Schrödinger’s Equation III

Greg Anderson
Department of Physics & Astronomy
Northeastern Illinois University

March 5, 2008
Overview

Quantum Mechanics
Infinite Square Well
Quantum Harmonic Oscillator
Molecular Spectra
Finite Square Well
Quantum Tunneling
Outline

- Recap
  - The wave function
  - Schrödinger’s Equation
  - The Infinite Square Well
- Qualitative solutions to Schrödinger’s Equation
  - Curvature of the wave functions
  - Classically forbidden & allowed regions
- The Quantum SHO
- The Finite Square Well
 Quantum Mechanics

Outline

Quantum Mechanics
The Schrödinger Equations
Acceptable Wave Functions $\psi(x)$
Compendium: The Infinite Square Well
Probability Distribution
Parity ($x \leftrightarrow -x$)
Parity II
Infinite Square Well
Quantum Harmonic Oscillator
Molecular Spectra
Finite Square Well
Quantum Tunneling
The Schrödinger Equations

Time Dependent Schrödinger equation

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}\]

Time Independent Schrödinger equation

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

where

\[\Psi(x, t) = \psi(x) e^{-iEt/\hbar}\]
Acceptable Wave Functions $\psi(x)$

An acceptable wave function must satisfy:

- $\psi(x)$ must satisfy the Schrödinger equation.
- $\psi(x)$ must be continuous.
- $d\psi/dx$ is (almost) always continuous.
- $\psi(x)$ must be single valued.
- The wave function must be normalizable.

$$1 = \int dx \, \psi^*(x)\psi(x)$$
Compendium: The Infinite Square Well

Probability Distribution Parity ($x \leftrightarrow -x$)

Wave functions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right),$$

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

Energy levels:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$
Quantum mechanics is probabilistic:

\[ P(x) = \Psi^*(x, t) \Psi(x, t) \]

The infinitesimal probability the particle will be found between \( x \) and \( x + dx \) is:

\[ dP = P(x)dx = \Psi^*(x, t) \Psi(x, t)dx \]

The probability that the particle will be found between \( a \) and \( b \):

\[ P_{ab} = \int_a^b \Psi^*(x, t) \Psi(x, t)dx \]
**Parity \((x \leftrightarrow -x)\)**

**Schrödinger’s equation**

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

Let \(x' = -x\), \(\frac{d}{dx} = -\frac{d}{dx'}\), \(\frac{d^2}{dx^2} = -\frac{d}{dx'}\).

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

For symmetric potentials \(V(x) = V(-x)\):

If \(\psi(x)\) solves Schrödinger’s equation, so does \(\psi(-x)\)
Parity II

Linear combinations of solutions to Schrödinger’s equation with the same energy \( E \) are solutions to Schrödinger’s equation.

Even and odd solutions:

\[
\psi_E(x) = \frac{1}{2} [\psi(x) + \psi(-x)], \quad \psi_E(x) = \psi_E(-x)
\]

\[
\psi_O(x) = \frac{1}{2} [\psi(x) - \psi(-x)], \quad \psi_O(x) = -\psi_O(-x)
\]

For symmetric potentials \( V(x) = V(-x) \):

- Solutions \( \psi(x) \) have a definite parity

\[
\psi(x) = \pm \psi(-x)
\]
Infinite Square Well

Outline
Quantum Mechanics

Infinite Square Well
Particle in an Infinite Well
Quantum Harmonic Oscillator
Molecular Spectra
Finite Square Well
Quantum Tunneling
Particle in an Infinite Well

Even wave functions
\[ x \psi_{2n-1}(x) = \sqrt{\frac{2}{L}} \cos \left( \frac{(2n-1)\pi x}{L} \right) \]

Odd wave functions
\[ \psi_{2n}(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{2n\pi x}{L} \right) \]

For the state \( \psi_n \)
\[ E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \]
Quantum Harmonic Oscillator
You can do everything with a bayonet except sit on it. – Napoleon

Taylor Series

\[ V(x) = \sum_{n=0}^{\infty} \frac{x^n}{n!} \frac{d^n V}{dx^n} \]

\[ = V(0) + V'(0)x + \frac{1}{2}V''(0)x^2 + \ldots \]

For small \( x \)

\[ V(x) \approx \frac{1}{2} \frac{d^2 V}{dx^2} x^2 = \frac{1}{2} Kx^2 \]

Force (Hooke’s Law):

\[ F = -\frac{dV}{dx} = -Kx \]
Classical Simple Harmonic Oscillator

Potential Energy

\[ V(x) = \frac{1}{2} K x^2 = \frac{1}{2} m \omega^2 x^2 \]

Newton II

\[ F = ma = m \ddot{x} = -Kx \]

\[ \ddot{x} = -\frac{K}{m} x \equiv -\omega^2 x \]

Energy is continuous

\[ x(t) = A \cos \omega t \]

\[ E = \frac{1}{2} m \omega^2 A^2 \]
Kinetic Energy:

\[ K = E - V = \frac{1}{2} m \omega^2 (A^2 - x^2) \]

\[ dt = \text{time spent in } dx. \]

Probability found in \( dx \):

\[ P(x) \propto \frac{dt}{v} \]
\[ \propto \frac{dx}{\sqrt{2(E-V)/m}} \]
\[ \propto \frac{dx}{\omega \sqrt{A^2 - x^2}} \]

\[ x(t) = A \cos \omega t \]
Curvature and Amplitude

Time-independent Schrödinger equation:

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

Rewriting Schrödinger’s equation:

\[\psi'' = -\frac{2m}{\hbar^2} (E - V)\psi\]

- \(E > V\): \(\text{sign } \psi'' = -\text{sign } \psi\)
- \(E = V\): \(\psi'' = 0\).
- \(E < V\): \(\text{sign } \psi'' = \text{sign } \psi\)
Curvature of Wave Function

A qualitative guide to Schrödinger's Equation:

\[
\text{Curvature of } \Psi = -\frac{2m}{\hbar^2} [E - V(x)] \Psi(x)
\]

Classically Forbidden vs. Allowed

- Allowed: \( E > V \) curve towards axis.
- Forbidden: \( E < V \) curve away from axis.

Probability of finding particle at \( x \):

\[
P \propto |\Psi|^2
\]
The Quantum SHO

Potential Energy

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

Quantized Energies

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \omega \]
Potential Energy

\[ V(x) = \frac{1}{2} k x^2 \]

Quantized Energies

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

\( n = 0, \) no nodes

\[ E_0 = \frac{1}{2} \hbar \omega \]
The Quantum SHO

Potential Energy

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

Quantized Energies

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

\( n = 1, \) 1 node

\[ E_1 = \frac{3}{2} \hbar \omega \]
The Quantum SHO

Potential Energy

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

Quantized Energies

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

\( n = 2, \) 2 nodes

\[ E_2 = \frac{5}{2}\hbar\omega \]
The Quantum SHO

Potential Energy

\[ V(x) = \frac{1}{2} m \omega^2 x^2 \]

Schrödinger’s Equation

\[ \psi'' = -\frac{2m}{\hbar^2} (E - V) \psi \]

Energies

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \omega \]
**SHO Wave Functions**

The SHO wave functions

\[ \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}} x \]

Corresponding to states with energy

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

The first few Hermite Polynomials \( H_n(\xi) \)

\[ H_0(\xi) = 1, \quad H_1(\xi) = 2\xi, \quad H_2(\xi) = 4\xi^2 - 2, \quad H_3(\xi) = 8\xi^3 - 12\xi \]
The first six Hermite polynomials:

\[ H_0(x) = 1 \quad \text{even} \]
\[ H_1(x) = 2x \quad \text{odd} \]
\[ H_2(x) = 4x^2 - 2 \quad \text{even} \]
\[ H_3(x) = 8x^3 - 12x \quad \text{odd} \]
\[ H_4(x) = 16x^4 - 48x^2 + 12 \quad \text{even} \]
\[ H_5(x) = 32x^5 - 160x^3 + 120x \quad \text{odd} \]

Rodrigues formula:

\[ H_n(x) = (-1)^n e^{x^2} \left( \frac{d}{dx} \right)^n e^{-x^2} \]
Hermite Polynomials

Outline
Quantum Mechanics
Infinite Square Well
Quantum Harmonic Oscillator
The Simple Harmonic Oscillator (SHO)
Classical Simple Harmonic Oscillator
Curvature and Amplitude
Curvature of Wave Function
The Quantum SHO
SHO Wave Functions
Hermite Polynomials

$H_1(x)$
$H_2(x)$
$H_3(x)$
$H_4(x)$
$H_5(x)$
\[ E_0 = \frac{1}{2} \hbar \omega \]

\[ \psi_0(\xi) = \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} H_0(\xi) e^{-\xi^2/2} \]
\[ E_1 = \frac{3}{2} \hbar \omega \]

\[ \psi_1(\xi) = \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{2}} H_1(\xi) e^{-\xi^2 / 2} \]

\[ |\psi_1|^2 \]

\[ \xi = \sqrt{\frac{m \omega}{\hbar}} x \]
\[ E_2 = \frac{5}{2} \hbar \omega \]

\[ \psi_2(\xi) = \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} \frac{1}{2\sqrt{2}} H_2(\xi) e^{-\xi^2/2} \]

\[ |\psi_2|^2 \]

\[ \xi = \sqrt{\frac{m \omega}{\hbar}} x \]
$|\psi_3|^2$

$\xi = \sqrt{\frac{m\omega}{\hbar}} x$
\[ |\psi_4|^2 \]

\[ \xi = \sqrt{\frac{m\omega}{\hbar}} x \]
\[ |\psi_5|^2 \]

\[ \xi = \sqrt{\frac{m\omega}{\hbar}} x \]
$|\psi_6|^2 = \sqrt{\frac{m\omega}{\hbar}} x$
\[ \xi = \sqrt{\frac{m \omega}{\hbar}} x \]

\[ |\psi_{10}|^2 \]
Molecular Spectra
Molecular Vibrations

The SHO provides a simple model for molecular vibrations.

Quantum Energies

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

Electric dipole radiation:

\[ \int dx \psi_n^*(x)x\psi_m(x) = 0, \]

unless \( n = m \pm 1 \). Selection Rules:

\[ \Delta n = \pm 1 \]
Molecular Energy Scales

- Rotational: $\Delta E \sim 10^{-3}$ eV
- Vibrational: $\Delta E \sim 10^{-1}$ eV
- Electronic: $\Delta E \sim$ eV
**The Finite Square Well**

Schrödinger’s Eq:

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

Bound States \( E < V_0 \):

\[ \alpha^2 = \frac{2m}{\hbar^2} (V_0 - E) > 0 \]

Regions I & III:

\[ \psi'' = +\alpha^2 \psi \]

Exponential solutions:

\[ \psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \]

Region II:

\[ \psi'' = -k^2 \psi, \quad k^2 = \frac{2m}{\hbar^2} E \]

Oscillating solutions:

\[ \psi(x) = C \sin(kx) + D \cos(kx) \]
The Finite Square Well (II)

Schrödinger’s Eq:
\[ \psi'' = \frac{2m}{\hbar^2} [V(x) - E] \psi \]

Bound States \( E < V_0 \):
\[ \alpha^2 = \frac{2m}{\hbar^2} (V_0 - E) > 0 \]

Regions I & III:
\[ \psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \]
\[ \lim_{x \to \infty} \psi_{III}(x) = 0 \]
\[ \lim_{x \to -\infty} \psi_{I}(x) = 0 \]

Exponential solutions:
\[ \psi_{I}(x) = Ae^{\alpha x}, \ psi_{III}(x) = Be^{-\alpha x} \]

Region II (Oscillating):
\[ \psi_{II}(x) = C \sin(kx) + D \cos(kx) \]
Matching Conditions

Continuous $\psi$:  
\[
\psi_I(-a) = \psi_{II}(-a) \\
\psi_{II}(a) = \psi_{III}(a)
\]

Continuous $\psi'$:  
\[
\psi'_I(-a) = \psi'_{II}(-a) \\
\psi'_{II}(a) = \psi'_{III}(a)
\]

Match even solutions ($A_I = B_{III}, C = 0$)  
\[
A e^{-\alpha a} = D \cos(ka) \\
\alpha A e^{-\alpha a} = kD \sin(ka)
\]

Dividing gives:  
\[
k \tan(ka) = \alpha
\]

For odd solutions ($A_I = -B_{III}, D = 0$)  
\[
-k \cot ka = \alpha
\]
The Transcendental Equation

For the even solutions:

\[
\tan ka = \alpha/k, \quad k^2 = \frac{2m}{\hbar^2} E, \quad \alpha^2 = \frac{2m}{\hbar^2} (V_0 - E)
\]

\[
\tan \left( \frac{\sqrt{2mE}}{\hbar} a \right) = \sqrt{\frac{V_0 - E}{E}} = \sqrt{\frac{2mV_0}{\hbar^2 k^2} - 1}
\]

For the odd solutions:

\[-\cot ka = \alpha/k\]
Graphical Solution

\[ tan(ka) - cot(ka) = \sqrt{\frac{2mV_0a^2}{\hbar^2}} (\frac{1}{(ka)^2}) - 1 \]

- **shallow well**
- **deeper well**

Outline
- Quantum Mechanics
  - Infinite Square Well
  - Quantum Harmonic Oscillator
  - Molecular Spectra
  - Finite Square Well
    - The Finite Square Well
    - The Finite Square Well (II)
    - Matching Conditions
    - The Transcendental Equation
- Graphical Solution
  - Quantum Corral
  - Quantum Tunneling

©2004, 2007 G. Anderson

Physics III – slide 33 / 38
Quantum Tunneling
Barrier Tunneling

Particle with $E < V_0$

$$\Delta E \Delta t \geq \hbar$$

Transmission Coefficient

$$T \propto e^{-2\kappa a}$$

$$\kappa = \sqrt{\frac{8\pi^2 m (V_0 - E)}{\hbar^2}}$$

$$\Delta E \Delta t \geq \hbar$$
Scanning tunneling microscopes (STM) are widely used in both industry and academic research.

Electron cloud extends above surface. When separation between tip and surface is a few atomic diameters, current flows.
Scanning Tunneling Microscope

A STM provides a 3D image of metal surfaces.

7 nm x 7 nm image of Cs on GaAs
NIST Physics Laboratory

35 nm x 35 nm Cs (small bumps) on Fe
NIST Physics Laboratory