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0521829526 - Fundamentals of Quantum Mechanics: For Solid State Electronics and Optics
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1 Classical mechanics vs. quantum mechanics

What is quantum mechanics and what does it do?

In very general terms, the basic problem that both classical Newtonian mechanics and quantum mechanics seek to address can be stated very simply: *if the state of a dynamic system is known initially and something is done to it, how will the state of the system change with time in response?*

In this chapter, we will give a brief overview of, first, how Newtonian mechanics goes about solving the problem for systems in the macroscopic world and, then, how quantum mechanics does it for systems on the atomic and subatomic scale. We will see qualitatively what the differences and similarities of the two schemes are and what the domain of applicability of each is.

1.1 Brief overview of classical mechanics

To answer the question posed above systematically, we must first give a more rigorous formulation of the problem and introduce the special language and terminology (in double quotation marks) that will be used in subsequent discussions. For the macroscopic world, common sense tells us that, to begin with, we should identify the "system" that we are dealing with in terms of a set of "static properties" that do not change with time in the context of the problem. For example, the mass of an object might be a static property. The change in the "state" of the system is characterized by a set of "dynamic variables." Knowing the initial state of the system means that we can specify the "initial conditions of these dynamic variables." What is done to the system is represented by the "actions" on the system. How the state of the system changes under the prescribed actions is then described by how the dynamic variables change with time. This means that there must be an "equation of motion" that governs the time-dependence of the state of the system. The mathematical solution of the equation of motion for the dynamic variables of the system will then tell us precisely the state of the system at a later time $t > 0$; that is to say, everything about what happens to the system after something is done to it.

For definiteness, let us start with the simplest possible "system": a single particle, or a point system, that is characterized by a single static property, its mass m. We assume that its motion is limited to a one-dimensional linear space (1-D, coordinate axis x, for example). According to Newtonian mechanics, the state of the particle at any time t is completely specified in terms of the numerical values of its position $x(t)$ and velocity $v_x(t)$, which is the rate of change of its position with respect to time, or $v_x(t) = \mathrm{d}x(t)/\mathrm{d}t$. All the other dynamic properties, such as linear momentum $p_x(t) = mv_x$, kinetic energy $T = (mv_x^2)/2$, potential energy $V(x)$, total energy $E = (T + V)$, etc. of this system depend only on x and v_x. "The state of the system is known initially" means that the numerical values of $x(0)$ and $v_x(0)$ are given. The key concept of Newtonian mechanics is that the action on the particle can be specified in terms of a "force", F_x, acting on the particle, and this force is proportional to the acceleration, $a_x = \mathrm{d}^2x / \mathrm{d}t^2$, where the proportionality constant is the mass, m, of the particle, or

$$F_x = ma_x = m\frac{\mathrm{d}^2x}{\mathrm{d}t^2}. \tag{1.1}$$

This means that once the force acting on a particle of known mass is specified, the second derivative of its position with respect to time, or the acceleration, is known from (1.1). With the acceleration known, one will know the numerical value of $v_x(t)$ at all times by simple integration. By further integrating $v_x(t)$, one will then also know the numerical value of $x(t)$, and hence what happens to the particle for all times. Thus, if the initial conditions on x and v_x are given and the action, or the force, on the particle is specified, one can always predict the state of the particle for all times, and the initially posed problem is solved.

The crucial point is that, because the state of the particle is specified by x and its first time-derivative v_x to begin with, in order to know how x and v_x change with time, one only has to know the second derivative of x with respect to time, or specify the force. This is a basic concept in calculus which was, in fact, invented by Newton to deal with the problems in mechanics.

A more complicated dynamic system is composed of many constituent parts, and its motion is not necessarily limited to any one-dimensional space. Nevertheless, no matter how complicated the system and the actions on the system are, the dynamics of the system can, in principle, be understood or predicted on the basis of these same principles. In the macroscopic world, the validity of these principles can be tested experimentally by direct measurements. Indeed, they have been verified in countless cases. The principles of Newtonian mechanics, therefore, describe the "*laws of Nature*" in the macroscopic world.

1.2 Overview of quantum mechanics

What about the world on the atomic and subatomic scale? A number of fundamental difficulties, both experimental and logical, immediately arise when trying to extend the principles of Newtonian mechanics to the atomic and subatomic scale. For example, measurements on atomic or subatomic particles carried out in the macroscopic world in general give results that are statistical averages over an ensemble of a large number of similarly prepared particles, not precise results on any particular particle. Also, the resolution needed to quantify or specify the properties of individual systems on the atomic and subatomic scale is generally many orders of magnitude finer than the scales and accuracy of any measurement process in the macroscopic world. This makes it difficult to compare the predictions of theory with direct measurements for specific atomic or subatomic systems. Without clear direct experimental evidence, there is no a priori reason to expect that it is *always* possible to specify the state of an atomic or subatomic particle at any particular time in terms of a set of simultaneously precisely measurable parameters, such as the position and velocity of the particle, as in the macroscopic world. The whole formulation based on the deterministic principles of Newtonian mechanics of the basic problem posed at the beginning of this discussion based on simultaneous precisely measurable position and velocity of a particular particle is, therefore, questionable. Indeed, while Newtonian mechanics had been firmly established as a valid theory for explaining the behaviors of all kinds of dynamic systems in the macroscopic world, experimental anomalies that could not be explained by such a theory were also found in the early part of the twentieth century. Attempts to explain these anomalies led to the development of quantum theory, which is a totally new way of dealing with the problems of mechanics and electrodynamics in the atomic and subatomic world.

A brief overview of the general approach of the theory in contrast to classical Newtonian mechanics is given here. All the assertions made in this brief overview will be explained and justified in detail in the following chapters. The purpose of the *qualitative* discussion in this chapter is simply to give an indication of the things to come, not a complete picture. A more formal description of the basic postulates and methodology of quantum mechanics will be given in the following chapter.

To begin with, according to quantum mechanics, the "state" of a system on the atomic and subatomic scale is not characterized by a set of dynamic variables each with a specific numerical value. Instead, it is completely specified by a "state function." The dynamics of the system is described by the time dependence of this state function. The relationship between this state function and various physical properties of the dynamic system that can be measured in the macroscopic world is also not as direct as in Newtonian mechanics, as will be clarified later.

The state function is a function of a set of chosen variables, called "canonic variables," of the system under study. For definiteness, let us consider again, for example, the case of a particle of mass m constrained to move in a linear space along the x axis. The state function, which is usually designated by the arbitrarily chosen symbol Ψ, is a function of x. That is, the state of the particle is specified by the functional dependence of the state function $\Psi(x)$ on the canonic variable x, which is the "possible position" of the particle. It is not specified by any particular values of x and v_x as in Newtonian mechanics. How the state of the particle changes with time is specified by $\Psi(x, t)$, or how $\Psi(x)$ changes explicitly with time, t. $\Psi(x, t)$ is often also referred to as the "wave function" of the particle, because it often has properties similar to those of a wave, even though it is supposed to describe the state of a "particle," as will be shown later.

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The state function can also be expressed alternatively as a function of another canonic variable "conjugate" to the position coordinate of the system, the linear momentum of the particle p_x, or $\Psi(p_{x,} t)$. The basic problem of the dynamics of the particle can be formulated in either equivalent form, or in either "representation." If the form $\Psi(x, t)$ is used, it is said to be in the "Schrödinger representation," in honor of one of the founders of quantum mechanics. If the form $\Psi(p_{x,} t)$ is used, it is in the "momentum representation." That the same state function can be expressed as a function of different variables corresponding to different representations is analogous to the situation in classical electromagnetic theory where a time-dependent electrical signal can be expressed either as a function of time, $\varepsilon(t)$, or in terms of its angular-frequency spectrum, $\varepsilon(\omega)$, in the Fourier-transform representation. There is a unique relationship between $\Psi(x, t)$ and $\Psi(p_{x,} t)$, much as that between $\varepsilon(t)$ and $\varepsilon(\omega)$. Either representation will eventually lead to the same results for experimentally measurable properties, or the "observables," of the system. Thus, as far as interpreting experimental results goes, it makes no difference which representation is used. The choice is generally dictated by the context of the problem or mathematical expediency. Most of the introductory literature on the quantum theory of electronic and optical devices tends to be based on the Schrödinger representation. That is what will be mostly used in this book also.

The "statistical," or probabilistic, nature of the measurement process on the atomic and subatomic scale is imbedded in the physical interpretation of the state function. For example, the wave function $\Psi(x, t)$ is in general a complex function of x and t, meaning it is a phasor of the form $\Psi = |\Psi|\, e^{i\phi}$ with an amplitude $|\Psi|$ and a phase ϕ. The magnitude of the wave function, $|\Psi(x, t)|$, gives statistical information on the results of measurement of the position of the particle. More specifically, "the particle" in quantum mechanics actually means a statistical "ensemble," or collection, of particles all in the same state, Ψ, for example. $|\Psi(x, t)|^2 dx$ is then interpreted as the probability of finding a particle in the ensemble in the spatial range from x to $x + dx$ at the time t. Unlike in Newtonian mechanics, we cannot speak of the precise position of a specific atomic or subatomic particle in a statistical ensemble of particles. The experimentally measured position must be viewed as an "expectation value," or the average value, of the probable position of the particle. An explanation of the precise meanings of these statements will be given in the following chapters.

The physical interpretation of the phase of the wave function is more subtle. It endows the particle with the "duality" of wave properties, as will be discussed later. The statistical interpretation of the measurement process and the wave–particle duality of the dynamic system represent fundamental philosophical differences between the quantum mechanical and Newtonian descriptions of "dynamic systems."

For the equation of motion in quantum mechanics, we need to specify the "action" on the system. In Newtonian mechanics, the action is specified in terms of the force acting on the system. Since the force is equal to the rate of decrease of the potential energy with the position of the system, or $\vec{F} = -\nabla V(\vec{r})$, the action on the system can be specified either in terms of the force acting on the system or the potential energy of the particle as a function of position $V(\vec{r})$. In quantum mechanics, the action on the dynamic system is generally specified by a physically "observable" property corresponding to the "potential energy operator," say $\hat{V}(\vec{r})$, as a function of the position of the system. For example, in the one-dimensional single-particle problem, $\hat{V}$ in the Schrödinger representation is a function of the variable x, or $\hat{V}(x)$. Since the position of a particle in general does not have a unique value in quantum mechanics, the important point is that $\hat{V}(x)$ gives the functional relationship between $\hat{V}$ and the position variable x. The force acting on the system is simply the negative of the gradient of the potential with respect to x; therefore, the two represent the same physical action on the system. Physically, $\hat{V}(x)$ gives, for example, the direction in which the particle position must change in order to lower its potential energy; it is, therefore, a perfectly reasonable way to specify the action on the particle.

In general, all dynamic properties are represented by "operators" that are functions of x and $\hat{p}_x$. As a matter of notation, a 'hat ∧' over a symbol in the language of quantum theory indicates that the symbol is mathematically an "operator," which in the Schrödinger representation can be a function of x and/or a differential operator involving x. For example, the operator representing the linear momentum, $\hat{p}_x$, in the Schrödinger representation is represented by an operator that is proportional to the first derivative with respect to x:

$$\hat{p}_x = -\mathrm{i}\,\hbar \frac{\partial}{\partial x}, \tag{1.2}$$

where $\hbar$ is the Planck's constant h divided by 2π. h is one of the fundamental constants in quantum mechanics and has the numerical value $h = 6.626 \times 10^{-27}$ erg-s. The reason for this peculiar equation, (1.2), is not obvious at this point. It is related to one of the basic "postulates" of quantum mechanics and one of its implications is the all-important "Heisenberg's uncertainty principle," as will be discussed in detail in later chapters.

The total energy of the system is generally referred to as the "Hamiltonian," and usually represented by the symbol $\hat{H}$, of the system. It is the sum of the kinetic energy and the potential energy of the system as in Newtonian mechanics:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x), \tag{1.3}$$

with the help of Eq. (1.2). The action on the system is, therefore, contained in the Hamiltonian through its dependence on $\hat{V}$.

The total energy, or the Hamiltonian, plays an essential role in the equation of motion dealing with the dynamics of quantum systems. *Because the state of the dynamic system in quantum mechanics is completely specified by the state function, it is only necessary to know its first time-derivative,* $\frac{\partial \Psi}{\partial t}$, *in order to predict how* Ψ *will vary with time, starting with the initial condition on* Ψ. The key equation of motion as postulated by Schrödinger is that the time-rate of change of the state function is proportional to the Hamiltonian "operating" on the state function:

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$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t}=\hat{H}\Psi. \tag{1.4}$$

In the Schrödinger representation for the one-dimensional single particle system, for example, it is a partial differential equation:

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t}=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\hat{V}(x)\right]\Psi, \tag{1.5}$$

by substituting Eq. (1.3) into Eq. (1.4). The time-dependent Schrödinger's equation, Eq. (1.4), or more often its explicit form Eq. (1.5), is the basic equation of motion in quantum mechanics that we will see again and again later in applications. Solution of Schrödinger's equation will then describe completely the dynamics of the system.

The fact that the basic equation of motion in quantum mechanics involves only the *first* time-derivative of something while the corresponding equation in Newtonian mechanics involves the *second* time-derivative of some key variable is a very interesting and significant difference. It is a necessary consequence of the fundamental difference in how the "state of a dynamic system" is specified in the two approaches to begin with. It also leads to the crucial difference in how the action on the system comes into play in the equations of motion: the total energy, $\hat{H}$, in the former case, in contrast to the force, $\vec{F}$, in the latter case.

Schrödinger's equation, (1.4), in quantum mechanics is analogous to Newton's equation of motion, Eq. (1.1), in classical mechanics. It is one of the key postulates that unlocks the wonders of the atomic and subatomic world in quantum mechanics. It has been verified with great precision in numerous experiments without exception. It can, therefore, be viewed as a *law of Nature* just as Newton's equation – 'F equals $m\,a$' – for the macroscopic world.

The problem is now reduced to a purely mathematical one. Once the initial condition $\Psi(x, t=0)$ and the action on the system are given, the solution of the Schrödinger equation gives the state of the system at any time t. Knowing $\Psi(x, t)$ at any time t also means that we can find the expectation values of all the operators corresponding to the dynamic properties of the system. Exactly how that is done mathematically will be described in detail in the following chapters. Since the state of the system is completely specified by the state function, the time dependent state function $\Psi(\vec{r}, t)$ contains all the information on the dynamics of the system that can be obtained by experimental observations. This is how the problem is formulated and solved according to the principles of quantum mechanics.

Further reading

For further studies at a more advanced level of the topics discussed in this and the following chapters of this book, we recommend the following.

On fundamentals of quantum mechanics

Bethe and Jackiw (1986); Bohm (1951); Cohen-Tannoudji, Diu and Laloë (1977); Dirac (1947).

On quantum theory of radiation

Glauber (1963); Heitler (1954).

On generalized angular momentum

Edmonds (1957); Rose (1956).

On atomic spectra and atomic structure

Condon and Shortley (1963); Herzberg (1944).

On molecules and molecular-orbital theory

Ballhausen and Gray (1964); Coulson (1961); Gray (1973); Pauling (1967).

On lasers and photonics

Siegman (1986); Shen (1984); Yariv (1989).

On solid state physics and semiconductor electronics

Kittel (1996); Smith (1964); Streetman (1995).

2 Basic postulates and mathematical tools

Basic scientific theories usually start with a set of hypotheses or “postulates.” There is generally no logical reason, apart from internal consistency, that can be given to justify such postulates absolutely. They come from ‘revelations’ in the minds of ‘geniuses,’ most likely with hints from Nature based on extensive careful observations. Their general validity can only be established through experimental verification. If numerous rigorously derived logical consequences of a very small set of postulates all agree with experimental observations without exception, one is inclined to accept these postulates as correct descriptions of the laws of Nature and use them confidently to explain and predict other natural phenomena. Quantum mechanics is no exception. It is based on a few postulates. For the purpose of the present discussion, we begin with three basic postulates involving: the “state functions,” “operators,” and “equations of motion.”

In this chapter, this set of basic postulates and some of the corollaries and related definitions of terms are introduced and discussed. We will first simply state these postulates and introduce some of the related mathematical tools and concepts that are needed to arrive at their logical consequences later. To those who have not been exposed to the subject of quantum mechanics before, each of these postulates taken by itself may appear puzzling and meaningless at first. It should be borne in mind, however, that it is the collection of these postulates as a whole that forms the foundations of quantum mechanics. The full interpretation, and the power and glory, of these postulates will only be revealed gradually as they are successfully applied to more realistic and increasingly complicated physical problems in later chapters.

2.1 State functions (Postulate 1)

The first postulate states that *the state of a dynamic system is completely specified by a state function.*

Even without a clear definition of what a state function is, this simple postulate already makes a specific claim: there *exists* an abstract state function that contains *all* the information about the state of the dynamic system. For this statement to have meaning, we must obviously provide a clear physical interpretation of the state function, and specify its mathematical properties. We must also give a prescription of how quantitative information is to be extracted from the state function and compared with experimental results.

The state function, which is often designated by a symbol such as Ψ, is in general a complex function (meaning a phasor, $|\Psi|\,e^{i\phi}$, with an amplitude and a phase). In terms of the motion of a single particle in a linear space (coordinate x), for example, $|\Psi|$ and ϕ in the Schrödinger representation are functions of the canonical variable x.

A fundamental distinction between classical mechanics and quantum mechanics is that, in classical mechanics, the state of the dynamic system is completely specified by the position and velocity of each constituent part (or particle) of the system. This presumes that the position and velocity of a particle can, at least in principle, be measured and specified precisely at each instant of time. The position and velocity of the particle at one instant of time are completely determined by the position and velocity of the particle at a previous instant. It is deterministic. That one can specify the state of a particle in the macroscopic world in this way is intuitively obvious, because one can see and touch such a particle. It is intuitively obvious that it is possible to measure its position and velocity simultaneously. And, if two particles are not at the same place or not moving with the same velocity, they are obviously not in the same state.

What about in the world on the atomic and subatomic scale where we cannot see or touch any particle directly? There is no assurance that our intuition on how things work in our world can be extrapolated to a much smaller world in which we have no direct sensorial experience. Indeed, in quantum mechanics, no a priori assumption is made about the possibility of measuring or specifying precisely the position and the velocity of the particle at the same time. In fact, as will be discussed in more detail later, according to "Heisenberg's uncertainty principle," it is decidedly not possible to have complete simultaneous knowledge of the two; a complete formulation of this principle will be given in connection with Postulate 2 in Section 2.2 below. Furthermore, quantum mechanics does not presume that measurement of the position of a particle will necessarily yield a particular value of x predictably. Knowing the particle is in the state Ψ, the most specific information on the position of the particle that one can hope to get by any possible means of measurement is that the probability of getting the value x_1 relative to that of getting the value x_2 is $|\Psi(x_1)|^2 : |\Psi(x_2)|^2$. In other words, the physical interpretation of the amplitude of the state function is that $|\Psi(x)|^2 dx$ is, in the language of probability theory, proportional to the probability of finding the particle in the range from x to $x + dx$ in any measurement of the position of the particle. If it is known for certain that there is one particle in the spatial range from $x = 0$ to $x = L$, then the probability distribution function $|\Psi(x)|^2$ integrated over this range must be equal to 1 and the wave function is said to be "normalized":

$$1 = \int_0^L \Psi(x)^* \Psi(x) dx = \int_0^L |\Psi(x)|^2 dx. \qquad (2.1)$$

If the wave function is normalized, the absolute value of the probability of finding the particle in the range from x to $x + dx$ is $|\Psi(x)|^2 dx$. Accordingly, there is also an

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average value, $\langle x\rangle_\Psi$, of the position of the particle in the state Ψ, which is called the "expectation value" of the position of the particle. It is an ordinary number given by:

$$\langle x\rangle_\Psi = \int_0^L \Psi^*(x)\, x\, \Psi(x)\, \mathrm{d}x = \int_0^L x\,|\Psi(x)|^2 \mathrm{d}x. \tag{2.2}$$

A "mean square deviation," Δx^2, from the average of the probable position of the particle can also be defined:

$$\Delta x^2 = \int_0^L \Psi(x)^*(x - \langle x\rangle_\Psi)^2 \Psi(x)\mathrm{d}x = \int_0^L (x - \langle x\rangle_\Psi)^2 |\Psi(x)|^2 \mathrm{d}x, \tag{2.3}$$

which gives a measure of the spread of the probability distribution function, $|\Psi(x)|^2$, of the position around the average value. In the language of quantum mechanics, $\Delta x \equiv \sqrt{\Delta x^2}$ as defined in (2.3) is called the "uncertainty" in the position x of the particle when it is in the state $\Psi(x)$. The definitions of the "average value" and the "mean square deviation," or "uncertainty," can also be generalized to any function of x, such as *any operator* in the Schrödinger representation, as will be discussed in Section 2.3.

A more detailed explanation of the above probabilistic interpretation of the amplitude of the state function is in order at this point. "$|\Psi(x)|^2$ is the probability distribution function of the position of the particle" implies the following. If there are a large number of particles all in the same state Ψ in a statistical ensemble and similar measurement of the position of the particles is made on each of the particles in the ensemble, the result of the measurements is that the ratio of the number of times a particle is found in the range from x to $x + \mathrm{d}x$, N_x, to the total number of measurements, N, is equal to $|\Psi(x)|^2\mathrm{d}x$. Stating it in another way, the number of times a particle is found in the differential range from x_1 to $x_1 + \mathrm{d}x$ to that in the range from x_2 to $x_2 + \mathrm{d}x$ is in the ratio of N_{x_1}: $N_{x_2} = |\Psi(x_1)|^2$: $|\Psi(x_2)|^2$. The expectation value of the position of the particle, $\langle x\rangle_\Psi$, is the average of the measured positions of the particles:

$$\langle x\rangle_\Psi = x_1 \frac{N_{x_1}}{N} + x_2 \frac{N_{x_2}}{N} + x_3 \frac{N_{x_3}}{N} + \cdots = \int_0^L x|\Psi(x)|^2 \mathrm{d}x,$$

as given by Eq. (2.2). The uncertainty, Δx, is the spread of the measured positions around the average value:

$$\begin{aligned}\Delta x^2 &= (x_1 - \langle x\rangle_\Psi)^2 \frac{N_{x_1}}{N} + (x_2 - \langle x\rangle_\Psi)^2 \frac{N_{x_2}}{N} \\ &\quad + (x_3 - \langle x\rangle_\Psi)^2 \frac{N_{x_3}}{N} + \cdots \\ &= \int_0^L (x - \langle x\rangle_\Psi)^2 |\Psi(x)|^2 \mathrm{d}x,\end{aligned}$$

as given by Eq. (2.3).