

## 2.2: The Postulates of Quantum Mechanics

There are only a small number of postulates of quantum mechanics. Upon them is built all of the conclusions of this powerful theory.

### Postulate 1

The state of a quantum-mechanical system is completely specified by a function  $\Psi(\mathbf{r}, t)$  that depends on the coordinates of the particle ( $\mathbf{r}$ ) and the time ( $t$ ). This function, called the wavefunction has the important property that

$$\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)dxdydz$$

is the probability of finding the particle within the infinitesimally small volume element  $dxdydz$  located at position  $\mathbf{r}$  at time  $t$ .

### Postulate 2

To every physical observable in classical mechanics, there corresponds an operator in quantum mechanics. This operator will be both linear and Hermitian.

### 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

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

It is important to note that the wavefunction describing the particle need not be an eigenfunction of the operator  $\hat{A}$ . However, well defined wavefunctions (those meeting the requirements of all of the postulates of quantum mechanics) will have the possibility of being described as a linear combination of eigenfunctions of any of the needed operators. The Superposition Principle is invaluable in working with this concept.

### Postulate 4

If a system is in a state described by a normalized wavefunction ( $\Psi$ ) then the average measured value of the observable corresponding to  $\hat{A}$  is given by

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\tau \quad \text{or} \quad \langle a \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

### Postulate 5

The wavefunction of a system evolves in time according to the time dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t)$$

Each of these postulates has important consequences and ramifications as to what quantum theory can (and cannot) tell us about a particle or system. In the remainder of this section, we will explore each postulate individually in order to lay a foundation of what quantum mechanics can predict for us about the nature of matter.

### Postulate 1: a Squared Wavefunction is a Probability Distribution

This postulate describes the commonly accepted interpretation of a wavefunction. First and foremost, a wavefunction is a mathematical function. It must be single valued in that for each point in space, there is only one value that can be calculated from the function. When considering all space which a particle may occupy, the squared wavefunction must create a smooth<sup>1</sup> and continuous probability distribution describing where the particle might be observed to be located. (for our purposes, "smooth" means that the first derivative of the function must be continuous.) Since the square of the wavefunction is a probability distribution for the location of the particle, any location in space where the squared wavefunction is zero, has a corresponding probability of zero that the particle will be observed at that location.

### ✓ Example 2.2.1

Consider a particle of mass  $m$  in box of length  $a$  that is prepared such that its wave function is given by

$$\psi(x) = \sqrt{\frac{30}{a^5}} \cdot x(a-x)$$

Calculate the probability that the particle will have a position measurement reveal the particle to be in the middle half of the box (with the measured position satisfying  $a/4 \leq x \leq 3a/4$ .)

#### Solution

The squared wavefunction gives the probability distribution for where the particle's position will be measured to be.

$$(\psi(x))^2 = \frac{30}{a^5} (a^2 x^2 - 2ax^3 + x^4)$$

The total probability will be given by the following integral.

$$\begin{aligned} P &= \int_{a/4}^{3a/4} [\psi(x)]^2 dx \\ &= \frac{30}{a^5} \int_{a/4}^{3a/4} (a^2 x^2 - 2ax^3 + x^4) dx \\ &= \frac{30}{a^5} \left[ \frac{a^2 x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right]_{a/4}^{3a/4} \\ &= \frac{30}{a^5} \left( \frac{27a^5}{192} - \frac{162a^5}{1024} + \frac{243a^5}{5120} - \frac{a^5}{192} + \frac{2a^5}{1024} - \frac{a^5}{5120} \right) \\ &= \frac{30}{a^5} \left( \frac{26a^5}{192} - \frac{164a^5}{1024} + \frac{242a^5}{5120} \right) \\ &= 0.520 \end{aligned}$$

Note that the final probability is unitless!

<sup>1</sup> The wavefunction will be smooth provided that the potential energy function is not discontinuous. A discontinuous potential energy function (such as a step function) will lead to a wavefunction that which single-valued, will not have a continuous first derivative, and therefore, not be "smooth" in the strictest sense.

The wavefunction contains all of the information about a system that is needed to understand how the system behaves and how it will behave in the future, at least within the limits of the quantum theory! Information on such properties as energy, momentum and position are all contained in the wavefunction.

## Postulate 2: Quantum Mechanical Operators

The second postulate describes the nature of quantum mechanical operators and their relationship to those properties of a system which we can observe. The operators are the tools that pull physical information from the wavefunction and reveal the properties of the quantum mechanical system. The following table shows some operators and their corresponding physically observable quantities.

	Physical Observable	One Dimension	Three Dimensions
$\hat{x}$	Position	$x$	$\mathbf{r}$
$\hat{p}$	Momentum	$-i\hbar \frac{d}{dx}$	$-i\hbar \vec{\nabla}$
$\hat{H}$	Energy	$\hat{T} + \hat{U}$	
$\hat{T}$	Kinetic	$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$	$-\frac{\hbar^2}{2m} \nabla^2$

	Physical Observable	One Dimension	Three Dimensions
$\hat{U}$	Potential	$U(x)$	$U(\mathbf{r})$

Each of these operators will have two very important properties. 1) Each is **linear** and 2) each is **Hermitian**. In one dimension, an operator ( $\hat{A}$ ) is defined to be linear if the following condition holds:

$$\hat{A}(af(x) + bg(x)) = a\hat{A}f(x) + b\hat{A}g(x)$$

where a and b are scalar values. An example of a linear operator is multiplication by a constant or a function. Taking a derivative (or integrating) is also a linear operation, as is adding a constant or a function. An example of a non-linear operator is taking a logarithm or raising a function to a power other than one.

The Hermitian nature of quantum mechanical operators has many important consequences. An operator ( $\hat{A}$ ) is Hermitian if it satisfies the following relationship:

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

for well-behaved <sup>2</sup> functions  $f$  and  $g$ , where the asterisk (\*) indicated the complex conjugate of the function or operator. Hermitian operators have the important properties that 1) their

<sup>2</sup> A well-behaved function is one that is normalizable and continuous over the relevant space of the problem.

### ✓ Example 2.2.1

Is the operator  $\frac{d}{dx}$  a Hermitian operator?

#### Solution

For an operator  $\hat{A}$  to be Hermitian, the following relationship must hold (for wellbehaved functions  $f$  and  $g$  :

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

So if we choose arbitrary functions  $f$  and  $g$ , we can evaluate the left-hand side of the above relationship by noting the pattern  $d(uv) = u dv + v du$  and integrating by parts. Using this approach

$$\int u dv = uv - \int v du$$

Making the substitutions that

$$u = g^* \\ dv = \frac{d}{dx} f dx$$

it should be clear that

$$du = \frac{d}{dx} g^* dx \\ v = f$$

So

$$\int g^* \frac{d}{dx} f dx = g^* f|_{-\infty}^{\infty} - \int f \frac{d}{dx} g^* dx$$

In order for  $f$  and  $g$  to meet the criteria that they are normalizable, they must vanish as  $x$  approaches  $\pm\infty$ . As such,

$$g^* f|_{-\infty}^{\infty} = 0$$

And we are left with

$$\int g^* \frac{d}{dx} f dx = - \int f \frac{d}{dx} g^* dx$$

Which clearly can not be true. Therefore, the operator  $\frac{d}{dx}$  is not Hermitian. You should, however, be able to use the same method to show that the operator  $\hat{A} = i \frac{d}{dx}$  is in fact Hermitian!

### Postulate 3: Measurable Values

Postulate three states that the only measurable values for a system are those values that are eigenvalues of the corresponding quantum mechanical operator. The first measurable value which we will explore is the energy of the system (see below.) Because the wavefunction provides a probability distribution, it also provides a means of predicting the statistics for a theoretical infinite set of measurements on a system. The ramifications of that point are developed in the discussion of the fourth postulate.

### Postulate 4: Expectation Values

An expectation value is an average value that would be expected based on an infinite number of measurements. Since wavefunctions give us probability information, it stands to reason that we can calculate a great deal of statistical information about a system based on the wavefunction and the corresponding operators. This will be discussed in detail in section D with regards to expectation values calculated for position, momentum and energy. It is important to note that the expectation value does not indicate the most probable measurement or observation that will be made, nor must it even give a value that can ever be measured; it just gives the average.

This postulate has very important (and controversial) ramifications. It forms the basis for how the Heisenberg Uncertainty Principle can be discussed. The problem is that quantum mechanics cannot tell you what will be measured, but rather only the probability that a certain value can be measured for a specific property. While a subtle point, it shakes the very nature of our intuition as to what it means for a system to have a certain property. In most cases, the properties we associate with classical particles do not even exist in quantum mechanical particles (at least in any sense to which we are accustomed) until those properties are measured. This has led to numerous debates as to the validity of quantum mechanics as a model, and even led one of the original developers of quantum theory (Erwin Schrödinger) to change his mind completely on the model.

### Postulate 5: the evolution of a system in time

The 5<sup>th</sup> postulate indicates how a system will evolve in time. It also gives the definition of the time dependent Schrödinger equation.

We will explore many of these properties based on the particle in a box problem in order to gain some insight into what quantum mechanics can and can not tell us about a system. The particle in a box problem actually has limited physical application (although it does have some), but does provide a "thought sandbox" in which we can explore the concepts, powers and limitations of the quantum theory. Hopefully then when we apply the theory to problems of greater chemical interest, we can focus more on the conclusions than on the specific mathematics.

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