

CHAPTER 2 QUANTUM THEORY OUTLINE

Homework Questions Attached

SECT	TOPIC
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|-----|--|
| 1. | Interpretation and Properties of Ψ |
| 2. | Operators and Eigenvalue Equations |
| 3. | Operators in Quantum Mechanics |
| 4. | The 1D Schrödinger Equation: Time Dependent and Independent Forms |
| 5. | Mathematical Preliminary: Probability Averages and Variance |
| 6. | Normalization of the Wavefunction |
| 7. | Mathematical Preliminary: Even and Odd Integrals |
| 8. | Eigenfunctions and Eigenvalues |
| 9. | Expectation Values: Application to an Harmonic Oscillator Wavefunction |
| 10. | Hermitian Operators |
| 11. | Orthogonality of Wavefunctions |
| 12. | Commutation of Operators |
| 13. | Differentiability and Completeness of the Wavefunctions |
| 14. | Dirac "Bra-Ket" Notation |

Chapter 2 Homework

1. Which of the following functions are normalizable over the indicated intervals? Normalize those functions which can be normalized.
 (a) $\exp(-ax^2)$ $(-\infty, \infty)$; (b) e^x $(0, \infty)$; (c) $e^{i\theta}$ $(0, 2\pi)$; (d) xe^{-3x} $(0, \infty)$
2. Determine whether each of the following functions is acceptable as a wavefunction over the indicated interval.
 (a) $1/x$ $(0, \infty)$; (b) $(1-x^2)^{-1}$ $(-1, 1)$; (c) $e^{-x}\cos(x)$ $(0, \infty)$; (d) $\tan^{-1}(x)$ $(0, \infty)$
3. Which of the following operators are Hermitian
 (a) i (b) $*$ (take complex conjugate) (c) e^{ix} (d) $-id/dx$
 (e) $i^2 d/dx$ (f) d^2/dx^2 (g) id^2/dx^2
4. True or False
 (a) Nondegenerate eigenfunctions of the same operator are orthogonal.
 (b) All Hermitian operators are real.
 (c) If two operators commute with a third, they will commute with each other.
 (d) $d\psi/dx$ must be continuous as long as the potential, $V(x)$, is finite.
 (e) If a wavefunction is simultaneously the eigenfunction of two operators, it will also be an eigenfunction of the product of the two operators.
5. Consider the following hypothetical PIB wavefunction: $\psi(x) = Ax(a-x)$ $0 \leq x \leq a$
 Calculate: (a) A ; (b) $\langle x^2 \rangle$; (c) $\langle p \rangle$; (d) $\langle p^2 \rangle$
6. Consider the functions: $\psi_1 = 1$; $\psi_2 = x$; $\psi_3 = x^2 - 1/3$.
 Show that all three functions are orthogonal over the interval $[-1, 1]$.
7. Calculate the commutator: $\left[\frac{d}{dx}, \frac{d}{dx} + x \right]$
8. Calculate the commutator: $[p_x, x^2]$
9. Classify the following operators as linear or nonlinear:
 (a) $3x^2 d^2/dx^2$; (b) $()^2$ (square the function); (c) $\int () dx$ (integrate the function);
 (d) $\exp()$ (exponentiate the function)
10. Which of the following functions are eigenfunctions of d^2/dx^2 ?
 For those that are eigenfunctions, determine the eigenvalues.
 (a) e^{2x} ; (b) x^2 ; (c) $\sin(8x)$; (d) $\sin(3x) - \cos(3x)$

11. Which of the following functions (defined from $-\infty$ to ∞) would be acceptable one-dimensional wavefunctions for a bound particle.

(a) $\exp(-ax)$; (b) $x \cdot \exp(-bx^2)$; (c) $i \cdot \exp(-bx^2)$; (d) $\sin(bx)$

DATA

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

$$R = 8.31 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg (electron mass)}$$

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$k \cdot N_A = R$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ atm.} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$\int_0^\infty e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$p^2(\text{oper}) = -\hbar^2 \frac{d^2}{dx^2}$$

Some “Concept Question” Topics

Refer to the PowerPoint presentation for explanations on these topics.

- Interpretation of ψ in one and three dimensions
- Required properties of a “well-behaved” wavefunction
- Linear operators
- Use of time dependent vs. time independent Schrödinger Equation
- Significance of whether or not ψ is an eigenfunction of an operator
- Significance of Hermitian operators
- Wavefunction orthogonality

- Linear combinations of degenerate wavefunctions
- Operator commutation and its significance
- Differentiability of the wavefunction, and its exception(s)
- Completeness of a set of wavefunctions

Chapter 2

Quantum Theory

Slide 1

Outline

- **Interpretation and Properties of ψ**
- Operators and Eigenvalue Equations
- Operators in Quantum Mechanics
- The 1D Schrödinger Equation: Time Depend. and Indep. Forms
- Math. Preliminary: Probability, Averages and Variance
- Normalization of the Wavefunction
- Math. Preliminary: Even and Odd Integrals
- Eigenfunctions and Eigenvalues
- Expectation Values (Application to HO wavefunction)
- Hermitian Operators

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Slide 2

Outline (Cont'd.)

- Orthogonality of Wavefunctions
- Commutation of Operators
- Differentiability and Completeness of the Wavefunctions
- Dirac "Bra-Ket" Notation

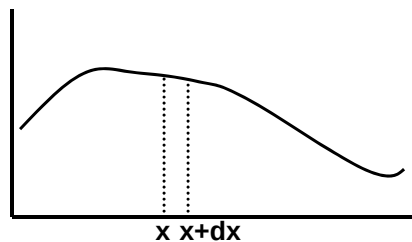
Slide 3

First Postulate: Interpretation of Ψ

One Dimension

Postulate 1: $\Psi(x,t)$ is a solution to the one dimensional Schrödinger Equation and is a well-behaved, square integrable function.

The quantity, $|\Psi(x,t)|^2 dx = \Psi^*(x,t)\Psi(x,t)dx$, represents the probability of finding the particle between x and $x+dx$.

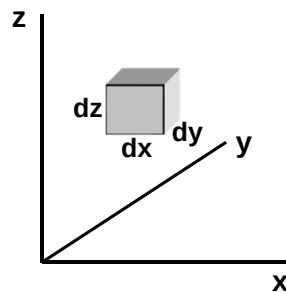


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Three Dimensions

Postulate 1: $\Psi(x,y,z,t)$ is a solution to the three dimensional Schrödinger Equation and is a well-behaved, square integrable function.

The quantity, $|\Psi(x,y,z,t)|^2 dx dy dz = \Psi^*(x,y,z,t)\Psi(x,y,z,t) dx dy dz$, represents the probability of finding the particle between x and $x+dx$, y and $y+dy$, z and $z+dz$.



Shorthand Notation

$$\Psi(x, y, z, t) \equiv \Psi(\vec{r}, t)$$

Two Particles

$$|\Psi(\vec{r}_1, \vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2$$

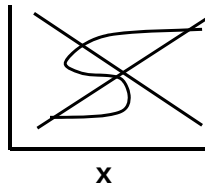
$$\text{where } d\vec{r}_1 d\vec{r}_2 = dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

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Required Properties of Ψ

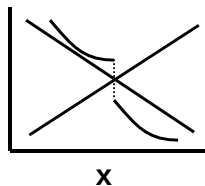
Finite $\Psi \not\rightarrow \infty$

Single Valued $\Psi(x)$



Continuous $\Psi(x)$

And derivatives must be continuous



Slide 6

Required Properties of Ψ

Vanish at endpoints (or infinity)

$$\Psi \rightarrow 0 \text{ as } \begin{array}{l} x \rightarrow \pm\infty \\ y \rightarrow \pm\infty \\ z \rightarrow \pm\infty \end{array}$$

Must be “Square Integrable”

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(\vec{r})|^2 dx dy dz < \infty \quad \text{or} \quad \int |\Psi(\vec{r})|^2 d\tau < \infty$$

Shorthand notation

Reason: Can “normalize” wavefunction

$$\int |\Psi(\vec{r})|^2 d\tau = 1$$

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Which of the following functions would be acceptable wavefunctions?

$$e^{-x^2} \quad -\infty < x < +\infty \quad \text{OK}$$

OK

$$e^{-x} \quad -\infty < x < +\infty$$

No - Diverges as $x \rightarrow -\infty$

$\sin^{-1} x$

No - Multivalued

i.e. $x = 1$, $\sin^{-1}(1) = \pi/2, \pi/2 + 2\pi, \dots$

$$e^{-|x|} \quad -\infty < x < +\infty$$

No - Discontinuous first derivative at $x = 0$.

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Operators and Eigenvalue Equations

One Dimensional Schrödinger Equation

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

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

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

Operator
Eigenvalue
Eigenfunction

This is an "Eigenvalue Equation"

$$\hat{A}f = af$$

Operator
Eigenvalue
Eigenfunction

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Linear Operators

A quantum mechanical operator must be linear

$$\hat{A}(c\phi + d\psi) = c\hat{A}\phi + d\hat{A}\psi$$

Operator	Linear ?
$x^2 \cdot$	Yes
$\sqrt{}$	No
$\log$	No
$\sin$	No
$\frac{d}{dx}$	Yes
$\frac{d^2}{dx^2}$	Yes

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Operator Multiplication

$$\hat{A}\hat{B}\phi \equiv \hat{A}(\hat{B}\phi)$$

First operate with $\hat{B}$, and then operate on the result with $\hat{A}$.

Note: $\hat{A}^2\phi \equiv \hat{A}(\hat{A}\phi) \neq (\hat{A}\phi)^2$

Example

$$\hat{A} = \frac{d}{dx} \quad \text{and} \quad \hat{B} = x$$

$$\hat{A}\hat{B}\phi = ?$$

$$\hat{A}\hat{B}\phi = x \frac{d\phi}{dx} + \phi$$

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Operator Commutation

$$\hat{A}\hat{B}\varphi \stackrel{?}{=} \hat{B}\hat{A}\varphi$$

Not necessarily!! If the result obtained applying two operators in opposite orders are the same, the operators are said to commute with each other.

Whether or not two operators commute has physical implications, as shall be discussed later, where we will also give examples.

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Eigenvalue Equations

$$\hat{A}f = af$$

$\hat{A}$	f	Eigenfunction?	Eigenvalue
3	x^2	Yes	3
x	$\sin(\beta x)$	No	
$\frac{d}{dx}$	$\sin(\beta x)$	No	
$\frac{d^2}{dx^2}$	$\sin(\beta x)$	Yes	$-\beta^2$ (All values of β allowed)
$\frac{d^2}{dx^2} - 4x^2$	$e^{\beta x^2}$	Only for $\beta = \pm 1$	2β (i.e. ± 2)

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Operators in Quantum Mechanics

Postulate 2: Every observable quantity has a corresponding linear, Hermitian operator.

The operator for position, or any function of position, is simply multiplication by the position (or function)

$$\text{i.e. } \hat{x} \equiv x \quad \text{i.e. } \hat{x}^2 \equiv x^2 \quad \text{etc.}$$

The operator for a function of the momentum, e.g. p_x , is obtained by the replacement:

$$\text{i.e. } \hat{p} \equiv \frac{\hbar}{i} \frac{\partial}{\partial x}$$

I will define Hermitian operators and their importance in the appropriate context later in the chapter.

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“Derivation” of the momentum operator

Wavefunction for a free particle (from Chap. 1)

$$\Psi = Ce^{i(kx - \omega t)} \quad \text{where} \quad k = \frac{2\pi}{\lambda} = \frac{2\pi}{\hbar/p} = \frac{p}{\hbar}$$

$$\frac{\partial \Psi}{\partial x} = ikCe^{i(kx - \omega t)} = ik\Psi = i\frac{p}{\hbar}\Psi$$

$$\frac{\hbar}{i} \frac{\partial \Psi}{\partial x} = p\Psi \quad \text{i.e.} \quad \hat{p} \equiv \frac{\hbar}{i} \frac{\partial}{\partial x}$$

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Some Important Operators (1 Dim.) in QM

Quantity	Symbol	Operator
Position	x	x
Potential Energy	$V(x)$	$V(x)$
Momentum	p_x (or p)	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
Kinetic Energy	$\frac{p_x^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Total Energy	$\frac{p_x^2}{2m} + V(x)$	$H \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

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Some Important Operators (3 Dim.) in QM

Quantity	Symbol	Operator
Position	$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$	$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$
Potential Energy	$V(x,y,z)$	$V(x,y,z)$
Momentum	$\vec{p} = p_x\vec{i} + p_y\vec{j} + p_z\vec{k}$	$\frac{\hbar}{i} \left(\vec{i} \frac{\partial}{\partial x} + \vec{j} \frac{\partial}{\partial y} + \vec{k} \frac{\partial}{\partial z} \right) = \frac{\hbar}{i} \nabla$
Kinetic Energy	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$
Total Energy	$\frac{p^2}{2m} + V(x,y,z)$	$H \equiv -\frac{\hbar^2}{2m} \nabla^2 + V(x,y,z)$
$\nabla \equiv \vec{i} \frac{\partial}{\partial x} + \vec{j} \frac{\partial}{\partial y} + \vec{k} \frac{\partial}{\partial z}$ $\nabla^2 \equiv \nabla \bullet \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$		

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The Schrödinger Equation (One Dim.)

Postulate 3: The wavefunction, $\Psi(x,t)$, is obtained by solving the time dependent Schrödinger Equation:

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right) \Psi(x,t)$$

If the potential energy is independent of time, [i.e. if $V = V(x)$], then one can derive a simpler time independent form of the Schrödinger Equation, as will be shown.

In most systems, e.g. particle in box, rigid rotator, harmonic oscillator, atoms, molecules, etc., unless one is considering spectroscopy (i.e. the application of a time dependent electric field), the potential energy is, indeed, independent of time.

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The Time-Independent Schrödinger Equation (One Dimension)

I will show you the derivation FYI. However, you are responsible only for the result.

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right) \Psi(x,t)$$

If V is independent of time, then so is the Hamiltonian, H .

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t) \quad \text{Assume that } \Psi(x,t) = \psi(x)f(t)$$

↓
On Board

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = \frac{1}{\psi(x)} H\psi(x) = E \quad (\text{the energy, a constant})$$

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$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = \frac{1}{\psi(x)} H\psi(x) = E \quad (\text{the energy, a constant})$$



On Board

$$H\psi(x) = E\psi(x)$$

**Time Independent
Schrödinger Equation**

$$\Psi(x,t) = \psi(x)f(t) = \psi(x)e^{-iEt/\hbar}$$

$$\text{Note that } \Psi^*(x,t)\Psi(x,t) = \psi^*(x)\psi(x)$$

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Continuous Distribution: $\bar{x} = \langle x \rangle = \int_{-\infty}^{\infty} xP(x)dx$ $\overline{x^2} = \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x)dx$
If normalized **If normalized**

Note: $\langle x^2 \rangle \geq \langle x \rangle^2$

Example: If $x_1 = 2$, $P(x_1)=0.5$ and $x_2 = 10$, $P(x_2) = 0.5$
 Calculate $\langle x \rangle$ and $\langle x^2 \rangle$

$$\langle x \rangle = 2 \cdot 0.5 + 10 \cdot 0.5 = 6$$

$$\langle x^2 \rangle = (2)^2 \cdot 0.5 + (10)^2 \cdot 0.5 = 52$$

Note that $\langle x \rangle^2 = 36$

It is always true that $\langle x^2 \rangle \geq \langle x \rangle^2$

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Variance

Below is a formal derivation of the expression for Standard Deviation.
 This is FYI only.

One requires a measure of the “spread” or “breadth” of a distribution.
 This is the variance, σ_x^2 , defined by:

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 P(x) dx$$

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x^2 - 2x\langle x \rangle + \langle x \rangle^2) P(x) dx$$

$$\sigma_x^2 = \int_{-\infty}^{\infty} x^2 P(x) dx - 2\langle x \rangle \int_{-\infty}^{\infty} x P(x) dx + \langle x \rangle^2 \int_{-\infty}^{\infty} P(x) dx$$

$$\sigma_x^2 = \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

Variance

$$\sigma_x = \sqrt{\sigma_x^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

Standard Deviation

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Example

$$\begin{aligned} P(x) &= Ax & 0 \leq x \leq 10 & \quad \text{Calculate: } A, \langle x \rangle, \langle x^2 \rangle, \sigma_x \\ P(x) &= 0 & x < 0, x > 10 \end{aligned}$$

$$\int_{-\infty}^{\infty} P(x) dx = \int_0^{10} A x dx = A \left[\frac{x^2}{2} \right]_0^{10} = A \cdot 50 = 1 \quad \longrightarrow \quad A = \frac{1}{50}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \int_0^{10} x A x dx = A \left[\frac{x^3}{3} \right]_0^{10} = \frac{1}{50} \frac{(10)^3}{3} = 6.67$$

$$\text{Note: } \langle x \rangle^2 = (6.67)^2 = 44.4$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) dx = \int_0^{10} x^2 A x dx = A \left[\frac{x^4}{4} \right]_0^{10} = \frac{1}{50} \frac{(10)^4}{4} = 50.0$$

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{50.0 - 44.4} = 2.37$$

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Normalization of the Wavefunction

For a quantum mechanical wavefunction: $P(x) = \psi^*(x)\psi(x)$

For a one-dimensional wavefunction to be normalized requires that:

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1$$

For a three-dimensional wavefunction to be normalized requires that:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^*(x, y, z)\psi(x, y, z)dx dy dz = 1$$

In general, without specifying dimensionality, one may write:

$$\int \psi^* \psi d\tau = 1$$

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Example: A Harmonic Oscillator Wave Function

Let's preview what we'll learn in Chapter 5 about the Harmonic Oscillator model to describe molecular vibrations in diatomic molecules.

The Hamiltonian: $H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$ μ = reduced mass
 k = force constant

A Wavefunction: $\psi(x) = Ae^{-\alpha x^2/2}$ $-\infty < x < \infty$

$$\alpha = \frac{\mu\omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$$

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Math Preliminary: Even and Odd Integrals

Integration Limits: $0 \rightarrow \infty$

Integration Limits: $-\infty \rightarrow \infty$

$$\int_0^{\infty} e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} e^{-\beta x^2} dx = 2 \int_0^{\infty} e^{-\beta x^2} dx$$

$$\int_0^{\infty} x e^{-\beta x^2} dx = \frac{1}{2\beta}$$

$$0$$

$$\int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} dx = 2 \int_0^{\infty} x^2 e^{-\beta x^2} dx$$

$$\int_0^{\infty} x^3 e^{-\beta x^2} dx = \frac{1}{2\beta^2}$$

$$0$$

$$\int_0^{\infty} x^4 e^{-\beta x^2} dx = \frac{3}{8\beta^2} \sqrt{\frac{\pi}{\beta}}$$

$$\int_{-\infty}^{\infty} x^4 e^{-\beta x^2} dx = 2 \int_0^{\infty} x^4 e^{-\beta x^2} dx$$

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Find the value of A that normalizes the Harmonic Oscillator oscillator wavefunction: $\psi(x) = Ae^{-\alpha x^2/2} \quad -\infty < x < \infty$

$$\int_0^\infty e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}$$

$$1 = \int_{-\infty}^{\infty} \psi^* \psi dx = \int_{-\infty}^{\infty} \psi^2 dx = \int_{-\infty}^{\infty} \left(Ae^{-\alpha x^2/2} \right)^2 dx = A^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$$

$$= A^2 \cdot 2 \int_0^\infty e^{-\alpha x^2} dx = A^2 \cdot 2 \cdot \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = A^2 \cdot \left(\frac{\pi}{\alpha} \right)^{1/2} = 1$$

$$A^2 = \left(\frac{\alpha}{\pi} \right)^{1/2} \longrightarrow \boxed{A = \left(\frac{\alpha}{\pi} \right)^{1/4}}$$

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Eigenfunctions and Eigenvalues

Postulate 4: If ψ_a is an eigenfunction of the operator $\hat{A}$ with eigenvalue a , then if we measure the property A for a system whose wavefunction is ψ_a , we always get a as the result.

Example

The operator for the total energy of a system is the Hamiltonian. Show that the HO wavefunction given earlier is an eigenfunction of the HO Hamiltonian. What is the eigenvalue (i.e. the energy)

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad \psi(x) = Ae^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\alpha = \frac{\mu\omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$$

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Preliminary: Wavefunction Derivatives

$$\psi(x) = Ae^{-\alpha x^2/2}$$

$$\frac{d\psi}{dx} = A \frac{d}{dx} (e^{-\alpha x^2/2}) = Ae^{-\alpha x^2/2} \frac{d(-\alpha x^2/2)}{dx} = Ae^{-\alpha x^2/2} (-2\alpha x/2)$$

$$\boxed{\frac{d\psi}{dx} = -A\alpha x e^{-\alpha x^2/2}}$$

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = -A\alpha \frac{d}{dx} (x e^{-\alpha x^2/2}) = -A\alpha \left[x \frac{d e^{-\alpha x^2/2}}{dx} + e^{-\alpha x^2/2} \frac{dx}{dx} \right] \\ &= -A\alpha \left[x e^{-\alpha x^2/2} (-2\alpha x/2) + e^{-\alpha x^2/2} \right] \end{aligned}$$

$$\boxed{\frac{d^2\psi}{dx^2} = -A\alpha \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right]}$$

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$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad \psi(x) = Ae^{-\alpha x^2/2} \quad -\infty < x < \infty \quad \frac{d^2\psi}{dx^2} = -\alpha A \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right]$$

$$\alpha = \frac{\mu\omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$$

$$H\psi = -\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2\psi = -\frac{\hbar^2}{2\mu} (-\alpha A) \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right] + \frac{1}{2} kx^2 Ae^{-\alpha x^2/2}$$

$$= -\frac{\hbar^2\alpha^2}{2\mu} x^2 \left(Ae^{-\alpha x^2/2} \right) + \frac{\hbar^2\alpha}{2\mu} \left(Ae^{-\alpha x^2/2} \right) + \frac{1}{2} kx^2 Ae^{-\alpha x^2/2}$$

$$= -\frac{\hbar^2\alpha^2}{2\mu} x^2\psi + \frac{\hbar^2\alpha}{2\mu}\psi + \frac{1}{2} kx^2\psi = x^2\psi \left[\frac{1}{2}k - \frac{\hbar^2\alpha^2}{2\mu} \right] + \frac{\hbar^2\alpha}{2\mu}\psi$$

To end up with a constant times ψ ,
this term must be zero.

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$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad \psi(x) = Ae^{-\alpha x^2/2} \quad -\infty < x < \infty \quad \frac{d^2\psi}{dx^2} = -\alpha A \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right]$$

$$\alpha = \frac{\mu\omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$$

$$H\psi = x^2\psi \left[\frac{1}{2}k - \frac{\hbar^2\alpha^2}{2\mu} \right] + \frac{\hbar^2\alpha}{2\mu}\psi$$

$$\alpha^2 = \frac{\mu^2\omega^2}{\hbar^2} = \frac{\mu^2(k/\mu)}{\hbar^2} = \frac{\mu k}{\hbar^2}$$

$$H\psi = x^2\psi \left[\frac{1}{2}k - \frac{\hbar^2}{2\mu} \left(\frac{\mu k}{\hbar^2} \right) \right] + \frac{\hbar^2\alpha}{2\mu}\psi$$

$$= x^2\psi \left[\frac{1}{2}k - \frac{1}{2}k \right] + \frac{\hbar^2\alpha}{2\mu}\psi = \frac{\hbar^2}{2\mu} \left(\frac{\mu\omega}{\hbar} \right) \psi$$

$$H\psi = \left(\frac{1}{2} \hbar\omega \right) \psi = \left(\frac{1}{2} \hbar\nu \right) \psi$$

$$\hbar\omega = \frac{h}{2\pi} \cdot 2\pi\nu = h\nu$$

$$E = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu$$

Because the wavefunction is an
eigenfunction of the Hamiltonian,
the total energy of the system
is known exactly.

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$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad \psi(x) = Ae^{-\alpha x^2/2} \quad -\infty < x < \infty$$

Is this wavefunction an eigenfunction of the potential energy operator?

$$\hat{V} = V(x) = \frac{1}{2} kx^2 \quad \text{No!! Therefore the potential energy cannot be determined exactly.}$$

Is this wavefunction an eigenfunction of the kinetic energy operator?

$$KE = \frac{\hat{p}^2}{2\mu} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} \quad \text{No!! Therefore the kinetic energy cannot be determined exactly.}$$

One can only determine the “average” value of a quantity if the wavefunction is not an eigenfunction of the associated operator. The method is given by the next postulate.

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Eigenfunctions of the Momentum Operator

Recall that the one dimensional momentum operator is: $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$

Is our HO wavefunction an eigenfunction of the momentum operator?

$$\psi(x) = Ae^{-\alpha x^2/2} \quad \text{No. Therefore the momentum of an oscillator in this eigenstate cannot be measured exactly.}$$

The wavefunction for a free particle is: $\Psi = Ce^{i(kx - \omega t)} \quad k = \frac{2\pi}{\lambda}$

Is the free particle wavefunction an eigenfunction of the momentum operator?

Yes, with an eigenvalue of $\hbar k$, which is just the de Broglie expression for the momentum.

Thus, the momentum is known exactly. However, the position is completely unknown, in agreement with Heisenberg's Uncertainty Principle.

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Outline

- Interpretation and Properties of ψ
- Operators and Eigenvalue Equations
- Operators in Quantum Mechanics
- The 1D Schrödinger Equation: Time Depend. and Indep. Forms
- Math. Preliminary: Probability, Averages and Variance
- Normalization of the Wavefunction
- Math. Preliminary: Even and Odd Integrals
- Eigenfunctions and Eigenvalues
- **Expectation Values (Application to HO wavefunction)**
- Hermitian Operators

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Expectation Values

Postulate 5: The average (or expectation) value of an observable with the operator $\hat{A}$ is given by

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

If ψ is normalized

Expectation values of eigenfunctions

It is straightforward to show that if ψ_a is eigenfunction of $\hat{A}$ with eigenvalue, a , then:

$$\langle a \rangle = a$$

$$\langle a^2 \rangle = a^2$$

$$\sigma_a = 0 \quad (\text{i.e. there is no uncertainty in } a)$$

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Expectation value of the position

$$\langle x \rangle = \frac{\int \psi^* \hat{x} \psi dx}{\int \psi^* \psi dx} = \frac{\int \psi^* x \psi dx}{\int \psi^* \psi dx} = \frac{\int x \psi^* \psi dx}{\int \psi^* \psi dx}$$

$$\langle x \rangle = \frac{\int x P(x) dx}{\int P(x) dx}$$

This is just the classical expression for calculating the average position.

The differences arise when one computes expectation values for quantities whose operators involve derivatives, such as momentum.

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Consider the HO wavefunction we have been using in earlier examples: $\psi(x) = A e^{-\alpha x^2/2}$ $-\infty < x < \infty$

$$\alpha = \frac{\mu \omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi \nu$$

Calculate the following quantities:

$\langle x \rangle$	$\langle p \rangle$	$\sigma_x \sigma_p$ (to demo. Unc. Prin.)
$\langle x^2 \rangle$	$\langle p^2 \rangle$	$\langle KE \rangle$
σ_x^2	σ_p^2	$\langle PE \rangle$

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Preliminary: Wavefunction Derivatives

$$\psi(x) = Ae^{-\alpha x^2/2}$$

$$\frac{d\psi}{dx} = A \frac{d}{dx} \left(e^{-\alpha x^2/2} \right) = Ae^{-\alpha x^2/2} \frac{d(-\alpha x^2/2)}{dx} = Ae^{-\alpha x^2/2} (-2\alpha x/2)$$

$$\boxed{\frac{d\psi}{dx} = -A\alpha x e^{-\alpha x^2/2}}$$

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = -A\alpha \frac{d}{dx} \left(x e^{-\alpha x^2/2} \right) = -A\alpha \left[x \frac{d e^{-\alpha x^2/2}}{dx} + e^{-\alpha x^2/2} \frac{dx}{dx} \right] \\ &= -A\alpha \left[x e^{-\alpha x^2/2} (-2\alpha x/2) + e^{-\alpha x^2/2} \right] \end{aligned}$$

$$\boxed{\frac{d^2\psi}{dx^2} = -A\alpha \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right]}$$

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$$\psi(x) = Ae^{-\alpha x^2/2} \quad A = \left(\frac{\alpha}{\pi} \right)^{1/4}$$

$$\langle x \rangle$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi dx = \int_{-\infty}^{\infty} A e^{-\alpha x^2/2} \cdot x \cdot A e^{-\alpha x^2/2} dx = A^2 \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx = 0$$

$$\langle x^2 \rangle$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^* x^2 \psi dx = \int_{-\infty}^{\infty} A e^{-\alpha x^2/2} \cdot x^2 \cdot A e^{-\alpha x^2/2} dx = A^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$$

$$= A^2 \cdot 2 \cdot \int_0^{\infty} x^2 e^{-\alpha x^2} dx = \left(\frac{\alpha}{\pi} \right)^{1/2} \cdot 2 \cdot \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{2\alpha}$$

$$\int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}}$$

$$\text{Also: } \sigma_x^2 = \frac{1}{2\alpha}$$

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$$\psi(x) = Ae^{-\alpha x^2/2} \quad \frac{d\psi}{dx} = -A\alpha x e^{-\alpha x^2/2} \quad \hat{p} = \frac{\hbar}{i} \frac{d}{dx}$$

<p>

$$\begin{aligned} \langle p \rangle &= \int_{-\infty}^{\infty} \psi^* \frac{\hbar}{i} \frac{d\psi}{dx} dx = \int_{-\infty}^{\infty} A e^{-\alpha x^2/2} \cdot \frac{\hbar}{i} (-A\alpha x e^{-\alpha x^2/2}) dx \\ &= -\frac{A^2 \alpha \hbar}{i} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx \\ \langle p \rangle &= 0 \end{aligned}$$

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$$\psi(x) = Ae^{-\alpha x^2/2} \quad \frac{d^2\psi}{dx^2} = -\alpha A \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right] \quad \hat{p}^2 = -\hbar^2 \frac{d^2}{dx^2}$$

<p²>

$$\begin{aligned} \langle p^2 \rangle &= \int_{-\infty}^{\infty} \psi^* (-\hbar^2) \frac{d^2\psi}{dx^2} dx = \int_{-\infty}^{\infty} A e^{-\alpha x^2/2} (-\hbar^2) (-\alpha A) \left[-\alpha x^2 e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right] dx \\ &= A^2 \hbar^2 \alpha \int_{-\infty}^{\infty} \left[-\alpha x^2 e^{-\alpha x^2} + e^{-\alpha x^2} \right] dx = A^2 \hbar^2 \alpha \left[\int_{-\infty}^{\infty} -\alpha x^2 e^{-\alpha x^2} dx + \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \right] \\ &= A^2 \hbar^2 \alpha \left[-\alpha \cdot 2 \cdot \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} + 2 \cdot \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right] = A^2 \hbar^2 \alpha \left[-\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} + 1 \sqrt{\frac{\pi}{\alpha}} \right] \end{aligned}$$

$$\begin{aligned} \int_0^{\infty} e^{-\beta x^2} dx &= \frac{1}{2} \sqrt{\frac{\pi}{\beta}} \\ \int_0^{\infty} x^2 e^{-\beta x^2} dx &= \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}} \end{aligned} \quad \langle p^2 \rangle = \sqrt{\frac{\alpha}{\pi}} \hbar^2 \alpha \left[+\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right] = \frac{\hbar^2 \alpha}{2} \quad \text{Also: } \sigma_p^2 = \frac{\hbar^2 \alpha}{2}$$

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$$\sigma_x^2 = \frac{1}{2\alpha} \quad \sigma_p^2 = \frac{\hbar^2 \alpha}{2}$$

Uncertainty Principle

$$\sigma_x^2 \sigma_p^2 = \frac{1}{2\alpha} \cdot \frac{\hbar^2 \alpha}{2} = \frac{\hbar^2}{4}$$

$$\sigma_x \sigma_p = \sqrt{\sigma_x^2 \sigma_p^2} = \frac{\hbar}{2}$$

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$$\langle p^2 \rangle = \frac{\hbar^2 \alpha}{2} \quad \langle x^2 \rangle = \frac{1}{2\alpha} \quad \alpha = \frac{\mu \omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}}$$

<KE>

$$\langle KE \rangle = \left\langle \frac{p^2}{2\mu} \right\rangle = \frac{\langle p^2 \rangle}{2\mu} = \frac{1}{2\mu} \frac{\hbar^2 \alpha}{2} = \frac{\hbar^2}{4\mu} \frac{\mu \omega}{\hbar} = \frac{1}{4} \hbar \omega = \frac{1}{4} \frac{h}{2\pi} \omega = \frac{1}{4} h\nu$$

<PE>

$$\begin{aligned} \langle PE \rangle &= \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} k \frac{1}{2\alpha} = \frac{k}{4\alpha} = \frac{k}{4\mu\omega/\hbar} \\ &= \frac{\hbar}{4} \frac{k}{\mu} \frac{1}{\omega} = \frac{\hbar}{4} \omega^2 \frac{1}{\omega} = \frac{1}{4} \hbar \omega = \frac{1}{4} h\nu \end{aligned}$$

Slide 52

Consider the HO wavefunction we have been using in earlier examples: $\psi(x) = Ae^{-\alpha x^2/2}$ $-\infty < x < \infty$

$$\alpha = \frac{\mu\omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$$

Calculate the following quantities:

$$\langle x \rangle = 0$$

$$\langle p \rangle = 0$$

$$\langle x^2 \rangle = 1/(2\alpha)$$

$$\langle p^2 \rangle = \alpha\hbar^2/2$$

$$\sigma_x^2 = 1/(2\alpha)$$

$$\sigma_p^2 = \alpha\hbar^2/2$$

$$\sigma_x\sigma_p = \hbar/2 \text{ (this is a demonstration of the Heisenberg uncertainty principle)}$$

$$\langle KE \rangle = \frac{1}{4}\hbar\omega = \frac{1}{4}h\nu$$

$$\langle PE \rangle = \frac{1}{4}\hbar\omega = \frac{1}{4}h\nu$$

Slide 53

Outline

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- **Hermitian Operators**

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Hermitian Operators

General

Definition: An operator $\hat{A}$ is Hermitian if it satisfies the relation:

$$\int \psi (\hat{A}\phi)^* d\tau = \int \phi^* \hat{A}\psi d\tau$$

“Simplified”

Definition ($\phi=\psi$): An operator $\hat{A}$ is Hermitian if it satisfies the relation:

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

So what?

Why is it important that a quantum mechanical operator be Hermitian?

It can be proven that if an operator $\hat{A}$ satisfies the “simplified” definition, it also satisfies the more general definition.

(“Quantum Chemistry”, I. N. Levine, 5th. Ed.)

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The eigenvalues of Hermitian operators must be real.

Proof: $\hat{A}\psi = a\psi$ and $\int \psi (\hat{A}\psi)^* d\tau = \int \psi^* \hat{A}\psi d\tau$

$$\int \psi (a\psi)^* d\tau = \int \psi^* a\psi d\tau$$

$$\int \psi a^* \psi^* d\tau = \int \psi^* a\psi d\tau$$

$$a^* \int \psi^* \psi d\tau = a \int \psi^* \psi d\tau$$

$$a^* = a$$

i.e. a is real

In a similar manner, it can be proven that the expectation values $\langle a \rangle$ of an Hermitian operator must be real.

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

Is the operator x (multiplication by x) Hermitian? Yes.

Is the operator ix Hermitian? No.

Is the momentum operator Hermitian? $\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$ Yes: I'll outline the proof

You are **NOT** responsible for the proof outlined below, but only for the result.

Math Preliminary: Integration by Parts

$$\frac{d(uv)}{dx} = u \frac{dv}{dx} + v \frac{du}{dx} \quad \int_{-\infty}^{\infty} u \frac{dv}{dx} dx = \int_{-\infty}^{\infty} \frac{d(uv)}{dx} dx - \int_{-\infty}^{\infty} v \frac{du}{dx} dx$$

$$u \frac{dv}{dx} = \frac{d(uv)}{dx} - v \frac{du}{dx}$$

$$\int_{-\infty}^{\infty} u \frac{dv}{dx} dx = [uv]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} v \frac{du}{dx} dx$$

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$$\int \psi (\hat{A}\psi)^* d\tau = \int \psi^* \hat{A}\psi d\tau \quad \int_{-\infty}^{\infty} u \frac{dv}{dx} dx = [uv]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} v \frac{du}{dx} dx$$

Is the momentum operator Hermitian? $\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$

The question is whether: $\int \psi \left(\frac{\hbar}{i} \frac{d\psi}{dx} \right)^* dx \stackrel{?}{=} \int \psi^* \frac{\hbar}{i} \frac{d\psi}{dx} dx$

$$\text{or: } \int \psi \frac{d\psi^*}{dx} dx \stackrel{?}{=} - \int \psi^* \frac{d\psi}{dx} dx$$

The latter equality can be proven by using Integration by Parts with: $u = \psi$ and $v = \psi^*$, together with the fact that both ψ and ψ^* are zero at $x = \pm\infty$. Next Slide

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$$\int_{-\infty}^{\infty} u \frac{dv}{dx} dx = [uv]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} v \frac{du}{dx} dx$$

$$\int \psi \left(\frac{\hbar}{i} \frac{d\psi}{dx} \right)^* dx = \int \psi^* \frac{\hbar}{i} \frac{d\psi}{dx} dx \quad ?? \quad \text{or:} \quad \int \psi \frac{d\psi^*}{dx} dx = - \int \psi^* \frac{d\psi}{dx} dx \quad ??$$

Let $u = \psi$ and $v = \psi^*$: $\int_{-\infty}^{\infty} \psi \frac{d\psi^*}{dx} dx = [\psi \psi^*]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx} dx$

$$= 0 - \int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx} dx \quad \text{Because } \psi \text{ and } \psi^* \text{ vanish at } x = \pm\infty$$

Therefore: $\int \psi \frac{d\psi^*}{dx} dx = - \int \psi^* \frac{d\psi}{dx} dx \quad ? \longrightarrow \int \psi \left(\frac{\hbar}{i} \frac{d\psi}{dx} \right)^* dx = \int \psi^* \frac{\hbar}{i} \frac{d\psi}{dx} dx$

Thus, the momentum operator IS Hermitian

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By similar methods, one can show that:

$\frac{d}{dx}$ is NOT Hermitian (see last slide)

$i \frac{d}{dx}$ IS Hermitian

$\frac{d^2}{dx^2}$ IS Hermitian (proven by applying integration by parts twice successively)

The Hamiltonian: $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$ IS Hermitian

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Outline (Cont'd.)

- Orthogonality of Wavefunctions
- Commutation of Operators
- Differentiability and Completeness of the Wavefunctions
- Dirac “Bra-Ket” Notation

Slide 61

Orthogonality of Eigenfunctions

Assume that we have two different eigenfunctions of the same Hamiltonian: $H\psi_i = E_i\psi_i$ and $H\psi_j = E_j\psi_j$

If the two eigenvalues, $E_i = E_j$, the eigenfunctions (aka wavefunctions) are **degenerate**. Otherwise, they are non-degenerate eigenfunctions

We prove below that non-degenerate eigenfunctions are **orthogonal** to each other.

Proof: $\int \psi_j^* H\psi_i d\tau = \int \psi_i (H\psi_j)^* d\tau$ Because the Hamiltonian is Hermitian

$$\int \psi_j^* E_i \psi_i d\tau = \int \psi_i (E_j \psi_j)^* d\tau = \int \psi_i E_j^* \psi_j^* d\tau$$

$$E_i \int \psi_j^* \psi_i d\tau = E_j^* \int \psi_i \psi_j^* d\tau = E_j \int \psi_j^* \psi_i d\tau$$

$$(E_i - E_j) \int \psi_j^* \psi_i d\tau = 0$$

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$$(E_i - E_j) \int \psi_j^* \psi_i d\tau = 0$$

Thus, if $E_i \neq E_j$ (i.e. the eigenfunctions are not degenerate, then:

$$\int \psi_j^* \psi_i d\tau = 0$$

We say that the two eigenfunctions are **orthogonal**

If the eigenfunctions are also normalized, then we can say that they are **orthonormal**.

$$\int \psi_j^* \psi_i d\tau = \delta_{ij}$$

δ_{ij} is the Kronecker Delta, defined by:

$$\begin{aligned} \delta_{ij} &= 1 & \text{if } i = j \\ \delta_{ij} &= 0 & \text{if } i \neq j \end{aligned}$$

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Linear Combinations of Degenerate Eigenfunctions

Assume that we have two different eigenfunctions of the same Hamiltonian: $H\psi_i = E_i\psi_i$ and $H\psi_j = E_j\psi_j$

If $E_j = E_i$, the eigenfunctions are degenerate. In this case, any linear combination of ψ_i and ψ_j is also an eigenfunction of the Hamiltonian

Proof: $\varphi = a\psi_i + b\psi_j$

$$H(a\psi_i + b\psi_j) = (aH\psi_i + bH\psi_j) = (aE_i\psi_i + bE_j\psi_j)$$

If $E_j = E_i$, $H(a\psi_i + b\psi_j) = E_i(a\psi_i + b\psi_j)$ or

$$H\varphi = E_i\varphi$$

Thus, any linear combination of degenerate eigenfunctions is also an eigenfunction of the Hamiltonian.

If we wish, we can use this fact to construct degenerate eigenfunctions that are orthogonal to each other.

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Outline (Cont'd.)

- Orthogonality of Wavefunctions
- **Commutation of Operators**
- Differentiability and Completeness of the Wavefunctions
- Dirac “Bra-Ket” Notation

Slide 65

Commutation of Operators

$$\hat{A}\hat{B}\varphi \stackrel{?}{=} \hat{B}\hat{A}\varphi$$

Not necessarily!! If the result obtained applying two operators in opposite orders are the same, the operators are said to commute with each other.

Whether or not two operators commute has physical implications, as shall be discussed below.

One defines the “commutator” of two operators as:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $[\hat{A}, \hat{B}]\varphi = 0$ for all φ , the operators commute.

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$$\hat{A} \quad \hat{B} \quad [\hat{A}, \hat{B}]$$

$$x \quad x^2 \quad 0 \quad \text{Operators commute}$$

$$3 \quad \frac{d}{dx} \quad 0 \quad \text{Operators commute}$$

$$\hat{p} = \frac{\hbar}{i} \frac{d}{dx} \quad \hat{x} = x \quad -i\hbar \quad \text{Operators DO NOT commute}$$

And so??

Why does it matter whether or not two operators commute?

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Significance of Commuting Operators

Let's say that two different operators, $\hat{A}$ and $\hat{B}$, have the same set of eigenfunctions, ψ_n :

$$\hat{A}\psi_n = a_n\psi_n \quad \text{and} \quad \hat{B}\psi_n = b_n\psi_n$$

This means that the observables corresponding to both operators can be exactly determined simultaneously.

Then it can be proven**

that the two operators commute; i.e. $[\hat{A}, \hat{B}] = 0$

Conversely, it can be proven that if two operators do **not** commute, then the operators **cannot** have simultaneous eigenfunctions.

This means that it is not possible to determine both quantities exactly; i.e. the product of the uncertainties is greater than zero.

**e.g. *Quantum Chemistry (5th. Ed.)*, by I. N. Levine, Sect. 5.1

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We just showed that the momentum and position operators do not commute: $[\hat{p}_x, \hat{x}] = -i\hbar \neq 0$

This means that the momentum and position of a particle cannot both be determined exactly; the product of their uncertainties is greater than 0.

$$\sigma_{p_x} \sigma_x > 0$$

If the position is known exactly ($\sigma_x=0$), then the momentum is completely undetermined ($\sigma_{p_x} \rightarrow \infty$), and vice versa.

This is the basis for the uncertainty principle, which we demonstrated above for the wavefunction for a Harmonic Oscillator, where we showed that $\sigma_p \sigma_x = \hbar/2$.

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Outline (Cont'd.)

- Orthogonality of Wavefunctions
- Commutation of Operators
- **Differentiability and Completeness of the Wavefunctions**
- Dirac "Bra-Ket" Notation

Slide 70

Differentiability and Completeness of the Wavefunction

Differentiability of ψ

It is proven in various texts** that the first derivative of the wavefunction, $d\psi/dx$, must be continuous.



This wavefunction would not be acceptable because of the sudden change in the derivative.

The one exception to the continuous derivative requirement is if $V(x) \rightarrow \infty$.

We will see that this property is useful when setting “Boundary Conditions” for a particle in a box with a finite potential barrier.

** e.g. *Introduction to Quantum Mechanics in Chemistry*, M. A. Ratner and G. C. Schatz, Sect. 2.7

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Completeness of the Wavefunction

$$H\psi_n = E\psi_n$$

The set of eigenfunctions of the Hamiltonian, ψ_n , form a “complete set”.

This means that any “well behaved” function defined over the same interval (i.e. $-\infty$ to ∞ for a Harmonic Oscillator, 0 to a for a particle in a box, ...) can be written as a linear combination of the eigenfunctions; i.e.

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n$$

We will make use of this property in later chapters when we discuss approximate solutions of the Schrödinger equation for multi-electron atoms and molecules.

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Outline (Cont'd.)

- Orthogonality of Wavefunctions
- Commutation of Operators
- Differentiability and Completeness of the Wavefunctions
- **Dirac “Bra-Ket” Notation**

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Dirac “Bra-Ket” Notation

A standard “shorthand” notation, developed by Dirac, and termed “bra-ket” notation, is commonly used in textbooks and research articles.

In this notation: $\int \varphi^* \hat{A} \psi d\tau \equiv \langle \varphi | \hat{A} | \psi \rangle$

$\langle \varphi |$ is the “bra”: It represents the complex conjugate part of the integrand

$|\psi\rangle$ is the “ket”: It represents the non-conjugate part of the integrand

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In Bra-Ket notation, we have the following:

“Scalar Product”
of two functions: $\int \psi_1^* \psi_2 d\tau \equiv \langle \psi_1 | \psi_2 \rangle$

Orthogonality: $\int \psi_i^* \psi_j d\tau \equiv \langle \psi_i | \psi_j \rangle = 0$

Normalization: $\int \psi_i^* \psi_i d\tau \equiv \langle \psi_i | \psi_i \rangle = 1$

Hermitian
Operators: $\int \phi^* \hat{A} \psi d\tau = \int \psi (\hat{A} \phi)^* d\tau \longrightarrow \langle \phi | \hat{A} | \psi \rangle = \langle \hat{A} \phi | \psi \rangle$

Expectation
Value: $\langle a \rangle = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle}$

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