

Max Planck (1858–1947)
Established equation $E = h \nu$



Louis De Broglie (1892-1987)
Attributed wave-like properties to particles

2

The postulates of quantum mechanics

2.1 The five postulates of quantum mechanics

The formulation of quantum mechanics, also called wave mechanics focuses on the wave function, $\Psi(x, y, z, t)$, which depends on the spatial coordinates x , y , z , and the time t . In the following sections we shall restrict ourselves to one spatial dimension x , so that the wave function depends solely on x . An

extension to three spatial dimensions can be done easily. The wave function $\Psi(x, t)$ and its complex conjugate $\Psi^*(x, t)$ are the focal point of quantum mechanics, because they provide a concrete meaning in the macroscopic physical world: The product $\Psi^*(x, t) \Psi(x, t) dx$ is the probability to find a particle, for example an electron, within the interval x and $x + dx$. The particle is described quantum mechanically by the wave function $\Psi(x, t)$. The product $\Psi^*(x, t) \Psi(x, t)$ is therefore called the **window of quantum mechanics to the real world**.

Quantum mechanics further differs from classical mechanics by the employment of **operators** rather than the use of **dynamical variables**. Dynamical variables are used in classical mechanics, and they are variables such as position, momentum, or energy. Dynamical variables are contrasted with **static variables** such as the mass of a particle. Static variables do not change during typical physical processes considered here. In quantum mechanics, dynamical variables are replaced by operators which act on the wave function. Mathematical operators are mathematical expressions that act on an operand. For example, (d/dx) is the differential operator. In the expression $(d/dx) \Psi(x, t)$, the differential operator acts on the wave function,

$\Psi(x, t)$, which is the operand. Such operands will be used to deduce the quantum mechanical wave equation or Schrödinger equation.

The postulates of quantum mechanics cannot be proven or deduced. The postulates are hypotheses, and, if no violation with nature (experiments) is found, they are called **axioms**, *i. e.* non-provable, true statements.

Postulate 1

The wave function $\Psi(x, y, z, t)$ describes the temporal and spatial evolution of a quantum-mechanical particle. The wave function $\Psi(x, t)$ describes a particle with one degree of freedom of motion.

Postulate 2

The product $\Psi^*(x, t) \Psi(x, t)$ is the probability density function of a quantum-mechanical particle. $\Psi^*(x, t) \Psi(x, t) dx$ is the probability to find the particle in the interval between x and $x + dx$. Therefore,

$$\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = 1 \quad (2.1)$$

If a wave function $\Psi(x, t)$ fulfills Eq. (2.1), then $\Psi(x, t)$ is called a *normalized* wave function. Equation (2.1) is the ***normalization condition*** and implies the fact that the particle must be located somewhere on the x axis.

Postulate 3

The wave function $\Psi(x, t)$ and its derivative $(\partial / \partial x) \Psi(x, t)$ are continuous in an isotropic medium.

$$\lim_{x \rightarrow x_0} \Psi(x, t) = \Psi(x_0, t) \quad (2.2)$$

$$\lim_{x \rightarrow x_0} \frac{\partial}{\partial x} \Psi(x, t) = \left. \frac{\partial}{\partial x} \Psi(x, t) \right|_{x=x_0} \quad (2.3)$$

In other words, $\Psi(x, t)$ is a continuous and continuously differentiable function throughout isotropic media. Furthermore, the wave function has to be finite and single valued throughout position space (for the one-dimensional case, this applies to all values of x).

Postulate 4

Operators are substituted for dynamical variables. The operators act on the wave function $\Psi(x, t)$. In classical mechanics, variables such as the position, momentum, or energy are called dynamical variables. In quantum mechanics *operators* rather than dynamical variables are employed. **Table 2.1** shows common dynamical variables and their corresponding quantum-mechanical operators

<i>Dynamical variable in classical mechanics</i>	<i>Quantum-mechanical operator</i>	
x	x	(2.4)
$f(x)$	$f(x)$	(2.5)
p	$\frac{\hbar}{i} \frac{\partial}{\partial x}$	(2.6)
$f(p)$	$f\left(\frac{\hbar}{i} \frac{\partial}{\partial x}\right)$	(2.7)
E_{total}	$-\frac{\hbar}{i} \frac{\partial}{\partial t}$	(2.8)

Table 2.1: Dynamical variables and their corresponding quantum-mechanical operators.

We next substitute quantum mechanical operators for dynamical variables in the total energy equation (see Eq. 1.2.6)

$$\frac{p^2}{2m} + U(x) = E_{\text{total}} . \quad (2.9)$$

Using the substitutions of Eqs. (2.4) to (2.8), and inserting the operand $\Psi(x, t)$, one obtains the Schrödinger or quantum mechanical wave equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + U(x) \Psi(x, t) = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(x, t) . \quad (2.10)$$

The Schrödinger equation is, mathematically speaking, a linear, second order, partial differential equation.

Postulate 5

The expectation value, $\langle \xi \rangle$, of any dynamical variable ξ , is calculated from the wave function according to

$$\langle \xi \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \xi_{\text{op}} \Psi(x, t) dx \quad (2.11)$$

where ξ_{op} is the operator of the dynamical variable ξ . The expectation value of a variable is also referred to as average value or ensemble average, and is denoted by the brackets $\langle \dots \rangle$. Equation (2.11) allows one to calculate expectation values of important quantities, such as the expectation values for position, momentum, potential energy, kinetic energy, etc.

The five postulates are a concise summary of the principles of quantum mechanics. The postulates have severe implications on the interpretation of *microscopic* physical processes. On the other hand, quantum-mechanics smoothly merges into newtonian mechanics for *macroscopic* physical processes.

The wave function $\Psi(x, t)$ depends on time. As will be seen in the Section on Schrödinger's equation, the time dependence of the wave function can be separated from the spatial dependence. The wave function can then be written as

$$\Psi(x, t) = \psi(x) e^{i\omega t} \quad (2.12)$$

where $\Psi(x)$ is stationary and it depends only on the spatial coordinate. The harmonic time dependence of $\Psi(x, t)$ is expressed by the exponential factor $\exp(i\omega t)$.

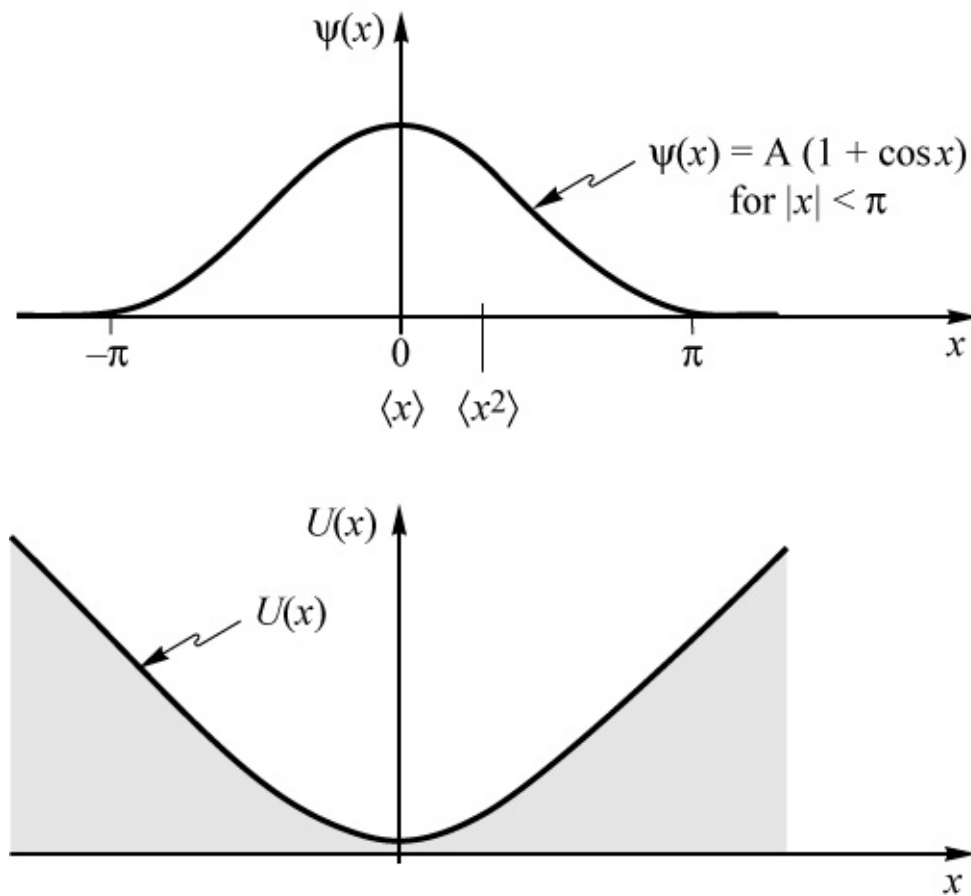


Fig. 2.1. Example for a one-dimensional wave function $\psi(x)$. Also shown is a corresponding potential function, $U(x)$. This potential function provides a driving force towards $x = 0$, that is towards minimum energy.

An example of a stationary wave function is shown in **Fig.** 2.1 and this wave function is used to illustrate some of the implications of the five postulates. It is assumed that a particle is described by the wave function

$$\psi(x) = A(1 + \cos x) \quad \text{for } |x| < \pi \quad (2.13)$$

$$\psi(x) = 0 \quad \text{for } |x| \geq \pi. \quad (2.14)$$

According to the second postulate, the wave function must be normalized, *i. e.*

$$\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = 1. \quad (2.15)$$

This condition yields the constant $A = 1 / \sqrt{3\pi}$ and thus the normalized wave function is given by

$$\psi(x) = \frac{1}{\sqrt{3\pi}} (1 + \cos x) \quad \text{for } |x| < \pi \quad (2.16)$$

$$\psi(x) = 0 \quad \text{for } |x| \geq \pi. \quad (2.17)$$

Note that $\psi(x)$ is a **continuous function** and is **continuously differentiable** throughout position space.

The potential energy of the particle, whose wave function is given by Eqs. (2.16) and (2.17), has a minimum probably around $x = 0$. A guess of such a potential is shown in the lower part of **Fig. 2.1**. A particle in such a potential experiences a force towards the potential minimum (see Eq. 2.4). Therefore, the corresponding wave function will be localized around the potential-minimum.

Next some expectation values associated with wave function shown in **Fig. 2.1** will be calculated using the fifth Postulate. The position expectation value of a particle described by the wave function $\psi(x)$ is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x) x \psi(x) dx \quad (2.18)$$

Note that x is now an operator, which acts on the wave function $\psi(x)$. Note further that $x \psi(x)$ is an odd function, and since $\psi^*(x)$ is even, the integrand $\psi^*(x) x \psi(x)$ is again an odd function. The integral over an odd function is zero, *i. e.*

$$\langle x \rangle = 0 \quad (2.19)$$

Thus, the expectation value of the position is zero. In other words, the probability to find the particle at any given time is highest at $x = 0$.

It is interesting to know, how far the wave function is distributed from its expectation value. In statistical mathematics, the standard deviation of any quantity, e. g. ξ , is defined as

$$\left(\langle \xi^2 \rangle - \langle \xi \rangle^2 \right)^{1/2}. \quad (2.20)$$

A measure of the spatial extent of the wave function is the standard deviation of the position of the particle. Hence, the spatial standard deviation of the particle on the x axis is given by

$$\sigma = \left(\langle x^2 \rangle - \langle x \rangle^2 \right)^{1/2}. \quad (2.21)$$

With $\langle x \rangle = 0$ one obtains

$$\langle x^2 \rangle = \int_{-\pi}^{\pi} \psi^*(x) x^2 \psi(x) dx = \frac{\pi^2}{3} - \frac{5}{2}. \quad (2.22)$$

The standard deviation $\sigma = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = (\langle x^2 \rangle)^{1/2}$ is shown in **Fig. 2.1** and it is a measure of the spatial extent of the wave function.

The expectation value of the **particle momentum** can be determined in an analogous way

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi(x) dx. \quad (2.23)$$

Evaluation of the integral yields $\langle p \rangle = 0$. In other words, the particle has no net momentum and it remains spatially at the same location, which is evident for a stationary wave function.

Similarly, the **expectation values** of **kinetic energy**, **potential energy**, and **total energy** can be calculated if $\psi(x)$ and $U(x)$ are known. The expectation values of these quantities are given by:

Kinetic energy:
$$\langle E_{\text{kin}} \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi(x) dx \quad (2.24)$$

Potential energy:

$$\langle U \rangle = \int_{-\infty}^{\infty} \psi^*(x) U(x) \psi(x) dx \quad (2.25)$$

Total energy:

$$\langle E_{\text{total}} \rangle = \langle E_{\text{kin}} \rangle + \langle U \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi(x) dx \quad (2.26)$$

2.2 The de Broglie hypothesis

The de Broglie hypothesis (de Broglie, 1923) is a significant milestone in the development of quantum mechanics because the dualism of waves and matter finds its synthesis in this hypothesis. Typical physical properties that had been associated with matter before the advent of quantum mechanics were *mass*, *velocity*, and *momentum*. On the other hand, *wavelength*, *phase-velocity*, and *group-velocity* had been associated with waves. The bridge

between the world of waves and the corpuscular world is the **de Broglie relation**

$$\lambda = h / p \quad (2.27)$$

which attributes a vacuum wavelength λ to a particle with momentum p . This relation, which de Broglie postulated in 1923, can also be written as

$$p = \hbar k \quad (2.28)$$

where $k = 2\pi / \lambda$ is the wavenumber. The kinetic energy of a classical particle can then be expressed in terms of its wavenumber, that is

$$E_{\text{kin}} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (2.29)$$

Four years after de Broglie's hypothesis, Davisson and Germer (1927) demonstrated experimentally that a wavelength can be attributed to an electron, *i. e.* a classical particle. They found, that a beam of electrons with momentum p and wavelength was diffracted by a Ni-crystal the same way as x-rays of the same wavelength λ . The relation between electron momentum p

and the x-ray wavelength λ , which yields the *same* diffraction pattern, is given by the de Broglie equation, Eq. (2.27). Thus, a bridge between particles and waves had been built. No longer could one think of electrons as pure particles or x-rays as pure waves. The nature of small particles has both, particle-like and wave-like characteristics. Analogously, a wave has both, wave-like and particle-like characteristics. This fact is known as the dual nature of particles and waves.

A simple **diffraction experiment** is illustrated in **Fig. 2.2** which shows a beam of particles incident on a screen having a narrow slit. A diffraction pattern is detected on a screen behind the slit as shown in the lower part. Electrons and x-rays with the same energy generate the same diffraction pattern. The diffraction pattern can be calculated by taking into account the constructive and destructive interference of waves.

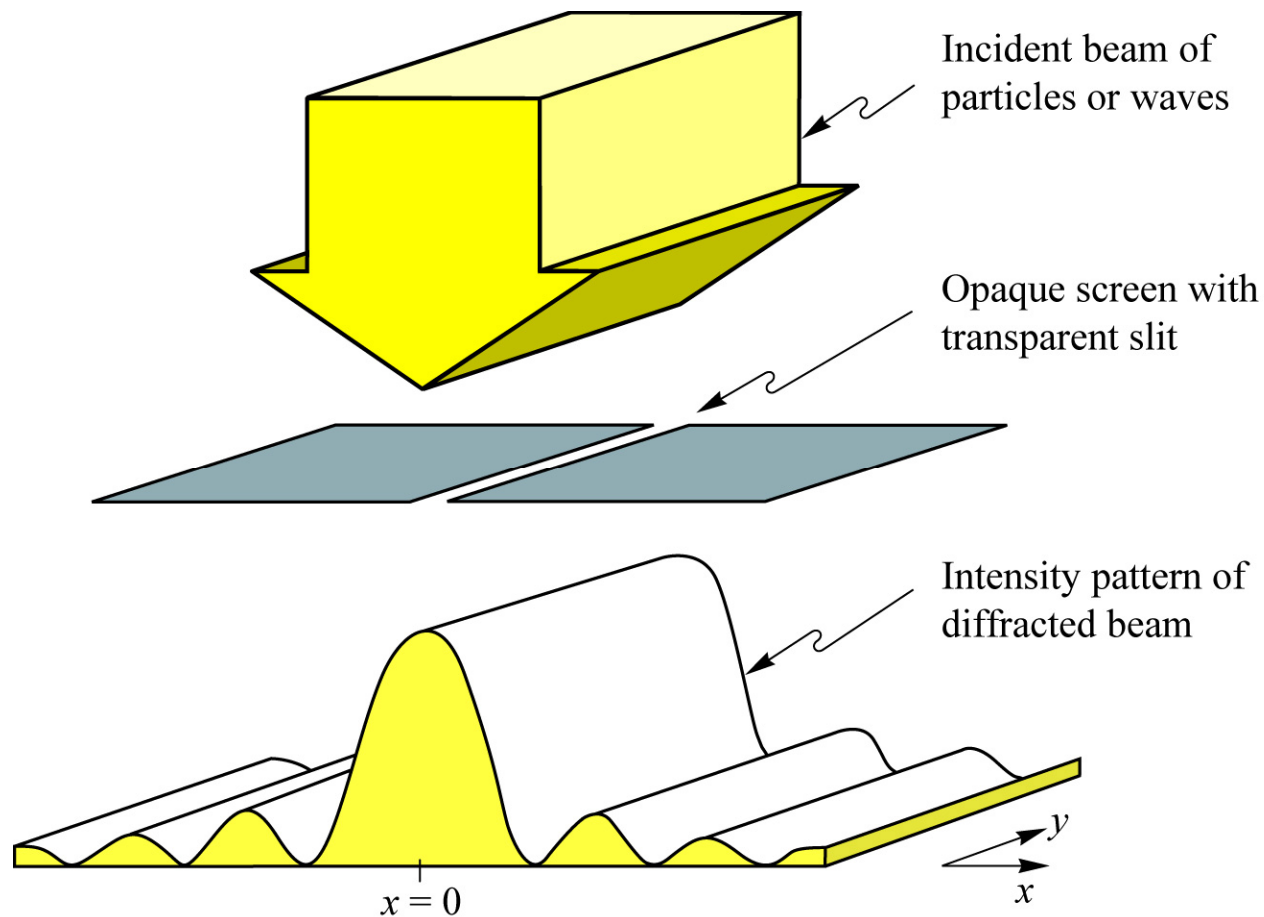


Fig. 2.2. Diffraction of a wave or beam of particles using a transparent slit in a screen. The intensity pattern of the diffracted beam is shown at the bottom.

The Davisson and Germer experiment further shows that the deterministic nature of classical mechanics is not valid for quantum mechanical particles. No longer is it possible to predict or calculate the exact trajectory of a particle. Instead, one can only calculate *probabilities* (expectation values). For

example, the position expectation value of an electron passing through the slit of **Fig. 2.2** is $\langle x \rangle = 0$.

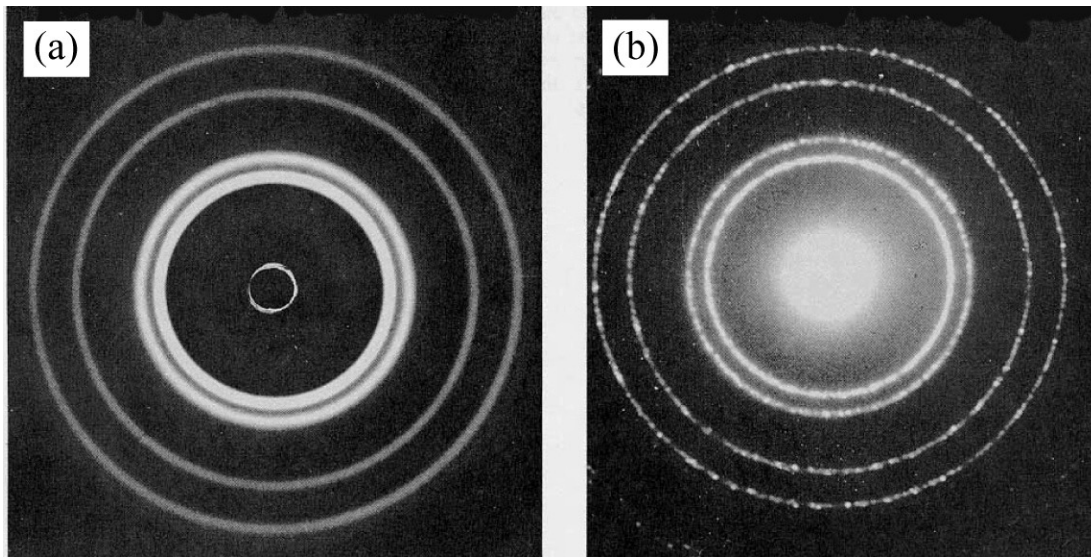


Fig. 2.3. Diffraction pattern of (a) an x-ray beam and (b) an electron beam passing through an Al foil.

Convincing experimental evidence of the wave nature of electrons is shown in **Fig. 2.3** which shows two very similar diffraction patterns, one obtained by a beam of x-rays and one by a beam of electrons when passing through an Al foil.

2.3 The Bohr–Sommerfeld quantization condition

During the years 1913-1918 Bohr developed a quantum mechanical model for the electronic states in a hydrogen atom (Bohr, 1913, 1918, 1922). This model supposes that the atom consists of a nucleus with positive charge e and one electron with charge $-e$. The motion of the electron is described by Newton's laws of classical mechanics and a quantum condition. Bohr specifically postulated that an atomic system can only exist in a certain series of electronic states corresponding to a series of discrete values for its energy, and that consequently any change in energy of the system, including the emission and absorption of photons, must take place by a complete transition of the electron between two such states. These states are called as the *stationary* electron states of the system. Bohr further postulated that the radiation absorbed or emitted during a transition between two states possesses a angular frequency ω , given by the relation

$$E_m - E_n = \hbar \omega \quad (2.30)$$

where $\hbar = h / (2\pi)$ is the reduced Planck constant and E_m and E_n are the energies of the two states (the m th state and the n th state) under consideration.

The quantum condition of Bohr can be visualized most easily in terms of the electron de Broglie wave orbiting the nucleus. (Historically, the de Broglie wave concept was postulated in 1925, *i. e.* about a decade *after* the development of Bohr's hydrogen atom model. However, the de Broglie wave concept is used here for convenience). **Fig. 2.4** shows a circular electron orbit of radius r . The electrostatic potential of the nucleus has symmetry and the electron is consequently moving with a constant velocity about the nucleus. Electronic orbitals are allowed, only if the circumference is an integer multiple of the electron de Broglie wavelength

$$S = (n + 1) \lambda \quad (n = 0, 1, 2, \dots) \quad (2.31)$$

where n is an integer and S is the circumference of the electron orbit. If this equation is fulfilled, the electron de Broglie wave is *interfering constructively* with itself as shown in **Fig. 2.4(b)**. Such orbits are called *allowed* orbits. If the latter equation is not fulfilled, the electron wave interferes *destructively* with itself as shown in **Fig. 2.4(c)**. Such orbits are called *forbidden or disallowed*.

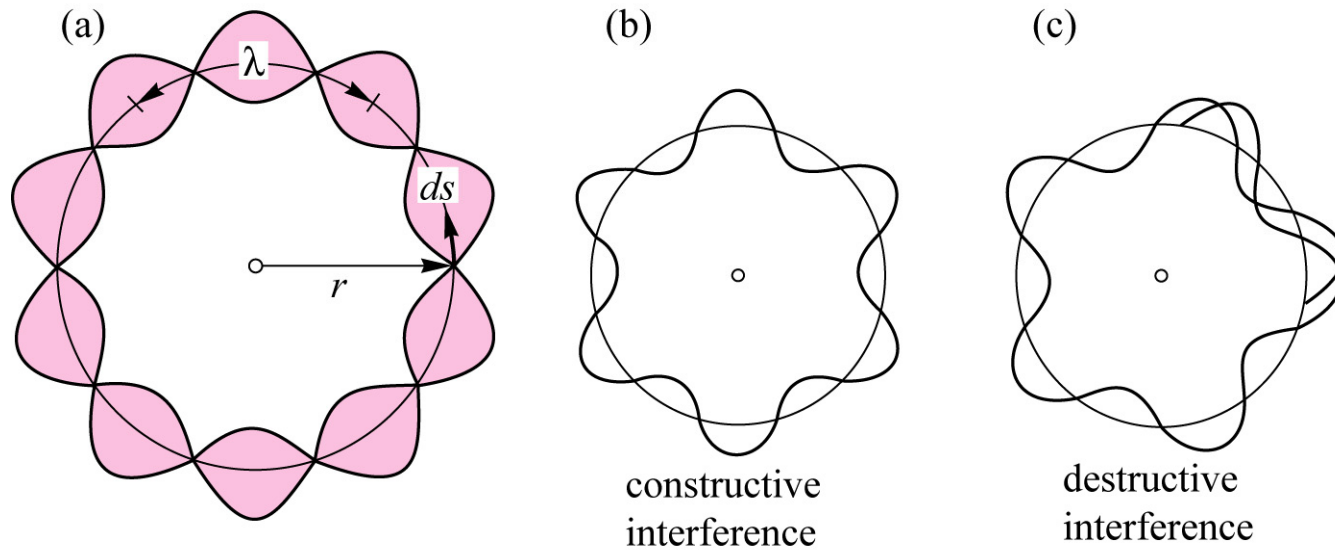


Fig. 2.4. (a) De Broglie wave representing an electron orbiting a nucleus. (b) Constructive interference of wave satisfying the Bohr-Sommerfeld quantum condition. (c) Destructive interference of wave not satisfying the quantum condition results in disallowed state.

Only circular orbits have been considered in Eq. (2.31), because the electron is assumed to move in a constant potential with constant momentum $p = h / \lambda$. However, the laws of classical mechanics also allow *elliptical* orbits. For example, the laws of planetary motion (Kepler's laws) allow for elliptical orbits of the planets around the sun. The nucleus is in one of the focal points of the ellipse as shown in **Fig. 2.5**. In such elliptical orbits the momentum is a function of the position. It is therefore necessary to generalize the quantum condition of Eq. (2.31) in order to make it applicable to orbits other than circular orbits.

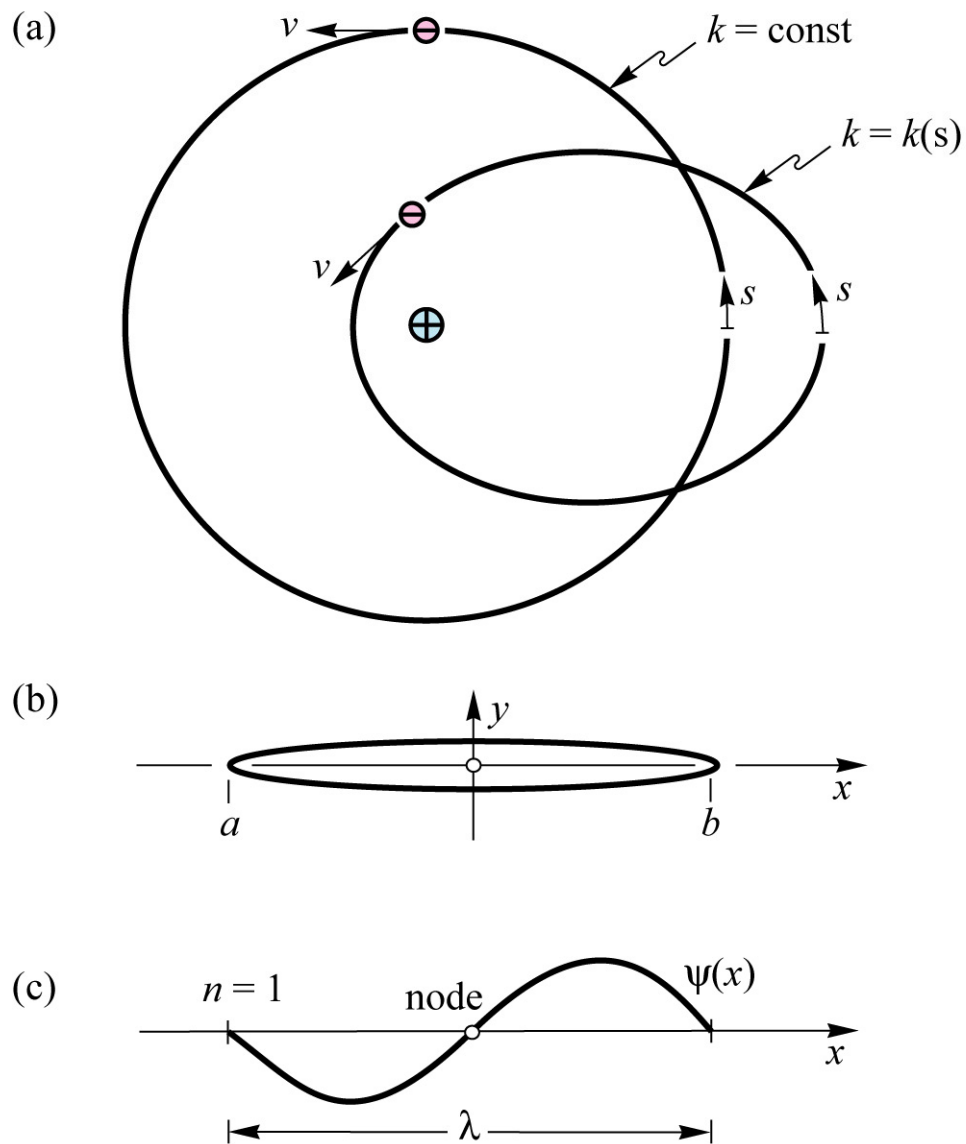


Fig. 2.5. Electrons can orbit the positively charged nucleus on a circular or elliptical curve. (a) The motion of electrons in Bohr's atom model is fully described by (i) classical laws (Kepler's laws of planetary motion) and (ii) the Bohr-Sommerfeld quantum condition. (b) The one-dimensional Bohr-Sommerfeld quantum condition can be obtained from an ellipsoid compressed onto the x axis. (c) Illustration of quantum state $n = 1$, where the number n is the number of nodes of the wave function.

A generalization of the quantum condition is obtained by first rearranging Eq. (2.31) and employing the wavenumber $k = 2\pi / \lambda$ according to

$$\frac{1}{2\pi} k S = n + 1 \quad (n = 0, 1, 2, \dots) . \quad (2.32)$$

Because k depends on the position for elliptical orbits an *integration* rather than a product must be employed

$$\oint_S k(s) ds = 2\pi (n + 1) \quad (n = 0, 1, 2, \dots) . \quad (2.33)$$

The integral is a closed line integral along the electron orbit S . Using the de Broglie relation $p = \hbar k$ one obtains.

$$\oint_S p(s) ds = 2\pi \hbar (n + 1) \quad (n = 0, 1, 2, \dots) \quad (2.34)$$

which is known as the **Bohr – Sommerfeld quantization condition**. The integral $\hbar^{-1} \oint p(s) ds$ is called the phase integral, since it provides the phase change of the electron wave during one complete orbit. The phase integral must have values of multiples of 2π in order to achieve constructive

interference of the electron wave with itself. The properties of the hydrogen atom and of hydrogenic impurities are discussed in greater detail in the Chapter on hydrogenic impurities.

The Bohr-Sommerfeld quantization condition has been derived for a system with three degrees of freedom. In a system with only one degree of freedom, the *one-dimensional Bohr-Sommerfeld condition* applies. To obtain this condition the ellipse shown in **Fig. 2.5(b)** is compressed to a line on the x axis. Thus, the particle is confined to the x axis. The line-integral of Eq. (2.34) can then be simplified to

$$\oint_S p(s) ds = \int_a^b p(x) dx + \int_b^a p(x) dx \quad (2.35)$$

Using the fact that the two integrals on the right-hand side of the equation are identical because of symmetry considerations, one obtains the **one-dimensional Bohr-Sommerfeld quantization condition**

$$\int_a^b p(x) dx = \pi \hbar (n + 1) \quad (n = 0, 1, 2, \dots) \quad (2.36)$$

Most wave functions are oscillating functions. Oscillating functions have locations of zero amplitude, *i. e.* **nodes**. It is convenient to name the wave functions by the number of nodes. Assume, for example, $n = 1$. Then the phase shift in Eq. (2.36) is 2π . The corresponding wave function has one node. Thus the wave function with the quantum number n has n nodes. The quantum number is identical with the **number of nodes** of that wave function.

If we choose $n = 1$ and assume $p(x) = p = \text{constant}$, then, using the de Broglie relation, Eq. (2.36) simplifies to

$$b - a = \lambda. \quad (2.37)$$

The corresponding wave function is shown in **Fig. 2.5(c)**, where the wave function has one node ($n = 1$) in the center. By convention, the nodes at the left and right end of the wave function are not counted.

Exercise: Bohr's hydrogen atom model. Many properties of the hydrogen atom can be calculated in terms of the Bohr model. It is based on classical mechanics as well as quantum mechanics. We assume that the electron orbits the hydrogen atom on a circular orbit with radius a_B . The *classical*

mechanics condition for the steady state is that the centrifugal force equals the centripetal (coulombic) force, *i. e.*

$$\frac{m v^2}{a_B} = \frac{e^2}{4 \pi \epsilon_0 a_B^2} \quad (2.38)$$

The *quantum mechanical condition* is that the electron wave must interfere constructively with itself (Bohr-Sommerfeld quantization condition), *i. e.*

$$2 \pi a_B = (n + 1) \lambda \quad \text{for } n = 0, 1, 2, \dots \quad (2.39)$$

Using Eqs. (2.38) and (2.39) and the de Broglie relation, calculate the Bohr radius, electron potential energy, kinetic energy, and ionization energy (*i. e.* Rydberg energy).

The results of the calculation are:

Bohr radius:
$$a_B = (n + 1)^2 \frac{4 \pi \epsilon_0 \hbar^2}{e^2 m} \quad (2.40)$$

Potential energy:
$$E_{\text{pot}} = \frac{-1}{(n+1)^2} \frac{e^4 m}{(4 \pi \epsilon_0 \hbar)^2} \quad (2.41)$$

Kinetic energy:
$$E_{\text{kin}} = \frac{1}{2} \frac{1}{(n+1)^2} \frac{e^4 m}{(4 \pi \epsilon_0 \hbar)^2} \quad (2.42)$$

Rydberg energy:
$$E_{\text{Ryd}} = \frac{1}{2} \frac{1}{(n+1)^2} \frac{e^4 m}{(4 \pi \epsilon_0 \hbar)^2} \quad (2.43)$$

The hydrogen atom potential, and the potential, kinetic, and Rydberg energy are illustrated in **Fig. 2.6**. For the ground state of the hydrogen atom, *i. e.* for $n = 0$, one obtains:

$a_B = 0.53 \text{ \AA}$	and $E_{\text{Ryd}} = 13.6 \text{ eV}$
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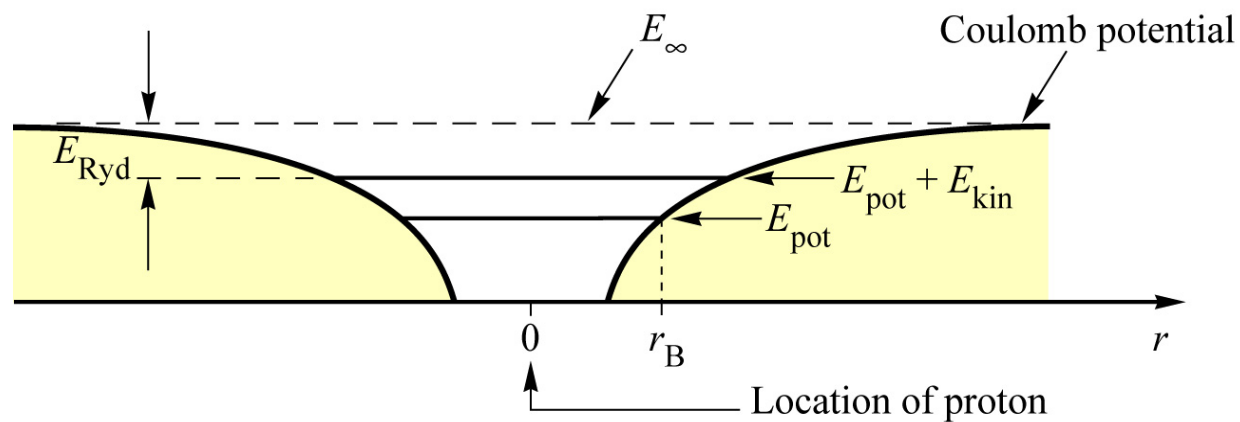


Fig. 2.6. Coulomb potential of a hydrogen atom. The energy of the electron orbiting the proton is the sum of potential and kinetic energy.

For consideration: *Erwin Schödinger on quantum rules.* “The appearance of quantum rules for the hydrogen atom is just as natural as is the existence of resonances for a vibrating string.” *Ann. Phys.* **79**, 361 (1926)
