

NPTEL ONLINE CERTIFICATION COURSES

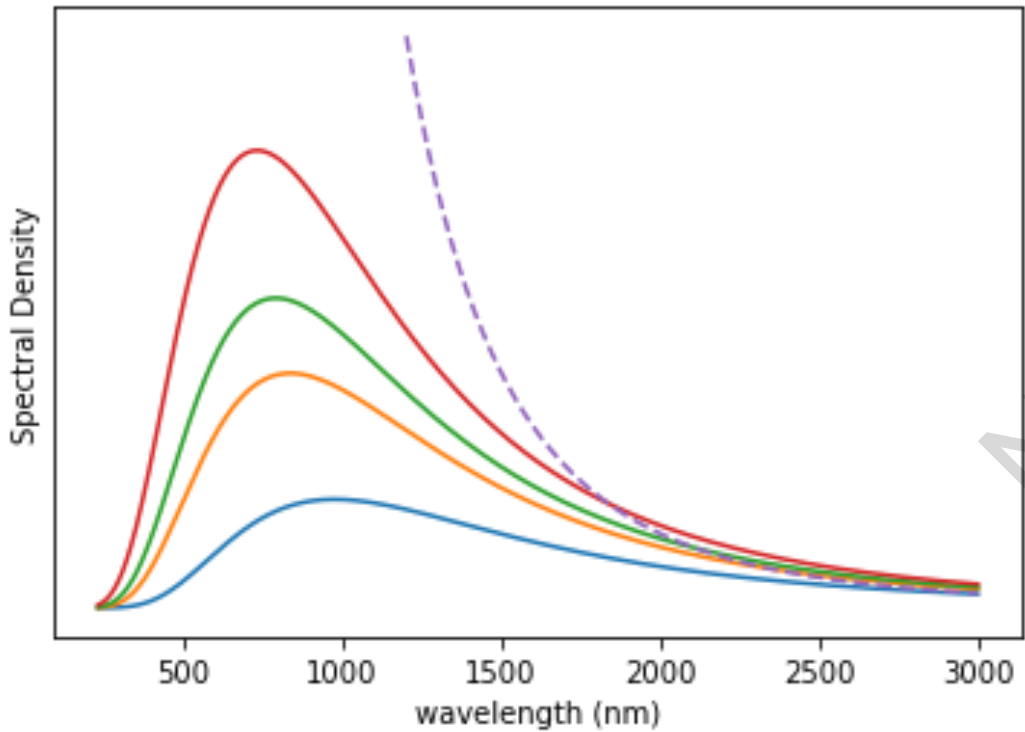
Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 01: Review of Quantum Chemistry

Origin of Quantum Mechanics

Blackbody Radiation



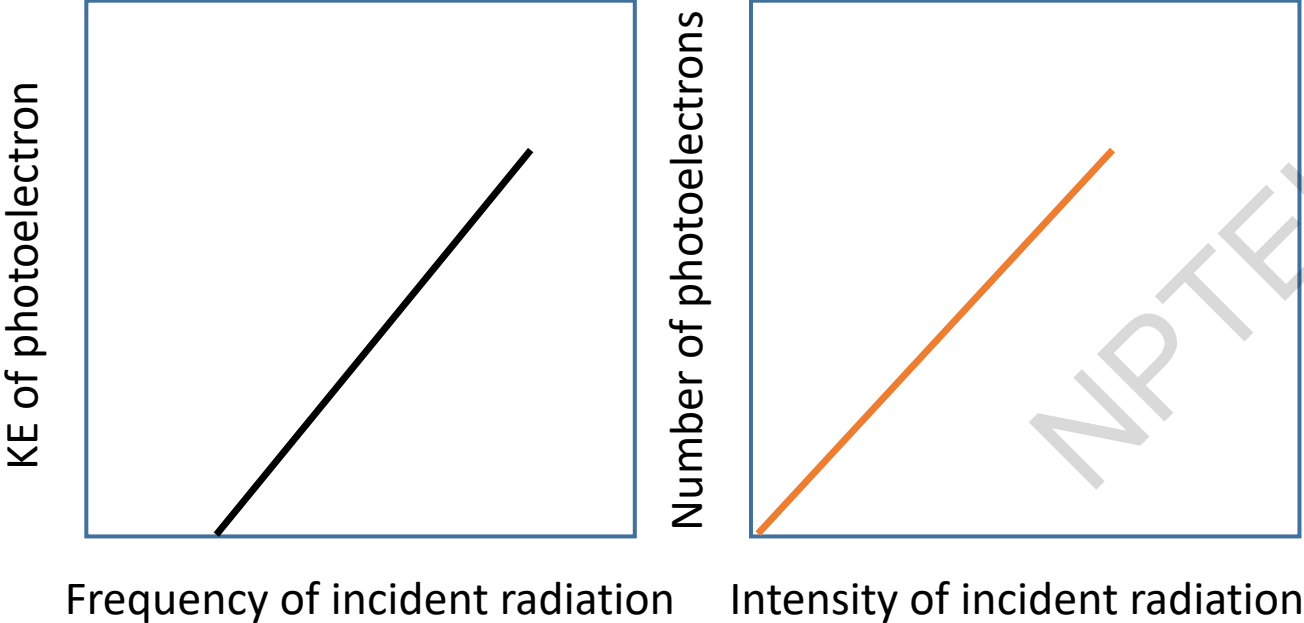
- $E \propto \nu$

$$E = \hbar \nu$$

$h = \text{Planck's const.}$

Origin of Quantum Mechanics

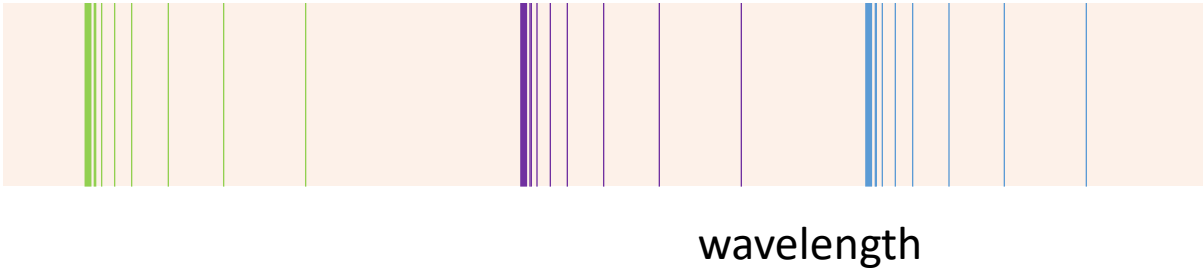
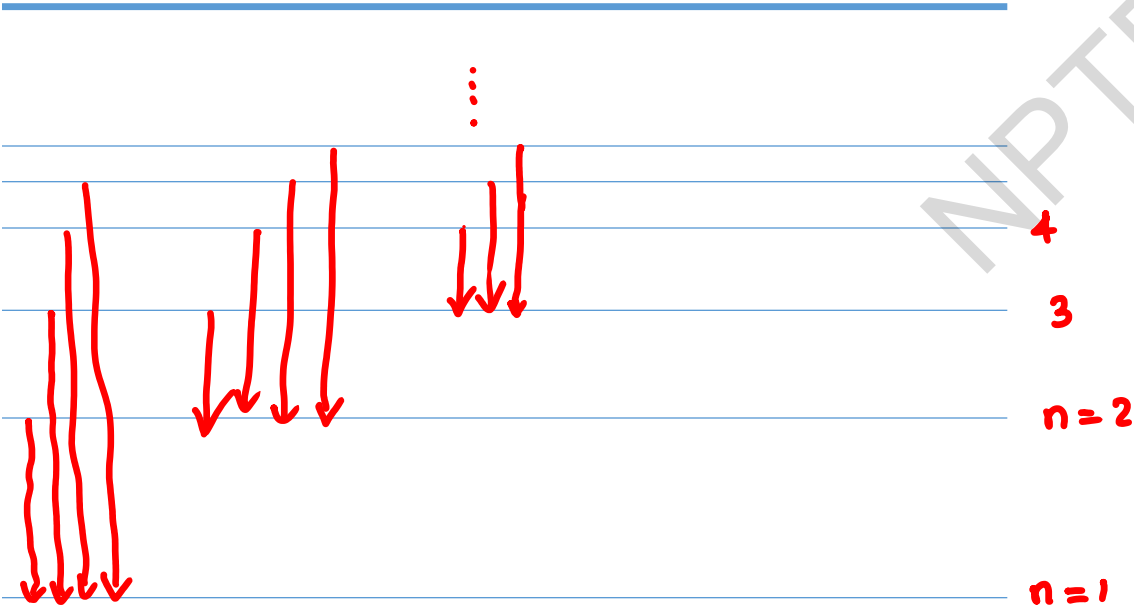
Photoelectric Effect



- $E \propto \nu$
 $E = h\nu$
- light is particle

Origin of Quantum Mechanics

Emission Spectra of Atoms



• angular momentum of e^- quantized

Origin of Quantum Mechanics

A few surprising experiments and two phenomenal ideas

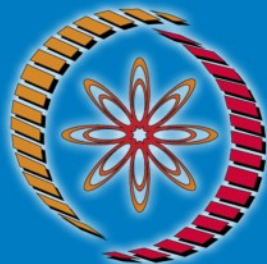
- de Broglie's hypothesis

$$\lambda = \frac{h}{p}$$

- Heisenberg's uncertainty principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$





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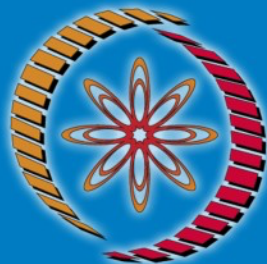
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Lecture 02: Postulates of Quantum Mechanics - I

Postulates of Quantum Mechanics

- 1 The state of a quantum mechanical system is completely specified by the **wave function** $\psi(x, t)$.
- 2 For every classical observable, there exists an **operator** $\hat{O}$ in quantum mechanics.
- 3 In any measurement of the observable associated with the operator, the only values that will ever be observed are the **eigenvalues of the operator**.





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Lecture 02: Postulates of Quantum Mechanics - I

Postulates of Quantum Mechanics

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Consequence of Postulate 3

Hermitian Operator $\langle \psi_m | \hat{A} | \psi_n \rangle = \langle \psi_n | \hat{A} | \psi_m \rangle^*$

$$\int \psi_m^* \hat{A} \psi_n d\tau = \int (\hat{A} \psi_m)^* \psi_n d\tau$$

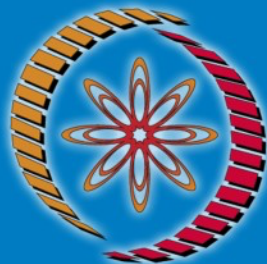
Hermitian Operators have:

1. Real eigenvalues
2. Complete set of orthonormal eigenfunctions

$$\langle \psi_m | \psi_n \rangle = \delta_{mn}$$

$$\phi = \sum_i c_i \psi_i \quad c_i = \langle \psi_i | \phi \rangle$$





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Lecture 03: Postulates of Quantum Mechanics - II

Postulates of Quantum Mechanics

- 1 The state of a quantum mechanical system is completely specified by the **wave function** $\psi(x, t)$.
- 2 For every classical observable, there exists an **operator** $\hat{O}$ in quantum mechanics.
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Consequence of Postulate 3

Hermitian Operator $\langle \psi_m | \hat{A} | \psi_n \rangle = \langle \psi_n | \hat{A} | \psi_m \rangle^*$

$$\int \psi_m^* \hat{A} \psi_n d\tau = \int (\hat{A} \psi_m)^* \psi_n d\tau$$

Hermitian Operators have:

1. Real eigenvalues
2. Complete set of orthonormal eigenfunctions

$$\langle \psi_m | \psi_n \rangle = \delta_{mn}$$

$$\phi = \sum_i c_i \psi_i \quad c_i = \langle \psi_i | \phi \rangle$$



Postulates of Quantum Mechanics

- 4 If a system is in a state described by a normalized wave function, then the **average value** of the observable corresponding to $\hat{A}$, is

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \int \psi^* \hat{A} \psi d\tau$$

- If the state of the system is an eigenfunction of the operator
- If the state of the system is **NOT** an eigenfunction of the operator



Commutation of Operators and Uncertainty Principle

If two operators A and B have a common complete set of eigenfunctions, then A and B commute and vice versa.

NPTEL



Some Exactly Solvable Models

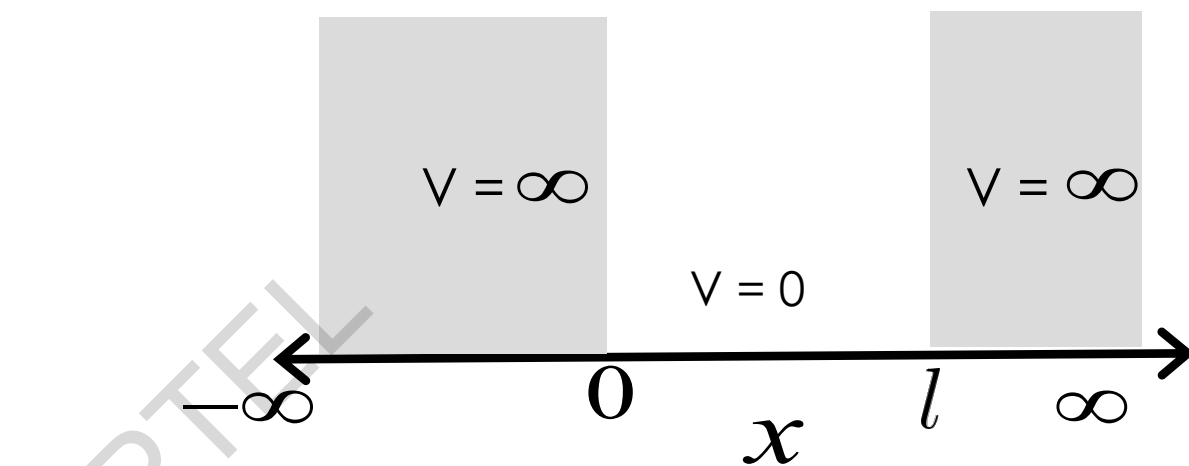
Particle in a box

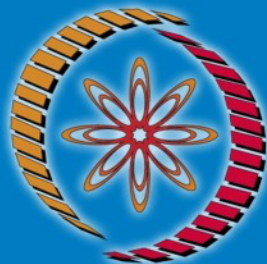
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\hat{H}\psi = E\psi$$

$$E_n = \frac{n^2 h^2}{8ml^2}$$

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





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Lecture 04: Exactly Solvable Models - I

Some Exactly Solvable Models

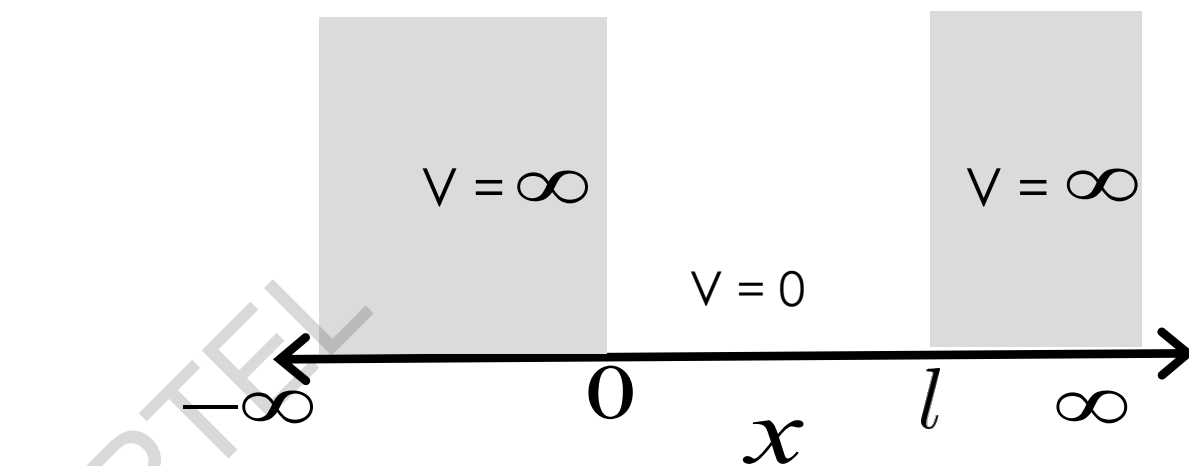
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Some Exactly Solvable Models

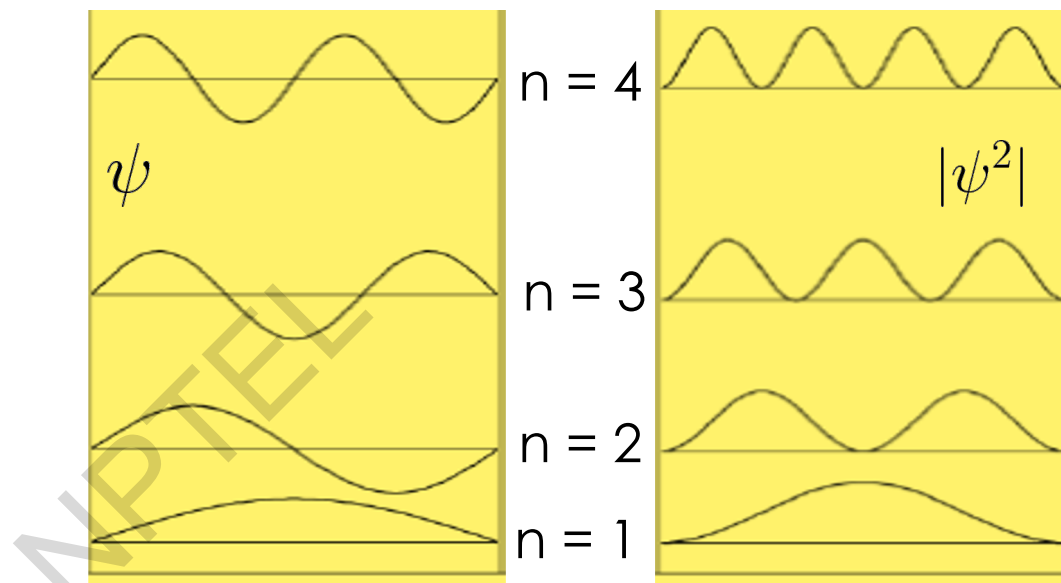
Particle in a box

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

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Some Exactly Solvable Models

Harmonic Oscillator

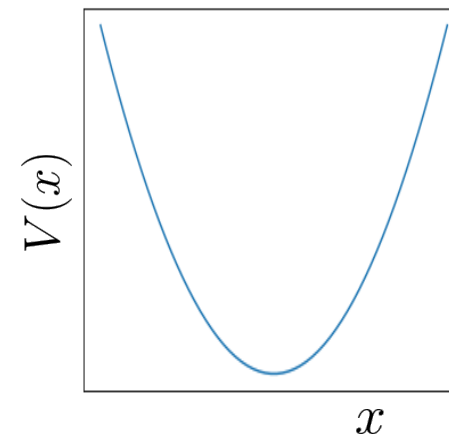
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2$$

$$\hat{H} \phi = E \phi$$

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

$$\phi_n = A_n \mathcal{H}_n(\rho) e^{-\rho^2/2}$$

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



Some Exactly Solvable Models

Harmonic Oscillator

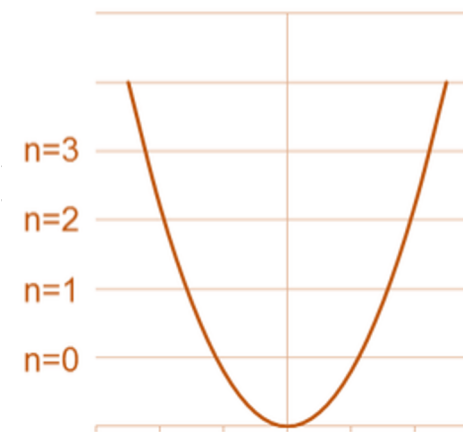
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2$$

$$\hat{H} \phi = E \phi$$

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

$$\phi_n = A_n \mathcal{H}_n(\rho) e^{-\rho^2/2}$$

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



Some Exactly Solvable Models

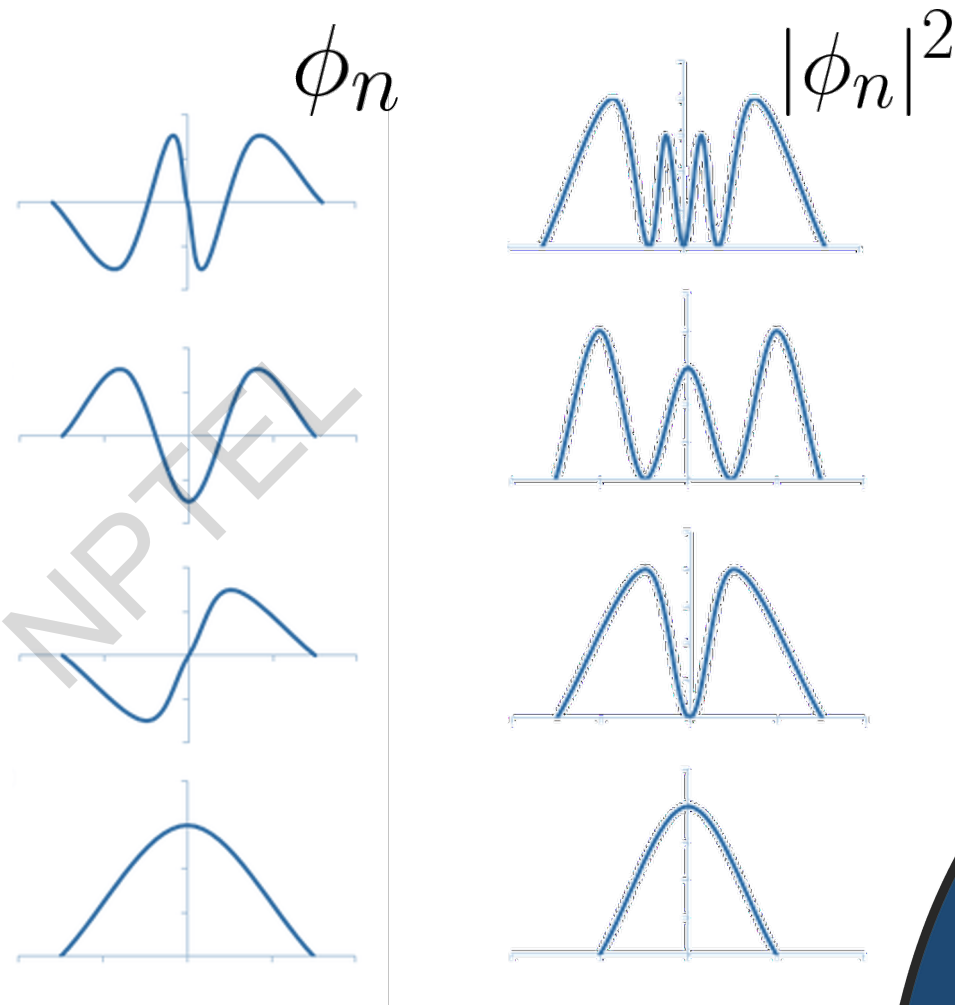
Harmonic Oscillator

$$\phi_n = A_n \mathcal{H}_n(\rho) e^{-\rho^2/2}$$

$$A_n = (2^n n! \sqrt{\pi})^{-1/2}$$

Hermite Polynomials

n	$\mathcal{H}_n(\rho)$
0	1
1	2ρ
2	$4\rho^2 - 2$
3	$8\rho^3 - 12\rho$



Angular Momentum Operator

$$\begin{aligned}L_x &= yp_z - zp_y \\L_y &= zp_x - xp_z \\L_z &= xp_y - yp_x \\L^2 &= L_x^2 + L_y^2 + L_z^2\end{aligned}$$

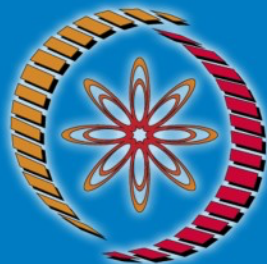
$$\begin{aligned}L_+ &= L_x + iL_y \\L_- &= L_x - iL_y\end{aligned}$$

Commutation Relations

$$\begin{aligned}[L_x, L_y] &= i\hbar L_z \\[L_y, L_z] &= i\hbar L_x \\[L_z, L_x] &= i\hbar L_y\end{aligned}$$

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$$





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Lecture 05: Exactly Solvable Models - II

Angular Momentum Operator

$$\begin{aligned}L_x &= yp_z - zp_y \\L_y &= zp_x - xp_z \\L_z &= xp_y - yp_x \\L^2 &= L_x^2 + L_y^2 + L_z^2\end{aligned}$$

$$\begin{aligned}L_+ &= L_x + iL_y \\L_- &= L_x - iL_y\end{aligned}$$

Commutation Relations

$$\begin{aligned}[L_x, L_y] &= i\hbar L_z \\[L_y, L_z] &= i\hbar L_x \\[L_z, L_x] &= i\hbar L_y\end{aligned}$$

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$$



Angular Momentum Operator

- Eigenvalues

$$L^2|Y_{l,m}\rangle = l(l+1)\hbar^2|Y_{l,m}\rangle$$

$$L_z|Y_{l,m}\rangle = m\hbar|Y_{l,m}\rangle$$

$$l = 0, 1, 2, \dots$$

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



Angular Momentum Operator

- Eigenfunctions

$$Y_{l,m} = \left(\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right)^{1/2} (1-x^2)^{|m|/2} \frac{d^{|m|}}{dx^{|m|}} P_l(x) \left(\frac{1}{\sqrt{2\pi}} e^{im\phi} \right)$$

$$x = \cos \theta$$

Legendre Polynomials

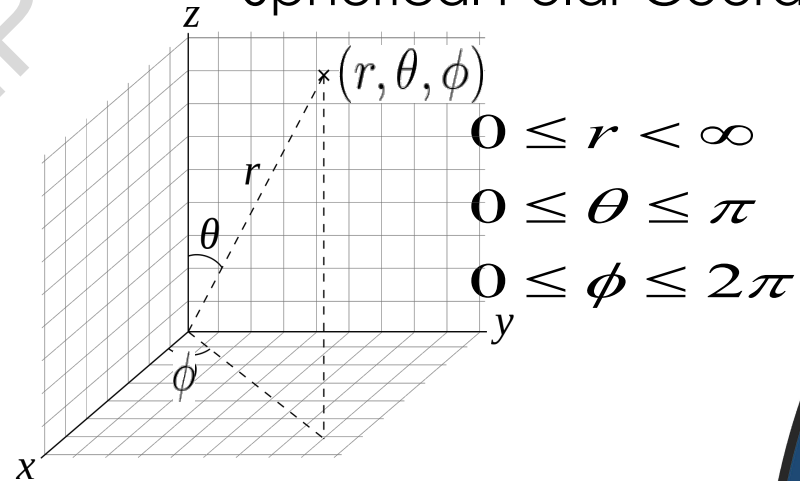
$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = (3x^2 - 1)/2$$

$$P_3(x) = (5x^3 - 3x)/2$$

Spherical Polar Coordinate



The Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(r)$$

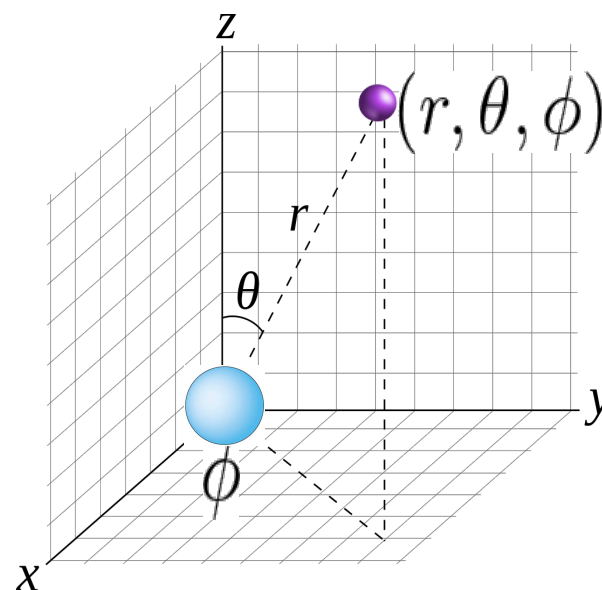
$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_{com}^2 - \frac{\hbar^2}{2\mu} \nabla^2 + V(r)$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{\hbar^2 r^2} L^2 \right) + V(r)$$

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

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$



$$0 \leq r < \infty$$

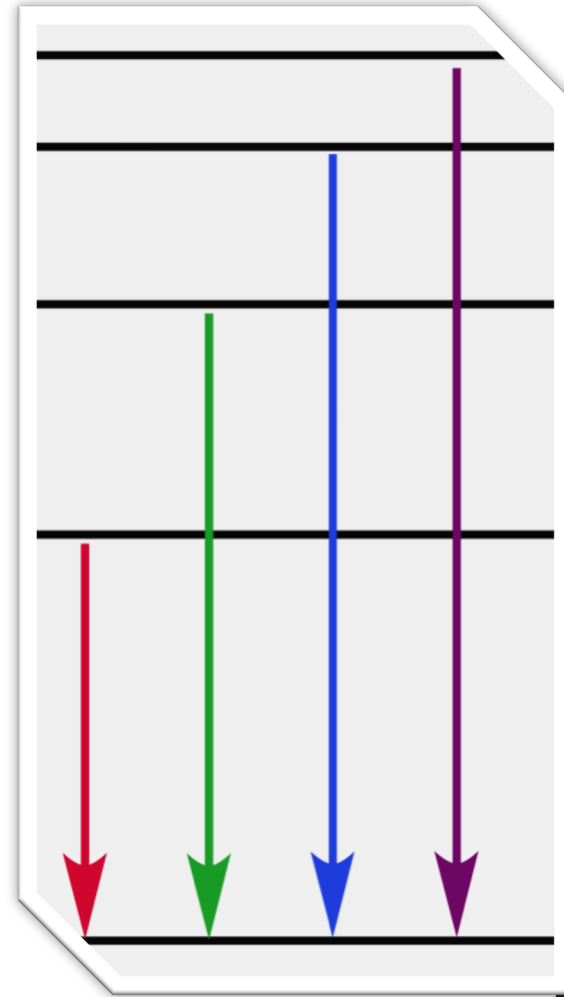
$$0 \leq \theta \leq \pi$$

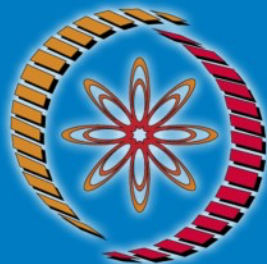
$$0 \leq \phi \leq 2\pi$$

The Hydrogen Atom

Eigenvalues and degeneracy

$$E_{nlm} = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}$$





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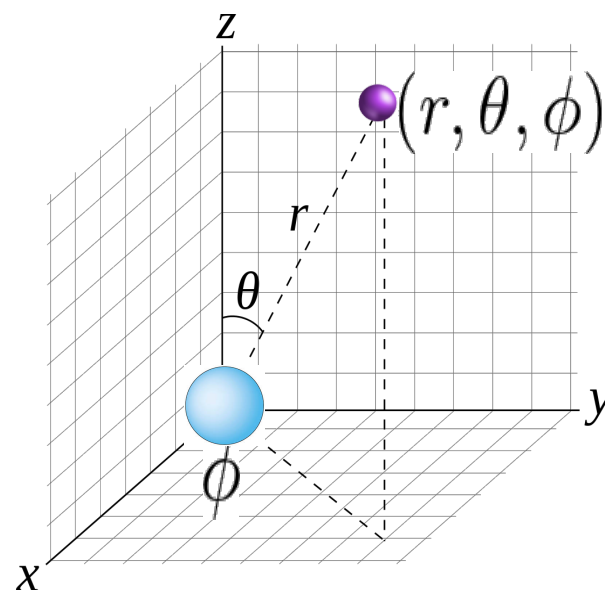
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Lecture 06: Exactly Solvable Models - III

The Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 + V(r)$$

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



$$0 \leq r < \infty$$

$$0 \leq \theta \leq \pi$$

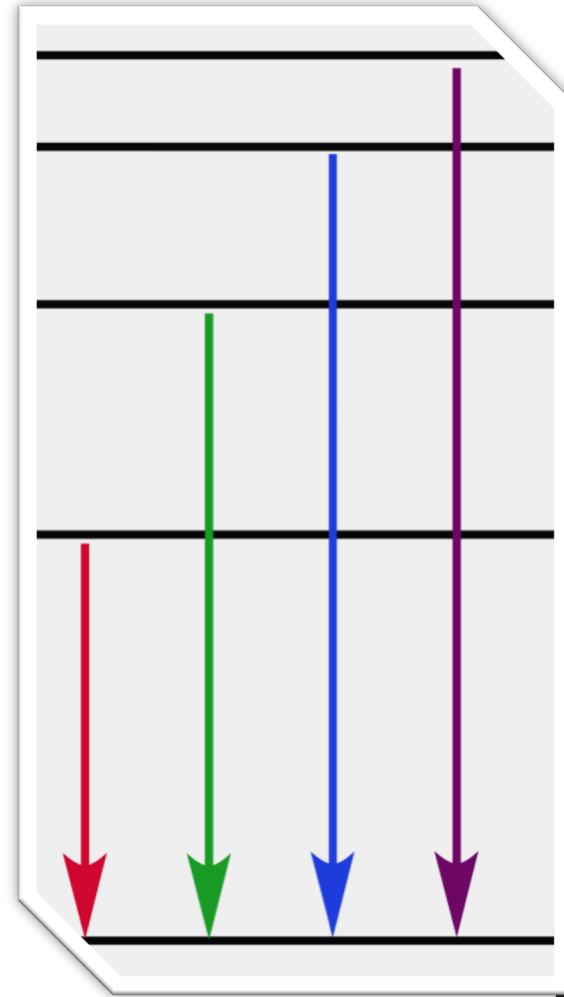
$$0 \leq \phi \leq 2\pi$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

The Hydrogen Atom

Eigenvalues and degeneracy

$$E_{nlm} = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}$$



The Hydrogen Atom Eigenfunctions

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

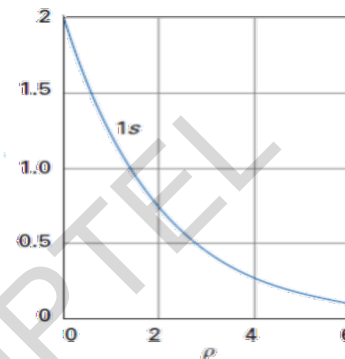
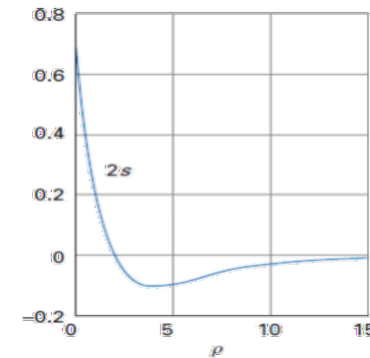
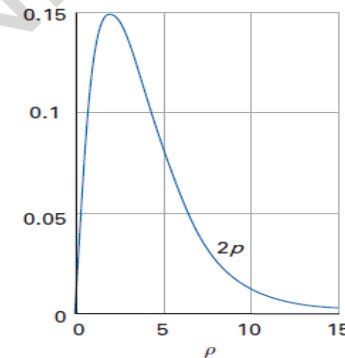
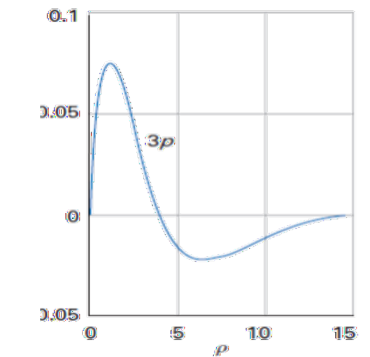
$$R_{20}(r) = \frac{1}{\sqrt{2}} \left(\frac{Z}{a}\right)^{3/2} \left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a}$$

$$R_{30}(r) = \frac{2}{3\sqrt{3}} \left(\frac{Z}{a}\right)^{3/2} \left(1 - \frac{2Zr}{3a} + \frac{2Z^2r^2}{27a^2}\right) e^{-Zr/3a}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}} \left(\frac{Z}{a}\right)^{3/2} \left(\frac{Zr}{a} - \frac{Z^2r^2}{6a^2}\right) e^{-Zr/3a}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}} \left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}$$



Radial Distribution Functions

$$P(r) = 4\pi r^2 |R(r)|^2 dr$$

