§13. POSTULATES OF QUANTUM MECHANICS

Now that some of the background has been established for formulating the electromagnetic field in terms of the quantum mechanical Hamiltonian, a small set of fundamental postulates will be given. These postulates form the basis of the quantum mechanical formalism developed over the past six decades. The complexities of quantum mechanics prohibits any detailed discussion of this subject. The intention of this section of the book is to given the read a quick overview of the vocabulary and lay the groundwork for the description of the quantum mechanical description of the electromagnetic field and its interaction with charges in a conductor.

At the quantum mechanical level, particles do not move along definitive paths imposed by a Euclidean coordinate system. Instead in each volume of space–time there exists a probability that at a given time, the particle may appear in an infinitesimal region $d^3\mathbf{r}$ with the probability $\rho d^3\mathbf{r} = \psi^* \psi d^3\mathbf{r}$.

§13.1 BASIC THEORETICAL CONCEPTS

The theory of Quantum Mechanics is fraught with complexities, confusion and improper interpretation. There is a rich set of literature which addresses the *interpretation* of quantum mechanics. The primary feature of the quantum description of nature is the indetermism of individual atomic level events [Holl95]. Regularities and their associated predicitibalities emerge only when large *ensembles* of events are considered. The problem is formulating a clear understanding of the theory is stated in…

> In prosecuting their quantization procedure, the Founding Fathers introduced the new notion of state not in *addition* to the classical state variables, but *instead* of them.

The result of the formulation is a wave function which characterizes the state of the system. Using this description of nature there is no mathematical mechanism to describe individual processes which results in indeterminism and unanalyzable behavior of atomic level processes.

The formalism of Quantum Mechanics developed in §12 — the Schrödinger equation and Hilbert vector space with the observables as operators in the vector space — was consolidated in the late 1920's by Heisenberg, Bohr and Pauli in the *Copenhagen School* of physics. For the purposes of this section, it will be this *theory* of quantum mechanics that will be used.

The Copenhagen School states that the magnitude of the state function ψ determines the probability density ρ and the phase angle of the complex function ψ describes the particles nonrelativistic motion through space–time. The probability distribution of the particle together with its propagation properties produce all the observable quantities of the quantum mechanical system.

> *The present paper seeks to establish a basis for theoretical quantum mechanics founded exclusively upon relationships between quantities that in principal are observable.*
>
> *— W. Heisenberg [Heis25]*

§13.2 THE FOUR POSTULATES OF QUANTUM MECHANICS (ACCORDING TO BOHR)

In quantum mechanics the definition of a system state is more subtle. The following postulates are considered fundamental in the quantum mechanical description of nature:

Postulate 1 — Each state of a physical system corresponds to an element, a state vector, in a Hilbert space $\mathbf{H}$ [1]. The length of the state vector $|u\rangle$ is unity, $\langle u|u\rangle = 1$. Elements that only differ by a phase factor $e^{i\phi}$ represent the same state of the physical system.

Postulate 2 — Given that the state of the physical system corresponds to the state vector $|u\rangle$, the probability that the system is observed in the state vector $|v\rangle$ is $|\langle v|u\rangle|^2$.

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[1] A Hilbert space $\mathbf{H}$ is a complex vector space, in which an inner product $\langle\cdot|\cdot\rangle$ is defined as a mapping of $\mathbf{H}$ x $\mathbf{H}$ on a set of complex numbers. The inner product should satisfy the following conditions for elements of the vector space (u, v, and w):

(1) $\langle u|u\rangle \ge 0$

(2) $\langle u|v+w\rangle = \langle u|v\rangle + \langle u|w\rangle$

(3) $\langle u|\alpha v\rangle = \alpha\langle u|v\rangle$

(4) $\langle u|v\rangle = \langle u|v\rangle^*$

Postulate 3 — Every observable [2] corresponds to a linear, Hermitian operator on a Hilbert space. The possible results of a measurement are the eigenvalues of the corresponding operator.

Postulate 4 — The operators associated with a coordinate q and its canonically-conjugate momentum p_i satisfy commutation rules $\left[q_i , p_j \right] = i\hbar\delta_{ij}$ where δ_{ij} equals 1 if $i = j$ and zero otherwise.

Postulate 5 — The development in time of the state vector is given by the first order differential equation $i\hbar \frac{d}{dt} \left| \psi(t) \right\rangle = \hat{H} \left| \psi(t) \right\rangle$, where $\hat{H}$ is a linear Hermitian operator. The non–relativistic limit $\hat{H}$ is the operator corresponding to a classical Hamiltonian. [3]

§13.2.1 Postulate 1 and Postulate 2

The state vectors of Postulate 1 and their probability densities in Postulate 2 represent observable value of Schrödinger's wave equation or eigenvalue of Heisenberg's matrix mechanics. In either case the state of the quantum system must be single valued, finite and continuous — that is a well behaved function for all values of the generalized coordinates and time.

A system is in a *stationary state* when its observed properties do not change with time. Wave functions representing stationary states have time–dependence which can be *factored* into a configuration independent

[2] The terminology used to describe a measurable physical quantity — dynamical variables — are called *observables*. These entities are distinguished from their mathematical counterparts and the operators they are represented by. In a number of quantum mechanics texts the term *observable* is used to denote any Hermitian operator which posses a complete set of eigenfunctions.

[3] The time dependent Schrödinger equation is the fundamental equation of motion in quantum theory, corresponding to Newton's equations in classical mechanics. In general the form the time dependent Schrödinger equation is $\hat{H}\psi = ih \frac{\partial \psi}{\partial t}$, where the Hamiltonian of the system under consideration is derived from the classical Hamiltonian. In addition the wave equation $\psi(\mathbf{r},t)$ is not necessarily an eigen state of the Hamiltonian. Its physical interpretation is that of a probability amplitude $\left|\psi(\mathbf{r},t)\right|^2 dr$ of a measurement of the position of a particle. The general solution to the Schrödinger equation is, $\psi = \sum_E c_E \mathbf{u}_E(\mathbf{r}) e^{-iEt/h}$, where $\mathbf{u}_E$ denotes the spatial part of the wave equation and c_E are constants determined from the knowledge of the wave function at $t = 0$.

portion and a configuration dependent portion. The configuration dependent portion then fully described the system.

In the Schrödinger formulation of quantum mechanics the wave function was originally through to represent a physical matter wave traveling through space and time. The square of this matter wave function represents the measure of the intensity of the wave function. The modern view of Schrödinger's wave function is that of a *probability density* function for the instantaneous occurrence of a specific configuration at a specific time. This view of the wave equation requires that a quantum state be *localized* within some finite region of the configuration space. The *norm* and *inner product* of the vector space developed in the previous section can be used to describe behavior of the quantum states.

§13.2.2 Postulate 3

An operator is a mathematical *prescription* for transforming one function into another in the same manner a function is a prescription for transforming one number into another. The action of an operator on the wave function can be associated with the process of *measuring* an observable of the quantum system. The result of this measurement is the result of the transformation of the state of the system *after* the measurement has been performed. In general the state of the quantum system is different after the measurement since the process of measuring produces an irreducible perturbation of the system.

§13.2.3 Postulate 4

Although the other four postulates are important concepts in quantum mechanics, the commutator of two canonical variables and their relationship to Planck's constant needs further explanation. In Postulate 4, the commutation rule $\left[q_j, p_i\right] = ic\delta_{ij}$ represents the quantum mechanical equivalent of the Poisson bracket notation of Eq. (8.27) and the subsequent commutator algebra.[4] The origin of Postulate 4 is based on

[4] In this description of the uncertainty principle, the constant c is used in place of the familiar $\hbar$. In many texts the notation uses $\hbar$ directly, skipped the historical developments in which the Plank's constant was not yet measured. For a historically correct development see [Mand92] §3.3 For an electron, $q = 5\times10^{-9}$ cm and $p = 2\times10^{-19}\ \mathrm{g\cdot cm/sec}$, which gives $\hbar \cong 6.626\times10^{-27}\ \mathrm{g\cdot cm/sec}$

experimental observations rather than theoretical formulation [Dira58], [Heis30], [Dira25].

Heisenberg was searching for a theory that involved only measurable quantities of the quantum mechanical system [Mehr82]. In order to answer the question: *what are the measurable quantities? What are the equations of motion for these quantities?* Heisenberg made the distinction between the values that are measured and the mathematics used to describe the equations of the quantities. His model for this theory was Einstein's special theory of relativity, which focused on *measurable quantities*. In correspondence between Einstein and Heisenberg, Einstein insisted it makes no sense to assume that what is measurable can be specified without an underlying theory, that ...

> It is the theory which decides what we can observe [Heis71].

Considering the commutator rule in its expanded form,

$$q_i p_j - p_j q_i = ic\delta_{ij}, \tag{13.1}$$

states that the position coordinate and the momentum coordinate when measured individually, produce real numbers with unlimited accuracy. It also states that the position and the momentum of a particle cannot be simultaneously measured with unlimited accuracy. If the momentum and the position values are represented by matrices P and Q then the Heisenberg uncertainty principle implies that,

$$\sqrt{\left\langle \left(Q - \langle Q \rangle\right)^2 \right\rangle} \sqrt{\left\langle \left(P - \langle P \rangle\right)^2 \right\rangle} \geq \frac{c}{2}. \tag{13.2}$$

Postulate 4 can be *derived* from Heisenberg's uncertainty principle [5] which states that the product of two dynamical variables is greater than or

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[5] Heisenberg's *Uncertainty Principle* is one of the more popular misunderstandings of modern science. Critics of this *unpredictable* description of nature have tried to interpret the uncertainty that appears in quantum mechanics as a consequence of the *ignorance* of the underlying physical process. However this ignorance may not be due to the inability of the observer to *measure* properly, but rather that the laws of nature — at the quantum mechanical level — set an absolute limit on the ability of the observer to predict the outcome of the measurement [Frit83]. Various descriptions of the principle can be found in the literature, including:

(1) It is not possible to measure both the position and the momentum of a particle accurately at the same time — This is somewhat misleading

equal to one half the magnitude of the expectation value of the Hermitian commutator,

$$\Delta k_1 \Delta k_2 \geq \tfrac{1}{2}\langle c \rangle . \tag{13.3}$$

This expression can also be stated as: *The product of the uncertainties for the position and momentum is never smaller than* $c/2$ [Jord86]. [6] In the context of the uncertainty principle, the *uncertainty*, ΔK of a variable

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(2) The properties of a classical particle are no longer valid in the quantum mechanical description of motion — This is much too pessimistic a view.

(3) Attempts to localize a particle, inevitably give it a *kick* of such probable intensity that the momentum of the particle is changed — This is wrong.

A *clear* description of the Heisenberg Uncertainty Principle is given in [Penr89] pp. 248–50. The summary simply says that a particle's position and momentum are described by its *Wave Packet* having coordinates in both position and momentum spaces. Since the particle is moving, the wave packet *evolves* with time. The position description and the momentum description of the particle are related by the Fourier transform of each other [Bagg92], [Heis89]. When a precise measurement is taken in one space, a *Dirac delta function* is used as a sampling device. The Fourier transform of this delta function in one space is *spread out* in the other space. The result is that the more precisely the sample in one space, the more imprecisely the information in the other space.

Heisenberg himself summarized the confusion over his principle:

> I remember discussions with Bohr which ... ended in almost despair; and when at the end of the discussion ... I repeated to myself again and again: Can nature possibly be as absurd as it seemed... ?

[6] The traditional expression of Heisenberg's uncertainty principal describes the relationship between two canonical variables, position q and momentum p, with $\Delta p \cdot \Delta q \geq \hbar$. A second relationship is often found in the literature, but usually is given without a full explanation of its consequences. That relationship is between energy E and time t, $\Delta t \cdot \Delta E \geq \hbar$. This uncertainty condition does not follow the canonical variable *rules* developed in this section. L. D. Landau was quoted as saying,

> ... there is obviously no such limitation ... I can measure the energy and look at my watch; then I know both the energy and time [Polk86].

Another way to view $\Delta t \cdot \Delta E \geq \hbar$ is to consider the uncertainty is terms of energy transfer. The limitation is on the measurement of the amount of energy transferred. As the system is *measured* for smaller amounts of time, the uncertainty in the amount of energy grows. This energy uncertainty relation is the basis of the electron *tunneling* observed in semiconductor devices. In *normal* electronics and electron can not penetrate a potential barrier that is of higher energy than the electron itself. An electron is allowed to *borrow* some energy to energy on the other side of the electric potential. Tunneling effects can be found in several areas of physics. The explanation of the alpha decays of heavy nuclei depends on tunneling. Such nuclei behave as if they have alpha particles confined inside them. Occasionally the alpha particle is *ejected* from the nucleus having penetrated as energy barrier which classically would have been insurmountable.

K is defined as the *root mean square* deviation from the mean [Heis27]. In a state $|u\rangle$, the mean value of K is,

$$\langle \mathsf{K} \rangle = \langle u | \mathsf{K} | u \rangle . \tag{13.4}$$

The mean value of the operator $\left(\mathsf{K} - \langle \mathsf{K} \rangle\right)^2$ is then the *mean square* deviation from the mean,

$$(\Delta \mathsf{K})^2 = \langle u | \left(\mathsf{K} - \langle \mathsf{K} \rangle\right)^2 | u \rangle , \tag{13.5}$$

and the uncertainty is then

$$\Delta \mathsf{K} = \sqrt{\langle u | \left(\mathsf{K} - \langle \mathsf{K} \rangle\right)^2 | u \rangle} . \tag{13.6}$$

If a new operator K' is introduced such that,

$$\mathsf{K}' = \mathsf{K} - \langle \mathsf{K} \rangle , \tag{13.7}$$

the commutator may then be written as,

$$i\left(\mathsf{K}_1 \mathsf{K}_2 - \mathsf{K}_2 \mathsf{K}_1\right) = i\left(\mathsf{K}_1' \mathsf{K}_2' - \mathsf{K}_2' \mathsf{K}_1'\right). \tag{13.8}$$

The uncertainty relation in Eq. (13.4) may be examined in more detail. If $|u\rangle$ is an arbitrary vector and λ is an arbitrary real constant, the magnitude of the vector $\left(\mathsf{K}_1' + i\lambda \mathsf{K}_2'\right)|u\rangle$ is greater than or equal to zero for all λ. Thus,

$$\langle u | \left(\mathsf{K}_1' - i\lambda \mathsf{K}_2'\right)\left(\mathsf{K}_1' + i\lambda \mathsf{K}_2'\right) | u \rangle \geq 0 , \tag{13.9}$$

with K_1' and K_2' being Hermitian operators. From this relation,

$$\lambda^2 (\Delta \mathsf{K}_2)^2 + \lambda \langle c \rangle + (\Delta \mathsf{K}_1)^2 \geq 0 , \tag{13.10}$$

for all λ. This may be rewritten as,

$$\left(\lambda \Delta \mathsf{K}_2 + \frac{\langle c \rangle}{2 \Delta \mathsf{K}_2}\right)^2 + \left[(\Delta \mathsf{K}_1)^2 - \frac{\langle c \rangle}{4 (\Delta \mathsf{K}_2)^2}\right] \geq 0 . \tag{13.11}$$

The inequality must hold in particular for the value of λ which makes the first term zero,

$$\lambda = -\langle c \rangle / 2 \Delta \mathsf{K}_1 \Delta \mathsf{K}_2 . \tag{13.12}$$

It follows that the second term is non–negative, so that,

$$\Delta K_1 \Delta K_2 \geq \tfrac{1}{2}\langle c \rangle . \tag{13.13}$$

The preceding development states that the results of a measurement of a dynamical variable in a physical system *prepared* by the measurement of another dynamical variables depends on the commutator of the two variables. [7]

> *The essential hypothesis of quantum mechanics concerns the specification of these commutators.*

In order to make this hypothesis explicit the difference between *classical* and *non–classical* dynamical variables must be made. The classical variables are defined in terms of the classical generalized coordinates of the system, q_i and the conjugate momentum p_i. The dynamical variable is then a function of these coordinates and momentum $K(q_i, p_i)$. Examples of these variables are energy, position, momentum and angular momentum of a particle.

The commutation rules for these classical variables can be expressed in terms of the Poisson bracket from classical mechanics. For two dynamical variables $K_1(q_i, p_i)$ and $K_2(q_i, p_i)$, the Poisson bracket is,

$$[K_1, K_2] = \sum_i \left\{ \frac{\partial K_1}{\partial q_i}\frac{\partial K_2}{\partial p_i} - \frac{\partial K_2}{\partial q_i}\frac{\partial K_1}{\partial p_i} \right\}. \tag{13.14}$$

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7 The concept of a quantum mechanical system *prepared* by the observation — intervention of an observer — has lead several authors to assert a connection between quantum mechanics and some forms of eastern mysticism [Zuka79], [Capr75]. The argument states that because position and momentum cannot be measured simultaneously the *observer* make a choice of one or the other through the act of measurement and that this choice is a conscious one that results in the mind of the observer becoming part of the observation process.

Eugene Wigner described the logical conclusion…

> It was not possible to formulate the laws of quantum mechanics in a fully consistent way without reference to the consciousness of the observer... Remarkably, the very study of the external world lead to the conclusion that the content of the consciousness is the ultimate reality [Wign67], pp. 172.

The argument of the connection between mysticism and quantum mechanics is arrived at through *reductive* means by demonstrating we are all *floating in a sea of mind* [Zuka79] From the view point of a physicists, the idea of an *observer*

The basic hypothesis a quantum mechanics is then that the commutator $[\mathsf{K}_1, \mathsf{K}_2]$ is $i\hbar$ times the dynamical variable $(\mathsf{K}_1, \mathsf{K}_2)$,

$$[(\mathsf{K}_1, \mathsf{K}_2)] = i\hbar(\mathsf{K}_1, \mathsf{K}_2), \quad (13.15)$$ [8]

where the constant c has now been replaced with Planck's constant $\hbar$, completing the development of Heisenberg's uncertainty principle. [9]

This expression is fundamental to the theory of quantum mechanics and is given here — stated as fact. However the development of this concept is tedious and requires an understanding of the mathematics of commutator matrices which is beyond the scope of this text. For those interested in the details of these development they can be found in [Dira58] §4 [Krag90] and [Heis30].

Heisenberg's emphasis on measurable quantities leads to some important conclusions about atomic physics. Through an unsuccessful attempt to describe the orbits of atoms, Heisenberg said the uncertainty principle ...

> …helped to convince me of one thing: that one ought to ignore the problem of electron orbits inside the atom [Heis71].

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[8] It is important to understand that the operator on the right–hand side of this expression must be Hermitian. If p and q are individually Hermitian, neither pq nor qp is Hermitian, since $(pq)^* = (qp)$. Therefore the classical variables pq is represented by the quantum operator $½(pq + qp)$, which is Hermitian.

[9] The use of the Poisson Bracket notation in quantum mechanics was introduced by P. A. M. Dirac in 1924. Dirac had made an unsuccessful attempt to introduce relativistic dynamics into Heisenberg's quantum theory [Krag90]. The idea of using the Poisson Bracket came *out of the blue* after Dirac reread Whittaker's *Analytical Dynamics*, [Whit37]. The notation in Whittaker's text reads (x, y). The *bracket* notation $[x, y]$ was reserved for the *Lagrangian* symbol defined as $\sum_k \left(\frac{\partial p_k}{\partial x}\frac{\partial q_k}{\partial y} - \frac{\partial q_k}{\partial x}\frac{\partial p_k}{\partial y} \right)$. Dirac replaced the Poisson Bracket with the square brackets, which in turn pervaded quantum mechanics [Dira83].

This *discovery* can be traced to the fact that Hamiltonian dynamics can be formulated using a non–commuting Poisson Bracket algebra. By connecting the Poisson Bracket with Heisenberg's *products* $(xy - yx) = i\hbar[x, y]$, the basis for Dirac's paper "The Fundamental Equations of Quantum Mechanics," was laid. This work in turn resulted in the seminal text [Dira25].

The uncertainty relations confirm the knowledge of an orbit would imply knowledge of both position and momentum. For an electron in a hydrogen atom, the product of the position and momentum uncertainties is so large when compared to the orbit radius and momentum, that the orbit is only roughly defined [Jord86].

§13.2.4 Postulate 5 and Schrödinger's Equation

Although the focus of this monograph is on the interaction of charged matter with the electromagnetic field, a *diversion* into the fundamentals of quantum mechanics will provide some background of later sections. In March of 1926 Erwin Schrödinger wrote down a differential equation that described a nonrelativistic particle moving in a potential. Schrödinger was guided by Hamilton's description of classical mechanics and de Broglie's [10] description of *matter waves* associated with the motion of atomic sized objects.

Using the formalism of special relativity de Broglie was able to equate space and time with momentum and energy. Planck's formula states that energy is related to frequency by $E = h\nu$. This relation also states that energy is related to the number of *vibrations* per unit of *time*. De Broglie proposed that *momentum* is similarly related to the number of *vibrations* per unit of *space*, which is simply the wavelength such that $p = h/\lambda$. the de Broglie wavelength is then $\lambda = h/p$.

de Broglie's equation states that the energy E of a *matter wave* [11] oscillates with frequency $\omega = E/\hbar$ with a wave function,

[10] Prince Louis Victor de Broglie was a nobleman from an illustrious family of France. As an amateur scientist unknown to the research community he wrote a doctoral dissertation — *Rescherche sur la théorie des quanta*, University of Paris, defended 25 November 1924 — that was sufficiently farfetched that the faculty of the Sorbonne was unable to evaluate it correctness [Serg80], [Crea86].

[11] In de Broglie's [d'Brog24] thesis, the wavelength of light is given as $\lambda = c/\nu$, where ν is the frequency of the light wave. In quantum mechanics energy is *quantized* in units of $E = \hbar\nu$ giving $\nu = E/\hbar$.

Substituting the quantum expression into the classical wavelength expression gives $\lambda = c\hbar/E$. Since Einstein had already concluded that $E = mc^2$, de Broglie expression becomes $\lambda = c\hbar/mc^2$ or $\lambda = \hbar/mc$. Since mass × velocity (mc) is equivalent to momentum, particles like electrons and protons also have momentum equal to their mass times velocity. Since Einstein showed that matter cannot travel at the speed of light the actual

$$\psi \propto e^{-i\omega t}\,, \tag{13.16}$$

which satisfies the differential equation,

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi\,. \tag{13.17}$$

If the matter wave has momentum $\mathbf{p}$, de Broglie's relation gives a wave number of $\mathbf{k} = \mathbf{p}/\hbar$ which describes the wave function in terms of its position as,

$$\psi \propto e^{i\mathbf{k}\cdot\mathbf{r}}\,, \tag{13.18}$$

which satisfies the relation,

$$-i\hbar\nabla\psi = \hbar\mathbf{k} = \mathbf{p}\psi\,.$$

Schrödinger *guessed* [12] the wave equation for a free particle with energy E would be,

$$E\psi = \frac{\mathbf{p}^2}{2m}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi\,. \tag{13.19}$$

An electron in a bounded potential well has potential energy $V(\mathbf{r})$ as well as kinetic energy due to its motion. [13] Schrödinger generalized the wave equation using the potential and kinetic energies to give,

$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\,, \tag{13.20}$$

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velocity in de Broglie's expression can be represented by υ, which when substituted gives the wavelength of a *matter wave* as, $\lambda = \hbar/mv$.

[12] It is impossible to derive — with any rigor — the quantum mechanical Schrödinger equation from classical mechanics. In most texts Schrödinger's equation is simply stated and then justified through its successful application. By following the reasoning given in Schrödinger's notebooks the classical equations of motion serve as the starting point for the *derivation*. When Schrödinger started to publish the results of his research, which are presented here, he elected to present a much more complex derivation, which did not refer to de Broglie waves or quantized energy [Crea86].

[13] The use of a *bounded potential well* for the evaluation of quantum mechanical problem is a traditional approach to the solution of boundary value problems. Through this technique, the quantum mechanics of the hydrogen atom can be examined. Beyond this simple problem though, the potential well solution has little to contribute to *unbounded* problems such as quantizing the free electromagnetic field.

which is Schrödinger's equation for a single particle with definite energy E. A more general time–dependent form can be obtained by eliminating E from the equation to give,

$$i\hbar\frac{\partial\psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi . \tag{13.21}$$

It is customary to write this equation in the form,

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi , \tag{13.22}$$

for the time–dependent case and,

$$H\psi = E\psi , \tag{13.23}$$

when the energy is known. In both forms H is the derivative operator,

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) . \tag{13.24}$$

§13.2.4.1 The Expectation Value of an Operator

In order to proceed with Schrödinger's description of the interaction between matter and fields, some further *diversions* are needed. Since the objects in quantum mechanics and the operators that work on them are statistical in nature the definition of the expectation value of an observable property is needed.

The expectation value of a property corresponding to an operator A is given by,

$$\langle A\rangle = \int \psi^*\psi d^3\mathbf{r} . \tag{13.25}$$

Differentiating Eq. (13.25) with respect to time gives,

$$\frac{d}{dt}\langle A\rangle = \int\left(\frac{\partial\psi^*}{\partial t}A\psi + \psi^* A\frac{\partial\psi}{\partial t} + \psi^*\frac{\partial A}{\partial t}\psi\right)d^3\mathbf{r} . \tag{13.26}$$

Substituting Eq. (13.22) and its complex conjugate, $i\hbar\frac{\partial\psi^*}{\partial t} = H\psi^*$ into Eq. (13.26) gives,

$$\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\int\left[(H\psi)^*(A\psi) - \psi^* AH\psi\right]d^3\mathbf{r} + \left\langle\frac{\partial A}{\partial t}\right\rangle . \tag{13.27}$$

Using the Hermitian conditions of H,

$$\int (H\psi)^* (A\psi) d^3\mathbf{r} = \int \psi^* H A \psi d^3\mathbf{r} . \tag{13.28}$$

Using Eq. (13.28), Eq. (13.27) reduces to,

$$\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\int \left[\psi^* (HA - AH)\psi\right] d^3\mathbf{r} + \left\langle \frac{\partial A}{\partial t}\right\rangle , \tag{13.29}$$

where $(HA - AH)$ is the commutator $[H, A]$ so,

$$\frac{d}{dt}\langle A\rangle = \langle [H, A]\rangle + \left\langle \frac{\partial A}{\partial t}\right\rangle . \tag{13.30}$$

§13.2.5 Lorentz Force Law from Schrödinger's Equation

In classical mechanics, Newton's equations of motion assume that at each instant of time a particle is located at definite position with a definite velocity, momentum and rate or change of momentum or force. In quantum mechanics, only the eigenvalues or expectation values of the equations of motion have precise values.

The expectation value can be used to *generalize* the description of motion and provide an expression for the Lorentz force law. The expectation value for a linear momentum equals the mass of the particle times the rate of change of the expectation value of its position. The expectation value for a force is given by the time rate of change of the expectation value of the corresponding momentum [Duff83].

Given a particle of mass m moving is a scalar potential V the time derivative of the expectation value for its position on the x–axis involves $[\mathsf{H}, x]$. Using the explicit form of the operator $[\mathsf{H}, x] = \mathsf{H}x - x\mathsf{H}$ gives the commutator as,

$$\begin{aligned}
[\mathsf{H}, x] &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)x + Vx + x\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - xV , \\
&= \frac{\hbar^2}{2m}\left(2\frac{\partial}{\partial x}\right), \\
&= \frac{\hbar}{im}\frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{\hbar}{im}\mathbf{p}x
\end{aligned} \tag{13.31}$$

Since x is constant in the partial derivatives with respect to t, $\partial x/\partial t = 0$, gives the expectation value of the momentum as,

$$m\frac{d}{dt}\langle x\rangle = m\left(\frac{i}{\hbar}\left\langle \frac{\hbar}{im}p_x\right\rangle + \langle 0\rangle\right) = \langle p_x\rangle. \tag{13.32}$$

The time rate of change of the expectation value of the x–component of the momentum p_x is given by $\left[\mathsf{H}, p_x\right]$ which using the explicit form gives,

$$\begin{aligned}\left[\mathsf{H}, p_x\right] &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\frac{\hbar}{i}\frac{\partial}{\partial x} + V\frac{\hbar}{i}\frac{\partial}{\partial x}+\cdots \\ &\cdots + \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{\hbar}{i}\frac{\partial}{\partial x}V, \\ &= -\frac{\hbar}{i}\frac{\partial V}{\partial x}.\end{aligned} \tag{13.33}$$

Since $\partial p_x/\partial t = 0$,

$$\frac{d}{dt}\langle p_x\rangle = \frac{i}{\hbar}\left\langle -\frac{\hbar}{i}\frac{\partial V}{\partial x}\right\rangle + \langle 0\rangle = -\left\langle \frac{\partial V}{\partial x}\right\rangle = \langle F_x\rangle. \tag{13.34}$$

Similar equations can be developed for the y and z components. In vector form the time derivative of the momentum is given as,

$$\frac{d}{dt}\langle \mathbf{p}\rangle = -\langle \nabla V\rangle = \langle \mathbf{F}\rangle, \tag{13.35}$$

which says that the rate of change of the expectation value of the momentum of the particle's *wave function* equals the expectation value of the force acting on the particle. Although this equation does not directly equate to Newtonian mechanics, since the particle's wave packet does not propagate with *unchanging certainty*, it does approximate Newtonian mechanics. Eq. (13.35) was derived in 1927 by Paul Ehrenfest (1886–1933) and is called Ehrenfest's theorem. [14] These equations are not the classical

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14 Ehrenfest's theorem can be stated in a general manner using the momenta and generalized coordinates that follow the expression $d\langle q_i\rangle/dt = (1/i\hbar)\langle[q_i, \mathsf{H}]\rangle$ and $d\langle p_i\rangle/dt = (1/i\hbar)\langle[p_i, \mathsf{H}]\rangle$. A system of particles placed in a conservative potential field can be represented by the Hamiltonian $\mathsf{H} = \sum_k \left(p_k^2/2m_k\right) + V(\mathbf{r}_k)$ where the momentum of the k^{th} particle is given as $F_k \equiv -\nabla_k V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Using the commutator relations developed

limit of the quantum mechanical equations of motion, since Eq. (13.35) holds for any state of a particle and since they are the equations for the expectation values about which the *uncertainty* occurs, the standard deviations Δx and $\Delta \mathbf{p}$ are no longer negligible. The classical limit only applies for states in which this uncertainty is negligible, so that the particles travel along well–defined trajectories [Gott66].

§13.2.5.1 Lorentz Force Derivation

The Schrödinger formulation can now be extended to a *field* which carries both energy and momentum — such as the electromagnetic field [Duff84]. This field may contribute its energy and momentum to a particle which interacts with it in the same way the classical electromagnetic fields interact with charged particles. The effect of this energy interaction can be represented by an *interaction coefficient* and a scalar potential. The momentum effect can be represented by a coefficient and a vector field.

Given a particle of mass m and velocity v moving in a field, the potential energy resulting from the interaction between the particle and the field is V and the total energy of the interaction is,

$$E = mv^2 + V \; . \tag{13.36}$$

If the particle were traveling in the absence of the field — it was a *free* particle — its linear momentum would be mv, but the interaction between the particle and the field alters the momentum by a factor dependent on the interaction coefficient q such that the momentum is now given by,

$$\mathbf{p} = mv + q\mathbf{A} \, , \tag{13.37}$$

which gives,

$$\begin{aligned} m^2v^2 &= mv \cdot mv = (\mathbf{p} - q\mathbf{A}) \cdot (\mathbf{p} - q\mathbf{A}), \\ &= \sum_j \left(p_j - qA_j \right)\left(p_j - qA_j \right). \end{aligned} \tag{13.38}$$

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previously $[\mathbf{r}_k, \mathrm{H}] = (i\hbar/m)\, p_k$ and $[p_k, \mathrm{H}] = i\hbar F_k$. Substituting these expressions into the original time derivative gives, $d\langle \mathbf{r}_k \rangle / dt = \langle p_k \rangle / m$ and $d\langle p_k \rangle / dt = \langle F_k \rangle$ which is Ehrenfest's theorem.

By combining the two previous expressions the quantum analog of Newton's Second law of motion can be given as, $\langle F_k \rangle = md^2 \langle \mathbf{r}_k \rangle / dt^2$ which states that the expectation value of the position and momentum coordinates are analogous to the classical laws of motion [Biln74].

Substituting Eq. (13.38) into Eq. (13.36) gives the Hamiltonian of the particle as,

$$E = \frac{1}{2m}\sum_j \left(p_j - qA_j\right)\left(p_j - qA_j\right) + V \equiv \mathsf{H} \quad , \tag{13.39}$$

which can be rewritten as,

$$\sum_j \left(p_j - qA_j\right)\left(p_j - qA_j\right) = 2m\left(E - V\right). \tag{13.40}$$

The operator for the j^{th} component of the momentum is given by,

$$\frac{\hbar}{i}\frac{\partial}{\partial x_j} = p_j \tag{13.41}$$

Since the vector field **A** is a function of position and possibly time it is generally independent of these components, which gives the corresponding operator for the vector field as,

$$\frac{\hbar}{i}\frac{\partial}{\partial x_j} - qA_j = p_j - qA_j . \tag{13.42}$$

Combining each side of Eq. (458) and summing over the *j* components and applying the result to the particles wave function ψ gives,

$$\begin{aligned}\sum_j \left(\frac{\hbar}{i}\frac{\partial}{\partial x_j} - qA_j\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x_j} - qA\right)\psi &= \sum_j \left(p_j - qA_j\right)\left(p_j - qA\right)\psi, \\ &= 2m\left(E - V\right)\psi.\end{aligned} \tag{13.43}$$

which is the Schrödinger equation for the motion of a particle is a field described by **A** and *V*.

The potential energy *V* of the field can be expressed as the interaction coefficient *q* times a scalar function ϕ such that,

$$V = q\phi . \tag{13.44}$$

The Hamiltonian then becomes,

$$\begin{aligned} \mathsf{H} &= \frac{1}{2m}\sum_j \left(p_j - qA_j\right)\left(p_j - qA_j\right) + q\phi, \\ &= \frac{1}{2m}(\mathbf{p} - q\mathbf{A})(\mathbf{p} - q\mathbf{A}) + q\phi, \\ &= \frac{1}{2m}\left[\mathbf{p}\cdot\mathbf{p} - q\left(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}\right) + q^2\mathbf{A}\cdot\mathbf{A}\right] + q\phi. \end{aligned} \tag{13.45}$$

The operator describing the motion of a particle with mass m and an interaction coefficient q traveling in a field described by $\mathbf{A}$ and ϕ is the Hamiltonian H [Duff84].

By restating the momentum as,

$$p_j = \frac{\hbar}{i}\frac{\partial}{\partial x_j} = \frac{\hbar}{i}\nabla_j\,, \tag{13.46}$$

allows the momentum to be represented as a vector,

$$\mathbf{p} = \frac{\hbar}{i}\nabla. \text{ [15]} \tag{13.47}$$

Since the momentum $\mathbf{p}$ is not a function of time,

$$\left\langle \frac{\partial \mathbf{p}}{\partial t} \right\rangle = 0\,. \tag{13.48}$$

Applying the momentum operator to the scalar wave equation gives,

$$\begin{aligned} \frac{i}{\hbar}[q\phi, \mathbf{p}]\psi = \frac{i}{\hbar}\left[q\phi, \frac{\hbar}{i}\nabla\right]\psi &= q\phi\nabla\psi - \nabla\left(q\phi\psi\right), \\ &= q\phi\nabla\psi - q\phi\nabla\psi - q\psi\nabla\phi, \\ &= -q\left(\nabla\phi\right)\psi. \end{aligned} \tag{13.49}$$

and applying the momentum operator to the vector field gives,

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[15] This *operator* notation of a vector can also be used for the kinetic energy and total system energy where $T = -\nabla^2/2m$ and $E = i\partial/\partial t$. These operators do not necessarily commute. From the definition $p_x = -i\partial/\partial x$ it follows $x\,p_x - p_x x = [x, p] = i$ where x is the position operator.

$$\frac{i}{\hbar}\left[\frac{1}{2m}\left(p_j-qA_j\right)\left(p_j-qA_j\right),\mathbf{p}\right]\psi=\cdots$$
$$\cdots=\frac{i}{\hbar}\left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right),\frac{\hbar}{i}\nabla_j\right]\psi,$$
$$=\frac{1}{2m}\left\{\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\nabla-\nabla\left[\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\right]\right\}\psi.$$
$$=\frac{1}{2m}\left[\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\nabla\psi-\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\nabla\psi-\cdots\right.$$
$$\left.\cdots-\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\psi-\left(-q\nabla A_j\right)\left(\frac{\hbar}{i}\nabla_j-qA_j\right)\psi\right]$$
$$=\frac{q}{2m}\left[\left(p_j-qA_j\right)\nabla A_j+\nabla A_j\left(p_j-qA_j\right)\right]\psi. \quad (13.50)$$

Using Eq. (13.50) the time derivative of the expectation value of the momentum operator is,

$$\begin{aligned}\frac{d}{dt}\langle\mathbf{p}\rangle&=\frac{q}{2m}\left\langle\sum\left[\left(p_j-qA_j\right)\left(\nabla A_j\right)+\left(\nabla A_j\right)\left(p_j-qA_j\right)\right]\right\rangle-q\left\langle\nabla\phi\right\rangle,\\&=\frac{1}{2}q\sum\left\langle\left(v_j\nabla A_j+\nabla A_j v_j\right)\right\rangle-q\left\langle\nabla\phi\right\rangle.\end{aligned} \quad (13.51)$$

where, $p_j-qA_j=mv_j$ has been introduced, which gives,

$$\frac{d}{dt}\langle\mathbf{p}\rangle=q\sum\left\langle v_j\right\rangle\nabla A_j-q\nabla\phi. \quad (13.52)$$

When the wave packet is small enough to make each ∇A_j and $\nabla\phi$ constant within the integrals then $\langle v\rangle=\mathbf{v}$ and $\langle v\rangle=\mathbf{v}$ which gives,

$$\begin{aligned}\frac{d}{dt}\mathbf{p}&=q\sum\nabla\left(v_jA_j-\phi\right),\\&=q\nabla\left(v_jA_j-\phi\right).\end{aligned} \quad (13.53)$$

By the *chain rule* of differentiation $\frac{d}{dt}=\frac{\partial}{\partial t}+v\cdot\nabla$ while differentiating $\mathbf{p}=mv+q\mathbf{A}$ gives,

$$\begin{aligned}\frac{d}{dt}\mathbf{p} &= \frac{d}{dt}(mv + q\mathbf{A}),\\ &= m\frac{dv}{dt} + q\left(\frac{\partial \mathbf{A}}{\partial t} + v \cdot \mathbf{A}\right).\end{aligned} \tag{13.54}$$

which converts Eq. (13.52) to,

$$\begin{aligned}m\frac{dv}{dt} &= q\left(-\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}\right) + q(\nabla v \cdot \mathbf{A} - v \cdot \nabla \mathbf{A}),\\ &= q\left(-\nabla\phi - \frac{\partial \mathbf{A}}{\partial t}\right) + qv \times (\nabla \times \mathbf{A}).\end{aligned} \tag{13.55}$$

Using the usual vector identity $A\times(B\times C) = B(A\cdot C) - (A\cdot B)C$ and defining the familiar Maxwell field potentials, $\mathbf{E} = -\nabla\phi - \partial\mathbf{A}/\partial t$ and $\mathbf{B} = \nabla\times\mathbf{A}$, gives the Lorentz force equation derived from Schrödinger's equation as,

$$m\frac{dv}{dt} = q(\mathbf{E} + v\times\mathbf{B}). \tag{13.56}$$

§13.2.5.2 Current Associated with Propagation

Before proceeding with *quantizing* the electromagnetic field, another example of a derivation from Schrödinger's equation will be useful. The propagation of energy and momentum through the classical electromagnetic field has a quantum mechanical counterpart. Starting with Schrödinger's equation for the motion of a quantum particle it can be shown the a *current* is associated with the propagation of the particle through space [Eise69].

Using the now familiar Hamiltonian $\mathsf{H} = T - V$ and the energy operator E an expression relating the two can be formed as,

$$E\psi = \mathsf{H}\psi, \tag{13.57}$$

so that,

$$i\frac{\partial\psi}{\partial t} = \mathsf{H}\psi = \left[-\frac{1}{2m}\nabla^2 + V(\mathbf{r},t)\right]. \tag{13.58}$$

If V is independent of t then putting $\psi(\mathbf{r},t) = u(\mathbf{r})g(t)$ allows the time and space components of the expression to be separated and rewritten as,

$$\frac{i}{g(t)}\frac{\partial g(t)}{\partial t}=\frac{1}{u(\mathbf{r})}\left[-\frac{1}{2m}\nabla^2+V(\mathbf{r})\right]u(\mathbf{r})=E\,, \tag{13.59}$$

where E is the energy eigenvalue. Solving this expression for the time component $g(t)$ gives,

$$\psi=u(\mathbf{r})e^{-iEt}\,. \tag{13.60}$$

The complex conjugate of the Schrödinger equation is given by,

$$i\frac{\partial\psi^*}{\partial t}=\left[-\frac{1}{2m}\nabla^2+V(\mathbf{r},t)\right]\psi^*\,, \tag{13.61}$$

The rate of change of the probability density $\rho=\psi^*\psi$ is given by,

$$\frac{\partial\rho}{\partial t}=\left(\frac{\partial\psi^*}{\partial t}\right)\psi+\psi^*\left(\frac{\partial\psi}{\partial t}\right)=-\frac{i}{2m}\left[\left(\nabla^2\psi^*\right)\psi-\psi^*\left(\nabla^2\psi\right)\right]. \tag{13.62}$$

The right–hand side of this expression can be written in terms of a *vector current* or *probability current*,

$$\mathbf{j}(\mathbf{r},t)=\frac{i}{2m}\left[\left(\nabla\psi^*\right)\psi-\psi^*\left(\nabla\psi\right)\right], \tag{13.63}$$

while the integral of the left–hand side gives the *current density* as,

$$\rho(\mathbf{r},t)=i\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right). \tag{13.64}$$

The divergence of the vector current is given as,

$$\nabla\cdot\mathbf{j}=\frac{i}{2m}\left[\left(\nabla^2\psi^*\right)\psi-\psi^*\left(\nabla^2\psi\right)\right]=-\frac{\partial\rho}{\partial t}. \tag{13.65}$$

Using the following definition for the divergence: the divergence of a vector function is the negative of the time rate of change in the *mass density* of the *fluid* for which the function is the momentum density [Duff84]. This allows the use Gauss's theorem for converting a surface integral into a volume integral gives,

$$\frac{\partial}{\partial t}\int\rho d^3\mathbf{r}=-\int_V\nabla\cdot\mathbf{j}\,d^3\mathbf{r}=-\oint_S\mathbf{j}dS\,. \tag{13.66}$$

by using the familiar Maxwell relation for current and charge, the conservation law of charges and currents can be restated as,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0\,. \tag{13.67}$$

> *I...never accept anything as true if I had not evident knowledge of its being so; that is, to accept only what presented itself to my mind so clearly and distinctly that I had no occasion to doubt it.*
>
> *— Rene Descartes in Discourse on Method [Elli66]*