# Knocking on the Devil's Door 

A Naive Introduction to Quantum Mechanics

Written and Illustrated by
Jeffrey F. Gold


Tachyon Publishing Company

# Knocking on the Devil's Door: A Naive Introduction to Quantum Mechanics 

Written and Illustrated by Jeffrey F. Gold

Created June 7, 1994
Run October 16, 1995
Copyright (c)1994, 1995

Illustrations © 1994, 1995 Jeffrey F. Gold.
ALDUS FREEHAND © 1992 Altsys.
$\mathrm{T}_{\mathrm{E}} \mathrm{X}$ is a trademark of the American Mathematical Society.

First printing, revised, March 1994
Second printing, revised, September 1995
Copyright © 1995 by Jeffrey F. Gold
This book is published by Tachyon Publishing Company, Inc. All rights reserved. This publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher or author. Printed in the United States of America.

This manuscript was prepared in $\mathrm{IAT}_{\mathrm{E}} \mathrm{X}$. All illustrations were prepared in ALDUS Freehand 3.11 © 1992 ALTSYS and exported into LATEX in a generic EPS (Encapsulated POSTSCRIPT) format and imported into $\mathrm{LAT}_{\mathrm{E}} \mathrm{X}$ using a dvialw driver.

Corrections and replies should be sent to jgold@physics.utah.edu. Updates of this manuscript may be obtained from http://www.math.utah.edu/~gold/quantum.html.

## Preface

Quantum Mechanics seems untenable. Many of the concepts that seem contrarian to our common experiences wash quantum mechanics in a dim light. Fortunately, this particular problem can be overcome, but the problem is exasperated by those who cannot teach quantum mechanics, or those who can't teach, period.

I am in the process of writing this short introduction so as to explain to myself the various underpinnings of quantum mechanics. I am currently working on a new approach to quantum mechanics, which I call Naive Quantum Mechanics or NQM, in the great tradition of Paul Halmos' book Naive Set Theory. The word naive is not meant to diminish or demean my own work, but to, perhaps, express my own naiveté in starting this project, my naiveté concerning the subject, and just maybe the naiveté we all have been harboring of the actual underlying principles of quantum mechanics. If it is successful, then maybe we'll all see it in print. If it isn't successful, it might have been worth the effort anyway. I might learn a lot about myself, and more importantly, I might learn something about other people.

Quantum mechanics in its present state, in my estimation, is inadequate. I believe this because it doesn't answer the question Why? in a wholly satisfactory manner (I like asking Why? and What?). When I say quantum mechanics is inadequate, I , of course, mean that quantum mechanics gives all the right answers and such, but the explanation is inadequate to describe the goings-on behind the curtain. What I am talking about exemplifies the difference between a descriptive theory and a prescriptive theory. It just seems that nothing of import has been achieved in this basic of sciences since the 1930's. And we have had a whole lot of time to do something about it. Naive Quantum Mechanics is my attempt to remedy this outstanding problem. Wish me luck!

Jeffrey F. Gold
Salt Lake City
September 1995

## Foreword

I hate Quantum Mechanics! That's not really true, but it may have gotten your attention. What I dislike is the pedagogy of QM, or what seems to be the case, the lack thereof. At first sight QM is mysterious, and in all seriousness, this is perpetuated by those who understand it, or seem to understand it, anyway.

In my short career, the things I've heard said about QM range from "nobody understands it" to "you're not meant to understand it." If they would have said "one is not meant to understand it," rather than (inadvertently?) point the finger, then maybe I wouldn't have taken offense. I always asked myself though, "if nobody undertands it, then why are they testing me on it?"

One might say that QM is just another religion, however, other religions have a redeeming quality in that they tell us that "some day you'll be forgiven and you'll understand everything." Quantum Mechanics just does not make that kind of promise.

In Quantum Mechanics there exist what are called non-commuting variables, like momentum and position, or energy and time. I've found that there exist two other non-commuting variables of QM. Much in the same way you can't measure both position and momentum simultaneously, it seems that "you can't both understand Quantum Mechanics and do it at the same time." Beside the amorous connotation here, what is meant is that one of the following hold: either "you understand QM, but can't do it" or "you can do QM, but you just can't understand it."

A serious problem with QM lies in the notation that is commonly used. For example, in some texts I have encountered, I've run into equations like $X|x\rangle=x|x\rangle$ (can't you just cancel the $|x\rangle$ 's?). I think it's terrible notation, especially for those who are just beginning to grasp the new language. It's just not clear as to what is an operator and what is a scalar. There are many other problems, probably too numerous to mention here. Maybe this naive introduction to QM is what's needed. Maybe not.

Jeffrey F. Gold
Salt Lake City
November 1992

## Acknowledgements

I would like to thank all the people who couldn't explain Quantum Mechanics for making this necessary.

IT IS NOTHING SHORT OF A MIRACLE THAT MODERN METHODS OF INSTRUCTION HAVE NOT YET ENTIRELY STRANGLED THE HOLY CURIOUSITY OF INQUIRY.

Albert Einstein

## Contents

Preface ..... i
Foreword ..... ii
Acknowledgements ..... iii
1 Waves and Particles ..... 1
Waves ..... 1
Wavelength and Wave Number ..... 1
Frequency and Period ..... 2
Moving Waves ..... 3
Particles ..... 3
Waves Acting like Particles ..... 3
Particles Acting like Waves ..... 4
2 Constructing the Schrödinger Equation ..... 5
Wave equation for Real Waves ..... 5
The Schrödinger Wave Equation ..... 8
Schrödinger Equation for Non-zero Potential. ..... 10
3 Applications of the Schrödinger Equation ..... 12
Standing Wave on a String ..... 12
A Free Particle ..... 14
The Square-Well Potential ..... 14
Square Well with Potential ..... 17
The Hydrogen Atom ..... 19
4 Operators ..... 22
The Momentum Operator ..... 22
The Energy Operator ..... 23
Hamiltonian Operator ..... 23
Hamiltonian Operator in Higher Dimensions ..... 23
Hamiltonian Operator in 2 Dimensions ..... 23
Hamiltonian Operator in 3 Dimensions ..... 24
Hamiltonian Operator in $n$ Dimensions ..... 24
Operator Theory ..... 24
5 Hilbert's Space ..... 25
Real Vector Spaces ..... 25
Complex Vector Spaces ..... 26
Hilbert's Space ..... 27
Bibliography ..... 28

## List of Figures

1.1 The Amplitude and Wavelength of a Sinusoidal Wave. ..... 2
3.1 A 1-dimensional Box. ..... 15
3.2 The Time-independent Solution of the Schrödinger Equation. ..... 18
5.1 Argand Diagram ..... 26

## Chapter 1

## Waves and Particles

One seldom recognizes the devil when he places his hand
ON YOUR SHOULDER.
Albert Speer

## Waves

A sinusoidal wave represents a periodic function. A periodic function is characterized by $f(x+n \lambda)=f(x)$, where $\lambda$ is the wavelength, and $n=\{0, \pm 1, \pm 2, \ldots\}$. Sinusoidal just means that the waves we will be describing can be characterized by sine and cosine functions. An example of a sinusoidal wave is illustrated in Fig. 1.

The amplitude of the wave is $\mathbf{A}$ and is measured from the equilibrium position on the $x$-axis to the point of maximum $y$-displacement. There is also such a thing as a peak-to-peak amplitude, but that merely represents twice the amplitude indicated here; our choice is arbitrary.

## Wavelength and Wave Number

If the whole function in Fig. 1 (supposing it is a rigid structure) moves with velocity $v$, then the time it takes for one wave to move past some point $\mathbf{P}$ on the $x$-axis is $T=\lambda / v$. What about the reciprocal $v / \lambda$ ? This tells us how many waves move past point $\mathbf{P}$ in unit time. This is called the frequency and is usually denoted by $\nu$ (or $f$ ), and so $v / \lambda=1 / T=\nu$.

Now suppose we form the ratio $x / \lambda$. This tells us how many waves fit into a length $x$. Its reciprocal, $\lambda / x$, tells us the wavelength in terms of some unit length decided by the units used.


Figure 1.1: The Amplitude and Wavelength of a Sinusoidal Wave.

Now let's make an analogy of this moving sinusoidal wave function with the rotation of a circle, with the following proviso: the passing of one wavelength corresponds to one rotation of a circle. If we imagine our circle to be a unit circle, that is, a circle with a radius of unit length, then the circumference of the circle is $2 \pi$. If the wave has moved one wavelength, then our circle has made one complete rotation of $2 \pi$ radians. Therefore, in our circle analogy, $x / \lambda$ represents the fraction of the circumference we have traversed, and $2 \pi(x / \lambda)$ represents the total distance (in terms of circumferences in radians) that have been traversed. The latter expression is usually written as $k x$, where $k=2 \pi / \lambda$ is called the wavenumber. It enumerates how many wavelengths fit onto the circumference of a unit circle.

Note that $\sin (k x)$ actually represents a stationary wave, that is, a nonmoving wave; $y=A \sin (k x)$ describes the $y$-displacement for all values of $x$ along the $x$-axis. We will have to introduce a parameter of time to make the wave move.

## Frequency and Period

There is another way of defining a wave, and that's in terms of time $t$. Remember the time it takes for one wave to pass point $\mathbf{P}$ is given by $T=\lambda / v$. How many waves pass point $\mathbf{P}$ per unit time? The frequency tells us that $v / \lambda=1 / T=\nu$. Again, we will make a comparison of this situation to the unit circle in terms of the parameter of time.

One time cycle $T$ of the wave corresponds to one rotation of a circle. The time circumference of the unit circle is $2 \pi$ time units. If the wave has moved the distance of one wavelength in time $T$, then our circle has made one complete rotation. Therefore, in our circle analogy, $2 \pi / T$ represents one time unit. The fraction $t / T$ represents the number of unit time periods $T$ the wave has moved in time $t$. Therefore, $2 \pi t / T$ represents the total number of time circumferences
that have been traversed in time $t$. The latter value $2 \pi t / T$ is usually written as $2 \pi t / T=2 \pi \nu t=\omega t$, where we have written $\omega=2 \pi \nu$. It counts how many wavelengths (having passed in time $t$ ) fit around the time circumference of the unit circle.

## Moving Waves

Now we are ready to define a moving wave. By changing our $x$ coördinate in time, we will have created a moving wave. The change in the $x$-coördinate $x$ is denoted by

$$
\begin{equation*}
x^{\prime}=x \pm v t \tag{1.1}
\end{equation*}
$$

or

$$
\begin{equation*}
x^{\prime}=x \pm\left(\frac{\omega}{k}\right) t \tag{1.2}
\end{equation*}
$$

since $v=\lambda / T=\nu \lambda=2 \pi \nu /(2 \pi / \lambda)=\omega / k$. This means that we may rewrite (1.2) as

$$
\begin{equation*}
k x^{\prime}=k x \pm \omega t \tag{1.3}
\end{equation*}
$$

Now, a moving wave, i.e., $\sin (k x) \xrightarrow{t} \sin \left(k x^{\prime}\right)$ may be described by $\sin (k x \pm \omega t)$. This means that in the time interval $t$, the wave has moved from $x$ to $x^{\prime}$.

## Particles

This section serves as a quick reminder of some concepts from classical mechanics. The momentum of a particle is given by

$$
\begin{equation*}
p=m v \tag{1.4}
\end{equation*}
$$

where $m$ is the mass of the particle and $v$ is its velocity. The kinetic energy is given by

$$
\begin{equation*}
E=\frac{1}{2} m v^{2}=\frac{p^{2}}{2 m} \tag{1.5}
\end{equation*}
$$

by the substitution $v=p / m$. The latter form, $p^{2} / 2 m$ will appear frequently in our discourse.

## Waves Acting like Particles

Waves acting like particles-the photoelectric effect-is the observation for which Albert Einstein won the Nobel Prize, not for the Special Theory of Relativity, as is commonly but incorrectly believed. The experiment which confirmed this postulate concerns light, and electrons in metal. If photons are targeted at a slab of metal, and if homogeneous absorption takes place, then one would
expect an electron to emerge from the metal after the entire slab of metal has absorbed the energy equivalent to the energy of one electron's binding energy.

Instead, what is seen is the following: the number of electrons that are emitted from the metal is proportional to the number of incident photons. Furthermore, the energies of the expatriated electrons (called photoelectrons) is

$$
\begin{equation*}
E=\hbar \omega-W, \tag{1.6}
\end{equation*}
$$

where $W$ is the work function (energy) required to remove the electrons from the metal, and $\hbar \omega$ is the energy of the incident photons. This suggests that individual photons are absorbed by the electrons. This created the so-called "quanta" notion of photons: rather than disperse the energy throughout the metal like a wave, the energy of the individual photons is imparted directly to individual electrons. This is quite contrary to the notion of light of consisting of waves, as we are familiar with them in, for example, geometric optics.

## Particles Acting like Waves

In 1927 an experiment was performed which clearly demonstrated that particles exhibit certain wave properties if subjected to experiments which test for wave characteristics. This had been anticipated by Louis DeBroglie, who combined the ideas of Max Planck and Albert Einstein, in a textbook example of Koestler's notion of bisociation. DeBroglie formulated this by equating the energy terms of Einstein and classical mechanics, $E=p c$ and $E=\hbar \omega$, respectively, to get

$$
\begin{equation*}
p c=\hbar \omega, \tag{1.7}
\end{equation*}
$$

or

$$
\begin{equation*}
p=\frac{\hbar \omega}{c}=\hbar\left(\frac{2 \pi \nu}{c}\right)=\hbar\left(\frac{2 \pi}{\lambda}\right)=\hbar k . \tag{1.8}
\end{equation*}
$$

This suggests that any object exhibiting momentum possesses a characteristic wavelength. For everyday objects, the wavelengths are too small to be measured, but for small masses such as electrons, the measurement of wavelengths yielded to experiment.

In the experiment of Davisson-Germer, electrons were targeted at a nickel crystal. If electrons exhibited only a particle behavior, then diffraction patterns inherent to wave phenomena would not have been observed. But they were, and the rest, they say, is history.

For a comprehensive history of Quantum Mechanics, the reader is advised to read Jammer [6].

## Chapter 2

## Constructing the Schrödinger Equation


#### Abstract

This equation has provided the basis of modern QuantumMECHANICS, IN WHICH IT SEEMS TO PLAY THE SAME PART AS do the equations established by Newton, Lagrange and Hamilton, in classical mechanics.


Max Planck

I have to qualify the title of this chapter by differentiating between constructing and deriving a wave equation because there is no method by which to derive a wave equation from first principles. One may construct a wave equation, however, from known equations of waves and working the problem backwards. A wave equation depends on the type of wave you are describing. The next two sections exemplify this point.

## Wave equation for Real Waves

The waves described in this section are real (non-complex): sine and cosine functions. We will consider a sine wave only because sine and cosine functions differ in phase only, that is, $\sin (x+\pi / 2)=\cos (x)$.

Suppose we have a wave of the form

$$
\begin{equation*}
Y=A \sin (k x-\omega t), \tag{2.1}
\end{equation*}
$$

where $k$ is the wave number, and $\omega$ is the frequency of the wave. Here, $x$ and $t$ denote position and time, respectively.

If we differentiate (2.1) with respect to $x$, we find that

$$
\begin{equation*}
\frac{d Y}{d x}=k A \cos (k x-\omega t) \tag{2.2}
\end{equation*}
$$

If we again differentiate with respect to $x$, we get

$$
\begin{equation*}
\frac{d^{2} Y}{d x^{2}}=-k^{2} A \sin (k x-\omega t)=-k^{2} Y \tag{2.3}
\end{equation*}
$$

where $Y$ in the last expression is our original wave function. By operating on our original wave with the operator $\frac{d^{2}}{d x^{2}}$, the result we got back was our original wave multiplied by some constant $-k^{2}$. Equation (2.3) is an eigenvalue equation with the eigenvalue $-k^{2}$.

Remark: A quick reminder. An example of an eigenvalue equation is given by the following: Suppose $(1,2)$ is a vector residing in 2 -space, then consider the operator

$$
\hat{O}=\left(\begin{array}{rr}
3 & 0  \tag{2.4}\\
8 & -1
\end{array}\right)
$$

When the operator operates on the vector $(1,2)$, we find that

$$
\left(\begin{array}{rr}
3 & 0  \tag{2.5}\\
8 & -1
\end{array}\right)\binom{1}{2}=\binom{3}{6}=3\binom{1}{2}
$$

The operator $\hat{O}$ merely rescaled the original vector $(1,2)$ by the factor 3 . We will explain more about eigenvalue equations in Chapter ??.

Let's get back to the original problem. Let me remind you, we have

$$
\left\{\begin{array}{l}
Y=A \sin (k x-\omega t)  \tag{2.6}\\
\frac{d Y}{d x}=k A \cos (k x-\omega t) \\
\frac{d^{2} Y}{d x^{2}}=-k^{2} A \sin (k x-\omega t)=-k^{2} Y
\end{array}\right.
$$

Now let's differentiate $Y$ with respect to time $t$; we get

$$
\left\{\begin{array}{l}
Y=A \sin (k x-\omega t)  \tag{2.7}\\
\frac{d Y}{d t}=-\omega A \cos (k x-\omega t) \\
\frac{d^{2} Y}{d x^{2}}=-\omega^{2} A \sin (k x-\omega t)=-\omega^{2} Y
\end{array}\right.
$$

To construct the wave equation we simply equate the last terms from the third rows of (2.6) and (2.7), i.e., we equate

$$
\begin{equation*}
\frac{d^{2} Y}{d x^{2}}=-k^{2} Y \tag{2.8}
\end{equation*}
$$

with

$$
\begin{equation*}
\frac{d^{2} Y}{d t^{2}}=-\omega^{2} Y \tag{2.9}
\end{equation*}
$$

Let's rewrite (2.8) as

$$
\begin{equation*}
-\frac{1}{k^{2}} \frac{d^{2} Y}{d x^{2}}=Y \tag{2.10}
\end{equation*}
$$

and (2.9) as

$$
\begin{equation*}
-\frac{1}{\omega^{2}} \frac{d^{2} Y}{d t^{2}}=Y \tag{2.11}
\end{equation*}
$$

Equating the two, we get

$$
\begin{equation*}
\frac{1}{k^{2}} \frac{d^{2} Y}{d x^{2}}=\frac{1}{\omega^{2}} \frac{d^{2} Y}{d t^{2}} \tag{2.12}
\end{equation*}
$$

or

$$
\begin{equation*}
\frac{d^{2} Y}{d x^{2}}=\frac{k^{2}}{\omega^{2}} \frac{d^{2} Y}{d t^{2}} \tag{2.13}
\end{equation*}
$$

That's the wave equation for real waves; it is usually written as

$$
\begin{equation*}
\frac{d^{2} Y}{d x^{2}}=\frac{1}{v^{2}} \frac{d^{2} Y}{d t^{2}} \tag{2.14}
\end{equation*}
$$

where we identify the velocity $v$ of the wave as

$$
\begin{equation*}
v=\frac{\omega}{k} . \tag{2.15}
\end{equation*}
$$

Remark: Another, perhaps shorter, way of (re)constructing the wave equation is by using the following mnemonic: the velocity $v$ is given by

$$
\begin{equation*}
v=\frac{d x}{d t} \tag{2.16}
\end{equation*}
$$

The square of the velocity is

$$
\begin{equation*}
v^{2}=\left(\frac{d x}{d t}\right)^{2} \tag{2.17}
\end{equation*}
$$

Now, if we imagine $v^{2}$ to be a differential operator, then we may rewrite it as

$$
\begin{equation*}
v^{2}=\left(\frac{d x}{d} \cdot \frac{d}{d t}\right)^{2}=\left(\frac{d}{d t} / \frac{d}{d x}\right)^{2}=\left(\frac{d}{d t}\right)^{2} /\left(\frac{d}{d x}\right)^{2}=\frac{d^{2}}{d t^{2}} / \frac{d^{2}}{d x^{2}} \tag{2.18}
\end{equation*}
$$

Now, operating on some dummy function $y=y(x, t)$, we find that

$$
\begin{equation*}
v^{2}=\frac{d^{2} y}{d t^{2}} / \frac{d^{2} y}{d x^{2}} \tag{2.19}
\end{equation*}
$$

which we may rewrite into the form

$$
\begin{equation*}
\frac{d^{2} y}{d x^{2}}=\frac{1}{v^{2}} \frac{d^{2} y}{d t^{2}} \tag{2.20}
\end{equation*}
$$

## The Schrödinger Wave Equation

We will soon find out that the Schrödinger equation does not resemble the wave equation for real waves. The procedure of construction will be the same, but our mathematical description of waves is different. We use the complex wave description - a plane wave model given by

$$
\begin{equation*}
\Psi=A e^{i(k x-\omega t)} \tag{2.21}
\end{equation*}
$$

Remember, Euler's equation tells us that

$$
\begin{equation*}
e^{i \theta}=\cos \theta+i \sin \theta \tag{2.22}
\end{equation*}
$$

This means that we can construct sine and cosine waves (real waves) from complex waves. For a complex function $z$ the real part is given by

$$
\begin{equation*}
\Re(z)=\frac{z+\bar{z}}{2}, \tag{2.23}
\end{equation*}
$$

and the imaginary part is given by

$$
\begin{equation*}
\Im(z)=\frac{z-\bar{z}}{2 i} \tag{2.24}
\end{equation*}
$$

We won't explore this now, however.
Let's differentiate $\Psi$ with respect to $x$ :

$$
\begin{equation*}
\frac{d \Psi}{d x}=i k A e^{i(k x-\omega t)} \tag{2.25}
\end{equation*}
$$

Also,

$$
\begin{equation*}
\frac{d^{2} \Psi}{d x^{2}}=-k^{2} A e^{i(k x-\omega t)}=-k^{2} \Psi \tag{2.26}
\end{equation*}
$$

If we differentiate with respect to time $t$, we find

$$
\begin{equation*}
\frac{d \Psi}{d t}=-i \omega A e^{i(k x-\omega t)} \tag{2.27}
\end{equation*}
$$

We will not need to take the second time derivative for reasons to be explained below. Note that all time and position derivatives give eigenvalues. So for the wave equation $\Psi$, the operators $\left(d / d x, d^{2} / d x^{2}, \ldots\right)$ and $\left(d / d t, d^{2} / d t^{2}, \ldots\right)$ operating on $\Phi$ all represent eigenvalue equations, because after operating on the function $\Phi$, the operators returned the original function $\Phi$ modified by some constant factor.

From Max Planck we learned that the energy of radiation is given by

$$
\begin{equation*}
E=\hbar \omega \tag{2.28}
\end{equation*}
$$

where $\hbar=h / 2 \pi$ and $\omega$ is the frequency of the radiation.
This means that if we multiply (2.27) by $\hbar$, we have

$$
\begin{equation*}
\hbar \frac{d \Psi}{d t}=-i \hbar \omega A e^{i(k x-\omega t)}=-i \hbar \omega \Psi, \tag{2.29}
\end{equation*}
$$

or

$$
\begin{equation*}
-\frac{h}{i} \frac{d \Psi}{d t}=\hbar \omega \Psi \tag{2.30}
\end{equation*}
$$

which we may also write as

$$
\begin{equation*}
i \hbar \frac{d \Psi}{d t}=\hbar \omega \Psi \tag{2.31}
\end{equation*}
$$

If we identify $i \hbar \frac{d}{d t}$ as an operator, then when it operates on $\Psi$, the result we get back is the energy eigenvalue of the wave.

Remark: We will designate the operator $i \hbar \frac{d}{d t}$ by the symbol $\hat{E}$, which creates the distinction between an operator $\hat{E}$ and a scalar $E$. Both will appear in our discussion.

Now, let's take a look at the other equation (the other equation you might have forgotten if I hadn't reminded you). The equation of interest is

$$
\begin{equation*}
\frac{d^{2} \Psi}{d x^{2}}=-k^{2} \Psi . \tag{2.32}
\end{equation*}
$$

From DeBroglie and wave mechanics we have learned that $p=\hbar k$, where $p$ is the momentum, and $k$, again, is the wave number. If we solve for $k$ we find $k=p / \hbar$. Substituting this into (2.32),

$$
\begin{equation*}
\frac{d^{2} \Psi}{d x^{2}}=-\frac{p^{2}}{\hbar^{2}} \Psi . \tag{2.33}
\end{equation*}
$$

In mechanics, momentum is defined as $p=m v$ and kinetic energy for a free particle is defined as $E=\frac{1}{2} m v^{2}$. The latter equation may also be written as $E=p^{2} / 2 m$. This is exactly what we'll need; let's divide both sides of (2.33) by $2 m$ :

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}=\frac{p^{2}}{2 m} \Psi, \tag{2.34}
\end{equation*}
$$

another energy eigenvalue equation!
If you imagine the left hand side of (2.34) to be represented by an operator $\hat{p}^{2} / 2 m$ operating on $\Psi$, then the result is just an eigenvalue, or scaling factor, times the original wavefunction $\Psi$. This is equivalent to the result we obtained earlier in (2.31). If we equate (2.31) and (2.34), we have constructed the Schrödinger Equation for a free particle (or for zero potential; more about zero potential later):

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}=i \hbar \frac{d \Psi}{d t}, \tag{2.35}
\end{equation*}
$$

which is usually written as

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}=\hat{E} \Psi \tag{2.36}
\end{equation*}
$$

where $\hat{E}$ is an operator, not the scalar $E=\hbar \omega$ although we could have written it that way. It doesn't really matter which way we write it because, in this case, after $\hat{E}$ operates on $\Psi$, we just end up getting the energy eigenvalue $\hbar \omega$ anyway.

In the equation

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}=\frac{\hat{p}^{2}}{2 m} \Psi, \tag{2.37}
\end{equation*}
$$

we have written the scalar $p$ in equation (2.34) as an operator $\hat{p}$. Perhaps we would like to know what form this operator takes. If we equate both sides of (2.37), by eliminating $\Psi$, then

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}=\frac{\hat{p}^{2}}{2 m} \tag{2.38}
\end{equation*}
$$

If $\hat{p}^{2}$ is really the square $\hat{p} \cdot \hat{p}$, then

$$
\begin{equation*}
\hat{p} \cdot \hat{p}=-\hbar^{2} \frac{d^{2}}{d x^{2}}, \tag{2.39}
\end{equation*}
$$

or

$$
\begin{equation*}
\hat{p}= \pm i \hbar \frac{d}{d x} \tag{2.40}
\end{equation*}
$$

since $d / d x$ operating on itself is $d / d x \cdot d / d x=d^{2} / d x^{2}$ and $(-i)^{2}=-1$. Which operator is it? The positive one, or the negative one? We define it as the negative one. We define it as the negative one so that when you operate on $\Psi$ with the operator $-i \hbar \frac{d}{d x}$, then the momentum eigenvalue is positive. (This calculation is done in Chapter 4).

Therefore, the momentum operator is given by

$$
\begin{equation*}
\hat{p}=-i \hbar \frac{d}{d x} . \tag{2.41}
\end{equation*}
$$

## Schrödinger Equation for Non-zero Potential.

Equation (2.36) we constructed was for a particle in a zero potential, or a free particle. If a particle resides in a potential, such as a charged particle in the vicinity of a neighboring charged particle or an external electric field, then its total energy is modified. It now also possesses a potential energy term, denoted by $V$, which we must include in the final analysis. The total energy then, for a bound particle, is $E+V$, or in the language of QM , we will write it as

$$
\begin{equation*}
E+V \rightarrow \hat{E}+\hat{V}=\frac{\hat{p}^{2}}{2 m}+\hat{V} \tag{2.42}
\end{equation*}
$$

It will turn out that in most cases, the potential operator $\hat{V}$ reduces to a mere multiplying function, that is to say, the potential is not normally an operator, and thus $\hat{V} \rightarrow V$.

Now, we may write the complete Schrödinger equation as

$$
\begin{equation*}
\left(-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}+V\right) \Psi=\hat{E} \Psi \tag{2.43}
\end{equation*}
$$

or

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}+V \Psi=\hat{E} \Psi \tag{2.44}
\end{equation*}
$$

Frequently you will see the latter equation written as

$$
\begin{equation*}
\hat{H} \Psi=\hat{E} \Psi, \tag{2.45}
\end{equation*}
$$

where we identify the $\hat{H}$ as the Hamiltonian operator

$$
\begin{equation*}
\hat{H}=-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}+V, \tag{2.46}
\end{equation*}
$$

and $\hat{E}$ as the energy operator $\hat{E}=-i \hbar d / d t$. More will be explained about the Hamiltonian operator in Chapter 4.

## Chapter 3

## Applications of the Schrödinger Equation


#### Abstract

An EXPERT IS SOMEONE WHO KNOWS SOME OF THE WORST MISTAKES THAT CAN BE MADE IN HIS SUBJECT, AND HOW TO AVOID THEM.


Werner Heisenberg

These are the easiest applications of the Schrödinger equation because of the contrived mathematical restrictions placed on the problems and the equation. However, these examples introduce the reader to the main concepts hereboundary conditions on partial differential equations. I work the problems from beginning to end, even putting in the mathematical minutiae, so that the reader can glimpse the points of interest, rather than worry about filling in the missing steps. Let's concentrate on the concepts here-not so much the mathematical formality. We will first solve the classical analogue of the Schrödinger equation, i.e., the wave equation, for the problem of a string fixed at both ends. This should ease us into the applications of the Schrödinger equation.

## Standing Wave on a String

We will apply the wave equation for real waves to the problem of a taut string fixed at both ends. Now, since we derived the wave equation from the known solutions for real waves, we need not again solve the equation

$$
\begin{equation*}
\frac{d^{2} Y(x, t)}{d x^{2}}=\frac{1}{v^{2}} \frac{d^{2} Y(x, t)}{d t^{2}} \tag{3.1}
\end{equation*}
$$

A possible solution is $Y(x, t)=B \sin (k x-\omega t)+B_{0} \sin (k x+\omega t)$, which represents two waves of differing amplitudes traveling in opposite directions. We include the opposite traveling wave so as to take into account the reflected waves. We will also assume that no dampening or any other energy loss takes place.

All we need to do now is place the boundary conditions on $Y(x, t)$. The boundary conditions are $Y(0, t)=0$ and $Y(d, t)=0$, where $d$ is the distance separating the two ends of the string. These conditions must hold since the string is not be driven at either node, i.e., the sites where it is clamped.

The first condition implies that

$$
\begin{equation*}
Y(0, t)=B \sin (-\omega t)+B_{0} \sin (\omega t)=\left(B_{0}-B\right) \sin (\omega t)=0, \tag{3.2}
\end{equation*}
$$

or that $B_{0}=B$. We expected this to be the case anyway, since the reflected wave would be of the same amplitude as the incident wave, because of our caveat that no energy losses take place upon reflection. Now we may rewrite $Y(x, t)$ as

$$
\begin{equation*}
Y(x, t)=B \sin (k x-\omega t)+B \sin (k x+\omega t) . \tag{3.3}
\end{equation*}
$$

$Y(x, t)$ may also be written as

$$
\begin{align*}
Y(x, t)= & B \sin (k x) \cos (-\omega t)+B \sin (-\omega t) \cos (k x)  \tag{3.4}\\
& +B \sin (k x) \cos (\omega t)+B \sin (\omega t) \cos (k x), \tag{3.5}
\end{align*}
$$

since $\sin (\alpha+\beta)=\sin (\alpha) \cos (\beta)+\sin (\beta) \cos (\alpha)$ and $\sin (\alpha-\beta)=\sin (\alpha) \cos (\beta)-$ $\sin (\beta) \cos (\alpha)$. Also, since $\sin (-\alpha)=-\sin (\alpha)$ and $\cos (-\alpha)=\cos (\alpha)$,

$$
\begin{align*}
Y(x, t)= & B \sin (k x) \cos (\omega t)-B \sin (\omega t) \cos (k x)  \tag{3.6}\\
& +B \sin (k x) \cos (\omega t)+B \sin (\omega t) \cos (k x)  \tag{3.7}\\
= & 2 B \sin (k x) \cos (\omega t) . \tag{3.8}
\end{align*}
$$

This shows that we have separated $Y(x, t)$ into two multiplicative terms

$$
\begin{equation*}
Y(x, t)=X(x) T(t), \tag{3.9}
\end{equation*}
$$

where $X(x)=2 \sin (k x)$ and $T(t)=\cos (\omega t)$.
The remaining boundary condition $Y(d, t)$ forces

$$
\begin{equation*}
X(d)=2 \sin (k d)=0, \tag{3.10}
\end{equation*}
$$

which implies that the argument of the $\sin$ function must be a multiple of $\pi$, or that $k d=n \pi$, where $n=\{0,1,2, \ldots\}$. Now we may write $k$ as $k_{n}=n \pi / d$, and

$$
\begin{equation*}
X(x)=2 \sin \left(\frac{n \pi x}{d}\right) . \tag{3.11}
\end{equation*}
$$

Thus,

$$
\begin{equation*}
Y(x, t)=2 \sin \left(\frac{n \pi x}{d}\right) \cos (\omega t) . \tag{3.12}
\end{equation*}
$$

## A Free Particle

Suppose we have a particle of mass $m$. Since the particle is not in a potential, we find that the particle must satisfy the Schrödinger equation

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}=E \Psi \tag{3.13}
\end{equation*}
$$

which we may rewrite as,

$$
\begin{equation*}
\frac{d^{2} \Psi}{d x^{2}}+\frac{2 m E}{\hbar^{2}} \Psi=0 . \tag{3.14}
\end{equation*}
$$

We have already solved this problem (backwards) to derive the Schrödinger equation, but we'll solve it formally. Let's try a solution of the form

$$
\begin{equation*}
\Psi=A e^{i k x} . \tag{3.15}
\end{equation*}
$$

This means that (3.2) becomes

$$
\begin{equation*}
-k^{2} A e^{i k x}+\frac{2 m E}{\hbar^{2}} A e^{i k x}=0 \tag{3.16}
\end{equation*}
$$

or

$$
\begin{equation*}
\left(\frac{2 m E}{\hbar^{2}}-k^{2}\right) A e^{i k x}=0, \tag{3.17}
\end{equation*}
$$

which implies that the coefficient $2 m E / \hbar^{2}-k^{2}=0$, or that

$$
\begin{equation*}
k=\sqrt{\frac{2 m E}{\hbar^{2}}} . \tag{3.18}
\end{equation*}
$$

If we make the substitution $E=p^{2} / 2 m$, we find the DeBroglie relation

$$
\begin{equation*}
k=\frac{p}{\hbar}, \tag{3.19}
\end{equation*}
$$

as expected.

## The Square-Well Potential

This problem is very similar, if not equivalent (mathematicians would say "isomorphic") to the problem of a taut string fixed at both ends. The difference is that the wave equation we use in this case is not the wave equation for real waves, but the wave equation for complex waves-Schrödinger's equation.

Suppose we have a 1-dimensional box in which to confine a particle between two impenetrable walls (that's the contrived mathematics!). To make the problem even easier, we apply no potential to the particle. We'll apply the


Figure 3.1: A 1-dimensional Box.

Schrödinger equation for a free particle (that's kind of a misnomer, since the particle is confined to the box). An idealized representation of this situation is illustrated in Figure 3.1.

The wave equation

$$
\begin{equation*}
i \hbar \frac{d \Psi}{d t}=-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}} \tag{3.20}
\end{equation*}
$$

will be applied to the complex wave

$$
\begin{equation*}
\Psi(x, t)=A e^{i(k x-\omega t)}=A e^{i k x} e^{-i \omega t} \tag{3.21}
\end{equation*}
$$

This separates the wavefunction $\Psi(x, t)$ into the product of two new functions, $\Phi(x)$ and $T(t)$. We may now write

$$
\begin{equation*}
\Psi(x, t)=\Phi(x) e^{-i \omega t}=\Phi(x) T(t) . \tag{3.22}
\end{equation*}
$$

Let's substitute this equation into (3.1):

$$
\begin{align*}
& i \hbar \frac{d \Psi}{d t}=-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}} \\
& i \hbar \frac{d\left[\Phi(x) e^{-i \omega t}\right]}{d t}=-\frac{\hbar^{2}}{2 m} \frac{d^{2}\left[\Phi(x) e^{-i \omega t}\right]}{d x^{2}} \\
& i \hbar \Phi(x) \frac{\left.d e^{-i \omega t}\right]}{d t}=-\frac{\hbar^{2}}{2 m} e^{-i \omega t} \frac{d^{2}[\Phi(x)]}{d x^{2}}  \tag{3.23}\\
& i \hbar \Phi(x)(-i \omega)\left[e^{-i \omega t}\right]=-\frac{\hbar^{2}}{2 m}\left[e^{-i \omega t}\right] \frac{d^{2}[\Phi(x)]}{d x^{2}} \\
& \hbar \omega \Phi(x)=-\frac{\hbar^{2}}{2 m} \frac{d^{2}[\Phi(x)]}{d x^{2}}
\end{align*}
$$

or

$$
\begin{equation*}
\frac{\hbar^{2}}{2 m} \frac{d^{2}[\Phi(x)]}{d x^{2}}+\hbar \omega \Phi(x)=0 . \tag{3.24}
\end{equation*}
$$

We may also write this as

$$
\begin{equation*}
\frac{d^{2}[\Phi(x)]}{d x^{2}}+\frac{2 m(\hbar \omega)}{\hbar^{2}} \Phi(x)=0, \tag{3.25}
\end{equation*}
$$

by multiplying through by the factor $2 m / \hbar^{2}$. Since $E=\hbar \omega$, we get

$$
\begin{equation*}
\frac{d^{2}[\Phi(x)]}{d x^{2}}+\frac{2 m E}{\hbar^{2}} \Phi(x)=0, \tag{3.26}
\end{equation*}
$$

or

$$
\begin{equation*}
\frac{d^{2}[\Phi(x)]}{d x^{2}}+k^{2} \Phi(x)=0, \tag{3.27}
\end{equation*}
$$

by making the substitution $E=p^{2} / 2 m=\hbar^{2} k^{2} / 2 m$.
We do not yet know what form $\Phi(x)$ takes inside the box, but we do know that $\Phi(x)$ cannot extend beyond the dimension (!) of the box; this constrains $\Phi(x)$ to equate to zero at the boundaries $x=0$ and $x=\lambda$; that is, we have the boundary conditions $\Phi(0)=0$ and $\Phi(\lambda)=0$ which must be satisfied.

Since the confined particle may exhibit travel in either $x$ direction, i.e., it has both positive and negative momentum, we write $\Phi(x)$ as

$$
\begin{equation*}
\Phi(x)=C e^{i k x}+C_{0} e^{-i k x}=C e^{i p x / \hbar}+C_{0} e^{-i p x / \hbar} . \tag{3.28}
\end{equation*}
$$

by making the substitution $k=p / \hbar$. Note also that we should expect the two constants $C$ and $C_{0}$ to eventually equate, since we can't really expect the two waves $e^{i k x}$ and $e^{-i k x}$ to exhibit different amplitudes. This can be heuristically argued as follows: When the wave (particle) is reflected from a boundary, the reflected wave (particle) is of the same amplitude as the incident wave (particle) since no dampening, or friction, or any other energy loss takes place.

If we substitute (3.28) into (3.27), we get

$$
\begin{equation*}
-k^{2} C e^{i k x}-k^{2} C_{0} e^{-i k x}+k^{2} C e^{i k x}+k^{2} C_{0} e^{-i k x}, \tag{3.29}
\end{equation*}
$$

or

$$
\begin{align*}
& -k^{2}\left(C e^{i k x}-C_{0} e^{-i k x}\right)+k^{2}\left(C e^{i k x}+C_{0} e^{-i k x}\right)  \tag{3.30}\\
& =-k^{2} \Phi(x)+k^{2} \Phi(x)=0 .
\end{align*}
$$

This solution will work.
Now, let's impose the first boundary condition, namely $\Phi(0)=0$. This implies that

$$
\begin{equation*}
\Phi(0)=C e^{0}+C_{0} e^{0}=C+C_{0}=0, \tag{3.31}
\end{equation*}
$$

which implies that $C_{0}=-C$. So, now we have

$$
\begin{align*}
\Phi(x) & =C e^{k x}-C e^{-k x}  \tag{3.32}\\
& =C\left(e^{k x}-e^{-k x}\right)  \tag{3.33}\\
& =C[\cos (k x)+i \sin (k x)-(\cos (-k x)+i \sin (-k x))] \tag{3.34}
\end{align*}
$$

which, because $\cos (-k x)=\cos (k x)$ and $\sin (-k x)=-\sin (k x)$, is equivalent to

$$
\begin{align*}
\Phi(x) & =C[\cos (k x)+i \sin (k x)-(\cos (k x)-i \sin (k x))]  \tag{3.35}\\
& =C[\cos (k x)+i \sin (k x)-\cos (k x)+i \sin (k x)]  \tag{3.36}\\
& =2 i C \sin (k x)  \tag{3.3}\\
& =D \sin (k x) . \tag{3.38}
\end{align*}
$$

where $D=2 i C$. Now, if we constrain $\Phi(x)$ to the boundary condition $\Phi(d)=0$, we get

$$
\begin{equation*}
\Phi(d)=D \sin \left(\frac{p d}{\hbar}\right)=0, \tag{3.39}
\end{equation*}
$$

which implies that the argument of the sine function must be a multiple of $\pi$. This means that

$$
\begin{equation*}
\frac{p d}{\hbar}=n \pi, \tag{3.40}
\end{equation*}
$$

where $n$ is an integer $n=\{1,2,3, \ldots\}$. This constrains the momentum $p$ to the quantized form

$$
\begin{equation*}
p_{n}=\frac{n \pi \hbar}{d}, \tag{3.41}
\end{equation*}
$$

meaning that the momentum can take on only discrete values $p_{n}$. This corresponds to fitting half-wave segments or multiples of half-wave segments into the 1-dimensional box, just like the string fixed at both ends. That is to say, multiples of half-wave segment are the only waves that fit into the box without destructively interfering with themselves.

Since the momentum $p_{n}$ is quantized, this also means that the energies $\Phi(x)$ are also quantized. Since $E=p^{2} / 2 m$, this implies that $E_{n}=p_{n}^{2} / 2 m$, or

$$
\begin{equation*}
E_{n}=\frac{n^{2} \pi^{2} \hbar^{2}}{2 m d^{2}} . \tag{3.42}
\end{equation*}
$$

Since the momentum is quantized, by the same token, the wavenumber is also quantized by $k \rightarrow k_{n}=p_{n} / \hbar$, or

$$
\begin{equation*}
k_{n}=\frac{n \pi}{d} . \tag{3.43}
\end{equation*}
$$

The solutions to the time-independent Schrödinger equation for $n=1,2,3$ are shown in Fig. 3.2.

## Square Well with Potential

The square-well potential with the potential energy term $\hat{V}$ is very similar to that of the original square-well potential problem. Schrödinger's equation is

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}+\hat{V} \Psi=E \Psi . \tag{3.44}
\end{equation*}
$$



Figure 3.2: The Time-independent Solution of the Schrödinger Equation.

Since in most instances $\hat{V}$ is a multiplying function, that is, $V \neq V(x, t)$, we may rewrite this as $\hat{V} \rightarrow V$, and

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}=(E-V) \Psi \tag{3.45}
\end{equation*}
$$

This is just like doing the original square well potential problem, except we replace $E$ with the term $E-V$, which means that

$$
\begin{equation*}
E_{n}-V=\frac{n^{2} \pi^{2} \hbar^{2}}{2 m d^{2}} \tag{3.46}
\end{equation*}
$$

or that the quantized energy $E_{n}$ is shifted by the amount $V$ as given by

$$
\begin{equation*}
E_{n}=\frac{n^{2} \pi^{2} \hbar^{2}}{2 m d^{2}}+V \tag{3.47}
\end{equation*}
$$

In the case that $V$ is a function of position and time, i.e., $V=V(x, t)$, we find that $V$ behaves more like an operator $\hat{V}$, than a multiplier. For example, suppose $V$ is the potential energy term $V=-\frac{e^{2}}{x}$, the electrostatic potential energy. Then, Schrödinger's equation reads

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m} \frac{d^{2} \Psi}{d x^{2}}+-\frac{e^{2}}{x} \Psi=\hat{E} \Psi \tag{3.48}
\end{equation*}
$$

Now we have a problem. If we rewrite the equation, we get

$$
\begin{equation*}
-\frac{\hbar^{2} x}{2 m} \frac{d^{2} \Psi}{d x^{2}}-e^{2} \Psi=x \hat{E} \Psi \tag{3.49}
\end{equation*}
$$

Solving (3.49) requires a more sophisticated approach, which we develop later. Remark: The placing of variables is very crucial. If we place $x$ after an operator, we are indicating that the operator is intended to operate on the variable, as well as the wavefunction $\Psi$. This we don't want to do. For example, suppose we did this, then $x \frac{d}{d x} \Psi \neq \frac{d}{d x}(x \Psi)$. The left-hand-side is $x \frac{d \Psi}{d x}$ while the right-hand-side is $x \frac{d \Psi}{d x}+\Psi$.

## The Hydrogen Atom

Bohr's idea is an extension of DeBroglie's insight of the wave nature of particles. Quantum particles exhibit a characteristic wavelength given by the momentum relation

$$
\begin{equation*}
p=\hbar k, \tag{3.50}
\end{equation*}
$$

where $\hbar$ is the modified Planck's constant, and $k=2 \pi / \lambda$ is the wavenumber. For a classical particle the momentum may be expressed as $p=m v$, which we may rewrite as

$$
\begin{equation*}
\lambda=\frac{2 \pi \hbar}{m}, \tag{3.51}
\end{equation*}
$$

indicating an inverse relationship between the wavelength $\lambda$ and the mass $m$.
What Bohr proposed was to fit DeBroglie's wavelengths into circular orbits. But he did this in an indirect way, by quantizing the angular momentum. He stated that

$$
\begin{equation*}
m v r=n \hbar, \tag{3.52}
\end{equation*}
$$

where $n$ is an integer. What this equation says is that the angular momentum is discretized into multiples of $\hbar$ by the happy accident that $\hbar$ has the proper units of angular momentum.

From classical physics, and this is why this type of argument is referred to as semi-classical reasoning, he also equated the simple Newtonian centrifugal force with the electrostatic term,

$$
\begin{equation*}
\frac{m v^{2}}{r}=\frac{e^{2}}{r^{2}}, \tag{3.53}
\end{equation*}
$$

where $e$ is magnitude of the charge of the electron and proton. Substituting (3.50) into (3.51), this gives us the velocity $v$ as

$$
\begin{equation*}
v=\frac{e^{2}}{n \hbar} \tag{3.54}
\end{equation*}
$$

and the relation

$$
\begin{equation*}
r=\frac{n^{2} \hbar^{2}}{e^{2} m} \tag{3.55}
\end{equation*}
$$

The equation for the velocity $v$ allows us to find the kinetic energy of the system by

$$
\begin{equation*}
K=\frac{1}{2} m v^{2}=\frac{e^{4} m}{2 \hbar^{2} n^{2}} \tag{3.56}
\end{equation*}
$$

and the potential energy by

$$
\begin{equation*}
V=-\frac{e^{2}}{r}=-\frac{e^{4} m}{\hbar^{2} n^{2}}=-2 K . \tag{3.57}
\end{equation*}
$$

Thus the total energy $E$ is given as the sum of the two energy terms, and equates to $E=K+(-2 K)=-K$. So the energy of the hydrogen atom can be discretized in terms of the integers $n$, by the relation

$$
\begin{equation*}
E_{n}=-\frac{1}{n^{2}}\left(\frac{e^{4} m}{2 \hbar^{2}}\right) . \tag{3.58}
\end{equation*}
$$

Equation (3.55) relating $r$ and $n$ states that

$$
\begin{equation*}
r=\frac{n^{2} \hbar^{2}}{e^{2} m}=n^{2}\left(\frac{\hbar^{2}}{e^{2} m}\right)=n^{2} r_{0} \tag{3.59}
\end{equation*}
$$

where we identify $r_{0}=0.527 \times 10^{-8} \mathrm{~cm}$ as Bohr's radius.
The differences in energy for any two $n$ 's, say $n_{0}$ and $n_{f}$ is given by

$$
\begin{equation*}
E_{n_{f}}-E_{n_{0}}=-\frac{e^{4} m}{2 \hbar^{2}}\left(\frac{1}{n_{f}^{2}}-\frac{1}{n_{0}^{2}}\right) . \tag{3.60}
\end{equation*}
$$

In fact, what Bohr had done using this simple model was to effect a derivation of the Rydberg constant $R$ in

$$
\begin{equation*}
R h c=\frac{e^{4} m}{2 \hbar^{2}}=2.1798741(13) \times 10^{-18} J \tag{3.61}
\end{equation*}
$$

which until now had only been derived empirically by Janne Rydberg, who expanded on earlier work by Johann Jakob Balmer.

The sequence of energy levels for the case where $n=1$ is the initial state is called the Lyman series, and the case $n=2$ is called the Balmer sequence. The cases $n=3,4$, and 5 are called the Ritz-Paschen, Brackett, and Pfund series, respectively.

The Balmer series is of special interest because the transitions are in the wavelength of visible light ( $4000 \AA-7000 \AA$ ), and thus perhaps the the first to be observed in early experiments.

The energy levels of the Balmer series are thus given by

$$
\begin{equation*}
E_{n}=-R\left(\frac{1}{n^{2}}-\frac{1}{4}\right) . \tag{3.62}
\end{equation*}
$$

Consisting of a single electron orbiting around a single proton, the hydrogen atom is the simplest atom to study spectroscopically. The most prominent spectroscopic line of hydrogen was recorded by Ångstrom in 1853 . The brightest line of the Balmer series is a red line known as the $\mathrm{H}-\alpha$ line, or Balmer- $\alpha$ line. Its corresponding wavelength is 656 nm . The extended hydrogen lines were measured by Sir William Higgins in 1881 as part of his spectroscopic studies of the hydrogen lines of stars. Observing a pure hydrogen spectrum is difficult because of the diatomic nature of hydrogen and the high energies it takes to dissociate such diatomic molecules. Mere thermal excitations provided by a simple flame are not enough to break these bonds; instead one has to rely on the more energetic means usually provided by a gas discharge method.

## Chapter 4

## Operators


#### Abstract

I REGARD IT AS AN INELEGANCE, OR IMPERFECTION, IN QUATERNIONS, OR RATHER IN THE STATE TO WHICH IT HAS BEEN HITHERTO UNFOLDED, WHENEVER IT BECOMES OR SEEMS TO BECOME NECESSARY TO HAVE RECOURSE TO X, Y, Z, ETC...


Sir William Rowan Hamilton (1805-1865)

As we have learned in the previous chapter, operators help us extract information from the wavefunction, e.g., the momentum operator $\hat{p}$ extracted the momentum eigenvalue, and the energy operator $\hat{E}$ extracted the energy eigenvalue. The Hamiltonian Operator extracts information regarding the total energy of the system.

## The Momentum Operator

In the last chapter we encountered the operator

$$
\begin{equation*}
\hat{p}=-i \hbar \frac{d}{d x} \tag{4.1}
\end{equation*}
$$

Since we really derived it from the square $\hat{p}^{2}$, let's verify that this does indeed give us a (positive) momentum eigenvalue. Let $\hat{p}$ operate on $\Psi$, our wavefunction:

$$
\begin{equation*}
\hat{p} \Psi=-i \hbar \frac{d}{d x} \cdot \Psi=-i \hbar \frac{d \Psi}{d x}=-i \hbar(i k) A e^{i(k x-\omega t)}=\hbar k \Psi=p \Psi \tag{4.2}
\end{equation*}
$$

which indeed gives us the (positive) momentum eigenvalue.

## The Energy Operator

The energy operator was derived in Chapter 2. For sake of continuity, we operate on $\Psi$ with $\hat{E}$ :

$$
\begin{equation*}
\hat{E} \Psi=\frac{\hbar}{i} \frac{d}{d t} \cdot \Psi=i \hbar \frac{d \Psi}{d t}=i \hbar(-i \omega) \Psi=\hbar \omega \Psi \tag{4.3}
\end{equation*}
$$

## Hamiltonian Operator

The Hamiltonian operator is given by

$$
\begin{equation*}
\hat{H}=-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}+\hat{V} \tag{4.4}
\end{equation*}
$$

If we apply the Hamiltonian operator to the wave function $\Psi=A e^{i(k x-\omega t)}$, we obtain

$$
\begin{align*}
\left(-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}+\hat{V}\right) \Psi & =-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}} \Psi+\hat{V} \Psi  \tag{4.5}\\
& =-\frac{\hbar^{2}}{2 m} \frac{d^{2}}{d x^{2}}\left(A e^{i(k x-\omega t)}\right)+\hat{V}\left(A e^{i(k x-\omega t)}\right)  \tag{4.6}\\
& =-\frac{\hbar^{2}}{2 m} k^{2} i^{2} A e^{i(k x-\omega t)}+\hat{V} A e^{i(k x-\omega t)}  \tag{4.7}\\
& =\left(\frac{\hbar^{2} k^{2}}{2 m}+\hat{V}\right) \Psi  \tag{4.8}\\
& =\left(\frac{p^{2}}{2 m}+\hat{V}\right) \Psi \tag{4.9}
\end{align*}
$$

where $p^{2} / 2 m$ is the kinetic energy and $\hat{V}$ is the potential energy. In most instances, the operator $\hat{V}$ is merely a multiplying function, rather than a function which "operates" on $\Psi$.

## Hamiltonian Operator in Higher Dimensions

The Hamiltonian Operator in 2 and 3 dimensions is very easy to conceptualize, and is also easy to extend to higher dimensions.

## Hamiltonian Operator in 2 Dimensions

The Hamiltonian for two dimensions is given by

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m}\left(\frac{d^{2}}{d x^{2}}+\frac{d^{2}}{d y^{2}}\right)+\hat{V} \tag{4.11}
\end{equation*}
$$

where the wave function $\Psi$ is given by $\Psi=A e^{i\left(k_{x} x+k_{y} y-\omega t\right)}$.

## Hamiltonian Operator in 3 Dimensions

The Hamiltonian for three dimensions is given by

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m}\left(\frac{d^{2}}{d x^{2}}+\frac{d^{2}}{d y^{2}}+\frac{d^{2}}{d z^{2}}\right)+\hat{V} \tag{4.12}
\end{equation*}
$$

where the wave function $\Psi$ is given by $\Psi=A e^{i\left(k_{x} x+k_{y} y+k_{z} z-\omega t\right)}$.

## Hamiltonian Operator in $n$ Dimensions

The Hamiltonian for $n$ dimensions is given by

$$
\begin{equation*}
-\frac{\hbar^{2}}{2 m}\left(\frac{d^{2}}{d x_{1}^{2}}+\frac{d^{2}}{d x_{2}^{2}}+\frac{d^{2}}{d x_{3}^{2}}+\ldots+\frac{d^{2}}{d x_{n}^{2}}\right)+\hat{V} \tag{4.13}
\end{equation*}
$$

where the wave function $\Psi$ is given by $\Psi=A e^{i(\vec{k} \cdot \vec{x}-\omega t)}$, where the wavenumber is given $\vec{k}=\left(k_{1}, k_{2}, \ldots, k_{n}\right)$ and the dimension vector is given by $\vec{x}=$ $\left(x_{1}, x_{2}, \ldots, x_{n}\right)$. The thing to note here, is that for each of the Hamiltonian operators, be it in two, or three, or $n$-dimensions, each $\frac{d^{2}}{d x_{i}^{2}}$ chooses only the terms containing $x_{i}$ in the wavefunction $\Psi$. This means that if there exist no cross terms like $x^{2} y, x y$, or $x y^{2}$, in the case of two dimensions, then each dimensional component is decoupled from the other dimensional components.

## Operator Theory

Operator Theory is also known by the names Linear Mapping, Linear Transformation, and Linear Operators. The axioms for linear operators are

$$
\begin{align*}
\hat{O}(f+g) & =\hat{O}(f)+\hat{O}(g)  \tag{4.14}\\
\hat{O}(\alpha f) & =\alpha \hat{O}(f) \tag{4.15}
\end{align*}
$$

for some functions $f$ and $g$ and a scalar $\alpha$.
Example: We have already seen that the differential operator $d / d x$ is a linear operator:

$$
\begin{align*}
\frac{d}{d x}[f(x)+g(x)] & =\frac{d}{d x}[f(x)]+\frac{d}{d x}[g(x)]  \tag{4.16}\\
\frac{d}{d x}[\alpha f(x)] & =\alpha \frac{d}{d x}[f(x)] \tag{4.17}
\end{align*}
$$

## Chapter 5

## Hilbert's Space

Physics is much too hard for physicists.
David Hilbert

## Real Vector Spaces

The vectors $(1,0,0),(0,1,0)$ and $(0,0,1)$ form a normal basis for 3 -space. This means that any vector $\vec{v}$ in 3 -space can be written in terms of a linear combination of these three vectors; that is

$$
\begin{equation*}
\vec{v}=\alpha_{1}(1,0,0)+\alpha_{2}(0,1,0)+\alpha_{3}(0,0,1) \tag{5.1}
\end{equation*}
$$

where $\alpha_{i} \in \mathbb{R}$. The term normal just means that the basis vectors are mutually perpendicular. The basis vectors given above are in fact orthonormal, meaning that they are also each of unit length.

Remark: One usually talks of vectors being perpendicular if they are confined to 3 -space; the extension of this idea to higher dimensions and complex vector spaces is to call such vectors orthogonal or normal or orthonormal (if appropriate).

The basis vectors $(1,0,0),(0,1,0)$ and $(0,0,1)$ are not unique. One can construct other basis vectors for 3 -space. The ones above are probably the nicest - it is easy to extract information about them and their orthonormality just by looking at them.

How do we determine that vectors are perpendicular or normal in other situations? We use the inner product (or dot product). If $\mathbf{v}_{1} \cdot \mathbf{v}_{2}=0$, then $\mathbf{v}_{1}$ and $\mathbf{v}_{2}$ are perpendicular. In terms of our original basis vectors, we can easily


Figure 5.1: Argand Diagram.
see that

$$
\begin{aligned}
& (1,0,0) \cdot(0,1,0)=0 \\
& (1,0,0) \cdot(0,0,1)=0 \\
& (0,1,0) \cdot(0,0,1)=0
\end{aligned}
$$

## Complex Vector Spaces

Suppose we have the vector $(i, 2+i, 3)$. Note that each entry of the vector is a complex entry; it just so happens that the real component of the first entry is 0 and the imaginary component of the third entry is 0 . What is the length of this vector? Remember the inner product should gives us this information:

$$
\begin{equation*}
\mathbf{v} \cdot \mathbf{v}=\|v\|^{2} \geq 0 . \tag{5.2}
\end{equation*}
$$

Let's try this for $(i, 2+i, 3)$ :

$$
\begin{equation*}
(i, 2+i, 3) \cdot(i, 2+i, 3)=i^{2}+(2+i)^{2}+3^{2}=-1+(3+4 i)+9=11+4 i . \tag{5.3}
\end{equation*}
$$

The length is imaginary; this doesn't tell us a thing. To remedy the situation, that is, to get a real, non-negative length, we will multiply the vector $v$ by its conjugate, rather than multiply it by itself.
Example: Let's try this instead:

$$
\begin{align*}
& (i, 2+i, 3) \cdot \overline{(i, 2+i, 3)} \\
= & (i, 2+i, 3) \cdot(\bar{i}, \overline{2+i}, \overline{3}) \\
= & (i, 2+i, 3) \cdot(-i, 2-i, 3)  \tag{5.4}\\
= & -i^{2}+\left(4-i^{2}\right)+9 \\
= & 1+5+9 \\
= & 15
\end{align*}
$$

Why does this work? It works because each entry is simply the sum of the square of the length of the real part and the square of the imaginary part. To see this, return to the idea of anq Argand diagram, as shown in Fig. 5.1. For the vector $a+b i$, the real component is $a$ and the imaginary component is $b$. Now, square each of them, and then add them the same way you would to find the square of the hypotenuse using Pythagoras' theorem.

## Hilbert's Space

The idea of vector spaces is extended to functions. Functions may be normal (or orthonormal) as well. But how does one define this?

In the vector spaces with which we feel most comfortable, we defined the inner product as $\mathbf{v}_{1} \cdot \mathbf{v}_{2}$, and this we used to test the orthogonality condition. In a Hilbert space we simply define the inner product of two functions $f(x)$ and $g(x)$ by

$$
\begin{equation*}
\langle f(x) \mid g(x)\rangle \equiv \int_{a}^{b} f^{*}(x) g(x) d x \tag{5.5}
\end{equation*}
$$

over some interval $[a, b]$. Here $f^{*}(x)$ means the complex conjugate of the function $f(x)$. We do this simply because Hilbert's Space includes complex functions and because we want a non-negative value of the inner product, as explained in the previous section.

## Bibliography

[1] Anton, Howard. Linear Algebra, 5th Edition. John Wiley \& Sons, New York, 1987.
[2] Cropper, William H. The Quantum Physicists and an Introduction to their Physics, Oxford University Press, New York, 1970.
[3] C. J. Davisson and L. H. Germer, Diffraction of Electrons by a Crystal of Nickel, Physical Review 30, 705 (1927).
[4] French, A. P. Vibrations and Waves, The M.I.T. Introductory Physics Series. W.W. Norton \& Company, New York, 1971.
[5] Goswami, Amit. Quantum Mechanics. Wm. C. Brown Publishers, Dubuque, Iowa, 1992.
[6] Jammer, Max. The History of QM.
[7] Liboff, Richard. Introductory Quantum Mechanics. Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1980.
[8] Bohm, David. Quantum Theory. Dover Publications, Inc., New York, 1959.
[9] Baggott, Jim. The Meaning of Quantum Theory. Oxford University Press, Oxford, 1992.
[10] Semat, Henry and Harvey E. White. Atomic Age Physics. Rhinehart \& Company, Inc., New York, 1959.
[11] Ikenberry, Ernest. Quantum Mechanics for Mathematicians and Physicists. Oxford University Press, Oxford, 1962.
[12] Kafatos, Menas and Robert Nadeau. The Conscious Universe. SpringerVerlag, New York, 1990.
[13] Albert, David Z. Quantum Mechanics and Experience. Harvard University Press, Cambridge, 1992.

