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Introduction to Quantum Chemistry: The Schrödinger Equation

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March 2021

1 Quantum Chemistry

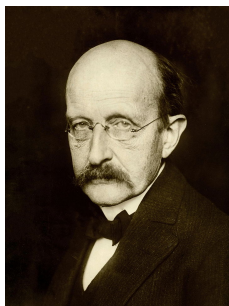
In the late seventeenth century, Isaac Newton discovered **classical mechanics**, the laws of motion of macroscopic objects. In the early twentieth century, physicists found that classical mechanics does not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms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

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.

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.



Planck in 1933

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.)



Interference electrons double slits

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

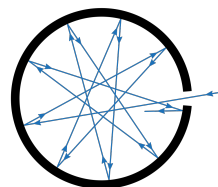
$$\lambda\nu = c \quad (1)$$

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** (\AA) and are now given in **nanometers** (nm):

$$1nm = 10^{-9}m, \quad 1\text{\AA} = 10^{-10}m = 0.1nm \quad (2)$$

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: $I = a\nu^3/e^{b\nu/T}$, where a and b are empirical constants, and $I d\nu$ 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: $I = a\nu^3/(e^{b\nu/T} - 1)$, 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 $h = 6.6 \times 10^{-34} \text{ J}\cdot\text{s}$.

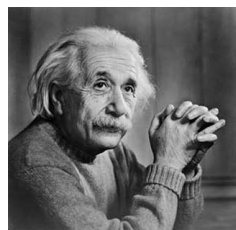


Planck in 1901

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 particle-like entities (called **photons**), with each photon having an energy

$$E_{\text{photon}} = h\nu \quad (3)$$



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. and T is the maximum kinetic energy of an emitted electron.

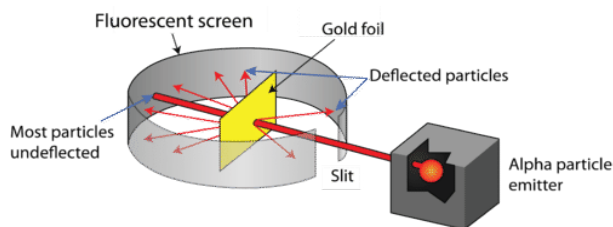
An increase in the light's frequency ν increases the photon energy and hence increases the kinetic energy of the emitted electron. An increase in light intensity at fixed frequency increases the rate at which photons strike the metal and hence increases the rate of emission of electrons, but does not change the kinetic energy of each emitted electron.

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 $h\nu_{vib}$, 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.

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.

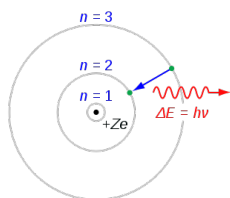
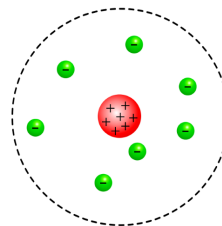
Starting in 1909, Rutherford, Geiger, and Marsden repeatedly passed a beam of alpha particles through a thin metal foil and observed the deflections of the particles by allowing them to fall on a fluorescent screen. Alpha particles are positively charged helium nuclei obtained from natural radioactive 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.



Rutherford's Gold Foil Experiment

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.

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

$$E_{upper} - E_{lower} = h\nu \quad (4)$$

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 (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 ν would have a wavelength

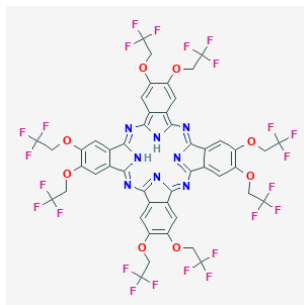
$$\lambda = \frac{h}{m\nu} = \frac{h}{p} \quad (5)$$

associated with it, where p is the linear momentum. De Broglie arrived at Eq. (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 (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.



De Broglie



$\text{C}_{48}\text{H}_{26}\text{F}_{24}\text{N}_8\text{O}_8$

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.

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.

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 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,

$$\Delta x \Delta p_x = pw \sin \alpha \quad (6)$$

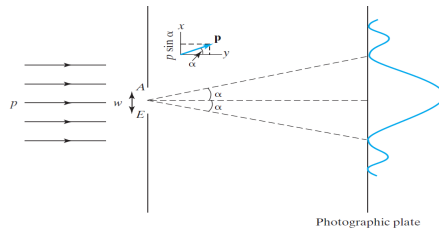


Figure 1: Diffraction of electrons by a slit.

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.

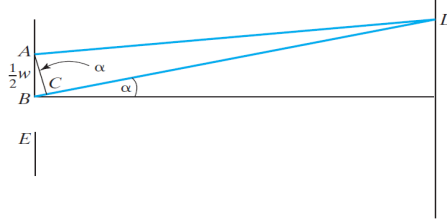


Figure 2: Calculation of first diffraction minimum.

Drawing AC in Fig. 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. (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

$$\Delta x \Delta p_x \approx h \quad (7)$$

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 (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, $\sin \alpha = \lambda/w$, 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.

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:

$$F = ma = m \frac{d^2x}{dt^2} \quad (8)$$

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 (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

$$x = g(t, c_1, c_2) \quad (9)$$

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

$$x_0 = g(t_0, c_1, c_2) \quad (10)$$

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

$$v_0 = \left. \frac{d}{dt}g(t, c_1, c_2) \right|_{t=t_0} \quad (11)$$

We may then use (10) and (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. (9) to predict the exact future motion of the particle.

As an example of Eqs. (8) to (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 (8) is $-mg = m d^2x/dt^2$, 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, $dx/dt = -gt + v_0 + gt_0$.

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 $x = x_0 - \frac{1}{2}g(t - t_0)^2 + v_0(t - t_0)$. 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

$$\frac{\partial V(x, t)}{\partial x} = -F(x, t) \quad (12)$$

For example, for a particle moving in the earth's gravitational field, $\partial V/\partial x = -F = mg$ 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. (9)–(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.



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

$$-\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t) \quad (13)$$

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

$$\hbar = \frac{h}{2\pi} \quad (14)$$

The concept of the wave function and the equation governing its change with time were discovered in 1926 by the Austrian physicist Erwin Schrödinger (1887–1961). In this equation, known as the **time-dependent Schrödinger equation** (or the **Schrödinger wave equation**), $i = \sqrt{-1}$, m is the mass of the particle, and $V(x, t)$ is the potential energy function of the system.



The time-dependent Schrödinger equation contains the first derivative of the wave function with respect to time and allows us to calculate the future wave function (state) at any time, if we know the wave function at time t_0 .

The wave function contains all the information we can possibly know about the system it describes. What information does Ψ give us about the result of a measurement of the x coordinate of the particle? We cannot expect Ψ to involve the definite specification of position that the state of a classical-mechanical system does. The correct answer to this question was provided by Max Born shortly after Schrödinger discovered the Schrödinger equation. Born postulated that for a one-particle, one-dimensional system,

$$|\Psi(x, t)|^2 dx \quad (15)$$

gives the *probability* at time t of finding the particle in the region of the x axis lying between x and $x + dx$. In (15) the bars denote the absolute value and dx is an infinitesimal length on the x axis. The function $|\Psi(x, t)|^2$ is the **probability density** for finding the particle at various places on the x axis. For example, suppose that at some particular time t_0 the particle is in a state characterized by the wave function $a e^{bx^2}$, where a and b are real constants. If we measure the particle’s position at time t_0 , we might get any value of x , because the probability density $a^2 e^{bx^2}$ is nonzero everywhere. Values of x in the region around $x = 0$ are more likely to be found than other values, since $|\Psi|^2$ is a maximum at the origin in this case.

To relate $|\Psi|^2$ to experimental measurements, we would take many identical non-interacting systems, each of which was in the same state Ψ . Then the

particle's position in each system is measured. If we had n systems and made n measurements, and if dn_x denotes the number of measurements for which we found the particle between x and $x + dx$, then dn_x/n is the probability for finding the particle between x and $x + dx$. Thus

$$\frac{dn_x}{n} = |\Psi|^2 dx$$

and a graph of $(1/n)dn_x/dx$ versus x gives the probability density $|\Psi|^2$ as a function of x . It might be thought that we could find the probability-density function by taking one system that was in the state Ψ and repeatedly measuring the particle's position. This procedure is wrong because the process of measurement generally changes the state of a system.

Quantum mechanics is *statistical* in nature. Knowing the state, we cannot predict the result of a position measurement with certainty; we can only predict the *probabilities* of various possible results. The Bohr theory of the hydrogen atom specified the precise path of the electron and is therefore not a correct quantum-mechanical picture.

Quantum mechanics does not say that an electron is distributed over a large region of space as a wave is distributed. Rather, it is the probability patterns (wave functions) used to describe the electron's motion that behave like waves and satisfy a wave equation.

Quantum mechanics provides the law of motion for microscopic particles. Experimentally, macroscopic objects obey classical mechanics. Hence for quantum mechanics to be a valid theory, it should reduce to classical mechanics as we make the transition from microscopic to macroscopic particles. Quantum effects are associated with the de Broglie wavelength $\lambda = h/mv$. Since h is very small, the de Broglie wavelength of macroscopic objects is essentially zero. Thus, in the limit $\lambda \rightarrow 0$, we expect the time-dependent Schrödinger equation to reduce to Newton's second law.

A similar situation holds in the relation between special relativity and classical mechanics. In the limit $v/c \rightarrow 0$, where c is the speed of light, special relativity reduces to classical mechanics. The form of quantum mechanics that we will develop will be nonrelativistic. A complete integration of relativity with quantum mechanics has not been achieved.

Historically, quantum mechanics was first formulated in 1925 by Heisenberg, Born, and Jordan using matrices, several months before Schrödinger's 1926 formulation using differential equations. Schrödinger proved that the Heisenberg formulation (called **matrix mechanics**) is equivalent to the Schrödinger formulation (called **wave mechanics**). In 1926, Dirac and Jordan, working independently, formulated quantum mechanics in an abstract version called *transformation theory* that is a generalization of matrix mechanics and wave mechanics. In 1948, Feynman devised the *path integral* formulation of quantum mechanics.

5 The Time-Independent Schrödinger Equation

The time-dependent Schrödinger equation (13) is formidable looking. Fortunately, many applications of quantum mechanics to chemistry do not use this equation. Instead, the simpler time-independent Schrödinger equation is used. We now derive the time-independent from the time-dependent Schrödinger equation for the one-particle, one-dimensional case.

We begin by restricting ourselves to the special case where the potential energy V is not a function of time but depends only on x . This will be true if the system experiences no time-dependent external forces. The time-dependent Schrödinger equation reads

$$-\frac{\hbar}{i} \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) \quad (16)$$

We now restrict ourselves to looking for those solutions of (16) that can be written as the product of a function of time and a function of x :

$$\Psi(x, t) = f(t) \psi(x) \quad (17)$$

Capital psi is used for the time-dependent wave function and lowercase psi for the factor that depends only on the coordinate x . States corresponding to wave functions of the form (17) possess certain properties that make them of great interest. Taking partial derivatives of (1.17), we have

$$\frac{\partial \Psi(x, t)}{\partial t} = \frac{df(t)}{dt} \psi(x), \quad \frac{\partial^2 \Psi(x, t)}{\partial x^2} = f(t) \frac{d^2 \psi(x)}{dx^2}$$

Substitution into (16) gives

$$\begin{aligned} -\frac{\hbar}{i} \frac{df(t)}{dt} \psi(x) &= -\frac{\hbar^2}{2m} f(t) \frac{d^2 \psi(x)}{dx^2} + V(x) f(t) \psi(x) \\ -\frac{\hbar}{i} \frac{1}{f(t)} \frac{df(t)}{dt} &= -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x) \end{aligned} \quad (18)$$

where we divided by $f\psi$. In general, we expect the quantity to which each side of (18) is equal to be a certain function of x and t . However, the right side of (18) does not depend on t , so the function to which each side of (18) is equal must be independent of t . The left side of (18) is independent of x , so this function must also be independent of x . Since the function is independent of both variables, x and t , it must be a constant. We call this constant E .

Equating the left side of (18) to E , we get

$$\frac{df(t)}{f(t)} = -\frac{iE}{\hbar} dt$$

Integrating both sides of this equation with respect to t , we have

$$\ln f(t) = -iEt/\hbar + C$$

where C is an arbitrary constant of integration. Hence

$$f(t) = e^C e^{-iEt/\hbar} = A e^{-iEt/\hbar}$$

where the arbitrary constant A has replaced e^C . Since A can be included as a factor in the function $\psi(x)$ that multiplies $f(t)$ in (17), A can be omitted from $f(t)$. Thus

$$f(t) = e^{-iEt/\hbar}$$

Equating the right side of (18) to E , we have

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (19)$$

Equation (19) is the **time-independent Schrödinger equation** for a single particle of mass m moving in one dimension.

What is the significance of the constant E ? Since E occurs as $[E - V(x)]$ in (19), E has the same dimensions as v , so E has the dimensions of energy. In fact, we postulate that E is the energy of the system. Thus, for cases where the potential energy is a function of X only, there exist wave functions of the form

$$\Psi(x, t) = e^{-iEt/\hbar} \psi(x) \quad (20)$$

and these wave functions correspond to states of constant energy E . Much of our attention in the next few chapters will be devoted to finding the solutions of (19) for various systems.

The wave function in (20) is complex, but the quantity that is experimentally observable is the probability density $|\Psi(x, t)|^2$. The square of the absolute value of a complex quantity is given by the product of the quantity with its complex conjugate, the complex conjugate being formed by replacing i with $-i$ wherever it occurs. Thus

$$|\Psi|^2 = \Psi^* \Psi \quad (21)$$

where the star denotes the complex conjugate. For the wave function (1.20),

$$\begin{aligned} |\Psi(x, t)|^2 &= [e^{-iEt/\hbar} \psi(x)]^2 e^{-iEt/\hbar} \psi(x) \\ &= e^{-iEt/\hbar} \psi(x)^* e^{-iEt/\hbar} \psi(x) \\ &= e^0 \psi(x)^* \psi(x) = \psi(x)^* \psi(x) \end{aligned} \quad (22)$$

$$|\Psi(x, t)|^2 = |\psi(x)|^2$$

In deriving (22), we assumed that E is a real number, so $E = E^*$.

Hence for states of the form (20), the probability density is given by $|\Psi(x)|^2$ and does not change with time. Such states are called **stationary states**. Since the physically significant quantity $|\Psi(x, t)|^2$, and since for stationary states $|\Psi(x)|^2 = |\psi(x)|^2$, the function $\psi(x)$ is often called the **wave function**, although the complete wave function of a stationary state is obtained by multiplying $\psi(x)$ by $e^{-iEt/\hbar}$. The term (stationary state) should not mislead the reader into thinking that a particle in a stationary state is at rest. What is stationary is the probability density $|\Psi(x)|^2$, not the particle itself.

We will be concerned mostly with states of constant energy (stationary states) and hence will usually deal with the time-independent Schrödinger equation (19). For simplicity we will refer to this equation as “the Schrödinger equation.” Note that the Schrödinger equation contains two unknowns: the allowed energies E and the allowed wave functions ψ . To solve for two unknowns, we need to impose additional conditions (called boundary conditions) on ψ besides requiring that it satisfy (19). The boundary conditions determine the allowed energies, since it turns out that only certain values of E allow ψ to satisfy the boundary conditions.

6 Probability

Probability plays a fundamental role in quantum mechanics. This section reviews the mathematics of probability.

There has been much controversy about the proper definition of probability. One definition is the following: If an experiment has n equally probable outcomes, m of which are favorable to the occurrence of a certain event A , then the probability that A occurs is m/n . Note that this definition is circular, since it specifies equally (probable) outcomes when *probability* is what we are trying to define. It is simply assumed that we can recognize equally probable outcomes. An alternative definition is based on actually performing the experiment many times. Suppose that we perform the experiment N times and that in M of these trials the event A occurs. The probability of A occurring is then defined as

$$\lim_{N \rightarrow \infty} \frac{M}{N}$$

Thus, if we toss a coin repeatedly, the fraction of heads will approach $1/2$ as we increase the number of tosses.

For example, suppose we ask for the probability of drawing a heart when a card is picked at random from a standard 52-card deck containing 13 hearts. There are 52 cards and hence 52 equally probable outcomes. There are 13 hearts and hence 13 favorable outcomes. Therefore, $m/n = 13/52 = 1/4$. The probability for drawing a heart is $1/4$.

In quantum mechanics we must deal with probabilities involving a continuous variable, for example, the x -coordinate. It does not make much sense to talk about the probability of a particle being found *at* a particular point such as $x = 0.5000\dots$, since there are an infinite number of points on the x axis, and for any finite number of measurements we make, the probability of getting *exactly* $x = 0.5000\dots$ is vanishingly small. Instead we talk of the probability of finding the particle in a tiny interval of the x -axis lying between x and $x + dx$, dx being an infinitesimal element of length. This probability will naturally be proportional to the length of the interval, dx , and will vary for different regions of the x axis. Hence the probability that the particle will be found between x and $x + dx$ is equal to $g(x)dx$, where $g(x)$ is some function that tells how the probability varies over the x axis. The function $g(x)$ is called the **probability density**, since it is

a probability per unit length. Since probabilities are real, nonnegative numbers, $g(x)$ must be a real function that is everywhere nonnegative. The wave function Ψ can take on negative and complex values and is not a probability density. Quantum mechanics postulates that the probability density is $|\Psi|^2$ [Eq. (15)].

What is the probability that the particle lies in some finite region of space $a \leq x \leq b$? To find this probability, we sum up the probabilities $|\Psi|^2 dx$ of finding the particle in all the infinitesimal regions lying between a and b . This is just the definition of the definite integral

$$\int_a^b |\Psi|^2 dx = Pr(a \leq x \leq b) \quad (23)$$

where Pr denotes a probability. A probability of 1 represents certainty. Since it is certain that the particle is somewhere on the x axis, we have the requirement

$$\int_{-\infty}^{\infty} |\Psi|^2 dx \quad (24)$$

When Ψ satisfies (24), it is said to be **normalized**. For a stationary state, $|\Psi|^2 = |\psi|^2$ and $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$.

7 Summary

The state of a quantum-mechanical system is described by a state function or wave function Ψ , which is a function of the coordinates of the particles of the system and of the time. The state function changes with time according to the time-dependent Schrödinger equation, which for a one-particle, one-dimensional system is Eq. (13). For such a system, the quantity $|\Psi(x, t)|^2$ gives the probability that a measurement of the particle's position at time t will find it between x and $x + dx$. The state function is normalized according to $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$. If the system's potential-energy function does not depend on t , then the system can exist in one of a number of stationary states of fixed energy. For a stationary state of a one-particle, one-dimensional system, $\Psi(x, t) = e^{-iEt/\hbar} \psi(x)$, where the time-independent wave function $\psi(x)$ is a solution of the time-independent Schrödinger equation (19).

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