Chapter 1
Sources

Abstract A brief presentation of the experimental origins of quantum mechanics is given. The key experiments leading to contradictions with accepted physical theories of matter and radiation, signaling a need for a thorough revision of classical mechanics and electrodynamics, are surveyed. The early attempts to resolve these controversies, formulated at the beginning of twentieth century and often named as the Old Quantum Theory, which mark the genesis of the modern quantum mechanics, are summarized. The specificity of the classical description of physical processes is briefly outlined and main suggestions addressed to a more general mechanics describing the elementary particles, atoms, and molecules are enumerated. The particle diffraction experiment is examined in some detail to pinpoint the essence of the wave–particle duality and to identify the key elements of the quantum description: the initial and final experiments, as well as the free evolution of the system dynamic state which separates them, without any interference from the measuring apparatus. The internal angular momentum of an elementary particle, called spin, is introduced. The emphasis in this historical background is on the development of the classical concepts into their more general quantum counterparts, rather than on their discontinuity in the two theories. On one hand, the classical (approximate) mechanics, in which some very small quantities such as the quantum of the physical action – measured by the Planck constant – are approximated by zero, provides the *geometric* optics limit of the quantum (exact) mechanics. On the other hand, the quantum description has to use the classical concepts due to a macroscopic character of the measuring devices, which adds to the intimate relationship between the two formulations.

1.1 Experimental Origins and Old Quantum Theory

At the current state of our understanding of matter the modern quantum mechanics plays a fundamental role in describing phenomena and processes in the surrounding world, particularly at the *microscopic* level of photons, elementary particles, atoms,

R.F. Nalewajski, *Perspectives in Electronic Structure Theory*,
DOI 10.1007/978-3-642-20180-6_1,

and molecules. It should be emphasized, however, that the complete theory of *macroscopic* objects, of dimensions perceived by our senses, also requires the quantum mechanical description of interactions between their constituent atoms and molecules since the quantum nature of these microscopic particles can be manifested also at the macroscopic level. Clearly, in the limit of very large masses and energies of macroscopic objects the predictions of quantum mechanics must be identical with those resulting from its classical analog. Thus, when supplemented by the laws of statistical thermodynamics the quantum mechanics gives rise to the complete description of the natural world.

It was born in the atmosphere of severe confusion at the beginning of twentieth century, when the accepted physical theories were challenged by numerous dilemmas resulting from a series of remarkable new experimental observations, which could not be explained by the classical mechanics and electrodynamics. The physics at the end of nineteenth century distinguished the categories of matter and radiation, and used separate laws to describe them: Newton's mechanics, to predict motions of material bodies, and the Maxwell equations of the electromagnetic theory of radiation, which unites the electric, magnetic, and optical phenomena. We recall at this point that the so-called *wave* optics becomes the *geometric* optics in the limit of infinitely small wavelength, $\lambda \to 0$, i.e., for infinitely large frequency, $\nu \to \infty$, of the monochromatic radiation.

Let us now briefly summarize the key stages of the development of quantum ideas in physics (see, e.g., van der Waerden 1968) with the experiment and intuitive insight ultimately leading to a new philosophy of science (Heisenberg 1949, 1958; Yourgrau and van der Merve 1979; Bohm 1980) with the *exact* determinism of classical predictions being replaced by the *statistical* determinism of quantum laws. This "revolution" has also led to a dramatically different way of thinking about the process of measurement, to a discovery of the universal character of the *particle–wave dualism* of both the radiation and matter, and a new definition of the mechanical state of microscopic systems. The crisis of classical physics was indeed observed first on the subatomic and atomic/molecular scales, in processes involving interactions of such objects with electromagnetic radiation, a diffraction of radiation and elementary particles, etc.

We begin this short survey with the problem of the black-body radiation, at equilibrium in the given temperature T, which could not be explained by the classical electrodynamics and eventually led to formulation in 1901 of the famous Planck's hypothesis of the *energy quantization*. The question was this: how much energy is present as radiation in the given volume of an empty space of a cavity in an object held at the definite temperature T, and how it is distributed as a function of the radiation frequency? The quantity describing such a distribution is called the radiation energy density $u(\nu, T)$, which measures the energy of the monochromatic radiation of frequency ν per unit volume of the cavity, in thermal equilibrium at absolute temperature T. The Rayleigh–Jeans law of 1900, $u(\nu, T) \propto \nu^2 T$, derived using the classical electrodynamics and statistical thermodynamics, is correct only for low frequencies (in the infrared region of the electromagnetic radiation spectrum) and it dramatically fails for high frequencies (in the ultraviolet region), where

the experimental data show a sharp drop in the energy distribution, with $u \to 0$ in the *geometric* optics limit of $v \to \infty$. This classical distribution has been obtained by first calculating the number of elementary oscillators (cavity standing waves) of the electromagnetic field, each corresponding to a particular frequency of radiation, and then ascribing them an average energy $k_B T$, where the Boltzmann constant $k_B = 1.381 \times 10^{-23}$ [J K^{-1}], in accordance with the classical energy *equi*-partition principle.

In order to overcome this discrepancy, also known as the *ultraviolet catastrophe*, which could not be explained by classical means, Planck has proposed that the energy of the elementary radiation oscillator of frequency v, is restricted to integral multiples of the *energy quantum*, $hv \equiv \hbar\omega$, where the new universal constant h has a dimension of the mechanical action [energy $\times$ time]; here, the radiation angular frequency $\omega = 2\pi v$ [radians/s] and the symbol $\hbar = h/2\pi$. In other words, this finite "grain" of the oscillator energy constitutes the smallest amount by which the oscillator energy can be increased or lowered. Hence, the energy absorbed by the elementary oscillators of the surrounding cavity can also be absorbed or emitted in integral multiples of such energy quanta, for all frequencies allowed by the cavity standing-wave boundary conditions, as implied by the condition of a thermal equilibrium in the black-body radiation problem: $\Delta E = hv$. This quantum (non-classical) assumption gives rise to the celebrated *Planck's distribution law*:

$$u(v, T) \propto v^3 [\exp(hv/k_B T) - 1]^{-1}, \tag{1.1}$$

which is in perfect agreement with experimental observations for the Planck constant (quantum portion of the physical action) $h = 6.626 \times 10^{-34}$ [Js] or $\hbar = h/2\pi = 1.055 \times 10^{-34}$ [Js].

It should be emphasized that this assumption was incompatible with the principles of classical physics. Thus, the agreement with experiment has been achieved only by introducing into the framework of the contemporary physics, in which the oscillator energy and mechanical action constitute the continuous dynamical quantities, the artificial "discrete" quantum condition, incompatible with the basic principles of the classical theory.

This energy quantization has been generalized in 1905 by Einstein into hypothesis of the elementary, localized (indivisible) portions of the electromagnetic energy, defining the radiation particles called *photons*, each containing Planck's portion of the energy: $E = hv$. This assumption provides the complete explanation of the *photoelectric effect* discovered by Hertz in 1886 and 1887. Photoelectrons are produced instantaneously, when the light of a frequency higher than some threshold value v_0 strikes any substance. This phenomenon is governed by the two laws formulated by Lenard in 1899–1902: (1) the number of photoelectrons is proportional to the intensity of the incident radiation; (2) their maximum velocity v and hence also the kinetic energy are affected only by the radiation frequency, and not by its intensity as predicted by the classical, wave theory of radiation. In Einstein's hypothesis the photoelectron energy of motion originates entirely from a single

photon, representing a localized corpuscle of the energy, and satisfies the energy conservation

$$\frac{1}{2}m_e v^2 = hv - hv_0, \tag{1.2}$$

where m_e denotes the mass of an electron and the threshold energy $\Phi = hv_0$ measures the so-called *work function* of the irradiated substance.

The electromagnetic radiation thus exhibits a dual character. On one hand, in the diffraction (interference) experiments, it behaves as a wave characterized by the frequency v [s^{-1}] or wave length $\lambda = c/v$, where c stands for the velocity of light in vacuum. On the other hand, as the localized particle of energy, it should be characterized by the linear momentum p. Using the relativistic expression for the energy, $E = m_f c^2 = p_f c = hv$, where m_f stands for the photon mass of motion (its rest mass vanishes), one obtains the relativistic expression for the photon momentum:

$$p_f = hv/c = h/\lambda \quad \text{or} \quad p_f = \hbar(2\pi/\lambda) \equiv \hbar k, \tag{1.3}$$

where k [m^{-1}] stands for the photon wave number.

In 1922 this corpuscular nature of radiation has been confirmed experimentally by Compton in the *X*-ray photon scattering by electrons. The collisions between photon (particle of radiation) and electron (particle of matter) have been shown to be governed by the conservation of the system energy and linear momentum, the two laws that govern any perfectly elastic collisions, e.g., of the billiard balls in the macroscopic world. It also follows from this experiment that any measurement of the particle position, effected by a scattering of light, influences the particle linear momentum; the more precise is this experiment, i.e., the shorter the wave of the incident radiation, the more perturbed is the particle motion after collision with the photon. This implies that in the microscopic world the measuring device and the object of measurement are not absolutely separable as it is implicitly assumed in the classical theory.

A second challenge to the established theory came from the atomic physics. In 1911 Rutherford had demonstrated, by scattering the α-radiation particles (nuclei of the helium atoms) on thin layers of heavy metals, that each atom contains the positively charged, heavy nucleus, with the estimated diameter of the order 10^{-15} [m], surrounded by light, negatively charged electrons, with the estimated diameter of the atom as a whole of the order 10^{-10} [m]. He also guessed that electrons are moving along the circular or elliptic trajectories around the nuclear attractor. This "planetary" model of an atom was in an obvious conflict with the accepted classical electrodynamics, which predicted that electrons moving on a circular orbit, thus being accelerated, should radiate electromagnetic energy and ultimately collapse onto the nucleus. Therefore, the very stability of such a "classical" atomic model has been put in doubt.

To remove this troubling inconsistency, in 1913 Bohr has followed the Planck approach of incorporating in the classical theory subsidiary quantum conditions

which contradicted it. He has achieved an excellent agreement with the available experimental data for the hydrogen atom by assuming that in the circular motion of an electron allowed are only specific, *stationary* orbits, on which the particle energy remains fixed. These *stationary* energy levels $\{E_n\}$ and corresponding radii $\{r_n\}$ are identified by the orbit *quantum number* $n = 1, 2, \ldots$. The energy is emitted/absorbed in the discrete manner, not continuously as predicted by the classical electrodynamics, only when electron makes a transition between the two stationary orbits. Emission takes place when electron "jumps" from an outer orbit, exhibiting larger radius, to an inner orbit of smaller radius, identified by the higher and lower values of n, respectively. Accordingly, the inner $\rightarrow$ outer transitions are possible only after absorbing the energy from an incident radiation. Bohr has used Planck's relation between the transition energy and frequency of the emitted/absorbed radiation:

$$\Delta E_{n\rightarrow n'} = E_{n'} - E_n = h\nu_{n\rightarrow n'}. \tag{1.4}$$

Bohr's quantum conditions, which determine the stationary orbits, can be formulated as those for the allowed, discrete values of the length of the electron angular momentum $\boldsymbol{l}_n = \boldsymbol{r}_n \times \boldsymbol{p}_n$,

$$l_n = |\boldsymbol{l}_n| = m_e v_n r_n = n\hbar, \tag{1.5}$$

where $\boldsymbol{r}_n$ denotes the electron position vector on nth orbit, and $\boldsymbol{p}_n = m_e \boldsymbol{v}_n$ stands for its linear momentum.

This model has been subsequently developed in 1915 and 1916 by Sommerfeld and Planck, who introduced the elliptic orbits and the spatial quantization of the angular momentum. This generalized planetary model still gave wrong predictions already for helium atom (*two*-electron system), which signaled that this *Old Quantum Theory* was far from the final formulation of the new, generalized mechanics of microscopic objects. It should be realized, however, that new physical ideas are always arrived at by understanding the novel in terms of the familiar. Clearly, Bohr's quantization rules, successful as they were, entail assumptions which are in conflict with the classical physics. For example, the latter predicts that an electron on the circular orbit should emit radiation and this contradicts the assumed stationary character of such a trajectory. Although it was clear already at the time of its invention that this *ad hoc* synthesis of the quantum elements with the classical theory has hardly any future as the consistent physical theory, Bohr's planetary model has turned out to be quite successful in explaining the observed series of spectral lines emitted by hydrogen. The predictive power of the model was quite limited, however, since – despite later improvements – it dramatically failed to explain the spectral data of *many* electron atoms.

Since the *micro*-objects escape perception by human sense organs, their observation always requires the measurement devices, the *macro*-objects which translate their interactions with the *micro*-objects in terms of macroscopic quantities. This points out to a subtle relationship between the quantum mechanics and classical

physics. In his celebrated *Correspondence Principle* Bohr has recognized that quantum mechanics must be consistent with classical mechanics. The classical limit corresponds to very large energies (quantum numbers), when such minute quantities as the Planck constant can be formally treated as zeros, in the $h \to 0$ limit.

In 1924 the quantum condition (1.5) of Bohr's model has gained a convincing interpretation in de Broglie's hypothesis of the *universal* character of the *particle–wave dualism*, which was first observed in the electromagnetic radiation. He suggested that the relations between corpuscular (E, p) and wave (ν, λ) attributes of material particles, which exhibit a nonzero rest mass, are the same as for photons, for which the rest mass vanishes (1.3). Therefore, there should also be a new, wave facet of electrons, linked to their more familiar corpuscular aspect by the associated relations:

$$E_\mathrm{e} = h\nu_\mathrm{e}, \quad p_\mathrm{e} = h\nu_\mathrm{e}/c = h/\lambda_\mathrm{e}. \tag{1.6}$$

The existence of such *matter waves* has been confirmed experimentally in 1927 by Davisson and Germer, who diffracted the electron beam on a crystal. This development has quantitatively verified the preceding relations thus demonstrating that the particle–wave duality constitutes a universal characteristic of nature, i.e., of all objects in the microworld, or the *micro-objects* for short, rather than being a monopoly of light. Apparently, in this scale of the linear dimensions 10^{-8}–10^{-15} [m], the differences between the material and radiation particles are significantly blurred. The hope was that in the final version of the quantum theory this important discovery will find a consistent synthesis and a more explicit dynamical expression. At this time it has not been understood yet as to how de Broglie's waves propagate and how they influence the motion of individual particles. They do offer, however, a solid basis for explaining Bohr's quantum condition of (1.5). More specifically, rewriting it in terms of the electron de Broglie's wavelength of an electron moving on nth stationary orbit, $\lambda_n = h/p_n$ (1.6), gives: $2\pi r_n = n\lambda_n$. This condition thus represents the classical criterion for the standing wave along the whole perimeter of the electron circular orbit. In other words, only on the stationary orbits of Bohr the constructive interference of de Broglie's (traveling) waves explains the stability of the electron distribution. Accordingly, the destructive interference of the de Broglie waves in an atom disallows any orbit which fails to satisfy this quantum condition.

Since science is concerned only with observable things one has to let the micro-particle to respond to some outside influence, in order to observe it. As we have already argued above, when examining the implications of the Compton experiment, the measurement process inadvertently modifies the state of the micro-object. A careful examination of the limitations imposed by this influence on the accuracies Δx and Δp_x of the simultaneous determination of the particle position (Cartesian) coordinate x and its conjugate linear momentum p_x, respectively, has led Heisenberg to formulate in 1926 and 1927 his famous *Uncertainty Principle*, also known as the *Principle of Indeterminacy*, which states that the limiting value of the product of

these two indeterminacies has a very small but finite value of the order of Planck's constant:

$$\Delta x \, \Delta p_x \geq \hbar. \tag{1.7}$$

The specific multiple of $\hbar$ in r.h.s. of the preceding inequality depends on the adopted measure of the measurement precision. For example, the *standard deviation* σ_A of physical quantity A, $\Delta A \cong \sigma_A = \left\langle (A - \langle A \rangle)^2 \right\rangle^{\frac{1}{2}} = \left(\langle A^2 \rangle - \langle A \rangle^2 \right)^{\frac{1}{2}}$, where $\langle A \rangle$ is the average, statistical expectation value of A and $\langle A^2 \rangle$ denotes the average value of its square, can be used to quantify the accuracy of such measurements. We shall use this familiar descriptor of a random variable later in this book, when formulating the Uncertainty Principle in terms of concepts of the molecular wave mechanics.

This limit to the fineness of our power to observe the atomic objects and the smallness of their accompanying disturbance in an act of measurement introduces the *absoluteness* to the distinction between the micro- and macro-objects. This limit can never be surpassed by an improved technique or increased skill of an observer, since a fraction of a photon is never observed. It is inherent in natural world and the dual particle–wave behavior, "anomalous" from the classical perspective, is not peculiar to light, but it is universally present in all material particles as well.

1.2 Classical–Mechanical Description and a Need for Its Revision in Generalized Mechanics

A necessity for a departure from the classical mechanics and its causality is thus clearly demonstrated by the experimental observations. The classical concepts have been proved to be inadequate to describe the molecular, atomic, and subatomic events. The uncertainty principle denies an observer the ability to simultaneously measure the conjugate components of the position and momentum vectors of micro-objects with arbitrary high precision. This contradicts the basic assumption of the classical mechanics, in the canonical formulation of the Hamilton equations of motion, where the exact knowledge of such quantities is required for the very definition of the particle dynamic state. According to the Heisenberg principle of indeterminacy such simultaneously (sharply) unobserved quantities are *unknowable*. Therefore, one is forced to resign from the classical concept of the particle trajectory, e.g., Bohr's orbit, which is unobservable thus belonging in the micro-world to a "metaphysical" rather than physical category.

Hence, the precise description of the time evolution of a micro-object, which requires an exact knowledge of its position and momentum at the given time, is unavailable in the quantum theory. This restriction does not reflect our technical inability of a precise measurement, but rather it signifies the incompatibility of the

two observations involved. Such physical quantities, which cannot be sharply defined simultaneously, are called the *complementary observables*. As we shall see later in the book, besides the complementary pair of the particle position and momentum, (x, p_x), there is a number of such relations in quantum physics: energy and time, (E, t), any two Cartesian components of the angular momentum, e.g., (l_x, l_y), etc.

The uncertainty relations give rise to *statistical* predictions of the quantum theory, in contrast to the *deterministic* predictions of the classical physics. In the macroscale of objects perceived by our senses, the statistical distribution of the alternative outcomes of a measurement, represented by the normal (Gaussian) distribution, can be made infinitely sharp in the limit of the Dirac *delta* function (Dirac 1967), which can be thought of as representing the ordinary Gauss curve of the probability theory in the limit of its vanishing variance. Therefore, the *statistical* (*multiple*-valued) determinism of quantum mechanics constitutes a natural extension of its limiting form in the *strict* (*single*-valued) determinism of the classical theory.

According to Bohr's *Complementarity Principle* both coexisting wave and particle aspects of all objects in the microworld are essential for their full description. However, the precise specification of one complementary observable rules out any specification of the other. Should the particle momentum be known exactly, $\Delta p_x \to 0$, one would then have no knowledge of its position whatsoever, $\Delta x \to \infty$; accordingly, when the object position is sharply defined, $\Delta x \to 0$, one looses all the knowledge about its momentum: $\Delta p_x \to \infty$. The principle operates not only in these limiting cases, but it also covers all intermediate, finite precisions of specifying the pairs of complementary observables. The more the precise localization of an electron (or photon) in space, when its momentum is not well specified, the more the particle-like behavior. Accordingly, the wave-like character is uncovered, when the particle localization is not well specified, i.e., when its momentum is determined more precisely.

As further articulated by Bohr and his Copenhagen School, all physical quantities such as position, momentum, angular momentum, energy, etc., have to be specified by measurement, which conveys information to our senses. It has to contain amplification mechanisms by which microscopic effects are translated into macroscopic effects accessible to our understanding. Indeed, all experiments in the atomic, nuclear, and subnuclear scales in the final analysis are described in classical terms, related to attributes of the macroscopic measuring apparatus. This emphasizes a unique, intimate relationship between the quantum mechanics and its classical limit, with the former being destined to use the concepts of the latter to describe the behavior of the micro-objects.

The indeterminacy principle also implies a relativity of the quantum description with respect to the adopted method of measurement, since the specific experimental device uncovers its own "projection" of the observed "reality." This also constitutes a natural extension of the classical relativity of the description of physical phenomena with respect to the adopted reference frame. This feature signifies a deeper, fully objective approach, which resigns from the subjective classical idealization of the exact separability of the observed object and the measuring device. It is implicitly assumed in the classical theory that the progress of a physical process is

independent of the experimental observations, which monitor its current stage. In other words, classical theory claims a lack of interference of the measuring device into the state of the probed mechanical system, i.e., the absolute separability of these two subsystems of an experimental arrangement.

Clearly, the physical objects evolve freely when undisturbed by an act of measurement, but finally we have to bring them into contact with the experimental apparatus to monitor their current (final) state. The progress of classical process is assumed to be independent whether they are observed experimentally or not, but in the realm of quantum mechanics the experimental monitoring is not without an influence, sometimes decisive, on the behavior of the observed micro-object. In the macroworld this influence can be practically neglected. For example, the perturbation of the airplane trajectory created by the photons of the illuminating radar radiation is nonexistent for all practical reasons. To summarize, the impression of the unequivocal determinism in the Newtonian mechanics is created by the very high masses and energies of the classical objects. It hardly implies the universality of this limiting macroconjecture of the absolute separability of the object and measuring device, to also cover the microworld where such small perturbations do matter.

The classical description also assumes the possibility of limitless gathering of simultaneous measurement information, i.e., the availability of the precise values of all mechanical properties of all constituent particles at the given time. In other words, this approach assumes that in principle at a given time all objects can be absolutely localized in space and their momenta can be determined with arbitrary precision, as can be any physical property of the dynamical system under consideration. Clearly, for practical reasons only, we are unable to reach this level of the precise specification of the mechanical microstate of all atoms/molecules in a macroscopic amount of matter. However, as claimed in the classical statistical thermodynamics, such detailed data are in principle knowable with arbitrary precision. Only due to the obvious "technical" difficulties of reaching this goal, and in view of the implications of the *Law of Large Numbers*, which renders such information irrelevant, we resort to familiar methods of the statistical mechanics in predicting the *average* descriptors of the system macrostate.

Let us briefly summarize the main suggestions addressed to the generalized mechanics capable of describing the behavior of micro-objects. As we have already argued in the preceding section, the relation between this, yet unknown, new mechanics and its classical analog should be similar to the relation between the *wave-* and *geometrical* optics; the former becomes the latter in the formal short-wave limit of $\lambda \to 0$ ($v \to \infty$), which is a characteristic of de Broglie's wave of a macro-object, when the free particle would not be diffracted but going along a straight rectilinear path, just as we expect classically. The new mechanics should thus include the classical mechanics as its limiting case for very large energies and hence also large values of its quantum numbers – or equivalently – in the formal limit of the vanishing quantum of the physical action: $h \to 0$. This can be argued more precisely by observing that the wave aspect of matter will be hidden from our sight, if de Broglie's wavelength λ is much lower than a characteristic length d involved in describing the motion of a body of momentum p: $\lambda/d = h/(dp) \ll 1$.

Thus, the $\lambda \to 0$ and $h \to 0$ limits are equivalent in identifying the range of applications of the classical mechanics. This postulate is known as Bohr's Correspondence Principle.

In contrast to old quantum theories, the general quantum theory must be internally consistent, i.e., all its experimental consequences must follow from the same axiomatic basis. It has to be capable of explaining all known experimental facts, rather than a narrow selection of such data. In the new mechanics we have to refrain from the classical definition of the system dynamic state, which uses the complementary observables. The new definition must instead be based only on the strictly knowable state parameters, which can be simultaneously determined with utmost precision. Clearly, such a positivistic attitude is a prerequisite of any sound physical theory.

The new definition of the mechanical state must be complete so that the results of all possible experiments performed on the microsystem can be extracted from it. In particular, it must offer means to predict the possible outcomes (spectrum) $\{a_i\}$ of any single measurement of quantity A, as well as the frequencies m_i (or probabilities) $\{p_i = m_i/m\}$ of these experimentally allowed values of the measured physical quantity in many repetitions $m = \sum_i m_i$ of the given experiment, performed on systems in the same dynamical state. This information on a multitude of measurements performed on replicas of the system then suffices to determine the statistical expectation value of the measured physical quantity:

$$\langle A \rangle = \sum\nolimits_i p_i \, a_i. \tag{1.8}$$

1.3 Implications from the Particle Diffraction Experiment

Let us consider the double-slit interference of photons or electrons, in analogy with Young's optical experiment. In this experimental arrangement the monochromatic stream of quantum particles falls on the opaque diaphragm with two slits O_1 and O_2. This experiment is crucial for distinguishing whether a perturbation traveling in space is of the particle or wave character.

The intensities $I_1(x)$ and $I_2(x)$ of two streams of the noninteracting particles passing through the openings O_1 and O_2, respectively, when the other slit is closed, upon reaching the screen $\mathcal{E}$ would produce the sum of such individual intensities (probabilities), $I_1(x) + I_2(x)$. The superposition of the corresponding waves $\psi_1(x) = |\psi_1(x)| \exp[\mathrm{i}\phi_1(x)]$ and $\psi_2(x) = |\psi_2(x)| \exp[\mathrm{i}\phi_2(x)]$,

$$\psi(x) = \psi_1(x) + \psi_2(x), \tag{1.9}$$

gives rise to the screen intensity distribution exhibiting the interference effects,

$$\begin{aligned} I(x) = |\psi(x)|^2 = \psi(x)\psi^*(x) = |\psi_1(x)|^2 + |\psi_2(x)|^2 + 2|\psi_1(x)||\psi_2(x)|\cos[\phi_1(x) - \phi_2(x)] \\ \equiv [I_1(x) + I_2(x)] + 2[I_1(x) I_2(x)]^{\frac{1}{2}} \cos[\phi_1(x) - \phi_2(x)] \equiv I^{add}(x) + I^{nadd}(x), \end{aligned} \tag{1.10}$$

because of the last, nonadditive (oscillatory) term $I^{nadd}(x)$. Above, we have identified the intensity of wave by the squared modulus of the scalar wave field $\psi(x)$, by analogy to the intensities of the electric, $E(x)$, or magnetic, $H(x)$, fields.

It has been established experimentally that the interference fringes are the statistical result of a very large number of independent particles hitting the screen, when each particle retains its individuality being finally deposited on a single grain of the photographic plate of the screen, at apparently random positions, hitting also the regions no classical particle could reach. The same interference pattern appears when a beam of particles goes through the slits simultaneously, and when single particles are scattered, one at a time, with the impact locations being observed in seemingly random fashion, now here, now there, over a length of time. The statistical determinism in this scattering of micro-objects, which give the impression of being truly indeterminable and chaotic, is only revealed after very many repetitions of such elementary, single-particle experiments, when the interference pattern finally emerges.

The appearance of interference depends critically on *both* slits being open, and it vanishes when one of them is closed, i.e., when a single particle goes definitely through one slit or the other, giving after many repetitions the separate distributions $I_1(x)$ or $I_2(x)$ on the screen. One thus concludes that the observance of interference denies us the determination of the slit through which the particle has actually passed. The interference pattern cannot be explained in the corpuscular representation, as a result of some collective effect of interactions between the beam particles. More specifically, by diminishing the density of the incident stream of particles, and hence also the number of particles passing through the slits in unit time, one changes such interactions, and this should affect the interference pattern on the screen. However, the experiment does not exhibit any influence of this kind; the diffraction pattern remains the same even in the limit of a single particle passing the slits at a time. The attempts to explain this phenomenon in the wave representation alone also fail, as the interference intensities, i.e., the wave determinism of the particle distribution is uncovered only after many repetitions of the single-particle scatterings performed at the specified dynamical conditions of the incident beam.

These apparent contradictions illustrate the wave–particle dualism of the micro-objects. Indeed, in accordance with the Heisenberg indeterminacy principle, it is impossible to simultaneously, sharply specify the particle momentum $p = h/\lambda$, which implies the knowledge of the interference pattern, and its position, which presupposes the knowledge of the slit, through which the particle has passed, when the other slit remains closed.

Therefore, there is a distinct *wave* causality in this at first glance "random" scattering of independent particles so that de Broglie's wave $\psi(x, t)$, or the *wave* (*state*) *function* for short, indeed describes in a statistical sense a movement of a single particle, with the wave intensity $I(x, t) = |\psi(x, t)|^2$ (1.10) measuring the chance of finding it hitting the screen at location x at time t. This probabilistic interpretation of the waves of matter is due to Born, who proposed in 1927 to call the intensity $I(x, t)$ the *probability density* of observing the particle at specified localization at the given time. As we shall see later in the book, in the modern

quantum mechanics this identification forms a basis for interpreting the system wave function, which carries the complete information about the dynamic state of the micro-object. It should also be emphasized that this function itself, the solution of the Schrödinger wave equation formulated in 1926, which governs the dynamics of microsystems, cannot be treated as a measure of the likelihood of finding a particle at the given position, since for that it should be positive everywhere, being then incapable of the destructive interference, which is the observed fact.

The *double*-slit diffraction of microparticles identifies two types of experiments involved in establishing the classical attributes of quantum systems. Let us examine the consecutive stages of a general setup in a thought experiment shown in Fig. 1.1. We denote the initial and final states (wave functions) of the quantum system, at time $t_0 \equiv 0$ and $t > 0$, respectively, by $\psi(x, t_0)$ and $\psi(x, t)$. The classical attributes of the initial state are determined by performing the so-called *initial experiment*, which in fact creates $\psi(x, t_0)$, e.g., the monochromatic beam of particles of the specified momentum. Thus, this first category of experiment in quantum mechanics always refers to the *future*, by preparing the quantum state the time evolution of which we intend to study.

In the period $t_0 \rightarrow t$ the system evolves freely, $\psi(x, t_0) \rightarrow \psi(x, t)$, without any perturbing influence from measuring devices. This wave deterministic process will be described by the Schrödinger equation of motion, which in the modern quantum mechanics replaces the Newton (Hamilton) equations of motion of the classical theory. As we shall see later in the book, this evolution of the state function in the

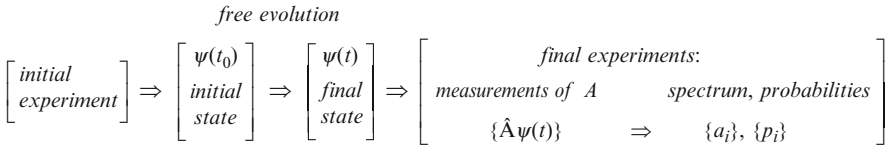

Fig. 1.1 Qualitative diagram of the *initial* and *final* experiments involved in preparing the initial state $\psi(t_0)$ and extracting the classical attributes of the final state $\psi(t)$ reached after free (undisturbed by measurement) evolution in the time interval $t_0 \rightarrow t$. The initial experiment arrangement, including the particle collimating slits and an appropriate velocity selector, transforms the polychromatic electron beam into its monochromatic component, thus preparing the initial state $\psi(t_0)$. In the time interval $t_0 \rightarrow t$ the system evolves freely, without any intervention from the measuring devices, in the specified dynamical conditions, e.g., when the particle motion is influenced by the force field generated by the external potential $v(x)$, in accordance with the *strictly* deterministic laws of quantum dynamics: $\psi(t_0) \rightarrow \psi(t)$. The statistically distributed classical attributes of the final state $\psi(t)$ are then extracted by performing the final experiment, using, e.g., the *double*-slit arrangement or a crystal as the measuring apparatus, which diffracts electrons to the movable detector or a photographic plate. This position-extraction experiment is an illustrative example of a general measurement-event of any physical observable A. The process of extracting the observed values $\{a_i\}$ (spectrum) of A in the *single*-particle experiments performed on the final state $\psi(t)$ has been symbolically depicted in the diagram as performance of the relevant mathematical operation $\hat{A}$ on $\psi(t)$, $\hat{A}\psi(t)$, with the operator $\hat{A}$ being specific for the measured quantity A. The observed spectrum $\{a_i\}$ of A and the associated probabilities $\{p_i = m_i/m\}$ can be determined only after many $m = (\sum_i m_i) \rightarrow \infty$ repetitions of the *single*-electron scatterings, with m_i denoting the frequency of observing a_i

specified dynamical conditions is strictly deterministic, with the given initial state $\psi(x, t_0)$ giving rise to a single final state $\psi(x, t)$.

The aim of the *final experiment* is to determine the classical descriptors of the quantum system in state $\psi(x, t)$. It should be stressed that after the particle has been localized on the screen, by using the photographic plate or some clever monitoring device, its dynamical state has been inadvertently and irreversibly destroyed as a result of the interaction with such an apparatus. Indeed the particle's precise localization denies us of any knowledge about the particle momentum. Thus, the final experiment can have implications only to the very *past* event, when the micro-object reaches the screen.

Due to the particle–wave duality, the link between $\psi(x, t)$ and possible outcomes of the final experiment is generally of the "*one-to-many*" type, thus giving rise to statistical predictions of specific values of classical descriptors of the system final state. Indeed, we cannot a priori predict, where the scattered electron hits the screen, but the final interference pattern, obtained after numerous repetitions of the single-electron diffractions, uniquely identifies the probability distribution $|\psi(x, t)|^2$ of the final state. It should be emphasized that only very numerous repetitions of the single-particle "experiment" together constitute the complete final experiment in quantum mechanics.

The preceding discussion prompts us to revise our ideas of causality (Heisenberg 1949, 1958; Born 1964; Bohm 1980; see also: Penrose 1989). Causality applies only to the micro-objects which are left undisturbed. Therefore, only the free-evolution in the chain of events depicted in Fig. 1.1 represents the causal stage, while the final measurement produces a disturbance in the state of the object serious enough to destroy any causal connection between the *separate* results of observations monitoring the object final state.

The statistical predictions and the indeterminism of quantum laws are a property inherent in nature, and should not be regarded as resulting from our temporary ignorance, which could be removed by some future theory, better and more complete. Although the modern quantum theory provides a thoroughly rational, coherent, and extremely successful description of micro-objects of the subatomic and atomic/molecular levels, one should not dogmatically rule out its future improvements and extensions, e.g., on the subnuclear level. However, as much as the quantum mechanics was forced upon the modern science by the physical rather than metaphysical necessity, these developments have to address future experimental findings, which could not be explained by the quantum theory. Indeed, as history teaches us, no matter how complete the description of the dynamical state may seem today, sooner or later new experimental facts will require us to improve the theoretical model and arrive at an even more general description, more detailed and usually more complex.

For example, all empirical evidence, including the *Stern–Gerlach experiment* and atomic spectra, points to the need for attributing to many elementary particles, notably electrons, protons, and neutrons, the intrinsic angular momentum, or *spin*, and the associated magnetic moment. Therefore, such particles can hardly be treated as mass points without any internal structure. Hence, for the complete

specification of their dynamic states one has to provide the relevant spin quantum numbers, which fix these internal degrees-of-freedom of such micro-objects. These new dynamical variables of entirely nonclassical origin have to be specified besides the remaining simultaneously measurable observables.

1.4 Particle Spin

In 1925 Uhlenbeck and Goudsmit hypothesized the existence of yet another internal attribute of atoms and elementary particles, called *spin* angular momentum and the associated intrinsic magnetic dipole moment, which complement such properties of these micro-objects as mass, electric dipole moment, moment of inertia, electric charge, etc. This internal state variable has been originally introduced to simplify the classification of atomic spectra. This goal has been achieved, when one envisaged the existence of the internal angular momentum $\boldsymbol{s}$ of an electron, called the spin, the length of which is quantized by the *half* integral quantum number $\mathfrak{s} = \frac{1}{2} : s = |\boldsymbol{s}| = [\mathfrak{s}(\mathfrak{s}+1)]^{\frac{1}{2}}\hbar$ (Fig. 1.2).

Confirmation of this experimental conjecture came in 1928 from the relativistic quantum theory of Dirac. The existence of the electronic spin also transpires from

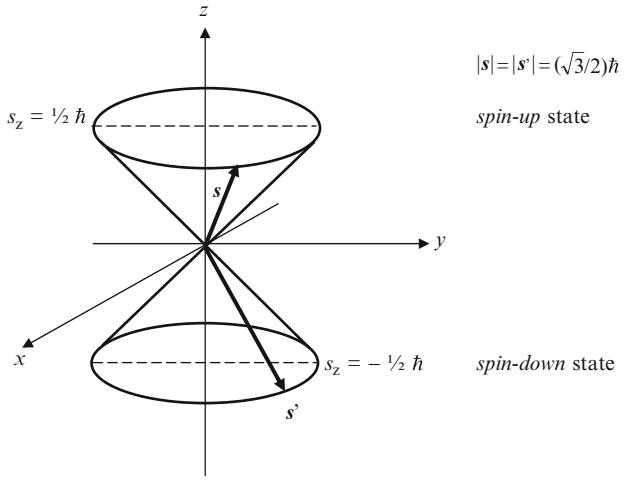

Fig. 1.2 The electron spin $\boldsymbol{s}$ can be characterized in quantum mechanics by two simultaneously observable attributes: its length $s = |\boldsymbol{s}| = [\mathfrak{s}(\mathfrak{s}+1)]^{\frac{1}{2}}\hbar = (\sqrt{3}/2)\hbar$, for the half-integral spin quantum number $\mathfrak{s} = \frac{1}{2}$, and its projection on the specified axis, say axis "z" of the Cartesian coordinate system: $s_z = \sigma\hbar$, where $\sigma = \pm\mathfrak{s}$. These two observables do not strictly specify the spin vector, but rather they define the whole family of admissible vector directions determining the cone surfaces shown in the diagram. The length and a single projection exhaust the complete list of simultaneously observed properties of any angular momentum in quantum mechanics. In other words, the direction of the angular momentum of the microparticle is not an observable

the earlier Stern–Gerlach experiment of 1921 in which a beam of silver atoms, containing a single, outermost spin-unpaired electron, produce two traces corresponding to the spin-up ($s_z = {}^1\!/_2\hbar$) and spin-down ($s_z = -{}^1\!/_2\hbar$) states (Fig. 1.2) of their valence electron, after being deflected in a nonuniform magnetic field.

These two spin states of a single electron can be uniquely specified by the quantum numbers determining the two simultaneously measurable attributes of the spin vector: $\mathfrak{s}$, for its length, and $\sigma = \pm\mathfrak{s}$, for its projection along the specified direction, say the "z" axis in Fig. 1.2: $s_z = \sigma\hbar$. They can be symbolically represented as the following "state vectors," in which one provides an explicit or symbolic specification of the state spin quantum numbers within the arrow-like symbol of Dirac:

$$\textit{spin}-\textit{up}\ \text{state:} \qquad |\,\alpha\,\rangle = |\mathfrak{s}, \sigma = +\mathfrak{s}\rangle = |\,{}^1\!/_2, +{}^1\!/_2\rangle = |\,+\,\rangle,$$

$$\textit{spin}-\textit{down}\ \text{state:} \quad |\,\beta\,\rangle = |\mathfrak{s}, \sigma = -\mathfrak{s}\rangle = |{}^1\!/_2, -{}^1\!/_2\rangle = |\,-\,\rangle.$$

1.5 Birth of Modern Quantum Mechanics

The consistent quantum mechanics (see, e.g., Messiah 1961; Davydov 1965; Dirac 1967; Merzbacher 1967; Cohen-Tannoudji et al. 1977; Fock 1986), which explains the origins of the quantization of the physical observables and introduces the generalized dynamics of quantum states, has emerged in 1926–1927 in two equivalent forms: the *Matrix Mechanics* of Heisenberg and the *Wave Mechanics* of Schrödinger. Although using quite different mathematical apparatuses, the matrix algebra and differential equations, respectively, these two rival theories gave rise to identical physical predictions, in complete agreement with all experimental data. It was clear, therefore, that these two approaches represent the same physical theory, as indeed demonstrated later by Schrödinger and Dirac (see, e.g., Buckley and Peat 1979).

Heisenberg discovered the need for a generally *noncommutative* multiplication of physical quantities in quantum mechanics, which gives rise to the position–momentum indeterminacy. The analogies with systems in classical mechanics, which are governed by the linear equations of motion, a consequence of the superposition relationships between states of vibrating strings or membranes, have led Schrödinger to establish the basic equations of the Wave Mechanics. The resulting equation of state is also linear in the unknowns, because of the assumption of the quantum superposition principle. In Heisenberg's approach the quantum states and physical observables are represented by the matrix vectors and square matrices, respectively, while in Schrödinger's treatment they are accordingly associated with functions and differential operators. The important contributions to the final form of the modern quantum theory have also been made by other

members of the Göttingen School, Born and Jordan, and by Dirac and Pauli, who invented the relativistic version of the quantum theory.

These revolutionary departures from principles of the classical theory, and particularly in the form of the quantum superposition of states demanding indeterminacy in the results of observations, are necessary to provide a sensible physical interpretation and to explain all known experimental facts. These new ideas find their expression through the introduction of a new mathematical formalisms as well as novel axioms and rules of manipulation. The two original formulations of the modern quantum mechanics can be united in a more general and abstract form of the quantum theory, which includes both the wave mechanics and matrix theory as its special cases. This "geometric" formulation requires the complex linear vector space, called the *Hilbert space*, in which vectors represent state functions. Both n-dimensional and $n \to \infty$ spaces are invoked, including the indenumerably infinite case of vectors corresponding to continuous variables. The matrix and wave function theories then appear as corresponding to different choices of the basic vectors in the Hilbert-space, which define the chosen reference frame for concepts and equations of quantum mechanics. This is similar to the relationship between the form of equations in classical physics and the adopted coordinate system in which they are formulated. With the increased elegance and mathematical abstractness of this unifying geometric formulation one also gains a great deal of understanding.

The geometric approach using Dirac's vector notation is the method chosen in the present short presentation of the principles of quantum mechanics. Its relation to the two original formulations will be briefly explored, emphasizing their equivalence in predicting the possible outcomes of experiments and the dynamical equation of motion. Since the wave mechanics appears to be conceptually simpler in chemical applications and directly connecting to the particle–wave dualism, a stronger emphasis will be made on this (nonrelativistic) version of the quantum theory. However, for reasons of convenience, in specific problems covered by the book the matrix theory will also be applied. In this study an emphasis is put on the conceptual developments rather than specific applications. For the solvable problems in quantum mechanics and quantum chemistry the reader is referred to specific textbooks and monographs (e.g., Flügge 1974; Szabo and Ostlund 1982; Atkins 1983; Levine 1983; McQuarrie 1983; Johnson and Pedersen 1986).

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