1 | Introduction

1.1 Introduction

Quantum mechanics is a mathematical description of how elementary particles move and interact in nature. It is based on the wave–particle dual description formulated by Bohr, Einstein, Heisenberg, Schrödinger, and others. The basic units of nature are indeed particles, but the description of their motion involves wave mechanics.

The important parameter in quantum mechanics is Planck's constant $h = 6.626 \times 10^{-34}$ J s. It is common to divide it by 2π, and to put a slash through the symbol: $\hbar = 1.054 \times 10^{-34}$ J s. Classical physics treated electromagnetic radiation as waves. It is particles, called *photons*, whose quantum of energy is $\hbar\omega$ where ω is the classical angular frequency. For particles with a mass, such as an electron, the classical momentum $m\vec{v} = \vec{p} = \hbar\mathbf{k}$, where the wave vector k gives the wavelength $k = 2\pi/\lambda$ of the particle. Every particle is actually a wave, and some waves are actually particles.

The *wave function* $\psi(\mathbf{r}, t)$ is the fundamental function for a single particle. The position of the particle at any time t is described by the function $|\psi(\mathbf{r}, t)|^2$, which is the probability that the particle is at position $\mathbf{r}$ at time t. The probability is normalized to one by integrating over all positions:

$$1 = \int d^3r |\psi(\mathbf{r}, t)|^2 \tag{1.1}$$

In classical mechanics, it is assumed that one can know exactly where a particle is located. Classical mechanics takes this probability to be

$$|\psi(\mathbf{r}, t)|^2 = \delta^3(\mathbf{r} - \mathbf{v}t) \tag{1.2}$$

The three-dimensional delta-function has an argument that includes the particle velocity $\mathbf{v}$. In quantum mechanics, we never know precisely where to locate a particle. There is always an uncertainty in the position, the momentum, or both. This uncertainty can be summarized by the *Heisenberg uncertainty principle*:

$$\Delta x \Delta p_x \geq \hbar \tag{1.3}$$

Table 1.1   Fundamental Constants and Derived Quantities

Name	Symbol	Value
Electron mass	m	$9.10938215 \times 10^{-31}$ kg
Electron charge	e	$1.602176487 \times 10^{-19}$ C
Planck's constant	h	$6.62606896 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054571628 \times 10^{-34}$ J s
Boltzmann's constant	k_B	$1.3806504 \times 10^{-23}$ J/K
Light speed	c	$299{,}792{,}458$ m/s
Atomic mass unit	AMU	$1.660538782 \times 10^{-27}$ kg
Bohr magneton	μ_B	$927.400915 \times 10^{-26}$ J/T
Neutron magnetic moment	μ_n	$-0.99623641 \times 10^{-26}$ J/T
Bohr radius	a_0	$0.52917720859 \times 10^{-10}$ m
Rydberg energy	E_{Ry}	13.605691 eV
Fine structure constant	α	$7.2973525376 \times 10^{-3}$
Compton wavelength	λ_c	$2.463102175 \times 10^{-12}$ m
Flux quantum	$\phi_0 = h/e$	$4.13566733 \times 10^{-15}$ T/m^2
Resistance quantum	h/e^2	$25{,}812.808$ Ω

Source: Taken from NIST web site http://physics.nist.gov/

where Δx is the uncertainty in position along one axis, Δp_x is the uncertainty in momentum along the same axis, and $\hbar$ is Planck's constant h divided by $2\pi(\hbar = h/2\pi)$, and has the value $\hbar = 1.05 \times 10^{-34}$ joules-second. Table 1.1 lists some fundamental constants.

1.2 Schrödinger's Equation

The exact form of the wave function $\psi(\mathbf{r}, t)$ depends on the kind of particle, and its environment. Schrödinger's equation is the fundamental nonrelativistic equation used in quantum mechanics for describing microscopic particle motions. For a system of particles, Schrödinger's equation is written as

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{1.4}$$

$$H = \sum_j \left[\frac{p_j^2}{2m_j} + U(\mathbf{r}_j, s_j) \right] \left(+ \sum_{i>j} V(\mathbf{r}_i - \mathbf{r}_j) \right) \tag{1.5}$$

The particles have positions $\mathbf{r}_i$, momentum $\mathbf{p}_j$, and spin s_j. They interact with a potential $U(\mathbf{r}_j, s_j)$ and with each other through the pair interaction $V(\mathbf{r}_i - \mathbf{r}_j)$. The quantity H is the Hamiltonian, and the wave function for a system of many particles is $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \cdot, \mathbf{r}_N; s_1, s_2, \ldots, s_N)$.

The specific forms for H depends on the particular problem. The relativistic form of the Hamiltonian is different than the nonrelativistic one. The relativistic Hamiltonian is discussed in chapter 11. The Hamiltonian can be used to treat a single particle, a collection of identical particles, or different kinds of elementary particles. Many-particle systems are solved in chapter 9.

No effort is made here to justify the correctness of Schrödinger's equation. It is assumed that the student has had an earlier course in the introduction to modern physics and quantum mechanics. A fundamental equation such as eqn. (1.4) cannot be derived from any postulate-free starting point. The only justification for its correctness is that its predictions agree with experiment. The object of this textbook is to teach the student how to solve Schrödinger's equation and to make these predictions. The students will be able to provide their own comparisons to experiment.

Schrödinger's equation for a single nonrelativistic particle of mass m, in the absence of a magnetic field, is

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \tag{1.6}$$

$$H = \frac{p^2}{2m} + V(\mathbf{r}) \tag{1.7}$$

The potential energy of the particle is $V(\mathbf{r})$. This potential is usually independent of the spin variable for nonrelativistic motions in the absence of a magnetic field. Problems involving spin are treated in later chapters. When spin is unimportant in solving Schrödinger's equation, its presense is usually ignored in the notation: the wave function is written as $\psi(\mathbf{r})$.

In quantum mechanics, the particle momentum is replaced by the derivative operator:

$$\mathbf{p} \rightarrow -i\hbar \vec{\nabla} \psi \tag{1.8}$$

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \tag{1.9}$$

Schrödinger's equation (1.4) is a partial differential equation in the variables $(\mathbf{r}, t)$. Solving Schrödinger's equation for a single particle is an exercise in ordinary differential equations. The solutions are not just mathematical exercises, since the initial and boundary conditions are always related to a physical problem.

Schrödinger's equation for a single particle is always an artificial problem. An equation with $V(\mathbf{r})$ does not ever describe an actual physical situation. The potential $V(\mathbf{r})$ must be provided by some other particles or by a collection of particles. According to Newton's third law, there is an equal and opposite force acting on these other particles, which are also reacting to this mutual force. The only situation in which one particle is by itself has $V = 0$, which is a dull example. Any potential must be provided by another particle, so

Schrödinger's equation is always a many-particle problem. Nevertheless, there are two reasons why it is useful to solve the one-particle problem using classical potentials. The first is that one has to learn using simple problems as a stepping stone to solving the more realistic examples. Secondly, there are cases where the one-particle Schrödinger's equation is an accurate solution to a many-particle problem: i.e., it describes the relative motion of a two-particle system.

1.3 Eigenfunctions

In solving the time-dependent behavior, for the one-particle Schrödinger's equation (1.8), an important subsidiary problem is to find the eigenvalues ε_n and eigenfunctions $\phi_n(\mathbf{r})$ of the time-independent Hamiltonian:

$$H\phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r}) \tag{1.10}$$

There is a silly convention of treating "eigenfunction" and "eigenvalue" as single words, while "wave function" is two words. The name wave function is usually reserved for the time-dependent solution, while eigenfunction are the solutions of the time-independent equation. The wave function may be a single eigenfunction or a linear combination of eigenfunctions.

The eigenfunctions have important properties that are a direct result of their being solutions to an operator equation. Here we list some important results from linear algebra: The Hamiltonian operator is always Hermitian: $H^\dagger = H$.

- Eigenvalues of Hermitian operators are always real.

- Eigenfunctions with different eigenvalues are orthogonal:

$$[\varepsilon_n - \varepsilon_m] \int d^3 r \phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}) = 0 \tag{1.11}$$

which is usually written as

$$\int d^3 r \phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}) = \delta_{nm} \tag{1.12}$$

These two statements are not actually identical. The confusing case is where there are several different states with the same eigenvalue. They do not have to obey eqn. (1.12), but they can be constructed to obey this relation. We assume that is the case.

- The eigenfunctions form a complete set:

$$\sum_n \phi_n^*(\mathbf{r}) \phi_n(\mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}') \tag{1.13}$$

These properties are used often. Orthogonality is important since it implies that each eigenfunction $\phi_n(\mathbf{r})$ is linearly independent of the others. Completeness is important, since any function $f(\mathbf{r})$ can be uniquely and exactly expanded in terms of these eigenfunctions:

$$f(\mathbf{r}) = \sum_n b_n \phi_n(\mathbf{r}) \tag{1.14}$$

$$b_n = \int d^3 r f(\mathbf{r}) \phi_n(\mathbf{r}) \tag{1.15}$$

The function of most interest is the wave function $\psi(\mathbf{r}, t)$. It can be expanded exactly as

$$\psi(\mathbf{r}, t) = \sum_n a_n \phi_n(\mathbf{r}) e^{-i\varepsilon_n t/\hbar} \tag{1.16}$$

$$i\hbar \frac{\partial \psi}{\partial t} = \sum_n a_n \varepsilon_n \phi_n(\mathbf{r}) e^{-i\varepsilon_n t/\hbar} = H\psi \tag{1.17}$$

The coefficients a_n depend on the initial conditions. They depend on neither $\mathbf{r}$ nor t. One example is when the system is in thermal equilibrium. If the particles obey Maxwell-Boltzmann statistics, the coefficients are

$$|a_n|^2 = \exp[-\beta(\varepsilon_n - \Omega)], \quad \beta = \frac{1}{k_B T} \tag{1.18}$$

and Ω is the grand canonical potential. Another example occurs during an experiment, where the system is prepared in a particular state, such as an atomic beam. Then the coefficients a_n are determined by the apparatus, and not by thermodynamics.

The wave function has a simple physical interpretation. The probability $P(\mathbf{r}, t)$ that the particle is at the position $\mathbf{r}$ at the time t is given by the square of the absolute magnitude of the wave function:

$$P(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2 \tag{1.19}$$

In quantum mechanics, there is no certainty regarding the position of the particle. Instead, the particle has a nonzero probability of being many different places in space. The likelihood of any of these possibilities is given by $P(\mathbf{r}, t)$. The particle is at only one place at a time.

The normalization of the wave function is determined by the interpretation of $P(\mathbf{r}, t)$ as a probability function. The particle must be someplace, so the total probability should be unity when integrated over all space:

$$1 = \int d^3 r P(\mathbf{r}, t) = \int d^3 r |\psi(\mathbf{r}, t)|^2 \tag{1.20}$$

The normalization also applies to the wave function. The eigenfunctions are also orthogonal, so that

$$1 = \int d^3 r |\psi(\mathbf{r}, t)|^2 = \sum_{n,m} a_n^* a_m e^{it(\varepsilon_n - \varepsilon_m)/\hbar} \int d^3 r \phi_n^* \phi_m \tag{1.21}$$

$$= \sum_n |a_n|^2 \tag{1.22}$$

The summation of the expansion coefficients $|a_n|^2$ must be unity. These coefficients

$$P_n = |a_n|^2, \quad \sum_n P_n = 1 \tag{1.23}$$

are interpreted as the probability that the particle is in the eigenstate $\phi_n(\mathbf{r})$.

The average value of any function $f(\mathbf{r})$ is obtained by taking the integral of this function over all of space, weighted by the probability $P(\mathbf{r}, t)$. The bracket notation denotes the average of a quantity:

$$\langle f \rangle (t) = \int d^3r f(\mathbf{r}) P(\mathbf{r}, t) \tag{1.24}$$

For example, the average potential energy $\langle V \rangle$ and the average position $\langle r \rangle$ are

$$\langle V \rangle = \int d^3r V(\mathbf{r}) P(\mathbf{r}, t) \tag{1.25}$$

$$\langle \mathbf{r} \rangle = \int d^3r \mathbf{r} P(\mathbf{r}, t) \tag{1.26}$$

A similar average can be taken for any other function of position.

There is no way to take an average of the particle velocity $\mathbf{v} = \dot{\mathbf{r}}$. Since $P(\mathbf{r}, t)$ does not depend on $\dot{\mathbf{r}}$, there is no way to average this quantity. So $\langle \dot{\mathbf{r}} \rangle$ does not exist. Instead, the average velocity is found by taking the time derivative of the average of $\mathbf{r}$, such as

$$\frac{\partial}{\partial t} \langle \mathbf{r} \rangle = \int d^3r \mathbf{r} \frac{\partial}{\partial t} P(\mathbf{r}, t) \tag{1.27}$$

$$= \int d^3r \mathbf{r} \left[\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right] \left(\tag{1.28} \right.$$

Now use Schrödinger's equation and its complex conjugate, to find

$$\frac{\partial \psi}{\partial t} = \frac{-i}{\hbar} \left[\left(\frac{\hbar^2 \nabla^2}{2m} + V \right] \psi \right. \tag{1.29}$$

$$\frac{\partial \psi^*}{\partial t} = \frac{i}{\hbar} \left[\left(\frac{\hbar^2 \nabla^2}{2m} + V \right] \psi^* \right. \tag{1.30}$$

which is used in $\partial \langle \mathbf{r} \rangle / \partial t$:

$$\frac{\partial}{\partial t} \langle \mathbf{r} \rangle = \frac{i\hbar}{2m} \int d^3r \mathbf{r} [\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*] \tag{1.31}$$

$$= \frac{i\hbar}{2m} \int d^3r \mathbf{r} \vec{\nabla} \psi [\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*] \tag{1.32}$$

The terms containing the potential energy V canceled. The equivalence of the last two expressions is found by just taking the derivative in the last expression. Each term in brackets generates a factor of $(\vec{\nabla} \psi^*) \cdot (\vec{\nabla} \psi)$, which cancels.

An integration by parts gives

$$\frac{\partial}{\partial t} \langle \mathbf{r} \rangle = -\frac{i\hbar}{2m} \int \left(d^3r [\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*] \cdot \vec{\nabla} \mathbf{r} \right. \tag{1.33}$$

If $\mathbf{A}$ is the quantity in brackets, then $(\mathbf{A} \cdot \vec{\nabla}) \mathbf{r} = \mathbf{A}$, so the final expression is

$$\frac{\partial}{\partial t} \langle \mathbf{r} \rangle = \frac{\hbar}{2mi} \int \left(d^3r [\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*] \right. \tag{1.34}$$

The integrand is just the definition of the particle current:

$$\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{2mi} [\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*] \tag{1.35}$$

$$\frac{\partial}{\partial t} \langle \mathbf{r} \rangle = \iint \left(d^3 r \mathbf{j}(\mathbf{r}, t) \right) \tag{1.36}$$

The function $\mathbf{j}(\mathbf{r}, t)$ is the particle current, which has the units of number of particles per second per unit area. If it is multiplied by the charge on the particle, it becomes the electrical current density $J = ej$, with units of amperes per area.

In the integral (1.34), integrate by parts on the second term in brackets. It then equals the first term:

$$\frac{\partial}{\partial t} \langle \mathbf{r} \rangle = \frac{1}{m} \iint \left(d^3 r \psi^* \left(\frac{\hbar}{i} \vec{\nabla} \psi \right) \psi \right) = \frac{\langle p \rangle}{m} \tag{1.37}$$

The momentum operator is $\mathbf{p} = \hbar \vec{\nabla}/i$, and the integral is the expectation value of the momentum. In quantum mechanics, the average value of the velocity is the average value of the momentum divided by the particle mass.

The expectation value of any derivative operator should be evaluated as is done for the momentum: the operator is sandwiched between ψ^* and ψ under the integral:

$$\langle O \rangle = \iint \left(d^3 r \psi^*(\mathbf{r}, t) O(\mathbf{r}) \psi(\mathbf{r}, t) \right) \tag{1.38}$$

Other examples are the Hamiltonian and the z-component of angular momentum:

$$\langle H \rangle = \iint \left(d^3 r \psi^*(\mathbf{r}, t) \left[\left(-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right] \psi(\mathbf{r}, t) \right) \tag{1.39}$$

$$\langle L_z \rangle = \frac{\hbar}{i} \int d^3 r \psi^*(\mathbf{r}, t) \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] \psi(\mathbf{r}, t) \tag{1.40}$$

Once the wave function is known, it can be used to calculate the average value of many quantities that can be measured.

The last relationship to be proved in this section is the equation of continuity:

$$0 = \frac{\partial}{\partial t} \rho(\mathbf{r}, t) + \vec{\nabla} \cdot \mathbf{j}(\mathbf{r}, t) \tag{1.41}$$

where $\rho(\mathbf{r}, t) \equiv P(\mathbf{r}, t)$ is the particle density and $\mathbf{j}(\mathbf{r}, t)$ is the particle current. The continuity equation is proved by taking the same steps to evaluate the velocity:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t} \psi^* \psi = \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \tag{1.42}$$

Use the above expressions (1.29, 1.30) for the time derivative of the wave functions. Again the potential energy terms cancel:

$$\frac{\partial \rho}{\partial t} = \frac{i\hbar}{2m} \vec{\nabla} \cdot \left[\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right] = -\vec{\nabla} \cdot \mathbf{j}(\mathbf{r}, t) \tag{1.43}$$

which proves the equation of continuity. Schrödinger's equation has been shown to be consistent with the equation of continuity as long as the density of particles is interpreted to be $\rho(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2$, and the current is eqn. (1.35).

1.4 Measurement

Making a measurement on a particle in a quantum system is a major disruption of the probability distribution. Suppose we have N identical particles, for example, atoms, in a large box. They will be in a variety of energy states. It is not possible to say which atom is in which state. If $\phi_n(\mathbf{r})$ is an exact eigenstate for an atom in this box, the wave function of an atom is

$$\psi(x, t) = \sum_n a_n \phi_n(\mathbf{r}) \exp[-it E_n/\hbar] \tag{1.44}$$

The amplitudes a_n, when squared ($P_n = |a_n|^2$), determine the probability of an atom being in the state with energy E_n.

Suppose we do a measurement on a single atom, to determine its energy. One might drill a small hole in the side of the box, which allows one atom to escape at a time. If one measures the energy of that particular atom, one will find a definite value E_j. The result of the measurement process is that one state, out of the many possible states, is selected.

Suppose that one measures the energy of the same atom at a later time. If its flight path has been undisturbed, one will again find the same energy E_j. After the first measurement of energy, the particle continues its motion starting from the eigenstate $\phi_j(\mathbf{r})$, and not from the distribution of eigenstates in $\psi(\mathbf{r}, t)$. Of course, the first measurement of energy may disrupt the flight path a bit, according to the uncertainly relation, so the second measurement may give a slightly different energy. The important point is that measurement disrupts the statistical distribution, and imposes a new initial condition for the particle motion.

1.5 Representations

In the early days of quantum mechanics, Schrödinger and Heisenberg each presented versions that appeared to be different. There was a lively debate on the virtues of each version, until it was shown by Dirac and Jordan that the two are mathematically identical. This history is well described by von Neumann. The two theories do not look identical, at least superficially. The two versions are described here briefly, and an equally brief explanation is given as to why they are identical.

Schrödinger's version is the one discussed so far in this chapter, and which is mainly treated in the early parts of this book. The Heisenberg version, which stresses operators rather than wave functions, is introduced in later chapters. Both versions are used extensively in modern physics, and both are important.

The measurable quantities in physics are always expectation values: they are the average quantities. If $F(\mathbf{r}, \mathbf{p})$ is some function of position $\mathbf{r}$ and momentum $\mathbf{p}$, then its expectation value is

$$\langle F \rangle(t) = \int d^3 r \psi^*(\mathbf{r}, t) F(\mathbf{r}, -i\hbar\nabla)\psi(\mathbf{r}, t) \tag{1.45}$$

The bracket on the left is a shorthand notation for taking the average over $\mathbf{r}$, as indicated on the right-hand side of the equation. The Schrödinger and Heisenberg versions of quantum mechanics are equivalent because they always give the same expectation values. The same result is obtained even as a function of time, so the two versions give the same result for the time derivatives of $\langle F \rangle(t)$.

1.5.1 Schrödinger Representation

This representation has two important features.

1. Wave functions $\psi(\mathbf{r}, t)$ depend on time, and the time development is governed by Schrödinger's equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi(\mathbf{r}, t) \tag{1.46}$$

$$\psi(\mathbf{r}, t) = e^{-iHt/\hbar}\psi(\mathbf{r}, t=0) \tag{1.47}$$

The second equation is a formal solution to eqn. (1.46).
2. Operators do not depend on time. Operators such as $\mathbf{r}$, $\mathbf{p}$, H, L_z are time independent.

In the Schrödinger representation, only the wave functions depend on time. The time derivative of an expectation value, such as (1.45), is

$$\frac{\partial}{\partial t}\langle F \rangle(t) = \int d^3 r \left[\left(\frac{\partial\psi^*(\mathbf{r}, t)}{\partial t}\right) F(\mathbf{r}, -i\hbar\nabla)\psi(\mathbf{r}, t)\right.$$
$$\left. + \psi^*(\mathbf{r}, t) F(\mathbf{r}, -i\hbar\nabla)\left(\frac{\partial\psi(\mathbf{r}, t)}{\partial t}\right)\right] \tag{1.48}$$

The derivatives are evaluated using eqn. (1.46), giving

$$\frac{\partial}{\partial t}\langle F \rangle(t) = \frac{i}{\hbar}\int d^3 r[(H\psi^*)F\psi - \psi^* F(H\psi)] \tag{1.49}$$

In the first term on the right, the positions of H and ψ^* can be interchanged. Recall that $H = p^2/2m + V$. The scalar V can be interchanged. The kinetic energy term is $-\hbar^2\nabla^2/2m$, which can be interchanged after a double integration by parts on the $\mathbf{r}$ variable. Then the time derivative is written as a commutator:

$$[H, F] = HF - FH \tag{1.50}$$

$$\frac{\partial}{\partial t}\langle F \rangle(t) = \frac{i}{\hbar}\int d^3 r \psi^*[H, F]\psi \tag{1.51}$$

The above equation can be summarized as

$$\frac{\partial}{\partial t}\langle F\rangle(t) = \left\langle \frac{i}{\hbar}[H, F]\right\rangle \tag{1.52}$$

The identical equation is found in the Heisenberg representation, as described below.

1.5.2 Heisenberg Representation

This representation has several important features:

1. Wave functions are independent of time $\psi(\mathbf{r})$.
2. Operators are time-dependent according to the prescription

$$F(\mathbf{r}, \mathbf{p}, t) = e^{iHt/\hbar} F(\mathbf{r}, \mathbf{p}) e^{-iHt/\hbar} \tag{1.53}$$

3. The expectation values are given by

$$\langle F\rangle(t) = \int d^3 r \psi^*(\mathbf{r}) F(\mathbf{r}, \mathbf{p}, t) \psi(\mathbf{r}) \tag{1.54}$$

$$= \int d^3 r \psi^*(\mathbf{r}) e^{iHt/\hbar} F(\mathbf{r}, \mathbf{p}) e^{-iHt/\hbar} \psi(\mathbf{r}) \tag{1.55}$$

The latter definition is formally identical to (1.45). The time derivative is also identical:

$$\frac{\partial}{\partial t} F(\mathbf{r}, \mathbf{p}, t) = \frac{i}{\hbar} e^{iHt/\hbar}[HF - FH] e^{-iHt/\hbar} \tag{1.56}$$

$$= \frac{i}{\hbar}[H, F(\mathbf{r}, \mathbf{p}, t)] \tag{1.57}$$

This equation is the fundamental equation of motion in the Heisenberg version of quantum mechanics. The focus of attention is on the operators and their development in time. Once the time development is determined, by either exact or approximate techniques, the expectation value of the operator may be evaluated using the integral in eqn. (1.55). The solution to the time development in (1.57) involves the solution of operator expressions. The Heisenberg version of quantum mechanics, with its emphasis on the manipulation of operators, appears to be very different than the Schrödinger's equation (1.29), which is a differential equation in $\mathbf{r}$-space.

Yet the two representations do make identical predictions. For the average of the time derivative of F, the Heisenberg representaton gives, from (1.57),

$$\left\langle \frac{\partial F}{\partial t}\right\rangle = \frac{i}{\hbar} \int d^3 r \psi^*(\mathbf{r}) e^{itH/\hbar}[H, F(\mathbf{r}, \mathbf{p})] e^{-itH/\hbar} \psi(\mathbf{r}) \tag{1.58}$$

This result is identical to the Schrödinger result in (1.51), just as the average value of F is the same as (1.45) and (1.55). The simularities of the two approaches is more apparent when using eqn. (1.47). The Hermitian conjugate of this expression is

$$\psi^\dagger(\mathbf{r}, t) = \psi^*(\mathbf{r}, t) e^{itH/\hbar} \tag{1.59}$$

and the expectation value of F in the Schrödinger representation is

$$\langle F \rangle = \int d^3 r \psi^{\dagger}(\mathbf{r}, t) F(\mathbf{r}, p) \psi(\mathbf{r}, t) \tag{1.60}$$

This Schrödinger result is identical to the Heisenberg result in (1.55). The two representations make identical predictions for the average values of operators and for all values of time. The two versions of quantum mechanics are equivalent in predicting measureable quantitites.

1.6 Noncommuting Operators

The important variables of classical mechanics usually exist as operators in quantum mechanics. A partial list of such operators is momentum $\mathbf{p}$, energy H, and angular momentum L_z. An important consideration between pairs of operators is whether they commute or do not commute.

An example of a pair of noncommuting operators in one dimension is the position x and momentum $p = -i\hbar d/dx$. Take some arbitrary function $f(x)$, and operate on it by the two combinations

$$xpf = -i\hbar x \frac{df}{dx} \tag{1.61}$$

$$pxf = -i\hbar \frac{d}{dx}(xf) = -i\hbar \left(f + x \frac{df}{dx} \right) (\tag{1.62}$$

Subtract these two results:

$$(xp - px)f = i\hbar f = [x, p]f \tag{1.63}$$

The bracket notation for the commutator is used in the second equality: $[A, B] \equiv (AB - BA)$. This notation was introduced in the prior section. The commutatior $[x, p]$, when operating on any function of x, gives $i\hbar$ times the same function of x. This result is usually written by omitting the function $f(x)$:

$$[x, p] = i\hbar \tag{1.64}$$

The presence of such a function is usually implied, even though it is customarily omitted. The position x and momentum p do not commute. They would be said to commute if $[x, p] = 0$.

A theorem in linear algebra states that if two operators commute, then it is possible to construct simultaneous eigenfunctions of both operators. For example, if two operators F and G commute, then it is possible to find eigenstates ϕ_n such that

$$F\phi_n = f_n \phi_n \quad G\phi_n = g_n \phi_n \tag{1.65}$$

where (f_n, g_n) are eigenvalues. The converse is also true, in that if two operators do not commute, then it is impossible to find simultaneous eigenvalues from the same eigenfunction.

It is impossible to find simultaneous eigenfunctions of x and p. There is no function ϕ_n that has the dual property that $x\phi_n = x_n\phi_n$, $p\phi_n = p_n\phi_n$. One can find an eigenfunction of x but it is not an eigenfunction of p, and vice versa. The statement that one cannot define simultaneous eigenvalues of x and p causes the uncertainly principle that $\Delta x \Delta p \geq \hbar$. A similar uncertainly principle exists between any pair of noncommuting operators.

The most important operator in quantum mechanics is the Hamiltonian H. The eigenfunctions of H are used extensively in wave functions and elsewhere. It is useful to ask whether these eigenfunctions are also exact eigenfunctions of other operators, such as momentum and angular momentum $\vec{L}$. The answer depends on whether these other operators commute with H. Angular momentum often commutes with H, and then one can construct simultaneous eigenstates of H and $\vec{L}$. The momentum p only occasionally commutes with H. Since p and $\vec{L}$ never commute, one can never find simultaneous eigenstates of all three operators.

An example is useful. Consider the Hamiltonian in three dimensions. The potential $V(r) = 0$.

$$H = \frac{p^2}{2m} = -\frac{\hbar^2 \nabla^2}{2m} \tag{1.66}$$

One choice of eigenfunction is the plane wave state $\phi(\mathbf{k}, \mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$, where A is a normalization constant. The eigenvalue of H is

$$H\phi(\mathbf{k}, \mathbf{r}) = -\frac{\hbar^2 \nabla^2}{2m}(Ae^{i\mathbf{k}\cdot\mathbf{r}}) = \varepsilon_k \phi(\mathbf{k}, \mathbf{r}), \quad \varepsilon_k = \frac{\hbar^2 k^2}{2m} \tag{1.67}$$

The plane wave solution is also an eigenfunction of the momentum operator, but not of the angular momentum:

$$\mathbf{p}\phi(\mathbf{k}, \mathbf{r}) = -i\hbar\nabla\phi(\mathbf{k}, \mathbf{r}) = \hbar\mathbf{k}\phi(\mathbf{k}, \mathbf{r}) \tag{1.68}$$

$$L_z\phi(\mathbf{k}, \mathbf{r}) = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\phi = \hbar(xk_y - yk_x)\phi(\mathbf{k}, \mathbf{r}) \tag{1.69}$$

The plane wave is an example of a simultaneous eigenfunction of H and $\mathbf{p}$.

Another choice of eigenfunction for H is the product of a spherical Bessel function $j_\ell(kr)$ and spherical harmonic angular function $Y_{\ell\psi}^m(\theta, \phi)$ in spherical coordinates:

$$\psi_{\ell m}(kr) = j_\ell(kr)Y_{\ell\psi}^m(\theta, \phi) \tag{1.70}$$

Readers unfamiliar with these functions should not worry: they are explained in chapter 5. This function is an exact eigenfunction of H and L_z, but not of momentum:

$$H\psi_{\ell m}(kr) = \varepsilon_k \psi_{\ell m}(kr) \tag{1.71}$$

$$L_z\psi_{\ell m}(kr) = \hbar m\psi_{\ell m}(kr) \tag{1.72}$$

Here is an example of simultaneous eigenfunctions of H and L_z.

The Hamiltonian of a "free particle," which is one with no potential ($V = 0$), has a number of eigenfunctions with the same eigenvalue ε_k. The eigenfunctions in (1.70), for

different values of (ℓ, m), where $(0 \geq \ell < \infty, -\ell \leq m \leq \ell)$, all have the same eigenvalue ε_k. Any linear combination of eigenstates with the same eigenvalues are still eigenfunctions of H. The plane wave state $\exp(i\mathbf{k} \cdot \mathbf{r})$ is a particular linear combination of these states. Some linear combinations are eigenfunctions of $\mathbf{p}$, while others are eigenfunctions of L_z. Since $\mathbf{p}$ and L_z do not commute, there are no eigenfunctions for both operators simultaneously.

References

1. J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton, University Press, Princeton, NJ, 1955) Translated from the German by R.T. Beyer
2. P.A.M. Dirac, *The Principles of Quantum Mechanics* (Oxford, University Press, Oxford, UK, 1958)

Homework

1. Prove that

$$e^L a e^{-L} = a + [L, a] + \frac{1}{2!}[L, [L, a]] + \frac{1}{3!}[L, [L, [L, a]]] + \cdots$$

where (a, L) are any operators.

2. If F is any operator that does not explicitly depend on time, show that $\partial \langle F \rangle / \partial t = 0$ in an eigenstate of H with discrete eigenvalues.