General Principles of Quantum Mechanics

CHEM 361B: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry
California State University, Fullerton

Lecture 7

Table of contents

1. ψ Completely Defines the State of a System
2. Linear Operators and Observables
3. Eigenfunctions and Eigenvectors
4. Operator Order
   - Expectation Values
   - The Uncertainty Principle

Learning Objective: Formalise the quantum mechanical principles we have discussed so far into 4 postulates of quantum mechanics.

References:

- McQuarrie §4.1 - 4.6

ψ Completely Defines the State of a System

Theorem (Postulate 1)

The state of a quantum-mechanical system is completely specified by a function $\Psi(\vec{r}, t)$ that depends on the coordinates of a particle and on time. This function, called the wave function, or state function, has the important property that $\Psi^*(\vec{r}, t)\Psi(\vec{r}, t)d\vec{r}$ is the probability that the particle lies in the volume element $d\vec{r}$ located at $\vec{r}$ at time t.

This is the postulate that defines the normalisation condition that the probability of finding the particle somewhere is certain:

$$\int_{\text{all space}} \Psi^*(\vec{r}, t)\Psi(\vec{r}, t)d\vec{r} = 1$$

Operators

An operator is a symbol that tells you to do something to whatever follows that symbol. For instance:

$$\frac{d}{dx}\left(x^2\right) = 2x$$

states take the derivative of x^2. If I instead write:

$$\hat{D}x^2 = 2x; \qquad \hat{D} = \frac{d}{dx}$$

then I am stating that $\hat{D}$ is a differential operator and I want to apply it to x^2. In both cases, I get the same result.

Operator Examples

Perform the following operations:

1. $\hat{A}(2x)$; $\quad \hat{A} = \frac{d^2}{dx^2}$
2. $\hat{A}(x^2)$; $\quad \hat{A} = \frac{d^2}{dx^2} + 2\frac{d}{dx} + 3$
3. $\hat{A}(xy^3)$; $\quad \hat{A} = \frac{\partial}{\partial y}$

Linear Operators

An operator is said to be linear if

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

For instance the integral operator is linear because

$$\int [c_1 f_1(x) + c_2 f_2(x)] = c_1 \int f_1(x) + c_2 \int f_2(x)$$

while the "square" operator ($\hat{S}x = x^2$) is not linear

$$\begin{aligned} \hat{S}[c_1 f_1(x) + c_2 f_2(x)] &= c_1^2 f_1^2(x) + 2c_1 c_2 f_1(x) f_2(x) + c_2^2 f_2^2(x) \\ &\neq c_1 f_1^2(x) + c_2 f_2^2(x) \end{aligned}$$

All QM Operators are Linear

Theorem (Postulate 2)

To every observable in classical mechanics there corresponds a linear operator in quantum mechanics

Some quantum mechanical operators include:

Observable		Operation	
Name	Symbol	Operator	Operation
Position	x	$\hat{X}$	x
Momentum	p_x	$\hat{P}_x$	$-i\hbar\frac{d}{dx}$
Total Energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$

Operators - Eigenfunctions and Eigenvalues

A problem that occurs frequently, called an eigenvalue problem, is the following: Given $\hat{Q}$, find a function $g(x)$ and a constant β such that

$$\hat{Q}g(x) = \beta g(x)$$

In this case $g(x)$ is called an eigenfunction, and β is called an eigenvalue. As another example, given the operator $\hat{D}^n$ (differentiate with respect to x n times), it is fairly evident that

$$f(x) = e^{\alpha x}$$

is an eigenfunction of this operator and α^n is its eigenvalue.

Operators and Observables

Theorem (Postulate 3)

In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigenvalue equation:

$$\hat{A}\Psi = a\Psi$$

The Hamiltonian

Revisiting the time independent Schrödinger equation it can be factored to be

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

If we denote the operator in the brakets by $\hat{H}$ then

$$\hat{H}\psi(x) = E\psi(x)$$

As a result, the Schrödinger equation has been formulated into an eigenfunction/eigenvalue problem where the Hamiltonian operator is

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

$\psi(x)$ is the eigenfunction and the energy E is the eigenvalue.

Deducing the Momentum Operator

The Hamiltonian operator suggests a correspondence between itself and the energy of the system. If $U(x) = 0$ then all the energy in the system is kinetic so the kinetic energy operator is defined as

$$\hat{K} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Classically, $K = \frac{p^2}{2m}$ so we can conclude that

$$\hat{P}_x^2 = -\hbar^2\frac{d^2}{dx^2}$$

When factored it gives

$$\hat{P}_x\hat{P}_x = \left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right)$$
$$\therefore \hat{P}_x = \left(-i\hbar\frac{d}{dx}\right)$$

Momentum Eigenfunction/Eigenvalue Example

We have deduced that the momentum operator is

$$\hat{P}_x = -i\hbar\frac{d}{dx}$$

Given the function $f(x) = e^{ikx}$ (recall that this is one of the solutions to
the wave equation) determine its eigenvalue when operated on by $\hat{P}_x$

Operators - Order can be important

Given two operators, $\hat{A}$ and $\hat{B}$, if they are applied sequentially to a function $f(x)$, then

$$\hat{A}\hat{B}f(x) = \hat{A}g(x) = h(x)$$

where

$$\hat{B}f(x) = g(x)$$

Operators are evaluated from right to left and can not necessarily be reversed. If it is the case that

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$$

then the operators $\hat{A}$ and $\hat{B}$ are said to commute.

Operator Order Examples

1. Given $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x^2$ (multiply by x^2) show that $\hat{A}$ and $\hat{B}$ do not commute.
2. Given $\hat{A} = \frac{d}{dx}$ and $\hat{B} = 2$ (multiply by 2) show that $\hat{A}$ and $\hat{B}$ do commute.

Note: When showing if operators commute, it helps to use a dummy function (eg f(x)) to have the operators operate on to keep everything straight.

Using Operators to Determine Expectation Values

To use an operator to determine an expectation value consider

$$\hat{X}\psi(x) = x\psi(x)$$

Since order is important, multiply the left hand side of both equations by $\psi^*(x)$ and integrate over all values of x to give

$$\begin{aligned}\int \psi^*(x)\hat{X}\psi(x)dx &= \int \psi^*(x)\ x\ \psi(x)\ dx \\ &= \int x\ \psi^*(x)\psi(x)\ dx \\ &= \langle x \rangle\end{aligned}$$

Using Operators to Determine Expectation Values (cont.)

Theorem (Postulate 4)

If the system is in a state described by the normalised wave function Ψ, then the average value of the observable corresponding to the operator $\hat{A}$ is given by

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi \, dx$$

Expectation Value Examples

Given $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ find

1. $\langle p \rangle$
2. $\langle p^2 \rangle$
3. σ_p

Non-Commuting Operators

Recall that operators are said to commute when

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$$

To test if operators do commute then evaluate the following expression

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0; \qquad \text{commute}$$
$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0; \qquad \text{do not commute}$$

Commutation Example

Verify if $\hat{X}$ (position operator) and $\hat{P}_x$ commute. If they do not commute then discuss the significance of the value obtained.

Note: $$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4}\left(\int \psi^* [\hat{A}, \hat{B}] \psi \ dx\right)^2$$

Summary

Quantum mechanical operators are linear and are eigenfunction/eigenvalue problems with ψ. For example, the Schrödinger equation can be written using the Hamiltonian

$$\hat{H}\psi(x) = E\psi(x)$$

where

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

To determine the expectation value of an observable

$$\langle a \rangle = \int \psi^*(x)\hat{A}\psi(x)dx$$

If two operators do not commute, then they can not both be known precisely simultaneously. The magnitude of the product of their uncertainties is

$$\sigma_A^2\sigma_B^2 \geq -\frac{1}{4}\left(\int \psi^*[\hat{A},\hat{B}]\psi \ dx\right)^2$$