

## Chapter 1

### INTRODUCTION

#### 1.1 What is Quantum Mechanics?

##### 1.1.1 What is Mechanics?

1. Classical Mechanics (Galileo, Newton, Lagrange, Hamilton)
2. Relativistic Mechanics (Einstein, Lorentz, Poincare)
3. Statistical Mechanics (Maxwell, Boltzmann, Gibbs)
4. Quantum Mechanics (Bohr, Schrödinger, Heisenberg, Dirac)

**Mechanics** - a statement of the rules for describing the evolution and observation (or measurement) of a particular class of dynamical systems.

**Dynamical System** - a set of elements possessing physical attributes, some of which are measurable and some of which may change as a function of time.

**Measurable Attributes** are often referred to as **observables**. To “measure an observable” means to assign a numerical value to it through some specified measurement process.

To state a given form of mechanics often entails the specification of four components, either implicitly, or in the form of **postulates** regarding:

1. **specification** - the means by which an arbitrary dynamical state of the system may be specified (in some sense, completely and uniquely).
2. **observables** - the types of measurements (or observables) that can be performed on the system when it is in an arbitrary dynamical state.
3. **measurement** - the possible outcomes associated with the measurement of an observable (or observables) when the system is in an arbitrary dynamical state. (Including, for example, what values can be obtained and what happens to the dynamical state during the measurement process.)
4. **evolution** - the rules governing the evolution of the system as it passes from one dynamical state into another.

It is to be emphasized that these four components are not generally something which one can expect to *derive*. Rather, they exist as postulates or axioms of the particular mechanics which they serve to *define*. It is the role of experiment to verify or refute the applicability of a postulated system of theoretical mechanics to a particular class of physical systems. When a sufficient degree of applicability to physical systems is experimentally demonstrated the corresponding postulates take on the cultural status of **physical laws**.

### 1.1.2 Postulates of Classical Mechanics:

#### Postulates of Classical Mechanics for Conservative Systems

(Lagrange formalism)

1. The instantaneous dynamical state of a system is determined through the specification of a set of  $N$  generalized coordinates and their associated velocities  $\{q_i(t), \dot{q}_i(t)\} = (q, \dot{q})$ .
2. Any function  $A(q, \dot{q})$  of the set  $(q, \dot{q})$  is, in principle, an observable of the dynamical system. The value of any observable is completely determined once the state of the system is specified.
3. It is, in principle, possible to simultaneously measure any or all of the dynamical variables of the system with arbitrary precision without disturbing its evolution; the values obtained will always be just those associated with the dynamical state at the time of measurement.
4. The evolution of the system is governed through the Lagrangian  $L(q, \dot{q})$  of the system through **the Euler-Lagrange equations**

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0. \quad (1.1)$$

In conservative systems the Lagrangian function is the difference  $T - V$  between the kinetic and potential energies of the system expressed as a function of the set  $(q, \dot{q})$ .

#### Postulates of Classical Mechanics for Conservative Systems

(Hamiltonian formalism)

1. The instantaneous dynamical state of a system is determined through the specification of a set of  $N$  generalized coordinates and their conjugate momenta  $\{q_i, p_i\} = (q, p)$ . The  $p_i$  are new variables defined through the Lagrangian:  $p_i = \partial L / \partial \dot{q}_i$ .
2. Any function  $A(q, p)$  of the set  $(q, p)$  is, in principle, an observable of the dynamical system, and its value is completely determined once the state of the system is specified.
3. It is, in principle, possible to simultaneously measure any or all of the dynamical variables of the system with arbitrary precision without disturbing its evolution; the values obtained will just be those associated with the dynamical state at the time of measurement.
4. The evolution of the state is governed through the Hamiltonian  $H(q, p)$  of the system through **Hamilton's equations** of motion

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad (1.2)$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}. \quad (1.3)$$

The Hamiltonian function,  $H = \sum_i p_i \dot{q}_i - L$ , is the total energy of the system expressed as a function of the canonical variables  $(q, p)$ .

The field of **Statistical Mechanics** recognizes that in some systems (e.g., those containing  $10^{23}$  particles) we may be unable to specify the exact dynamical state of the system (nor, usually, would we want to). Instead, one settles for a statistical description. For a classical system possessing a large number of generalized coordinates and momenta, we have the following:

### Postulates of Classical Statistical Mechanics

1. All available information about the instantaneous dynamical state of the system is contained in a **probability density function** (or **state function**)  $\rho(q, p, t)$ , defined so that the differential  $dP = \rho(q, p, t) d^N q d^N p$  represents the probability of finding the actual dynamical state of the system in an infinitesimal cell of classical phase space centered at the point  $(q, p)$ . The requirement that the dynamical system be in one of its dynamical states necessitates the normalization condition

$$\int \rho(q, p, t) d^N q d^N p = 1. \quad (1.4)$$

2. Any function  $A(q, p)$  of the set  $(q, p)$  is, in principle, an observable of the dynamical system. In general, its value is completely determined only if the actual dynamical state of the system is completely specified (which it may never be).
3. It is, in principle, possible to simultaneously measure any or all of the dynamical variables of the system with arbitrary precision (although in practice this may never occur). It is not, in general, possible to predict what values will be obtained during the measurement, because the actual dynamical state prior to measurement is not known. If  $\rho(q, p)$  is specified, however, it is possible to predict the average value associated with a large number of measurements of an observable  $A$  when performed on a set of similarly prepared systems

$$\langle A \rangle = \int \rho(q, p, t) A(q, p) d^N q d^N p. \quad (1.5)$$

It is also generally possible to predict the probability that any given value will be obtained. For example, if we let  $P_a(q, p)$  denote a function that equals unity at all points where  $A(q, p) = a$  and is equal to zero otherwise, then the probability that the value  $a$  is obtained upon measurement of the observable  $A$  will be  $P(a) = \langle P_a \rangle$ .

Immediately after a measurement of an observable  $A$  yielding a specific value  $a$ , the uncertainty associated with the actual dynamical state of the system has been reduced, since the system must now be in a state consistent with the value obtained. Thus the state function  $\rho(q, p)$  **collapses** upon measurement to those parts of phase space consistent with the value obtained. Taking into account the normalization, this implies the reduction

$$\rho(q, p) \rightarrow \frac{P_a(q, p)\rho(q, p)}{\langle P_a \rangle}. \quad (1.6)$$

4. Each point in phase space evolves classically. This gives rise to a change in  $\rho(q, p, t)$ , whose evolution is governed by **Liouville's equation** of motion

$$\frac{\partial \rho}{\partial t} = [H, \rho] = \sum_i \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i}. \quad (1.7)$$

**Comment:** The quantum mechanics developed by Schrödinger, Heisenberg, and Dirac is not intrinsically different in that, as a formalism, it sets out the four basic requirements normally associated with any type of mechanics. There are, however, elements of it which seem odd when looked at from the point of view of classical mechanics. These odd aspects, however, have been deliberately built into the structure of quantum mechanics to make it agree with experimental observations performed on a large (and growing) class of physical systems. Our goal is to enumerate and explore the consequences of the basic postulates of quantum mechanics. To this end, we review experiments that led up to what is perhaps the earliest “essentially correct” version of quantum mechanics, namely, the wave mechanics of Schrödinger.

## 1.2 The Development of Wave Mechanics

### Electromagnetic Waves and Photons

The earliest quantitative theory of light was due to Newton: Light is a collection of particles or *corpuscles*. But Newton’s predictions could also be obtained through a wave description (Huygens). Maxwell appeared to clear things up definitively: Light is an Electromagnetic Wave. Unfortunate Problem: Classical statistical mechanics applied to Maxwell’s electrodynamics was found to be in *profound* conflict with experimental observations regarding the blackbody spectrum and the photoelectric effect. This led Planck and Einstein to *reintroduce* Newton’s original concept of light as a particle, i.e., a **photon**, each containing a quantized amount of energy

$$E = \hbar\omega = h\nu \quad (1.8)$$

related to the frequency of the associated wave, and a momentum

$$\vec{p} = \hbar\vec{k} \quad (1.9)$$

related to the corresponding wavevector. In this construction, the quantity  $\hbar = h/2\pi = 1.054 \times 10^{-34}$ Js was an empirical, but obviously fundamental constant required by the new theory.

Thus, at the turn of the century, there were two entirely different classes of experiment: one class leading to the conclusion that light is a wave, one to the conclusion that light is a particle. Taken together, the experimental evidence had elements which both confirmed and refuted both of these disparate classical pictures. The new mechanics to be developed had the task of reconciling these experimental observations in a unified way. To demonstrate some of the features necessary for such a reconciliation, we consider two examples: the double slit experiment, and the passage of light through a polarizing filter.

### The Double Slit Experiment

Monochromatic plane waves of light are separated into two components by passing through a pair of slits, and recombined to form an interference pattern.

According to classical wave theory, this pattern results because the intensity at the screen is *not* the sum of the intensities from each slit, i.e.,

$$S \neq S_1 + S_2. \quad (1.10)$$

Rather, the intensity at any point depends upon the square of the total field at that point; recall that it is the electric fields (or wave amplitudes) that obey a superposition principle, not the intensities:

$$S = |E|^2 = |\vec{E}_1 + \vec{E}_2|^2. \quad (1.11)$$

How about the particle picture? Are photons irrelevant to this experiment? Not at all. When the intensity of the light is reduced, and the screen replaced with an array of photodetectors, it is found that light energy striking the screen arrives in discrete “lumps”, as apparently random single events. It is only after a large number of such events are recorded that the former interference pattern becomes evident. The intensity at any given point on the screen, as reflected in the interference pattern, reflects the *average* number of photons per unit time striking that point. This leads to important unresolved questions: With what do individual photons interfere? If light is a collection of particles how can we explain the non-additive nature of the individual intensities associated with each slit? What do we make of the experimental fact that any attempt to determine the slit through which the photons actually pass destroys the interference pattern? The reconciliation of these classically disparate ideas leads to Bohr’s concept of *wave-particle duality*:

**Wave-particle duality** - The phenomena we call “light” seems to behave simultaneously like a wave and like a collection of particles. On the one hand, the wave amplitude, represented by the electric field  $\vec{E}(r, t)$  at each point, evolves **deterministically** according to Maxwell’s equations; but it carries with it all information regarding the relative **probability** (or probability density) of detecting one of the associated particles (i.e., the photons) at that point. The probability density of detecting a particle at a given point is proportional to the squared modulus  $|E(r, t)|^2$  (i.e., to the intensity) of the wave amplitude.

#### Comments:

1. Note that the smoothly-evolving wave amplitude is a *field* that contains all possible information about any *statistical predictions* that can be made regarding anticipated experimental measurements. The wave amplitude, therefore, can be viewed as representing the dynamical state of the system, in analogy to the phase space probability density function  $\rho(q, p, t)$  which plays a similar role in statistical mechanics.
2. The linearity of Maxwell’s equations, which govern the evolution of the wave amplitude, implies a principle of **superposition**: If  $\vec{E}_1(r, t)$  and  $\vec{E}_2(r, t)$  are two separate solutions to Maxwell’s equations (i.e. acceptable dynamical states of the system) then a linear superposition (or linear combination)

$$\vec{E}(r, t) = \lambda_1 \vec{E}_1 + \lambda_2 \vec{E}_2 \quad (1.12)$$

of these solutions is also a solution, i.e., it is also an acceptable dynamical state of the system. Such a superposition principle turns out to be one of the essential features associated with the dynamical states of all quantum mechanical systems.

Closely related to the superposition principle is the associated principle of **spectral decomposition**, which we illustrate through another experiment.

#### Polarization of Light Through a Filter

A plane electromagnetic wave, traveling along the  $z$ -axis and linearly polarized along a transverse direction represented by a unit vector

$$\hat{u} = \cos \theta \hat{x} + \sin \theta \hat{y}. \quad (1.13)$$

encounters an ideal polarizing filter lying in the  $xy$ -plane with its transmission axis pointing along the  $x$  - axis. Classical wave analysis says that we can *decompose* the electric

field into components  $E \cos \theta$  and  $E \sin \theta$  along any direction of interest. The latter component is absorbed, the former passes through. The light emerging from the filter is then polarized in the  $x$ -direction with an intensity  $S \propto |E_x|^2 = E^2 \cos^2 \theta$ .

How about the photons? As before, at low intensities the light emerging from the apparatus appears in discrete “lumps”, at random time intervals. Any given photon either passes through or it doesn’t. It is not possible to tell for certain if a photon will get through, but the statistics of the process indicate that the *probability* of any single photon getting through is  $p_x = \cos^2 \theta$ . These observations lead to the following additional characterization of the measurement process:

1. The result of a measurement process is always one of a certain set of **eigenvalues** associated with the particular quantity being measured. The set of eigenvalues for a given observable is called its **spectrum**. (Here the eigenvalue of the observable is equal to one if an incident photon passes through the polarizer and is equal to zero if it does not.)
2. To each eigenvalue of an observable there corresponds at least one dynamical state, referred to as an **eigenstate** of the observable. When the particle is known to be definitely in one of the eigenstates at the time of measurement, the result will be the corresponding eigenvalue with unit probability. (Here the eigenstates are states of linear polarization  $|\hat{x}\rangle$  corresponding to eigenvalue 1, and states of linear polarization  $|\hat{y}\rangle$  corresponding to eigenvalue 0.)
3. The *superposition principle* allows the particle to be in a linear superposition of different eigenstates, the linear coefficients of which we call the *amplitude* to be in that eigenstate.
4. The principle of *spectral decomposition* goes further and demands that an arbitrary state of the system can be spectrally decomposed in this manner, i.e., written as a linear superposition of the eigenstates of any observable quantity. Thus, we could have oriented our detector along any direction in the  $xy$  plane and performed a similar decomposition.
5. In general, the result of a measurement on an arbitrary state is uncertain. However, the relative *probability* that the measured value will turn out to be a given eigenvalue is proportional to the square of the amplitude for it to be in that eigenstate. (Here the superposition state is essentially represented by the polarization vector and can be written, using a notation that we will develop more fully later,

$$|u\rangle = |\hat{x}\rangle \cos \theta + |\hat{y}\rangle \sin \theta.$$

We measure 1 with probability  $\cos^2 \theta$ , and 0 with probability  $\sin^2 \theta$ .)

6. Immediately after an ideal measurement, the particle is (with unit probability) in an eigenstate consistent with the particular eigenvalue measured. (Only photons which are  $x$ -polarized emerge from the polarizer.)

**Comments:** This last part implies a non-deterministic reduction or “collapse” of the state of the system to one which is consistent with the result of the measurement process. This is also similar to what happens with the probability density function  $\rho(q, p, t)$  in statistical mechanics except for one important difference: in quantum mechanics this reduction occurs *even when the dynamical state is known exactly*. In the above example, the wave incident on the filter is completely and uniquely characterized by its polarization vector and intensity. There is no additional information that can be given that would

characterize it further, without performing a measurement that would irreversibly *alter* the dynamical state. Implication: In quantum mechanics it is *not* generally true that the value of a dynamical quantity can be precisely measured without perturbing the evolution of the system in the process.

### Matter Waves

The de Broglie hypothesis: just as there are particle properties associated with “classical waves” of electromagnetism, so there are wave-like properties associated with material particles. Verification: Davisson and Germer showed that electrons could be made to exhibit wavelike interference and diffraction effects, just like light. In analogy to the photon, one is led to associate with a free material particle of momentum  $\vec{p}$ , a wave of wavevector  $\vec{k}$  related to it through the same relation  $\vec{p} = \hbar\vec{k}$  as applies to photons, and with a corresponding wavelength

$$\lambda = \frac{2\pi}{|k|}, \quad (1.14)$$

and frequency

$$\omega = \frac{E}{\hbar} = \frac{p^2}{2m\hbar}. \quad (1.15)$$

By applying our conclusions regarding light directly to the case of material particles one obtains, along with an additional evolution equation postulated by Schrödinger, what is often referred to as “Wave Mechanics”.

## 1.3 The Wave Mechanics of Schrödinger

### 1.3.1 Postulates of Wave Mechanics for a Single Spinless Particle

1. All possible information about the quantum state of a particle at time  $t$  is contained in a complex-valued **wave function**  $\psi(\vec{r}, t)$ . The wave function  $\psi(\vec{r}, t)$  gives the **probability amplitude** for finding the particle at the point  $\vec{r}$  at time  $t$ . Specifically, the probability  $dP$  of finding the particle in a differential volume element  $d^3r$  centered at  $\vec{r}$  at time  $t$  is proportional to the squared modulus of the corresponding probability amplitude:

$$dP = \rho(\vec{r}, t)d^3r = |\psi(\vec{r}, t)|^2 d^3r \quad (1.16)$$

The function  $\rho(\vec{r}, t) = |\psi(\vec{r}, t)|^2$  in this expression is the associated **probability density**. The normalization of the wave function is often chosen so that the probability of finding the particle somewhere in the universe is equal to 1. This necessitates the normalization condition

$$\int |\psi(\vec{r}, t)|^2 d^3r = 1, \quad (1.17)$$

i.e., the wave function is “square normalized to unity”.

2. For each observable or measurable quantity  $\mathcal{A}$  of the system there is associated a linear self-adjoint operator  $A$ , that action of which on the wave function  $\psi(\vec{r})$  is to replace it with another function  $\psi_A(\vec{r}) = A\psi$ . For example, the particle’s momentum  $\vec{p}$  is associated with the operator  $\vec{P} = -i\hbar\vec{\nabla}$ . When measuring any given observable  $A$ , there are only a certain set of values  $\{a\}$ , referred to as eigenvalues, which may be obtained. The set  $\{a\}$  of eigenvalues is referred to as the *spectrum* of  $A$ . For

each eigenvalue  $a$  there is at least one normalized wave function  $\phi_a(\vec{r})$ , referred to as an eigenfunction of  $\mathcal{A}$ , which satisfies the **eigenvalue equation** for the associated linear operator, i.e.,  $A\phi_a(\vec{r}) = a\phi_a(\vec{r})$ . The set of eigenfunctions associated with any observable are sufficiently **complete**, that the wave function  $\psi(\vec{r})$  for an arbitrary state of the system may be “spectrally decomposed”

$$\psi(\vec{r}) = \sum_{\{a\}} c_a \phi_a(\vec{r}), \quad (1.18)$$

into a linear superposition of the eigenstates associated with that observable, for a unique set of complex constants  $c_a$ . Normalization of the wave function  $\psi$  and the eigenfunctions  $\phi_a$  lead to a normalization condition for the amplitudes, i.e.,  $\sum_{\{a\}} |c_a|^2 = 1$ .

3. Measurement of  $A$  when the particle is in the state corresponding to the eigenfunction  $\phi_a(\vec{r})$  will yield the value  $a$  with unit probability. Indeed, it is only when the system is in a state represented by such an eigenfunction that it can properly be said to actually possess the property associated with that observable. The result of measuring the observable  $A$  on the system when it is in an arbitrary state  $\psi = \sum_{\{a\}} c_a \phi_a$ , will be one of the eigenvalues represented in the decomposition of that state. The probability of measuring a particular eigenvalue  $a$  is proportional to the square of the corresponding probability amplitude. In particular, with the normalization convention introduced above,

$$P(a) = |c_a|^2. \quad (1.19)$$

Thus,  $c_a$  is referred to as the **amplitude** that a measurement of  $A$  will yield the value  $a$ . Immediately after an ideal measurement which yields the value  $a$  for the observable  $A$ , the system will be in an eigenfunction  $\phi_a$  consistent with the value obtained. For this reason,  $c_a$  is also referred to as the amplitude that a measurement of  $A$  will find the system in the state  $\phi_a$ .

4. Between measurements the wave function evolves smoothly and deterministically according to **Schrödinger’s equation of motion**. For a single particle with no internal structure Schrödinger’s equation takes the form

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = H\psi(\vec{r}, t) \quad (1.20)$$

where the **Hamiltonian**  $H$  appearing in the evolution equation is a differential operator obtained from the corresponding classical Hamiltonian function  $H(\vec{r}, \vec{p}, t)$  by replacing all occurrences of the momentum  $\vec{p}$  by the **momentum operator**  $\vec{P} = -i\hbar\vec{\nabla}$ . Thus, for example, a particle of mass  $m$  moving in a scalar potential energy  $U(\vec{r}, t)$  has a classical Hamiltonian function

$$H(\vec{r}, \vec{p}, t) = \frac{p^2}{2m} + U(\vec{r}, t)$$

which leads to the usual form of the Schrodinger equation

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2 \nabla^2}{2m} \psi(\vec{r}, t) + U(\vec{r}, t) \psi(\vec{r}, t).$$

On the other hand, for a particle of charge  $e$  moving in an electromagnetic field with scalar potential energy  $U = e\phi(\vec{r}, t)$  and vector potential  $\vec{A}$  the classical Hamiltonian takes the form

$$H(\vec{r}, \vec{p}, t) = \frac{1}{2m} \left( \vec{p} - \frac{e}{c} \vec{A} \right)^2 + U(\vec{r}, t)$$



which gives the Schrodinger equation in the form

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \frac{1}{2m} \left( -i\hbar \vec{\nabla} - \frac{e}{c} \vec{A}(\vec{r}, t) \right)^2 \psi(\vec{r}, t) + U(\vec{r}, t) \psi(\vec{r}, t).$$

**Comments:** It should be mentioned that in writing the second and third postulates, as stated above, we have implicitly assumed that the spectrum of the observable  $A$  is **discrete**, i.e., the eigenvalues take on only isolated “quantized” values, and that the associated eigenfunctions are square-normalizeable to unity, like the wave function itself. In fact, many observables of interest (such as the particle’s position, momentum, and kinetic energy) have eigenvalues that can take on any value in some continuous set (or union of continuous sets). Such observables are said to have a **continuous spectrum**. Occasionally, we encounter observables that have a **mixed spectrum**, i.e., they have both a discrete part and a continuous part (the eigenfunctions of the hydrogen atom are a case in point, with the bound electronic states corresponding to the discrete part, and the unbound, or “scattering states” being associated with a continuum of positive allowed energies). In the case of an observable with a continuous spectrum it turns out that the eigenfunctions are not square-normalizeable to unity, and that other mathematically convenient normalization conventions are required. Expansion of the wave function  $\psi$  in the appropriately normalized eigenfunctions  $\phi_a(\vec{r})$  of an observable with a continuous spectrum takes the form of a “continuous summation”, i.e., an integral, so that

$$\psi(\vec{r}) = \int da c(a) \phi_a(\vec{r}) \quad (1.21)$$

where the integration is over the entire range of eigenvalues in the spectrum of the observable. Then, rather than talk about a probability  $P(a)$ , it is more appropriate to speak of the probability density

$$\rho(a) = |c(a)|^2 \quad (1.22)$$

to obtain an eigenvalue in the range  $a$  to  $a + da$  upon measurement of  $A$ .

In fact, with this modification, much of the description in the first postulate can be viewed as an application of the second and third postulates to a specific observable, namely that corresponding to the particle’s location  $\vec{r}$  in space, which in the Schrödinger theory is associated with the linear operator  $\vec{R}$  that simply multiplies the wave function by  $\vec{r}$ , i.e.,

$$\vec{R}\psi(\vec{r}) = \vec{r}\psi(\vec{r}). \quad (1.23)$$

The *spectrum* of the position observable  $\vec{R}$  is the set of all vectors  $\{\vec{r}\} \in R^3$  where a particle could be found if we attempted to measure its position. To each such point  $\vec{r}'$  in space, there is an *eigenfunction* of position  $\phi_{\vec{r}'}(\vec{r})$ , corresponding to a particle which is known, with unit probability to be at that point. Leaving questions of normalization aside, an obvious candidate for such an eigenfunction is the delta function located at the point  $\vec{r}'$ , i.e.,

$$\phi_{\vec{r}'}(\vec{r}) = \delta(\vec{r} - \vec{r}'). \quad (1.24)$$

(See the appendix of this chapter for a discussion of the properties of the delta function.) The principle of spectral decomposition then demands that the wave function  $\psi(\vec{r})$  representing an arbitrary dynamical state be expandable in these eigenfunctions of the position operator. That such a decomposition is, in fact, possible follows from the identity

$$\psi(\vec{r}) = \int d^3 r' \psi(\vec{r}') \phi_{\vec{r}'}(\vec{r}) = \int d^3 r' \psi(\vec{r}') \delta(\vec{r} - \vec{r}'), \quad (1.25)$$

which is precisely of the form (1.21) with the continuous expansion coefficients  $c(\vec{r})$  being given by the values of the wave function itself. It follows from this decomposition, then, that  $\psi(\vec{r})$  represents the amplitude for the particle to be found at  $\vec{r}$ , with  $|\psi(\vec{r})|^2$  giving the associated probability density.

The postulates stated above have also been purposely simplified to avoid some important technical questions that arise when, for example, there are more than one linearly independent eigenfunction associated with a given observable. Such details will be ironed out in the next chapter where we formally present the postulates of quantum mechanics in a way that is applicable to *arbitrary* quantum mechanical systems. The postulates given above will then be seen to represent a special, but important, case of the more general formalism. Indeed, we will often find it useful to illustrate the general features of the theory using examples taken from the quantum mechanics of a single particle moving in 3-dimensions. To that end, and to more fully set the stage for the formal development of the next chapter, it is useful to first spend a little time exploring some of the consequences of the postulates enumerated above.

### 1.3.2 Schrödinger's Mechanics for Conservative Systems

When the potential  $V(\vec{r})$  is independent of time (so that  $\partial V/\partial t = 0$ ) the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi \quad (1.26)$$

is governed by a Hamiltonian operator

$$H = -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) \quad (1.27)$$

which is itself independent of time. It is customary under these circumstances to employ the method of separation of variables and thus to seek solutions to Schrödinger's equation having the *separable* form

$$\psi(\vec{r}, t) = \phi(\vec{r})\chi(t). \quad (1.28)$$

Substitution into Schrödinger's equation

$$i\hbar\phi\frac{d\chi}{dt} = \chi H\phi \quad (1.29)$$

and a subsequent division by  $\psi = \phi\chi$  yields

$$\frac{i\hbar}{\chi}\frac{d\chi}{dt} = \frac{1}{\phi}H\phi \quad (1.30)$$

Note: the right hand side is a time-independent function of  $\vec{r}$ ; the left-hand side is independent of  $\vec{r}$ . They both must equal some constant,  $E$  having units of energy, thus

$$\frac{i\hbar}{\chi}\frac{d\chi}{dt} = \frac{1}{\phi}H\phi = E = \hbar\omega_E. \quad (1.31)$$

Here we have introduced another form of this constant  $\omega_E = E/\hbar$  having units of frequency.

The time-dependence of the assumed solution is governed by the first-order equation

$$\frac{i\hbar}{\chi}\frac{d\chi}{dt} = E = \hbar\omega_E \quad (1.32)$$

which has the solution

$$\chi_E(t) = \chi_E(0) \exp\left(-\frac{iEt}{\hbar}\right) = \chi(0)e^{-i\omega_E t} \quad (1.33)$$

A convenient choice is to set  $\chi(0) = 1$ , letting  $\phi(\vec{r})$  absorb any multiplicative constants. Thus, if separable solutions exist, they will have the form

$$\psi_E(\vec{r}, t) = \phi_E(\vec{r})e^{-i\omega_E t} \quad (1.34)$$

where the spatial function obeys a second-order differential equation which we can write in operator form as

$$H\phi_E(\vec{r}) = E\phi_E(\vec{r}), \quad (1.35)$$

which, after re-inserting the spatial dependence, becomes

$$-\frac{\hbar^2}{2m}\nabla^2\phi_E + V(\vec{r})\phi_E = E\phi_E(\vec{r}). \quad (1.36)$$

### Comments:

1. This latter equation is the **eigenvalue equation** for the **Hamiltonian** operator  $H$ . In Schrödinger's theory,  $H$  represents that observable associated with the **total energy** of the system (as does the corresponding function in classical mechanics). Some author's refer to this last equation as "Schrödinger's equation", or the "time-independent Schrödinger equation". To avoid confusion, we shall reserve the term "Schrödinger equation" *exclusively* for the *evolution equation* appearing in the postulates, and simply refer to this last equation as the "energy eigenvalue equation".
2. In any specific problem, various physical conditions can restrict the values of  $E$  for which physically acceptable solutions exist. Such *regularity* conditions include, e.g., normalizability, differentiability, and the requirement that there be finite energy content in any finite region of space.
3. The values of  $E$  for which acceptable solutions exist we identify with the energy eigenvalues of the system. A measurement made of the energy when the system is in the state  $\psi_E$  will yield the value  $E$  with unit probability. The set of allowed energies  $\{E\}$  is the spectrum of  $H$ , or the energy spectrum of the system.
4. Such energy eigenstates are also commonly referred to as **stationary states** since the associated probability density function

$$\rho(\vec{r}, t) = |\psi(\vec{r}, t)|^2 = |\phi_E(\vec{r})e^{-i\omega_E t}|^2 = |\phi_E(\vec{r})|^2 \quad (1.37)$$

is, in fact, independent of time, as are any other measurable properties.

### 1.3.3 The Principle of Superposition and Spectral Decomposition

The linearity of Schrödinger's equation assures us that any superposition of stationary solutions is also a solution to the evolution equation. Nonetheless, one may ask: Is such a superposition of stationary solutions a solution to the energy eigenvalue equation? Is such a superposition of stationary solutions a stationary solution? Generally, the answer is "no", for both of these questions. To explore this, let us enumerate the acceptable stationary solutions using an index  $n = 1, 2, \dots$ . Thus, we assume solutions to the energy eigenvalue equation of the form

$$H\phi_n = E_n\phi_n = \hbar\omega_n\phi_n \quad (1.38)$$

which correspond to stationary solutions of Schrödinger's equation of the form

$$\psi_n(\vec{r}, t) = \phi_n(\vec{r})e^{-i\omega_n t}. \quad (1.39)$$

A general solution to Schrödinger's equation can then be written as a linear combination

$$\psi(\vec{r}, t) = \sum_n c_n \phi_n(\vec{r}) e^{-i\omega_n t} \quad (1.40)$$

where  $\omega_n = E_n/\hbar$ , and the  $c_n$  are arbitrary complex numbers. Such a state is not stationary, nor is it a state of well defined energy, since it is a superposition of states of many different energies, but it does obey Schrödinger's equation of motion (Proof: left as an exercise.) The principle of spectral decomposition (as applied to the energy of the system which is assumed to be an observable) demands that an arbitrary state of the system be expressible as a superposition of energy eigenstates. Note that if we know the numbers  $c_n$  associated with the wave function at some arbitrary time  $t = 0$ , during which

$$\psi(\vec{r}, 0) = \sum_n c_n \phi_n(\vec{r}) = \sum_n c_n(0) \phi_n(\vec{r}) \quad (1.41)$$

then at later times we can write

$$\psi(\vec{r}, t) = \sum_n c_n(t) \phi_n(\vec{r}) \quad (1.42)$$

where  $c_n(t) = c_n e^{-i\omega_n t}$ , thereby guaranteeing that such a decomposition in the eigenfunctions  $\{\phi_n(\vec{r})\}$  is possible at all later times. These developments raise another interesting point. According to the postulates, the dynamical state is specified through the wave function  $\psi(\vec{r}, t)$ . But now we see that if we know the energy eigenfunctions  $\{\phi_n(\vec{r})\}$  we can specify the wave function in *two* ways:

1. Specify  $\psi(\vec{r})$  for all values of  $\vec{r}$ , or
2. Specify the coefficients  $c_n$  for all values of the index  $n$ .

In either case we have to specify an infinite number of complex values. This allows us to envision representing the dynamical state using, e.g., a column vector

$$\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \\ \vdots \end{pmatrix} \quad (1.43)$$

On the other hand, this is really no different than arranging all the values of the wave function in some sort of array

$$\begin{pmatrix} \psi(\vec{r}_1) \\ \psi(\vec{r}_2) \\ \vdots \\ \psi(\vec{r}_n) \\ \vdots \end{pmatrix} \quad (1.44)$$

except for the fact that the values defining the wave function are indexed by the *continuous* (or *noncountable*) infinity of points in  $R^3$  rather than by the discrete (or countable) infinity of points in the set  $Z$  of integers. Thus, although it initially seems more natural to refer to and think of the collection of values  $\{\psi(\vec{r})\}$  as a *function* rather than a column vector, this difference is not really very large.

The main point of this comparison is to introduce the idea that the actual “state” of the quantum system may be associated with a more *fundamental* mathematical object than the wave function introduced in Schrödinger’s version of quantum mechanics. Indeed, the wave function is just one possible (infinite) set of numbers that can be used to represent the underlying object (which we will refer to as a state vector), in the same way, e.g., that displacement vectors  $\vec{r}$  in  $R^3$  have an existence that is independent of the particular coordinates (and coordinate system) which are used to represent them. We will pursue this idea quite vigorously in a short while. For now, however, it is useful to develop an example.

#### 1.3.4 The Free Particle

We consider a particle subject to no forces at all, i.e., a free particle. The potential associated with a particle subject to no forces is a constant, which we can take to be zero. In this limit the energy operator consists only of the kinetic energy operator

$$T \equiv H_0 \equiv -\frac{\hbar^2}{2m}\nabla^2 \quad (1.45)$$

and the energy eigenvalue equation  $H\phi = E\phi$  takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\phi_E(\vec{r}) - E\phi_E(\vec{r}) = 0. \quad (1.46)$$

Multiplying through by  $-2m/\hbar^2$ , we can write this in the form

$$\nabla^2\phi_k + k^2\phi_k = 0 \quad (1.47)$$

where we have re-expressed the energy using a constant

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (1.48)$$

in terms of which

$$E \equiv E_k = \frac{\hbar^2 k^2}{2m}. \quad (1.49)$$

In this form, the free particle energy eigenvalue equation is referred to as the *Helmholtz* equation, which has solutions that can be separated in many different coordinates systems, but for the moment we will focus on applying the method of separation of variables to the cartesian coordinates  $x, y$ , and  $z$ . That is, we assume that

$$\phi_k(\vec{r}) = X(x)Y(y)Z(z) \quad (1.50)$$

and substitute into the Helmholtz equation to obtain (after dividing by  $\phi = XYZ$  )

$$\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} = -k^2 \quad (1.51)$$

This equation demands that the individual terms on the left each equal a constant, which we denote by  $-k_x^2$ ,  $-k_y^2$ , and  $-k_z^2$ , respectively, the sum of which add up to  $-k^2$ . Thus we end up with three ordinary differential equations

$$X'' + k_x^2 X = 0 \quad (1.52)$$

$$Y'' + k_y^2 Y = 0 \quad (1.53)$$

$$Z'' + k_z^2 Z = 0 \quad (1.54)$$

which have the solutions

$$X(x) = A_x e^{ik_x x} \quad (1.55)$$

$$Y(y) = A_y e^{ik_y y} \quad (1.56)$$

$$Z(z) = A_z e^{ik_z z} \quad (1.57)$$

The product of these gives the free particle energy eigenfunctions in the form we seek:

$$\phi_{\vec{k}}(\vec{r}) = A e^{i(k_x x + k_y y + k_z z)} = A e^{i\vec{k} \cdot \vec{r}} \quad (1.58)$$

where we have introduced a vector  $\vec{k}$ , with components  $k_x$ ,  $k_y$ , and  $k_z$ , which labels the particular solution. Note that these second order differential equations actually have two linearly independent solutions, e.g.,  $A e^{\pm i k_x x}$ , but if we interpret the solution  $A e^{+i k_x x}$  as a plane wave traveling with wavevector  $k_x$ , then we automatically obtain *both* solutions by allowing  $k_x$  to take both positive and negative values. Thus, the complete set of solutions is obtained by considering all possible wavevectors  $\vec{k} \in R^3$ . Combining this with the time dependence associated with this energy eigenstate, we obtain the stationary solutions for the free particle, namely

$$\psi_{\vec{k}}(\vec{r}, t) = A e^{i\vec{k} \cdot \vec{r}} e^{-i\omega_k t} = A e^{i(\vec{k} \cdot \vec{r} - \omega_k t)} \quad (1.59)$$

where

$$\omega_k = \frac{E_k}{\hbar} = \frac{\hbar k^2}{2m}. \quad (1.60)$$

Thus, the free particle energy eigenstates are plane waves traveling along the direction associated with the wavevector  $\vec{k}$  which labels the solution. Note that the energy spectrum associated with the free particle is the set of values

$$E_{\vec{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \vec{k} \cdot \vec{k} \quad (1.61)$$

which includes all possible positive energies, as in the classical theory. We exclude negative energies, which would require imaginary wavevectors, because they would be associated with wavefunctions that would grow exponentially in some directions of space, and thus are unsuitable. As it is, the wave functions that we have produced are not entirely well-behaved, since they are not square-normalizable. We will address this difficulty in a moment. First, we observe that these free-particle eigenstates (i.e., eigenstates of the free-particle Hamiltonian) are also eigenstates of the momentum operator,

$$\vec{P} = -i\hbar \vec{\nabla}, \quad (1.62)$$

which is a *vector* operator, i.e., a collection of three operators  $\{P_x, P_y, P_z\}$  that transform like the components of a vector. The eigenvalue equation for the momentum operator takes the form

$$\vec{P}\phi = \vec{p}\phi, \quad (1.63)$$

where the vector  $\vec{p}$  in this expression represents a vector eigenvalue appropriate to the vector operator. Our plane wave solutions obey this equation, since

$$\vec{P}\phi_{\vec{k}}(\vec{r}) = -i\hbar \vec{\nabla} A e^{i\vec{k} \cdot \vec{r}} = -i\hbar (i\vec{k}) A e^{i\vec{k} \cdot \vec{r}} = \hbar \vec{k} A e^{i\vec{k} \cdot \vec{r}} \quad (1.64)$$

or

$$\vec{P}\phi_{\vec{k}}(\vec{r}) = \vec{p}_{\vec{k}} \phi_{\vec{k}}(\vec{r}), \quad (1.65)$$

where  $\vec{p}_{\vec{k}} = \hbar \vec{k}$ . Thus, Schrödinger's wave mechanics recovers, as a special case, the hypothesis of deBroglie: with every free material particle of momentum  $\vec{p}$ , we can associate a plane wave of wavevector  $\vec{k} = \vec{p}_{\vec{k}}/\hbar$ , and frequency  $\omega = \hbar k^2/2m$ .

### Normalization Conventions for Free Particle Eigenstates

We now turn to the question of the normalization constant. The question is, what value should we assign to the constant  $A$  in (1.59) so that the probability of finding the particle somewhere in the universe is equal to one. A naive attempt to determine the magnitude of the normalization constant would lead us to evaluate the integral

$$\int d^3r \rho(\vec{r}, t) = \int d^3r |\psi_{\vec{k}}(\vec{r}, t)|^2 = \int d^3r |A|^2, \quad (1.66)$$

which illustrates the problem. If  $|A|^2$  is finite then the integral over all space diverges. If we set  $A$  equal to zero, then the wave function vanishes everywhere. Does this mean that our solutions are, in fact, unacceptable? We are reluctant to let them go, since they recover the classical spectrum so nicely, and moreover, they do allow us to obtain information about the *relative probabilities* of finding the particle in some region of space. That is, if the particle is in one of these free particle eigenstates, then the probability to find the particle in any given volume is simply proportional to the volume of the associated region. The only problem is that, since the particle can be *anywhere*, the relative probability of finding it in some *particular* volume is exceedingly small when compared to the volume of the universe. Physically, this does not seem so implausible. We are thus encouraged to seek a reasonable *normalization convention* for these states that will allow us to deal with them in a mathematically consistent fashion. In fact, two such conventions are commonly adopted:

1. *Box Normalization* - In this convention, the wave function is assumed to be confined to a very large square box of volume  $V$ , with appropriate boundary conditions imposed at the edges of the box. A useful convention is to make the value of the wave function equal at opposite faces, a choice referred to as *periodic boundary conditions*. Thus, one sets

$$\phi_{\vec{k}}(\vec{r}) = \begin{cases} V^{-1/2} e^{i\vec{k}\cdot\vec{r}} & \text{for } \vec{r} \in V \\ 0 & \text{for } \vec{r} \notin V \end{cases} \quad (1.67)$$

In this way the wave function is square-normalized to unity. Unfortunately, this convention has the drawback that it *discretizes* the free particle spectrum of both the energy and the momentum, since the boundary conditions require that only wavelengths that just fit within the dimensions of the box are allowed. This quantization of the free particle spectrum is unfortunate, and can be avoided by employing the following alternative convention.

2. *Delta Function Normalization* - In this approach, one gives up the attempt to produce a square-normalized wave function, but instead chooses the normalization constant for mathematical convenience. Specifically, we choose the constant  $A$  so that the set of functions  $\{\phi_{\vec{k}}(\vec{r})\}$  for all wavevectors  $\vec{k}$  form a *generalized orthonormal set* of functions on  $R^3$ .

To understand what this means we need to define the concept of an orthonormal set.

**Orthonormal Set of Functions** - A set of functions  $\{\phi_n(x)\}$  labeled by a discrete index  $n$  is said to form an orthonormal set of functions on the interval  $(a, b)$  if

$$\int_a^b dx \phi_n^*(x) \phi_m(x) = \delta_{n,m} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{if } n \neq m \end{cases} . \quad (1.68)$$

Similar definitions can obviously be given for an orthonormal set of functions on the whole axis, or for functions in higher dimensions. Thus, a set of functions  $\{\phi_n(\vec{r})\}$  labeled by a discrete index  $n$  is said to form an orthonormal set of functions on  $R^3$  if

$$\int d^3 r \phi_n^*(\vec{r}) \phi_m(\vec{r}) = \delta_{n,m}, \quad (1.69)$$

where here and everywhere which follows, *an integral with no limits implies a definite integration over all values associated with the integration variable* (in this case over all vectors in  $R^3$ ). Note that the box-normalization convention described above produces a discrete set of functions which form an orthonormal set over the volume of the box in which they are contained.

**Generalized Orthonormal Set** - A set (or family) of functions  $\{\phi_\alpha(x)\}$  labeled by a *continuous* index  $\alpha \in R$  is said to form an orthonormal set of functions on the real axis if

$$\int dx \phi_\alpha^*(x) \phi_{\alpha'}(x) = \delta(\alpha - \alpha'). \quad (1.70)$$

This is clearly the continuous analog of the expression above involving the Kronecker delta function defined on the integers. Similar definitions can obviously be given for an orthonormal set of functions in higher dimensions. Thus, a set of functions  $\{\phi_\alpha(\vec{r})\}$  labeled by a continuous index  $\alpha$  is said to form an orthonormal set of functions on  $R^3$  if

$$\int d^3 r \phi_\alpha^*(\vec{r}) \phi_{\alpha'}(\vec{r}) = \delta(\alpha - \alpha'). \quad (1.71)$$

A set of functions obeying this relation we will refer to as being Dirac normalized. This is clearly the sort of thing which we need for the plane waves, since it implies that when  $\alpha = \alpha'$ , the modulus-squared integral diverges (as do the plane waves for a nonzero value of  $A$ ). This definition specifies the particular way in which the integral diverges for two neighboring members of the set as one approaches the other (i.e., in a way which is proportional to the delta function). To apply this to the plane waves, we simply need to generalize the continuous index  $\alpha$  into a vector  $\vec{k}$  drawn from a continuous set of vectors in  $R^3$ . Thus, the Dirac normalization condition for the plane waves involves choosing the constant  $A$  such that

$$\int d^3 r \phi_{\vec{k}}^*(\vec{r}) \phi_{\vec{k}'}(\vec{r}) = \delta(\vec{k} - \vec{k}'). \quad (1.72)$$

Inserting the expression for the plane waves we obtain the normalization condition

$$\int d^3 r \phi_{\vec{k}}^*(\vec{r}) \phi_{\vec{k}'}(\vec{r}) = |A|^2 \int d^3 r e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \delta(\vec{k} - \vec{k}') \quad (1.73)$$

In this expression, the three dimensional delta function must be constructed from the product of three delta functions in  $k_x, k_y,$  and  $k_z$ . A change of variable in the plane wave representation of the delta function

$$\delta(x - x') = \int \frac{dk}{2\pi} e^{ik(x-x')} \quad (1.74)$$

in which we interchange the roles of  $k$  and  $x$  leads to the result that

$$\int \frac{dx}{2\pi} e^{i(k'_x - k_x)x} = \delta(k_x - k'_x) \quad (1.75)$$



and similarly for the remaining cartesian components of  $\vec{k}$ . Combining these results we deduce that

$$\int \frac{d^3 r}{(2\pi)^3} e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \delta(\vec{k} - \vec{k}'). \quad (1.76)$$

Comparison with our normalization relation reveals  $|A|^2 = (2\pi)^{-3}$  to be the relation we seek. Choosing  $A$  real and positive we deduce that the set of Dirac normalized plane waves takes the form

$$\phi_{\vec{k}}(\vec{r}) = \frac{e^{i\vec{k} \cdot \vec{r}}}{(2\pi)^{3/2}}. \quad (1.77)$$

With this convention for the free particle eigenstates we retain a continuous spectrum for both momentum and energy, but we give up the strict probabilistic interpretation associated with the wave function. In practice, this does not turn out to be so important, since a real particle is inevitably in a superposition of free particle states. Such a superposition of states *can* be normalized.

We will often find it convenient to work through examples in lower dimensions. Thus, e.g., we will have occasion to refer to a particle moving in one-dimension, and therefore described by a wave function  $\psi(x)$ . A free-particle in one dimension is then associated with eigenstates which are one-dimensional plane waves. A review of the analysis given above reveals that the appropriate normalization for one-dimensional plane waves is

$$\phi_k(x) = \frac{e^{ikx}}{(2\pi)^{1/2}}. \quad (1.78)$$

### 1.3.5 Superpositions of Plane Waves and the Fourier Transform

The superposition principle implies that a superposition of stationary solutions to the free particle Schrödinger equation is itself a solution to that equation. Thus, a possible solution to Schrödinger's equation of motion can be written

$$\psi(\vec{r}, t) = \int d^3 k \hat{\psi}(\vec{k}) \phi_{\vec{k}}(\vec{r}) e^{-i\omega_k t}. \quad (1.79)$$

This state evolves from another one which at  $t = 0$  has the form

$$\psi(\vec{r}) = \int d^3 k \hat{\psi}(\vec{k}) \phi_{\vec{k}}(\vec{r}). \quad (1.80)$$

It is useful to write this expansion in the form

$$\psi(\vec{r}, t) = \int d^3 k \hat{\psi}(\vec{k}, t) \phi_{\vec{k}}(\vec{r}), \quad (1.81)$$

where  $\hat{\psi}(\vec{k}, t) = \hat{\psi}(\vec{k}, 0)e^{-i\omega_k t}$  is the amplitude (in this continuous superposition) of the state associated with the free particle eigenstate of wavevector  $\vec{k}$ . In the theory,  $dP = \rho(\vec{k})d^3 k = |\hat{\psi}(\vec{k})|^2 d^3 k$  is the probability that a momentum measurement will yield a value in an infinitesimal neighborhood of  $\vec{p}_{\vec{k}} = \hbar\vec{k}$ . The principle of spectral decomposition demands, in fact, that an arbitrary state of the system admit such an expansion in free particle eigenstates. This is actually guaranteed by Fourier's theorem which states that any sufficiently regular function  $\psi(\vec{r}, t)$  admits a Fourier expansion

$$\psi(\vec{r}, t) = \int \frac{d^3 k}{(2\pi)^{3/2}} \hat{\psi}(\vec{k}, t) e^{i\vec{k} \cdot \vec{r}} \quad (1.82)$$

in plane waves, where the expansion function  $\hat{\psi}(\vec{k}, t)$ , referred to as the Fourier transform of  $\psi(\vec{r}, t)$ , is given by the relation

$$\hat{\psi}(\vec{k}, t) = \int \frac{d^3 r}{(2\pi)^{3/2}} \hat{\psi}(\vec{r}, t) e^{-i\vec{k}\cdot\vec{r}}. \quad (1.83)$$

Verification of these expressions follows from the plane-wave expansion for the delta function. That is, if we insert the expansion for  $\hat{\psi}(\vec{k}, t)$  into that for  $\psi(\vec{r}, t)$ , being careful to use a different integration variable

$$\psi(\vec{r}, t) = \int \frac{d^3 k}{(2\pi)^{3/2}} \int \frac{d^3 r'}{(2\pi)^{3/2}} \psi(\vec{r}', t) e^{-i\vec{k}\cdot\vec{r}'} e^{i\vec{k}\cdot\vec{r}} \quad (1.84)$$

and re-order the integration

$$\psi(\vec{r}, t) = \int d^3 r' \psi(\vec{r}', t) \int \frac{d^3 k}{(2\pi)^3} e^{-i\vec{k}\cdot(\vec{r}'-\vec{r})} \quad (1.85)$$

we recognize the expansion for  $\delta(\vec{r}-\vec{r}')$ . Thus,

$$\psi(\vec{r}, t) = \int d^3 r' \psi(\vec{r}', t) \delta(\vec{r}-\vec{r}') = \psi(\vec{r}, t). \quad (1.86)$$

Note, that a plane wave expansion of the wave function is always possible, even when the Hamiltonian is *not* that associated with a free particle, since all we are doing, in a sense, is expanding in the eigenstates of the momentum operator, or equivalently, of the kinetic energy operator. Since these are observable quantities, the principle of spectral decomposition demands that such an expansion be possible independent of the Hamiltonian of the system. In the particular case in which the Hamiltonian *is* that of a free particle, however, we know in addition that the time dependence has a particularly simple form, namely,

$$\hat{\psi}(\vec{k}, t) = \hat{\psi}(\vec{k}, 0) e^{-i\omega_k t}, \quad (1.87)$$

where  $\omega_k = E_k/\hbar = \hbar k^2/2m$ .

We conclude with the observation that this example of the free particle has again shown that there is more than one way to represent the dynamical state of the system. By Schrödinger's *postulate*, the dynamical state at time  $t$  is described by the wave function  $\psi(\vec{r}, t)$ . However, it is clear from the discussion above, that all information in the wave function is also contained in its Fourier transform: if we have  $\hat{\psi}(\vec{k}, t)$  we can always construct  $\psi(\vec{r}, t)$ . This must be true for *any* observable, not just momentum and/or kinetic energy. Hence the particular set of numbers used to represent the state of the system can be chosen to correspond to a particular observable which one might be interested in analyzing. This is similar to the idea of choosing a convenient coordinate system in  $R^3$  in which to solve a particular problem in classical mechanics. In what follows, we construct a formalism for quantum mechanics which does not choose at the outset any particular coordinate system, but which recognizes that the wave function  $\psi(\vec{r}, t)$ , its Fourier transform  $\hat{\psi}(\vec{k}, t)$ , or any other set of expansion coefficients  $\{c_n(t)\}$ , simply give a means of *representing* an object (what we will refer to as the state vector) that has an existence independent of the means that may be chosen to do so.