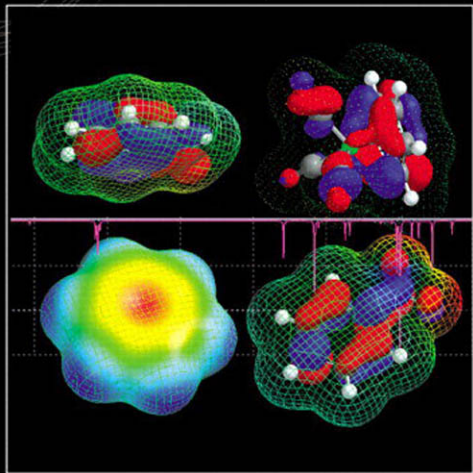


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Quantum Chemistry



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Quantum Chemistry

by Ira N. Levine *Brooklyn College, City College of New York*

SEVENTH EDITION

Quantum Chemistry

Ira N. Levine

Chemistry Department, Brooklyn College, City University of New York

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Preface

This book is intended for first-year graduate and advanced undergraduate courses in quantum chemistry. This text provides students with an in-depth treatment of quantum chemistry, and enables them to understand the basic principles. The limited mathematics background of many chemistry students is taken into account, and reviews of necessary mathematics (such as complex numbers, differential equations, operators, and vectors) are included. Derivations are presented in full, step-by-step detail so that students at all levels can easily follow and understand. A rich variety of homework problems (both quantitative and conceptual) is given for each chapter.

NEW TO THIS EDITION

The following improvements were made to the seventh edition:

- Thorough updates reflect the **latest quantum chemistry research** and methods of computational chemistry, including many new literature references.
- **New problems** have been added to most chapters, including additional computational problems in Chapters 15 and 16.
- Explanations have been revised in areas where students had difficulty.
- **Color** has been added to figures to increase the visual appeal of the book.
- The computer programs in the Solutions Manual and the text were changed from BASIC to C++.
- The text is enlivened by references to modern research in quantum mechanics such as the Ozawa reformulation of the uncertainty principle and the observation of interference effects with very large molecules.

New and expanded material in the seventh edition includes

- New theoretical and experimental work on the uncertainty principle (Section 5.1).
- The CM5 and Hirshfeld-I methods for atomic charges (Section 15.7).
- Static and dynamic correlation (Section 16.1).
- Expanded treatment of extrapolation to the complete-basis-set (CBS) limit (Sections 15.5, 16.1 and 16.4).
- Use of the two-electron reduced density matrix (Section 16.2).
- The DFT-D3 method (Section 16.5).
- The VV10 correlation functional for dispersion (Section 16.5).
- The W1-F12 and W2-F12 methods (Section 16.6).
- Dispersion (stacking) interactions in DNA (Section 16.8).
- The MP2.5, MP2.X, SCS(MI)-CCSD, and SCS(MI)-MP2 methods (Section 16.8).
- An expanded discussion of calculation of NMR shielding constants and spin-spin coupling constants including linear scaling (Section 16.9).
- Fragmentation methods (Section 16.10).
- The PM6-D3H4 and PM7 methods (Section 17.4).

Resources: Optional Spartan Student Edition molecular modeling software provides access to a sophisticated molecular modeling package that combines an easy-to-use graphical interface with a targeted set of computational functions. A solutions manual for the end-of-chapter problems in the book is available at <http://www.pearsonhighered.com/advchemistry>.

The extraordinary expansion of quantum chemistry calculations into all areas of chemistry makes it highly desirable for all chemistry students to understand modern methods of electronic structure calculation, and this book has been written with this goal in mind.

I have tried to make explanations clear and complete, without glossing over difficult or subtle points. Derivations are given with enough detail to make them easy to follow, and wherever possible I avoid resorting to the frustrating phrase “it can be shown that.” The aim is to give students a solid understanding of the physical and mathematical aspects of quantum mechanics and molecular electronic structure. The book is designed to be useful to students in all branches of chemistry, not just future quantum chemists. However, the presentation is such that those who do go on in quantum chemistry will have a good foundation and will not be hampered by misconceptions.

An obstacle faced by many chemistry students in learning quantum mechanics is their unfamiliarity with much of the required mathematics. In this text I have included detailed treatments of the needed mathematics. Rather than putting all the mathematics in an introductory chapter or a series of appendices, I have integrated the mathematics with the physics and chemistry. Immediate application of the mathematics to solving a quantum-mechanical problem will make the mathematics more meaningful to students than would separate study of the mathematics. I have also kept in mind the limited physics background of many chemistry students by reviewing topics in physics.

Previous editions of this book have benefited from the reviews and suggestions of Leland Allen, N. Colin Baird, Steven Bernasek, James Bolton, W. David Chandler, Donald Chesnut, R. James Cross, Gary DeBoer, Douglas Doren, David Farrelly, Melvyn Feinberg, Gordon A. Gallup, Daniel Gerrity, David Goldberg, Robert Griffin, Tracy Hamilton, Sharon Hammes-Schiffer, James Harrison, John Head, Warren Hehre, Robert Hinde, Hans Jaffé, Miklos Kertesz, Neil Kestner, Harry King, Peter Kollman, Anna Krylov, Mel Levy, Errol Lewars, Joel Liebman, Tien-Sung Tom Lin, Ryan McLaughlin, Frank Meeks, Robert Metzger, Charles Millner, John H. Moore, Pedro Muiño, William Palke, Sharon Palmer, Kirk Peterson, Gary Pfeiffer, Russell Pitzer, Oleg Prezhdo, Frank Rioux, Kenneth Sando, Harrison Shull, James J. P. Stewart, Richard Stratt, Fu-Ming Tao, Ronald Terry, Alexander Van Hook, Arieh Warshel, Peter Weber, John S. Winn, and Michael Zerner.

Reviewers for the seventh edition were

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 Scott Kirkby, East Tennessee State University
 Jorge Morales, Texas Technical University
 Ruben Parra, DePaul University
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I wish to thank all these people and several anonymous reviewers for their helpful suggestions.

I would greatly appreciate receiving any suggestions that readers may have for improving the book.

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The Schrödinger Equation

1.1 Quantum Chemistry

In the late seventeenth century, Isaac Newton discovered **classical mechanics**, the laws of motion of macroscopic objects. In the early twentieth century, physicists found that classical mechanics does not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms and molecules. The behavior of such particles is described by a set of laws called **quantum mechanics**.

Quantum chemistry applies quantum mechanics to problems in chemistry. The influence of quantum chemistry is evident in all branches of chemistry. Physical chemists use quantum mechanics to calculate (with the aid of statistical mechanics) thermodynamic properties (for example, entropy, heat capacity) of gases; to interpret molecular spectra, thereby allowing experimental determination of molecular properties (for example, molecular geometries, dipole moments, barriers to internal rotation, energy differences between conformational isomers); to calculate molecular properties theoretically; to calculate properties of transition states in chemical reactions, thereby allowing estimation of rate constants; to understand intermolecular forces; and to deal with bonding in solids.

Organic chemists use quantum mechanics to estimate the relative stabilities of molecules, to calculate properties of reaction intermediates, to investigate the mechanisms of chemical reactions, and to analyze and predict nuclear-magnetic-resonance spectra.

Analytical chemists use spectroscopic methods extensively. The frequencies and intensities of lines in a spectrum can be properly understood and interpreted only through the use of quantum mechanics.

Inorganic chemists use ligand field theory, an approximate quantum-mechanical method, to predict and explain the properties of transition-metal complex ions.

Although the large size of biologically important molecules makes quantum-mechanical calculations on them extremely hard, biochemists are beginning to benefit from quantum-mechanical studies of conformations of biological molecules, enzyme–substrate binding, and solvation of biological molecules.

Quantum mechanics determines the properties of nanomaterials (objects with at least one dimension in the range 1 to 100 nm), and calculational methods to deal with nanomaterials are being developed. When one or more dimensions of a material fall below 100 nm (and especially below 20 nm), dramatic changes in the optical, electronic, chemical, and other properties from those of the bulk material can occur. A semiconductor or metal object with one dimension in the 1 to 100 nm range is called a *quantum well*; one with two dimensions in this range is a *quantum wire*; and one with all three dimensions in this range is a *quantum dot*. The word *quantum* in these names indicates the key role played by quantum mechanics in determining the properties of such materials. Many

people have speculated that nanoscience and nanotechnology will bring about the “next industrial revolution.”

The rapid increase in computer speed and the development of new methods (such as density functional theory—Section 16.4) of doing molecular calculations have made quantum chemistry a practical tool in all areas of chemistry. Nowadays, several companies sell quantum-chemistry software for doing molecular quantum-chemistry calculations. These programs are designed to be used by all kinds of chemists, not just quantum chemists. Because of the rapidly expanding role of quantum chemistry and related theoretical and computational methods, the American Chemical Society began publication of a new periodical, the *Journal of Chemical Theory and Computation*, in 2005.

“Quantum mechanics . . . underlies nearly all of modern science and technology. It governs the behavior of transistors and integrated circuits . . . and is . . . the basis of modern chemistry and biology” (Stephen Hawking, *A Brief History of Time*, 1988, Bantam, chap. 4).

1.2 Historical Background of Quantum Mechanics

The development of quantum mechanics began in 1900 with Planck’s study of the light emitted by heated solids, so we start by discussing the nature of light.

In 1803, Thomas Young gave convincing evidence for the wave nature of light by observing diffraction and interference when light went through two adjacent pinholes. (*Diffraction* is the bending of a wave around an obstacle. *Interference* is the combining of two waves of the same frequency to give a wave whose disturbance at each point in space is the algebraic or vector sum of the disturbances at that point resulting from each interfering wave. See any first-year physics text.)

In 1864, James Clerk Maxwell published four equations, known as Maxwell’s equations, which unified the laws of electricity and magnetism. Maxwell’s equations predicted that an accelerated electric charge would radiate energy in the form of electromagnetic waves consisting of oscillating electric and magnetic fields. The speed predicted by Maxwell’s equations for these waves turned out to be the same as the experimentally measured speed of light. Maxwell concluded that light is an electromagnetic wave.

In 1888, Heinrich Hertz detected radio waves produced by accelerated electric charges in a spark, as predicted by Maxwell’s equations. This convinced physicists that light is indeed an electromagnetic wave.

All electromagnetic waves travel at speed $c = 2.998 \times 10^8$ m/s in vacuum. The frequency ν and wavelength λ of an electromagnetic wave are related by

$$\lambda\nu = c \quad (1.1)$$

(Equations that are enclosed in a box should be memorized. The Appendix gives the Greek alphabet.) Various conventional labels are applied to electromagnetic waves depending on their frequency. In order of increasing frequency are radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays. We shall use the term **light** to denote any kind of electromagnetic radiation. Wavelengths of visible and ultraviolet radiation were formerly given in **angstroms** (Å) and are now given in **nanometers** (nm):

$$1 \text{ nm} = 10^{-9} \text{ m}, \quad 1 \text{ Å} = 10^{-10} \text{ m} = 0.1 \text{ nm} \quad (1.2)$$

In the 1890s, physicists measured the intensity of light at various frequencies emitted by a heated blackbody at a fixed temperature, and did these measurements at several temperatures. A *blackbody* is an object that absorbs all light falling on it. A good

approximation to a blackbody is a cavity with a tiny hole. In 1896, the physicist Wien proposed the following equation for the dependence of blackbody radiation on light frequency and blackbody temperature: $I = av^3/e^{bv/T}$, where a and b are empirical constants, and $I dv$ is the energy with frequency in the range ν to $\nu + d\nu$ radiated per unit time and per unit surface area by a blackbody, with $d\nu$ being an infinitesimal frequency range. Wien's formula gave a good fit to the blackbody radiation data available in 1896, but his theoretical arguments for the formula were considered unsatisfactory.

In 1899–1900, measurements of blackbody radiation were extended to lower frequencies than previously measured, and the low-frequency data showed significant deviations from Wien's formula. These deviations led the physicist Max Planck to propose in October 1900 the following formula: $I = av^3/(e^{bv/T} - 1)$, which was found to give an excellent fit to the data at all frequencies.

Having proposed this formula, Planck sought a theoretical justification for it. In December 1900, he presented a theoretical derivation of his equation to the German Physical Society. Planck assumed the radiation emitters and absorbers in the blackbody to be harmonically oscillating electric charges (“resonators”) in equilibrium with electromagnetic radiation in a cavity. He assumed that the total energy of those resonators whose frequency is ν consisted of N indivisible “energy elements,” each of magnitude $h\nu$, where N is an integer and h (**Planck's constant**) was a new constant in physics. Planck distributed these energy elements among the resonators. In effect, this restricted the energy of each resonator to be a whole-number multiple of $h\nu$ (although Planck did not explicitly say this). Thus the energy of each resonator was **quantized**, meaning that only certain discrete values were allowed for a resonator energy. Planck's theory showed that $a = 2\pi h/c^2$ and $b = h/k$, where k is Boltzmann's constant. By fitting the experimental blackbody curves, Planck found $h = 6.6 \times 10^{-34} \text{ J} \cdot \text{s}$.

Planck's work is usually considered to mark the beginning of quantum mechanics. However, historians of physics have debated whether Planck in 1900 viewed energy quantization as a description of physical reality or as merely a mathematical approximation that allowed him to obtain the correct blackbody radiation formula. [See O. Darrigol, *Centaurus*, **43**, 219 (2001); C. A. Gearhart, *Phys. Perspect.*, **4**, 170 (2002) (available online at employees.csbsju.edu/cgearhart/Planck/PQH.pdf); S. G. Brush, *Am. J. Phys.*, **70**, 119 (2002) (www.punsterproductions.com/~sciencehistory/cautious.htm).] The physics historian Kragh noted that “If a revolution occurred in physics in December 1900, nobody seemed to notice it. Planck was no exception, and the importance ascribed to his work is largely a historical reconstruction” (H. Kragh, *Physics World*, Dec. 2000, p. 31).

The concept of energy quantization is in direct contradiction to all previous ideas of physics. According to Newtonian mechanics, the energy of a material body can vary continuously. However, only with the hypothesis of quantized energy does one obtain the correct blackbody-radiation curves.

The second application of energy quantization was to the photoelectric effect. In the *photoelectric effect*, light shining on a metal causes emission of electrons. The energy of a wave is proportional to its intensity and is not related to its frequency, so the electromagnetic-wave picture of light leads one to expect that the kinetic energy of an emitted photoelectron would increase as the light intensity increases but would not change as the light frequency changes. Instead, one observes that the kinetic energy of an emitted electron is independent of the light's intensity but increases as the light's frequency increases.

In 1905, Einstein showed that these observations could be explained by regarding light as composed of particlelike entities (called **photons**), with each photon having an energy

$$E_{\text{photon}} = h\nu \quad (1.3)$$

When an electron in the metal absorbs a photon, part of the absorbed photon energy is used to overcome the forces holding the electron in the metal; the remainder appears as kinetic energy of the electron after it has left the metal. Conservation of energy gives $h\nu = \Phi + T$, where Φ is the minimum energy needed by an electron to escape the metal (the metal's *work function*), and T is the maximum kinetic energy of an emitted electron. An increase in the light's frequency ν increases the photon energy and hence increases the kinetic energy of the emitted electron. An increase in light intensity at fixed frequency increases the rate at which photons strike the metal and hence increases the rate of emission of electrons, but does not change the kinetic energy of each emitted electron. (According to Kragh, a strong "case can be made that it was Einstein who first recognized the essence of quantum theory"; Kragh, *Physics World*, Dec. 2000, p. 31.)

The photoelectric effect shows that light can exhibit particlelike behavior in addition to the wavelike behavior it shows in diffraction experiments.

In 1907, Einstein applied energy quantization to the vibrations of atoms in a solid element, assuming that each atom's vibrational energy in each direction (x, y, z) is restricted to be an integer times $h\nu_{\text{vib}}$, where the vibrational frequency ν_{vib} is characteristic of the element. Using statistical mechanics, Einstein derived an expression for the constant-volume heat capacity C_V of the solid. Einstein's equation agreed fairly well with known C_V -versus-temperature data for diamond.

Now let us consider the structure of matter.

In the late nineteenth century, investigations of electric discharge tubes and natural radioactivity showed that atoms and molecules are composed of charged particles. Electrons have a negative charge. The proton has a positive charge equal in magnitude but opposite in sign to the electron charge and is 1836 times as heavy as the electron. The third constituent of atoms, the neutron (discovered in 1932), is uncharged and slightly heavier than the proton.

Starting in 1909, Rutherford, Geiger, and Marsden repeatedly passed a beam of alpha particles through a thin metal foil and observed the deflections of the particles by allowing them to fall on a fluorescent screen. Alpha particles are positively charged helium nuclei obtained from natural radioactive decay. Most of the alpha particles passed through the foil essentially undeflected, but, surprisingly, a few underwent large deflections, some being deflected backward. To get large deflections, one needs a very close approach between the charges, so that the Coulombic repulsive force is great. If the positive charge were spread throughout the atom (as J. J. Thomson had proposed in 1904), once the high-energy alpha particle penetrated the atom, the repulsive force would fall off, becoming zero at the center of the atom, according to classical electrostatics. Hence Rutherford concluded that such large deflections could occur only if the positive charge were concentrated in a tiny, heavy nucleus.

An atom contains a tiny (10^{-13} to 10^{-12} cm radius), heavy nucleus consisting of neutrons and Z protons, where Z is the atomic number. Outside the nucleus there are Z electrons. The charged particles interact according to Coulomb's law. (The nucleons are held together in the nucleus by strong, short-range nuclear forces, which will not concern us.) The radius of an atom is about one angstrom, as shown, for example, by results from the kinetic theory of gases. Molecules have more than one nucleus.

The chemical properties of atoms and molecules are determined by their electronic structure, and so the question arises as to the nature of the motions and energies of the electrons. Since the nucleus is much more massive than the electron, we expect the motion of the nucleus to be slight compared with the electrons' motions.

In 1911, Rutherford proposed his planetary model of the atom in which the electrons revolved about the nucleus in various orbits, just as the planets revolve about the sun. However, there is a fundamental difficulty with this model. According to classical

electromagnetic theory, an accelerated charged particle radiates energy in the form of electromagnetic (light) waves. An electron circling the nucleus at constant speed is being accelerated, since the direction of its velocity vector is continually changing. Hence the electrons in the Rutherford model should continually lose energy by radiation and therefore would spiral toward the nucleus. Thus, according to classical (nineteenth-century) physics, the Rutherford atom is unstable and would collapse.

A possible way out of this difficulty was proposed by Niels Bohr in 1913, when he applied the concept of quantization of energy to the hydrogen atom. Bohr assumed that the energy of the electron in a hydrogen atom was quantized, with the electron constrained to move only on one of a number of allowed circles. When an electron makes a transition from one Bohr orbit to another, a photon of light whose frequency ν satisfies

$$E_{\text{upper}} - E_{\text{lower}} = h\nu \quad (1.4)$$

is absorbed or emitted, where E_{upper} and E_{lower} are the energies of the upper and lower states (conservation of energy). With the assumption that an electron making a transition from a free (ionized) state to one of the bound orbits emits a photon whose frequency is an integral multiple of one-half the classical frequency of revolution of the electron in the bound orbit, Bohr used classical mechanics to derive a formula for the hydrogen-atom energy levels. Using (1.4), he got agreement with the observed hydrogen spectrum. However, attempts to fit the helium spectrum using the Bohr theory failed. Moreover, the theory could not account for chemical bonds in molecules.

The failure of the Bohr model arises from the use of classical mechanics to describe the electronic motions in atoms. The evidence of atomic spectra, which show discrete frequencies, indicates that only certain energies of motion are allowed; the electronic energy is quantized. However, classical mechanics allows a continuous range of energies. Quantization does occur in wave motion—for example, the fundamental and overtone frequencies of a violin string. Hence Louis de Broglie suggested in 1923 that the motion of electrons might have a wave aspect; that an electron of mass m and speed v would have a wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (1.5)$$

associated with it, where p is the linear momentum. De Broglie arrived at Eq. (1.5) by reasoning in analogy with photons. The energy of a photon can be expressed, according to Einstein's special theory of relativity, as $E = pc$, where c is the speed of light and p is the photon's momentum. Using $E_{\text{photon}} = h\nu$, we get $pc = h\nu = hc/\lambda$ and $\lambda = h/p$ for a photon traveling at speed c . Equation (1.5) is the corresponding equation for an electron.

In 1927, Davisson and Germer experimentally confirmed de Broglie's hypothesis by reflecting electrons from metals and observing diffraction effects. In 1932, Stern observed the same effects with helium atoms and hydrogen molecules, thus verifying that the wave effects are not peculiar to electrons, but result from some general law of motion for microscopic particles. Diffraction and interference have been observed with molecules as large as $\text{C}_{48}\text{H}_{26}\text{F}_{24}\text{N}_8\text{O}_8$ passing through a diffraction grating [T. Juffmann et al., *Nat. Nanotechnol.*, **7**, 297 (2012)]. A movie of the buildup of an interference pattern involving $\text{C}_{32}\text{H}_{18}\text{N}_8$ molecules can be seen at www.youtube.com/watch?v=vCiOMQIRU7I.

Thus electrons behave in some respects like particles and in other respects like waves. We are faced with the apparently contradictory “wave–particle duality” of matter (and of light). How can an electron be both a particle, which is a localized entity, and a wave, which is nonlocalized? The answer is that an electron is neither a wave nor a particle, but something else. An accurate pictorial description of an electron's behavior is impossible

using the wave or particle concept of classical physics. The concepts of classical physics have been developed from experience in the macroscopic world and do not properly describe the microscopic world. Evolution has shaped the human brain to allow it to understand and deal effectively with macroscopic phenomena. The human nervous system was not developed to deal with phenomena at the atomic and molecular level, so it is not surprising if we cannot fully understand such phenomena.

Although both photons and electrons show an apparent duality, they are not the same kinds of entities. Photons travel at speed c in vacuum and have zero rest mass; electrons always have $v < c$ and a nonzero rest mass. Photons must always be treated relativistically, but electrons whose speed is much less than c can be treated nonrelativistically.

1.3 The Uncertainty Principle

Let us consider what effect the wave–particle duality has on attempts to measure simultaneously the x coordinate and the x component of linear momentum of a microscopic particle. We start with a beam of particles with momentum p , traveling in the y direction, and we let the beam fall on a narrow slit. Behind this slit is a photographic plate. See [Fig. 1.1](#).

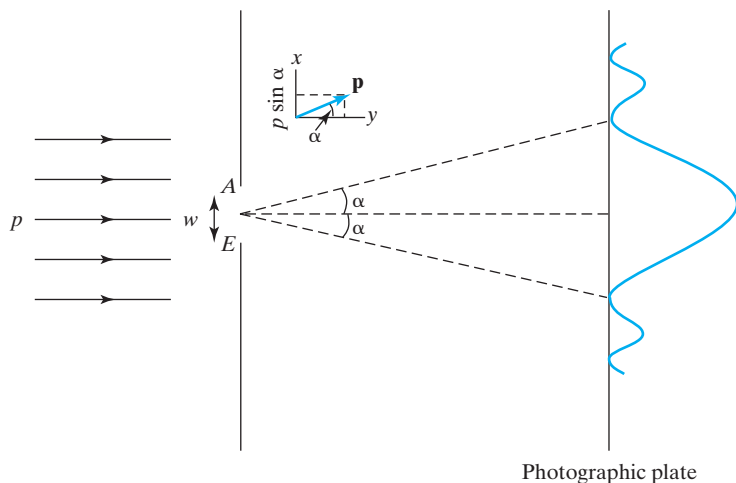
Particles that pass through the slit of width w have an uncertainty w in their x coordinate at the time of going through the slit. Calling this spread in x values Δx , we have $\Delta x = w$.

Since microscopic particles have wave properties, they are diffracted by the slit producing (as would a light beam) a diffraction pattern on the plate. The height of the graph in [Fig. 1.1](#) is a measure of the number of particles reaching a given point. The diffraction pattern shows that when the particles were diffracted by the slit, their direction of motion was changed so that part of their momentum was transferred to the x direction. The x component of momentum p_x equals the projection of the momentum vector \mathbf{p} in the x direction. A particle deflected upward by an angle α has $p_x = p \sin \alpha$. A particle deflected downward by α has $p_x = -p \sin \alpha$. Since most of the particles undergo deflections in the range $-\alpha$ to α , where α is the angle to the first minimum in the diffraction pattern, we shall take one-half the spread of momentum values in the central diffraction peak as a measure of the uncertainty Δp_x in the x component of momentum: $\Delta p_x = p \sin \alpha$.

Hence at the slit, where the measurement is made,

$$\Delta x \Delta p_x = pw \sin \alpha \quad (1.6)$$

FIGURE 1.1 Diffraction of electrons by a slit.



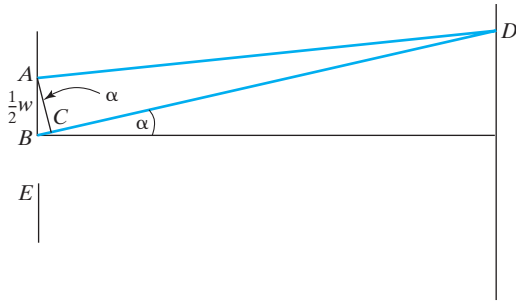


FIGURE 1.2 Calculation of first diffraction minimum.

The angle α at which the first diffraction minimum occurs is readily calculated. The condition for the first minimum is that the difference in the distances traveled by particles passing through the slit at its upper edge and particles passing through the center of the slit should be equal to $\frac{1}{2}\lambda$, where λ is the wavelength of the associated wave. Waves originating from the top of the slit are then exactly out of phase with waves originating from the center of the slit, and they cancel each other. Waves originating from a point in the slit at a distance d below the slit midpoint cancel with waves originating at a distance d below the top of the slit. Drawing AC in **Fig. 1.2** so that $AD = CD$, we have the difference in path length as BC . The distance from the slit to the screen is large compared with the slit width. Hence AD and BD are nearly parallel. This makes the angle ACB essentially a right angle, and so angle $BAC = \alpha$. The path difference BC is then $\frac{1}{2}w \sin \alpha$. Setting BC equal to $\frac{1}{2}\lambda$, we have $w \sin \alpha = \lambda$, and Eq. (1.6) becomes $\Delta x \Delta p_x = p\lambda$. The wavelength λ is given by the de Broglie relation $\lambda = h/p$, so $\Delta x \Delta p_x = h$. Since the uncertainties have not been precisely defined, the equality sign is not really justified. Instead we write

$$\Delta x \Delta p_x \approx h \quad (1.7)$$

indicating that the product of the uncertainties in x and p_x is of the order of magnitude of Planck's constant.

Although we have demonstrated (1.7) for only one experimental setup, its validity is general. No matter what attempts are made, the wave-particle duality of microscopic "particles" imposes a limit on our ability to measure simultaneously the position and momentum of such particles. The more precisely we determine the position, the less accurate is our determination of momentum. (In **Fig. 1.1**, $\sin \alpha = \lambda/w$, so narrowing the slit increases the spread of the diffraction pattern.) This limitation is the **uncertainty principle**, discovered in 1927 by Werner Heisenberg.

Because of the wave-particle duality, the act of measurement introduces an uncontrollable disturbance in the system being measured. We started with particles having a precise value of p_x (zero). By imposing the slit, we measured the x coordinate of the particles to an accuracy w , but this measurement introduced an uncertainty into the p_x values of the particles. The measurement changed the state of the system.

1.4 The Time-Dependent Schrödinger Equation

Classical mechanics applies only to macroscopic particles. For microscopic "particles" we require a new form of mechanics, called **quantum mechanics**. We now consider some of the contrasts between classical and quantum mechanics. For simplicity a one-particle, one-dimensional system will be discussed.

In classical mechanics the motion of a particle is governed by Newton's second law:

$$F = ma = m \frac{d^2x}{dt^2} \quad (1.8)$$

where F is the force acting on the particle, m is its mass, and t is the time; a is the acceleration, given by $a = dv/dt = (d/dt)(dx/dt) = d^2x/dt^2$, where v is the velocity. Equation (1.8) contains the second derivative of the coordinate x with respect to time. To solve it, we must carry out two integrations. This introduces two arbitrary constants c_1 and c_2 into the solution, and

$$x = g(t, c_1, c_2) \quad (1.9)$$

where g is some function of time. We now ask: What information must we possess at a given time t_0 to be able to predict the future motion of the particle? If we know that at t_0 the particle is at point x_0 , we have

$$x_0 = g(t_0, c_1, c_2) \quad (1.10)$$

Since we have two constants to determine, more information is needed. Differentiating (1.9), we have

$$\frac{dx}{dt} = v = \frac{d}{dt}g(t, c_1, c_2)$$

If we also know that at time t_0 the particle has velocity v_0 , then we have the additional relation

$$v_0 = \left. \frac{d}{dt}g(t, c_1, c_2) \right|_{t=t_0} \quad (1.11)$$

We may then use (1.10) and (1.11) to solve for c_1 and c_2 in terms of x_0 and v_0 . Knowing c_1 and c_2 , we can use Eq. (1.9) to predict the exact future motion of the particle.

As an example of Eqs. (1.8) to (1.11), consider the vertical motion of a particle in the earth's gravitational field. Let the x axis point upward. The force on the particle is downward and is $F = -mg$, where g is the gravitational acceleration constant. Newton's second law (1.8) is $-mg = md^2x/dt^2$, so $d^2x/dt^2 = -g$. A single integration gives $dx/dt = -gt + c_1$. The arbitrary constant c_1 can be found if we know that at time t_0 the particle had velocity v_0 . Since $v = dx/dt$, we have $v_0 = -gt_0 + c_1$ and $c_1 = v_0 + gt_0$. Therefore, $dx/dt = -gt + gt_0 + v_0$. Integrating a second time, we introduce another arbitrary constant c_2 , which can be evaluated if we know that at time t_0 the particle had position x_0 . We find (Prob. 1.7) $x = x_0 - \frac{1}{2}g(t - t_0)^2 + v_0(t - t_0)$. Knowing x_0 and v_0 at time t_0 , we can predict the future position of the particle.

The classical-mechanical potential energy V of a particle moving in one dimension is defined to satisfy

$$\frac{\partial V(x, t)}{\partial x} = -F(x, t) \quad (1.12)$$

For example, for a particle moving in the earth's gravitational field, $\partial V/\partial x = -F = mg$ and integration gives $V = mgx + c$, where c is an arbitrary constant. We are free to set the zero level of potential energy wherever we please. Choosing $c = 0$, we have $V = mgx$ as the potential-energy function.

The word **state** in classical mechanics means a specification of the position and velocity of each particle of the system at some instant of time, plus specification of the forces

acting on the particles. According to Newton's second law, given the state of a system at any time, its future state and future motions are exactly determined, as shown by Eqs. (1.9)–(1.11). The impressive success of Newton's laws in explaining planetary motions led many philosophers to use Newton's laws as an argument for philosophical determinism. The mathematician and astronomer Laplace (1749–1827) assumed that the universe consisted of nothing but particles that obeyed Newton's laws. Therefore, given the state of the universe at some instant, the future motion of everything in the universe was completely determined. A super-being able to know the state of the universe at any instant could, in principle, calculate all future motions.

Although classical mechanics is deterministic, many classical-mechanical systems (for example, a pendulum oscillating under the influence of gravity, friction, and a periodically varying driving force) show chaotic behavior for certain ranges of the systems' parameters. In a chaotic system, the motion is extraordinarily sensitive to the initial values of the particles' positions and velocities and to the forces acting, and two initial states that differ by an experimentally undetectable amount will eventually lead to very different future behavior of the system. Thus, because the accuracy with which one can measure the initial state is limited, prediction of the long-term behavior of a chaotic classical-mechanical system is, in practice, impossible, even though the system obeys deterministic equations. Computer calculations of solar-system planetary orbits over tens of millions of years indicate that the motions of the planets are chaotic [I. Peterson, *Newton's Clock: Chaos in the Solar System*, Freeman, 1993; J. J. Lissauer, *Rev. Mod. Phys.*, **71**, 835 (1999)].

Given exact knowledge of the present state of a classical-mechanical system, we can predict its future state. However, the Heisenberg uncertainty principle shows that we cannot determine simultaneously the exact position and velocity of a microscopic particle, so the very knowledge required by classical mechanics for predicting the future motions of a system cannot be obtained. We must be content in quantum mechanics with something less than complete prediction of the exact future motion.

Our approach to quantum mechanics will be to *postulate* the basic principles and then use these postulates to deduce experimentally testable consequences such as the energy levels of atoms. To describe the **state** of a system in quantum mechanics, we postulate the existence of a function Ψ of the particles' coordinates called the **state function** or **wave function** (often written as **wavefunction**). Since the state will, in general, change with time, Ψ is also a function of time. For a one-particle, one-dimensional system, we have $\Psi = \Psi(x, t)$. The wave function contains all possible information about a system, so instead of speaking of “the state described by the wave function Ψ ,” we simply say “the state Ψ .” Newton's second law tells us how to find the future state of a classical-mechanical system from knowledge of its present state. To find the future state of a quantum-mechanical system from knowledge of its present state, we want an equation that tells us how the wave function changes with time. For a one-particle, one-dimensional system, this equation is postulated to be

$$-\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t)\Psi(x, t) \quad (1.13)$$

where the constant \hbar (**h-bar**) is defined as

$$\hbar \equiv \frac{h}{2\pi} \quad (1.14)$$