

## 1.1: Describing a System Quantum Mechanically

As a starting point it is useful to review the postulates of quantum mechanics, and use this as an opportunity to elaborate on some definitions and properties of quantum systems.

### 1. The Wavefunction

Quantum mechanical matter exhibits wave-particle duality in which the particle properties emphasize classical aspects of the object's position, mass, and momentum, and the wave properties reflect its spatial delocalization and ability to interfere constructively or destructively with other particles or waves. As a result, in quantum mechanics the physical properties of the system are described by the wavefunction  $\Psi$ . The wavefunction is a time-dependent complex probability amplitude function that is itself not observable; however, it encodes all properties of the system's particles and fields. Depending on the context, particle is a term that will refer to a variety of objects—such as electron, nucleons, and atoms—that fill space and have mass, but also retain wavelike properties. Fields refer to a variety of physical quantities that are continuous in time and space, which have energy and influence the behavior of particles.

In the general sense, the wavefunction, or state, does not refer to a three dimensional physical space in which quantum particles exist, but rather an infinite dimensional linear vector space, or Hilbert space, that accounts for all possible observable properties of the system. We can represent the wavefunction in physical space,  $\Psi(\mathbf{r})$  by carrying out a projection onto the desired spatial coordinates. As a probability amplitude function, the wavefunction describes the statistical probability of locating particles or fields in space and time. Specifically, we claim that the square of the wavefunction is proportional to a probability density (probability per unit volume). In one dimension, the probability of finding a particle in a space between  $x$  and  $x+dx$  at a particular time  $t$  is

$$P(\mathbf{x}, t)dx = \Psi^*(\mathbf{x}, t)\Psi(\mathbf{x}, t)dx \quad (1.1.1)$$

We will always assume that the wavefunctions for a particle are properly normalized, so that  $\int P(\mathbf{x}, t)dx = 1$ .

### 2. Operators

Quantum mechanics parallels Hamilton's formulation of classical mechanics, in which the properties of particles and fields are described in terms of their position and momenta. Each particle described by the wavefunction will have associated with it one or more degrees of freedom that are defined by the dimensionality of the problem. For each degree of freedom, particles which are described classically by a position  $x$  and momentum  $p_x$  will have associated with it a quantum mechanical operator  $\hat{x}$  or  $\hat{p}_x$  which will be used to describe physical properties and experimental observables. Operators correspond to dynamical variables, whereas static variables, such as mass, do not have operators associated with them. In practice there is a quantum/classical correspondence which implies that the quantum mechanical behavior can often be deduced from the classical dynamical equations by substituting the quantum mechanical operator for the corresponding classical variables. In the case of position and momenta, these operators are  $x \rightarrow \hat{x}$  and  $\hat{p}_x = -i\hbar(\partial/\partial x)$ . Table 1 lists some important operators that we will use. Note that time does not have an operator associated with it, and for our purposes is considered an immutable variable that applies uniformly to the entire system.

Table 1.1.1: lists some important operators that we will use. Note that time does not have an operator associated with it, and for our purposes is considered an immutable variable that applies uniformly to the entire system.

		Classical variable	Operator
Position	(1D)	$x$	$\hat{x}$
	(3D)	$r$	$\hat{r}$
Linear momentum	(1D)	$p_x$	$\hat{p}_x = -i\hbar(\partial/\partial x)$
	(3D)	$p$	$\hat{p} = -i\hbar\nabla$
Function of position and momentum	(1D)	$f(x, p_x)$	$f(\hat{x}, \hat{p}_x)$
Angular momentum	(3D)	$\vec{L} = \vec{r} \times \vec{p}$	$\hat{L} = -i\hbar\vec{r} \times \vec{\nabla}$
z-component of orbital angular momentum			$\hat{L}_z = -i\hbar(\partial/\partial\phi)$

(1.1.2)

What do operators do? Operators map one state of the system to another—also known as acting on the wavefunction:

$$\hat{A}\Psi_0 = \Psi_A \quad (1.1.3)$$

Here  $\Psi_0$  is the initial wavefunction and  $\Psi_A$  refers to the wavefunction after the action of the operator  $\hat{A}$ . Whereas the variable  $x$  represents a position in physical space, the operator  $\hat{x}$  maps the wavefunction from Hilbert space onto physical space. Operators also represent a mathematical operation on the wavefunction that influences or changes it, for instance moving in time and space. Operators may be simply multiplicative, as with the operator  $\hat{x}$ , or they may take differential or integral forms. The gradient  $\nabla$ , divergence  $\nabla \cdot$ , and curl  $\nabla \times$  are examples of differential operators, whereas Fourier and Laplace transforms are integral operators.

When writing an operator, it is always understood to be acting on a wavefunction to the right. For instance, the operator  $\hat{p}_x$  says that one should differentiate the wavefunction to its right with respect to  $x$  and then multiply the result by  $-i\hbar$ . The operator  $\hat{x}$  simply means multiply the wavefunction by  $x$ . Since operators generally do not commute, a series of operators must be applied in the prescribed right-to-left order.

$$\hat{B}\hat{A}\Psi_0 = \hat{B}\Psi_A = \Psi_{B,A} \quad (1.1.4)$$

One special characteristic of operators that we will look for is whether operators are Hermitian. A Hermitian operator obeys the equality  $\hat{A} = \hat{A}^*$ .

Of particular interest is the Hamiltonian,  $\hat{H}$ , an operator corresponding to the total energy of the system. The Hamiltonian operator describes all interactions between particles and fields, and thereby determines the state of the system. The Hamiltonian is a sum of the total kinetic and potential energy for the system of interest,  $\hat{H} = \hat{T} + \hat{V}$ , and is obtained by substituting the position and momentum operators into the classical Hamiltonian. For one particle under the influence of a potential,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\hat{r}, t) \quad (1.1.5)$$

Notation: In the following chapters, we will denote operators with a circumflex only when we are trying to explicitly note its role as an operator, but otherwise we take the distinction between variables and operators to be understood.

### 3. Eigenvalues and Eigenfunctions

The properties of a system described by mapping with the operator  $\hat{A}$  can only take on the values  $a$  that satisfy an eigenvalue equation

$$\hat{A}\Psi = a\Psi \quad (1.1.6)$$

For instance, if the state of the system is  $\Psi(x) = e^{ipx/\hbar}$ , the momentum operator  $\hat{p}_x = -i\hbar(\partial/\partial x)$  returns the eigenvalue  $p$  (a scalar) times the original wavefunction. Then  $\Psi(x)$  is said to be an eigenfunction of  $\hat{p}_x$ . For the Hamiltonian, the solutions to the eigenvalue equation

$$\hat{H}\Psi = E\Psi \quad (1.1.7)$$

yield possible energies of the system. The set of all possible eigenvectors are also known as the eigenstates  $\psi_1$ . Equation (6) is the time-independent Schrödinger equation (TISE).

### 4. Linear Superposition

The eigenstates of  $\hat{A}$  form a complete orthonormal basis. In Hilbert space the wavefunction is expressed as a linear combination of orthonormal functions,

$$\Psi = \sum_{i=0}^{\infty} c_i \psi_i \quad (1.1.8)$$

where  $c_i$  are complex numbers. The eigenvectors  $\psi_1$  are orthogonal and complete:

$$\int_{-\infty}^{+\infty} d\tau \psi_i^* \psi_j = \delta_{ij} \quad (1.1.9)$$

and

$$\sum_{i=0}^{\infty} |c_i|^2 = 1 \quad (1.1.10)$$

The choice of orthonormal functions in which to represent the system is not unique and is referred to as selecting a basis set. The change of basis set is effectively a transformation that rotates the wavefunction in Hilbert space.

## 5. Expectation Values

The outcome of a quantum measurement cannot be known with arbitrary accuracy; however, we can statistically describe the probability of measuring a certain value. The measurement of a value associated with the operator is obtained by calculating the expectation value of the operator

$$\langle A \rangle = \int d\tau \Psi^* \hat{A} \Psi \quad (1.1.11)$$

Here the integration is over Hilbert space. The brackets  $\langle \dots \rangle$  refer to an average value that will emerge from a large series of measurements on identically prepared systems. Whereas  $\langle A \rangle$  is an average value, the variance in a distribution of values measured can be calculated from  $\Delta A = \langle A^2 \rangle - \langle A \rangle^2$ . Since an observable must be real valued, operators corresponding to observables are Hermitian:

$$\int d\tau \Psi^* \hat{A} \Psi = \int d\tau \hat{A}^* \Psi^* \Psi \quad (1.1.12)$$

As a consequence, a Hermitian operator must have real eigenvalues and orthogonal eigenfunctions.

## 6. Commutators

Operators are associative but not necessarily commutative. Commutators determine whether two operators commute. The commutator of two operators  $\hat{A}$  and  $\hat{B}$  is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (1.1.13)$$

If we first make an observation of an eigenvalue  $a$  for  $\hat{A}$ , one cannot be assured of determining a unique eigenvalue  $b$  for a second operator  $\hat{B}$ . This is only possible if the system is an eigenstate of both  $\hat{A}$  and  $\hat{B}$ . This would allow one to state that  $\hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi$  or alternatively  $[\hat{A}, \hat{B}]\psi = 0$ . If the operators commute, the commutator is zero, and  $\hat{A}$  and  $\hat{B}$  have simultaneous eigenfunctions. If the operators do not commute, one cannot specify  $a$  and  $b$  exactly, however, the variance in their uncertainties can be expressed as  $\Delta A^2 \Delta B^2 \geq \left\langle \frac{1}{2} [\hat{A}, \hat{B}] \right\rangle^2$ . As an example, we see that  $\hat{p}_x$  and  $\hat{p}_y$  commute, but  $\hat{x}$  and  $\hat{p}_x$  do not. Thus we can specify the momentum of a particle in the  $x$  and  $y$  coordinates precisely, but cannot specify both the momentum and position of a particle in the  $x$  dimension to arbitrary resolution. We find that  $[\hat{x}, \hat{p}_x] = i\hbar$  and  $\Delta x \Delta p_x \geq \hbar/2$ .

Note that for the case that the Hamiltonian can be written as a sum of commuting terms, as is the case for a set of independent or separable coordinates or momenta, then the total energy is additive in eigenvalues for each term, and the total eigenfunctions can be written as product states in the eigenfunctions for each term.

## 7. Time Dependence

The wavefunction evolves in time as described by the time-dependent Schrödinger equation (TDSE):

$$-i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (1.1.14)$$

In the following chapter, we will see the reasoning that results in this equation.

## 8. Readings

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