Exactly Solvable Problems in QM

Particle in a Box, Harmonic Oscillator, Finite Barrier, Particle on a Sphere, and the Hydrogen Atom

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Outline

1. Particle in a Box
2. Quantum Harmonic Oscillator
3. Finite Potential Barrier
4. Particle on a Sphere
5. The Hydrogen Atom

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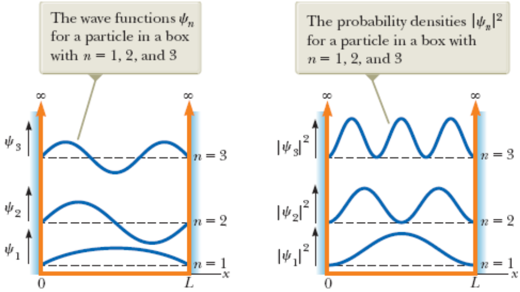
Particle in a Box

The Setup

- Consider a point particle of mass m confined in a one-dimensional box of length L. The potential energy $V(x)$ inside the box is zero, and infinite outside:

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$



Particle in a Box

Schrödinger Equation for 1D Box

- The time-independent Schrödinger equation inside the box is:

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

- The boundary conditions are $\psi(0) = 0$ and $\psi(L) = 0$.
- Sine functions satisfy the Schrödinger equation and the boundary conditions.

Particle in a Box

Solution to the Schrödinger Equation

- The general solution to the Schrödinger equation is:

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

where n is a positive integer. The normalization condition gives:

$$\int_0^L |\psi_n(x)|^2 \, dx = 1 \quad \Rightarrow \quad A = \sqrt{\frac{2}{L}}$$

- Substituting the solutions in the Schrödinger equation, we obtain the following quantized energy levels:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Particle in a Box

Solution to the Schrödinger Equation

- For a symmetric infinite square well

$$V(x) = \begin{cases} 0 & \text{for } -\frac{L}{2} < x < \frac{L}{2} \\ \infty & \text{otherwise} \end{cases}$$

- solutions can be classified through their parity: with respect to the origin:

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

  - $n = 1, 3, 5, \ldots$

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

  - $n = 2, 4, 6, \ldots$

Particle in a Box

Two- and Three-Dimensional Boxes

- For a particle in a 2D $L_x \times L_y$ box, the potential is:

$$V(x,y) = \begin{cases} 0 & \text{for } 0 < x < L_x \text{ and } 0 < y < L_y \\ \infty & \text{otherwise} \end{cases}$$

- The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2}\right) = E\psi(x,y)$$

with solutions

$$\psi_{n_x,n_y}(x,y) = \sqrt{\frac{4}{L_xL_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right) \qquad n_x, n_y = 1, 2, \cdots$$

and with energy levels

$$E_{n_x,n_y} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

Particle in a Box

Two- and Three-Dimensional Boxes

- Finally in a 3D box, we have

$$\psi_{n_x,n_y,n_z}(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

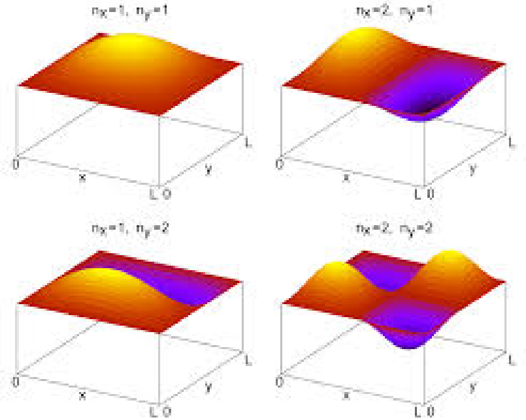
- The energy levels are

$$E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

Particle in a Box

Two- and Three-Dimensional Boxes

- Some solutions for the 2D box can be visualized as follows:



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2 Quantum Harmonic Oscillator

3 Finite Potential Barrier

4 Particle on a Sphere

5 The Hydrogen Atom

Quantum Harmonic Oscillator

Introduction

- The quantum harmonic oscillator describes a particle subject to a restoring force proportional to its displacement.
- The potential energy for a harmonic oscillator is:

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

  where m is the mass of the particle and ω is the angular frequency of oscillation.
- The time-independent Schrödinger equation for a harmonic oscillator is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi(x) = E\psi(x)$$

- Rearranging gives:

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2mE}{\hbar\omega} - \frac{m^2\omega^2 x^2}{\hbar}\right)\psi(x) = 0$$

Quantum Harmonic Oscillator

Solution to the Schrödinger Equation

- Introduce a dimensionless variable ξ defined by:

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

- The Schrödinger equation becomes:

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(E' - \xi^2\right)\psi(\xi) = 0$$

  where $E' = \frac{2E}{\hbar\omega}$.

- The solution to the dimensionless Schrödinger equation is:

$$\psi_n(\xi) = N_n e^{-\xi^2/2} H_n(\xi)$$

  where $H_n(\xi)$ are the Hermite polynomials and N_n is a normalization constant:

$$N_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

Quantum Harmonic Oscillator

Solution to the Schrödinger Equation

- The energy levels of the quantum harmonic oscillator are quantized and given by:

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

where $n = 0, 1, 2, \ldots$ is a non-negative integer.

- The wavefunctions are:

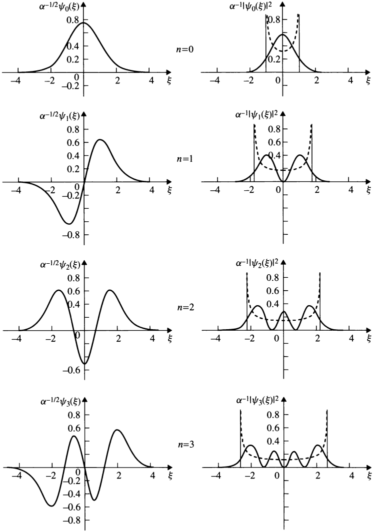
$$\psi_n(x) = \sqrt{\frac{m\omega}{\pi\hbar}}\frac{1}{\sqrt{2^n n!}}e^{-m\omega x^2/(2\hbar)}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

where H_n are Hermite polynomials. For $n = 0$:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{-m\omega x^2/(2\hbar)}$$

Quantum Harmonic Oscillator

Solution to the Schrödinger Equation



Quantum Harmonic Oscillator

The correspondence principle

- The classical probability density, $P_c(x)$ is given by

$$P_c(x) = \frac{1}{T}\frac{2dx}{v} = \frac{dx}{\pi(x_0^2 - x^2)^{\frac{1}{2}}}$$

  - T: period
  - x_0: amplitude of the periodic motion

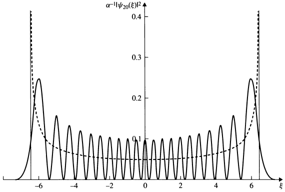


Figure 4.19 Comparison of the quantum mechanical position probability density for the state $n = 20$ of a linear harmonic oscillator (solid curve) with the probability density of the corresponding classical oscillator (dashed curve), having a total energy $E_{n=20} = (41/2)\hbar\omega$.

- Classical and quantum mechanics agree for large quantum numbers

Quantum Harmonic Oscillator

2D Harmonic Oscillator

- For a two-dimensional (isotropic) harmonic oscillator with potential:

$$V(x, y) = \frac{1}{2} m\omega^2 (x^2 + y^2)$$

- The time-independent Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2}\right) + \frac{1}{2} m\omega^2 (x^2 + y^2)\psi(x, y) = E\psi(x, y)$$

Quantum Harmonic Oscillator

2D Harmonic Oscillator

- The energy levels are:

$$E_{n_x,n_y} = (n_x + n_y + 1)\,\hbar\omega$$

where n_x and n_y are non-negative integers. The wavefunctions are:

$$\psi_{n_x,n_y}(x,y) = \psi_{n_x}(x)\psi_{n_y}(y)$$

with:

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

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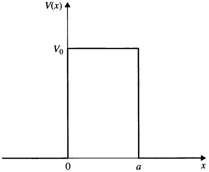
Finite Potential Barrier

Introduction

- Consider a particle of energy E approaching a potential barrier of height V_0 and width a. The potential $V(x)$ is given by:

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

- Some of the incoming wave function is expected to pass through the barrier and the rest to be reflected.



Finite Potential Barrier

Schrödinger Equation and Boundary Conditions

- The time-independent Schrödinger equation is:

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

- In regions:
  - For $x < 0$ (Region I): $V(x) = 0$

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

  - For $0 \leq x \leq a$ (Region II): $V(x) = V_0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi(x) = E\psi(x)$$

  - For $x > a$ (Region III): $V(x) = 0$

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

Finite Potential Barrier

Solution in Region I and III

- In regions I and III, the solutions have a forward and a backward moving free particle portion, but with different ratios.

$$\psi_I(x) = Ae^{ikx} + Be^{-ikx}$$
$$\psi_{III}(x) = Ce^{ikx} + De^{-ikx}$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$. $D = 0$ assuming a particle incident to the left of the barrier (boundary condition).

- The boundary conditions at $x = 0$ and $x = a$ require continuity of $\psi(x)$ and $\frac{d\psi(x)}{dx}$.

Finite Potential Barrier

Solution in Region II

- In Region II ($0 \leq x \leq a$), the Schrödinger equation becomes:

$$\frac{d^2\psi_{II}(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2}\psi_{II}(x)$$

- Define $\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$, where κ is real for $E < V_0$. The wavefunction in this region is:

$$\psi_{II}(x) = Fe^{\kappa x} + Ge^{-\kappa x}$$

- Thus the wave function in this region does not have a sinusoidal character but a decaying profile.

Finite Potential Barrier

Matching Boundary Conditions

- For continuity, the solutions and their derivatives must match at the two boundaries.
- At $x = 0$:

$$\psi_I(0) = \psi_{II}(0) \implies A + B = F + G$$

$$\left.\frac{d\psi_I(x)}{dx}\right|_{x=0} = \left.\frac{d\psi_{II}(x)}{dx}\right|_{x=0} \implies ik(A - B) = \kappa(F - G)$$

- At $x = a$:

$$\psi_{II}(a) = \psi_{III}(a) \implies Ce^{ikaa} = Fe^{\kappa a} + Ge^{-\kappa a}$$

$$\left.\frac{d\psi_{II}(x)}{dx}\right|_{x=a} = \left.\frac{d\psi_{III}(x)}{dx}\right|_{x=a} \implies ikCe^{i\kappa a} = \kappa(Fe^{\kappa a} - Ge^{-\kappa a})$$

Finite Potential Barrier

Transmission and Reflection Coefficients (case E<V_0)

- Define the transmission coefficient T and reflection coefficient R:

$$R = \frac{|B|^2}{|A|^2} = \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)}\right]^{-1}$$

$$T = \frac{|C|^2}{|A|^2} = \left[1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)}\right]^{-1}$$

- The coefficients are related by $R + T = 1$

Finite Potential Barrier

Visualization of Solutions (case E<V_0)

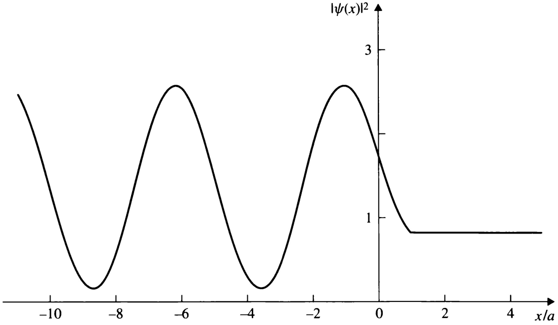
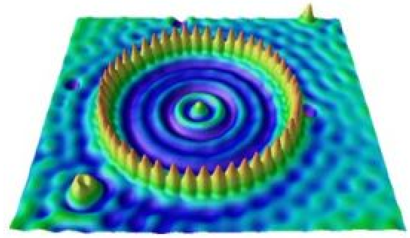


Figure 4.5 The modulus square of the wave function, $|\psi(x)|^2$, for the case of a rectangular barrier such that $mV_0a^2/\hbar^2 = 0.25$. The incident particle energy is $E = 0.75V_0$. The coefficient A in (4.73a) has been taken to be $A = 1$.

Finite Potential Barrier

Application: scanning tunnelling microscope



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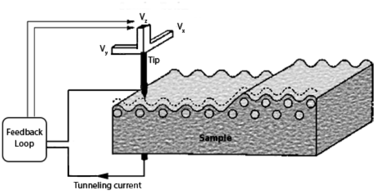

scheme of a STM

- Electrical voltage is applied between a needle and the surface. Current will flow according to the equation above for the transmission coefficient (case $\kappa a >> 1$).
  - sensitive measure of the height of the needle above the surface

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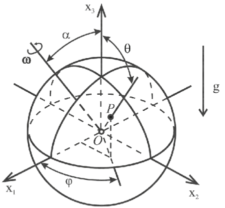
Particle on a Sphere

Introduction



- Consider a particle of mass μ constrained to move on the surface of a sphere.
- The particle's wave function must satisfy the Schrödinger equation in spherical coordinates.
- Boundary conditions are applied on the spherical surface, leading to quantization.

Particle on a Sphere

Spherical Coordinates

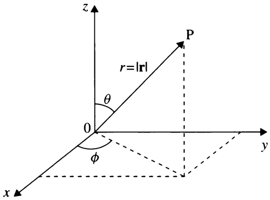


Figure 6.1 The spherical polar coordinates (r, θ, ϕ) of a point P. The position vector of P with respect to the origin is **r**.

- The spherical coordinates (r, θ, ϕ) are used for the spherical surface.
- The position vector is given by $\mathbf{r} = r\hat{r}$ where r is the radius of the sphere.
- The angular coordinates θ (polar angle) and ϕ (azimuthal angle) describe the position on the surface.

Particle on a Sphere

Schrödinger Equation on a Sphere

- The Laplacian operator ∇^2 in spherical coordinates is:

$$\nabla^2 = \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

- The Schrödinger equation in spherical coordinates for a particle on a sphere of radius a is:

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta,\phi) = E\psi(\theta,\phi)$$

where $I = \mu a^2$ is the moment of inertia.

Particle on a Sphere

Separation of Variables

- The wave function $\psi(\theta, \phi)$ can be separated into:

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

- Substituting into the Schrödinger equation and dividing by ψ:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2} = -\frac{2IE}{\hbar^2}$$

Particle on a Sphere

Azimuthal Equation

- The azimuthal part $\Phi(\phi)$ satisfies:

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0$$

  where m is the azimuthal quantum number.

- The solution is:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

- The quantum number m is an integer.

Particle on a Sphere

Polar Equation

- The polar part $\Theta(\theta)$ satisfies:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[\frac{2IE}{\hbar^2}-\frac{m^2}{\sin^2\theta}\right]\Theta=0$$

- This is the associated Legendre differential equation.
- Solutions are the associated Legendre functions $P_l^{|m|}(\cos\theta)$.

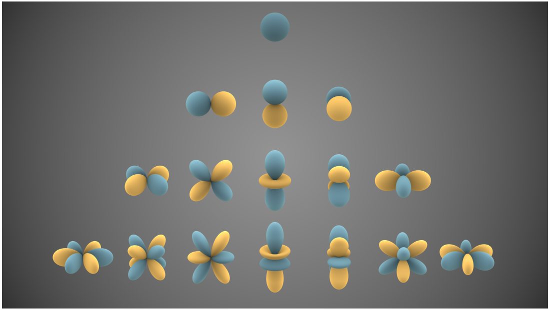
Particle on a Sphere

Spherical Harmonics

- The solutions to Schrödinger equation are the spherical harmonics:

$$Y_l^m(\theta,\phi) = N_l^m P_l^m(\cos\theta)e^{im\phi}$$

where N_l^m is a normalization constant, $P_l^m(\cos\theta)$ are Legendre polynomials.



real spherical harmonics

Particle on a Sphere

Properties of Spherical Harmonics

- Spherical harmonics are complete and orthonormal set of functions:

$$\int_0^{2\pi}\int_0^{\pi} Y_l^m(\theta,\phi)Y_{l'}^{m'*}(\theta,\phi)\sin\theta\, d\theta\, d\phi = \delta_{ll'}\delta_{mm'}$$

- They are eigenfunctions of the square of the orbital angular momentum operator and of a component of the angular momentum:

$$\hat{L}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m$$

$$\hat{L}_z Y_l^m = \hbar m Y_l^m$$

- The eigenvalue l is a non-negative integer and m ranges from $-l$ to l.

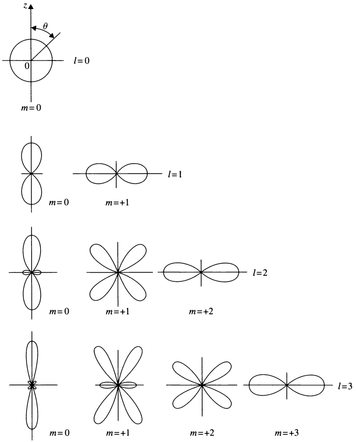
Particle on a Sphere

Low order spherical harmonics

l	m	Spherical harmonic $Y_{lm}(\theta,\phi)$
0	0	$Y_{0,0} = \dfrac{1}{(4\pi)^{1/2}}$
1	0	$Y_{1,0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta$
	±1	$Y_{1,\pm1} = \mp\left(\dfrac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$
2	0	$Y_{2,0} = \left(\dfrac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	±1	$Y_{2,\pm1} = \mp\left(\dfrac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$
	±2	$Y_{2,\pm2} = \left(\dfrac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
3	0	$Y_{3,0} = \left(\dfrac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
	±1	$Y_{3,\pm1} = \mp\left(\dfrac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1) e^{\pm i\phi}$
	±2	$Y_{3,\pm2} = \left(\dfrac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
	±3	$Y_{3,\pm3} = \mp\left(\dfrac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

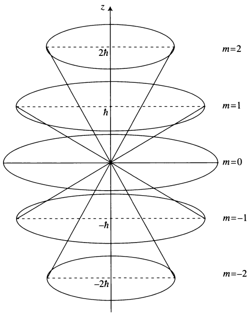
Particle on a Sphere

Polar plots of probability distribution $|Y_{lm}(\theta\phi)|^2 = \frac{1}{2\pi}|\Theta_{lm}(\theta)|^2$



Particle on a Sphere

Angular Momentum Quantization



- Angular momentum in quantum mechanics is quantized
- Vector model: vector **L** of length $\hbar\sqrt{l(l+1)}$ precesses about the quantization axis.
  - allowed projections on this axis are given by $\hbar m$

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The Hydrogen Atom

Introduction

- The hydrogen atom is the simplest atom consisting of a single electron bound to a nucleus by the Coulomb force.
- The system is central to quantum mechanics and explains atomic spectra.
- We use spherical coordinates (r, θ, ϕ) to account for the spherical symmetry of the problem.

The Hydrogen Atom

The Schrödinger Equation

- The time-independent Schrödinger equation for the hydrogen atom in spherical coordinates is:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0 r}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

- μ is the reduced mass of the electron-nucleus system: $\mu = \frac{m_e m_p}{m_e + m_p}$
- The potential energy is given by the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

The Hydrogen Atom

Separation of Variables

- We separate the wavefunction $\psi(r, \theta, \phi)$ into radial and angular components:
$$\psi(r, \theta, \phi) = R_{El}(r) Y_l^m(\theta, \phi)$$
- The angular part $Y_l^m(\theta, \phi)$ is given by a spherical harmonics.
- The radial part $R_{El}(r)$ satisfies a radial eigenvalue equation.

The Hydrogen Atom

The Radial Equation

- The radial part of the Schrödinger equation is:

$$\frac{d^2 u_{El}(r)}{dr^2} + \left[\frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right) - \frac{l(l+1)}{r^2}\right] u_{El}(r) = 0$$

- Here, $u_{El}(r) = rR_{El}(r)$ is the reduced radial wavefunction, and l is the orbital angular momentum quantum number.
- This equation can be solved to find the energy levels and wavefunctions.

The Hydrogen Atom

Energy Levels

- The energy levels of the hydrogen atom are quantized and given by:

$$E_n = -\frac{\mu e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}$$

- n is the principal quantum number and can take integer values $n = 1, 2, 3, \ldots$
- The energy levels are inversely proportional to n^2, resulting in the characteristic spectral lines.

The Hydrogen Atom

Quantum Numbers

- The hydrogen atom wavefunctions are described by three quantum numbers:
  - n: principal quantum number
  - l: orbital angular momentum quantum number
  - m: magnetic quantum number
- These quantum numbers determine the energy, shape, and orientation of the electron's probability distribution.

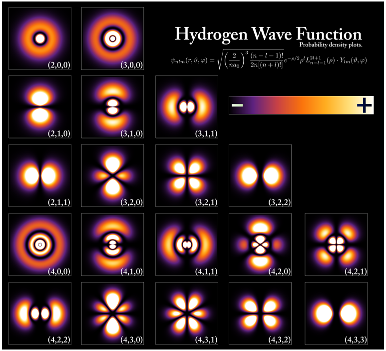
The Hydrogen Atom

Wave Functions

- The wavefunction $\psi_{nlm}(r, \theta, \phi)$ is the product of radial and angular parts:
$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$
- The radial part $R_{nl}(r)$ depends on the principal quantum number n and the orbital angular momentum l.
- The angular part $Y_l^m(\theta, \phi)$ is a spherical harmonic that depends on l and m.

The Hydrogen Atom

Visualization of Orbitals



- The probability density for finding the electron in the hydrogen atom is given by $|\psi_{nlm}(r, \theta, \phi)|^2$.
- Different quantum numbers give rise to different orbital shapes.
- The radial part influences the size of the orbital, while the angular part determines the shape.

The Hydrogen Atom

Degeneracy of Energy Levels

- Each energy level E_n is degenerate, meaning multiple states share the same energy.
- The degeneracy is determined by the quantum numbers l and m, which range from:

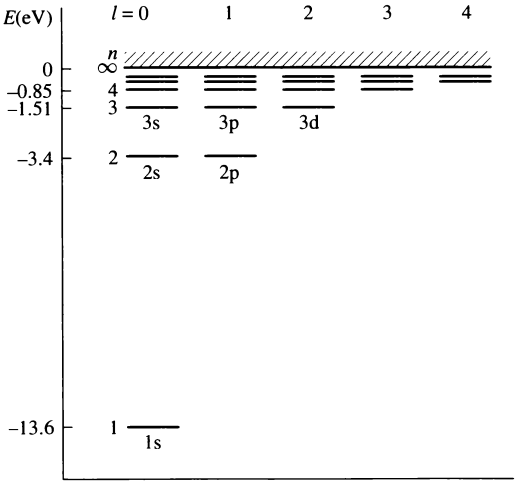
$$l = 0, 1, 2, \ldots, n - 1$$

$$m = -l, -l + 1, \ldots, l$$

- The total degeneracy for a given n is n^2.

The Hydrogen Atom

Energy level diagram



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Selection Rules and Transitions

- Electrons can transition between energy levels by absorbing or emitting a photon.
- The allowed transitions are governed by selection rules:
  - $\Delta l = \mp 1$
  - $\Delta m = 0, \mp 1$
- These rules explain the observed spectral lines in hydrogen's emission and absorption spectra.