

treatment of quantum mechanics in this book, but instead to present just enough of the essential inputs of quantum mechanics to keep our story on the track in an understandable way. This means, of course, that I cannot present a “completely modern treatment” of many of the topics of this book; I am content to let the formalisms come later in other courses if the students’ interest moves in that direction. Rather in this treatment I attempt to open up the subject to those who would be quite unprepared to translate the formalisms into meaningful concepts.

These remarks emphasize that this book is being written for students rather than for experts (in any sense) in the fields involved. In this day of intense specialization I think it still likely that experts in some areas may well find themselves in the character of students in another, and for them this book may be helpful. Also, although the book has developed out of a context of students with backgrounds in materials science and metallurgy, I hope that it will be helpful to a wide variety of students in undergraduate curricula in the sciences and engineering.

Particular aspects of this book may prove helpful. (1) I have tried to make the purely mathematical problems less troublesome by showing how the results lead to one another rather than leaving all such inferences to the student. For many students mathematical development produces a formidable barrier against conceptual understanding, but I believe that quantitative description puts down more roots than a purely qualitative description. There are, of course, places where the detailed mathematical derivation of a significant result cannot be given because it is beyond the scope of this book. I have tried, however, to keep the number of such places as small as possible. (2) I have provided a constant comparison between the SI and Gaussian unit systems wherever this seems at all desirable, particularly in those cases for which differences in the unit system used introduce numerical constants differing from unity. Absolute limitation in presentation to one system of units only, even the MKS or SI systems, closes to the student a considerable body of relevant literature in the past (and also the present) simply because the Gaussian system of units may continue to be used there. (3) Problems to be worked out by the student and illustrations are provided to bridge the gap between the abstract formulation of the subject development and the application of this development to specific algebraic and numerical problems.

I wish to thank my own teachers; the many classes that have endured the development of these notes, in particular, the class of 1979–1980, who helped to eliminate the errors in the original manuscript for this book; and especially Dr. Julio Aranovich, whose notes for this course on magnetic properties were very helpful to me.

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1 | *Particles and Waves*

Almost everyone grows up with a kind of intuitive knowledge of what is meant by speaking of “a particle.” However remote mathematical abstractions of a particle may be, we have all handled stones, baseballs, billiard balls, and other similar entities whose motion is part of our everyday experience. When this concept is extended to the planets of the solar system, these planets are so far away that we readily think of them as particles despite their great size. We naturally think of atoms as small particles of matter, and when we come to realize that electric charge exists in small units known as electrons, we readily attribute particlelike behavior to electrons as well. We are comfortable in this framework and resist being told that such particles may have to be thought of in a quite different way.

Waves are a somewhat different concept, a little harder to grasp and a little further from our everyday experience. Of course, we know about ocean waves and waves moving across a wheat field, but our contact with these waves is more on the holistic and emotional level. They seem less tangible to us than the “real” stuff, the water and the wheat, that is doing the moving. Still, since light is clearly not made up of particles according to our everyday experience, we are willing to attribute the concept of a wave to light motion, although we feel less at home than with our more immediate working concepts.

At least we can reassure ourselves that on the basis of everyday experience, there are particles and there are waves, and we can certainly tell the difference between them. Once we have the “true” description of a phenomenon, we

will know whether to categorize it as particle motion or wave motion. And we will certainly be making a mistake if we try to blur the distinction between these categories.

It is exactly this strongly ingrained intuitive reaction that makes the subject matter of electrical, optical, and magnetic properties of materials such a challenge, if we decide to depart from a purely phenomenological summary of effects and measurable parameters. For it is the very essence of the thought of the past 65 years that we should *not* think of particles and waves in mutually exclusive terms, but that we should realize that each way of looking at the situation may be appropriate under some conditions and inappropriate under others. To the insistent question, "But after all, is the electron a particle or a wave?" we must reply that it is neither. An electron is an electron, no more and no less. Perhaps in time we shall know more of its "internal structure," but everything we know today leads us to believe that "particle" and "wave" are useful words to *describe* different aspects of the properties of an electron, but are not suitable to describe in any kind of ultimate sense what an electron *is*. In fact, we are reminded of a fundamental point: We can do no other than to describe the unknown in terms of the known, and this very fact prevents us from ever grasping more than a partial truth of the universe, if by "truth" we mean simply "what is objectively there."

The thoughtful student of electronic properties is therefore led to some rather revolutionary reevaluation of the nature of science, compared to what he or she may have been led to believe from earlier science education. Unless the existence of this revolution is realized at the outset, the student in non-electronic fields may simply feel that he or she is being unnecessarily confused, and may reject the whole field of knowledge in favor of other fields where the more classical and intuitive concepts can be retained without modification.

This need to rethink the capabilities of scientific models is accentuated by the recognition that there are certain kinds of questions that wave or particle models simply cannot answer. In dealing with the reflection of light from a material, for example, we can correctly calculate the reflection and transmission of light using a wave model, including only the proper boundary conditions at the interface and the appropriate parameters for the material. But we can say nothing, on the basis of this model, about what happens in detail to the light interactions with the material. In is often true that particular scientific models have the capability of giving meaningful answers only to specific kinds of questions. We must often learn to accept this situation, either as an expression of our own present limitations or of the nature of the world itself, without feeling that available information or insight is being deliberately withheld.

In this book we have chosen the wavelike properties of all of matter as an integrating theme into which we can weave such themes as crystal lattice

vibrations (with their effect on electron mobility and electrical and thermal conductivity), electromagnetic waves (with their effect on optical reflection and absorption), and electronic transport in solids (with its dependence on the wavelike properties of electrons). Our choice of the wavelike emphasis is not meant to imply that this is an ultimately true mode of description, but simply that it is a convenient way to see correlations between apparently quite different phenomena, and to bridge the gap between classical perspectives and more modern quantum views. Nor is our choice meant to imply in any sense that the wavelike emphasis is a unique approach to the problems of modern electronic behavior; again, it rather affords a visualizable context within which to view a situation which can otherwise become rather mathematically abstract.

CLASSICAL VIEWS OF ELECTRONS, LIGHT, AND ENERGY

An electron has three basic properties: a charge q , which forms the basis for electrical properties, a mass m , and a spin, a non-classical kind of self angular momentum responsible for a wide variety of magnetic properties. The ratio of charge to mass q/m can be accurately measured. For example, if we impart energy to electrons by passing them through a potential difference ϕ , then we can consider them to be particles with kinetic energy $\frac{1}{2}mv^2 = q\phi$. If we then allow these electrons to be deflected by a magnetic field (the force on an electron moving with velocity \mathbf{v} in a magnetic field \mathbf{B} is given in SI units by $\mathbf{F} = q\mathbf{v} \times \mathbf{B}$), and measure the radius of curvature R of the path that they travel, we can determine the ratio q/m by equating the centripetal and magnetic forces on the electron:

$$mv^2/R = qvB \quad (1.1S)\dagger$$

to obtain

$$q/m = 2\phi/R^2B^2 \quad (1.2S)$$

Our view of light as a wave motion is consistent with our knowledge of phenomena such as light diffraction or interference, and with its apparently massless character. Our sense that all positive values of energy are allowed is consistent with our everyday experience of moving objects and their kinetic energy.

† Throughout this book we give major equations in both Gaussian and SI units (see Appendix B). Any equation whose *specific form* depends on the unit system used will be specifically labeled "G" for Gaussian, or "S" for SI units. Thus Eq. (1.1S) is in SI units. If no label is given, the *form* of the equation is independent of the unit system used.

Underlying much of the subject matter relevant to the behavior of electrons in solids, however, is the realization that came early in the present century that a profoundly different view of the properties of electrons, light, and energy is needed to account for a wide variety of other phenomena that began to be observed. Electrons were seen to exhibit wavelike as well as particlelike properties, light was seen to exhibit particlelike as well as wavelike properties, and the energies allowed for electrons in confined systems were seen to be restricted to a range of discrete values. All of these revolutionary changes can be interpreted by adopting a thoroughgoing wavelike view of matter.

SOME CHALLENGING OBSERVATIONS

Some very simple experimental and theoretical observations are involved in setting forth the need for a much broader view than that held by the classical view. Here we summarize a few of these to indicate the general nature of the need for a reinterpretation of classical ideas.

The wavelike properties of electrons were dramatically suggested by the electron diffraction experiments of C. Davisson and L. H. Germer in 1927, and by G. P. Thomson in 1928. It was found that electrons diffracted from a crystalline solid showed constructive interference corresponding to the Bragg conditions (developed for x rays in 1913):

$$n\lambda = 2d \sin \theta \quad (1.3)$$

where n is an integer, d is the spacing between crystal lattice planes, θ the angle between the electron beam and the crystal surface, and λ the apparent wavelength of the electrons. The value of λ was found to depend on the energy of the electrons in the beam. Correspondence could be achieved by associating the de Broglie wavelength $\lambda = h/p$ with electrons with momentum p . Here h is Planck's constant with a numerical value of 6.6256×10^{-34} J sec. The kinetic energy of free electrons is therefore given by

$$p^2/2m = h^2/2m\lambda^2 \quad (1.4)$$

A summary of particlelike and wavelike properties is given in Table 1.1 together with the correlation proposed between them.

Position and momentum can be considered to be complementary quantities, such that complete knowledge of the one removes the possibility of knowledge of the other. This expresses itself in the Heisenberg Indeterminacy Principle. The product of the indeterminacy in the position Δx and the indeterminacy in the momentum $\Delta p = h[\Delta(1/\lambda)]$ is shown by quantum mechanics to be greater than or equal to $\hbar = h/2\pi$. If the information we have were to provide us with exact information about the lo-

TABLE 1.1 Particle and Wave Properties^a

| Particlelike | Wavelike | Correlation |
|--|--|---|
| Has a position in space; its' location can be specified by giving spatial coordinates. | Is extended in space; spatial characteristics are specified by a wavelength λ . | Heisenberg indeterminacy principle: $\Delta x \cdot \Delta(1/\lambda) \geq 1/2\pi$ |
| | | Totally particlelike: $\Delta x = 0, \Delta(1/\lambda) = \infty$ |
| | | Totally wavelike: $\Delta(1/\lambda) = 0, \Delta x = \infty$. |
| Has a momentum given by $p = mv$. | Momentum is described in terms of a wave number $k = 2\pi/\lambda$ | If particlelike momentum is mv , wavelike wavelength is $\lambda = h/mv$ where v is the group velocity of the corresponding waves. |
| Has kinetic and potential energy given by $E = \frac{1}{2}mv^2 + V$ | Has an angular frequency $\omega = 2\pi\nu$. | If particlelike energy is E , wavelike frequency is $\omega = E/\hbar$. |
| Can take on all values of energy $E \geq 0$. | Can exhibit all frequencies ω if the wave is effectively infinite, i.e., unconfined. | Can exhibit all energies $E = \hbar\omega \geq 0$ if the "wave" is effectively infinite, i.e., a free particle" with $V = 0$. |
| | Can exhibit only a set of discrete frequencies ω_i if the wave is finite, i.e., confined to a specific region of space. | Can exhibit only a set of discrete energies $E_i = \hbar\omega_i$ if the "wave" is confined, i.e., if the "particle" is constrained by $V \neq 0$. |

^a A comparison of particlelike and wavelike properties and the correlation between them when both are used in appropriate circumstances to describe the behavior of entities with particlelike and wavelike properties, e.g., an electron.

cation of an electron, i.e., the information suitable for particle behavior, then we could know nothing about its equivalent wavelength, its wavelike behavior. Similarly if the information we have were to provide us with exact information about the wavelength of an electron, i.e., information implying extension in space like a wave, then we could know nothing about its position.

Another key link between particle and wave properties is provided by the relationship between energy E , a familiar particle property, and the wave frequency ν , $E = h\nu = \hbar\omega$, which results from the recognition that energy exchanges in interaction with a wave must occur in integral multiples of a basic quantum of energy, $h\nu = \hbar\omega$.

Both particlelike and wavelike models had been proposed for light through

the years, although a wavelike model had gained dominance. The existence of particlelike properties was shown, however, by the photoelectric effect. In 1887 Hertz showed that a metallic surface would emit electrons if illuminated with light of a very short wavelength. In 1905 Einstein interpreted the phenomena in terms of the energy relationship

$$h\omega = \frac{1}{2}mv^2 + q\phi \quad (1.5)$$

and was subsequently awarded the Nobel Prize for this work. In Eq. (1.5), $\hbar = h/2\pi$, $\omega = 2\pi\nu$ is the angular frequency of the light with frequency ν , and $q\phi$ is the work function of the metal, corresponding to the height of a potential barrier at the surface of the metal that electrons in the metal must overcome in order to escape into vacuum. Unless the frequency of the illuminating light is at least $q\phi/\hbar$, no electrons are emitted regardless of what intensity of light is used. If the quantity $\hbar\omega$ is larger than $q\phi$, the excess energy is carried off by the emitted electron as kinetic energy. The results are as if light energy came in small bundles of $\hbar\omega$ each (called photons) and interaction with electrons in the solid occurred through absorption of such discrete energy bundles. A similar phenomenon is observed in the emission of x rays as the result of bombarding a metal with electrons; the maximum frequency of the emitted x rays is proportional to the accelerating voltage (hence the energy) of the electrons used.

A number of experimental observations led to the conclusion that allowed energy levels for electrons in solids must be restricted to a discontinuous set of allowed discrete levels rather than being continuous as classically expected. The classical theory of an electron moving in an orbit about a positively charged nucleus indicates that the moving electron should be continuously radiating energy and hence be spiraling in towards the nucleus. Not only does experimental evidence indicate that atoms are stable, but the emitted light coming from atoms suitably excited is in the form of a series of discrete lines rather than a continuous spectrum. In 1885 Balmer provided some kind of coherence to the vast intricacies of atomic spectra by showing that the spectral emission lines from hydrogen could be categorized by the expression

$$\lambda = 3645.6 \frac{n^2}{n^2 - 4} \times 10^{-10} \text{ m} \quad (1.6)$$

where $n = 3, 4, 5, \dots$ and these lines became known as the Balmer series. Up to 1926 the amount of spectral emission data grew tremendously, resembling more and more a giant cryptogram awaiting its Rosetta Stone to

break the code. Bohr's model of the hydrogen atom in 1913 is one of the best known attempts to "crack the code."

Even more direct observations, however, lead to the conclusion that the energy levels for electrons in solids must be a discrete set (said to be quantized). Consider a box containing a monatomic gas with all the atoms of the gas in motion.† If additional energy is supplied to this gas, the additional energy might be distributed in one or both of two ways: an increase in the kinetic energy of the atoms, or an increase in the internal energy of the atoms. If we measured the specific heat of the gas, i.e., the energy required to increase the temperature of the gas by 1°K, and if we calculated the expected increase in kinetic energy, we could determine how much of the energy supplied to the gas had increased the internal energy of the atoms. If we do this, we see that no energy has gone into the internal energy of the atoms, i.e., when we raise the temperature of the gas, *all* of the additional energy given to the gas appears in the kinetic energy of the atoms. What does this mean? One interpretation would be that at least a certain minimum energy ΔE is required before it is possible to increase the internal energy of the atoms, and that the value of the ΔE is much larger than the available thermal energy kT at room temperature, where k is Boltzmann's constant = 1.38×10^{-23} J/degree, and T is the absolute temperature. A continuum of allowed energy states apparently does not exist for the internal energies of an atom, but the atom will stay in its lowest energy state unless we provide at least an energy ΔE . In practice, typical values of ΔE are several electron volts, whereas kT at room temperature is 0.025 eV, since $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$.

Similar conclusions are indicated by experiments involving the scattering of electrons by gases, following the experiments of Franck and Hertz in 1914. If electrons are accelerated through a monatomic gas such as He at reduced pressure, and if the number of electrons collected after passing through the gas is measured as a function of the energy of the collected electrons, it is found that either (a) electrons suffer only elastic scattering and lose no energy, or (b) electrons suffer inelastic scattering and lose energy markedly if their energy is equal to one of a set of discrete values increasing in magnitude up to the ionization energy of the gas atoms. This result may be interpreted as showing that in the electron-atom interaction, only energies corresponding to specific energy differences inside the atom can be absorbed from the impinging electrons.

† See N. Mott, On teaching quantum phenomena, *Contemp. Phys.* 5, 401 (1964), for a helpful treatment.

THE NEW APPROACH†

In the early summer of 1925 Werner Heisenberg was on the island of Heligoland recovering from an attack of hay fever. While there, he invented a way of describing physical quantities using sets of time-dependent complex numbers, which seemed able to provide a framework within which the new phenomena could be described. Within a few months, this approach (which came to be known as matrix mechanics) was developed by others such as Born and Jordan into a full treatment of these problems.

Quite independently, Erwin Schroedinger had been working on the same problem from a somewhat different perspective. At the end of January 1926 he completed Part 1 of "Quantization as an eigenvalue problem." Over the next 6 months he published Parts 2-4 of this major work, and in a very brief space of time the atomic cryptogram seemed to have been deciphered. A very brief introduction is given in Appendix D. Between the publication of Parts 2 and 3, Schroedinger showed that his approach and that of Heisenberg were equivalent although apparently quite different. Between Parts 3 and 4, Schroedinger applied the new method to the linear harmonic oscillator and showed also that particlelike behavior could be simulated by sums of waves (wave packets). By the time Part 4 was published in June 1926, he had developed the complete time-dependent equation and time-dependent perturbation theory, an approximate method needed to calculate time-dependent effects.

We can get a feeling for the underlying ideas in this development by considering the following question: Why is the energy of electrons *in* an atom quantized (an expression used to indicate that only discrete values of energy are allowed, rather than a continuous range of energies), whereas the energy of free electrons is not? That is, why can free electrons take on any positive value of energy, but electrons in atoms are restricted to discrete discontinuous values? It appears from this state of affairs that electron energies are quantized when the electron is confined (as in an atom), but are not quantized when the electron is unconfined, i.e., free. What kind of a system shows this kind of effect? Looking ahead through the material of the next couple of chapters, we are led to realize that there is a curious analogy with waves in a string, depending on whether the ends of the string are fixed or free. When the string has fixed ends, the frequency spectrum of waves is quantized, i.e., only certain values of frequency (the normal modes) are allowed; when the ends are not fixed, these restrictions on allowed frequencies are re-

†For historical background, see, for example, M. Jammer, "The Philosophy of Quantum Mechanics," Wiley, New York, 1974.

moved. If the electron in an atom had wavelike properties and behaved something like a wave in a string with fixed ends, then these properties of quantization, coupled with the identification of $E = h\nu$, might be directly expected. It is with this kind of thinking in mind that we explore the properties of wave systems and see the effects of considering that matter itself partakes of wave properties.

TOPICS FOR DISCUSSION

1.1 Is it necessary, or even reasonable, to suppose that phenomena occurring at sizes much smaller than those encountered in everyday life should be describable by the same models as are useful for everyday life?

1.2 Which of the following interpretations of a scientific theory do you prefer and why?

(a) A system of mathematical propositions designed to represent as simply, as completely, and as exactly as possible a whole group of experimental correlations.

(b) A system of mathematical propositions such as (a) but also including a unifying principle that permits prediction of as yet unobserved effects.

(c) A system of mathematical propositions such as (a) and (b), but also including a suitable "picture" or model for the theory.

1.3 Should we maintain a distinction between behavior and essence: If an electron behaves like a particle, is it then a particle? Or if it behaves like a wave, is it then a wave?

1.4 If one were to ask, "What is the location of an electron if we know that it is moving with a specific velocity?" would this be a meaningful question? Would you prefer to believe that electrons actually have specific positions and velocities simultaneously but the world is such that we can't know them, or that electrons are entities such that thinking in terms of simultaneous position and velocity is an inappropriate thing to do?

SUGGESTED BACKGROUND READING

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2 | *General Properties of Waves*

In this chapter we describe the basic properties of waves and common useful ways of describing them. The various systems we are considering can have their properties summarized in wave equations. We can determine the dependence of frequency on wavelength for the wave system by calculating the conditions necessary for a harmonic wave to be a solution of the wave equation, and we can take into account boundary conditions that may limit the allowed frequencies to certain discrete values. We use the simple problem of waves in a string to illustrate these concepts and finally fantasize a little about what might happen if the wave properties of a string were extended naïvely to electrons or other atomic particles.

BASIC WAVE PROPERTIES

We are concerned particularly with three kinds of wave systems: wave motion in crystalline solids to describe the periodic vibrations of the atoms, electromagnetic waves corresponding to the classical view of light, and electron waves derived from a basic wavelike view of matter itself. Sound waves are long-wavelength longitudinal lattice waves that travel with a velocity of about 10^5 cm/sec; light waves are transverse waves with a velocity of 3×10^{10} cm/sec in a vacuum regardless of the wavelength of the wave. Regardless of their specific physical origin, however, all wave systems share certain features in common.