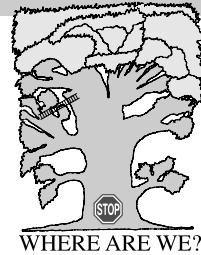


# Chapter 1

# THE MAGIC OF QUANTUM MECHANICS



## Where are we?

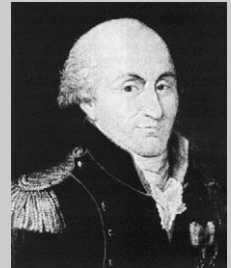
We are at the beginning of all the paths, at the base of the TREE.

## An example

Since 1911 we have known that atoms and molecules are built of two kinds of particles: electrons and nuclei. Experiments show the particles may be treated as point-like objects of certain mass and electric charge. The electronic charge is equal to  $-e$ , while the nuclear charge amounts to  $Ze$ , where  $e = 1.6 \cdot 10^{-19}$  C and  $Z$  is a natural number. Electrons and nuclei interact according to the Coulomb law, and classical mechanics and electrodynamics predict that *any atom or molecule is bound to collapse in a matter of a femtosecond* emitting an infinite amount of energy. Hence, according to the classical laws, the complex matter we see around us (also our bodies) should simply not exist at all.

However, atoms and molecules do exist, and their existence may be described in detail by quantum mechanics using what is known as the wave function. The axioms of quantum mechanics provide the rules for the derivation of this function and for the calculation of all the observable properties of atoms and molecules.

Charles Augustin de Coulomb (1736–1806), French military engineer, one of the founders of quantitative physics. In 1777 he constructed a torsion balance for measuring very weak forces, with which he was able to demonstrate the inverse square law for electric and magnetic forces. He also studied charge distribution on the surfaces of dielectrics.



## What is it all about

History of a revolution ( $\Delta$ )	p. 4
Postulates ( $\Delta$ )	p. 15
The Heisenberg uncertainty principle ( $\Delta$ )	p. 34
The Copenhagen interpretation ( $\otimes$ )	p. 37
How to disprove the Heisenberg principle? The Einstein–Podolsky–Rosen recipe ( $\otimes$ )	p. 38
Is the world real? ( $\otimes$ )	p. 40
• Bilocation	

<b>The Bell inequality will decide (✕)</b>	<b>p. 43</b>
<b>Intriguing results of experiments with photons (✕)</b>	<b>p. 46</b>
<b>Teleportation (✕)</b>	<b>p. 47</b>
<b>Quantum computing (✕)</b>	<b>p. 49</b>

Any branch of science has a list of axioms, on which the entire construction is built.<sup>1</sup> For quantum mechanics, six such axioms (postulates) have been established. The postulates have evolved in the process of reconciling theory and experiment, and may sometimes be viewed as non-intuitive. These axioms stand behind any tool of quantum mechanics used in practical applications. They also lead to some striking conclusions concerning the reality of our world, for example, the possibilities of bilocation, teleportation, and so on. These unexpected conclusions have recently been experimentally confirmed.

**Why is this important?**

The axioms given in this chapter represent the *foundation* of quantum mechanics, and justify all that follows in this book. In addition, our ideas of what the world is really like acquire a new and unexpected dimension.

**What is needed?**

- Complex numbers (necessary).
- Operator algebra and vector spaces, Appendix B, p. 895 (necessary).
- Angular momentum, Appendix F, p. 955 (recommended).
- Some background in experimental physics: black body radiation, photoelectric effect (recommended).

**Classical works**

The beginning of quantum theory was the discovery, by Max Planck, of the electromagnetic *energy quanta emitted* by a black body. The work was published under the title: “*Über das Gesetz der Energieverteilung im Normalspektrum*”<sup>2</sup> in *Annalen der Physik*, 4 (1901) 553. ★ Four years later Albert Einstein published a paper “*Über die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt*” in *Annalen der Physik*, 17 (1905) 132, in which he explained the photoelectric effect by assuming that the energy is *absorbed* by a metal as quanta of energy. ★ In 1911 Ernest Rutherford discovered that atoms are composed of a massive nucleus and electrons: “*The Scattering of the  $\alpha$  and  $\beta$  Rays and the Structure of the Atom*”, in *Proceedings of the Manchester Literary and Philosophical Society*, IV,

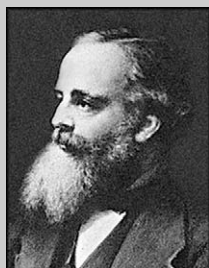
<sup>1</sup>And which are not expected to be proved.  
<sup>2</sup>Or “*On the Energy Distribution Law in the Normal Spectrum*” with a note saying that the material had already been presented (in another form) at the meetings of the German Physical Society on Oct. 19 and Dec. 14, 1900.  
On p. 556 one can find the following historical sentence on the total energy denoted as  $U_N$ : “*Hierzu ist es notwendig,  $U_N$  nicht als eine stetige, unbeschränkt teilbare, sondern als eine diskrete, aus einer ganzen Zahl von endlichen gleichen Teilen zusammengesetzte Grösse aufzufassen*”, which translates as: “*Therefore, it is necessary to assume that  $U_N$  does not represent any continuous quantity that can be divided without any restriction. Instead, one has to understand that it as a discrete quantity composed of a finite number of equal parts.*”

55 (1911) 18. ★ Two years later Niels Bohr introduced a planetary model of the hydrogen atom in “*On the Constitution of Atoms and Molecules*” in *Philosophical Magazine*, Series 6, vol. 26 (1913). ★ Louis de Broglie generalized the corpuscular and wave character of any particle in his PhD thesis “*Recherches sur la théorie des quanta*”, Sorbonne, 1924. ★ The first mathematical formulation of quantum mechanics was developed by Werner Heisenberg in “*Über quantentheoretischen Umdeutung kinematischer und mechanischer Beziehungen*”, *Zeitschrift für Physik*, 33 (1925) 879. ★ Max Born and Pascual Jordan recognized matrix algebra in the formulation [in “*Zur Quantenmechanik*”, *Zeitschrift für Physik*, 34 (1925) 858] and then all three [the famous “*Drei-Männer Arbeit*” entitled “*Zur Quantenmechanik. II.*” and published in *Zeitschrift für Physik*, 35 (1925) 557] expounded a coherent mathematical basis for quantum mechanics. ★ Wolfgang Pauli introduced his “two-valuedness” for the non-classical electron coordinate in “*Über den Einfluss der Geschwindigkeitsabhängigkeit der Elektronenmasse auf den Zeemaneffekt*”, published in *Zeitschrift für Physik*, 31 (1925) 373, the next year George Uhlenbeck and Samuel Goudsmit described their concept of particle spin in “*Spinning Electrons and the Structure of Spectra*”, *Nature*, 117 (1926) 264. ★ Wolfgang Pauli published his famous exclusion principle in “*Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren*” which appeared in *Zeitschrift für Physik B*, 31 (1925) 765. ★ The series of papers by Erwin Schrödinger “*Quantisierung als Eigenwertproblem*” in *Annalen der Physik*, 79 (1926) 361 (other references in Chapter 2) was a major advance. He proposed a different mathematical formulation (from Heisenberg’s) and introduced the notion of the wave function. ★ In the same year Max Born, in “*Quantenmechanik der Stossvorgänge*” which appeared in *Zeitschrift für Physik*, 37 (1926) 863 gave an interpretation of the wave function. ★ The uncertainty principle was discovered by Werner Heisenberg and described in “*Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik*”, *Zeitschrift für Physik*, 43 (1927) 172. ★ Paul Adrien Maurice Dirac reported an attempt to reconcile quantum and relativity theories in a series of papers published from 1926–1928 (references in Chapter 3). ★ Albert Einstein, Boris Podolsky and Natan Rosen proposed a test (then a Gedanken or thinking-experiment, now a real one) of quantum mechanics “*Can quantum-mechanical description of physical reality be considered complete?*” published in *Physical Review*, 47 (1935) 777. ★ Richard Feynman, Julian Schwinger and Shinichiro Tomonaga independently developed quantum electrodynamics in 1948. ★ John Bell, in “*On the Einstein–Podolsky–Rosen Paradox*”, *Physics*, 1 (1964) 195 reported inequalities which were able to verify the very foundations of quantum mechanics. ★ Alain Aspect, Jean Dalibard and Gérard Roger in “*Experimental Test of Bell’s Inequalities Using Time-Varying Analyzers*”, *Physical Review Letters*, 49 (1982) 1804 reported measurements which violated the Bell inequality and proved the non-locality or/and (in a sense) non-reality of our world. ★ Akira Tonomura, Junji Endo, Tsuyoshi Matsuda and Takeshi Kawasaki in “*Demonstration of Single-Electron Buildup of an Interference Pattern*”, *American Journal of Physics*, 57 (1989) 117 reported direct electron interference in a two-slit experiment. ★ Charles H. Bennett, Gilles Brassard, Claude Crépeau, Richard Jozsa, Asher Peres and William K. Wootters, in “*Teleporting an unknown quantum state via dual classical and Einstein–Podolsky–Rosen channels*” in *Physical Review Letters*, 70 (1993) 1895 designed a teleportation experiment, which has subsequently been successfully accomplished by Dik Bouwmeester, Jian-Wei Pan, Klaus Mattle, Manfred Eibl, Harald Weinfurter and Anton Zeilinger, “*Experimental Quantum Teleportation*” in *Nature*, 390 (1997) 575.

## 1.1 HISTORY OF A REVOLUTION

The end of the nineteenth century saw itself as a proud period for physics, which seemed to finally achieve a state of coherence and clarity. Physics at that time believed the world consisted of two kingdoms: a kingdom of particles and a kingdom of electromagnetic waves.

James Clerk Maxwell (1831–1879), British physicist, professor at the University of Aberdeen, Kings College, London, and Cavendish Professor in Cambridge. His main contributions are his famous equations for electromagnetism (1864), and the earlier discovery of velocity distribution in gases (1860).



Motion of particles had been described by Isaac Newton's equation, with its striking simplicity, universality and beauty. Similarly, electromagnetic waves had been accurately described by James Clerk Maxwell's simple and beautiful equations.

Young Planck was advised to abandon the idea of studying physics, because everything had already been discovered.

*This beautiful idyll was only slightly in-*

*complete, because of a few annoying details: the strange black body radiation, the photoelectric effect and the mysterious atomic spectra.* Just some rather exotic problems to be fixed in the near future...

As it turned out, they opened a New World. The history of quantum theory, one of most revolutionary and successful theories ever designed by man, will briefly be given below. Many of these facts have their continuation in the present textbook.

### Black body radiation

#### 1900 – Max Planck

Max Planck wanted to understand black body radiation. The black body may be modelled by a box, with a small hole, Fig. 1.1. We heat the box up, wait for the system to reach a stationary state (at a fixed temperature) and see what kind of electromagnetic radiation (intensity as a function of frequency) comes out of the hole. In 1900 Rayleigh and Jeans<sup>3</sup> tried to apply classical mechanics to this problem, and calculated correctly that the black body would emit electromagnetic radiation having a distribution of frequencies. However, the larger the frequency the larger its intensity, leading to what is known as ultraviolet catastrophe, an absurd conclusion. Experiment contradicted theory (Fig. 1.1).

At a given temperature  $T$  the intensity distribution (at a given frequency  $\nu$ , Fig. 1.1.b) has a single maximum. As the temperature increases, the maximum should shift towards higher frequencies (a piece of iron appears red at 500 °C, but bluish at 1000 °C). Just like Rayleigh and Jeans, Max Planck was unable to derive

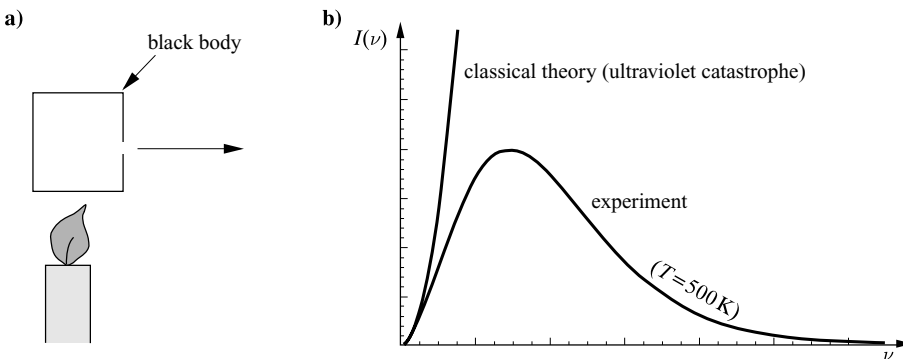
<sup>3</sup>James Hopwood Jeans (1877–1946), British physicist, professor at the University of Cambridge and at the Institute for Advanced Study in Princeton. Jeans also made important discoveries in astrophysics (e.g., the theory of double stars).

Max Karl Ernst Ludwig Planck (1858–1947), German physicist, professor at the universities in Munich, Kiel and Berlin, first director of the Institute of Theoretical Physics in Berlin. Planck was born in Kiel, where his father was a university professor of law. Max Planck was a universally talented school pupil, then an outstanding physics student at the University of Berlin, where he was supervised by Gustav Kirchhoff and Hermann Helmholtz. Music was his passion throughout his life, and he used to play piano duets with Einstein (who played the violin). This hard-working, middle-aged, old-fashioned, professor of thermodynamics made a major breakthrough as if in an act of scientific desperation. In 1918 Planck received the Nobel Prize “for services rendered to the advancement of Physics by his discovery of energy quanta”. Einstein recalls jokingly Planck’s reported lack of full confidence in general relativity theory: “Planck was one of the most out-



standing people I have ever known, (...) In reality, however, he did not understand physics. During the solar eclipse in 1919 he stayed awake all night, to see whether light bending in the gravitational field will be confirmed. If he understood the very essence of the general relativity theory, he would quietly go to bed, as I did”. (Cited by Ernst Straus in “Einstein: A Centenary Volume”, p. 31).

John William Strutt, Lord Rayleigh (1842–1919), British physicist, Cavendish Professor at Cambridge, contributed greatly to physics (wave propagation, light scattering theory – Rayleigh scattering). In 1904 Rayleigh received the Nobel Prize “for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies”.



**Fig. 1.1.** Black body radiation. (a) As one heats a box to temperature  $T$ , the hole emits electromagnetic radiation with a wide range of frequencies. The distribution of intensity  $I(\nu)$  as a function of frequency  $\nu$  is given in Fig. (b). There is a serious discrepancy between the results of classical theory and the experiment, especially for large frequencies. Only after assuming the existence of energy quanta can theory and experiment be reconciled.

quanta

Planck constant

this simple qualitative picture from classical theory – something had to be done. On 14 December 1900, the generally accepted date for the birth of quantum theory, Planck presented his theoretical results for the black body treated as an ensemble of harmonic oscillators. With considerable reluctance he postulated<sup>4</sup> that matter cannot emit radiation otherwise than by equal portions (“*quanta*”) of energy  $h\nu$ , proportional to the frequency  $\nu$  of vibrations of a single oscillator of the black body. The famous Planck constant  $h$  followed soon after ( $h = 6.62607 \cdot 10^{-34}$  J s; but in this book, we will use a more convenient constant<sup>5</sup>  $\hbar = \frac{h}{2\pi}$ ). It is exactly this hypothesis about energy quanta that led to the agreement of theory with experiment and the elimination of the ultraviolet catastrophe.

## Photoelectric effect

### 1905 – Albert Einstein

photon

The second worrying problem, apart from the black body, was the photoelectric effect.<sup>6</sup> Light knocks electrons<sup>7</sup> out of metals, but only when its frequency exceeds a certain threshold. Classical physics was helpless. In classical theory, light energy should be stored in the metal in a continuous way and *independent of the frequency used, after a sufficient period of time, the electrons should be ejected from the metal*. Nothing like that was observed. Einstein introduced the idea of electromagnetic radiation quanta as *particles*, later baptised *photons* by Gilbert Lewis. Note that Planck’s idea of a quantum concerned energy transfer *from the black body to the electromagnetic field*, while Einstein introduced it *for the opposite direction* with the energy corresponding to Planck’s quantum. Planck considered the quantum as a portion of energy, while for Einstein the quantum meant a particle.<sup>8</sup> Everything became clear: energy goes to electrons by *quanta* and this is why only quanta ex-

<sup>4</sup>He felt uncomfortable with this idea for many years.

<sup>5</sup>Known as “h bar”.

<sup>6</sup>Experimental work on the effect had been done by Philipp Eduard Anton Lenard (1862–1947), German physicist, professor at Breslau (now Wrocław), Köln and Heidelberg. Lenard discovered that the number of photoelectrons is proportional to the intensity of light, and that their kinetic energy *does not depend at all on the intensity*, depending instead on the *frequency* of light. Lenard received the Nobel Prize in 1905 “*for his work on cathode rays*”. A faithful follower of Adolf Hitler, and devoted to the barbarous Nazi ideas, Lenard terrorized German science. He demonstrates that scientific achievement and decency are two separate human characteristics.

<sup>7</sup>The electron was already known, having been predicted as early as 1868 by the Irish physicist George Johnstone Stoney (1826–1911), and finally discovered in 1897 by the British physicist Joseph John Thomson (1856–1940). Thomson also discovered a strange pattern: the number of electrons in light elements was equal to about one half of their atomic mass. Free electrons were obtained much later (1906). The very existence of atoms was still a hypothesis. The atomic nucleus was to be discovered only in 1911. Physicists were also anxious about the spectra of even the simplest substances such as hydrogen. Johann Jacob Balmer, a teacher from Basel, was able to design an astonishingly simple formula which fitted perfectly some of the observed lines in the hydrogen spectrum (“*Balmer series*”). All that seemed mysterious and intriguing.

<sup>8</sup>It is true that Einstein wrote about “*point-like quanta*” four years later, in a careful approach identifying the quantum with the particle. Modern equipment enables us to count photons, the individual particles of light. The human eye is also capable of detecting 6–8 photons striking a neuron.

Gilbert Newton Lewis (1875–1946), the greatest American chemist, who advanced American chemistry internationally through his research and teaching. In a 1926 article in *Nature* Lewis introduced the name of the “photon”. He also developed an early theory of chemical bonding (“Lewis structures”) based on counting the valence electrons and forming “octets” from them. The idea that atoms in molecules tend to form octets in order to complete their electron shells turned out to be surprisingly useful in predicting bond patterns in molecules. A drawback of this concept is that it was not related to the ideas of theoretical physics. It is an example of an



extremely clever concept rather than of a coherent theory. Lewis also introduced a new definition of acids and bases, which is still in use.

ceeding some threshold (the binding energy of an electron in the metal) are able to eject electrons from a metal.

### 1911 – Ernest Rutherford

Rutherford proved experimentally that an atom has massive nucleus, but it is however very small when compared to the size of the atom. The positive charge is concentrated in the nucleus, which is about  $10^{-13}$  cm in size. The density of the nuclear matter boggles the imagination:  $1\text{ cm}^3$  has a mass of about 300 million tonnes. This is how researchers found out that an atom is composed of a massive nucleus and electrons.

atomic nucleus

## The model of the hydrogen atom

### 1913 – Niels Bohr

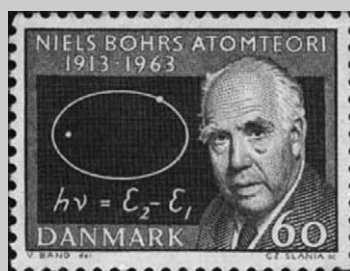
Atomic spectra were the third great mystery of early 20th century physics. Even interpretation of the spectrum of the hydrogen atom represented a challenge. At the age of 28 Bohr proposed (in 1913) a simple planetary model of this atom, in which the electron, contrary to classical mechanics, did not fall onto the nucleus. Instead, it changed its orbit with accompanying absorption or emission of energy quanta. Bohr assumed that angular orbital momentum is quantized and that the centrifugal force is compensated by the Coulomb attraction between the electron and the nucleus. He was able to reproduce part of the spectrum of the hydrogen

In 1905, the accuracy of experimental data was too poor to confirm Einstein's theory as the only one which could account for the experimental results. Besides, the wave nature of light was supported by thousands of crystal clear experiments. Einstein's argument was so breathtaking (...particles???), that Robert Millikan decided to falsify experimentally Einstein's hypothesis. However, after ten years of investigations, Millikan acknowledged that he was forced to support undoubtedly Einstein's explanation “however absurd it may look” (*Rev. Modern Phys.* 21 (1949) 343). This conversion of a sceptic inclined the Nobel Committee to grant Einstein the Nobel Prize in 1923 “for his work on the elementary charge of electricity and on the photo-electric effect”.

Niels Hendrik Bohr (1885–1962), Danish physicist, a professor at Copenhagen University, played a key role in the creation and interpretation of quantum mechanics (see end of this chapter). Bohr was born in Copenhagen, the son of a professor of physiology. He graduated from Copenhagen university and in 1911 obtained his doctorate there. Then he went to Cambridge to work under the supervision of J.J. Thomson, the discoverer of the electron. The collaboration did not work out, and in 1912 Bohr began to cooperate with Ernest Rutherford at the University of Manchester. In Manchester Niels Bohr made a breakthrough by introducing a planetary model of hydrogen atom. He *postulated* that the angular orbital momentum must be quantized. Using this Bohr reproduced the experimental spectrum of hydrogen atom with high accuracy. In 1922 Bohr received the Nobel Prize “for his investigation of the structure of atoms”. In the same year he became the father of Aage Niels Bohr – a future winner of the Nobel Prize (1975, for studies of the structure of nuclei). In October 1943, Bohr and his family fled from Denmark to Sweden,



and then to Great Britain and the USA, where he worked on the Manhattan Project. After the war the Bohr family returned to Denmark.



atom very accurately. Bohr then began work on the helium atom, which turned out to be a disaster, but he was successful again with the helium cation<sup>9</sup>  $\text{He}^+$ .

Niels Bohr played an inspiring role in the development and popularization of quantum mechanics. His Copenhagen Institute for Theoretical Physics, founded in 1921, was the leading world centre in the twenties and thirties, where many young theoreticians from all over the world worked on quantum mechanical problems.<sup>10</sup> Bohr, with Werner Heisenberg, Max Born and John von Neumann, contributed greatly to the elaboration of the philosophical foundations of quantum mechanics. According to this, quantum mechanics represents a coherent and complete model of reality (“the world”), and the discrepancies with the classical mechanics have a profound and fundamental character,<sup>11</sup> and both theories coincide in the limit  $\hbar \rightarrow 0$  (where  $\hbar$  is the Planck constant), and thus the predictions of quantum

<sup>9</sup>Bohr did not want to publish without good results for all other atoms, something he would never achieve. Rutherford argued: “Bohr, you explained hydrogen, you explained helium, people will believe you for other atoms”.

<sup>10</sup>John Archibald Wheeler recalls that, when he first came to the Institute, he met a man working in the garden and asked him where he could find Professor Bohr. The gardener answered: “That’s me”.

<sup>11</sup>The centre of the controversy was that quantum mechanics is indeterministic, while classical mechanics is deterministic, although this indeterminism is not all it seems. As will be shown later in this chapter, quantum mechanics is a *fully deterministic theory in the Hilbert space* (the space of all possible wave functions of the system), its indeterminism pertains to the physical space in which we live.



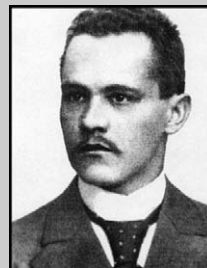
mechanics reduce to those of classical mechanics (known as Bohr's correspondence principle).

## "Old quantum theory"

### 1916 – Arnold Sommerfeld

In 1916 Arnold Sommerfeld generalized the Bohr quantization rule beyond the problem of the one-electron atom. Known as "old quantum theory", it did not represent any coherent theory of general applicability. As a matter of fact, this quantization was achieved by assuming that for every periodic variable (like an angle), an integral is equal to an integer times the Planck constant.<sup>12</sup> Sommerfeld also tried to apply the Bohr model to atoms with a single valence electron (he had to modify the Bohr formula by introducing the quantum defect, i.e. a small change in the principal quantum number, see p. 179).

Arnold Sommerfeld (1868–1951), German physicist, professor at the Mining Academy in Clausthal, then at the Technical University of Aachen, in the key period 1906–1938, was professor at Munich University. Sommerfeld considered not only circular (Bohr-like) orbits, but also elliptical ones, and introduced the angular quantum number. He also investigated X rays and the theory of metals. The sci-



entific father of many Nobel Prize winners he did not get this distinction himself.

## Waves of matter

### 1923 – Louis de Broglie

In his doctoral dissertation, stuffed with mathematics, Louis de Broglie introduced the concept of "waves of matter". He postulated that not only photons, but *also any other particle*, has, besides its corpuscular characteristics, some wave properties (those corresponding to light had been known for a long, long time). According to de Broglie, the wave length corresponds to momentum  $p$ ,

dualism

Louis Victor Pierre Raymond de Broglie (1892–1987) was studying history at the Sorbonne, carefully preparing himself for a diplomatic career. His older brother Maurice, a radiographer, aroused his interest in physics. The first World War (Louis did his military service in a radio communications unit) and the study of history delayed his start in physics. He was 32 when he presented his doctoral dissertation, which embarrassed his supervisor, Paul Langevin. The thesis, on the wave nature of all particles, was so revolutionary, that only a positive opinion from Einstein, who was asked by Langevin to take a look of the dissertation, con-



vinced the doctoral committee. Only five years later (in 1929), Louis de Broglie received the Nobel Prize "for his discovery of the wave nature of electrons".

<sup>12</sup>Similar periodic integrals were used earlier by Bohr.

$$p = \frac{h}{\lambda}$$

where  $h$  is again the Planck constant! What kind of momentum can this be, in view of the fact that momentum depends on the laboratory coordinate system chosen? Well, it is the momentum measured in the same laboratory coordinate system as that used to measure the corresponding wave length.

## Electron–photon scattering

1923 – Arthur Compton<sup>13</sup>

It turned out that an electron–photon collision obeys the same laws of dynamics as those describing collision of two particles: the energy conservation law and the momentum conservation law. This result confirmed the wave–corpuscular picture emerging from experiments.

## Discovery of spin

1925 – George E. Uhlenbeck and Samuel A. Goudsmit

Two Dutch students explained an experiment (Stern–Gerlach) in which a beam of silver atoms passing through a magnetic field split into two beams. In a short paper, they suggested that the silver atoms have (besides their orbital angular momentum) an additional internal angular momentum (spin), *similar* to a macroscopic body, which besides its centre-of-mass motion, also has a rotational (spinning) motion.<sup>14</sup> Moreover, the students demonstrated that the atomic spin follows from the spin of the electrons: among the 47 electrons of the silver atom, 46 have their spin compensated (23 “down” and 23 “up”), while the last “unpaired” electron gives the net spin of the atom.

## Pauli Exclusion Principle

1925 – Wolfgang Pauli<sup>15</sup>

Pauli postulated that *in any system two electrons cannot be in the same state* (including their spins). This “Pauli exclusion principle” was deduced from spectroscopic data (some states were not allowed).

<sup>13</sup> Arthur Holly Compton (1892–1962), American physicist, professor at the universities of Saint Louis and Chicago. He obtained the Nobel Prize in 1927 “*for the discovery of the effect named after him*”, i.e. for investigations of electron–photon scattering.

<sup>14</sup> Caution: *identifying* the spin with the rotation of a rigid body leads to physical inconsistencies.

<sup>15</sup> Pauli also introduced the idea of spin when interpreting spectra of atoms with a single valence electron. He was inspired by Sommerfeld, who interpreted the spectra by introducing the quantum number  $j = l \pm \frac{1}{2}$ , where the quantum number  $l$  quantized the orbital angular momentum of the electron. Pauli described spin as *a bivalent non-classical characteristic of the electron* [W. Pauli, *Zeit. Phys. B* 3 (1925) 765].

## Matrix quantum mechanics

### 1925 – Werner Heisenberg

A paper by 24 year old Werner Heisenberg turned out to be a breakthrough in quantum theory.<sup>16</sup> Max Born recognized matrix algebra in Heisenberg's formulation (who, himself, had not yet realised it) and in the same year a more solid formulation of the new mechanics ("matrix mechanics") was proposed by Werner Heisenberg, Max Born and Pascual Jordan.<sup>17</sup>

## Schrödinger equation

### 1926 – Erwin Schrödinger

In November 1925, Erwin Schrödinger delivered a lecture at the Technical University in Zurich (ETH), in which he presented the results of de Broglie. Professor Peter Debye stood up and asked the speaker:

Peter Joseph Wilhelm Debye, more exactly, Peter Josephus Wilhelmus Debye (1884–1966), Dutch physicist and chemist, professor in the Technical University (ETH) of Zurich (1911, 1920–1937) as well as at Göttingen, Leipzig and Berlin, won the Nobel Prize in chemistry in 1936 "for his contribution to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases". Debye emigrated to the USA in 1940, where he obtained a professorship at Cornell University in Ithaca, NY (and remained in this beautiful town to the end of his life). His memory is still alive there. Pro-



fessor Scheraga remembers him as an able chair in seminar discussions, in the tradition of the Zurich seminar of 1925.

<sup>16</sup>On June 7, 1925, Heisenberg was so tired after a bad attack of hay fever that he decided to go and relax on the North Sea island of Helgoland. Here, he divided his time between climbing the mountains, learning Goethe's poems by heart and (despite his intention to rest) hard work on the spectrum of the hydrogen atom with which he was obsessed. It was at night on 7 or 8 June that he saw something – the beginning of the new mechanics. In later years he wrote in his book *"Der Teil und das Ganze"*: *"It was about three o'clock in the morning when the final result of the calculation lay before me. At first I was deeply shaken. I was so excited that I could not think of sleep. So I left the house and awaited the sunrise on the top of a rock."* The first man with whom Heisenberg shared his excitement a few days later was his schoolmate Wolfgang Pauli, and, after another few days, also with Max Born.

<sup>17</sup>Jordan, despite his talents and achievements, felt himself underestimated and even humiliated in his native Germany. For example, he had to accept a position at Rostock University, which the German scientific elite used to call the "Outer-Mongolia of Germany". The best positions seemed to be reserved. When Hitler came to power, Jordan became a fervent follower...

Max Born (1882–1970), German physicist, professor at the universities of Göttingen, Berlin, Cambridge and Edinburgh, born in Breslau (now Wrocław) to the family of a professor of anatomy in Breslau. Born studied first in Breslau, then at Heidelberg and Zurich. He received his PhD in physics and astronomy in 1907 at Göttingen, where he began his swift academic career. Born obtained a chair at the University of Berlin in 1914, and returned to Göttingen in 1921, where he founded an outstanding school of theoretical physics, which competed with the famous institute of Niels Bohr in Copenhagen. Born supervised Werner Heisenberg, Pascual Jordan and Wolfgang Pauli. It was Born who recognized, in 1925, that Heisenberg's quantum mechanics could be formulated in terms of matrix algebra. Together with Heisenberg and Jordan, he created the first consistent quantum theory (the famous "*drei-Männer Arbeit*"). After



Schrödinger's formulation of quantum mechanics, Born proposed the probabilistic interpretation of the wave function. Despite such seminal achievements, the Nobel Prizes in the thirties were received by his colleagues. Finally, when in 1954 Born obtained the Nobel Prize "*for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wave-function*", there was a great relief among his famous friends.

"*You are telling us about waves, but where is the wave equation in your talk?*" Indeed, there wasn't any! Schrödinger began to work on this and the next year formulated what is now called wave mechanics based on the wave equation. Both formulations, Heisenberg's and Schrödinger's<sup>18</sup> turned out to be equivalent and are now known as the foundation for (non-relativistic) quantum mechanics.

## Statistical interpretation of wave function

### 1926 – Max Born

Max Born proposed interpreting the square of the complex modulus of Schrödinger's wave function as the probability density for finding the particle.

## Uncertainty principle

### 1927 – Werner Heisenberg

Heisenberg concluded that it is not possible to measure simultaneously the position ( $x$ ) and momentum ( $p_x$ ) of a particle with any desired accuracy. The more exactly we measure the position (small  $\Delta x$ ), the larger the error we make in measuring the momentum (large  $\Delta p_x$ ) and *vice versa*.

<sup>18</sup>And the formulation proposed by Paul A.M. Dirac.

## Electron diffraction

1927 – Clinton Davisson, Lester H. Germer, George Thomson<sup>19</sup>

Davisson and Germer, and Thomson, demonstrated in ingenious experiments that indeed electrons do exhibit wave properties (using crystals as diffraction gratings).

## The birth of quantum chemistry

1927 – Walter Heitler, Fritz Wolfgang London

Walter Heitler and Fritz Wolfgang London convincingly explained why two neutral atoms (like hydrogen) attract each other with a force so strong as to be comparable with the Coulomb forces between ions. Applying the Pauli exclusion principle when solving the Schrödinger equation is of key importance. Their paper was received on June 30, 1927, by *Zeitschrift für Physik*, and this may be counted as the birthday of quantum *chemistry*.<sup>20</sup>

## Dirac equation for the electron and positron

1928 – Paul Dirac

Paul Dirac made a magnificent contribution to quantum theory. His main achievements are the foundations of quantum electrodynamics and construction of the relativistic wave equation (1926–1928) which now bears his name. The equation not only described the electron, but also its anti-matter counterpart – the positron (predicting anti-matter). Spin was also inherently present in the equation.

## Quantum field theory

1929 – Werner Heisenberg and Wolfgang Pauli

These classmates developed a theory of matter, and the main features still survive there. In this theory, the elementary particles (the electron, photon, and so on) were viewed as excited states of the corresponding fields (the electron field, electromagnetic field and so on).

<sup>19</sup>Clinton Joseph Davisson (1881–1958), American physicist at Bell Telephone Laboratories. He discovered the diffraction of electrons with L.H. Germer, and they received the Nobel Prize in 1937 “for their experimental discovery of the diffraction of electrons by crystals”. The prize was shared with G.P. Thomson, who used a different diffraction method. George Paget Thomson (1892–1975), son of the discoverer of the electron, Joseph John Thomson, and professor at universities in Aberdeen, London and Cambridge.

<sup>20</sup>The term “quantum chemistry” was first used by Arthur Haas in his lectures to the Physicochemical Society of Vienna in 1929 (A. Haas, “*Die Grundlagen der Quantenchemie. Eine Einleitung in vier Vorträgen*”, Akademische Verlagsgesellschaft, Leipzig, 1929).

anti-matter

## Discovery of anti-matter (the positron)

1932 – Carl Anderson<sup>21</sup>

One of Dirac's important results was the observation that his relativistic wave equation is satisfied, not only by the electron but also by a mysterious unknown particle, the positive electron (positron). This anti-matter hypothesis was confirmed by Carl Anderson, who found the positron experimentally – a victorious day for quantum theory.

## Quantum electrodynamics

1948 – Richard Feynman, Julian Schwinger, Shinichiro Tomonaga<sup>22</sup>

The Dirac equation did not take all the physical effects into account. For example, the strong electric field of the nucleus polarizes a vacuum so much, that electron–positron pairs emerge from the vacuum and screen the electron–nucleus interaction. The quantum electrodynamics (QED) developed independently by Feynman, Schwinger and Tomonaga accounts for this, and for similar effects, and brings theory and experiment to an agreement of unprecedented accuracy.

## Bell inequalities

1964 – John Bell

The mathematician John Bell proved that, if particles have certain properties *before measurement* (so that they were small but *classical objects*), then the measurement results would have to satisfy some inequalities which contradict the predictions of quantum mechanics (further details at the end of this chapter).

## Is the world non-local?

1982 – Alain Aspect

Experiments with photons showed that the Bell inequalities are *not* satisfied. This means that either there is *instantaneous communication* even between extremely distant particles (“entangled states”), or that the particles *do not have some definite properties* before the measurement is performed (more details at the end of this chapter).

## Teleportation of the photon state

1997 – Anton Zeilinger

A research group at the University of Innsbruck used entangled quantum states (see p. 39) to perform teleportation of a photon state<sup>23</sup> that is, to prepare at a

<sup>21</sup>More details in Chapter 3.

<sup>22</sup>All received the Nobel Prize in 1965 “for their fundamental work in quantum electrodynamics, with fundamental implications for the physics of elementary particles”.

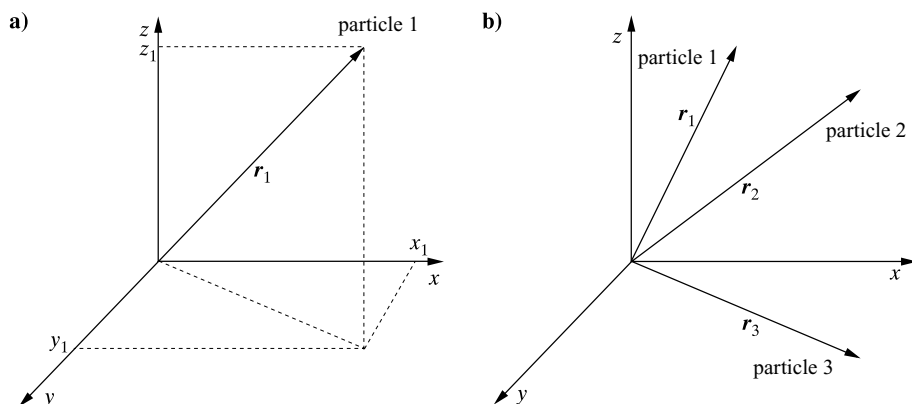
<sup>23</sup>D. Bouwmeester, J. Pan, K. Mattle, M. Eibl, H. Weinfurter, A. Zeilinger, *Nature* 390 (1997) 575.

distance any state of a photon with simultaneous disappearance of this state from the teleportation site (details at the end of this chapter).

## 1.2 POSTULATES

All science is based on a number of axioms (postulates). Quantum mechanics is based on a system of axioms that have been formulated to be as simple as possible and yet reproduce experimental results. Axioms are not supposed to be proved, their justification is efficiency. Quantum mechanics, the foundations of which date from 1925–26, still represents the basic theory of phenomena within atoms and molecules. This is the domain of chemistry, biochemistry, and atomic and nuclear physics. Further progress (quantum electrodynamics, quantum field theory, elementary particle theory) permitted deeper insights into the structure of the atomic nucleus, but did not produce any fundamental revision of our understanding of atoms and molecules. Matter as described at a non-relativistic<sup>24</sup> quantum mechanics represents a system of electrons and nuclei, treated as point-like particles with a definite mass and electric charge, moving in three-dimensional space and interacting by *electrostatic* forces.<sup>25</sup> This model of matter is at the core of quantum chemistry, Fig. 1.2.

The assumptions on which quantum mechanics is based are given by the following postulates I–VI. For simplicity, we will restrict ourselves to a single particle



**Fig. 1.2.** An atom (molecule) in non-relativistic quantum mechanics. A Cartesian (“laboratory”) coordinate system is introduced into three-dimensional space (a). We assume (b) that all the particles (electrons and nuclei) are point-like (figure shows their instantaneous positions) and interact only by electrostatic (Coulomb) forces.

<sup>24</sup> Assuming that the speed of light is infinite.

<sup>25</sup> Yes, we take only electrostatics, that is, Coulomb interactions. It is true that a moving charged particle creates a magnetic field, which influences its own and other particles’ motion. This however (the Lorentz force) is taken into account in the *relativistic* approach to quantum mechanics.

moving along a single coordinate axis  $x$  (the mathematical foundations of quantum mechanics are given in Appendix B on p. 895).

### Postulate I (on the quantum mechanical state)

wave function

The state of the system is described by the *wave function*  $\Psi = \Psi(x, t)$ , which depends on the coordinate of particle  $x$  at time  $t$ . Wave functions in general are complex functions of real variables. The symbol  $\Psi^*(x, t)$  denotes the complex conjugate of  $\Psi(x, t)$ . The quantity

$$p(x, t) = \Psi^*(x, t)\Psi(x, t) dx = |\Psi(x, t)|^2 dx \quad (1.1)$$

gives the *probability that at time  $t$  the  $x$  coordinate of the particle lies in the small interval  $[x, x + dx]$*  (Fig. 1.3.a). The probability of the particle being in the interval  $(a, b)$  on the  $x$  axis is given by (Fig. 1.3.b):  $\int_a^b |\Psi(x, t)|^2 dx$ .

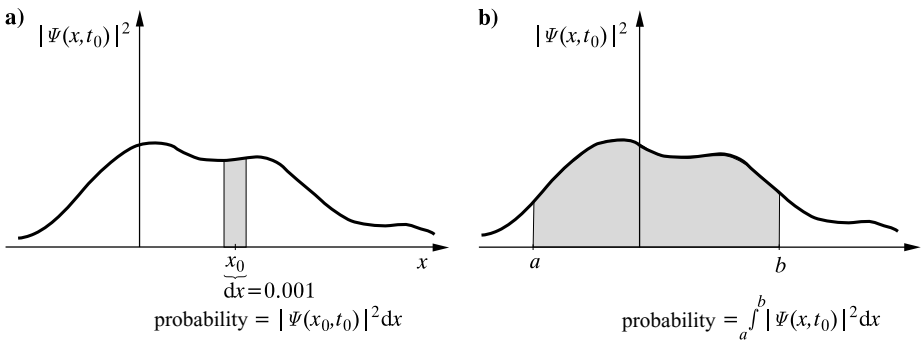
statistical  
interpretation  
probability  
density

The probabilistic interpretation of the wave function was proposed by Max Born.<sup>26</sup> By analogy with the formula: mass = density  $\times$  volume, the quantity  $\Psi^*(x, t)\Psi(x, t)$  is called the *probability density* that a particle at time  $t$  has position  $x$ .

normalization

In order to treat the quantity  $p(x, t)$  as a probability, at any instant  $t$  the wave function must satisfy the *normalization condition*:

$$\int_{-\infty}^{\infty} \Psi^*(x, t)\Psi(x, t) dx = 1. \quad (1.2)$$



**Fig. 1.3.** A particle moves along the  $x$  axis and is in the state described by the wave function  $\Psi(x, t)$ . Fig. (a) shows how the probability of finding particle in an *infinitesimally small* section of the length  $dx$  at  $x_0$  (at time  $t = t_0$ ) is calculated. Fig. (b) shows how to calculate the probability of finding the particle at  $t = t_0$  in a *section*  $(a, b)$ .

<sup>26</sup>M. Born, *Zeitschrift für Physik* 37 (1926) 863.



All this may be generalized for more complex situations. For example, in three-dimensional space, the wave function of a single particle depends on position  $\mathbf{r} = (x, y, z)$  and time:  $\Psi(\mathbf{r}, t)$ , and the *normalization condition* takes the form

$$\begin{aligned} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \Psi^*(x, y, z, t) \Psi(x, y, z, t) &\equiv \int \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) dV \\ &\equiv \int \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d^3\mathbf{r} = 1. \end{aligned} \quad (1.3)$$

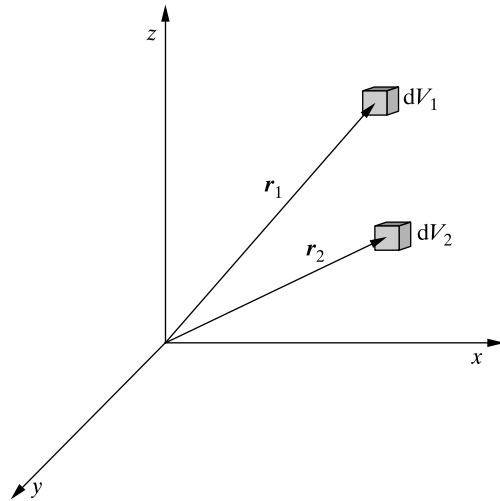
When integrating over whole space, for simplicity, the last two integrals are given without the integration limits, but they are there *implicitly*, and this convention will be used by us throughout the book unless stated otherwise.

For  $n$  particles (Fig. 1.4), shown by vectors  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$  in three-dimensional space, the interpretation of the wave function is as follows. The probability  $P$ , that at a given time  $t = t_0$ , particle 1 is in the domain  $V_1$ , particle 2 is in the domain  $V_2$  etc., is calculated as

$$\begin{aligned} P &= \int_{V_1} dV_1 \int_{V_2} dV_2 \dots \int_{V_n} dV_n \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t_0) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t_0) \\ &\equiv \int_{V_1} d^3\mathbf{r}_1 \int_{V_2} d^3\mathbf{r}_2 \dots \int_{V_n} d^3\mathbf{r}_n \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t_0) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t_0). \end{aligned}$$

Often in this book we will perform what is called the normalization of a function, which is required if a probability is to be calculated. Suppose we have a unnormal-

normalization



**Fig. 1.4.** Interpretation of a many-particle wave function, an example for two particles. The number  $|\psi(\mathbf{r}_1, \mathbf{r}_2, t_0)|^2 dV_1 dV_2$  represents the probability that at  $t = t_0$  particle 1 is in its box of volume  $dV_1$  shown by vector  $\mathbf{r}_1$  and particle 2 in its box of volume  $dV_2$  indicated by vector  $\mathbf{r}_2$ .

ized function<sup>27</sup>  $\psi$ , that is

$$\int_{-\infty}^{\infty} \psi(x, t)^* \psi(x, t) dx = A, \quad (1.4)$$

with  $0 < A \neq 1$ . To compute the probability  $\psi$  must be normalized, i.e. multiplied by a *normalization constant*  $N$ , such that the new function  $\Psi = N\psi$  satisfies the normalization condition:

$$1 = \int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = N^* N \int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx = A|N|^2.$$

Hence,  $|N| = \frac{1}{\sqrt{A}}$ . How is  $N$  calculated? One person may choose it as equal to  $N = \frac{1}{\sqrt{A}}$ , another:  $N = -\frac{1}{\sqrt{A}}$ , a third:  $N = e^{1989i} \frac{1}{\sqrt{A}}$ , and so on. There are, therefore, an infinite number of legitimate choices of the *phase*  $\phi$  of the wave function  $\Psi(x, t) = e^{i\phi} \frac{1}{\sqrt{A}} \psi$ . Yet, when  $\Psi^*(x, t) \Psi(x, t)$ , is calculated, everyone will obtain *the same* result,  $\frac{1}{A} \psi^* \psi$ , because the phase disappears. In most applications, this is what will happen and therefore the computed physical properties will not depend on the choice of phase. There are cases, however, where the phase will be of importance.

## Postulate II (on operator representation of mechanical quantities)

The mechanical quantities that describe the particle (energy, the components of vectors of position, momentum, angular momentum, etc.) are represented by linear operators acting in Hilbert space (see Appendix B). There are two important examples of the operators: the operator of the particle's position  $\hat{x} = x$  (i.e. multiplication by  $x$ , or  $\hat{x} = x \cdot$ , Fig. 1.5), as well as the operator of the ( $x$ -component) momentum  $\hat{p}_x = -i\hbar \frac{d}{dx}$ , where  $i$  stands for the imaginary unit.

Note that the mathematical form of the operators is always defined with respect to a *Cartesian* coordinate system.<sup>28</sup> From the given operators (Fig. 1.5) the operators of some other quantities may be constructed. The potential energy operator  $\hat{V} = V(x)$ , where  $V(x)$  [the multiplication operator by the function  $\hat{V}f = V(x)f$ ] represents a function of  $x$  called a potential. The kinetic energy operator of a single particle (in one dimension)  $\hat{T} = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ , and in three dimensions:

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} = -\frac{\hbar^2}{2m} \Delta, \quad (1.5)$$

<sup>27</sup>Eq. (1.2) not satisfied.

<sup>28</sup>Although they may then be transformed to other coordinates systems.

Mechanical quantity	Classical formula	Operator acting on $f$
coordinate	$x$	$\hat{x}f \stackrel{\text{def}}{=} xf$
momentum component	$p_x$	$\hat{p}_x f \stackrel{\text{def}}{=} -i\hbar \frac{\partial f}{\partial x}$
kinetic energy	$T = \frac{mv^2}{2} = \frac{p^2}{2m}$	$\hat{T}f = -\frac{\hbar^2}{2m}\Delta f$

Fig. 1.5. Mechanical quantities and the corresponding operators.

where the Laplacian  $\Delta$  is

$$\Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (1.6)$$

and  $m$  denotes the particle's mass. The total energy operator, or *Hamiltonian* is the most frequently used:

Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}. \quad (1.7)$$

An important feature of operators is that they may not *commute*,<sup>29</sup> i.e. for two particular operators  $\hat{A}$  and  $\hat{B}$  one *may* have  $\hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$ . This property has important physical consequences (see below, postulate IV and the Heisenberg uncertainty principle). Because of the possible non-commutation of the operators, transformation of the classical formula (in which the commutation or non-commutation did not matter) may be non-unique. In such a case, from all the possibilities one has to choose an operator which is Hermitian. The operator  $\hat{A}$  is Hermitian if, for any functions  $\psi$  and  $\phi$  from its domain, one has

commutation

$$\int_{-\infty}^{\infty} \psi^*(x) \hat{A} \phi(x) dx = \int_{-\infty}^{\infty} [\hat{A} \psi(x)]^* \phi(x) dx. \quad (1.8)$$

Using what is known as *Dirac notation*, Fig. 1.6, the above equality may be written in a concise form:

$$\langle \psi | \hat{A} \phi \rangle = \langle \hat{A} \psi | \phi \rangle. \quad (1.9)$$

In Dirac notation<sup>30</sup> (Fig. 1.6) the key role is played by vectors *bra*:  $\langle |$  and *ket*:  $| \rangle$  denoting respectively  $\psi^* \equiv \langle \psi |$  and  $\phi \equiv | \phi \rangle$ . Writing the bra and ket as  $\langle \psi | | \phi \rangle$

bra and ket

<sup>29</sup>Commutation means  $\hat{A}\hat{B} = \hat{B}\hat{A}$ .  
<sup>30</sup>Its deeper meaning is discussed in many textbooks of quantum mechanics, e.g., A. Messiah, “*Quantum Mechanics*”, vol. I, Amsterdam (1961), p. 245. Here we treat it as a convenient tool.

$\int \psi^* \phi \, d\tau \equiv \langle \psi   \phi \rangle$	Scalar product of two functions
$\int \psi^* \hat{A} \phi \, d\tau \equiv \langle \psi   \hat{A} \phi \rangle$ or $\langle \psi   \hat{A}   \phi \rangle$	Scalar product of $\psi$ and $\hat{A} \phi$ or a matrix element of the operator $\hat{A}$
$\hat{Q} =  \psi\rangle \langle \psi $	Projection operator on the direction of the vector $\psi$
$1 = \sum_k  \psi_k\rangle \langle \psi_k $	Spectral resolution of identity. Its sense is best seen when acting on $\chi$ : $\chi = \sum_k  \psi_k\rangle \langle \psi_k   \chi \rangle = \sum_k  \psi_k\rangle c_k.$

Fig. 1.6. Dirac notation.

denotes  $\langle \psi | \phi \rangle$ , or the scalar product of  $\psi$  and  $\phi$  in a unitary space (Appendix B), while writing it as  $|\psi\rangle \langle \phi|$  means the operator  $\hat{Q} = |\psi\rangle \langle \phi|$ , because of its action on function  $\xi = |\xi\rangle$  shown as:  $\hat{Q}\xi = |\psi\rangle \langle \phi | \xi \rangle = |\psi\rangle \langle \phi | \xi \rangle = c\psi$ , where  $c = \langle \phi | \xi \rangle$ .

The last formula in Fig. 1.6 (with  $\{\psi_k\}$  standing for the complete set of functions) represents what is known as “spectral resolution of identity”, best demonstrated when acting on an arbitrary function  $\chi$ :

$$\chi = \sum_k |\psi_k\rangle \langle \psi_k | \chi \rangle = \sum_k |\psi_k\rangle c_k.$$

spectral  
resolution of  
identity

We have obtained the decomposition of the function (i.e. a vector of the Hilbert space)  $\chi$  on its components  $|\psi_k\rangle c_k$  along the basis vectors  $|\psi_k\rangle$  of the Hilbert space. The coefficient  $c_k = \langle \psi_k | \chi \rangle$  is the corresponding scalar product, the basis vectors  $\psi_k$  are normalized. This formula says something trivial: any vector can be retrieved when adding *all* its components together.

Postulate III (on time evolution of the state)

time evolution

TIME-DEPENDENT SCHRÖDINGER EQUATION  
The time-evolution of the wave function  $\Psi$  is given by the equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H} \Psi(x, t), \tag{1.10}$$

where  $\hat{H}$  is the system Hamiltonian, see eq. (1.7).

$\hat{H}$  may be time-dependent (energy changes in time, interacting system) or time-independent (energy conserved, isolated system). Eq. (1.10) is called the time-dependent Schrödinger equation (Fig. 1.7).

$$\begin{array}{c}
 \Psi(x, t_0) \\
 \downarrow \\
 \hat{H}\Psi(x, t_0) \\
 \downarrow \\
 i\hbar \left( \frac{\partial \Psi}{\partial t} \right)_{t=t_0} \\
 \downarrow \\
 \Psi(x, t_0 + dt) = \Psi(x, t_0) - \frac{i}{\hbar} \hat{H}\Psi dt
 \end{array}$$

**Fig. 1.7.** Time evolution of a wave function. Knowing  $\Psi(x, t)$  at a certain time  $t = t_0$  makes it possible to compute  $\hat{H}\Psi(x, t_0)$ , and from this (using eq. (1.10)) one can calculate the time derivative  $\frac{\partial \Psi(x, t_0)}{\partial t} = -\frac{i\hat{H}\Psi(x, t_0)}{\hbar}$ . Knowledge of the wave function at time  $t = t_0$ , and of its time derivative, is sufficient to calculate the function a little later ( $t = t_0 + dt$ ):  $\Psi(x, t_0 + dt) \cong \Psi(x, t_0) + \frac{\partial \Psi}{\partial t} dt$ .

When  $\hat{H}$  is *time-independent*, the general solution to (1.10) can be written as

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \Psi_n(x, t), \quad (1.11)$$

where  $\Psi_n(x, t)$  represent special solutions to (1.10), that have the form

$$\Psi_n(x, t) = \psi_n(x) e^{-i\frac{E_n}{\hbar}t}, \quad (1.12)$$

and  $c_n$  stand for some constants. Substituting the special solution into (1.10) leads to<sup>31</sup> what is known as the *time-independent Schrödinger equation*:

time-  
independent  
Schrödinger  
equation

### SCHRÖDINGER EQUATION FOR STATIONARY STATES

$$\hat{H}\psi_n = E_n\psi_n, \quad n = 1, 2, \dots, M. \quad (1.13)$$

The equation represents an example of an *eigenvalue equation of the operator*; the functions  $\psi_n$  are called the eigenfunctions, and  $E_n$  are the eigenvalues of the operator  $\hat{H}$  ( $M$  may be finite or infinite). It can be shown that  $E_n$  are real (see Appendix B, p. 895). The eigenvalues are the permitted energies of the system,

<sup>31</sup>  $i\hbar \frac{\partial \Psi_n(x, t)}{\partial t} = i\hbar \frac{\partial \psi_n(x) e^{-i\frac{E_n}{\hbar}t}}{\partial t} = i\hbar \psi_n(x) \frac{\partial e^{-i\frac{E_n}{\hbar}t}}{\partial t} = i\hbar \psi_n(x) (-i\frac{E_n}{\hbar}) e^{-i\frac{E_n}{\hbar}t} = E_n \psi_n e^{-i\frac{E_n}{\hbar}t}$ . However,  $\hat{H}\Psi_n(x, t) = \hat{H}\psi_n(x) e^{-i\frac{E_n}{\hbar}t} = e^{-i\frac{E_n}{\hbar}t} \hat{H}\psi_n(x)$ , because the Hamiltonian does not depend on  $t$ . Hence, after dividing both sides of the equation by  $e^{-i\frac{E_n}{\hbar}t}$  one obtains the time independent Schrödinger equation.

and the corresponding eigenfunctions  $\Psi_n$  are defined in eqs. (1.12) and (1.13). These states have a special character, because the probability given by (1.1) does not change in time (Fig. 1.8):

$$p_n(x, t) = \Psi_n^*(x, t)\Psi_n(x, t) dx = \psi_n^*(x)\psi_n(x) dx = p_n(x). \quad (1.14)$$

stationary states

Therefore, in determining these states, known as *stationary states*, one can apply the time-independent formalism based on the Schrödinger equation (1.13).

### Postulate IV (on interpretation of experimental measurements)

This postulate pertains to ideal measurements, i.e. such that no error is introduced through imperfections in the measurement apparatus. We assume the measurement of the physical quantity  $A$ , represented by its time-independent operator  $\hat{A}$  and, for the sake of simplicity, that the system is composed of a single particle (with one variable only).

- The result of a single measurement of a mechanical quantity  $A$  can *only* be an eigenvalue  $a_k$  of the operator  $\hat{A}$ .

The eigenvalue equation for operator  $\hat{A}$  reads

$$\hat{A}\phi_k = a_k\phi_k, \quad k = 1, 2, \dots, M. \quad (1.15)$$

quantization

The eigenfunctions  $\phi_k$  are orthogonal<sup>32</sup> (cf. Appendix on p. 895). When the eigenvalues do not form a continuum, they are *quantized*, and then the corresponding eigenfunctions  $\phi_k$ ,  $k = 1, 2, \dots, M$ , satisfy the orthonormality relations:<sup>33</sup>

$$\int_{-\infty}^{\infty} \phi_k^*(x)\phi_l(x) dx \equiv \langle \phi_k | \phi_l \rangle \equiv \langle k | l \rangle = \delta_{kl} \equiv \begin{cases} 1, & \text{when } k = l, \\ 0, & \text{when } k \neq l, \end{cases} \quad (1.16)$$

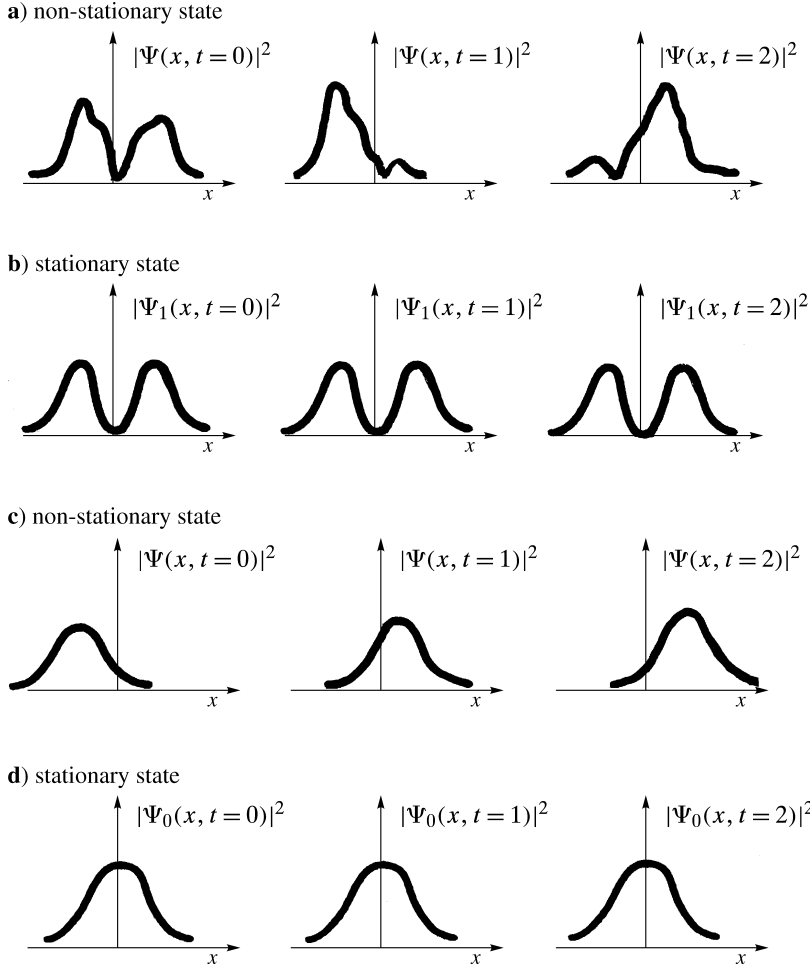
where we have given several equivalent notations of the scalar product, which will be used in the present book,  $\delta_{kl}$  means the Kronecker delta.

- Since eigenfunctions  $\{\phi_k\}$  form the complete set, then the wave function of the system may be expanded as ( $M$  is quite often equal to  $\infty$ )

$$\psi = \sum_{k=1}^M c_k \phi_k, \quad (1.17)$$

<sup>32</sup>If two eigenfunctions correspond to the same eigenvalue, they are not necessarily orthogonal, but they *can* still be orthogonalized (if they are linearly independent, see Appendix J, p. 977). Such orthogonal functions still remain the eigenfunctions of  $\hat{A}$ . Therefore, *one can always construct the orthonormal set of the eigenfunctions of a Hermitian operator.*

<sup>33</sup>If  $\phi_k$  belong to continuum they cannot be normalized, but still can be made mutually orthogonal.



**Fig. 1.8.** Evolution of a starting wave function  $\Psi$  for a system shown as three snapshots ( $t = 0, 1, 2$ ) of  $|\Psi(x, t)|^2$ . In cases (a) and (c) it is seen that  $|\Psi(x, t)|^2$  changes considerably when the time goes on: in (a) the function changes its overall shape, in (c) the function preserves its shape but travels along  $x$  axis. Both cases are therefore *non-stationary*. Cases (b) and (d) have a remarkable property that  $|\Psi(x, t)|^2$  does not change at all in time. Hence, they represent examples of the *stationary* states. The reason why  $|\Psi(x, t)|^2$  changes in cases (a) and (c) is that  $\Psi(x, t)$  does not represent a pure stationary state [as in (b) and (d)], but instead is a linear combination of some stationary states.

where the  $c_k$  are in general, complex coefficients. From the normalization condition for  $\psi$  we have<sup>34</sup>

$$\sum_{k=1}^M c_k^* c_k = 1. \quad (1.18)$$

<sup>34</sup>  $\langle \psi | \psi \rangle = 1 = \sum_{k=1}^M \sum_{l=1}^M c_k^* c_l \langle \phi_k | \phi_l \rangle = \sum_{k,l=1}^M c_k^* c_l \delta_{kl} = \sum_{k=1}^M c_k^* c_k$ .

According to the axiom, the probability that the result of the measurement is  $a_k$ , is equal to  $c_k^* c_k$ .

collapse

If the wave function that describes the state of the system has the form given by (1.17) and does not reduce to a single term  $\psi = \phi_k$ , then the result of the measurement of the quantity  $A$  *cannot* be foreseen. We will measure *some* eigenvalue of the operator  $\hat{A}$ , but cannot predict which one. After the measurement is completed the wave function of the system represents the eigenstate that corresponds to the measured eigenvalue (known as the *collapse of the wave function*). According to the axiom, the only thing one may say about the measurements is that the *mean value*  $\bar{a}$  of the quantity  $A$  (from many measurements) is to be compared with the following theoretical result<sup>35</sup> (Fig. 1.9)

$$\bar{a} = \sum_{k=1}^M c_k^* c_k a_k = \langle \psi | \hat{A} \psi \rangle, \quad (1.19)$$

where the normalization of  $\psi$  has been assumed.

If we have a special case,  $\psi = \phi_k$  (all coefficients  $c_l = 0$ , except  $c_k = 1$ ), the measured quantity is exactly equal  $a_k$ . From this it follows that if the wave function is an eigenfunction of operators of several quantities (this happens when the operators commute, Appendix B), then all these quantities when measured, produce with certainty, the eigenvalues corresponding to the eigenfunction.

mean value

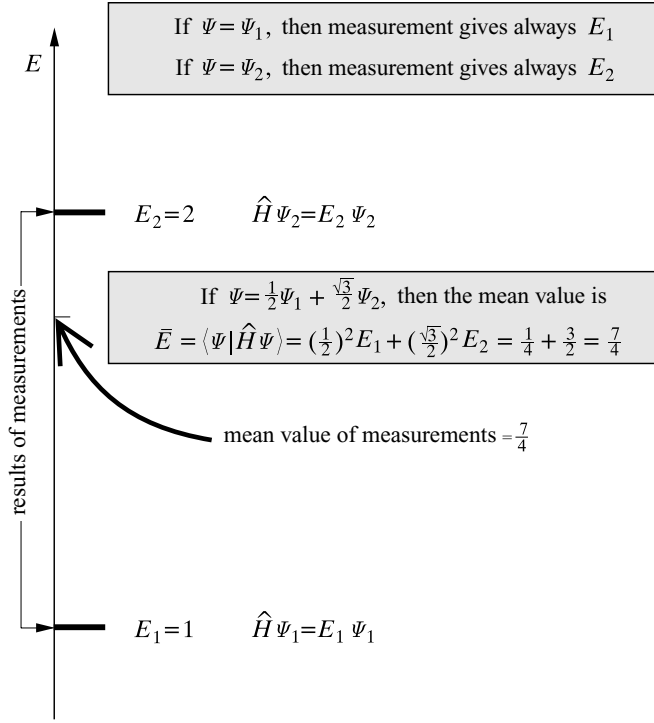
The coefficients  $c$  can be calculated from (1.17). After multiplying by  $\phi_l^*$  and integration, one has  $c_l = \langle \phi_l | \psi \rangle$ , i.e.  $c_l$  is identical to the overlap integral of the function  $\psi$  describing the state of the system and the function  $\phi_l$  that corresponds to the eigenvalue  $a_l$  of the operator  $\hat{A}$ . *In other words, the more the eigenfunction corresponding to  $a_l$  resembles the wave function  $\psi$ , the more frequently  $a_l$  will be measured.*

<sup>35</sup>

$$\begin{aligned} \langle \psi | \hat{A} \psi \rangle &= \left\langle \sum_{l=1}^M c_l \phi_l \left| \hat{A} \sum_{k=1}^M c_k \phi_k \right. \right\rangle = \sum_{k=1}^M \sum_{l=1}^M c_k^* c_l \langle \phi_l | \hat{A} \phi_k \rangle \\ &= \sum_{k=1}^M \sum_{l=1}^M c_k^* c_l a_k \langle \phi_l | \phi_k \rangle = \sum_{k=1}^M \sum_{l=1}^M c_k^* c_l a_k \delta_{kl} = \sum_{k=1}^M c_k^* c_k a_k. \end{aligned}$$

In case of degeneracy ( $a_k = a_l = \dots$ ) the probability is  $c_k^* c_k + c_l^* c_l + \dots$ . This is how one computes the mean value of anything. Just take all possible distinct results of measurements, multiply each by its probability and sum up all resulting numbers.





**Fig. 1.9.** The results of measurements of a quantity  $A$  are the eigenvalues of the operator  $\hat{A}$ :  $E_1$  and  $E_2$ .

## Postulate V (spin angular momentum)

spin

**Spin of elementary particles.** As will be shown in Chapter 3 (about relativistic effects) spin angular momentum will appear in a natural way. However, in nonrelativistic theory the existence of spin is *postulated*.<sup>36</sup>

An elementary particle has, besides its orbital angular momentum  $\mathbf{r} \times \mathbf{p}$ , an internal angular momentum (analogous to that associated with the rotation of a body about its own axis) called spin  $\mathbf{S} = (S_x, S_y, S_z)$ . Two quantities are measurable: the square of the spin length:  $|\mathbf{S}|^2 = S_x^2 + S_y^2 + S_z^2$  and one of its components, by convention,  $S_z$ . These quantities only take some particular values:  $|\mathbf{S}|^2 = s(s+1)\hbar^2$ ,  $S_z = m_s\hbar$ , where the spin magnetic quantum number  $m_s = -s, -s+1, \dots, s$ .

<sup>36</sup>This has been forced by experimental facts, e.g., energy level splitting in a magnetic field suggested two possible electron states connected to internal angular momentum.

Enrico Fermi (1901–1954), Italian physicist, professor at universities in Florence, Rome, New York, and in 1941–1946 at the University of Chicago. Fermi introduced the notion of statistics for the particles with a half-integer spin number (called fermions) during the Florence period. Dirac made the same discovery independently, hence this property is called the Fermi–Dirac statistics. Young Fermi was notorious for being able to derive a formula from any domain of physics faster than someone sent to find it in textbooks. His main topic was nuclear physics. He played an important role in the A bomb construction in Los Alamos, and in 1942 he built the world’s first nuclear reactor on a tennis court at the University of Chicago.



Fermi was awarded the Nobel Prize in 1938 “for his demonstration of the existence of new radioactive elements and for results obtained with them, especially with regard to artificial radioactive elements”.

The spin quantum number  $s$ , characteristic of the type of particle<sup>37</sup> (often called simply its spin), can be written as:  $s = \frac{n}{2}$ , where  $n$  may be zero or a natural number (“an integer or half-integer” number). The particles with a half-integer  $s$  (e.g.,  $s = \frac{1}{2}$  for electron, proton, neutron, neutrino) are called fermions, the particles with an integer  $s$  (e.g.,  $s = 1$  for deuteron, photon;<sup>38</sup>  $s = 0$  for meson  $\pi$  and meson K) are called bosons.

fermions

bosons

The magnetic<sup>39</sup> spin quantum number  $m_s$  quantizes the  $z$  component of the spin angular momentum.

Satyendra Nath Bose (1894–1974), Indian physicist, professor at Dakka and Calcutta, first recognized that particles with integer spin number have different statistical properties. Einstein contributed to a more detailed description of this statistics.



Thus, a particle with spin quantum number  $s$  has an additional (spin) degree of freedom, or an additional coordinate – *spin coordinate*  $\sigma$ . The spin coordinate differs widely from a spatial coordinate, because it takes only  $2s + 1$  discrete values (Fig. 1.10) associated to  $-s, -s + 1, \dots, 0, \dots, +s$ .

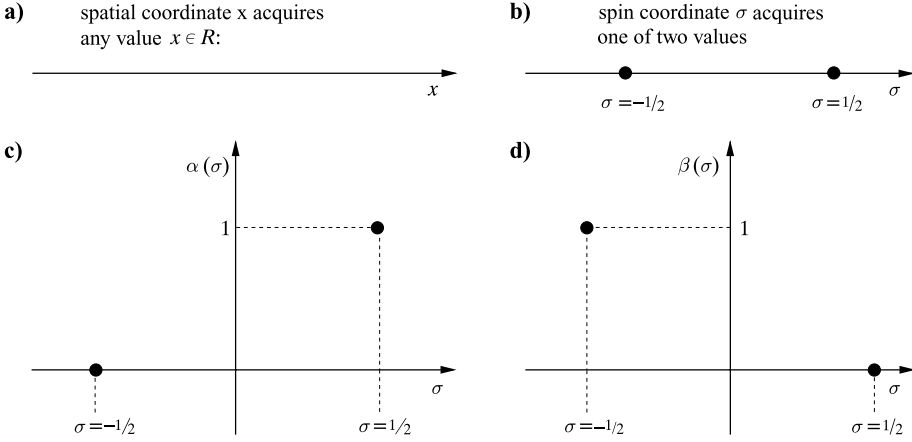
Most often one will have to deal with electrons. For electrons, the spin coordinate  $\sigma$  takes two values, often called

“up” and “down”. We will (arbitrarily) choose  $\sigma = -\frac{1}{2}$  and  $\sigma = +\frac{1}{2}$ , Fig. 1.11.a,b.

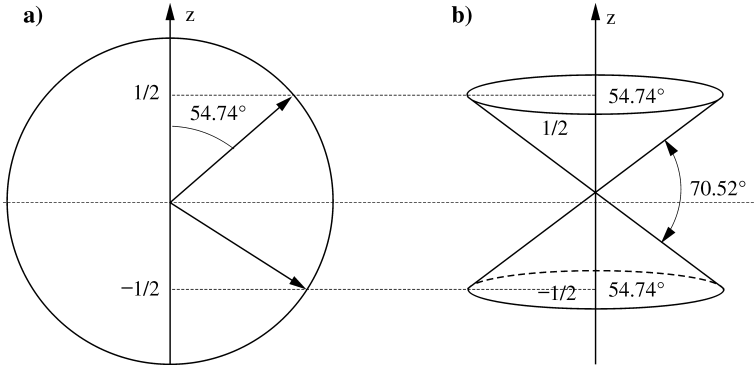
<sup>37</sup>Note, the length of the spin vector for an elementary particle is given by Nature once and for all. Thus, if there is any relation between the spin and the rotation of the particle about its own axis, it has to be a special relation. One cannot change the angular momentum of such a rotation.

<sup>38</sup>The photon represents a particle of zero mass. One can show that, instead of three possible  $m_s$  one has only two:  $m_s = 1, -1$ . We call these two possibilities “polarizations” (“parallel” and “perpendicular”).

<sup>39</sup>The name is related to energy level splitting in a magnetic field, from which the number is deduced. A non-zero  $s$  value is associated to the magnetic dipole, which in magnetic field acquires  $2s + 1$  energetically non-equivalent positions.



**Fig. 1.10.** Main differences between the spatial coordinate ( $x$ ) and spin coordinate ( $\sigma$ ) of an electron. (a) the spatial coordinate is *continuous*: it may take any value being a real number (b) the spin coordinate  $\sigma$  has a granular character (*discrete* values): for  $s = \frac{1}{2}$  it can take only one of two values. One of the values is represented by  $\sigma = -\frac{1}{2}$ , the other to  $\sigma = \frac{1}{2}$ . Figs. (c,d) show, respectively, two widely used basis functions in the spin space:  $\alpha(\sigma)$  and  $\beta(\sigma)$ .



**Fig. 1.11.** Diagram of the spin angular momentum vector for a particle with spin quantum number  $s = \frac{1}{2}$ . The only measurable quantities are the spin length  $\sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$  and the projection of the spin on the quantization axis (chosen as coincident with the vertical axis  $z$ ), which takes only the values  $-s, -s+1, \dots, +s$  in units  $\hbar$ , i.e.  $S_z = -\frac{1}{2}\hbar, \frac{1}{2}\hbar$  (a). Possible positions of the spin angular momentum with respect to the quantization axis  $z$  (b) since the  $x$  and  $y$  components of the spin remain indefinite, one may visualize the same by locating the spin vector (of constant length  $\sqrt{s(s+1)}\hbar$ ) *anywhere* on a cone surface that assures a given  $z$  component. Thus, one has  $2s+1=2$  such cones.

According to the postulate (p. 25), the square of the spin length is always the same and equal to  $s(s+1)\hbar^2 = \frac{3}{4}\hbar^2$ . The maximum projection of a vector on a chosen axis is equal to  $\frac{1}{2}\hbar$ , while the length of the vector is larger, equal to  $\sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$ . We conclude that the vector of the spin angular momentum

makes an angle  $\theta$  with the axis, with  $\cos \theta = \frac{1}{2} / \frac{\sqrt{3}}{2} = \frac{1}{\sqrt{3}}$ . From this one obtains<sup>40</sup>  $\theta = \arccos \frac{1}{\sqrt{3}} \approx 54.74^\circ$ . Fig. 1.11.b shows that the spin angular momentum has indefinite  $x$  and  $y$  components, while always preserving its length and projection on the  $z$  axis.

**Spin basis functions for  $s = \frac{1}{2}$ .** One may define (see Fig. 1.10.c,d) the complete set of orthonormal basis functions of the spin space of an electron:

$$\alpha(\sigma) = \begin{cases} 1 & \text{for } \sigma = \frac{1}{2} \\ 0 & \text{for } \sigma = -\frac{1}{2} \end{cases} \quad \text{and} \quad \beta(\sigma) = \begin{cases} 0 & \text{for } \sigma = \frac{1}{2} \\ 1 & \text{for } \sigma = -\frac{1}{2} \end{cases}$$

or, in a slightly different notation, as orthogonal unit vectors:<sup>41</sup>

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

$\alpha$  and  $\beta$  spin  
functions

Orthogonality follows from

$$\langle \alpha | \beta \rangle \equiv \sum_{\sigma} \alpha(\sigma)^* \beta(\sigma) = 0 \cdot 1 + 1 \cdot 0 = 0.$$

Similarly, normalization means that

$$\langle \alpha | \alpha \rangle \equiv \sum_{\sigma} \alpha(\sigma)^* \alpha(\sigma) = \alpha\left(-\frac{1}{2}\right)^* \alpha\left(-\frac{1}{2}\right) + \alpha\left(\frac{1}{2}\right)^* \alpha\left(\frac{1}{2}\right) = 0 \cdot 0 + 1 \cdot 1 = 1$$

etc.

Pauli matrices

We shall now construct operators of the spin angular momentum.

The following definition of spin operators is consistent with the postulate about spin.

$$\hat{S}_x = \frac{1}{2} \hbar \sigma_x$$

$$\hat{S}_y = \frac{1}{2} \hbar \sigma_y$$

$$\hat{S}_z = \frac{1}{2} \hbar \sigma_z,$$

where the Pauli matrices of rank 2 are defined as:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

<sup>40</sup>In the general case, the spin of a particle may take the following angles with the quantization axis:  $\arccos \frac{m_s}{\sqrt{s(s+1)}}$  for  $m_s = -s, -s+1, \dots, +s$ .

<sup>41</sup>In the same spirit as wave functions represent vectors: vector components are values of the function for various values of the variable.

Indeed, after applying  $\hat{S}_z$  to the spin basis functions one obtains:

$$\begin{aligned}\hat{S}_z|\alpha\rangle &\equiv \hat{S}_z \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\hbar|\alpha\rangle, \\ \hat{S}_z|\beta\rangle &\equiv \hat{S}_z \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2}\hbar \begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\frac{1}{2}\hbar|\alpha\rangle.\end{aligned}$$

Therefore, functions  $\alpha$  and  $\beta$  represent the eigenfunctions of the  $\hat{S}_z$  operator with corresponding eigenvalues  $\frac{1}{2}\hbar$  and  $-\frac{1}{2}\hbar$ . How to construct the operator  $\hat{S}^2$ ? From Pythagoras' theorem, after applying Pauli matrices one obtains:

$$\begin{aligned}\hat{S}^2|\alpha\rangle &= \hat{S}^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} = (\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \frac{1}{4}\hbar^2 \left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \frac{1}{4}\hbar^2 \begin{pmatrix} 1+1+1 & 0+0+0 \\ 0+0+0 & 1+1+1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \left[ \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \right] |\alpha\rangle.\end{aligned}$$

The function  $|\beta\rangle$  gives an identical eigenvalue.

Therefore, both basis functions  $\alpha$  and  $\beta$  represent the eigenfunctions of  $\hat{S}^2$  and correspond to the same eigenvalue. Thus, the definition of spin operators through Pauli matrices gives results identical to those postulated for  $S^2$  and  $S_z$ , and the two formulations are equivalent. From Pauli matrices, it follows that the functions  $\alpha$  and  $\beta$  are not eigenfunctions of  $\hat{S}_x$  and  $\hat{S}_y$  and that the following relations are satisfied<sup>42</sup>

$$\begin{aligned}[\hat{S}^2, \hat{S}_z] &= 0, \quad [\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \\ [\hat{S}_y, \hat{S}_z] &= i\hbar\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y,\end{aligned}$$

Wolfgang Pauli (1900–1958), German physicist, professor in Hamburg, at Technical University of Zurich, Institute for Advanced Studies in Princeton (USA), son of a physical chemistry professor in Vienna and a classmate of Werner Heisenberg. At the age of 20 he wrote a famous 200-page article on relativity theory for *Mathematical Encyclopedia*, afterwards edited as a book. A year later Pauli defended his doctoral dissertation under the supervision of Sommerfeld in Munich.



The renowned Pauli exclusion principle was proposed in 1924. Wolfgang Pauli received the Nobel Prize in 1945 “for the discovery of the Exclusion Principle, also called the Pauli Principle”.

<sup>42</sup>These formulae are easy to memorize, since the sequence of the indices is always “rotational”, i.e.  $x, y, z, x, y, z, \dots$

which is in agreement with the general properties of angular momenta<sup>43</sup> (Appendix on p. 955).

**Spin of non-elementary particles.** The postulate on spin pertains to an elementary particle. What about a system composed of such particles? Do they have spin? Spin represents angular momentum (a vector) and therefore the angular momentum vectors of elementary particles have to be added. A system composed of a number of elementary particles (each with its spin  $s_i$ ) has as a measurable quantity (an observable quantity), the square

$$|\mathbf{S}|^2 = S(S+1)\hbar^2$$

of the total spin vector,

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \cdots + \mathbf{s}_N,$$

and one of the components of  $\mathbf{S}$  (denoted by  $S_z = \sum_{i=1}^N s_{iz} = \hbar \sum_{i=1}^N m_{si}$ ):

$$S_z = M_S \hbar, \quad \text{for } M_S = -S, -S+1, \dots, S,$$

where the number  $S$  stands (as in the case of a single particle) for an integer or half-integer non-negative number. Particular values of  $S$  (often called simply the spin) and of the spin magnetic number  $M_S$  depend on the directions of vectors  $s_i$ . It follows that no excitation of a non-elementary boson (that causes another summing of the individual spin vectors) can change the particle to a fermion and *vice versa*. Systems with an even number of fermions are always bosons, while these with an odd number of fermions are always fermions.

**Nuclei.** The ground states of the important *nuclei*  $^{12}\text{C}$  and  $^{16}\text{O}$  correspond to  $S=0$ , while those of  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$  have  $S = \frac{1}{2}$ .

**Atoms and molecules.** Does an atom as a whole represent a fermion or a boson? This depends on which atom and which molecule. Consider the hydrogen atom, composed of two fermions (proton and electron, both with spin number  $\frac{1}{2}$ ). This is sufficient to deduce that here we are dealing with a boson. For similar reasons,

<sup>43</sup>Also, note that the mean values of  $S_x$  and  $S_y$  are both equal to zero in the  $\alpha$  and  $\beta$  state, e.g., for the  $\alpha$  state one has

$$\langle \alpha | \hat{S}_x | \alpha \rangle = \left\langle \alpha \left| \frac{1}{2} \hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right| \right\rangle = \frac{1}{2} \hbar \langle \alpha | \beta \rangle = 0.$$

This means that in an external vector field (of direction  $z$ ), when the space is no longer isotropic, only the projection of the total angular momentum on the field direction is conserved. A way to satisfy this is to recall the behaviour of a top in a vector field. The top rotates about its own axis, but the axis precesses about the field axis. This means that the total electron spin momentum moves on the cone surface making an angle of  $54.74^\circ$  with the external field axis in  $\alpha$  state and an angle  $180^\circ - 54.74^\circ$  in the  $\beta$  state. Whatever the motion, it must satisfy  $\langle \alpha | \hat{S}_x | \alpha \rangle = \langle \alpha | \hat{S}_y | \alpha \rangle = 0$  and  $\langle \beta | \hat{S}_x | \beta \rangle = \langle \beta | \hat{S}_y | \beta \rangle = 0$ . No more information is available, but one may imagine the motion as a precession just like that of the top.

the sodium atom with 23 nucleons (each of spin  $\frac{1}{2}$ ) in the nucleus and 11 electrons moving around it, also represents a boson.

When one adds together two electron spin vectors  $s_1 + s_2$ , then the maximum  $z$  component of the spin angular momentum will be (in  $\hbar$  units):  $|M_S| = |m_{s1} + m_{s2}| = \frac{1}{2} + \frac{1}{2} = 1$ . This corresponds to the vectors  $s_1, s_2$ , called “parallel” to each other, while the minimum  $|M_S| = |m_{s1} + m_{s2}| = \frac{1}{2} - \frac{1}{2} = 0$  means an “antiparallel” configuration of  $s_1$  and  $s_2$  (Fig. 1.12).

The first situation indicates that for the state with parallel spins  $S = 1$ , for this  $S$  the possible  $M_S = 1, 0, -1$ . This means there are three states:  $(S, M_S) = (1, 1), (1, 0), (1, -1)$ . If no direction in space is privileged, then all the three states correspond to the same energy (triple degeneracy). This is why such a set of three states is called a *triplet state*. The second situation witnesses the existence of a state with  $S = 0$ , which obviously corresponds to  $M_S = 0$ . This state is called a *singlet state*.

triplet

singlet

Let us calculate the angle  $\omega$  between the individual electronic spins:

$$\begin{aligned} |S|^2 &= (s_1 + s_2)^2 = s_1^2 + s_2^2 + 2s_1 \cdot s_2 \\ &= s_1^2 + s_2^2 + 2s_1 \cdot s_2 \cos \omega \\ &= \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \cdot 2 + 2 \sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)} \sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)} \hbar^2 \cos \omega \\ &= \left( \frac{3}{2} + \frac{3}{2} \cos \omega \right) \hbar^2 = \frac{3}{2} (1 + \cos \omega) \hbar^2. \end{aligned}$$

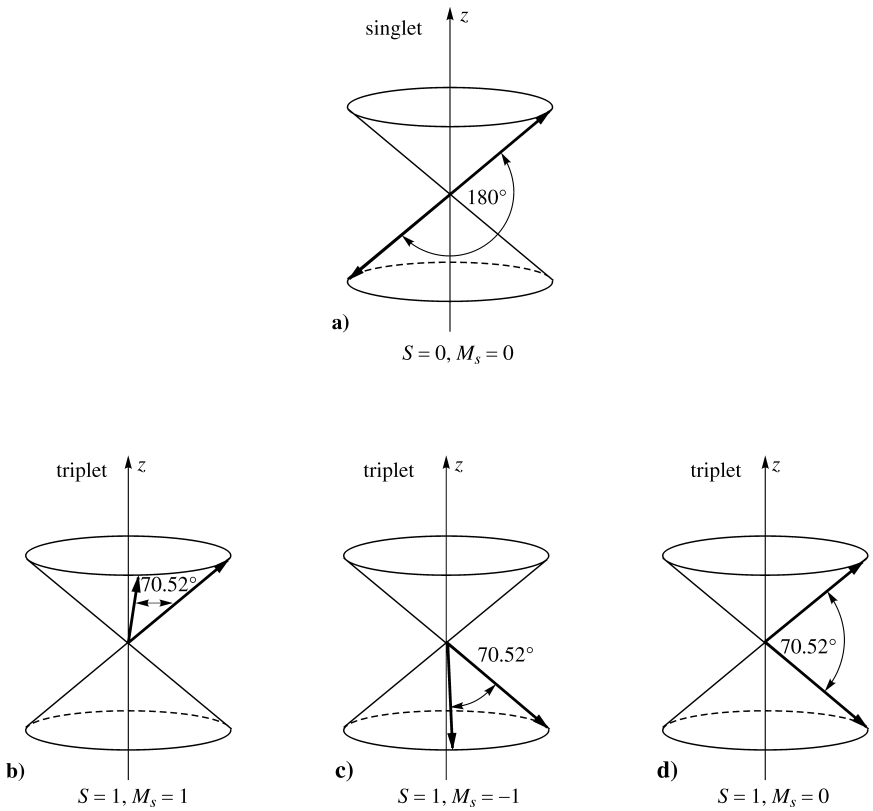
#### SINGLET AND TRIPLET STATES:

For the singlet state  $|S|^2 = S(S+1)\hbar^2 = 0$ , hence  $1 + \cos \omega = 0$  and  $\omega = 180^\circ$ . *This means the two electronic spins in the singlet state are antiparallel.* For the triplet state  $|S|^2 = S(S+1)\hbar^2 = 2\hbar^2$ , and hence  $\frac{3}{2}(1 + \cos \omega)\hbar^2 = 2\hbar^2$ , i.e.  $\cos \omega = \frac{1}{3}$ , or  $\omega = 70.52^\circ$ , see Fig. 1.12. *Despite forming the angle  $\omega = 70.52^\circ$  the two spins in the triplet state are said to be “parallel”.*

The two electrons which we have considered may, for example, be part of a hydrogen molecule. Therefore, when considering electronic states, we may have to deal with singlets or triplets. However, in the same hydrogen molecule we have two protons, whose spins may also be “parallel” (orthohydrogen) or antiparallel (parahydrogen). In parahydrogen the nuclear spin is  $S = 0$ , while in orthohydrogen  $S = 1$ . In consequence, there is only one state for parahydrogen ( $M_S = 0$ ), and three states for orthohydrogen ( $M_S = 1, 0, -1$ ).<sup>44</sup>

parahydrogen  
and  
orthohydrogen

<sup>44</sup>Since all the states have very similar energies (and therefore at high temperatures the Boltzmann factors are practically the same), there are three times as many molecules of orthohydrogen as of parahydrogen. Both states (ortho and para) differ slightly in their physicochemical characteristics.



**Fig. 1.12.** Spin angular momentum for a system with two electrons (in general, particles with  $s = \frac{1}{2}$ ). The quantization axis is arbitrarily chosen as the vertical axis  $z$ . Then, the spin vectors of individual electrons (see Fig. 1.11.b) may be thought to reside somewhere on the upper cone that corresponds to  $m_{s1} = \frac{1}{2}$ , or on the lower cone corresponding to  $m_{s1} = -\frac{1}{2}$ . For two electrons there are two spin eigenstates of  $\hat{S}^2$ . One has total spin quantum number  $S = 0$  (singlet state); the other is triply degenerate (triplet state), and the three components of the state have  $S = 1$  and  $S_z = 1, 0, -1$  in  $\hbar$  units. In the singlet state (a) the vectors  $s_1$  and  $s_2$  remain on the cones of different orientation, and have the opposite (“antiparallel”) orientations, so that  $s_1 + s_2 = \mathbf{0}$ . Although their exact positions on the cones are undetermined (and moreover the cones themselves follow from the arbitrary choice of the quantization axis in space), they are always pointing in opposite directions. The three triplet components (b,c,d) differ by the direction of the total spin angular momentum (of constant length  $\sqrt{S(S+1)}\hbar = \sqrt{2}\hbar$ ). The three directions correspond to three projections  $M_s\hbar$  of spin momentum:  $\hbar, -\hbar, 0$  for Figs. b, c, d, respectively. In each of the three cases the angle between the two spins equals  $\omega = 70.52^\circ$  (although in textbooks – including this one – they are said to be “parallel”. In fact they are not, see the text).

### Postulate VI (on the permutational symmetry)

Unlike classical mechanics, quantum mechanics is radical: it requires that two particles of the same kind (two electrons, two protons, etc.) should play the same role in the system, and therefore in its description enshrined in the wave



function.<sup>45</sup> Quantum mechanics *guarantees* that the roles played in the Hamiltonian by two identical particles are identical. Within this philosophy, exchange of the labels of two identical particles (i.e. the exchange of their coordinates  $x_1, y_1, z_1, \sigma_1 \leftrightarrow x_2, y_2, z_2, \sigma_2$ . In short,  $1 \leftrightarrow 2$ ) leads, at most, to a change of the phase  $\phi$  of the wave function:  $\psi(2, 1) \rightarrow e^{i\phi} \psi(1, 2)$ , because in such a case  $|\psi(2, 1)| = |\psi(1, 2)|$  (and this guarantees equal probabilities of both situations). However, when we exchange the two labels once more, we have to return to the initial situation:  $\psi(1, 2) = e^{i\phi} \psi(2, 1) = e^{i\phi} e^{i\phi} \psi(1, 2) = (e^{i\phi})^2 \psi(1, 2)$ . Hence,  $(e^{i\phi})^2 = 1$ , i.e.  $e^{i\phi} = \pm 1$ . *Postulate VI says that  $e^{i\phi} = +1$  refers to bosons, while  $e^{i\phi} = -1$  refers to fermions.*<sup>46</sup>

The wave function  $\psi$  which describes identical *bosons* (i.e. spin integer particles)  $1, 2, 3, \dots, N$  has to be *symmetric* with respect to the exchange of coordinates  $x_i, y_i, z_i, \sigma_i$  and  $x_j, y_j, z_j, \sigma_j$ , i.e. if  $x_i \leftrightarrow x_j, y_i \leftrightarrow y_j, z_i \leftrightarrow z_j, \sigma_i \leftrightarrow \sigma_j$ , then  $\psi(1, 2, \dots, i, \dots, j, \dots, N) = \psi(1, 2, \dots, j, \dots, i, \dots, N)$ . If particles  $i$  and  $j$  denote identical *fermions*, the wave function must be *antisymmetric*, i.e.  $\psi(1, 2, \dots, i, \dots, j, \dots, N) = -\psi(1, 2, \dots, j, \dots, i, \dots, N)$ .

bosons –  
symmetric  
function

fermions –  
antisymmetric  
function

Let us see the probability density that two identical fermions occupy the same position in space and, additionally, that they have the same spin coordinate ( $x_1, y_1, z_1, \sigma_1) = (x_2, y_2, z_2, \sigma_2)$ . We have:  $\psi(1, 1, 3, 4, \dots, N) = -\psi(1, 1, 3, 4, \dots, N)$ , hence  $\psi(1, 1, 3, 4, \dots, N) = 0$  and, of course,  $|\psi(1, 1, 3, 4, \dots, N)|^2 = 0$ . Conclusion: two electrons of the same spin coordinate (we will sometimes say: “of the same spin”) avoid each other. This is called the exchange or Fermi hole around each electron.<sup>47</sup> The reason for the hole is the antisymmetry of the electronic wave function, or in other words, the Pauli exclusion principle.<sup>48</sup>

Pauli exclusion  
principle

Thus, the probability density of finding two identical fermions *in the same position* and with *the same spin coordinate* is equal to zero. There is no such restriction for two identical bosons or two identical fermions with *different* spin coordinates. They can be at the same point in space.

<sup>45</sup>Everyday experience in classical world tells us the opposite, e.g., a car accident involving a Mercedes does not cause all copies of that particular model to have identical crash records.

<sup>46</sup>The postulate requires more than just making identical particles indistinguishable. It requires that *all* pairs of the identical particles follow the same rule.

<sup>47</sup>Besides that any two electrons avoid each other because of the same charge (Coulombic hole). Both holes (Fermi and Coulomb) have to be reflected in a good wave function. We will come back to this problem in Chapter 10.

<sup>48</sup>The Pauli exclusion principle is sometimes formulated in another way: two electrons cannot be in the same state (including spin). The connection of this strange phrasing (what does electron state mean?) with the above will become clear in Chapter 8.

Bose  
condensation

This is related to what is known as Bose condensation.<sup>49</sup>

\* \* \*

Among the above postulates, the strongest controversy has always been associated with Postulate IV, which says that, except of some special cases, one cannot predict the result of a particular single measurement, but only its probability. More advanced considerations devoted to Postulate IV lead to the conclusion that there is no way (neither experimental protocol nor theoretical reasoning), to predict when and in which direction an excited atom will emit a photon. This means that quantum mechanics is not a deterministic theory.

The indeterminism appears however only in the physical space, while in the space of all states (Hilbert space) everything is perfectly deterministic. The wave function evolves in a deterministic way according to the time-dependent Schrödinger equation (1.10).

The puzzling way in which indeterminism operates will be shown below.

### 1.3 THE HEISENBERG UNCERTAINTY PRINCIPLE

Consider two mechanical quantities  $A$  and  $B$ , for which the corresponding Hermitian operators (constructed according to Postulate II),  $\hat{A}$  and  $\hat{B}$ , give the commutator  $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = i\hat{C}$ , where  $\hat{C}$  is a Hermitian operator.<sup>50</sup> This is what happens for example for  $A = x$  and  $B = p_x$ . Indeed, for any differentiable function  $\phi$  one has:  $[\hat{x}, \hat{p}_x]\phi = -x\hbar\phi' + i\hbar(x\phi)' = i\hbar\phi$ , and therefore the operator  $\hat{C}$  in this case means simply multiplication by  $\hbar$ .

From axioms of quantum mechanics one can prove that a product of errors (in the sense of standard deviation) of measurements of two mechanical quantities is greater than or equal to  $\frac{1}{2}\langle[\hat{A}, \hat{B}]\rangle$ , where  $\langle[\hat{A}, \hat{B}]\rangle$  is the mean value of the commutator  $[\hat{A}, \hat{B}]$ .

This is known as the Heisenberg uncertainty principle.

<sup>49</sup>Carried out by Eric A. Cornell, Carl E. Wieman and Wolfgang Ketterle (Nobel Prize 2001 “for discovering a new state of matter”). In the Bose condensate the bosons (alkali metal atoms) are in the same place in a peculiar sense. The total wave function for the bosons was, to a first approximation, a product of *identical* nodeless wave functions for the particular bosons (this assures proper symmetry). Each of the wave functions extends considerably in space (the Bose condensate is as large as a fraction of a millimetre), but all have been centred *in the same point in space*.

<sup>50</sup>This is guaranteed. Indeed,  $\hat{C} = -i[\hat{A}, \hat{B}]$  and then the Hermitian character of  $\hat{C}$  is shown by the following chain of transformations  $\langle f|\hat{C}g\rangle = -i\langle f|[\hat{A}, \hat{B}]g\rangle = -i\langle f|(\hat{A}\hat{B} - \hat{B}\hat{A})g\rangle = -i\langle(\hat{B}\hat{A} - \hat{A}\hat{B})f|g\rangle = \langle -i(\hat{A}\hat{B} - \hat{B}\hat{A})f|g\rangle = \langle \hat{C}f|g\rangle$ .

Werner Karl Heisenberg (1901–1976) was born in Würzburg (Germany), attended high school in Munich, then (with his friend Wolfgang Pauli) studied physics at the Munich University under Sommerfeld's supervision. In 1923 he defended his doctoral thesis on turbulence in liquids. Reportedly, during the doctoral examination he had problems writing down the chemical reaction in lead batteries. He joined the laboratory of Max Born at Göttingen (following his friend Wolfgang) and in 1924 the Institute of Theoretical Physics in Copenhagen working under the supervision of Niels Bohr. A lecture delivered by Niels Bohr decided the future direction of his work. Heisenberg later wrote: *"I was taught optimism by Sommerfeld, mathematics in Göttingen, physics by Bohr"*. In 1925 (only a year after being convinced by Bohr) Heisenberg developed a formalism, which became the first successful quantum theory. Then, in 1926 Heisenberg, Born and Jordan elaborated the formalism, which resulted in a coherent theory ("matrix mechanics"). In 1927 Heisenberg obtained a chair at Leipzig University, which he held until 1941 (when he became director of the Kaiser Wilhelm Physics Institute in Berlin). Heisenberg received the Nobel Prize in 1932 *"for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen"*.

In 1937 Werner Heisenberg was at the height of his powers. He was nominated professor and got married. However, just after returning from his honeymoon, the rector of the university called him, saying that there was a problem. In the SS weekly an article by Prof. Johannes Stark (a Nobel Prize winner and faithful Nazi) was about to appear claiming that Professor Heisenberg is not such a good patriot as he pretends, because he socialized in the past with Jewish physicists. . .



Soon Professor Heisenberg was invited to SS headquarters at Prinz Albert Strasse in Berlin. The interrogation took place in the basement. On the raw concrete wall there was the interesting slogan *"Breathe deeply and quietly"*. One of the questioners was a Ph.D. student from Leipzig, who had once been examined by Heisenberg. The terrified Heisenberg told his mother about the problem. She recalled that in her youth she had made the acquaintance of Heinrich Himmler's mother. Frau Heisenberg paid a visit to Frau Himmler and asked her to pass a letter from her son to Himmler. At the beginning Himmler's mother tried to separate her maternal feelings for her beloved son from politics. She was finally convinced after Frau Heisenberg said *"we mothers should care about our boys"*. After a certain time, Heisenberg received a letter from Himmler saying that his letter "coming through unusual channels" has been examined especially carefully. He promised to stop the attack. In the *post scriptum* there was a precisely tailored phrase: *"I think it best for your future, if for the benefit of your students, you would carefully separate scientific achievements from the personal and political beliefs of those who carried them out. Yours faithfully, Heinrich Himmler"* (after D. Bodanis, *"E = mc<sup>2</sup>"*, Fakty, Warsaw, 2001, p. 130).

Werner Heisenberg did not carry out any formal proof, instead he analyzed a Gedankenexperiment (an imaginary ideal experiment) with an electron interacting with an electromagnetic wave ("Heisenberg's microscope").

The formal proof goes as follows.

Recall the definition of the variance, or the square of the standard deviation  $(\Delta A)^2$ , of measurements of the quantity  $A$ :

$$(\Delta A)^2 = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2, \quad (1.20)$$

where  $\langle X \rangle$  means the mean value of many measurements of the quantity  $X$ . The *standard deviation*  $\Delta A$  represents the width of the distribution of  $A$ , i.e. measures the error made. Eq. (1.20) is equivalent to

$$(\Delta A)^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle, \quad (1.21)$$

because  $\langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle = \langle \hat{A}^2 - 2\hat{A}\langle \hat{A} \rangle + \langle \hat{A} \rangle^2 \rangle = \langle \hat{A}^2 \rangle - 2\langle \hat{A} \rangle^2 + \langle \hat{A} \rangle^2 = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2$ . Consider the product of the standard deviations for the operators  $\hat{A}$  and  $\hat{B}$ , taking into account that  $\langle \hat{u} \rangle$  denotes (Postulate IV) the integral  $\langle \Psi | \hat{u} | \Psi \rangle$  according to (1.19). One obtains (denoting  $\hat{A} = \hat{A} - \langle \hat{A} \rangle$  and  $\hat{B} = \hat{B} - \langle \hat{B} \rangle$ ; of course,  $[\hat{A}, \hat{B}] = [\hat{A}, \hat{B}]$ ):

$$(\Delta A)^2 \cdot (\Delta B)^2 = \langle \Psi | \hat{A}^2 | \Psi \rangle \langle \Psi | \hat{B}^2 | \Psi \rangle = \langle \hat{A} \Psi | \hat{A} \Psi \rangle \langle \hat{B} \Psi | \hat{B} \Psi \rangle,$$

where the Hermitian character of the operators  $\hat{A}$  and  $\hat{B}$  is used. Now, let us use the Schwarz inequality (Appendix B)  $\langle f_1 | f_1 \rangle \langle f_2 | f_2 \rangle \geq |\langle f_1 | f_2 \rangle|^2$ :

$$(\Delta A)^2 \cdot (\Delta B)^2 = \langle \hat{A} \Psi | \hat{A} \Psi \rangle \langle \hat{B} \Psi | \hat{B} \Psi \rangle \geq |\langle \hat{A} \Psi | \hat{B} \Psi \rangle|^2.$$

Next,

$$\begin{aligned} \langle \hat{A} \Psi | \hat{B} \Psi \rangle &= \langle \Psi | \hat{A} \hat{B} | \Psi \rangle = \langle \Psi | [\hat{A}, \hat{B}] + \hat{B} \hat{A} | \Psi \rangle = i \langle \Psi | \hat{C} | \Psi \rangle + \langle \Psi | \hat{B} \hat{A} | \Psi \rangle \\ &= i \langle \Psi | \hat{C} | \Psi \rangle + \langle \hat{B} \Psi | \hat{A} \Psi \rangle = i \langle \Psi | \hat{C} | \Psi \rangle + \langle \hat{A} \Psi | \hat{B} \Psi \rangle^*. \end{aligned}$$

Hence,

$$i \langle \Psi | \hat{C} | \Psi \rangle = 2i \operatorname{Im} \{ \langle \hat{A} \Psi | \hat{B} \Psi \rangle \}$$

This means that  $\operatorname{Im} \{ \langle \hat{A} \Psi | \hat{B} \Psi \rangle \} = \frac{\langle \Psi | \hat{C} | \Psi \rangle}{2}$ , which gives  $|\langle \hat{A} \Psi | \hat{B} \Psi \rangle| \geq \frac{|\langle \Psi | \hat{C} | \Psi \rangle|}{2}$ . Hence,

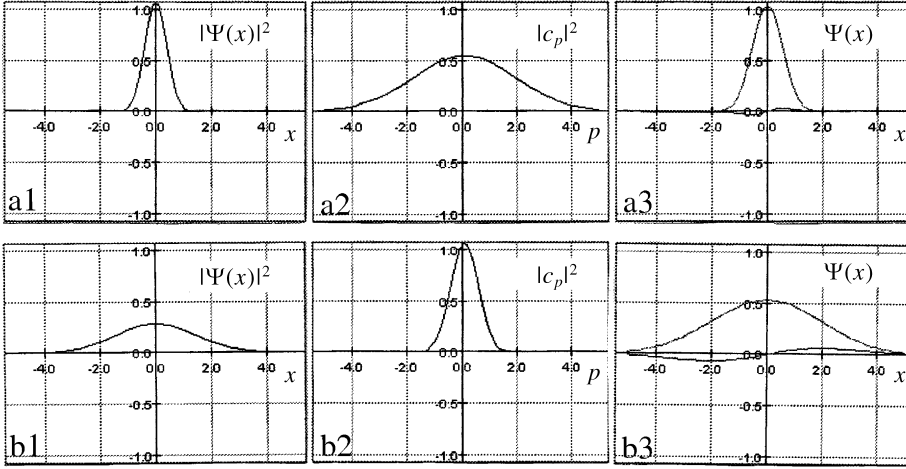
$$(\Delta A)^2 \cdot (\Delta B)^2 \geq |\langle \hat{A} \Psi | \hat{B} \Psi \rangle|^2 \geq \frac{|\langle \Psi | \hat{C} | \Psi \rangle|^2}{4} \quad (1.22)$$

or, taking into account that  $|\langle \Psi | \hat{C} | \Psi \rangle| = |\langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle|$  we have

$$\Delta A \cdot \Delta B \geq \frac{1}{2} |\langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle|. \quad (1.23)$$

There are two important special cases:

- (a)  $\hat{C} = 0$ , i.e. the operators  $\hat{A}$  and  $\hat{B}$  commute. We have  $\Delta A \cdot \Delta B \geq 0$ , i.e. *the errors can be arbitrarily small*. Both quantities therefore *can be* measured simultaneously without error.
- (b)  $\hat{C} = \hbar$ , as in the case of  $\hat{x}$  and  $\hat{p}_x$ . Then,  $(\Delta A) \cdot (\Delta B) \geq \frac{\hbar}{2}$ .



**Fig. 1.13.** Illustration of the Heisenberg uncertainty principle. (a1)  $|\Psi(x)|^2$  as function of coordinate  $x$ . Wave function  $\Psi(x)$  can be expanded in the infinite series  $\Psi(x) = \sum_p c_p \exp(ipx)$ , where  $p$  denotes the momentum. Note that each individual function  $\exp(ipx)$  is an eigenfunction of momentum, and therefore if  $\Psi(x) = \exp(ipx)$ , a measurement of momentum gives exactly  $p$ . If however  $\Psi(x) = \sum_p c_p \exp(ipx)$ , then such a measurement yields a given  $p$  with the probability  $|c_p|^2$ . Fig. (a2) shows  $|c_p|^2$  as function of  $p$ . As one can see a broad range of  $p$  (large uncertainty of momentum) assures a sharp  $|\Psi(x)|^2$  distribution (small uncertainty of position). Simply the waves  $\exp(ipx)$  to obtain a sharp peak of  $\Psi(x)$  should exhibit a perfect constructive interference in a small region and a destructive interference elsewhere. This requires a lot of different  $p$ 's, i.e. a broad momentum distribution. Fig. (a3) shows  $\Psi(x)$  itself, i.e. its real (large) and imaginary (small) part. The imaginary part is non-zero because of small deviation from symmetry. Figs. (b1–b3) show the same, but this time a narrow  $p$  distribution gives a broad  $x$  distribution.

In particular, for  $\hat{A} = \hat{x}$  and  $\hat{B} = \hat{p}_x$ , if quantum mechanics is valid, *one cannot measure the exact position and the exact momentum of a particle*. When the precision with which  $x$  is measured increases, the particle's momentum has so wide a distribution that the error in determining  $p_x$  is huge, Fig. 1.13.<sup>51</sup>

## 1.4 THE COPENHAGEN INTERPRETATION

In the 1920s and 1930s, Copenhagen for quantum mechanics was like Rome for catholics, and Bohr played the role of the president of the Quantum Faith Congregation.<sup>52</sup> The picture of the world that emerged from quantum mechanics was “diffuse” compared to classical mechanics. In classical mechanics one could mea-

<sup>51</sup>There is an apocryphal story about a police patrol stopping Professor Heisenberg for speeding. The policeman asks: “Do you know how fast you were going when I stopped you?” Heisenberg answered: “I have no idea, but can tell you precisely where you stopped me”.

<sup>52</sup>Schrödinger did not like the Copenhagen interpretation. Once Bohr and Heisenberg invited him for a Baltic Sea cruise and indoctrinated him so strongly, that Schrödinger became ill and stopped participating in their discussions.

sure a particle's position and momentum with a desired accuracy,<sup>53</sup> whereas the Heisenberg uncertainty principle states that this is simply *impossible*.

Bohr presented a philosophical interpretation of the world, which at its foundation had in a sense a *non-reality of the world*.

According to Bohr, before a measurement on a particle is made, *nothing* can be said about the value of a given mechanical quantity, unless the wave function represents an eigenfunction of the operator of this mechanical quantity. Moreover, except in this case, the particle *does not have* any fixed value of mechanical quantity at all.

collapse

decoherence

A measurement gives a value of the mechanical property ( $A$ ). Then, according to Bohr, after the measurement is completed, the state of the system changes (the so called *wave function collapse* or, more generally, *decoherence*) to the state described by *an eigenfunction of the corresponding operator  $\hat{A}$* , and as the *measured value one obtains the eigenvalue corresponding to the wave function*. According to Bohr, there is no way to foresee which eigenvalue one will get as the result of the measurement. However, one can calculate the *probability* of getting a particular eigenvalue. This probability may be computed as the square of the overlap integral (cf. p. 24) of the initial wave function and the eigenfunction of  $\hat{A}$ .

## 1.5 HOW TO DISPROVE THE HEISENBERG PRINCIPLE? THE EINSTEIN–PODOLSKY–ROSEN RECIPE

EPR  
"experiment"

The Heisenberg uncertainty principle came as a shock. Many scientists felt a strong imperative to prove that the principle is false. One of them was Albert Einstein, who used to play with ideas by performing some (as he used to say) imaginary ideal experiments (in German *Gedankenexperiment*) in order to demonstrate internal contradictions in theories. Einstein believed in the reality of our world. With his colleagues Podolsky and Rosen ("EPR team") he designed a special Gedankenexperiment.<sup>54</sup> It represented an attempt to disprove the Heisenberg uncertainty principle and to show that one *can* measure the position and momentum of a particle *without any error*. To achieve this, the gentlemen invoked a second particle.

The key statement of the whole reasoning, given in the EPR paper, was the following: "*If, without in any way disturbing a system, we can predict with certainty (i.e. with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity*". EPR considered

<sup>53</sup>This is an exaggeration. Classical mechanics also has its own problems with uncertainty. For example, obtaining the same results for a game of dice would require a perfect reproduction of the initial conditions, which is never feasible.

<sup>54</sup>A. Einstein, B. Podolsky, N. Rosen, *Phys. Rev.* 47 (1935) 777.

a coordinate system fixed in space and two particles: 1 with coordinate  $x_1$  and momentum  $p_{x1}$  and 2 with coordinate  $x_2$  and momentum  $p_{x2}$ , the total system being in a state with a well defined total momentum:  $P = p_{x1} + p_{x2}$  and well defined relative position  $x = x_1 - x_2$ . The meaning of the words “well defined” is that, according to quantum mechanics, there is a possibility of the *exact measurement* of the two quantities ( $x$  and  $P$ ), because the two operators  $\hat{x}$  and  $\hat{P}$  do commute.<sup>55</sup> At this point, Einstein and his colleagues and the great interpreters of quantum theory, agreed.

We now come to the crux of the real controversy.

The particles interact, then separate and fly far away (at any time we are able to measure exactly both  $x$  and  $P$ ). When they are extremely far from each other (e.g., one close to us, the other one millions of light years away), we begin to suspect that each of the particles may be treated as free. Then, we decide to measure  $p_{x1}$ . However, after we do it, we know *with absolute certainty the momentum of the second particle*  $p_{x2} = P - p_{x1}$ , and this knowledge has been acquired *without any perturbation of particle 2*. According to the above cited statement, one has to admit that  $p_{x2}$  represents an element of physical reality. So far so good. However, we *might have decided* with respect to particle 1 to measure its *coordinate*  $x_1$ . If this happened, then we would know *with absolute certainty the position of the second particle*,  $x_2 = x - x_1$ , without perturbing particle 2 at all. Therefore,  $x_2$ , as  $p_{x2}$ , is an element of physical reality. The Heisenberg uncertainty principle says that it is *impossible* for  $x_2$  and  $p_{x2}$  to be exactly measurable quantities. Conclusion: the Heisenberg uncertainty principle is wrong, and quantum mechanics is at least incomplete!

A way to defend the Heisenberg principle was to treat the two particles as an indivisible total system and reject the supposition that the particles are independent, even if they are millions light years apart. This is how Niels Bohr defended himself against Einstein (and his two colleagues). He said that the state of the total system in fact never fell apart into particles 1 and 2, and still is in what is known as *entangled quantum state*<sup>56</sup> of the system of particles 1 and 2 and

entangled states

any measurement influences the state of the system as a whole, *independently of the distance of particles 1 and 2*.

This reduces to the statement that measurement manipulations on particle 1 influence the results of measurements on particle 2. This correlation between measurements on particles 1 and 2 has to take place *immediately, regardless of the space*

<sup>55</sup>Indeed,  $\hat{x}\hat{P} - \hat{P}\hat{x} = (\hat{x}_1 - \hat{x}_2)(\hat{p}_{x1} + \hat{p}_{x2}) - (\hat{p}_{x1} + \hat{p}_{x2})(\hat{x}_1 - \hat{x}_2) = [\hat{x}_1, \hat{p}_{x1}] - [\hat{x}_2, \hat{p}_{x2}] + [\hat{x}_1, \hat{p}_{x2}] - [\hat{x}_2, \hat{p}_{x1}] = +i\hbar - i\hbar + 0 - 0 = 0$ .

<sup>56</sup>To honour Einstein, Podolsky and Rosen the entanglement of states is sometimes called the EPR effect.

that separates them. This is a shocking and non-intuitive feature of quantum mechanics. This is why it is often said, also by specialists, that quantum mechanics cannot be understood. One can apply it successfully and obtain an excellent agreement with experiment, but there is something strange in its foundations. This represents a challenge: an excellent theory, but based on some unclear foundations.

In the following, some precise experiments will be described, in which it is shown that quantum mechanics is right, however absurd it looks.

## 1.6 IS THE WORLD REAL?

### BILOCATION

Assume that the world (stars, Earth, Moon, you and me, table, proton, etc.) exists objectively. This one may suspect from everyday observations. For example, the Moon is seen by many people, who describe it in a similar way.<sup>57</sup> Instead of the Moon, let us begin with something simpler: how about electrons, protons or other elementary particles? This is an important question because the world as we know it – including the Moon – is mainly composed of protons.<sup>58</sup> Here one encounters a mysterious problem. I will try to describe it by reporting results of several experiments.

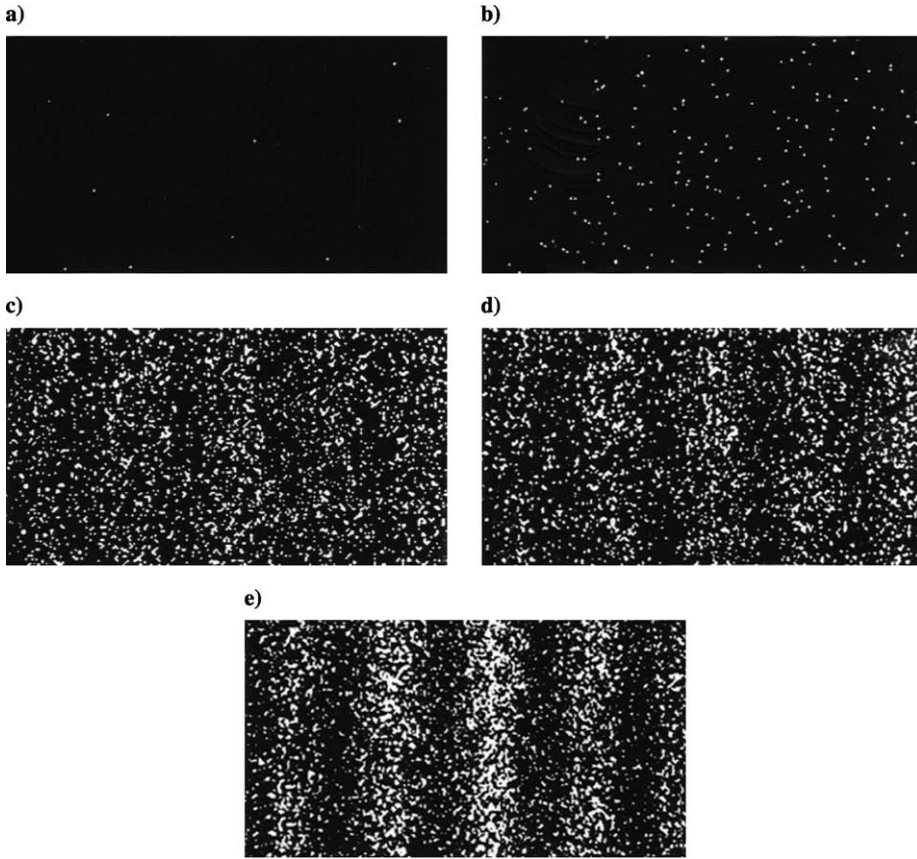
Following Richard Feynman,<sup>59</sup> imagine two slits in a wall. Every second (the time interval has to be large enough to be sure that we deal with properties of a *single* particle) we send an electron towards the slits. There is a screen behind the two slits, and when an electron hits the screen, there is a flash (fluorescence) at the point of collision. Nothing special happens. Some electrons will not reach the screen at all, but traces of others form a pattern, which seems quite chaotic. The experiment looks monotonous and boring. Just a flash here, and another there. One cannot predict where a particular electron will hit the screen. But suddenly we begin to suspect that there is some regularity in the traces, Fig. 1.14.

<sup>57</sup>This may indicate that the Moon exists independently of our observations and overcome importunate suspicions that the Moon ceases to exist, when we do not look at it. Besides, there are people who claim to have seen the Moon from very close and even touched it (admittedly through a glove) and this slightly strengthens our belief in the Moon's existence. First of all, one has to be cautious. For example, some chemical substances, hypnosis or an ingenious set of mirrors may cause some people to be convinced about the reality of some phenomena, while others do not see them. Yet, would it help if even everybody saw? We should not verify serious things by voting. The example of the Moon also intrigued others, cf. D. Mermin, "*Is the Moon there, when nobody looks?*", *Phys. Today* 38 (1985) 38.

<sup>58</sup>In the darkest communist times a colleague of mine came to my office. Conspiratorially, very excited, he whispered: "*The proton decays!!!*" He just read in a government newspaper that the lifetime of proton turned out to be finite. When asked about the lifetime, he gave an astronomical number, something like  $10^{30}$  years or so. I said: "*Why do you look so excited then and why all this conspiracy?*" He answered: "*The Soviet Union is built of protons, and therefore is bound to decay as well!*"

<sup>59</sup>After Richard Feynman, "The Character of Physical Law", MIT Press, 1967.





**Fig. 1.14.** Two-slit electron interference pattern registered by Akira Tonomura. (a) 10 electrons (b) 100 electrons (c) 3000 electrons – one begins to suspect something (d) 20000 electrons – no doubt, we will have a surprise (e) 70000 electrons – here it is! Conclusion: there is only one possibility – each electron went through the two slits. Courtesy of Professor Akira Tonomura.

A strange pattern appears on the screen: a number of high concentrations of traces is separated by regions of low concentration. This resembles the interference of waves, e.g., a stone thrown into water causes interference behind two slits: an alternation of high and low amplitude of water level. Well, but what has an electron in common with a wave on the water surface? The interference on water was possible, because there were two sources of waves (the Huygens principle) – two slits.

The common sense tells us that nothing like this could happen with the electron, because, firstly, the electron could not pass through *both* slits, and, secondly, unlike the waves, the electron has hit a tiny spot on the screen (transferring its energy). Let us repeat the experiment with a *single* slit. The electrons

Christiaan Huygens (1629–1695), Dutch mathematician, physicist and astronomer. Huygens was the first to construct a useful pendulum clock.



go through the slit and make flashes on the screen here and there, but there is only a single major concentration region (just facing the slit) fading away from the centre (with some minor minima).

This result should make you feel faint. Why? You would like the Moon, a proton or an electron to be solid objects, wouldn't you? All investigations made

so far indicate that the electron is a point-like elementary particle. If, in the experiments we have considered, the electrons were to be divided into two classes: those that went through slit 1 and those that passed slit 2, then the electron patterns would be different. The pattern with the two slits *had to be* the sum of the patterns corresponding to only one open slit (facing slit 1 and slit 2). *We do not have that picture.*

The *only* explanation for this interference of the electron with itself is that with the two slits open it went through *both*.

Clearly, the two parts of the electron united somehow and caused the flash at a single point on the screen. The quantum world is really puzzling. Despite the fact that the wave function is delocalized, the measurement gives its single point position (decoherence). How could an electron pass simultaneously through two slits? We do not understand this, but this is what happens.

Maybe it is possible to pinpoint the electron passing through two slits? Indeed, one may think of the Compton effect: a photon collides with an electron, changes its direction and this can be detected (“a flash on the electron”). When one prepares two such ambushes at the two open slits, it turns out that the flash is *always on a single slit, not on both*. This cannot be true! If it were true, then the pattern would be of a NON-interference character (and had to be the sum of the two one-slit patterns), but we have the interference. No. There is no interference. *Now*, the pattern does not show the interference. The interference was when the electrons were not observed. When we observe them, there is no interference.<sup>60</sup> Somehow we perturb the electron's momentum (the Heisenberg principle) and the interference disappears.

We have to accept that the electron passes through two slits. This is a blow to those who believe in the reality of the world. Maybe it only pertains to the electron, maybe the Moon is something completely different? A weak hope. The same thing

<sup>60</sup>Even if an electron has been pinpointed just *after* passing the slit region, i.e. already on the screen side (leaving the slit system *behind*). One might think it is too late, it has already passed the interference region. This has serious consequences, known as the problem of “*delayed choice*” (cf. the experiments with photons at the end of this chapter).

happens to proton. Sodium atoms were also found to interfere.<sup>61</sup> A sodium atom, of diameter of a few Å, looks like an ocean liner, when compared to a child's toy boat of a tiny electron (42 000 times less massive). And this ocean liner passed through two slits separated by thousands of Å. A similar interference was observed for the fullerene,<sup>62</sup> a giant C<sub>60</sub> molecule (in 2001 also for C<sub>70</sub>), about million times more massive than the electron. It is worth noting that after such adventure the fullerene molecule remained intact: somehow all its atoms, with the details of their chemical bonds, preserved their nature. There is something intriguing in this.

## 1.7 THE BELL INEQUALITY WILL DECIDE

John Bell proved a theorem in 1964 that pertains to the results of measurements carried out on particles and some of the inequalities they have to fulfil. The theorem pertains to the basic logic of the measurements and is valid independently of the kind of particles and of the nature of their interaction. The theorem soon became very famous, because it turned out to be a useful tool allowing us to verify some fundamental features of our knowledge about the world.

Imagine a launching gun<sup>63</sup> (Fig. 1.15), which ejects a series of pairs of identical rectangular bars flying along a straight line (no gravitation) in opposite directions (opposite velocities). The axes of the bars are always parallel to each other and always perpendicular to the straight line. The launching machine is constructed in such a way that it can rotate about the straight line, and that any two launching series are absolutely identical. At a certain distance from the launching machine there are two rectangular slits A and B (the same on both sides). If the bar's longer axis coincides with the longer dimension of the slit then the bar will go through for sure and will be registered as "1", i.e. "it has arrived" by the detector. If the bar's longer axis coincides with the shorter axis of the slit, then the bar will not go through for sure, and will be detected as "0". For other angles between the bar and slit axes the bar will sometimes go through (when it fits the slit), sometimes not (when it does not fit the slit).<sup>64</sup>

John Stuart Bell (1928–1990), Irish mathematician at Centre Européen de la Recherche Nucleaire (CERN) in Geneva. In the 1960s Bell reconsidered an old controversy of locality versus non-locality, hidden variables, etc., a subject apparently exhausted after exchange of ideas between Einstein and Bohr.

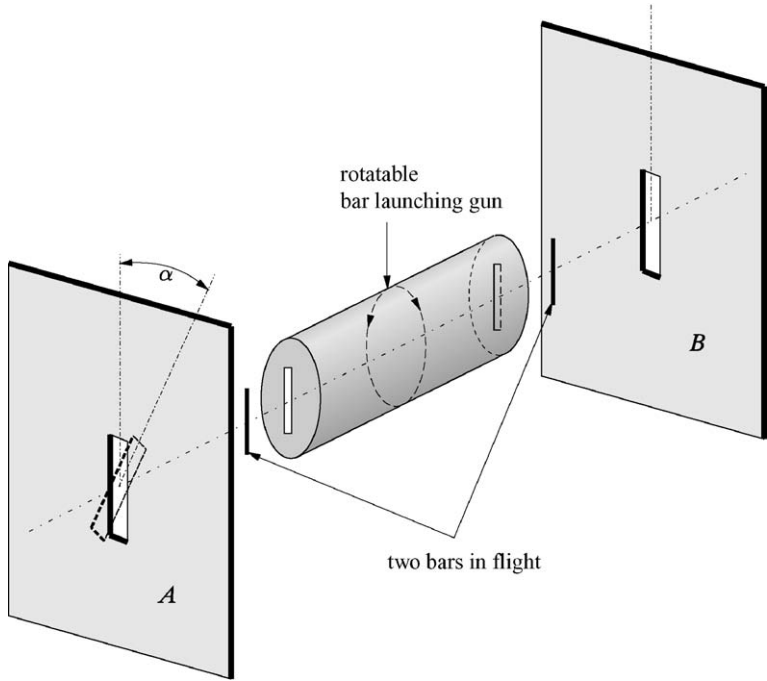


<sup>61</sup>To observe such phenomena the slit distance has to be of the order of the de Broglie wave length,  $\lambda = h/p$ , where  $h$  is the Planck constant, and  $p$  is the momentum. Cohen-Tannoudji lowered the temperature to such an extent that the momentum was close to 0, and  $\lambda$  could be of the order of thousands of Å.

<sup>62</sup>M. Arndt, O. Nairz, J. Voss-Andreae, C. Keller, G. van der Zouw, A. Zeilinger, *Nature* 401 (1999) 680.

<sup>63</sup>See, e.g., W. Kolos, Proceedings of the IV Castel Gandolfo Symposium, 1986.

<sup>64</sup>Simple reasoning shows that for a bar of length  $L$ , two possibilities: "to go through" and "not to go through" are equally probable (for a bar of zero width) if the slit width is equal to  $\frac{L}{\sqrt{2}}$ .



**Fig. 1.15.** Bell inequalities. A bar launching gun adopts some positions when rotating about the axis. Each time the full magazine of bars is loaded. The slits also may be rotated about the axis. The bars arrive at slits A and B. Some will go through and be detected.

Having prepared the launching gun (our magazine contains 16 pairs of bars) we begin our experiments. Four experiments will be performed. Each experiment will need the full magazine of bars. In the first experiment the two slits will be parallel. This means that the fate of both bars in any pair will be exactly the same: if they go through, they will both do it, if they are stopped by the slits, they will both be stopped. Our detectors have registered (we group the 16 pairs in clusters of 4 to make the sequence more transparent):

Experiment I (angle 0)				
Detector A:	1001	0111	0010	1001
Detector B:	1001	0111	0010	1001

Now, we repeat Experiment I, but this time slit A will be rotated by a small angle  $\alpha$  (Experiment II). At the slit B nothing has changed, and therefore we must obtain there exactly the same sequence of zeros and ones as in Experiment I. At slit A, however, the results may be different. Since the rotation angle is small, the difference list will be short. We might get the following result

Experiment II (angle  $\alpha$ )

Detector A:                    10**11**   0111   0010   **0001**

Detector B:                    1001   0111   0010   1001

There are two differences (highlighted in bold) between the lists for the two detectors.

Now for Experiment III. This time slit A comes back to its initial position, but slit B is rotated by  $-\alpha$ . Because of our perfect gun, we must obtain at detector A the same result as in Experiment I. However, at B we find some difference with respect to Experiments I and II:

Experiment III (angle  $-\alpha$ )

Detector A:                    1001   0111   0010   1001

Detector B:                    1001   **0011**   0110   1001

There are two differences (bold) between the two detectors.

We now carry out Experiment IV. We rotate slit A by angle  $\alpha$ , and slit B by angle  $-\alpha$ . Therefore, at Detector A we obtain the same results as in Experiment II, while at Detector B – the same as in Experiment III. Therefore, we detect:

Experiment IV (angle  $2\alpha$ )

Detector A:                    10**11**   0111   0010   **0001**

Detector B:                    1001   **0011**   0110   1001

Now there are four differences between Detector A and Detector B. In Experiment IV *the number of differences could not be larger (Bell inequality)*. In our case it could be four or fewer. When would it be fewer? When accidentally the bold figures (i.e. the differences of Experiments II and III with respect to those of Experiment I) coincide. In this case this would be counted as a difference in Experiments II and III, while in Experiment IV it would not be counted as a difference.

Thus, we have demonstrated

**BELL INEQUALITY:**

$$N(2\alpha) \leq 2N(\alpha), \quad (1.24)$$

where  $N$  stands for the number of measurement differences. The Bell inequality was derived under assumption that whatever happens at slit A it does not influence that which happens at slit B (this is how we constructed the counting tables) and that the two flying bars have, maybe unknown for the observer, only a real (definite) direction in space (the same for both bars).

It would be interesting to perform a real experiment similar to Bell's to confirm the Bell inequality. This opens the way for deciding in a physical experiment whether:

- elementary particles are classical (though extremely small) objects that have some well defined attributes irrespective of whether we observe them or not (Einstein's view)
- elementary particles do not have such attributes and only measurements themselves make them have measured values (Bohr's view).

## 1.8 INTRIGUING RESULTS OF EXPERIMENTS WITH PHOTONS

Aspect et al., French scientists from the Institute of Theoretical and Applied Optics in Orsay published the results of their experiments with photons.<sup>65</sup> The excited calcium atom emitted pairs of photons (analogues of our bars), which moved in opposite directions and had the same polarization. After flying about 6 m they both met the polarizers – analogues of slits A and B in the Bell procedure. A polarizer allows a photon with polarization state  $|0\rangle$ , or “parallel” (to the polarizer axis), always pass through, and always rejects any photon in the polarization state  $|1\rangle$ , or “perpendicular” (indeed perpendicular to the above “parallel” setting). When the polarizer is rotated about the optical axis by an angle, it will pass through a percentage of the photons in state  $|0\rangle$  and a percentage of the photons in state  $|1\rangle$ . When both polarizers are in the “parallel” setting, there is perfect correlation between the two photons of each pair, i.e. exactly as in Bell's Experiment I. In the photon experiment, this correlation was checked for 50 million photons every second for about 12 000 seconds.

Bell's experiments II–IV have been carried out. Common sense indicates that, even if the two photons in a pair have random polarizations (perfectly correlated though always the same – like the bars), they still have *some* polarizations, i.e. maybe unknown but definite (as in the case of the bars, i.e. what E, P and R believed happens). *Hence, the results of the photon experiments would have to fulfil the Bell inequality.* However, the photon experiments have shown that the Bell inequality is violated, but still the results are in accordance with the prediction of quantum mechanics.

There are therefore only two possibilities (compare the frame at the end of the previous section):

- (a) either the measurement on a photon carried out at polarizer A (B) results in some *instantaneous interaction* with the photon at polarizer B(A), or/and
- (b) the polarization of any of these photons is completely *indefinite* (even if the polarizations of the two photons are fully correlated, i.e. the same) and only the *measurement on one of the photons at A (B) determines its polarization*, which

<sup>65</sup> A. Aspect, J. Dalibard, G. Roger, *Phys. Rev. Lett.* 49 (1982) 1804.

results in the automatic determination of the polarization of the second photon at B(A), even if they are separated by millions of light years.

Both possibilities are sensational. The first assumes a strange form of communication between the photons or the polarizers. This communication must be propagated with a velocity *exceeding* the speed of light, because an experiment was performed in which the polarizers were switched (this took something like 10 nanoseconds) *after* the photons started (their flight took about 40 nanoseconds). Despite this, communication between the photons did exist.<sup>66</sup> The possibility b) as a matter of fact represents Bohr's interpretation of quantum mechanics: elementary particles do not have definite attributes (e.g., polarization).

As a result there is dilemma: either the world is “non-real” (in the sense that the properties of particles are not determined before measurement) or/and there is instantaneous (i.e. faster than light) communication between particles which operates independently of how far apart they are (“non-locality”).

This dilemma may make everybody's metaphysical shiver!

## 1.9 TELEPORTATION

The idea of teleportation comes from science fiction and means:

- *acquisition of full information* about an object located at A,
- *its transmission* to B,
- *creation* (materialization) of an identical object at B
- and *at the same time, the disappearance* of the object at A.

At first sight *it seems* that this contradicts quantum mechanics. The Heisenberg uncertainty principle says that it is not possible to prepare a perfect copy of the object, because, in case of mechanical quantities with non-commuting operators (like positions and momenta), there is *no way to have them measured exactly*, in order to rebuild the system elsewhere with the same values of the quantities.

The trick is, however, that the quantum teleportation we are going to describe, *will not violate* the Heisenberg principle, because the mechanical quantities needed *will not be measured and the copy made based on their values*.

The teleportation protocol was proposed by Bennett and coworkers,<sup>67</sup> and applied by the Anton Zeilinger group.<sup>68</sup> The latter used the entangled states (EPR effect) of two photons described above.<sup>69</sup>

teleportation

<sup>66</sup>This again is the problem of delayed choice. It seems that when starting the photons have a knowledge of the *future* setting of the apparatus (the two polarizers)!

<sup>67</sup>C.H. Bennett, G. Brassard, C. Crépeau, R. Josza, A. Peres, W.K. Wootters, *Phys. Rev. Letters* 70 (1993) 1895.

<sup>68</sup>D. Bouwmeester, J. Pan, K. Mattle, M. Eibl, H. Weinfurter, A. Zeilinger, *Nature* 390 (1997) 575.

<sup>69</sup>A UV laser beam hits a barium borate crystal (known for its birefringence). Photons with parallel polarization move along the surface of a cone (with the origin at the beam-surface collision point),

Assume that photon A (number 1) from the entangled state belongs to Alice, and photon B (number 2) to Bob. Alice and Bob introduce a common fixed coordinate system. Both photons have *identical* polarizations in this coordinate system, *but neither Alice nor Bob know which*. Alice may measure the polarization of her photon and send this information to Bob, who may prepare his photon in that state. This, however, does not amount to teleportation, because the original state could be a linear combination of the  $|0\rangle$  (parallel) and  $|1\rangle$  (perpendicular) states, and in such a case Alice's measurement would "falsify" the state due to wave function collapse (it would give either  $|0\rangle$  or  $|1\rangle$ ), cf. p. 23.

Since Alice and Bob have two entangled photons of the same polarization, then let us assume that the state of the two photons is the following superposition:<sup>70</sup>  $|00\rangle + |11\rangle$ , where the first position in every ket pertains to Alice's photon, the second to Bob's.

qubit Now, Alice wants to carry out teleportation of her additional photon (number 3) in an unknown quantum state  $\phi = a|0\rangle + b|1\rangle$  (known as *qubit*), where  $a$  and  $b$  stand for *unknown* coefficients<sup>71</sup> satisfying the normalization condition  $a^2 + b^2 = 1$ . Therefore, the state of three photons (Alice's: the first and the third position in the three-photon ket, Bob's: the second position) will be  $[|00\rangle + |11\rangle][a|0\rangle + b|1\rangle] = a|000\rangle + b|001\rangle + a|110\rangle + b|111\rangle$ .

Alice prepares herself for teleportation of the qubit  $\phi$  corresponding to her second photon. She first prepares a device called the *XOR gate*.<sup>72</sup>

XOR gate What is the XOR gate? The device manipulates two photons, one is treated as the steering photon, the second as the steered photon. The device operates thus: if the steering photon is in state  $|0\rangle$ , then no change is introduced for the state of the steered photon. If, however, the steering photon is in the state  $|1\rangle$ , the steered photon will be switched over, i.e. it will be changed from  $|0\rangle$  to  $|1\rangle$  or from  $|1\rangle$  to  $|0\rangle$ . Alice chooses the photon in the state  $\phi$  as her steering photon, and photon 1 as her steered photon.

After the XOR gate is applied, the state of the three photons will be as follows:  $a|000\rangle + b|101\rangle + a|110\rangle + b|011\rangle$ .

Hadamard gate Alice continues her preparation by using another device called the *Hadamard gate* that operates on a single photon and does the following

$$\begin{aligned} |0\rangle &\rightarrow \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle), \\ |1\rangle &\rightarrow \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle). \end{aligned}$$

the photons with perpendicular polarization move on another cone, the two cones intersecting. From time to time a single UV photon splits into two equal energy photons of different polarizations. Two such photons when running along the intersection lines of the two cones, *and therefore not having a definite polarization* (i.e. being in a superposition state composed of both polarizations) represent the two entangled photons.

<sup>70</sup>The teleportation result does not depend on the state.

<sup>71</sup>Neither Alice nor Bob will know these coefficients up to the end of the teleportation procedure, but still Alice will be able to send her qubit to Bob!

<sup>72</sup>Abbreviation of "*eXclusive OR*".



Alice applies this operation to her photon 3, and after that the three-photon state is changed to the following

$$\begin{aligned}
 & \frac{1}{\sqrt{2}}[a|000\rangle + a|001\rangle + b|100\rangle - b|101\rangle + a|110\rangle + a|111\rangle + b|010\rangle - b|011\rangle] \\
 &= \frac{1}{\sqrt{2}}[|0(a|0\rangle + b|1\rangle)0\rangle + |0(a|0\rangle - b|1\rangle)1\rangle - |1(a|1\rangle + b|0\rangle)0\rangle \\
 &\quad + |1(a|1\rangle - b|0\rangle)1\rangle]. \tag{1.25}
 \end{aligned}$$

There is a superposition of four three-photon states in the last row. Each state shows the state of Bob's photon (number 2 in the ket), at any given state of Alice's two photons. Finally, Alice carries out the measurement of the polarization states of her photons (1 and 3). This inevitably causes her to get (for each of the photons) either  $|0\rangle$  or  $|1\rangle$  (collapse). This causes her to know the state of Bob's photon from the three-photon superposition (1.25):

- Alice's photons 00, i.e. Bob has his photon in state  $(a|0\rangle + b|1\rangle) = \phi$ ,
- Alice's photons 01, i.e. Bob has his photon in state  $(a|0\rangle - b|1\rangle)$ ,
- Alice's photons 10, i.e. Bob has his photon in state  $(a|1\rangle + b|0\rangle)$ ,
- Alice's photons 11, i.e. Bob has his photon in state  $(a|1\rangle - b|0\rangle)$ .

Then Alice calls Bob and tells him the result of her measurements of the polarization of her two photons. Bob has derived (1.25) as we did.

Bob knows therefore, that if Alice tells him 00 this means that the teleportation is over: he already has his photon in state  $\phi$ ! If Alice sends him one of the remaining possibilities, he would know exactly what to do with his photon to prepare it in state  $\phi$  and he does this with his equipment. *The teleportation is over: Bob has the teleported state  $\phi$ , Alice has lost her photon state  $\phi$  when performing her measurement (wave function collapse).*

Note that to carry out the successful teleportation of a photon state Alice had to communicate something to Bob.

## 1.10 QUANTUM COMPUTING

Richard Feynman pointed out that contemporary computers are based on the “all” or “nothing” philosophy (two bits:  $|0\rangle$  or  $|1\rangle$ ), while in quantum mechanics one may also use a linear combination (superposition) of these two states with arbitrary coefficients  $a$  and  $b$ :  $a|0\rangle + b|1\rangle$ , a qubit. Would a quantum computer based on such superpositions be better than traditional one? The hope associated with quantum

computers relies on a multitude of quantum states (those obtained using variable coefficients  $a, b, c, \dots$ ) and possibility of working with many of them using a single processor. It was (theoretically) proved in 1994 that quantum computers could factorize natural numbers much faster than traditional computers. This sparked intensive research on the concept of quantum computation, which uses the idea of entangled states. According to many researchers, any entangled state (a superposition) is extremely sensitive to the slightest interaction with the environment, and as a result decoherence takes place very easily, which is devastating for quantum computing.<sup>73</sup> First attempts at constructing quantum computers were based on protecting the entangled states, but, after a few simple operations, decoherence took place.

In 1997 Neil Gershenfeld and Isaac Chuang realized that any routine nuclear magnetic resonance (NMR) measurement represents nothing but a simple quantum computation. The breakthrough was recognizing that a qubit may be also represented by the huge number of molecules in a liquid.<sup>74</sup> The nuclear spin angular momentum (say, corresponding to  $s = \frac{1}{2}$ ) is associated with a magnetic dipole moment and those magnetic dipole moments interact with an external magnetic field and with themselves (Chapter 12). An isolated magnetic dipole moment has two states in a magnetic field: a lower energy state corresponding to the antiparallel configuration (state  $|0\rangle$ ) and of higher energy state related to the parallel configuration (state  $|1\rangle$ ). By exposing a sample to a carefully tailored nanosecond radiowave impulse one obtains a rotation of the nuclear magnetic dipoles, which corresponds to their state being a superposition  $a|0\rangle + b|1\rangle$ .

Here is a prototype of the XOR gate. Take chloroform<sup>75</sup> [ $^{13}\text{CHCl}_3$ ]. Due to the interaction of the magnetic dipoles of the proton and of the carbon nucleus (both either in parallel or antiparallel configurations with respect to the external magnetic field) a radiowave impulse of a certain frequency causes the carbon nuclear spin magnetic dipole to rotate by  $180^\circ$  *provided* the proton spin dipole moment is parallel to that of the carbon. Similarly, one may conceive other logical gates. The spins changes their orientations according to a sequence of impulses, which play the role of a computer program. There are many technical problems to overcome in “liquid quantum computers”: the magnetic interaction of distant nuclei is very weak, decoherence remains a worry and for the time being, limits the number of operations to several hundred. However, this is only the beginning of a new computer technology. It is most important that chemists know the future computers well – they are simply molecules.

<sup>73</sup>It pertains to an entangled state of (already) distant particles. When the particles interact strongly the state is more stable. The wave function for  $\text{H}_2$  also represents an entangled state of two electrons, yet the decoherence does not take place even at short internuclear distances. As we will see, entangled states can also be obtained in liquids.

<sup>74</sup>Interaction of the molecules with the environment does not necessarily result in decoherence.

<sup>75</sup>The NMR operations on spins pertain in practise to a tiny fraction of the nuclei of the sample (of the order of 1 : 1000000).

## Summary

Classical mechanics was unable to explain certain phenomena: black body radiation, the photoelectric effect, the stability of atoms and molecules as well as their spectra. Quantum mechanics, created mainly by Werner Heisenberg and Erwin Schrödinger, explained these effects. The new mechanics was based on six postulates:

- Postulate I says that all information about the system follows from the wave function  $\psi$ . The quantity  $|\psi|^2$  represents the probability density of finding particular values of the coordinates of the particles, the system is composed of.
- Postulate II allows *operators* to be ascribed to mechanical quantities (e.g., energy). One obtains the operators by writing down the classical expression for the corresponding quantity, and replacing momenta (e.g.,  $p_x$ ) by momenta operators (here,  $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ ).
- Postulate III gives the time evolution equation for the wave function  $\psi$  (time-dependent Schrödinger equation  $\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$ ), using the energy operator (*Hamiltonian*  $\hat{H}$ ).
- Postulate IV pertains to ideal measurements. When making a measurement of a quantity  $A$ , one can obtain only *an eigenvalue of the corresponding operator  $\hat{A}$* . If the wave function  $\psi$  represents an eigenfunction of  $\hat{A}$ , i.e. ( $\hat{A}\psi = a\psi$ ), then one obtains always as a result of the measurement the eigenvalue corresponding to  $\psi$  (i.e.,  $a$ ). If, however, the system is described by a wave function, which *does not represent any eigenfunction of  $\hat{A}$* , then one obtains also an eigenvalue of  $\hat{A}$ , but there is no way to predict which eigenvalue. The only thing one can predict is the mean value of many measurements, which may be computed as  $\langle \psi | \hat{A} | \psi \rangle$  (for the normalized function  $\psi$ ).
- Postulate V says that an elementary particle has an internal angular momentum (spin). One can measure only two quantities: the square of the spin length  $s(s+1)\hbar^2$  and one of its components  $m_s\hbar$ , where  $m_s = -s, -s+1, \dots, +s$ , with spin quantum number  $s \geq 0$  characteristic for the type of particle (integer for bosons, half-integer for fermions). The spin magnetic quantum number  $m_s$  takes  $2s+1$  values.
- Postulate VI has to do with symmetry of the wave function with respect to the different labelling of identical particles. If one exchanges the labels of two identical particles (we sometimes call it the exchange of all the coordinates of the two particles), then for two identical fermions the wave function has to change its sign (antisymmetric), while for two identical bosons the function does not change (symmetry). As a consequence, two identical fermions with the same spin coordinate cannot occupy the same point in space.

Quantum mechanics is one of the most peculiar theories. It gives numerical results that agree extremely well with experiments, but on the other hand the relation of these results to our everyday experience sometimes seems shocking. For example, it turned out that a particle or even a molecule may somehow exist in two locations (they pass through two slits simultaneously), but when one checks that out they are always in one place. It also turned out that

- either a particle has no definite properties (“*the world is unreal*”), and the measurement fixes them somehow
- or/and, there is instantaneous communication between particles however distant they are from each other (“*non-locality of interactions*”).

It turned out that in the Bohr–Einstein controversy Bohr was right. The Einstein–Podolsky–Rosen paradox resulted (in agreement with Bohr’s view) in the concept of entangled states. These states have been used experimentally to teleport a photon state without

violating the Heisenberg uncertainty principle. Also the entangled states stand behind the idea of quantum computing: with a superposition of two states (qubit)  $a|0\rangle + b|1\rangle$  instead of  $|0\rangle$  and  $|1\rangle$  as information states.

### Main concepts, new terms

wave function (p. 16)	symmetric function (p. 33)
operator of a quantity (p. 18)	Heisenberg uncertainty principle (p. 36)
Dirac notation (p. 19)	Gedankenexperiment (p. 38)
time evolution equation (p. 20)	EPR effect (p. 38)
eigenfunction (p. 21)	entangled states (p. 39)
eigenvalue problem (p. 21)	delayed choice (p. 42)
stationary state (p. 22)	interference of particles (p. 42)
measurement (p. 22)	bilocation (p. 42)
mean value of an operator (p. 24)	Bell inequality (p. 43)
spin angular momentum (p. 25)	experiment of Aspect (p. 46)
spin coordinate (p. 26)	teleportation (p. 47)
Pauli matrices (p. 28)	logical gate (p. 47)
symmetry of wave function (p. 33)	qubit (p. 48)
antisymmetric function (p. 33)	XOR and Hadamard gates (p. 48)

### From the research front

Until recently, the puzzling foundations of quantum mechanics could not be verified directly by experiment. As a result of enormous technological advances in quantum electronics and quantum optics it became possible to carry out experiments on single atoms, molecules, photons, etc. It was possible to carry out teleportation of a photon state across the Danube River. Even molecules such as fullerene were subjected to successful interference experiments. Quantum computer science is just beginning to prove that its principles are correct.

### Ad futurum

Quantum mechanics has been proved in the past to give excellent results, but its foundations are still unclear.<sup>76</sup> There is no successful theory of decoherence, that would explain why and how a delocalized state becomes localized after the measurement. It is possible to make fullerene interfere, and it may be that in the near future we will be able to do this with a virus.<sup>77</sup> It is interesting that fullerene passes instantaneously through two slits with its whole complex electronic structure as well as nuclear framework, although the de Broglie wave length is quite different for the electrons and for the nuclei. Visibly the “overweighted” electrons interfere differently from free ones. After the fullerene passes the slits, one sees it in a single spot on the screen (decoherence). It seems that there are cases when even strong interaction does not make decoherence necessary. Sławomir Szymański presented his theoretical and experimental results<sup>78</sup> and showed that the functional group  $-\text{CD}_3$  exhibits a delocalized state (which corresponds to its rotation instantaneously in both directions, a coherence) and, which makes the thing more peculiar, interaction with the environment *not only does not destroy the coherence, but makes it more robust*. This type of phenomenon might fuel investigations towards future quantum computer architectures.

<sup>76</sup>A pragmatic viewpoint is shared by the vast majority: “do not wiseacre, just compute!”

<sup>77</sup>As announced by Anton Zeilinger.

<sup>78</sup>S. Szymański, *J. Chem. Phys.* 111 (1999) 288.

## Additional literature

“The Ghost in the atom: a discussion of the mysteries of quantum physics”, P.C.W. Davies and J.R. Brown, eds, Cambridge University Press, 1986.

Two BBC journalists interviewed eight outstanding physicists: Alain Aspect (photon experiments), John Bell (Bell inequalities), John Wheeler (Feynman’s PhD supervisor), Rudolf Peierls (“Peierls metal-semiconductor transition”), John Taylor (“black holes”), David Bohm (“hidden parameters”) and Basil Hiley (“mathematical foundations of quantum physics”). It is most striking that all these physicists give *very* different theoretical interpretations of quantum mechanics (summarized in Chapter I).

R. Feynman, “QED – the Strange Theory of Light and Matter”, Princeton University Press, Princeton (1985).

Excellent popular presentation of quantum electrodynamics written by one of the outstanding physicists of the 20th century.

A. Zeilinger, “Quantum teleportation”, *Scientific American* 282 (2000) 50.

The leader in teleportation describes this new domain.

N. Gershenfeld, I.L. Chuang, “Quantum computing with molecules”, *Scientific American* 278 (1998) 66.

First-hand information about NMR computing.

Ch.H. Bennett, “Quantum Information and Computation”, *Physics Today* 48 (1995) 24.

Another first-hand description.

## Questions

- The state of the system is described by the wave function  $\psi$ . If  $|\psi|^2$  is computed by inserting some particular values of the coordinates, then one obtains:
  - the probability of finding the system with these coordinates;
  - a complex number;
  - 1;
  - the probability density of finding the system with these coordinates.
- The kinetic energy operator (one dimension) is equal to:
  - $\frac{mv^2}{2}$ ;
  - $-i\hbar \frac{\partial}{\partial x}$ ;
  - $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ ;
  - $\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ .
- The length of the electron spin vector is equal to:
  - $\sqrt{\frac{3}{4}}\hbar$ ;
  - $\frac{1}{2}\hbar$ ;
  - $\pm \frac{1}{2}\hbar$ ;
  - $\hbar$ .
- The probability density of finding two identical fermions in a single point and with the same spin coordinate is:
  - $> 0$ ;
  - 0;
  - 1;
  - 1/2.
- The measurement error  $\Delta A$  of quantity  $A$ , which the Heisenberg uncertainty principle speaks about is equal to:
  - $\Delta A = \sqrt{\langle \psi | \hat{A} \psi \rangle}$ ;
  - $\Delta A = \sqrt{\langle \psi | \hat{A}^2 \psi \rangle - \langle \psi | \hat{A} \psi \rangle^2}$ ;
  - $\Delta A = \langle \psi | (\hat{A}^2 - \hat{A}) \psi \rangle$ ;
  - $\Delta A = \langle \psi | \hat{A} \psi \rangle$ .
- The Heisenberg uncertainty principle  $\Delta A \cdot \Delta B \geq \frac{\hbar}{2}$  pertains to:
  - any two mechanical quantities  $A$  and  $B$ ;
  - such mechanical quantities  $A$  and  $B$ , for which  $\hat{A}\hat{B} = \hat{B}\hat{A}$ ;
  - such mechanical quantities  $A$  and  $B$ , for which the operators do not commute;
  - only to a coordinate and the corresponding momentum.

7. The product of the measurement errors for a coordinate and the corresponding momentum is:  
a)  $\geq \frac{\hbar}{2}$ ; b)  $> \frac{\hbar}{2}$ ; c)  $= \frac{\hbar}{2}$ ; d)  $> \hbar$ .
8. The Einstein–Podolsky–Rosen experiment aimed at falsifying the Heisenberg uncertainty principle:  
a) measuring the coordinate of the first particle and the momentum of the second particle; b) measuring exactly the coordinates of two particles; c) measuring exactly the momenta of two particles; d) by exact measuring whatever one chooses: either the coordinate or the momentum of a particle (one of two particles).
9. Entangled states mean:  
a) the real and imaginary parts of the wave function; b) a single state of two separated particles causing dependence of the results of measurements carried out on both particles; c) a product of the wave function for the first and for the second particle; d) wave functions with a very large number of nodes.
10. The experiment of Aspect has shown that:  
a) the world is local; b) the photon polarizations are definite before measurement; c) the world is non-local or/and the photon polarizations are indefinite before measurement; d) the Bell inequality is satisfied for photons.

**Answers**

1d, 2c, 3a, 4b, 5b, 6c, 7a, 8d, 9b, 10c