Chapter 5 – 1D Problems: Bound States

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Modern Physics (Summer 2020)
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Agenda

1. Some General Properties of Solutions to 1D Stationary Schrödinger Equation

2. Examples
   - Rectangular Finite Potential
   - Harmonic Oscillator
   - Triangular Semi-Infinite Potential Well
   - NH_3 Molecule

Some General Properties of Solutions to 1D Stationary Schrödinger Equation

General Features of Solutions to 1D Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x)$$

(1) If $V^*(x) = V(x)$, then the solutions to the stationary Schrödinger equation can be chosen to be real-valued functions.

(2) If $V(x) = V(-x)$, i.e. $\hat{P}V(x) = V(x)$ where $\hat{P}$ is the parity operator (see Problem Set), then the solutions to the stationary Schrödinger equation can be chosen to be even/odd functions of x.

* If the eigenvalues of $\hat{H}$ are not degenerate (i.e. to each eigenvalue there belongs only one eigenfunction) wave functions are either even or odd.

Schrödinger Equation and Shape of Wave Function

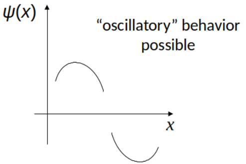
How to sketch the graph of a solution (wave function) to the Schrödinger equation without actually solving it?

Rewrite Schrödinger equation as

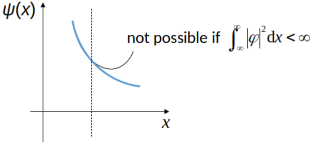
$$\boxed{\psi''(x) = -\frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x)}$$

and recall that the second derivative determines whether the ψ is concave or convex.

If $E > V(x)$, then ψ'' and ψ have opposite signs

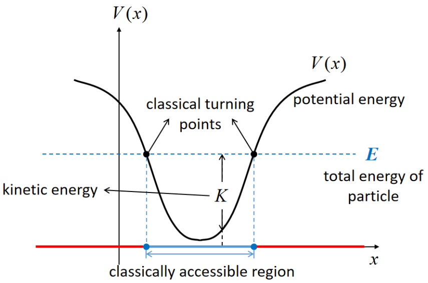


If $E < V(x)$, then ψ'' and ψ have the same sign



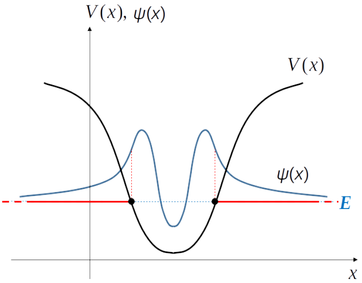
Wave Function of Particle in Potential Well

Classical particle



Zero probability of finding the particle in the classically forbidden region (indicated by the red line), but non-zero in classically accessible region.

Quantum particle



Non-zero probability of finding the particle in the classically forbidden region (indicated by the red line).

[$\psi(x)$ is shifted upwards on this graph]

Bound States in 1D

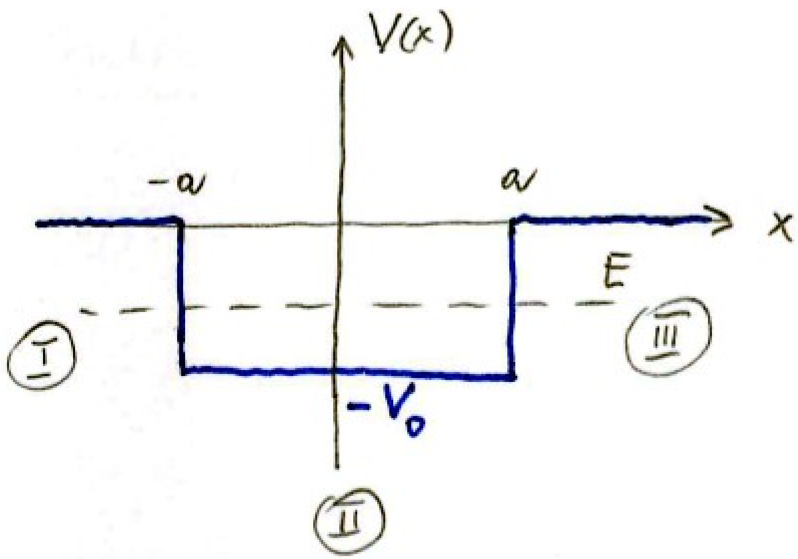
EXAMPLES

Example 1

Finite-depth Potential Well

Finite-depth potential well

$$V(x) = \begin{cases} -V_0 & \text{for } -a \leq x \leq a \\ 0 & \text{otherwise} \end{cases}$$



$V_0 > 0$

We are interested in bound states

$-V_0 < E < 0$

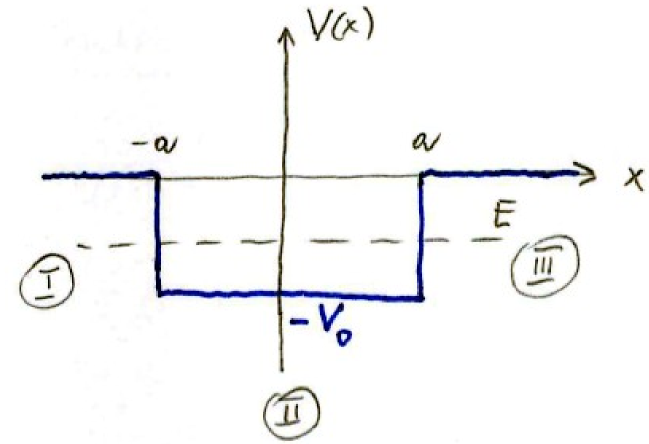
stationary Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \Leftrightarrow \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0$$

Region I

Region I $\quad (V(x) = 0)$

$(x < -a)$



$$\frac{d^2\psi_I(x)}{dx^2} - \varkappa^2 \psi_I(x) = 0 \qquad \text{where} \quad \varkappa^2 = -\frac{2mE}{\hbar^2} > 0$$

Solution

$$\psi_I(x) = A e^{\varkappa x} + \cancel{\tilde{A} e^{-\varkappa x}}$$

ψ has to be normalizable $\Rightarrow \psi \xrightarrow{x \to -\infty} 0$, hence $\tilde{A} = 0$

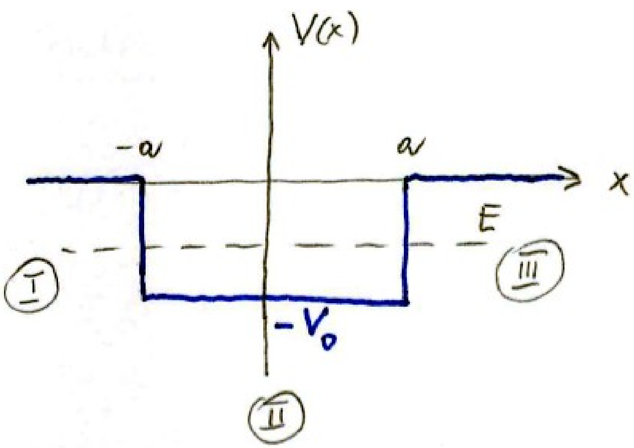
$$\boxed{\psi_I(x) = A e^{\varkappa x}}$$

Regions III and II

Region III ($V(x) \equiv 0$)

($x > a$)

$$\boxed{\psi_{III}(x) = B e^{-\varkappa x}}$$



Region II ($V(x) = -V_0$)

($-a \le x \le a$)

$$\frac{d^2\psi_{III}(x)}{dx^2} + k^2\psi_{III}(x) = 0$$

where $k^2 = \frac{2m}{\hbar^2}(E + V_0) > 0$

$$k = \sqrt{\frac{2m}{\hbar^2}(E + V_0)}$$

$$\boxed{\psi_{III}(x) = C_1 \cos kx + C_2 \sin kx}$$

Finite-depth potential well. Continuity conditions

Potential energy is symmetric, wave functions either even or odd

even ($C_2 = 0;\ B = A$)

$$\psi(x) = \begin{cases} A\,e^{\varkappa x}, & x < -a \\ C_1 \cos kx, & -a \le x \le a \\ A\,e^{-\varkappa x}, & x > a \end{cases}$$

odd ($C_1 = 0;\ B = -A$)

$$\psi(x) = \begin{cases} A\,e^{\varkappa x}, & x < -a \\ C_2 \sin kx, & -a \le x \le a \\ -A\,e^{-\varkappa x}, & x > a \end{cases}$$

Continuity of ψ and ψ' at $x = \pm a$

$$\psi_{I}(-a) = \psi_{II}(-a)$$

$$\psi_{I}'(-a) = \psi_{II}'(-a)$$

symmetry

enough to enforce continuity at, e.g., $x = -a$

Finite-depth potential well. Continuity conditions

Continuity of wave function and its derivative at $x = -a$ yields

even

$$\begin{cases} A e^{-\varkappa a} = C_1 \cos ka \\ \varkappa A e^{-\varkappa a} = C_1 k \sin ka \end{cases}$$

$$\Downarrow$$

$$\varkappa = k \tan ka \quad / \cdot a$$

$$\boxed{\varkappa a = ka \tan ka} \quad (1)$$

odd

$$\begin{cases} A e^{-\varkappa a} = -C_2 \sin ka \\ \varkappa A e^{-\varkappa a} = C_2 k \cos ka \end{cases}$$

$$\Downarrow$$

$$\varkappa = -k \cot ka \quad / \cdot a$$

$$\boxed{\varkappa a = -ka \cot ka} \quad (2)$$

Recall how we defined k and κ

$$k^2 = \frac{2m}{\hbar^2}(E + V_0) \qquad \varkappa^2 = -\frac{2m}{\hbar^2}E$$

Hence

$$\boxed{(ka)^2 + (\varkappa a)^2 = \frac{2ma^2}{\hbar^2}V_0} \quad (3)$$

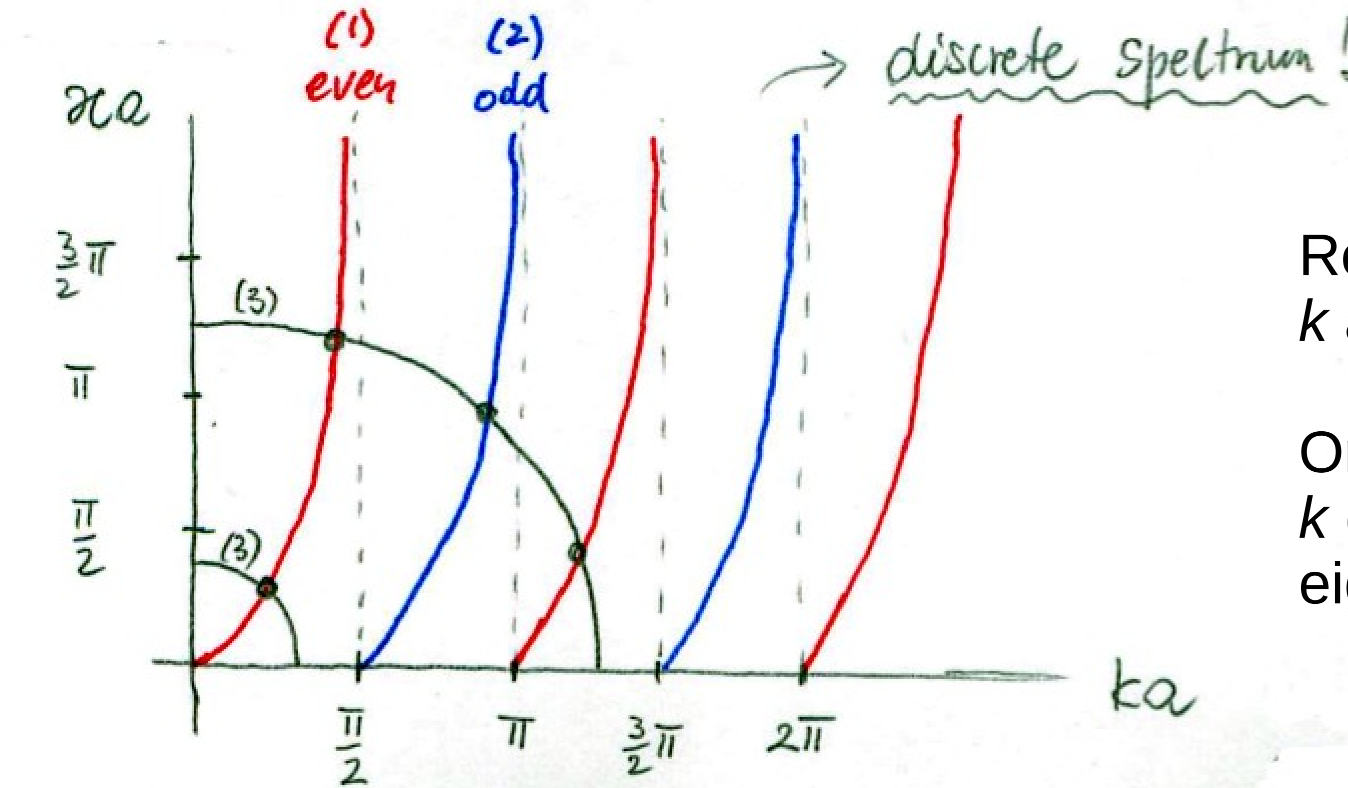
Solution: energy levels

$$\boxed{\kappa a = ka \tan ka} \qquad (1)$$

$$\boxed{\kappa a = -ka \cot ka} \qquad (2)$$

$$\boxed{(ka)^2 + (\kappa a)^2 = \frac{2ma^2}{\hbar^2} V_0} \qquad (3)$$

Need to be solved numerically. But graphical solution is useful to look at



Remember that
k and κ contain E!

Once we know
k (or κ) we know the eigen-energy, e.g. from

$$k^2 = \frac{2m}{\hbar^2}(E + V_0)$$

https://www.st-andrews.ac.uk/physics/quvis/simulations_phys/ph19_Finite_Well.html

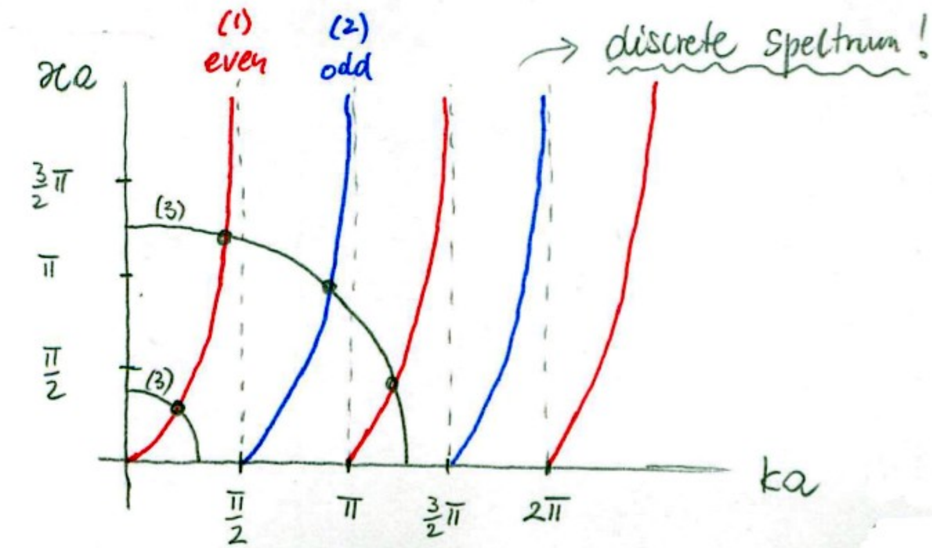
Discussion: energy levels and symmetry of ψ

Features

- **discrete spectrum**: energy is quantized

$$(ka)^2 + (\varkappa a)^2 = \frac{2ma^2}{\hbar^2}V_0$$

- finite number of bound states, depending on well parameters (width *a*, depth $-V_0$)
- for any combination of well parameters (width *a*, depth $-V_0$) **always at least one bound state**
- states with *even* and *odd* wave functions alternate
- **ground-state wave function** is ***even***



Wave functions

even ($C_2 = 0$; $B = A$)

$$\psi(x) = \begin{cases} A e^{\kappa x}, & x < -a \\ C_1 \cos kx, & -a \le x \le a \\ A e^{-\kappa x}, & x > a \end{cases}$$

odd ($C_1 = 0$; $B = -A$)

$$\psi(x) = \begin{cases} A e^{\kappa x}, & x < -a \\ C_2 \sin kx, & -a \le x \le a \\ -A e^{-\kappa x}, & x > a \end{cases}$$

Express C_1 and C_2 in terms of A (using the equations implied by continuity conditions)...

even

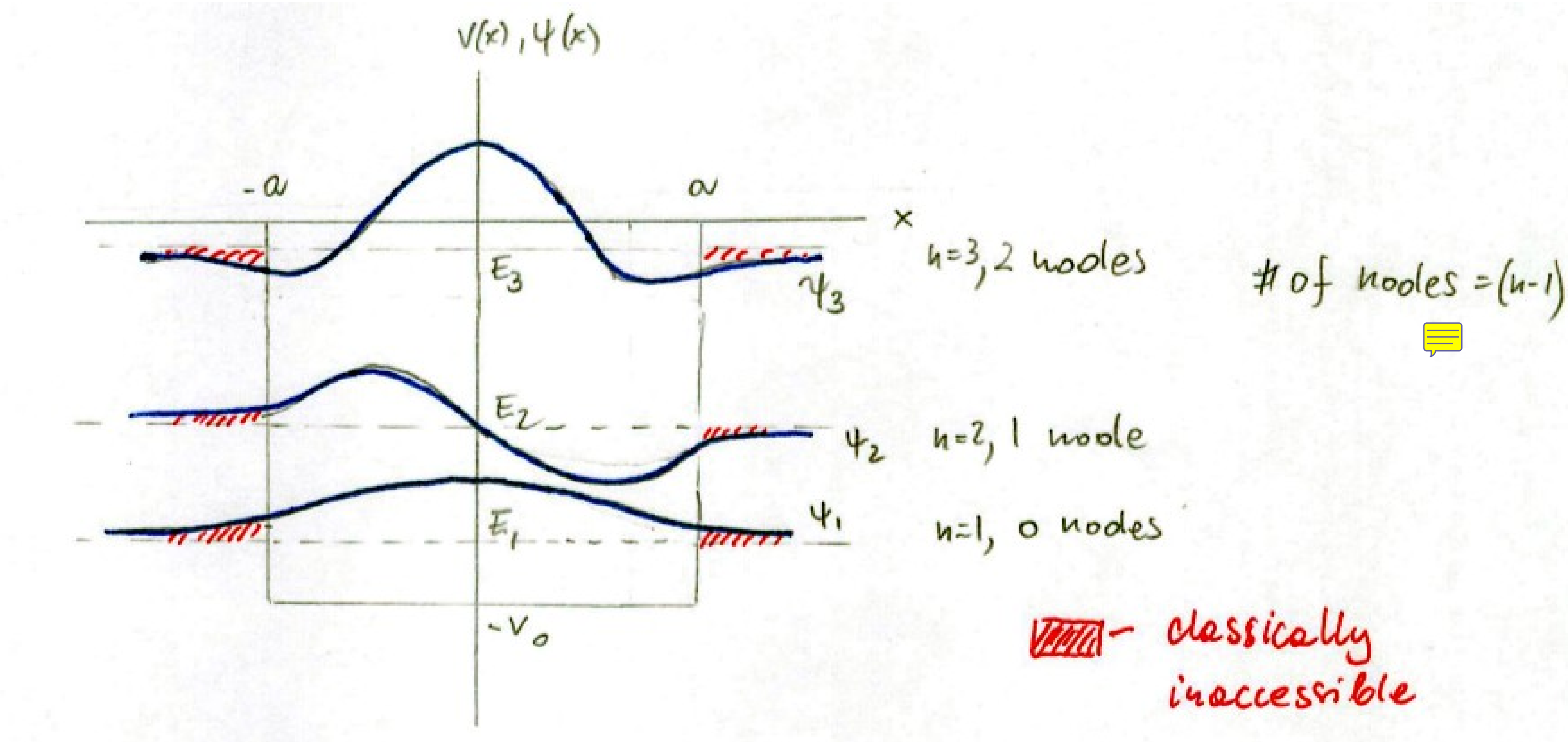
$$\psi(x) = \begin{cases} A e^{\kappa x}, & x < -a \\ A \dfrac{e^{-\kappa a}}{\cos ka} \cos kx, & -a \le x \le a \\ A e^{-\kappa x}, & x > a \end{cases}$$

odd

$$\psi(x) = \begin{cases} A e^{\kappa x}, & x < -a \\ -A \dfrac{e^{-\kappa a}}{\sin ka} \sin kx, & -a \le x \le a \\ -A e^{-\kappa x}, & x > a \end{cases}$$

...and normalize, to find A.

Discussion: wave functions



Observations:

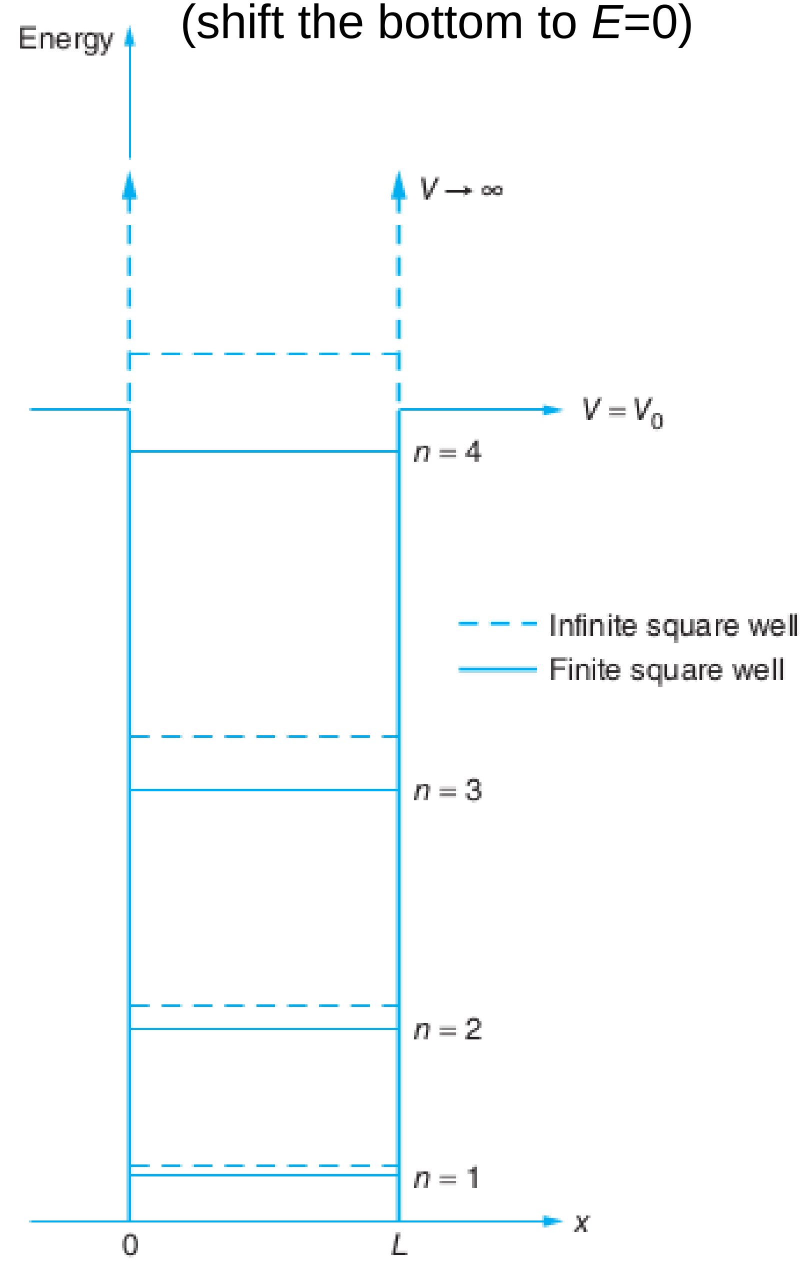
- non-zero probability, that a quantum particle penetrates classically forbidden regions
- states with *even/odd* wave functions alternate

Discussion: finite vs infinite well

Key points

- infinite number of bound states in the infinite well vs. limited number of bound states in the finite-depth well
- the corresponding energy levels are lower in the finite-depth well
- probability of finding the particle in the classically-forbidden region is zero for the infinite well and non-zero for the finite well

comparison with infinite well (shift the bottom to E=0)



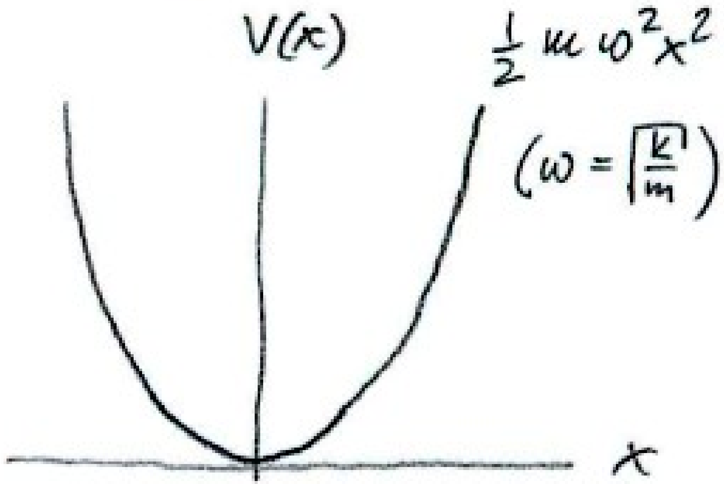
Example 2

Quantum Harmonic Oscillator

Quantum harmonic oscillator

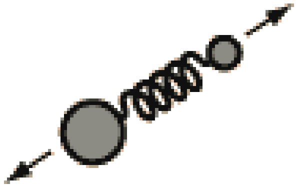
Schrödinger equation (stationary) for the harmonic oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) = E\,\psi(x)$$



Comments:

- Important in atomic/solid state physics:
  oscillations of diatomic molecules and crystal lattice;
  theory of heat capacity...

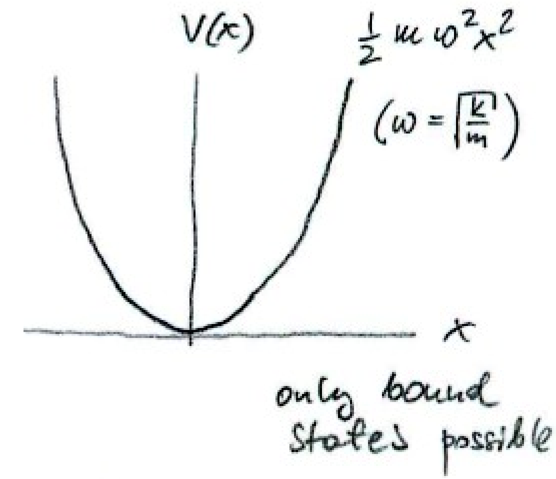


x=0 represents the equilibrium separation between the nuclei.

- Why so important?
  Can be used to approximate *small* oscillations
  around equilibrium in an arbitrarily shaped potential well.

Solution*

stationary Schrödinger equation



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

introduce dimensionless position $\xi = x/\sqrt{\frac{\hbar}{m\omega}}$. Then

$$\frac{d}{dx} = \frac{d\xi}{dx}\frac{d}{d\xi} = \sqrt{\frac{m\omega}{\hbar}}\frac{d}{d\xi} \quad \text{and} \quad \frac{d^2}{dx^2} = \frac{m\omega}{\hbar}\frac{d^2}{d\xi^2}$$

and the stationary Schrödinger equation reads

$$-\frac{\hbar\omega}{2}\frac{d^2\psi(\xi)}{d\xi^2} + \frac{\hbar\omega}{2}\xi^2\psi(\xi) = E\psi(\xi)$$

or, equivalently,

$$\frac{d^2\psi(\xi)}{d\xi^2} + \Big(\underbrace{\frac{2E}{\hbar\omega}}_{=\varepsilon} - \xi^2\Big)\psi(\xi) = 0$$

Solution*

$$\frac{d^2\psi(\xi)}{d\xi^2} + \Big(\underbrace{\frac{2E}{\hbar\omega}}_{=\varepsilon} - \xi^2\Big)\psi(\xi) = 0$$

How to solve this 2nd order linear ODE?

First, look at the corresponding asymptotic equation $(\xi \to \pm\infty)$

$$\tilde{\psi}''(\xi) - \xi^2 \tilde{\psi}(\xi) \sim 0$$

Guess a solution... $\tilde{\psi}(\xi) = e^{-\frac{1}{2}\xi^2}$ (cannot be $e^{\frac{1}{2}\xi^2}$)

...and check $\tilde{\psi}'(\xi) = -\xi e^{-\frac{1}{2}\xi^2}$; $\tilde{\psi}''(\xi) = -e^{-\frac{1}{2}\xi^2} + \xi^2 e^{-\frac{1}{2}\xi^2} \sim \xi^2 e^{-\frac{1}{2}\xi^2}$ ✓

Look for solutions of the full equation in the form

$$\psi(\xi) = e^{-\frac{1}{2}\xi^2}\, v(\xi)$$

↳ function that does not increase faster than $e^{\frac{1}{2}\xi^2}$ as $\xi \to \pm\infty$

Solution*

Calculate the derivatives...

$$\psi'(\xi) = -\xi e^{-\frac{1}{2}\xi^2}\vartheta(\xi) + e^{-\frac{1}{2}\xi^2}\vartheta'(\xi)$$

$$\psi''(\xi) = -e^{-\frac{1}{2}\xi^2}\vartheta(\xi) + \xi^2 e^{-\frac{1}{2}\xi^2}\vartheta(\xi) - \xi e^{-\frac{1}{2}\xi^2}\vartheta'(\xi) +$$

$$- \xi e^{-\frac{1}{2}\xi^2}\vartheta'(\xi) + e^{-\frac{1}{2}\xi^2}\vartheta''(\xi) = (\xi^2-1)e^{-\frac{1}{2}\xi^2}\vartheta(\xi) - 2\xi e^{-\frac{1}{2}\xi^2}\vartheta'(\xi) + e^{-\frac{1}{2}\xi^2}\vartheta''(\xi)$$

and plug back into the original (full) equation

$$\frac{d^2\psi(\xi)}{d\xi^2} + \Big(\underbrace{\frac{2E}{\hbar\omega}}_{=\varepsilon} - \xi^2\Big)\psi(\xi) = 0$$

to get

$$\vartheta''(\xi) - 2\xi\vartheta'(\xi) + (\varepsilon - 1)\vartheta(\xi) = 0$$

Hermite equation
(recall ODE class)
solution – Frobenius method

Solution*

$$v''(\xi) - 2\xi v'(\xi) + (\varepsilon - 1) v(\xi) = 0$$

Hermite equation (recall ODE class)

solution – Frobenius method

Wave function is normalizable iff $v(\xi) = \sum_{k=0} a_k \xi^{k+r}$ terminates

i.e. $v(\xi)$ is a polynomial. This happens if $\varepsilon - 1 = 2n$, where $n = 0, 1, 2, \ldots$

Then $v(\xi)$ is denoted as $H_n(\xi)$ and is called the Hermite polynomial

Hence, normalizable solutions of the S.E. exist if

$$\varepsilon = \varepsilon_n = 2n + 1$$

$$\psi(\xi) = \psi_n(\xi) = C_n e^{-\frac{1}{2}\xi^2} H_n(x) \qquad n = 0, 1, 2, \ldots$$

Results

Solution: energies and wave functions

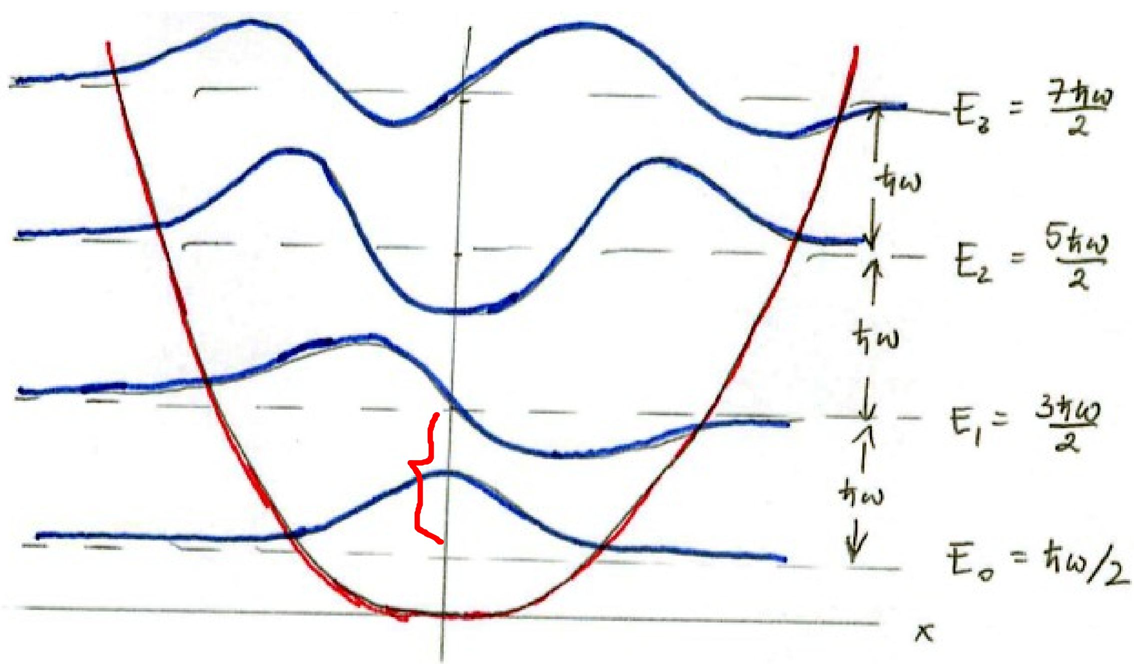
$$E = E_n = \hbar\omega\left(n + \tfrac{1}{2}\right)$$

$$\psi(x) = \psi_n(x) = C_n\, e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)^2} H_n\!\left(\frac{x}{x_0}\right) \qquad n = 0, 1, 2, \ldots$$

where $C_n = \dfrac{1}{\sqrt{2^n n!\, x_0 \sqrt{\pi}}}$ and $x_0 = \sqrt{\hbar/m\omega}$

$$\psi_1(x) = \frac{1}{\sqrt{2 x_0 \sqrt{\pi}}}\left(2\frac{x}{x_0}\right) e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)^2}$$

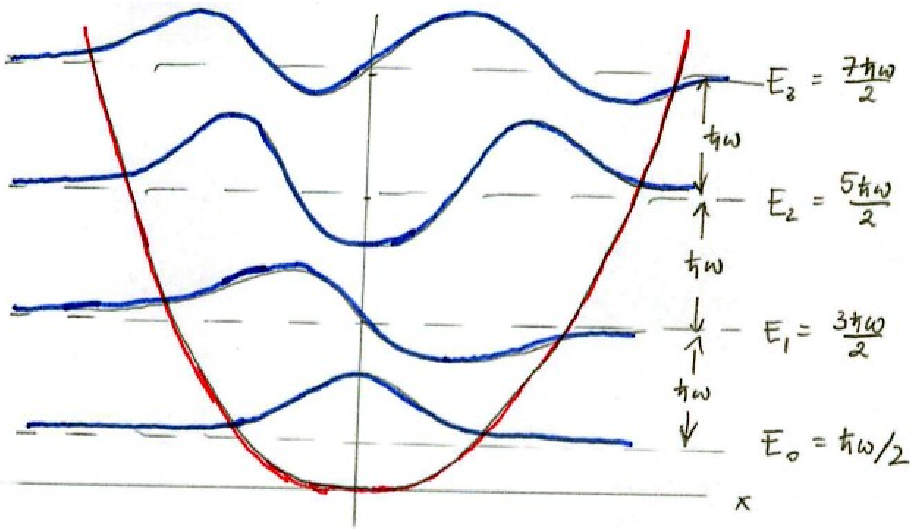
$$\psi_0(x) = \frac{1}{\sqrt{x_0 \sqrt{\pi}}}\, e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)^2}$$



https://www.st-andrews.ac.uk/physics/quvis/simulations_html5/sims/QuantumOscillator/oscillator2.html

Discussion

Features



- equally-spaced energy levels

- the energy of the ground state (state with the lowest energy) is not zero, oscillations never disappear (*zero-point vibrations*)

- non-zero probability, that a quantum particle penetrates the classically forbidden region

- states *with even/odd* wave functions alternate; ground-state wave function is *even* (no nodes)

- the ground state wave function of the harmonic oscillator saturates the Heisenberg uncertainty principle, i.e. in the ground state

$$\Delta_x \Delta_p = \frac{\hbar}{2}$$

Appendix*: Properties of Hermite polynomials

- few first polynomials

$$H_0(\xi)=1; \quad H_1(\xi)=2\xi; \quad H_2(\xi)=4\xi^2-2; \quad H_3(\xi)=8\xi^3-12\xi$$

- orthogonality with weight $e^{-\xi^2}$

$$\int_{-\infty}^{\infty} H_n(\xi) H_m(\xi)\, e^{-\xi^2} d\xi = 2^n n! \sqrt{\pi}\, \delta_{nm}$$

- recurrence relations

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2n H_{n-1}(\xi)$$
$$H_n'(\xi) = 2n H_{n-1}(\xi)$$

- generating function

$$e^{2\xi t - t^2} = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n$$

- Rodriguez formula

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

Example 3*

Triangular Semi-infinite Potential Well

Triangular well

Quantum particle (charge)
in a uniform electric field

$$V(x) = \begin{cases} \infty & \text{for } x \le 0 \\ q\,\mathcal{E}\,x & \end{cases}$$

$\mathcal{E}$: electric field

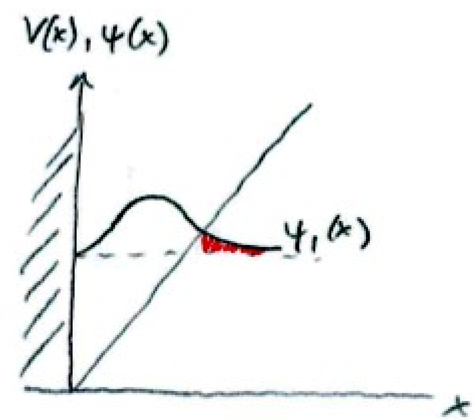
q: electric charge

Solution: wave functions and energies

$$\psi_n(x) = \begin{cases} 0 & \text{for } x \le 0 \\ C \cdot \mathrm{Ai}\left(\sqrt[3]{\dfrac{2m}{(\hbar q \mathcal{E})^2}}\,(q\mathcal{E}x - E_n) \right) & \text{for } x > 0 \end{cases}$$

C: normalization constant

Ai: Airy function (special function)



$$E_n = \sqrt[3]{\frac{\hbar^2}{2m}} \left[\frac{3\pi q \mathcal{E}}{2} \left(n - \frac{1}{4} \right) \right]^{2/3} \qquad n = 1, 2, \ldots$$

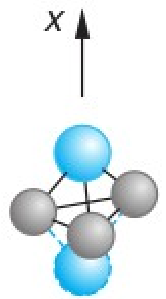
Extra Example

Double-well potential

(NH_3 molecule)

NH_3 molecule

Structure of the NH_3 molecule



The H atoms form a plane;
the N atom (in two equivalent positions) is colored in blue

Source:
P.A. Tipler, *Modern Physics*

Source:
R.P Feynman,
The Feynman Lectures on Physics

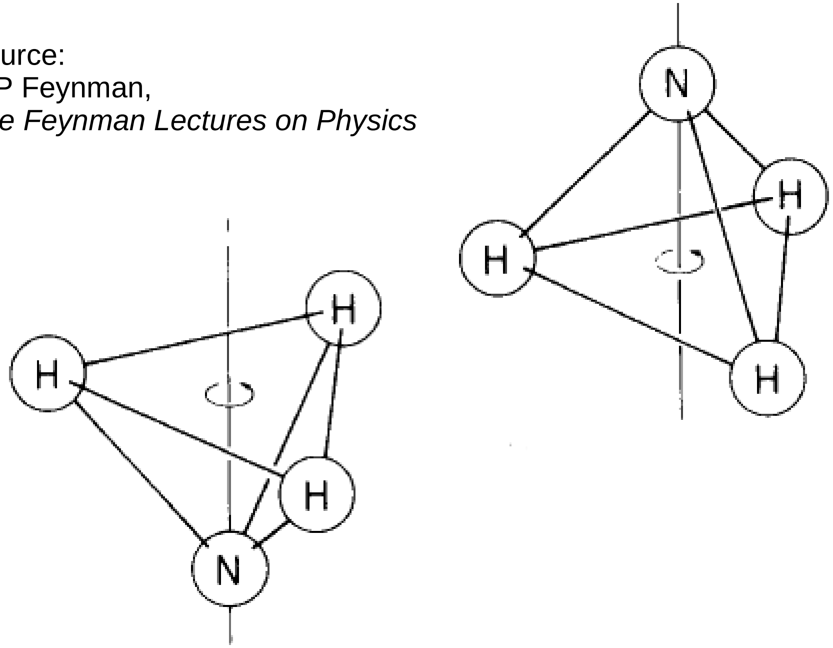


Fig. 8-1. Two equivalent geometric arrangements of the ammonia molecule.

Observation

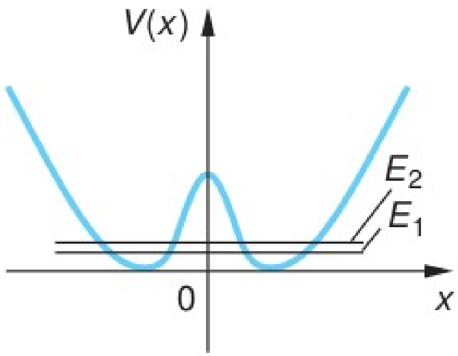
The NH_3 molecule oscillates back and forth, with frequency

f = 2.3786 x 10^{10} Hz,

between the two equivalent geometric arrangements.

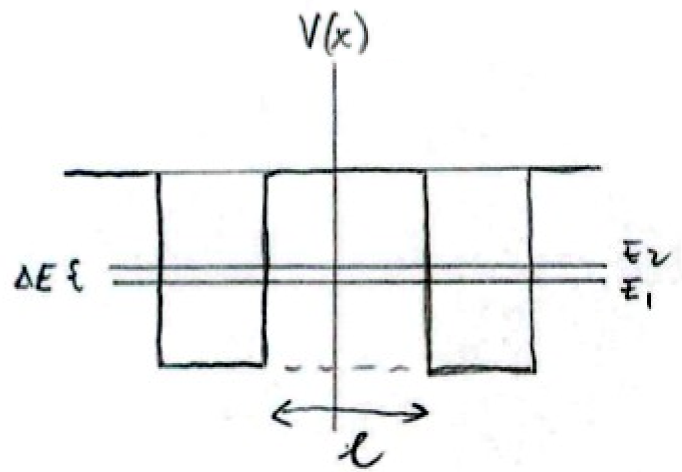
How to model?

A particle in a double-well potential



Energies and wave functions in a double-well

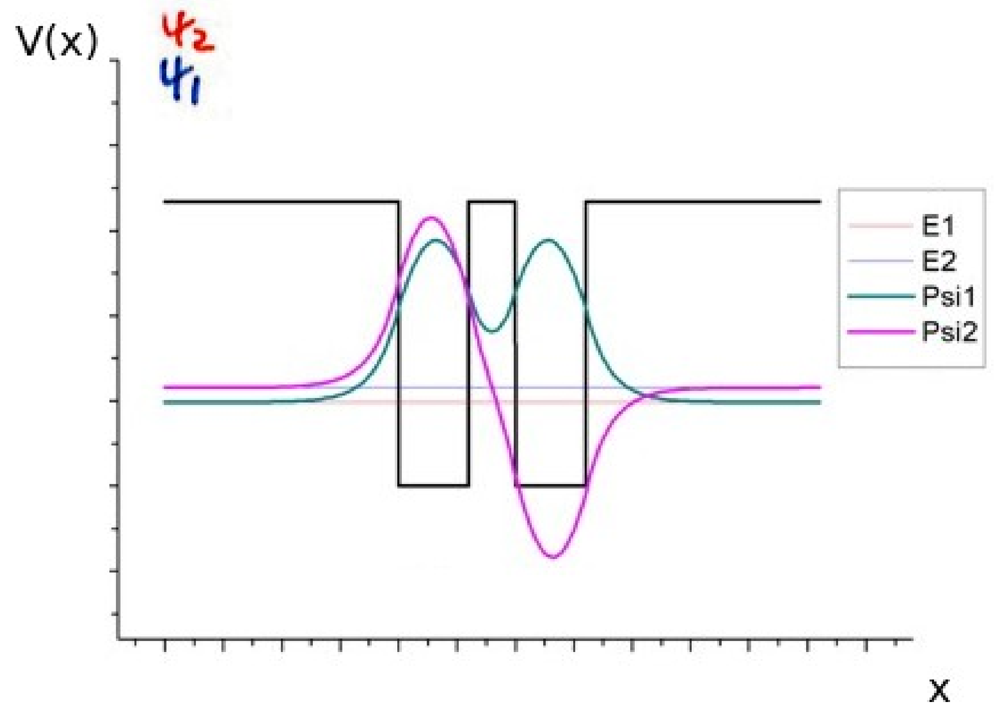
For simplicity, consider a rectangular double-well. For the two lowest-lying states, the separation between the ground-state and first excited state energies depends on the width *l* of the barrier between the wells



For *l* $\rightarrow \infty$ (large separation),
we have $\Delta E \rightarrow 0$ (two independent wells)

Ground-state
wave function – even with no nodes;

First excited state
wave function – odd with one node



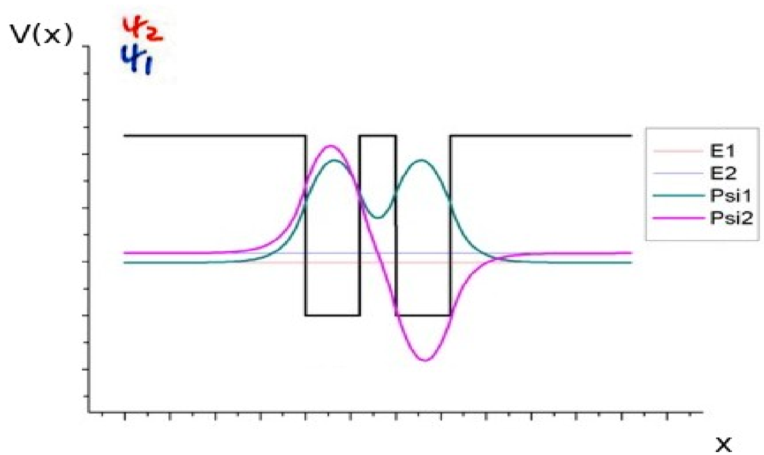
Time-evolution and tunneling

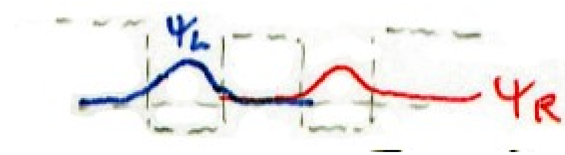
Use the wave functions of the ground state and first excited state to design two linear combinations representing the molecule in the two equivalent geometric arrangements

“particle in the the left well” = “N atom above the plane”

and

“particle in the the right well” = “N atom below the plane”.





These linear combinations are

$$\psi_L = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$$

$$\psi_R = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$$

Are they eigenfunctions of the double-well Hamiltonian?

Time-evolution and tunneling

Of course not! They have no definite energy, but the average energy in both is the same.

What happens if we start with the NH_3 molecule in the state

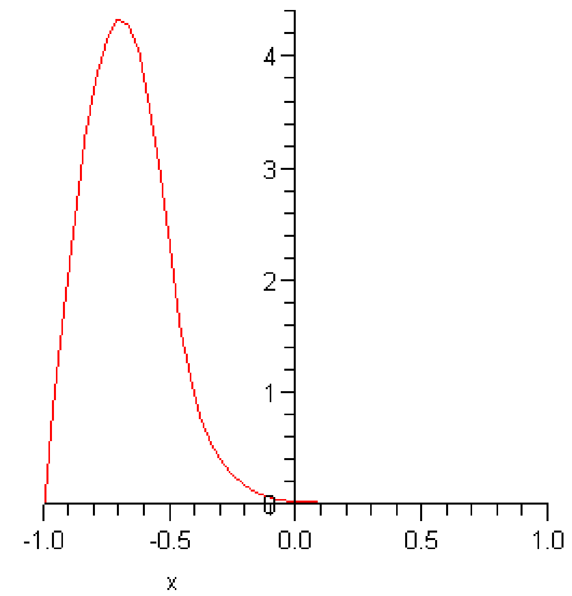
$$\Psi(x,0) = \psi_L(x) = \frac{1}{\sqrt{2}}\left(\psi_1(x) + \psi_2(x)\right)$$

It evolves according to

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left(e^{-\frac{i}{\hbar}E_1 t}\psi_1(x) + e^{-\frac{i}{\hbar}E_2 t}\psi_2(x)\right)$$

and, after some time *T*, it becomes

$$\Psi(x,T) = \psi_R = \frac{1}{\sqrt{2}}\left(\psi_1 - \psi_2\right)$$



The NH_3 molecule oscillates back and forth between two equilibrium configurations.

http://www.hep.manchester.ac.uk/u/forshaw/BoseFermi/images/Double%20Well_45.gif