

A Development of Quantum Mechanics

Based on Symmetry Considerations

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George H. Duffey

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Preface

The theory of quantum mechanics continues to appear arbitrary and abstruse to new students; and to many veterans, it has become acceptable and useable only because it is familiar. Yet, this theory is at the basis of all modern physics, chemistry, and engineering, describing, as it does, the behavior of the submicroscopic particles making up all matter. So it needs to be presented more effectively to a diverse audience.

The primary question is, I believe, 'What can be considered self-evident?' Indeed, what do certain key experiments reveal about the workings of nature? How can we consider that some probabilities are not a result of our ignorance, but instead, fundamental properties?

We must pay particular attention to the subject of what we can do, what we cannot do, and what we can and cannot observe. We can prepare a homogeneous beam of almost independent particles by boiling electrons out of a metal and accelerating them by a given potential drop. We cannot follow an electron individually in the beam without introducing conditions that destroy the beam's homogeneity, but we can determine when electrons arrive at a given position.

Such arrivals are found to be governed by probability. In the homogeneous beam, the resulting probability density ρ is constant. There is thus symmetry over displacement along the beam, and similarly, over time. But to describe propagation along the beam, we need an independent function. A simple choice is to consider ρ , the square of the absolute value of a complex function Ψ . The phase of the function is involved in describing propagation.

To be consistent, we make each infinitesimal change $d\Psi$ meet the symmetry requirements over space and time. We also suppose that, for pure motion in one direction, each part of Ψ exerts the same effect on $d\Psi$ as each other part. Furthermore, the influences on $d\Psi$ vary directly with Ψ . We thus have a simple symmetry over Ψ .

To determine whether the constructed form is suitable, we again turn to experiment. Investigators find that homogeneous beams are diffracted exactly as this Ψ would be. Furthermore, one of the parameters in the theory satisfies de Broglie's equation, which photons in light are known to obey.

From photoelectric determinations, we induce a relationship for the other

parameter. In Chapter 3 we consider how the arguments need to be modified to allow for a varying potential. In Chapter 4 this discussion is expanded to cover motion over more than one variable.

Translatory motion is considered first because it is the simplest. Rotatory motion is in many respects similar, so it is considered next. Symmetry arguments are invoked in constructing the variation of Ψ over θ from that over φ . The simplest kind of varying field is that for the harmonic oscillator; so its treatment appears next. Then we go to the hydrogen-like atom, the model in terms of which other atoms and nuclei are understood.

Operator theory is developed only after we have gained some confidence in treating the simpler systems.

Because particles of the same species are indistinguishable, a corresponding symmetry exists in multiparticle systems. This has profound effects on the properties of such systems in atoms, molecules, and thermodynamic arrays.

The material is all presented at a level suitable for junior and senior students in physics and chemistry. Engineers who work with molecular, atomic, and electronic processes would also benefit from the course.

There are nearly 20 problems at the end of each chapter. These have been developed through actual use in undergraduate classes.

General Introduction

In our early years, we develop a commonsense view of the world based on inductions from the experiences we have in common with all other people. Each individual conceives a reality external to himself or herself in which objects occupy definite positions in space at any given time. These move, and accelerate or decelerate, in response to the action of forces.

The replacement of qualitative observations with quantitative ones, made with the help of various instruments, has led to more and more profound inductions: the science of geometry developed from the measurement of agricultural fields and other areas; Newtonian mechanics developed from astronomical observations and measurements; Maxwellian electromagnetism developed from electrical studies and measurements; and the Law of Definite Proportions, an indirect support for the atomic theory of matter developed from chemical measurements.

When particles of matter were found to make tracks through supersaturated vapor, and in a photographic plate, the atomic theory seemed to be confirmed. However, no mechanics in which electrons, protons, or neutrons traced out individual mathematical curves proved to be satisfactory. A revolution in physical science was necessary. This developed slowly. In order to explain black-body radiation, Planck had to assume that a solid transferred energy to the electromagnetic field in discrete amounts, quanta. Einstein suggested that such quanta persisted in the field as photons and was thus able to explain the photoelectric effect. The young de Broglie saw that Einstein's equation implied a relationship between wavelength and particle momentum. He suggested that this might also apply to particles with a rest mass. Finally, Heisenberg and Schrödinger developed a suitable mechanics for such particles.

Now, all these theories are induced from experimental observations. Consequently, they appear only as a way of explaining the data on which they are based. New results, at a deeper level, may very well require modifications or additions — even a new revolution. Study the following material with these reservations in mind.

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Chapter 1

Quantization of Translatory Motion

1.1. Background Remarks on Time and Space

Each of us learns about the physical world through (a) experiencing various processes in one's own body, (b) interacting with external objects close at hand and far away, (c) constructing and manipulating devices, (d) observing and measuring reactions of the resulting instruments, and (e) studying accounts of the experiences, manipulations, and measurements of others.

A person's mind, first of all, notes an *order* in impressions that are recorded. Each perception is recognized as occurring either before, simultaneously with, or after each other one. The senses also recognize mechanisms that repeat a certain process again and again. The cycles of such a process occur in sequence and can be counted. Furthermore, an observer can associate any given stimulus with a particular cycle, as long as the mechanism is operating. Since parameters in the machine may presumably be altered to make the length of a cycle as small as the observer wishes, there appears to be no limit to the precision with which he can thus pinpoint a given event.

An engineer can design a cyclic mechanism to be nearly free of secular changes and split each of its cycles into parts that are apparently equivalent in duration. The resulting machine is called a clock. Experimenters find that a good mechanism does not seem to be affected by a change in position alone. A constant times the number of cycles, or fractional cycles, executed by the clock within a given interval is taken as the *time* to be associated with the interval.

A second clock that behaves as the first one can be constructed. This can be synchronized with the first clock in the neighborhood of a given body. An experimenter can then move the second clock slowly to a different body to establish a time scale there corresponding to that already existing on the first body. Reducing the sizes of the bodies probably does not destroy the possibility of making this correspondence; in our calculations we will presume that it can be done.

The mind also receives evidence of the *coexistence* of things through the eyes, ears, and tactile nervous system. Furthermore, it finds that the sources of the stimuli map onto a three-dimensional *space* at any given time. Measuring rods, compasses, and protractors can be constructed and manipulated to study this

space. Insofar as an observer can tell, such devices are not altered by a change in position alone, or by a change in time. Measurements with such tools show that the Pythagorean theorem holds to a high degree of accuracy in macroscopic situations. So for these at least, the space is Euclidean and Cartesian coordinate frames are adequate.

A person can keep such a frame in uniform rectilinear motion with respect to three or more noncolinear force-free bodies that maintain constant separations from each other. The frame is then said to be *inertial*. Each reference frame that we will employ will not differ in the pertinent properties from an inertial system during the significant intervals of time.

With available rays, an observer can only survey macroscopic and microscopic parts of space. The submicroscopic elements making up any discernible region need not be divisible into an arbitrary number of parts and may contain deviations from the Pythagorean theorem, as long as the elements fit together to yield the apparently Euclidean regions that are found. Similarly, the subchronometric elements of time add to give an apparently smooth uniform flow of the variable t ; but each such small element need not be infinitely divisible and may fluctuate from the corresponding element at another location in some unknown manner. Since these deviations from uniformity and homogeneity are not directly observable, we will assume that they are not present. However, they might have to be considered in a more comprehensive theory.

A macroscopic object can be broken into smaller parts, each of the parts divided into still smaller parts, and so on, at any given time. At some stage in the process, however, one reaches seemingly indivisible units that can be associated with separated points in space. These basic constituents of matter are called *particles*. Similar to an object, a particle is characterized by a mass and a charge. Furthermore, it may possess a property analogous to angular momentum — a spin — and classifying attributes such as hypercharge.

1.2. The Statistical Nature of Position, Velocity, and Momentum

In classical mechanics, it is assumed that each particle in a given system moves as a *point* through a space that is locally Euclidean and through a time that is uniform. A definite, smooth *curve* is traced out by the particle at a determinable varying rate. This curve is called the path or trajectory of the particle.

No device can locate a particle and determine its velocity and momentum at any given time with exactness. Not only are there errors in transforming the interactions with the particle to numbers, but the interactions themselves introduce errors. Classically, the uncertainties were attributed to the measurement process. Calculations of various observable effects proceeded. Many of these failed, however.

The interchange of energy between vibrational modes of a solid and the electromagnetic field did not follow the classical laws. Interactions of the electromagnetic field with electrons in a molecule or in a condensed phase resulted in discontinuous

changes. The existence of stable atomic and molecular states could not be explained. Little could be done with nuclear states. The behavior of such a simple system as a homogeneous beam of particles was inexplicable.

On the other hand, considering some of the uncertainty to be an essential attribute of the particles leads to a viable theory. A person does violence to a system of particles when he assumes that each follows a definite trajectory.

In our analysis, we will assume that the space and time of the laboratory can be infinitely subdivided, as in elementary calculus, and imposed on the system under consideration. And, if a particle were at a certain point in this space at a certain time with a given velocity, it is presumed to possess a kinetic energy T and a potential energy V calculated in the same way as the corresponding classical quantities. An isolated set of particles arranged in a particular way with given velocities similarly exhibits a T and V equivalent to the classical kinetic and potential energies that such a set would have. The sum of these energies is the total energy E for the system.

If a person prepares a set of equivalent potential fields and employs an instrument to introduce an identical particle into each in the same manner, he always obtains a statistical distribution of initial positions and initial velocities. The distributions persist over time. A set of such systems that is large enough so that adding more members does not appreciably alter the statistical weight of any pertinent value of a property is said to form an *ensemble*. An observer can presumably study an ensemble and determine the probability that the particle is in a given small volume d^3r of the reference space at a chosen time t . Here, radius vector r is drawn from the origin to the center of the differential volume. Dividing the probability by the volume yields the *probability density* ρ for the particle. A system of particles, and ensembles of such a system, can be considered similarly. The probability that the first particle is in volume d^3r_1 , the second in d^3r_2 , ..., the n th in d^3r_n may be determined and the corresponding probability densities calculated.

Also determinable are the statistical kinetic energy and momentum of a particle in a beam. Since these properties are independent of the density ρ at the point of measurement, but are related to particle movements in the beam, one needs an additional real function.

Essentially, two things have to be represented: distribution of the density and unidirectional movements of the particles. However, a single complex function can describe what one can know of both attributes very simply. The probability density is related directly to the square of the absolute value of the function, while the particle propagation is embodied in the phase angle. Indeed, we will find that the relationship

$$\rho = (\text{constant}) \Psi^* \Psi \quad (1.1)$$

serves except when Einstein's relativity needs to be taken into account. Then, four complex functions are needed, rather than only one.

Symmetry considerations will enable us, in principle, to complete the formulation. In particular, we will consider how $d\Psi$ depends on Ψ , on coordinates, and on

time. Except in special circumstances where another choice is convenient, the constant in (1.1) will be set equal to 1. We call Ψ the *state function*, or *wave function*, for the given particle (or particles).

The principle of *continuity*, that small causes produce small effects, is applied, not to each individual particle, but to the probability density and to the state function. So whenever the influences that act on a particle vary smoothly with the coordinates and time, the corresponding probability density varies smoothly. And, the state function is analytic wherever the relevant V is analytic.

Since observable properties are determined by the way the pertinent particles are distributed in space, on the average, and by how they propagate, these properties are derivable from state functions. Indeed, we have the theorem of *wholeness* or *completeness*: The function Ψ for a particle (or particles) represents the state of the corresponding system to the extent that this state can be determined.

From the standpoint of probability, the simplest system imaginable is one in which free movement occurs in a single direction with a constant ρ . Employing a source with constant intensity and accelerating energy, or velocity selection, one can also assume that the propagation properties are as uniform as possible.

Since ρ would be constant along such a beam, the magnitude of Ψ would be constant. The phase angle, however, would vary to represent the propagation. This variation must be introduced in a way consistent with the prevailing symmetries, as we will see in the next section.

In general, we have to consider particles subject to a varying potential V . But as long as the variations are not abrupt, we may assume that the motion across an infinitesimal element is effectively at constant V , and the results obtained for the homogeneous beam and its reflection may be applied within the element.

1.3. A State Function Governing Translation

Freely moving particles do not distinguish between the different points traversed in space or time; each point is equivalent in its average effect on a particle. Furthermore, a homogeneous beam, in which the particles move freely with the same momentum, possesses a Ψ made up of uniform parts. The resulting symmetries enable us to construct a credible state function.

Let us consider a system of equivalent particles traveling freely in one direction at one velocity (or momentum). Furthermore, let us suppose that the probability density ρ is constant throughout the region under consideration. Following the discussion in Section 1.2, we assume that all behavior of a typical particle is described by the factor of ρ labeled Ψ . This function Ψ presumably varies smoothly, so formal differentiation leads to the result

$$d\Psi = \frac{\partial\Psi}{\partial x} dx + \frac{\partial\Psi}{\partial y} dy + \frac{\partial\Psi}{\partial z} dz + \frac{\partial\Psi}{\partial t} dt \quad (1.2)$$

in which x, y, z are Cartesian coordinates of an inertial frame and t is the time.

For the pure motion we are studying, there is no reason to expect any part of Ψ to exert a different effect on $d\Psi$ than any other equivalent part. The simplest way to incorporate this symmetry is to make $d\Psi$ homogeneously linear in Ψ . Furthermore, each point in the given region and time interval is assumed to be like any other point in the region and interval. So the change in Ψ on going from one point to the next needs to be independent of the initial point. But the change must depend on

$$dx, dy, dz, dt. \quad (1.3)$$

By symmetry, multiplying each of these small changes by a factor should multiply the effects on $d\Psi$ by the factor. The infinitesimal $d\Psi$ therefore depends linearly on each of the infinitesimals in set (1.3).

For simplicity, however, let us go to axes X', Y', Z' for which the direction of the X' axis is that of the motion. Then the only spatial coordinate affecting Ψ is x' in the region of interest. And by the arguments just given, the variation in the state function is linear in dx' , linear in dt , and homogeneously linear in Ψ . We thus have

$$d\Psi = \kappa\Psi dx' + \gamma\Psi dt \quad (1.4)$$

where κ and γ are parameters to be identified. Our argument allows κ and γ to be imaginary or complex, so we may alternatively consider

$$d\Psi = ik\Psi dx' - i\omega\Psi dt. \quad (1.5)$$

Let us separate variables in (1.5)

$$\frac{d\Psi}{\Psi} = i\kappa dx' - i\omega dt \quad (1.6)$$

and integrate

$$\Psi = A e^{ikx'} e^{-i\omega t}. \quad (1.7)$$

Imposing (1.1) with the constant taken equal to 1, as we commonly do in normalizing functions, yields the probability density

$$\rho = \Psi^* \Psi = A^* (e^{ikx'})^* (e^{-i\omega t})^* A e^{ikx'} e^{-i\omega t}. \quad (1.8)$$

This reduces to an expression independent of x' and t only if k and ω are real (κ and γ imaginary). Since such independence exists in the homogeneous propagating beam, we assume that k and ω are real in the beam. Then (1.8) reduces to

$$\rho = A^* A. \quad (1.9)$$

A general displacement may be written as

$$dr = dx\hat{x} + dy\hat{y} + dz\hat{z}. \quad (1.10)$$

Element dx' is the component of dr in the direction of motion. If e is the unit vector pointing in this direction and ke is written as k , then

$$k dx' = ke \cdot dr = k \cdot dr \quad (1.11)$$

and

$$kx' = ke \cdot r = k \cdot r. \quad (1.12)$$

The expression governing pure translation (1.7) now becomes

$$\Psi = A e^{ik \cdot r} e^{-i\omega t} = A e^{i(k \cdot r - \omega t)}. \quad (1.13)$$

A given phase of this Ψ travels with a given value of the angle

$$kx' - \omega t = k \cdot r - \omega t = a. \quad (1.14)$$

Indeed, the corresponding coordinate x' obeys the equation

$$x' = \frac{\omega}{k} t + \frac{a}{k}, \quad (1.15)$$

which yields

$$\frac{dx'}{dt} = \frac{\omega}{k} = w. \quad (1.16)$$

for the *phase velocity* w . Parameter ω is called the *angular frequency* with respect to time t ; and parameter k , the *wavevector* for the motion.

In the unprimed Cartesian coordinate system, parameter k has the components

$$k = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}. \quad (1.17)$$

Since

$$k \cdot r = k_x x + k_y y + k_z z, \quad (1.18)$$

formula (1.13) expands to

$$\Psi = A e^{ik_x x} e^{ik_y y} e^{ik_z z} e^{-i\omega t} \quad (1.19)$$

and (1.5) to

$$d\Psi = ik_x \Psi dx + ik_y \Psi dy + ik_z \Psi dz - i\omega \Psi dt. \quad (1.20)$$

Equation (1.20) describes how Ψ varies within the homogeneous beam, for a general orientation of axes; Equation (1.19) describes the resulting coherent wave function.

Example 1.1. What is the periodicity of the exponential function?

The exponential function is related to trigonometric functions by the identity

$$e^{i\alpha} \equiv \exp i\alpha = \cos \alpha + i \sin \alpha.$$