• Simple harmonic oscillator $V(x) = \frac{1}{2} \omega^2 x^2$
  - End result

• Numerical solution of Schrödinger's Equation

\[ E/\hbar \omega \]
Recap:

The simple harmonic oscillator potential $V(x) = \frac{1}{2} cx^2$:

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

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

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

$\psi(\xi) = \sum_{j=0}^{\infty} a_j \xi^j e^{-\xi^2/2}$ solve 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!

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

$\Rightarrow a_{j+2} = \frac{2(j-n)}{(j+2)(j+1)} a_j$
• **Solve in 4 steps:**

1) Quantitative \( \Psi(x) \)

2) Consider large \( x \) i.e large \( \xi \)

3) Solve at all \( x \) i.e all \( \xi \)

4) Make sure \( \Psi(\xi) \) can be normalized
   
   \[
   \Rightarrow \text{ require } \Psi(\xi) \xrightarrow{\xi \to \pm \infty} 0 \Rightarrow \text{quantized allowed energy } E_n
   \]
End result:

\[ \psi_n(x) = H_n(s) e^{-s^2/2} = \sum_{j=0}^{n} a_j s^j e^{-s^2/2} \]

Recursion formula:

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

\( s^2, 2n+1 \) for even wave functions: \( n = 0, 2, 4, \ldots \)

\( \begin{align*}
\text{start } a_0 \neq 0, a_1 = 0 \\
\Rightarrow H_0(s) = a_0 \\
\Rightarrow \psi_0 = a_0 e^{-s^2/2} \\
\Rightarrow H_2(s) = a_0 (1-2s^2) \\
\Rightarrow \psi_2 = a_0 (1-2s^2) e^{-s^2/2}
\end{align*} \)

\( \Rightarrow \) for odd wave functions: \( n = 1, 3, 5, \ldots \)

\( \begin{align*}
\Rightarrow H_1(s) = a_1 s \\
\Rightarrow \psi_1 = a_1 s e^{-s^2/2} \\
\text{start with } a_1 \neq 0, a_0 = 0
\end{align*} \)
<table>
<thead>
<tr>
<th>(n) = # of nodes</th>
<th>(E_n)</th>
<th>(\Psi_n(S))</th>
<th>Hermite Polynomial (H_n(S))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(\frac{1}{2} k_0)</td>
<td>(a_0 e^{-S^2/2})</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>(\frac{3}{2} k_0)</td>
<td>(a_1 S e^{-S^2/2})</td>
<td>2 (S)</td>
</tr>
<tr>
<td>2</td>
<td>(\frac{5}{2} k_0)</td>
<td>(a_2 (1 - 2S^2)e^{-S^2/2})</td>
<td>4 (S^2 - 2)</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{7}{2} k_0)</td>
<td>(a_3 (S - 2S^3)e^{-S^2/2})</td>
<td>(8S^3 - 12S)</td>
</tr>
</tbody>
</table>

\(\Psi_n(S)\) = \(\left(\frac{2n}{\pi k_0}\right)^{1/4} \sqrt{\frac{1}{2^n n!}} H_n(S) e^{-S^2/2}\)  \(\omega = \sqrt{\frac{\omega_c}{m}}\)  \(n = 0, 1, 2, \ldots\)

\(E_n = (n + \frac{1}{2}) k_0 S\)

\(S = \sqrt{\frac{2n\omega}{k_0}} \times \)
Atomic molecule vibration

Near equilibrium: simple harmonic

reduced mass, $\mu$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$

$E_n = (n + \frac{1}{2}) \hbar \omega$
Example: CO$_2$

Molecular structure of Carbon Dioxide

The asymmetric stretch mode

The bending mode

The symmetric stretch mode

2349 cm$^{-1}$  
(001)

$egin{align*}
\text{1388 cm}^\text{1} & \quad (100) \\
\text{667 cm}^\text{1} & \quad (010)
\end{align*}$

\[ \{ \hbar \omega \} \]

Symmetric stretch mode  Bending mode  Asymmetric stretch mode

(000)

The first few vibrational energy levels of the CO$_2$ molecule
Molecule vibration and rotation:
Example: $\text{H}_2\text{O}$

- $v_1$: symmetric stretch
- $v_3$: asymmetric stretch
- $v_2$: bend
- $x$, $y$, $z$: librations
Numerical Solution of the time-indep. Schrödinger Equ.

Intro:

→ Timeindep. S.E.: \( \hat{H} \psi = E \psi \)
  
  Eigenvalue problem: both \( \psi \) and \( E \) are unknown.

→ Solved S.E. in analytical form for \( 0 \) square well and for \( \text{S.H. O.} \).

→ 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
Numerical solution of the time-independent S.E.

**Step 1:** Fix energy \( E \) at some trial value \( E^t \)

\( \Rightarrow \) Get differential equation

\[
\frac{d^2 \Psi}{dx^2} = -\frac{2m}{\hbar^2} (E^t - V(x)) \Psi(x)
\]

**Step 2:** Solve diff. eqn. numerically or compute

\( \Rightarrow \Psi(x) \)

**Step 3:** Check if trial value for particle energy \( E^t \)

is approximate allowed, i.e. if \( \Psi(x) \) is

normalizable
Recall:

- If trial $E^t$ is slightly below allowed eigenstate energy value $E_n$
  \[ V = 0 \] \[ (V(x) - E) \text{ is too large outside the well} \]
  \[ E^t < E_n \rightarrow |\text{curvature}| \text{ is too large outside well} \]
  \[ \Rightarrow \psi(x) \text{ curves away from x-axis without crossing it and goes to } +\infty - \infty \]

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

- If trial $E^t$ is slightly above allowed energy $E_n$
  \[ (V(x) - E) \text{ is too small outside well} \]
  \[ |\text{curvature}| \text{ is too small outside well} \]
  \[ \Rightarrow \psi(x) \text{ crosses x-axis and then goes to } +\infty - \infty \]
\text{= 1)} \quad \text{require } \psi(x) \to 0 \text{ for large and small } x \text{ outside well}

\text{= 2)} \quad \text{use # of nodes inside well and use sign-change outside well of } \psi(x) \text{ to serve (for } E_n, n \text{ 1)}

\underline{\text{Step 4:}} \quad \text{based on results from step 3, generate new } E^* \text{ and go back to step 1 until valid solution } \psi_n, E_n \text{ is found}

\underline{\text{Step 5:}} \quad \text{normalize } \psi_n \text{ is found}
(2) Dimensionless form of the S.E.

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

\( \Rightarrow \) both to choose convenient, dimensionless units so that values are of the order of one

\[ \Rightarrow \text{get dimensionless form of the S.E.:} \]

\[ \frac{d^2 \psi(\tilde{x})}{d\tilde{x}^2} = -\left[ \tilde{E} - \tilde{V}(\tilde{x}) \right] \psi(\tilde{x}) \]

with changed variables (dimensionless!)

\[ \tilde{x} = \frac{x}{A} \]

units of length for the system

\[ \tilde{V} = \frac{V}{\hbar^2}, \quad \tilde{E} = \frac{E}{\hbar^2} \quad \text{energies in some "natural" unit of energy of the system} \]
Note: To get above dimensionless S.E., need
\[ B = \frac{L^2}{2 \pi A^2} \]

Example: square well of width \( L \)

1) Choose \( \bar{x} = \frac{x}{L} \)

\[ \bar{E} = \frac{E}{B} = \frac{E}{\frac{L^2}{2 \pi L^2}} = \frac{\bar{E}}{\frac{1}{2 \pi}} \]

\[ \overline{\bar{E}} = \sqrt{\frac{\bar{E}^2}{2 \pi}} \]

2) Once \( \Psi(\bar{x}) \) and \( \bar{E} \) found \( \rightarrow \) convert back to conventional units

\[ \Psi(x), E \]
3. **Approximate difference Equation**

To solve dimensional less S.E. $\rightarrow$ approximate S.E. by a difference equation

- Compute values of $\Psi(\vec{x})$ only at certain, discrete, equally spaced values along the coordinate $\vec{x}$

\[
\vec{x} \rightarrow \vec{x}_j = j \cdot \Delta \vec{x}
\]

Set of points $\vec{x}_j$ is called a mesh or grid

Grid spacing $\Delta \vec{x}$

Jth mesh point

Needs to be small compared to the length scales in given potential
\( \Psi \) at these points: \( \Psi(x) \rightarrow \Psi(x_j) = \Psi_j \)

potential energy at these points: \( V(x) \rightarrow V(x_j) = V_j \)

to discrete S.E., must find an approximate expression of the second derivative \( \frac{d^2 \Psi}{dx^2} \)
in terms of the \( \Psi_j \):

\[
\Rightarrow \quad \frac{d^2 \Psi}{dx^2} \bigg|_{x_j} \approx \frac{\Psi_{j+1} - 2 \Psi_j + \Psi_{j-1}}{\Delta x^2}
\]

\[
\Rightarrow \quad \Psi_{j+1} = \left\{ 2 - \Delta x^2 \left[ E - V_j \right] \right\} \Psi_j - \Psi_{j-1}
\]

difference eqn approximation of S.E.!

\( \Rightarrow \) can calculate \( \Psi_{j+1} \) from \( \Psi_j \) and \( \Psi_{j-1} \)!
Derive approximation for $d^2 \psi / d\bar{x}^2$:

Use Taylor expansion:

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

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

Add these two equations:

$= \psi_{j+1} + \psi_{j-1} = 2\psi_j + \Delta x^2 \frac{d^2\psi}{d\bar{x}^2}|_{x_j}$

$= \frac{d^2\psi}{d\bar{x}^2}|_{x_j} \approx \psi_{j+1} - 2\psi_j + \psi_{j-1}$

$= \Delta x^2$

Insert this into the dimensionless S.E.

Gives: $\frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{\Delta x^2} \approx - \left[ E - V_j \right] \psi_j$
4) **Solving the Discretized S.E.:**

- Pick trial value for particle energy $E$
  (see discussion above)

- Need two starting values (S.E. is a 2nd order diff. eqn.!
  $\Psi_0$ and $\Psi_1$

- From $\Psi_0$ and $\Psi_1$, calculate $\Psi_2$
  From $\Psi_1$ and $\Psi_2$, "" $\Psi_3$
  From $\Psi_2$ and $\Psi_3$, "" $\Psi_4$
  
  Upto some max. index $\infty$: $\Psi_\infty = \Psi(E_\infty)$

Out of well
How to find initial starting values $\Psi_0$ and $\Psi_1$?

**Example 1:** Potential with infinite well.

- $V(x)$, $\infty$ to 0
- $x$ to $\infty$

Know: $\Psi_0 = \Psi(0) = 0$ at infinite wall

Choose $\Psi_1 \neq 0 \Rightarrow \Psi_1$ determines initial slope of $\Psi(x)$

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

**Example 2:** Symmetric potentials

- For even functions $\Psi$:
  - have zero slope at center of well
  - choose $\Psi_0 = \Psi_1 \neq 0$

- For odd functions $\Psi$:
  - have $\Psi(\text{center}) = 0$ and
  - $\frac{d\Psi}{dx} \bigg|_{\text{center}} \neq 0 \Rightarrow$ choose $\Psi_0 = 0$ and $\Psi_1 \neq 0$
5) Normalizing $\psi(x)$:

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

=) for discretized values:

\[
\text{require: } \sum_{j=-\infty}^{+\infty} |\psi_j|^2 \Delta x = 1
\]

Note: $\Delta x = \Delta \bar{x} \cdot A$