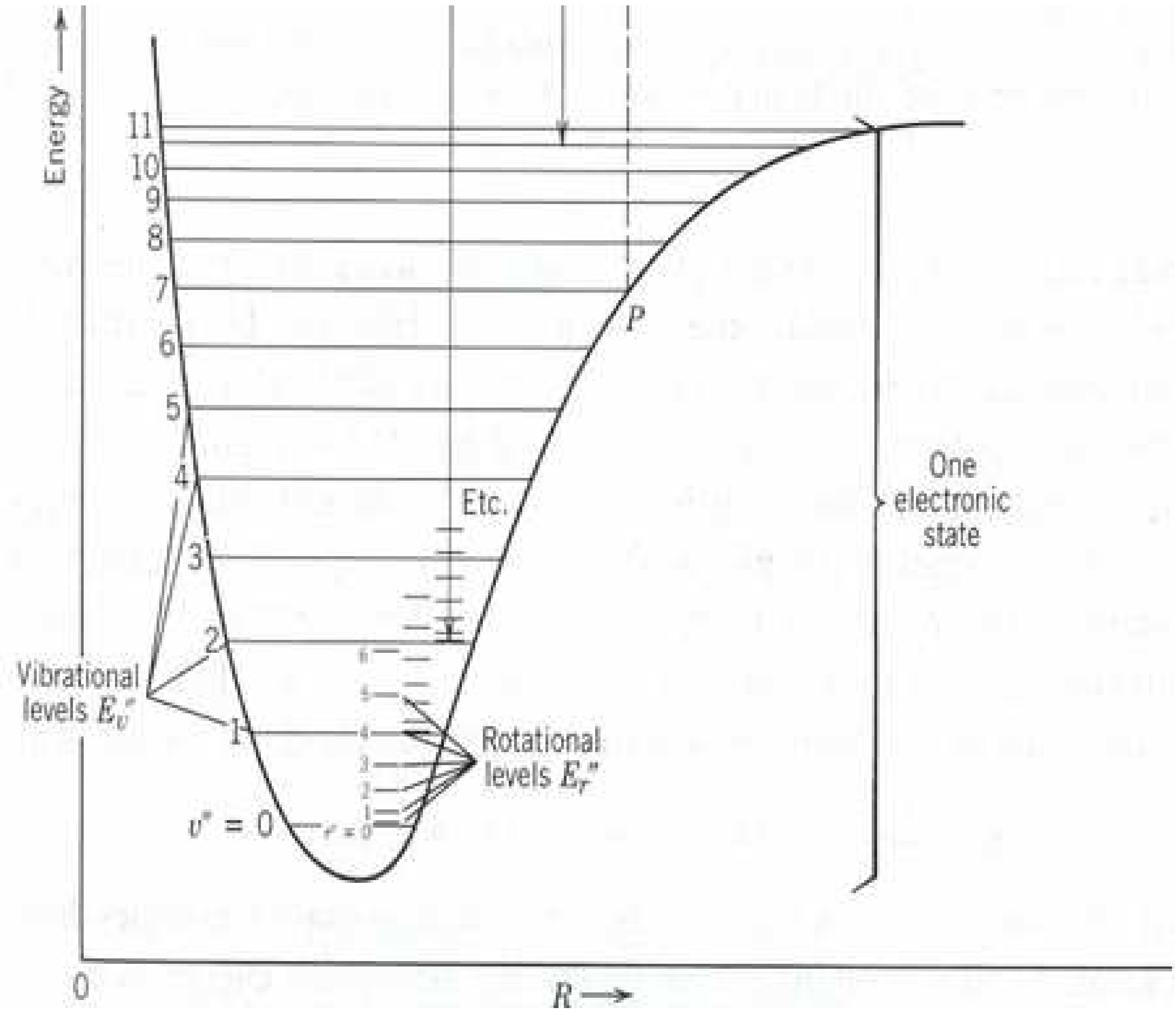
Example: CO_2



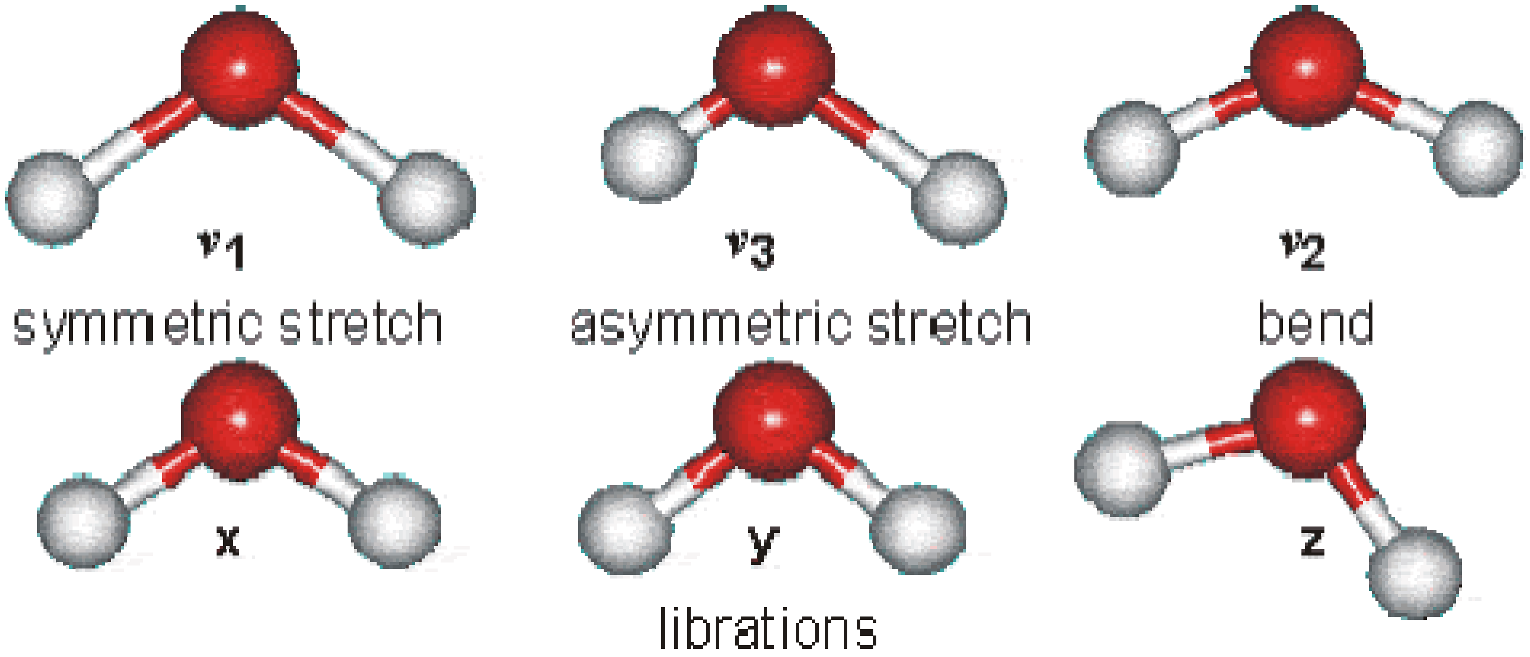


The first few vibrational energy levels of the CO2 molecule

Molecule vibration and rotation:



Example: H_2O


ν_1
symmetric stretch
ν_3
asymmetric stretch
ν_2
bend
x
y
z
librations

$II_{2,6}$ Numerical Solution of the time-indep. Schrödinger Equ.:

Intro:

→ Time-indep. S.E: $\hat{H}\psi = E\psi$

eigenvalue problem: both ψ and E are unknown

→ Solved S.E. in analytical form for ∞ square well and for S.H.O.

→ But: for most physically realistic potentials the S.E. cannot be solved in analytical form!

→ Solution: use numerical approximation methods on computer!

→ Here: will discuss one of the simple methods

→ <u>Numerical solution</u> of <u>the time-indep. S.E.</u>

<u>step 1:</u> fix energy E at some trail value E^t

⇒ get differential equation

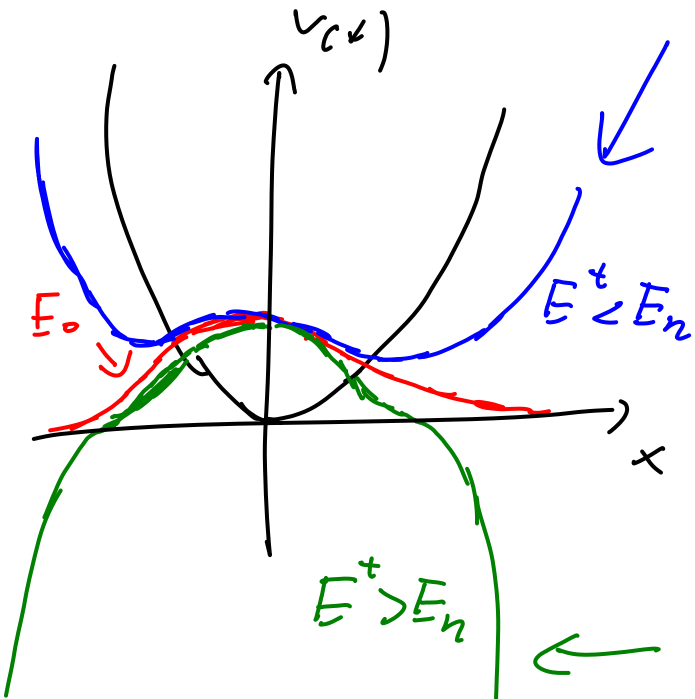
$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E^t - V(x)\right)\psi(x)$$

<u>step 2:</u> solve diff. equ. numerically on computer

⇒ $\psi(x)$

<u>step 3:</u> check if tail value for particle energy E^t is approximat. allowed, i.e. if $\psi(x)$ is <u>normalizable</u>

Recall:



- if trail E^t is slightly below allowed eigenstate energy value E_n

$\Rightarrow$ $(V(x) - E)$ is too large outside the well

$\Rightarrow$ |curvature| is too large outside well

$\Rightarrow$ $\psi(x)$ curves away from x-axis without crossing it and goes to + or − ∞

- if trail E^t is slightly above allowed energy E_n

$\Rightarrow$ $(V(x) - E)$ is too small outside well

$\Rightarrow$ |curvature| is too small outside well

$\Rightarrow$ $\psi(x)$ crosses x-axis and then goes to + or − ∞

note: sign of $\psi(x)$ changes outside the well when E^t crosses allowed energy E_n

$\Rightarrow$ require $\psi(x) \to \approx 0$ for large and small x
outside well

$\Rightarrow$ use # of nodes inside well and use sign-
changes outside well of $\psi(x)$ to search for E_n's

step 4: based on results from step 3, generate
new E^t and go back to step 1 until
valid solution ψ_n, E_n is found

step 5: normalize ψ_n's found

② Dimensionless form of the S.E.

→ time indep. S.E.: $\dfrac{d^2\psi(x)}{\underset{\substack{\uparrow\\ x\,\approx\,\text{nm}}}{dx^2}} = -\underbrace{\dfrac{2m}{\hbar}}_{\text{large}}\,[\underbrace{E - V(x)}_{\text{small}\,\approx\,\text{eV}}]\,\psi(x)$

⇒ better to choose convenient, dimensionless units so that values are of the order of one

⇒ get dimensionless form of the S.E.:

$$\frac{d^2}{d\bar{x}^2}\psi(\bar{x}) = -[\bar{E} - \bar{V}(\bar{x})]\,\psi(\bar{x})$$

with changed variables (dimensionless!)

$\bar{x} = \dfrac{x}{A}$ } distance measured in some "natural" units of length for the system under investigation

$\bar{V} = \dfrac{V}{B}$; $\bar{E} = E/B$ } energies in some "natural" unit of energy of the system

Note: to get above dimensionless S.E., need

$$B = \frac{\hbar^2}{2mA^2}$$

Example: square well of width L

$\Rightarrow$ choose $\bar{x} = \frac{x}{L}$

$\Rightarrow$ $\bar{E} = \frac{E}{B} = \frac{E}{\frac{\hbar^2}{2mL^2}}$ $\qquad \bar{V} = V/\hbar^2/2mL^2$

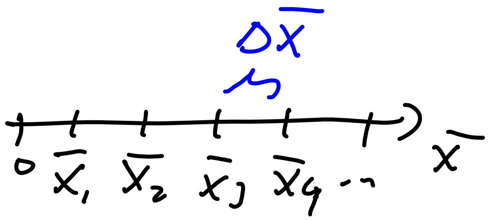
$\Rightarrow$ once $\psi(\bar{x})$ and $\bar{E}$ found $\rightarrow$ convert back to conventional units

$\Rightarrow \psi(x)$, E

3 Approximate difference Equation:

to solve dimensionless S.E. $\longrightarrow$ approximate S.E. by a difference-equation

$\rightarrow$ compute values of $\psi(\bar{x})$ only at certain, discrete, equally spaced values along the coordinate $\bar{x}$



set of points $\bar{x}_j$ is called a mesh or grid

$$\bar{x} \longrightarrow \bar{x}_j = j \cdot \underbrace{\Delta\bar{x}}_{\text{grid spacing}}$$

jth mesh point

grid spacing needs to be small compared to other length scales in given potential

⇝ ψ at these points $\psi(\bar{x}) \to \psi(\bar{x}_j) \equiv \psi_j$

⇝ potential energy at these points: $\bar{V}(\bar{x}) \to \bar{V}(\bar{x}_j) = \bar{V}_j$

⇝ to discretize S.E., must find an approximate expression of the second derivative $\frac{d^2\psi}{dx^2}$ in terms of the ψ_j's:

$$\Rightarrow \left.\frac{d^2\psi}{d\bar{x}^2}\right|_{\bar{x}_j} \simeq \frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{\Delta\bar{x}^2}$$

see next page

⇒ for S.E.

$$\boxed{\Rightarrow \psi_{j+1} = \left\{2 - \Delta\bar{x}^2\left[\bar{E} - \bar{V}_j\right]\right\}\psi_j - \psi_{j-1}}$$

difference eqn approximation of S.E.!

⇒ can calculate ψ_{j+1} from ψ_j and ψ_{j-1} !

Derive approximation for $d^2\psi/dx^2$:

use Taylor expansion:

$$\psi_{j+1} = \psi(\bar{x}_j + \Delta\bar{x}) \approx \psi(\bar{x}_j) + \Delta\bar{x} \left.\frac{d\psi}{d\bar{x}}\right|_{\bar{x}_j} + \frac{\Delta\bar{x}^2}{2} \left.\frac{d^2\psi}{d\bar{x}^2}\right|_{\bar{x}_j}$$

$$\psi_{j-1} = \psi(\bar{x}_j - \Delta\bar{x}) \approx \psi(\bar{x}_j) - \Delta\bar{x} \left.\frac{d\psi}{d\bar{x}}\right|_{\bar{x}_j} + \frac{\Delta\bar{x}^2}{2} \left.\frac{d^2\psi}{d\bar{x}}\right|_{\bar{x}_j}$$

add these two equations:

$$\Rightarrow \psi_{j+1} + \psi_{j-1} = 2\psi_j + \Delta\bar{x}^2 \left.\frac{d^2\psi}{d\bar{x}^2}\right|_{\bar{x}_j}$$

$$\Rightarrow \left.\frac{d^2\psi}{d\bar{x}^2}\right|_{\bar{x}_j} \approx \frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{\Delta\bar{x}^2}$$

$\Rightarrow$ insert this into the dimensionless S.E

gives: $\dfrac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{\Delta\bar{x}^2} \approx -[\bar{E} - \bar{V}_j]\psi_j$

(4) Solving the Discretized S.E.:

- pick trail value for particle energy E (see discussion above)
- need two starting valus (S.E. is a 2^{nd} order diff. equ.!)

$$\psi_0 \text{ and } \psi_1$$

- from ψ_0 and ψ_1 $\longrightarrow$ calculate ψ_2

  from ψ_1 and ψ_2 $\longrightarrow$ " ψ_3

  from ψ_2 and ψ_3 $\longrightarrow$ " ψ_4

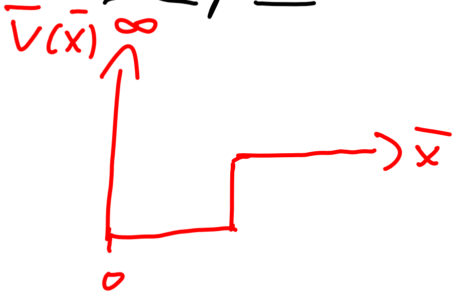
  ⋮

  up to some max. index n : $\psi_n = \psi(\bar{x}_n)$

  outside of well

→ How to find initial starting values ψ_0 and ψ_1?

Example 1: Potential with infinite wall:

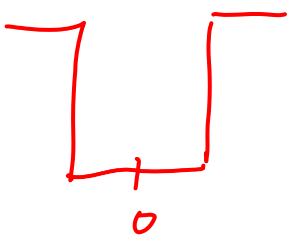


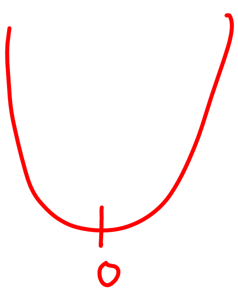
Know: $\psi_0 = \psi(0) = 0$ at ∞ wall

choose $\psi_1 \neq 0$ ⇒ ψ_1 determines initial slope of $\psi(\bar{x})$

(later re-adjusted to normalize $\psi(x)$)

Example 2: Symmetric potentials





- for even functions ψ:
  - have zero slope at center of well

    ⇒ choose $\psi_0 = \psi_1 \neq 0$
- for odd functions ψ:
  - have $\psi(\text{center}) = 0$ and $\left.\frac{d\psi}{dx}\right|_{\text{center}} \neq 0$ ⇒ choose $\psi_0 = 0$ and $\psi_1 \neq 0$

⑤ Normalizing $\psi(x)$:

require: $\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1$

$\Rightarrow$ for discretized values:

require: $\boxed{\sum_{j=-\infty}^{+\infty} |\psi_j|^2 \Delta X = 1}$

<u>note</u>: $\Delta X = \Delta\bar{X} \cdot A$