3 Foundation of Quantum Theory

Since electrons possess both wave and particle properties, treating an electron like a pure particle (classical physics) is insufficient to describe the nature of electrons. New framework must be developed. Erwin Schrödinger developed this framework for quantum mechanics. In this chapter, we attempt to recreate postulates of quantum mechanics from simple inspiration.

3.1 What if Electrons Behave like Waves

Because e^{-1} is a wave, classical wave equation can be applied.

$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v}\frac{\partial^2 u}{\partial t^2}$ Solution: $u(x,t) = \psi(x)\cos(\omega t)$

Plug the solution into the differential equation.

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0 \quad \Rightarrow \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

$$\Downarrow$$

angular frequency $\omega = 2\pi\nu$

velocity $v = \lambda\nu$

(by de Broglie) $= \frac{h}{p}\nu$

$= \frac{h\nu}{\sqrt{2m(E-V)}}$

$$\left.\begin{array}{l}\omega = 2\pi\nu \\ v = \frac{h\nu}{\sqrt{2m(E-V)}}\end{array}\right\} \Big\uparrow \quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\uparrow$$

standard form
of
time independent
Schrödinger Eq

total E

$$\uparrow$$

$$E = \frac{p^2}{2m} + V \Rightarrow p = \sqrt{2m(E-V)}$$

At this point, we can also see that the term $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$ must represent kinetic energy. Because the kinetic energy can be written as $T = \frac{p^2}{2m}$, we can also relate momentum p to $i\hbar\frac{d\psi}{dx}$

3.2 Postulates of Quantum Mechanics (Time independent)

Postulate: A statement, also known as an axiom, is taken to be true without proof. Following are the minimum statements required for quantum mechanical study (time independent) of any molecules.

1. The state of the system is completely specified by $\psi(x)$ where $\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1$, $\psi(x)$ is twice differentiable almost everywhere.
2. To every observable, there is a corresponding linear Hermitian operator in quantum mechanics.
3. The observable associated with operator $\hat{A}$ satisfy
   $\hat{A}\psi = a\psi$.
   $\uparrow \quad \nwarrow$
   operator real number
4. The average of the observable for $\hat{A}$ is
   $\langle A \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A}\psi dx$
5. ψ is a solution of Schrödinger equation $\hat{H}\psi = E\psi$

① What does $\psi(x)$ represent?

The probability distribution we use in classical statistical mechanics, $f : \mathbb{R} \to \mathbb{R}$

$\psi(x)$, in Quantum Mechanics, $\psi : \mathbb{R} \to \mathbb{C}$, is a complex valued function

Because imaginary numbers are useless for real life, $\psi(x)$ is meaningless.
It turns out that
$|\psi(x)|^2 = \psi^*(x)\psi(x)$ represents probability of finding particle (electron) at position x.

$\uparrow$

amplitude or absolute value

$\Downarrow$

$\int \psi^*(x)\psi(x)dx = 1$ Probability must be normalized

3.3 Operator

3.3.1 What is an operator?

Definition: An operator is a mapping that acts on the elements of a space to produce other elements of the same space

<u>Example</u>

$f(x) = 3x^2 \leftarrow$ function

function operator function

$$f(x) \rightarrow \underset{\hat{D}}{\boxed{\frac{d}{dx}}} \rightarrow f'(x)$$

$\frac{df}{dx} = \underline{6x}$

$\searrow$

function

3.3.2 Linear operator

Concept of “Linear” $\cdots$ Linearity

Function version (in linear algebra):

The map f is linear function if and only if it satisfies the following properties: For any scalar constant a,

1. $f(x + y) = f(x) + f(y)$
2. $f(ax) = af(x)$

Note that $f(x) = 3.5x$ is a linear function in this sense. However, usual linear function $f(x) = ax + b$ does not qualify as a linear function because it does not satisfy the second condition, if b is not zero. For $f(x)$ to be linear, b must be equal to zero.

Operator version:

$\hat{A}$ is linear if and only if it satisfies the following properties: For any scalar constant a,

1. $\hat{A}(f + g) = \hat{A}f + \hat{A}g$
2. $\hat{A}(af) = a\hat{A}f$

<u>*HW*</u> Show 1) integration, and 2) differentiation are linear operators.

3.3.3 Hermitian Operator

In matrix language,
A is Hermitian if $A = (A^T)^*$.
The following matrix is Hermitian, as the reader can check:

$$\begin{bmatrix} 2 & 2+i & i \\ 2-i & 3 & -2i \\ -i & 2i & 4 \end{bmatrix}$$

In operator language,
$\hat{A}$ is Hermitian if the linear operator $\hat{A}$ satisfies
$\int f^*(\hat{A}g)dx = \int g(\hat{A}f)^*dx$

As mentioned in the Math Prerequisite section, a function is a column vector and the operator maps this vector to another vector (i.e., an n x n matrix). Therefore, the resulting function is also a column vector. Multiplication of this vector with the complex conjugate function vector from the left followed by integration is essentially the dot product.
By setting g & f to be vectors, and
$\hat{A}$ as a matrix,
$\int f^*hdx$ is a dot product, where $h = \hat{A}g$. Now

$$\int f^*(\hat{A}g)dx = [f^*]^T [A] [g]$$

Since $[A]$ is Hermitian,
$[A] = \left[A^T\right]^*$, and replace $[A]$ with $\left[A^T\right]^*$:

$$= [f^*]^T \underbrace{\left[A^T\right]^*}_{A} [g]$$

$$= ([A][f])^{*T} [g] .$$

Because the output is 1 x 1, we have

$$= \left(([A][f])^{*T} [g])\right)^T$$

$$= [g]^T ([A][f])^*$$

as desired.

Example: Is the position operator, x, Hermitian?
Let $\hat{A} = x$
$\int f^*(\hat{A}g)dx = \int f^*(xg)dx = \int f^* x^* g dx$
$\uparrow x$ real $\Rightarrow x = x^*$
$= \int g(xf)^* dx$
$= \int g(\hat{A}f)^* dx$ //

Example: Is the Derivative operator Hermitian?
Let $\hat{A} = \frac{d}{dx}$.
$\int f^*(\hat{A}g)dx = \int f^*(\frac{dg}{dx})dx$
by using integration by parts, $\int uv'dx = uv - \int u'vdx$,
$= f^*g|_{-\infty}^{\infty} - \int g\frac{df^*}{dx}dx$
$= -\int g(\hat{A}f)^* dx$
$\neq \int g(\hat{A}f)^* dx \Rightarrow\Leftarrow$
//
See the HW hint below for the position of complex conjugate

HW Is the momentum operator Hermitian?
The momentum operator $\hat{p}$ is given by
$\hat{p} := -i\hbar\frac{d}{dx}$
Hint: $\frac{d}{dx}$ itself has no meaning. $\frac{df^*}{dx} = (\frac{df}{dx})^*$ if $f : R \to \mathbb{C}$. This can be visualized easily by creating some function on excel by taking 1 column (real number) as an input and set 2 column as the output (real part and imaginary part). Then, take the small difference. Once you are convinced on above equality , you can easily prove $-i\hbar\frac{df^*}{dx} = (i\hbar\frac{df}{dx})^*$

Example: Is the potential energy operator Hermitian?
Let $\hat{A} =$ V(x), a pure function of position x.
$\int f^*(\hat{A}g)dx = \int f^*(Vg)dx = \int f^*V^*gdx (\leftarrow V real, V = V^*)$
$= \int g(Vf)^* dx$
$= \int g(\hat{A}f)^* dx$ //

3.3.4 The Hamiltonian Operator

Classical

$$
\begin{aligned}
H &= \frac{p^2}{2m} + V(x) \\
&= \frac{(mv)^2}{2m} + V(x) \\
&= \frac{1}{2}mv^2 + V(x) \\
&= K.E. + V(x)
\end{aligned}
$$

Quantum Mechanics

$$
\begin{aligned}
\hat{H} &= \frac{\hat{p}^2}{2m} + \hat{V} \\
&= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V} \\
&= \hat{T} + \hat{V}
\end{aligned}
$$

where $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ and the kinetic energy operator $\hat{T}$ is defined by $\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$.

Is the K.E. operator Hermitian?
$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$
\begin{aligned}
\int f^*(\hat{T}g)dx &= -\frac{\hbar^2}{2m}\int f^*\frac{d^2g}{dx^2}dx \\
&= -\frac{\hbar^2}{2m}\left(f^*\frac{dg}{dx}|_{-\infty}^{\infty} - \int \frac{dg}{dx}\frac{df^*}{dx}dx\right) \\
&= \frac{\hbar^2}{2m}\int \frac{df^*}{dx}\frac{dg}{dx}dx \\
&= \frac{\hbar^2}{2m}\left(g\frac{df}{dx}|_{-\infty}^{\infty} - \int g\frac{d^2f^*}{dx^2}dx\right) \\
&= -\frac{\hbar^2}{2m}\left(\int g\frac{d^2}{dx^2}f^*dx\right) \\
&= \int g(\hat{T}f)^*dx \quad //
\end{aligned}
$$

Theorem If $\hat{A}$ is Hermitian, then for any real constant a in $\mathbb{R}$, $a\hat{A}$ is Hermitian.

$$\begin{aligned}
\int f^*\big(a\hat{A}g\big)dx &= a\int f^*\big(\hat{A}g\big)dx \\
&= a\int g\big(\hat{A}f\big)^* dx \\
&= \int g\big(a\hat{A}f\big)^* dx \quad //
\end{aligned}$$

Theorem If $\hat{A}$ & $\hat{B}$ are Hermitian, then $\hat{C}=\hat{A}+\hat{B}$ is Hermitian.

$$\begin{aligned}
\int f^*\big(\hat{C}g\big)dx &= \int f^*\big(\hat{A}g+\hat{B}g\big)dx \\
&= \int f^*\big(\hat{A}g\big)dx + \int f^*\big(\hat{B}g\big)dx \\
&= \int g\big(\hat{A}f\big)^* dx + \int g\big(\hat{B}f\big)^* dx \\
&= \int g\big(\hat{A}f+\hat{B}f\big)^* dx \\
&= \int g\big(\hat{C}f\big)^* dx \quad //
\end{aligned}$$

We note from the previous two pages that $\hat{T}=\hat{T}+\hat{V}$ is Hermitian.

3.4 Eigenvalues

3.4.1 The Eigenvalue for a Matrix

For a given matrix A and , we look for a vector v that satisfies this equation:
$[A]\,[v] = a\,[v]$
$\uparrow$ $\uparrow$ $\nwarrow$
matrix number vector

Any vector that satisfies this equation is called the eigenvector for the matrix A, which has the corresponding eigenvalue a.
The spectral theorem has a deep connection to the quantum mechanics. In linear algebra, the theorem states that
"If an $n \times n$ matrix A is real & symmetric, then there exists n independent eigenvectors, and & all of those eigenvalues are real."
<u>note</u> A is said to be symmetric if $A = A^T$.
Since the entries of A are real numbers, $a_{ij} = a^*_{ij}$.
Thus, A is Hermitian. This should sound like postulates 2 & 3.

<u>Laboratory 0</u>
see appendix

3.4.2 Eigenvalues for Operators

$\hat{A}f$	$=$	a	f
$\uparrow$		$\uparrow$	$\uparrow$
The operator acts like a matrix.		#	The function acts like a vector. "For given operator A, we look for f that satisfies this equation."

<u>Ex</u> $\hat{H}\psi = E\psi$
For Hamiltonian operator $\hat{H}$, we look for function ψ that satisfy this equation.
Because nature tends to look for the lowest E, we look for a wavefunction ψ with the lowest E.
$\uparrow$
Goal of Quantum Mechanics.

In Quantum Mechanics, every operator must be Hermitian. Every Hermitian operator has real eigenvalues. This comes as no surprise, because we observe only real quantities.

Theorem The eigenvalue of any Hermitian operator is a real number.
Proof: Recall that every Hermitian operator $\hat{A}$ satisfies $\int f^*\big(\hat{A}g\big)dx = \int g\big(\hat{A}f\big)^*dx$
By choosing $f = g$,
$\int f^*\big(\hat{A}f\big)dx = \int f^*\big(af\big)dx = a\int f^*fdx$
$\Downarrow$ $\hat{A}$ Hermitian
$\int f\big(\hat{A}f\big)^*dx = a^*\int ff^*dx$
So, $a = a^*$, which implies that a is a real number. //
We found that the eigenvalue for ψ is real, in agreement with postulate 5

Theorem The Eigenfunctions of the Quantum Mechanics operator are orthogonal. (Simple case where all eigenvalues are different. Note that wavefunctions are normalized by postulate.)
Let ψ_n & ψ_m be eigenfunctions of $\hat{A}$.
Let λ_n and λ_m be their eigenvalues, respectively.
Since $\hat{A}$ is Hermitian,

$$\begin{aligned}\int \psi_n^*\hat{A}\psi_m dx &= \int \psi_n^*\big(\hat{A}\psi_m\big)dx = \lambda_m\int \psi_n^*\psi_m dx \\ &= \int \psi_m\big(\hat{A}\psi_n\big)^*dx = \lambda_n\int \psi_n^*\psi_m dx\end{aligned}$$

If $n \neq m$, then $\int \psi_n^*\psi_m dx = 0 \leftarrow$ orthogonal
If $n = m$, then $\int \psi_n^*\psi_m dx = 1 \leftarrow$ requirement
So, $\{\psi_n\}$ is orthonormal set.

3.5 The Commutative Property of the Operator

Case - Numbers

$a \cdot b = b \cdot a$ #'s commute.

Case - Matrices Matriices sometimes commute; however, they do not always commute.

$$\begin{bmatrix}1 & 1\\2 & 2\end{bmatrix}\begin{bmatrix}1 & 2\\1 & 2\end{bmatrix} \neq \begin{bmatrix}1 & 2\\1 & 2\end{bmatrix}\begin{bmatrix}1 & 1\\2 & 2\end{bmatrix} \text{ non-commutative}$$

$$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}\begin{bmatrix}1 & 2\\1 & 2\end{bmatrix} = \begin{bmatrix}1 & 2\\1 & 2\end{bmatrix}\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} \text{ commutative}$$

Case - Operators

Just like matrices, operators, only sometimes, commute.

$\hat{P}_x\hat{x}\psi = \big(-i\hbar\frac{d}{dx}\big)x\psi = -i\hbar\big(x\frac{d\psi}{dx} + \psi\big)$

$\hat{x}\hat{P}_x\psi = x\big(-i\hbar\frac{d}{dx}\big)\psi = -i\hbar x\frac{d\psi}{dx}$

$\hat{P}_x\hat{x} - \hat{x}\hat{P}_x = -i\hbar\hat{I}$, where $\hat{I}$ is the identity operator. It preserves its operand.

Here we define commutator of a pair of matrices $\hat{A}$ and $\hat{B}$ to be

$\big[\hat{A}, \hat{B}\big] = \hat{A}\hat{B} - \hat{B}\hat{A} \leftarrow$ commutator

• If you are interested in classical analogue, please read Poisson blacket.

When

$\big[\hat{A}, \hat{B}\big] = 0,$

you do not have to worry about violating uncertainty principle. See appendix for explanation.

Example

We have

$\big[\hat{P}_x, y\big] = \big(-i\hbar\big)\frac{d}{dx}y\psi - \big(y\big)\big(-i\hbar\big)\frac{d}{dx}\psi.$

$= \emptyset$

Thus, you can obtain the eigenvalue of P_x & y simultaneously.

$\big[\hat{P}_x, x\big] = i\hbar\hat{I} \neq 0$, which means that you can't get an accurate eigenvalue for both P_x & x at once.

3.6 Generalization to Time Dependent Quantum Mechanics

$$\widehat{H}\psi = i\hbar\frac{\partial\psi(x,t)}{\partial t}\cdots 1)$$

Recall that the Shrödinger Equation was inspired by the classical wave equation

$\downarrow$ Standard form (time independent Shrödinger Equation)

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

We show 1) implies 2) if $\psi(x,t) = \psi(x)f(t)$.
Then,

$$\begin{aligned}
\widehat{H}\big(\psi(x)f(t)\big) &= i\hbar\frac{\partial}{\partial t}\big(\psi(x)f(t)\big)\\
f(t)\widehat{H}\psi(x) &= \psi(x)i\hbar\frac{\partial f}{\partial t}\\
\underbrace{\frac{1}{\psi(x)}\widehat{H}\psi(x)}_{\text{depends only on x}} &= \underbrace{\frac{1}{f(t)}i\hbar\frac{\partial}{\partial t}f(t)}_{\text{depends only on t}} = \underset{\text{must be constant}}{\underset{\downarrow}{E}}\\
\widehat{H}\psi &= E\psi \qquad //
\end{aligned}$$

In general, the solution to time dependent Shrödinger Equation is not always separable.
For example, Let $\phi_1(x)$ & $\phi_2(x)$ be solutions of the time independent. Shrödinger Equation then the solution of time dependent Shrödinger Equation is

$$\psi(x,t) = \frac{1}{\sqrt{2}}\big(\phi_1(x)e^{-iE_1t/\hbar} + \phi_2(x)e^{-iE_2t/\hbar}\big)$$

This solution is not separable.
But separating variables, we can generate a base that can be used to create the solution.