

Quantum Mechanics for Nanostructures

Vladimir V. Mitin, Dmitry I. Sementsov
and Nizami Z. Vagidov

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The properties of new nanoscale materials, their fabrication and applications, as well as the operational principles of nanodevices and systems, are solely determined by quantum-mechanical laws and principles. This textbook introduces engineers to quantum mechanics and the world of nanostructures, enabling them to apply the theories to numerous nanostructure problems.

The book covers the fundamentals of quantum mechanics, including uncertainty relations, the Schrödinger equation, perturbation theory, and tunneling. These are then applied to a quantum dot, the smallest artificial atom, and compared with the case of hydrogen, the smallest atom in nature. Nanoscale objects with higher dimensionality, such as quantum wires and quantum wells, are introduced, as well as nanoscale materials and nanodevices. Numerous examples throughout the text help students to understand the material.

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Preface

Nanoelectronics is a field of fundamental and applied science, which is rapidly progressing as a natural development of microelectronics towards nanoscale electronics. The modern technical possibilities of science have reached such a level that it is possible to manipulate single molecules, atoms, and even electrons. These objects are the building blocks of nanoelectronics, which deals with the processes taking place in regions of size comparable to atomic dimensions. However, the physical laws which govern electron behavior in nanoobjects significantly differ from the laws of classical physics which define the operation of a large number of complex electronic devices, such as, for example, cathode-ray tubes and accelerators of charged particles. The laws that govern electron behavior in nanoobjects, being of quantum-mechanical origin, very often seem to be very strange from a common-sense viewpoint. The quantum-mechanical description of electron (or other microparticle) behavior is based on the idea of the *wave-particle duality of matter*. The wave properties of the electron, which play a significant role in its motion in small regions, require a new approach in the description of the electron's dynamic state on the nanoscale. Quantum mechanics has developed a fundamentally new probabilistic method of description of particle motion taking into account its wave properties. This type of description is based on the notion of a wavefunction, which is not always compatible with the notion of a particle's trajectory. This makes electron behavior harder to understand.

The main objects of research in nanoelectronics are quantum-dimensional structures such as *quantum wells*, *quantum wires*, and *quantum dots*, where electron motion is limited in one, two, and three directions, respectively. The size of these quantum-mechanical objects is comparable to the *electron de Broglie wavelength*. In such structures electronic properties become different from those of bulk materials: new so-called low-dimensional effects become apparent. Quantum-mechanical laws govern various processes and define a significant modification of the energy spectrum, which is the main characteristic of an electronic system. The energy spectrum which characterizes the electron motion in the limited region becomes discrete. The structures with such an energy spectrum are the basis for the development of new types of nanoelectronic devices.

The physics of quantum-dimensional structures is currently developing rapidly and is beginning to form a separate field with quantum mechanics

as its basis. Only a small number of undergraduate engineering students take quantum-mechanics courses. However, there are only a few textbooks that are simple enough to understand for a wide range of engineering students, who would like to learn theoretical methods of analysis of the electronic properties of low-dimensional structures. While writing the current textbook we pursued two main goals: to present the main low-dimensional structures clearly from the physical point of view and to teach the reader the basics of quantum-mechanical analysis of the properties of such structures. Therefore, the experimental and theoretical material which will help the reader to understand the quantum-mechanical concepts applied to *nanostuctures* is presented. Special attention is paid to the physical interpretation of quantum-mechanical notions. Theoretical material as well as the mathematical apparatus of quantum mechanics necessary for carrying out quantum-mechanical calculations independently is presented.

The book is written in such a way that it can be used by students who have studied classical physics to a sufficient extent as well as by students who have not had such an opportunity. The book consists of eight chapters and three appendices. The appendix material contains the main aspects of classical physics (particle dynamics, oscillations and waves in crystals, and electromagnetic fields and waves) which students can use while studying quantum mechanics.

In Chapter 1 we give a review of milestones in the development of *nanotechnology* and *nanoscience*. The main types of nanostructures are described and it is substantiated why it is necessary to use quantum physics for the description of their properties.

In Chapter 2 the main experimental facts which required the introduction of such unusual (for classical physics) notions as *wave-particle duality and uncertainty relationships*, among others, are described. The main notions and principles of the quantum-mechanical description are introduced. The Schrödinger equation – the main equation of non-relativistic quantum mechanics – is discussed in detail and its validity for the description of nanostructures is presented.

In Chapter 3 the solutions of the stationary Schrödinger equation are obtained for several important cases of one-dimensional motion. The main peculiarities of free electron motion as well as confined electron behavior are discussed. The main advantage of these solutions is in explanation and quantitative definition of the discrete energy levels of an electron when it moves in potential wells of various profiles.

In Chapter 4 the peculiarities of electron motion for structures wherein electron motion is confined in two and three dimensions are considered. It is shown that the discrete electron energy levels are characteristic for electron motion in potential wells of particular dimensionalities, in contrast to the continuous energy spectrum of a free electron. The structure's dimensionality and potential profile define the positioning of energy levels in the discrete energy spectrum.

The calculation of electron quantum states in various types of nanostructures generally encounters big mathematical difficulties. Therefore, approximate methods become very important for finding solutions of the Schrödinger equation. We consider in Chapter 5 several important and widely used approximate methods for calculation of electron wavefunctions, energy states, and transition probabilities between quantum states.

Chapter 6 is dedicated to finding wavefunctions, the geometry of electron clouds corresponding to them, and energy spectra of the simplest atoms and molecules using approximate methods.

When the size of the potential well is several times larger than the distance between atoms in a crystal, a fundamental reconstruction of the energy spectrum, which leads to a change in the physical properties of nanostructures, takes place. In Chapter 7 the main peculiarities of the electron energy spectrum in low-dimensional quantum structures (quantum wells, wires, and dots) as well as in periodic structures (superlattices) consisting of these low-dimensional nanostructures are considered.

In the last chapter – Chapter 8 – we consider the main methods of fabrication and characterization of nanostructures as well as their prospective applications in modern nanoelectronics.

Practically all chapters and appendices contain a large number of detailed examples and homework problems, which the authors hope will help students to acquire a deeper understanding of the material presented.

The authors have many professional colleagues and friends from different countries who must be acknowledged. Without their contributions and sacrifices this work would not have been completed. Special thanks go to the Division of Undergraduate Education of the National Science Foundation for the partial support of this work through its Course, Curriculum and Laboratory Improvement Program (Program Director Lance Z. Perez). The authors would like especially to thank Professor Athos Petrou for his editorial efforts in a critical reading of this book and for many valuable comments and suggestions. The authors also would like to thank undergraduate student Brian McSkimming for his thorough reading of the manuscript and helpful comments. We would like to thank undergraduate student Jonathan Bell for his help in preparation of figures.

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Notation

Symbols

A – amplitude
 A_{wf} – work function
 a – lattice constant
 a – acceleration
 $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ – basis vectors
 \mathbf{B} – magnetic flux density
 \mathbf{C} – wrapping vector
 C – capacitance
 c – speed of light in vacuum
 D – superlattice period
 \mathbf{D} – electric displacement
 \mathbf{d} – translation vector
 E – energy of a particle
 E_c – bottom of conduction band
 E_g – bandgap
 E_i – ionization energy
 E_v – bottom of valence band
 E_F – Fermi energy
 \mathbf{E} – electric field intensity
 e – elementary charge
 \mathbf{e}_r – unit vector directed along radius vector \mathbf{r}
 $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ – unit coordinate vectors
 \mathbf{F}_{gr} – gravitational force
 \mathbf{F}_L – Lorentz force
 \mathbf{F}_m – magnetic force
 \mathbf{F}_e – electric force
 g – acceleration due to gravity; density of states
 \mathbf{H} – magnetic field intensity
 H_n – Hermite polynomials
 $\hat{\mathcal{H}}$ – Hamiltonian operator
 h – Planck's constant
 \hbar – reduced Planck constant

I – current
 I_T – tunneling current
 $\mathbf{i}, \mathbf{j}, \mathbf{k}$ – unit coordinate vectors
 K – kinetic energy; superlattice wavenumber
 k – spring constant; wavenumber
 \mathbf{k} – wavevector
 k_B – Boltzmann's constant
 $k_e = 1/(4\pi\epsilon_0)$ – coefficient in SI system
 l – orbital quantum number
 \mathbf{L} – angular momentum
 L_x, L_y, L_z – dimensions of a sample
 m – orbital magnetic quantum number
 m^* – effective mass of an electron
 m_0 – mass of particle at rest
 m_e – electron mass in vacuum
 m_s – magnetic quantum number
 N – number of states
 N_A – Avogadro constant
 n – principal quantum number; concentration
 \mathbf{P} – Poynting vector
 \mathcal{P} – pressure
 P – probability
 \mathbf{p} – momentum
 \mathbf{q} – wavevector
 Q – charge
 q – charge of a particle
 R – universal gas constant
 r – magnitude of radius vector
 r_1 – first Bohr radius
 \mathbf{r} – coordinate vector
 R_∞ – Rydberg's constant
 \mathbf{R}_c – radius vector of center of mass
 \mathbf{S} – spin
 S – cross-section
 t – time
 T – time period; ambient temperature
 \mathcal{T}_d – translation operator
 U – potential energy; applied voltage
 U_0 – height of potential barrier
 U_G – gate voltage
 u – displacement of atoms from their equilibrium positions
 V – volume
 v – velocity

v_{gr} – group velocity
 v_{ph} – phase velocity
 V_c – velocity of center of mass
 W – work done by a force
 $X(r)$ – radial function
 x, y, z – spatial coordinates
 Y_{ml} – spherical harmonics
 α – angle; Madelung constant
 β – force constant; $b/(2m)$
 γ – gyromagnetic ratio
 δ – logarithmic decrement of damping
 $\delta(x)$ – Dirac's delta-function
 ϵ – dielectric constant of the medium; relative deformation
 ϵ_0 – permittivity of free space
 ε – energy
 ϕ – electrostatic field potential
 φ – azimuthal angle; chiral angle; phase difference
 λ – wavelength; parameter in characteristic equation
 λ_{Br} – de Broglie wavelength
 μ – magnetic permeability; magnetic moment
 μ_l – orbital magnetic moment
 μ_B – Bohr magneton
 $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ – Laplace operator
 ψ – stationary wavefunction
 Ψ – time-dependent wavefunction
 Ω – angular velocity of a particle
 ω – frequency
 ω_e – frequency of electron oscillations
 ω_q – frequency of harmonic oscillator
 ρ – three-dimensional density
 τ – torque
 θ – polar angle

Chapter 1

The nanoworld and quantum physics

1.1 A review of milestones in nanoscience and nanotechnology

It is extremely difficult to write the history of nanotechnology for two reasons. First, because of the vagueness of the term “nanotechnology.” For example, nanotechnology is very often not a technology in the strictest sense of the term. Second, people have always experimented with nanotechnology even without knowing about it. Ironically enough, we can say that the medieval alchemists were the founding fathers of nanoscience and nanotechnology. They were the first researchers who tried to obtain gold from other metals. The ancient Greek philosopher Democritus also can be considered as a father of modern nanotechnology, since he was the first to use the name “atom” to characterize the smallest particle of matter. The red and ruby-red opalescent glasses of ancient Egypt and Rome, and the stained glasses of medieval Europe, can be considered as the first materials obtained using nanotechnology. An exhibition at the British Museum includes the Lycurgus cup made by the ancient Romans. The glass walls of the cup contain nanoparticles of gold and silver, which change the color of the glass from dark red to light gold when the cup is exposed to light. In 1661 the Irish chemist Robert Boyle for the first time stated that everything in the world consists of “corpuscles” – the tiniest particles, which in different combinations form all the varied materials and objects that exist.

In modern history the first practical breakthrough in nanotechnology was made by the American inventor George Eastman, who in 1884 fabricated the first roll film for a camera. This film contained a photosensitive layer of silver bromide nanoparticles. In 1931 the German physicists Max Knoll and Ernst Ruska developed an electron microscope, which for the first time allowed one to study nanoobjects.

The development of modern optical, microelectronic, material science, chemical, biological, and other technologies, which took into account quantum-dimensional effects, and, subsequently, the development of the main concepts and methods for the formation and control of nanoparticles has accelerated at an

explosive rate. This development was based on the achievements and discoveries made by researchers in diverse fields of science.

The notion of “nanotechnology” was introduced for the first time by Richard Feynman in 1959 in his famous Caltech lecture “There’s plenty of room at the bottom: an invitation to enter a new field of physics.” Richard Feynman imagined the world of the nanoscale where the fundamental laws of quantum physics define the behavior of a single atom and control the formation of different structures from individual atoms. This vision of the great scientist ushered in the modern era of nanotechnology. The main achievements of this era are the following.

In 1952, L. V. Radushkevich and V. M. Lukyanovich published the first clear images of 50-nm-diameter carbon nanotubes. Carbon nanotubes were rediscovered many times after that.

In 1966, Robert Young suggested the use of piezomotors for positioning; these are currently used to move the tip in scanning-tunneling microscopes (STMs) and atomic-force microscopes (AFMs) with an accuracy of 10^{-2} – 10^{-3} nm.

In 1968, Alfred Cho and John Arthur developed the theoretical foundations of nanotechnology for the processing of surfaces.

In 1974, the Japanese physicist Norio Taniguchi in his report “On the basic concept of nanotechnology” coined the term “nanotechnology,” which he suggested using to name all the processes which take place in objects of size less than 1 μm .

In 1981, Gerd Binnig and Heinrich Röhler developed their first STM, which enabled them to see individual atoms.

In 1985, Robert Curl, Harold Kroto, and Richard Smalley discovered fullerene – a molecule that resembles a soccer ball and contains 60 carbon atoms. This discovery accelerated the development of the fabrication technology of other carbon nanomaterials such as carbon nanotubes.

In 1986, the atomic-force microscope was introduced by Gerd Binnig, Calvin Quate, and Christoph Gerber. The same year the book *Engines of Creation*, by Eric Drexler which has been called the Bible of nanoscience, was published. Eric Drexler described in his book molecular self-replicating robots, which can assemble molecules, decompose molecules, record in a nanocomputer’s memory programs for self-replication, and realize these programs. The predictions for a 20-year period made in this book are incredibly becoming reality. Also in 1986, the American physicist Arthur Ashkin invented *optical tweezers* – the device for manipulation of microobjects and nanoobjects with the help of a focussed laser beam.

In 1987, the French physicist Jean-Marie Lehn introduced the notions of “self-organization” and “self-assembly.”

In 1990, Donald Eigler showed that it is possible to develop a molecular automaton. With the help of STM he wrote on one of the crystallographic edges of nickel the name of his company “IBM” using 35 individual xenon atoms.

Further studies showed that it is possible to fix atoms to the surfaces of other materials. Submolecular assembly became a reality from this moment on.

In 1991, the first artificial metamaterial, which was called by its creator, the American physicist Eli Yablonovich, “photonic crystal,” was produced.

In 1998, the Dutch physicist Cees Dekker fabricated the first field-effect nanotransistor, which was based on a carbon nanotube. The technology for fabrication of nanotubes of length larger than 300 nm was developed.

In 1999, the American physicists Mark Reed and James Tour formulated the principles of the manipulation of a single molecule as well as chains of molecules.

In 2000, the principles of nanotomography, i.e., the creation of three-dimensional images of the inner structure of matter with a resolution of 100 nm, were developed.

In 2001, IBM researchers developed the first examples of logical circuits constructed on the basis of carbon-nanotube field-effect transistors.

In 2002, Cees Dekker created the first bionanostructure – a synthesis of a carbon nanotube and a DNA molecule.

In 2003, an international team of researchers deciphered the sequence of the human genome.

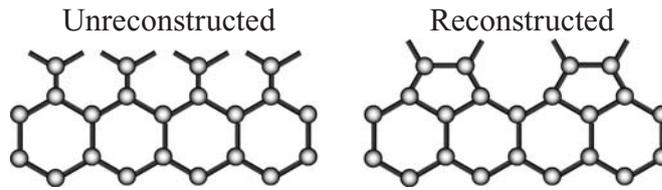
In 2004, British and Russian scientists obtained the first samples of graphene – a single layer of graphite, which has a two-dimensional hexagonal lattice.

In 2001–2005 a team of American scientists deciphered the mechanism of the replication of genetic information by cells.

In 2007 an international group of physicists from the USA, Germany, and Holland developed a scanning-electron microscope with subatomic resolution of 0.05 nm. The same year a group of American scientists developed the technology of scanning nanolithography with a resolution of 12 nm and a recording speed of more than 1 mm s^{-1} .

At present it is commonly accepted that Nobel laureate Richard Feynman in his lecture “There’s plenty of room at the bottom” was the first to relate nanostructures and nanotechnology. In his lecture Feynman suggested that in the future it will be possible to move individual atoms with the help of devices of the same size. Using such devices, macroobjects can be assembled atom by atom, making the fabrication process cheaper by several orders of magnitude. It will be enough to supply these nanorobots with the necessary amount of molecules and write a program for the fabrication of the required product. In his lecture Feynman also mentioned the prospects of nanochemistry for the synthesis of new materials. As soon as physicists create these devices, which will be able to operate with individual atoms, most of the traditional methods of chemical synthesis will be replaced by the methods of atomic assembly. The development of such a technology at the atomic scale will help to solve many problems of chemistry and biology. One can only wonder how the great scientist envisioned the enormous potential of nanotechnology.

Figure 1.1 Reconstruction of Si surface.



1.2 Nanostructures and quantum physics

The prefix “nano” means one billionth part of something. Therefore, from the formal point of view nanostructures can be any objects with size (at least in one of the directions) of the order of 100 nm or less. Thus, nanostructures are objects whose sizes range from individual atoms (the size of an atom is about 0.1 nm) to large clusters consisting of up to 10^8 atoms or molecules. The transition of material structures from macroscale to nanoscale results in sharp changes of their properties. These changes are due to two reasons. The first reason is the increase of the proportion of surface atoms in the structure. The surface of the material can be considered as a special state of matter. The higher the proportion of atoms on the surface, the stronger are effects connected with the surface of a specimen. The ratio of the number of atoms located within a thin near-surface layer (~ 1 nm) to the total number of atoms in a specimen increases with decreasing volume of the specimen. Also the surface atoms are under conditions, which are very different from the conditions for the bulk atoms, because they are bound to the neighboring atoms in a different way. Atoms in the surface layer have some of their chemical bonds broken and therefore they are free to make new bonds. This results in a tendency of those electrons which do not form a pair to form a bond either with atoms of some other type that the surface adsorbs or with atoms of the same type.

If the surface is clean and smooth and there are no other atoms then the surface atoms establish bonds with each other. In the simplest case neighboring atoms of a surface layer unite to give so-called *dimers* (or pairs). The atoms of each dimer approach each other and at the same time move away from the other neighboring atoms which have formed dimers. Therefore, the lattice constant of the surface changes. Such a process is called *reconstruction*. As a result of atomic reconstruction a new type of atomic arrangement occurs at the surface (see Fig. 1.1). Also for those atoms at the edges of monatomic terraces and cavities, where the number of neighboring atoms is much smaller than that in the bulk volume, there exist special conditions. For example, the interaction of electrons with the free surface creates specific near-surface energy states. These facts lead us to consider the near-surface layer as a new state of matter.

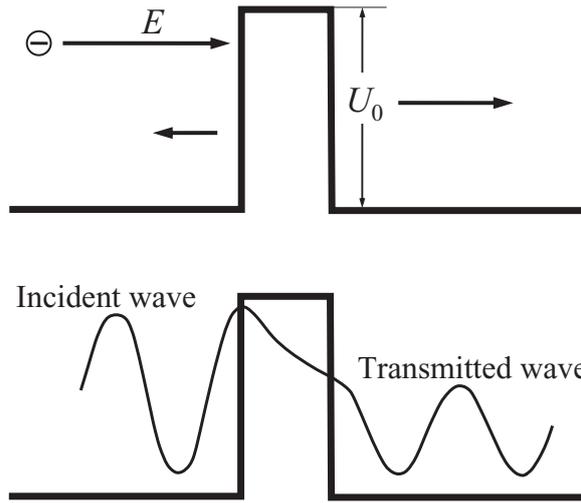
Less clear is the second group of dimensional effects, which can be explained only by using a quantum-mechanical description. As will be shown further on, this group of effects is related to a significant increase of quantum effects when

the size of the region where an electron moves significantly decreases. Therefore, the properties of nanoparticles strongly change compared with the properties of macroparticles of the same material. This happens mostly at characteristic sizes of 10–100 nm. According to quantum mechanics an electron can be presented as a wave, whose physical meaning will be explained in the following chapters of the book. The propagation of an electron wave in nanosize structures and its interaction with the boundary surfaces lead to the effects of energy quantization, interference of incident and reflected waves, and tunneling through potential barriers. Such a wave, which corresponds to a freely moving electron in an ideal crystalline material, can propagate in any direction. The situation radically changes when an electron is confined within a structure, whose size, L , along one of the directions of propagation is limited and is comparable to the electron de Broglie wavelength. In this case the electron cannot propagate in this specific direction and the electron can be described by a standing wave: only an integer number of electron half-wavelengths can fit within the structure of length L . This leads to the existence of non-zero discrete values of energy that an electron can have in this direction, i.e., the electron energy in this direction is no longer continuous but instead its spectrum consists of a set of separate energy levels. As a result, quantum confinement of electron motion increases the electron minimum energy. In the case of nanometer length of L the distance between energy levels exceeds the energy of thermal motion of the electron, which allows control of the electron energy by external fields. If in the two other directions the size of the structure is not limited, the energy of electron motion in these directions is not quantized and the electron may have any energy values. All this leads to the situation when the electric properties of nanosize structures differ from the well-known bulk properties of the materials from which the nanostructures are fabricated.

The self-interaction of electron waves in nanosize structures as well as their interaction with inhomogeneities and interfaces can be accompanied by the phenomenon of interference, which resembles the interference of electromagnetic waves. The distinctive feature of electron waves is that they are charged waves because the electron is a charged particle. This allows one to control the propagation of electron waves in nanostructures by the application of electric and magnetic fields.

The wave nature of microscopic particles, including electrons, is manifested by their ability to penetrate through an obstacle even when the particle's energy is lower than the height of the potential barrier of the corresponding obstacle. This phenomenon is called *tunneling* and it is a purely quantum phenomenon. According to classical mechanics an electron with energy E that encounters an obstacle with the potential barrier $U_0 > E$ on its path will reflect from this obstacle. However, the electron as a wave is transmitted through the obstacle (see Fig. 1.2). Quantum confinement in nanostructures specifically affects the processes of tunneling in them. Thus, the quantization of electron energy in very

Figure 1.2 An electron with energy E tunneling through the potential barrier U_0 ($U_0 > E$).



thin and periodically arranged potential wells leads to the electron tunneling through these structures only having a certain energy, i.e., tunneling has a *resonance character*. Another such effect is *single-electron tunneling* when a charge is transmitted in an external electric field in portions equal to the charge of a single electron. After each tunneling event the system returns to its initial state. The quantum effects discussed above are widely used in nanoelectronic devices and elements of informational systems, but applications of electron quantum phenomena are not limited to these systems and devices. Currently active research is continuing in this direction.

The development of nanotechnology, which includes molecular-beam epitaxy, modern methods of molecular-beam lithography, diagnostics of nanoobjects, scanning-electron microscopy, scanning-tunneling microscopy, and atomic-force microscopy, is providing fundamentally new tools for the development of the elements of silicon, heterostructure, carbon, and nanomagnetic electronics. Nanotechnology that uses effects of self-organization, and molecular and atomic self-assembly, has become an alternative to the fabrication of macroobjects. The elemental basis of nanoelectronics includes a large number of structures and devices whose operation is based on various physical principles. Considering a variety of prospective directions, special attention must be paid to three of them: (1) the direction related to information technologies, (2) carbon nanotubes, and (3) nanoelectromechanical systems (NEMSs).

When considering any transport process (electric current, thermal conductivity, etc.), we assign the carriers a certain effective mean-free-path length, l . For a characteristic size of the structure $L \gg l$ the scattering of carriers takes place in the bulk of structure and it does not depend on the geometry and the size of the object. If, on the other hand, $L \leq l$, then the situation radically changes and all

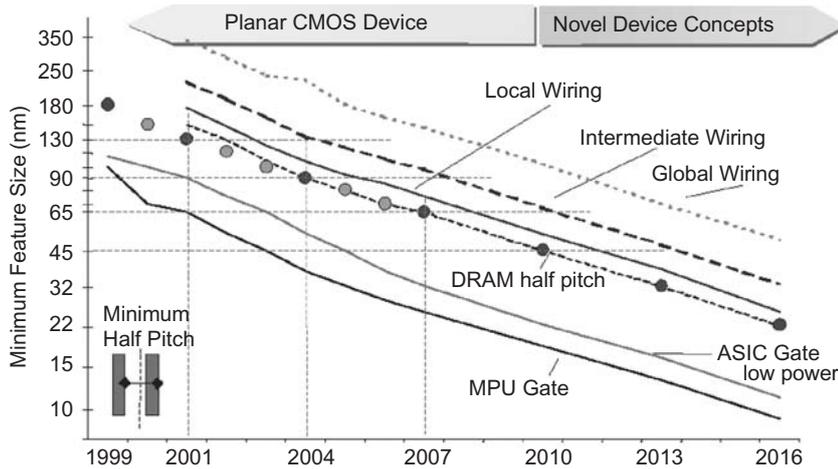


Figure 1.3 Technology nodes and minimum feature sizes from the ITRS 2002 Roadmap: MPU, microprocessing unit; ASIC, application-specific integrated circuit.

transport characteristics depend on the size of a specimen. Some of these effects can be described within the framework of classical physics, but there is a group of size effects that can be understood only on the basis of quantum mechanics.

Any achievements in nanoscience first of all are considered in terms of how they can be applied to the information technologies. Despite increasing difficulties, a very high rate of improvement of all significant parameters of electronics has been maintained during the last few decades. The most revolutionary achievements approach quantum limits when the working elements become a single electron, a single spin, a single quantum of energy, and so on. This may increase the speed of operations to close to 1 THz (10^{12} operations per second) and the writing density to about 10^3 Tbit cm^{-2} , which is significantly higher than the existing values, and energy consumption may be reduced by several orders of magnitudes. Having such a density of writing, we can store on a disk the size of a wristwatch a whole library (see Fig. 1.3 for the trends in miniaturization).

Quantum phenomena are currently widely used in nanoelectronic elements for information systems. However, utilization of the electron quantum properties is not limited to this. It is important to understand that the nanoscale is not just the next step in miniaturization. The behavior of nanostructures, in comparison with individual atoms and molecules, shows important changes, which cannot be explained by the traditional models and theories. The development of these new fields of science undoubtedly will lead to further scientific progress.

This book introduces the reader to the main ideas and laws of quantum mechanics using numerous examples, such as how to calculate energy spectra and other physical characteristics of certain types of nanostructures. In this book the authors had no intention to cover all the aspects of modern quantum physics and nanoelectronics because this task cannot be accomplished without deeper knowledge of subjects such as solid-state physics, the physics of semiconductors,

and statistical physics. Nevertheless, the authors hope that this first acquaintance with quantum physics for most of the readers of this book will be useful in their future professional careers and will encourage them to study quantum phenomena at a higher level.

1.3 Layered nanostructures and superlattices

Atoms and molecules until recently were considered the smallest building bricks of matter. As the latest achievements of nanotechnology show, materials can be built not only from single elements but also from whole blocks. Clusters and nanoparticles may serve as such building blocks. Crystalline materials that consist of nanoscale blocks are called *bulk nanocrystalline materials*. These materials may have unique properties. For example, from everyday life we know that, if a material is durable, then it can be simultaneously fragile. The best example of a very durable but fragile material is glass. It turns out that some nanocrystalline materials are especially durable and elastic simultaneously. The unique mechanical properties of nanocrystalline materials in many respects are connected with the existence of an interface between nanoparticles. Such materials have properties that differ from those of the corresponding bulk material.

Below we discuss a class of nanocrystalline materials known as *superlattices*. There are different types of superlattices. Those of one type – heterostructure superlattices – can be grown by alternating layers of two different semiconductor materials, e.g., GaAs and AlGaAs, which have very similar lattice constants. Therefore, heterostructure superlattices can be referred to as *layered structures*. The main elements of the layered structures are two types of layers: (1) the layer of the so-called *narrow-bandgap semiconductor* (GaAs) and (2) the layer of the *wide-bandgap semiconductor* (AlGaAs). These two elements can be used to create another layered structure called a *quantum well*. A thin layer of GaAs between two layers of AlGaAs creates a potential well for an electron, where its motion is restricted. In the next chapters of the book we will consider theoretically the electron motion in such layered structures (see Fig. 1.4).

More generally, superlattices are structures with periodic repetition along one, two or three directions of regions with different values of some physical quantity (dielectric or magnetic permeability, the type and mobility of carriers, the work function, elasticity, and so on). Periodicity along one direction of such a layered structure results in a *one-dimensional superlattice*. If there is a periodicity along two directions, then the superlattice is *two-dimensional*. An example of such a superlattice is a two-dimensional system of quantum wires of a semiconductor formed on the surface of another semiconductor. In such a two-dimensional material the electric properties of material periodically change along two directions. In a *three-dimensional superlattice* the periodicity of physical properties can be observed along three directions.

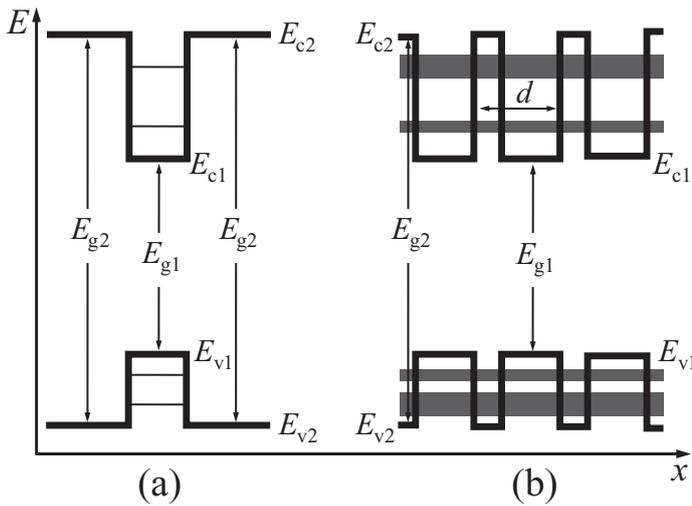


Figure 1.4 The energy bandstructure of a semiconductor quantum well (a) and a type-I heterostructure superlattice (b): E_{g1} and E_{g2} are the bandgaps, E_{c1} and E_{c2} are the bottoms of the conduction bands, and E_{v1} and E_{v2} are the tops of the valence bands of narrow-bandgap and wide-bandgap semiconductors, respectively; d is the period of the heterostructure superlattice.

Semiconductor superlattices, which consist of thin semiconductor layers alternating in one direction, i.e., heterostructure superlattices, have a wide range of applications. The period of such a superlattice usually is much larger than the lattice constant but is smaller than the electron mean free path. Such a structure possesses, in addition to a periodic potential of the crystalline lattice, a potential due to the alternating semiconductor layers. The existence of such a potential significantly changes the energy bandstructure of the semiconductors from which the superlattice is formed. A very important peculiarity of a superlattice is the existence of its own *minibands*. These peculiarities become apparent when studying optical and electric properties of semiconductor superlattices. Since semiconductor superlattices have special physical properties, we can consider superlattices as a new type of semiconductor materials.

The superlattices can be of several types. The most common are *heterostructure* superlattices and *modulation-doped* superlattices. A heterostructure superlattice is a representative of layered nanostructures: it consists of epitaxially grown alternating layers of different semiconductors, which have similar lattice constants. Historically the first heterostructure superlattices were grown for the semiconductor system GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$. The success in the growth of such a superlattice was due to the fact that Al has the same valence and ionic radius as Ga, and therefore the incorporation of Al does not cause noticeable distortions of the crystalline structure of the material. At the same time Al may sufficiently modulate the amplitude of the superlattice potential. Depending on the relative position of the semiconductor energy bands, heterostructure superlattices can be divided into two main types: type I and type II. GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ superlattices belong to the first type. The conduction-band minimum and the maximum of the valence band for GaAs are situated inside of the bandgap of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (see Fig. 1.4). Such band alignment leads to a periodic system of quantum wells

for current carriers in GaAs, which are separated from each other by potential barriers created by $\text{Al}_x\text{Ga}_{1-x}\text{As}$. The depth of the quantum wells for electrons is defined by the difference between the minima of the conduction bands of the two semiconductor materials, and the depth for quantum wells for holes is given by the difference between the maxima of the valence bands.

In the type-II heterostructure superlattices the minimum of the conduction band of one semiconductor is situated in the energy bandgap of the second, and the maximum of the valence band of the second semiconductor lies in the bandgap of the first. A representative of this type of superlattice is the system $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaSb}_{1-y}\text{As}_y$.

In modulation-doped superlattices the periodic potential is formed by the alternating layers of n- and p-types of the same semiconductor. These layers can be separated by undoped layers. The most common material for fabrication of modulation-doped superlattices is GaAs.

Besides heterostructure and modulation-doped superlattices, other types of superlattice are possible: they differ by the way in which the modulation potential is created. In spin superlattices, the semiconductor material is doped with magnetic impurities. A periodic potential occurs in such superlattices when an external magnetic field is applied. A superlattice potential can be created also by periodic deformation of a specimen in the field of a powerful ultrasound wave and an electromagnetic standing wave. Superlattices have a wide range of applications in diverse semiconductor devices. The most striking example is their use in cascade semiconductor lasers.

1.4 Nanoparticles and nanoclusters

Nanoparticles are atomic or molecular structures, whose size is equal to 100 nm or less. Such nanoobjects consist of 10^8 or fewer atoms (or molecules). Their properties differ from the properties of bulk materials consisting of the same atoms (or molecules). Nanoparticles whose size is equal to 10 nm or less that contain up to 10^3 atoms are called *nanoclusters* or, simply, *clusters*. Numerous studies have shown that for a given material there exist clusters having only a certain number of particles. This means that clusters consisting of these numbers of particles are the most stable ones. The corresponding numbers are called *magic numbers*. The set of magic numbers shows how clusters (from the smallest to the biggest) are formed from individual particles. An example of this structure of stable clusters is the *closest packing* of identical spheres.

The first magic number is 13, which corresponds to the packing when the internal sphere is surrounded by 12 spheres of the same radius. If subsequent shells of identical spheres are also filled, then their total number corresponds to the following magic numbers: 55, 147, 309, 567, and so on. The number of particles, N_n , in the n th shell can be calculated using the following formula:

$$N_n = 10n^2 + 2. \quad (1.1)$$

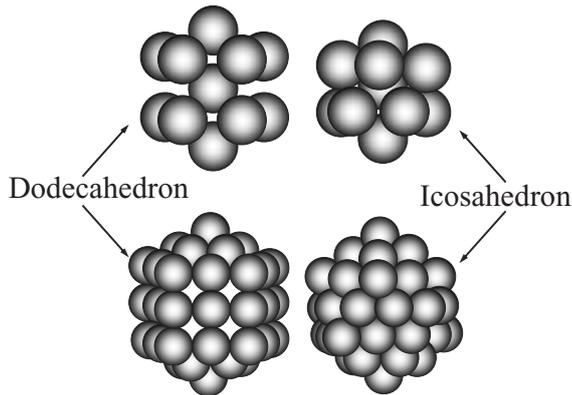


Figure 1.5 Clusters of 13 and 55 nanoparticles.

Thus, in the first shell there are 12 spheres ($N_1 = 12$) around a single sphere and, therefore, the magic number is equal to 13. In the second shell there are 42 spheres ($N_2 = 42$) and, by adding this number to 13, we obtain the next magic number which is equal to 55. In this case the cluster has the form of an *icosahedron* and this structure is the most stable. In some cases clusters have the form of a *dodecahedron*. Both types of packing of spheres are shown in Fig. 1.5. Such clusters are formed mostly during growth under vacuum conditions from liquid or gaseous phases.

Many physical properties of nanoparticles or nanoclusters differ from the properties of a bulk material consisting of the same type of atoms. Thus, nanoparticles and nanoclusters have a crystalline structure slightly different from the bulk crystal, which is due to the significant influence of the surface of the specimen. For example, gold nanoclusters of size 3–5 nm crystallize not having a face-centered cubic lattice as bulk gold does, but as an icosahedral structure. Let us estimate the number of surface atoms in a cluster that consists of N atoms and whose form is close to spherical. The volume of such a cluster is

$$V \approx \frac{4\pi}{3} R^3 = V_0 N, \quad (1.2)$$

where R is the radius of a sphere and V_0 is the volume that *corresponds* to an individual atom. Note, it is not the volume of the atom itself! Let us assume that the volume V_0 can be presented as a sphere of radius a . Therefore,

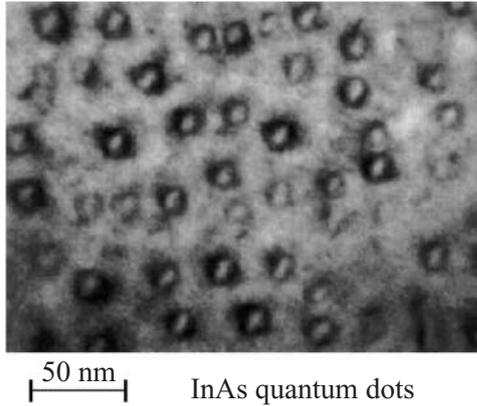
$$V_0 = \frac{4\pi}{3} a^3. \quad (1.3)$$

For the structure's closest packing the parameter a is almost equal to the radius of an atom. Then, from Eqs. (1.2) and (1.3), we find that the size of a cluster and the radius of an individual atom are related as

$$R = a N^{1/3}. \quad (1.4)$$

For most clusters the size of constituent atoms is close to $a \approx 0.1$ nm. From Eq. (1.4) it follows that a cluster that consists of 10^3 atoms has a size of about $R \approx 1$ nm. For a cluster that consists of molecules this size is significantly larger.

Figure 1.6 A scanning electron microscope image of InAs quantum dots in a GaAs matrix.



The surface area, S , is a very important characteristic of a cluster. Let us estimate S for a cluster with a spherical surface:

$$S \approx 4\pi R^2 = 4\pi a^2 N^{2/3}. \quad (1.5)$$

The number of atoms on the surface of a cluster, N_S , is connected with the surface area, S , as

$$S \approx S_0 N_S = 4\pi a^2 N_S, \quad (1.6)$$

where $S_0 = 4\pi a^2$ is the area that corresponds to an individual atom on the surface of a cluster. Let us find the ratio of the number of atoms, N_S , on the surface of a cluster to the number of atoms, N , in a cluster using Eqs. (1.2) and (1.6):

$$\frac{N_S}{N} = \frac{S V_0}{S_0 V} = \frac{3V_0}{R S_0} = \frac{a}{R} = \frac{1}{N^{1/3}}. \quad (1.7)$$

As we see from the above expressions, the proportion of atoms on the surface of a cluster rapidly decreases with increasing cluster size. Noticeable influence of the surface occurs at a cluster size less than 100 nm.

The formation of energy bands of crystals is manifested by the quantum-dimensional effects, which become apparent when the size of the region of electron motion is comparable to the electron de Broglie wavelength in the material. In metals this wavelength is about 0.5 nm, whereas in semiconductors this wavelength can be up to 1 μm . Therefore, quantum-dimensional effects can be observed at much larger sizes of semiconductor nanoparticles than for metal nanoparticles. In semiconductor clusters called quantum dots electrons are confined in all three directions. Such individual quantum dots or their arrays are frequently created in the matrix of some other semiconductor material. In this case quantum dots are regularly positioned as “islands” of one semiconductor on the surface of the other semiconductor. Figure 1.6 shows the example of an InAs quantum-dot array grown on the surface of GaAs.

The discreteness of electron energy in an individual quantum dot allows one to call it an *artificial atom*. On the basis of quantum dots highly-efficient miniature sources of light can be developed. By varying the size and composition of quantum dots new light-emitting diodes (LEDs) of different colors may be fabricated. Owing to the tunneling effect, electron transport along a chain of quantum dots is possible. This can be used for the development of numerous electronic devices.

In semiconductor devices of micrometer size it is necessary to control (including turn on and turn off) the current, which corresponds to the flux of hundreds of thousands of electrons. With the help of quantum dots we can control the motion of single electrons, which opens new possibilities for the further miniaturization of semiconductor devices and further decrease of power consumption.

Example 1.1. Estimate the size of a spherical nanocluster of water consisting of 100 atoms. Estimate the area and diameter of monomolecular water film that is formed when the nanocluster is spread over the surface of a sample.

Reasoning. The number of molecules, N , in a water cluster of volume V and mass m is defined by the following equation:

$$N = \frac{m}{\mu} N_A, \quad (1.8)$$

where $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant and μ is the molar mass of a molecule. The volume of one molecule of water, V_0 , can be estimated according to the following formula:

$$V_0 = \frac{V}{N} = \frac{V\mu}{mN_A} = \frac{\mu}{\rho N_A} = \frac{4}{3}\pi r_0^3, \quad (1.9)$$

where $\mu = 18 \text{ g mol}^{-1}$ is the molar mass of water and $\rho = 1 \text{ g cm}^{-3}$ is the density of water. From Eq. (1.9) we can find the radius of a molecule, r_0 :

$$r_0 = \left(\frac{3\mu}{4\pi\rho N_A} \right)^{1/3} \approx 0.2 \text{ nm}. \quad (1.10)$$

Let us write the relationship that connects the cluster's volume, V , and radius, R , with the radius of a water molecule, r_0 :

$$V = \frac{4}{3}\pi R^3 = N \frac{4}{3}\pi r_0^3. \quad (1.11)$$

From Eq. (1.11) we find the cluster's radius, R :

$$R = N^{1/3} r_0 \approx 0.9 \text{ nm}. \quad (1.12)$$

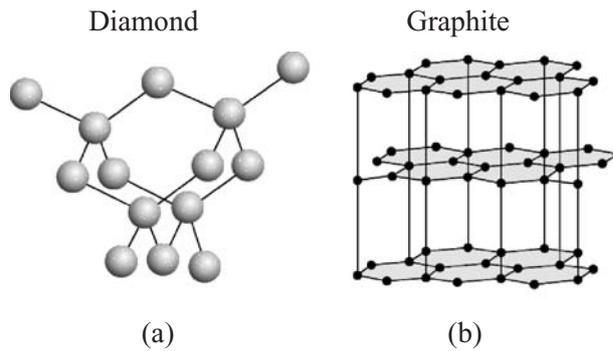
Since the diametral cross-section of a molecule is defined as

$$S_0 = \pi r_0^2, \quad (1.13)$$

the area of the water spot is defined by the following expression:

$$S = \pi R_s^2 = N\pi r_0^2 \approx 12.6 \text{ nm}^2, \quad (1.14)$$

Figure 1.7 The crystalline structures of diamond (a) and graphite (b).



where R_S is the radius of the water spot which occurred after spreading of the water cluster. From the last expression we find R_S :

$$R_S = N^{1/2}r_0 \approx 2 \text{ nm.} \quad (1.15)$$

1.5 Carbon-based nanomaterials

Carbon (C) is an element of group IV of the Periodic Table of the elements. Therefore, it has four valence electrons. It is widespread and it is the basis of living matter, but there is only 0.19% of carbon in the Earth's crust. The ability of atoms of the same chemical element to combine in different spatial configurations is called *allotropy*. Carbon possesses this property in full measure: there are several allotropic forms of carbon. First of all are diamond and graphite, which are shown in Fig. 1.7. In the diamond crystal each carbon atom is in the site of a tetrahedral lattice with average distance between atoms equal to 0.154 nm. Four valence electrons of each carbon atom form four strong C—C bonds. It is difficult to break them since there are no conduction electrons: diamond crystal is a dielectric. For the same reason diamond has exceptional hardness and a high melting temperature ($T_{\text{mt}} = 3277 \text{ K}$).

Another allotropic form of carbon is graphite, which has exceptionally different physical properties from those of diamond. Graphite is a soft black substance consisting of easily flaked layers, which are called *graphene sheets*. Within the plane of a graphene sheet carbon atoms have strong covalent bonds with each other. These bonds form the lattice consisting of regular *hexagons*. However, in contrast to the case of diamond, in graphite only *three electrons* participate in establishing bonds. The fourth electron of each carbon atom does not participate in the formation of interatomic bonds and therefore it is free. This makes graphite such a good conductor. There is only a weak attraction between graphite layers due to van der Waals forces. The weakness of the attraction between graphite layers results in their easy sliding with respect to each other. Therefore, they can be easily flaked apart.

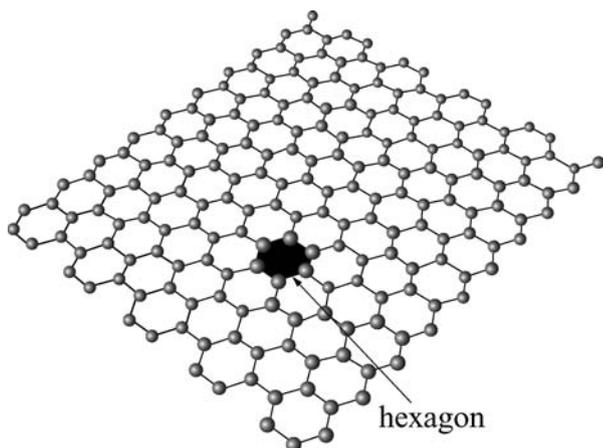
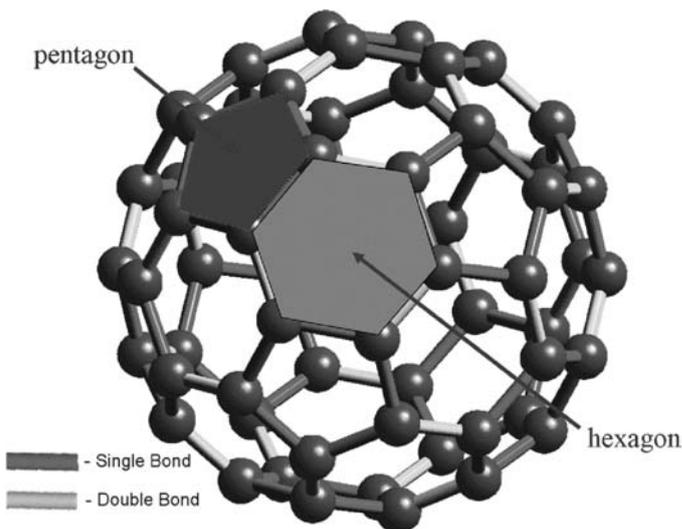


Figure 1.8 A schematic model of graphene in the form of a two-dimensional hexagonal lattice.

1.5.1 Graphene

Although graphite had been known for a long time, researchers managed to obtain single graphite layers and study them only in 2004. The material, which is one gigantic two-dimensional plane carbon molecule of monatomic width, was called *graphene* (see Fig. 1.8). Thus, graphene is a *two-dimensional crystal*, which consists of a single layer of carbon atoms composed in a *hexagonal lattice*. The properties of graphene turned out to be amazing. It is well known that graphite is a *semimetal*, i.e., it does not have a *bandgap*. The *bandstructure* of graphene also does not have a bandgap. At the points of intersection of *valence band* and *conduction band* the energy spectrum, $E(\mathbf{k})$, of electrons and holes has a linear dependence. A similar spectrum is possessed by *photons*, whose mass at rest is equal to zero. Therefore, it is said that the *effective mass* of electrons and holes in graphene near the intersection point is equal to zero. However, let us note that, despite the fact that photons and massless carriers in graphene have similarities, there are significant differences between them that make carriers in graphene unique. First of all, electrons and holes are *fermions* and they possess charge. There are no analogs for these massless charged fermions among known elementary particles. Second, graphene possesses unusual physical and chemical properties. Since the effective mass of electrons in graphene tends to zero, they have a high mobility, 100 times larger than the mobility of electrons and holes in crystalline silicon – the most widely used material in nanoelectronics. This explains the gigantic thermal conductivity and good electrical conductivity of graphene. These properties, together with the transparency and outstanding mechanical properties, make graphene a prospective material for nanotechnology. Using graphene as a basis, a new class of materials with extreme consumer properties can be developed. However, the most interesting effects are the electronic properties of graphene since their application opens new possibilities for

Figure 1.9 A three-dimensional model of a C_{60} fullerene molecule (or buckyball).



the development of elements for nanoelectronics. Thus, depending on the type of substrate and geometrical dimensions, the electronic properties of graphene may be either metallic or semiconducting.

1.5.2 Fullerenes

In 1990, one more crystalline modification of carbon called *fullerite* was discovered. Fullerite has as a structural unit not a carbon atom, as in the case of graphene or a carbon nanotube, but a molecule of *fullerene*. Fullerenes are a new class of carbon material, whose molecules have the form of skeleton structures reminding one of a soccer ball. In such molecules carbon atoms are at the vertices of regular pentagons and hexagons, which are placed on the surface of a sphere or a spheroid (see Fig. 1.9). Different fullerene molecules can consist of 28, 32, 50, 60, 70, 76, and so on carbon atoms. Although there are various geometrical forms of fullerenes, quantum-mechanical calculations of stable carbon structures show that their formation obeys certain rules. Stable carbon clusters have the form of polyhedra. The outer electron shell of an individual carbon atom provides stable bonds, which result in the formation of carbon pentagons or hexagons. The most stable fullerene molecule is C_{60} . The skeleton of the C_{60} molecule consists of 12 regular pentagons and 20 inequilateral hexagons. Each hexagon has three pentagons and three hexagons as its neighbors, whereas pentagons have as neighbors only hexagons. Such a structure provides the C_{60} molecule with an extraordinary stability. During the formation of closed geometrical figures pentagons provide the bending of a graphene sheet. The length of C—C bonds depends on the boundary on which they are located. The length of this bond at

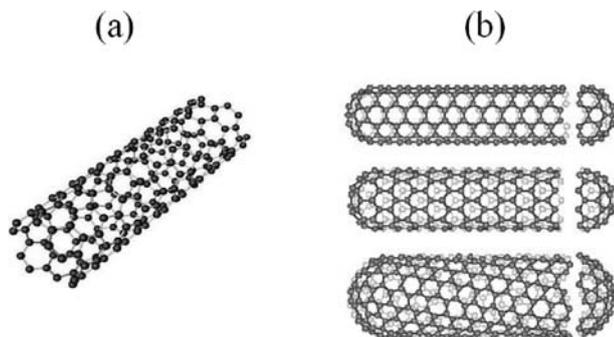


Figure 1.10
Three-dimensional
models of carbon
nanotubes: (a) open and
(b) closed nanotubes.

the hexagon–hexagon boundary is equal to 0.132 nm and it is a double covalent bond. The length of the bond on the hexagon–pentagon boundary is equal to 0.144 nm and it is a single covalent bond. Three electrons of each carbon atom participate in the formation of the fullerene structure. The fourth electron has a free chemical bond. Therefore, these molecules possess the important property of adsorbing atoms of other materials (for example, atoms of hydrogen or fluorine).

In the fullerite crystalline structure, C_{60} fullerene molecules are attracted to each other by the weak van der Waals forces. In the face-centered cubic lattice the centers of C_{60} molecules are at a distance of 1 nm from each other. In the unit cell of fullerite 26% of the volume between spherical molecules of fullerene is hollow. Atoms of alkali elements can be easily placed in this empty space. The C_{60} crystal is a dielectric, but, when it is doped with atoms of alkali elements, it becomes a conductor. Thus, doping of this crystal with potassium forms a K_3C_{60} compound. In this compound the potassium is in an ionized state and each C_{60} molecule acquires an additional three electrons weakly connected with the molecule moving around the crystal, which makes the compound a conductor. On decreasing the temperature to $T_{cr} = 18$ K, a doped K_3C_{60} fullerite undergoes a transition into a superconducting state. The record temperature for the superconducting transition for $CHBr_3C_{60}$ of $T_{cr} = 117$ K has been demonstrated recently by researchers from IBM. In another crystal, $CHCl_3C_{60}$, the critical temperature was $T_{cr} = 80$ K. The measured lattice parameters of crystalline samples of the above-mentioned fullerites are 14.45 Å and 14.28 Å, respectively.

1.5.3 Carbon nanotubes

After the discovery of fullerenes it was established that graphene sheets can, under certain conditions, roll up into tubes. These objects were called *carbon nanotubes*. Carbon nanotubes are hollow elongated cylindrical structures of diameter from one to several tens of nanometers. The ideal carbon nanotube is rolled up into a cylindrical graphene sheet. There are different forms of carbon

nanotubes. Carbon nanotubes can be classified as single-walled or multiwalled, chiral and non-chiral, long and short, and so on. Carbon nanotubes can be open and closed, as shown in Fig. 1.10. Nanotubes are unusually strong with respect to stretching and flexing. Under high mechanical stress carbon nanotubes cannot be torn or broken. They just reconstruct their structure. Carbon nanotubes possess important properties for practical applications: they can sustain electric high-density currents, change their properties when they adsorb other atoms or molecules, emit electrons from their ends at low temperatures, and so on. Carbon is not the only material for the growth of nanotubes. So far nanotubes of boron nitride, boron and silicon carbides, and silicon oxide have been grown.

The authors recommend the following textbooks on quantum mechanics for further reading.

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Chapter 2

Wave–particle duality and its manifestation in radiation and particle behavior

2.1 Blackbody radiation and photon gas

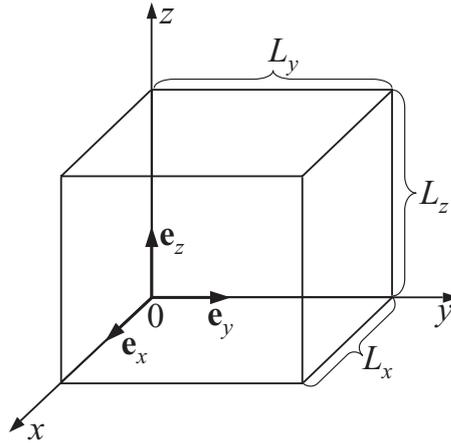
2.1.1 Thermal radiation

Heated bodies emit electromagnetic radiation over a wide frequency range because a part of their internal energy transforms into radiation energy. This type of radiation is called *thermal radiation* and it is caused by the supply of energy to the radiating body. If we place several bodies, heated to different temperatures, in a closed cavity with perfectly reflecting walls, then after a certain period of time the whole system will transfer to a state of thermal equilibrium with all bodies having the same temperature T . The notion of temperature, T , is introduced to characterize the amount of average kinetic energy, E_{kin} , of thermal motion of a body's particles. Energy in the Système International (SI) units is measured in joules (J) and temperature in degrees Kelvin (K). The temperature can be introduced as

$$T = \frac{2}{3} \frac{E_{\text{kin}}}{k_{\text{B}}}, \quad (2.1)$$

where $k_{\text{B}} = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is known as *Boltzmann's constant*. When the temperature of all bodies in the system becomes the same, then the energy emitted by the body becomes equal to the energy absorbed by the same body, and such a state of the system does not change with time. At the same time the radiation emitted by the heated bodies and cavity is in thermodynamical equilibrium, and therefore it is called *equilibrium radiation* (it is also known as *blackbody radiation*). Numerous experimental studies of this radiation have shown that its spectrum is continuous, i.e., the frequency interval of this radiation spans the entire electromagnetic spectrum. The distribution of energy of blackbody radiation significantly depends on the temperature of the radiation-emitting body. With increasing temperature the maximum of this distribution shifts to the region of higher frequencies and at the same time the total energy emitted by a body in the entire spectral range increases. Thus, bodies at room temperature

Figure 2.1 A cavity containing thermal radiation.



($T = 300$ K) emit energy with a maximum in the invisible infrared part of the spectrum (the wavelength is about $\lambda \approx 14 \mu\text{m}$). The surface of the Sun, which has the temperature $T \approx 6000$ K, has a maximum of radiation in the region of visible light ($\lambda \approx 0.5 \mu\text{m}$). During a nuclear explosion the temperatures attained are $T \approx 10^7$ K. Therefore, most of the energy of the explosion is carried away by highly penetrating X-ray radiation ($\lambda \approx 10^{-4} \mu\text{m}$).

The distribution of blackbody radiation of frequency ω is characterized by the spectral density u_ω , which has the dimension $[\text{J s m}^{-3}]$. The magnitude $u_\omega d\omega$ defines the energy of the radiation per unit volume in the interval of frequencies from ω to $\omega + d\omega$. The spectral density, $u_\omega(T)$, of blackbody radiation is a universal function of frequency and temperature, and it does not depend on the nature of the radiation-emitting body. Since this function describes the distribution of energy of an electromagnetic field, for a long time it was believed that it could be calculated on the basis of classical concepts. However, all the attempts to do this did not succeed.

2.1.2 The number of states and density of states

Let us consider a cavity with ideally reflecting walls, which has the form of a rectangular parallelepiped with edge lengths L_α , where $\alpha = x, y$, and z . In such a cavity the blackbody radiation as an electromagnetic field can exist only in the form of a superposition of standing electromagnetic waves, which have nodes at the walls of the cavity. Let us define the number of such standing waves which can be established in the cavity (see Fig. 2.1). The conditions for standing-wave formation along each of the axes are

$$L_x = n_x \frac{\lambda_x}{2}, \quad L_y = n_y \frac{\lambda_y}{2}, \quad L_z = n_z \frac{\lambda_z}{2}, \quad (2.2)$$

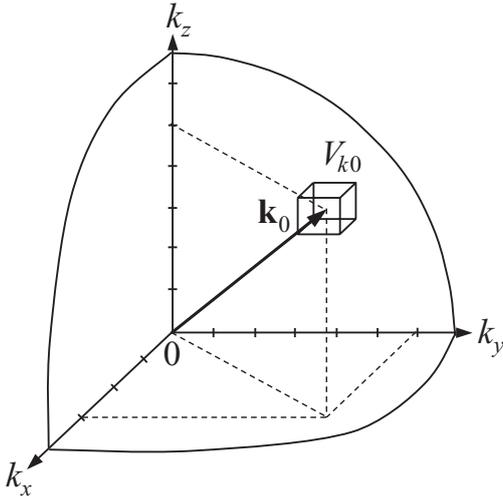


Figure 2.2 The region of k -space which corresponds to standing electromagnetic waves with positive components of the wavevector, \mathbf{k} .

where n_α are positive integer numbers, i.e., each length L_α between reflecting walls has to contain an integer number of half-waves with the wavelength λ_α along the corresponding direction. For the standing wave which is established in an arbitrary direction, its wavevector can be presented as

$$\mathbf{k} = k_x \mathbf{e}_x + k_y \mathbf{e}_y + k_z \mathbf{e}_z. \quad (2.3)$$

Taking into account that

$$k_\alpha = \frac{2\pi}{\lambda_\alpha} \quad (2.4)$$

(see Eq. (B.58) from Appendix B), the projections of a wavevector \mathbf{k} onto each of the coordinate axes take the form

$$k_\alpha = \frac{\pi n_\alpha}{L_\alpha}.$$

As a result the expression for the wavevector of an arbitrarily directed standing wave can be written in the following form:

$$\mathbf{k} = \pi \left(\frac{n_x}{L_x} \mathbf{e}_x + \frac{n_y}{L_y} \mathbf{e}_y + \frac{n_z}{L_z} \mathbf{e}_z \right). \quad (2.5)$$

In wavevector space (k -space) (see Fig. 2.2) the point with projections k_x , k_y , and k_z is defined by three numbers (n_x , n_y , and n_z), and corresponds to a standing wave. As a result we can assign for each standing wave in k -space a volume, V_{k0} :

$$V_{k0} = \frac{\pi^3}{L_x \times L_y \times L_z}. \quad (2.6)$$

This volume is often referred to as a *unit* or *primitive cell*. The wavenumber of such a standing wave, $k = |\mathbf{k}|$, is defined as

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2} = \pi \sqrt{\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}}. \quad (2.7)$$

Blackbody radiation in a rectangular cavity can be considered as a sum of standing electromagnetic waves with different wavelengths and frequencies. Their values are defined by the set of numbers n_α and L_α . Let us define the number of standing waves in the cavity with wavenumbers less than the given value of k . For this purpose let us select in k -space a sphere of radius k with volume V_k :

$$V_k = \frac{4\pi k^3}{3}. \quad (2.8)$$

Each point inside this sphere, (k_x, k_y, k_z) , or more precisely each primitive cell, corresponds to two independent standing waves with fixed frequencies and with orthogonal polarizations. For positive numbers n_α all three projections of the wavevector, k_α , are positive, i.e., they are within the first octant of the space of wavenumbers. The number of standing waves, Z_k , that correspond to 1/8 of a sphere, which is the above-mentioned octant, can be defined as 2/8 of the ratio of V_k and V_{k0} (Eqs. (2.8) and (2.6)). The factor of 2 is due to the two polarizations of waves (more details about waves and their polarizations are discussed in Appendix B):

$$Z_k = \frac{2}{8} \frac{4}{3} \frac{\pi k^3}{(\pi^3/L_x L_y L_z)} = \frac{L_x L_y L_z}{3\pi^2} k^3. \quad (2.9)$$

Taking into account the relation between the wavenumber and frequency, $\omega = ck$, we can find the number of standing waves, Z_ω , corresponding to the entire frequency interval from 0 to ω :

$$Z_\omega = \frac{V}{3\pi^2 c^3} \omega^3, \quad (2.10)$$

where $V = L_x L_y L_z$ is the volume of the cavity. We can find the number of standing waves corresponding to an infinitesimal interval of frequencies from ω to $\omega + d\omega$ by differentiating Eq. (2.10):

$$dZ_\omega = V \frac{\omega^2}{\pi^2 c^3} d\omega. \quad (2.11)$$

Let us introduce the *density of states*, N_ω , i.e., the number of standing waves corresponding to a unit volume of the cavity and to a frequency interval $d\omega$:

$$N_\omega = \frac{1}{V} \frac{dZ_\omega}{d\omega} = \frac{\omega^2}{\pi^2 c^3}. \quad (2.12)$$

Taking into account Eq. (2.12), we can write the expression for the *spectral density of blackbody radiation*, u_ω , defined as

$$u_\omega(T) = N_\omega \langle \varepsilon_\omega \rangle = \frac{\omega^2}{\pi^2 c^3} \langle \varepsilon_\omega \rangle, \quad (2.13)$$

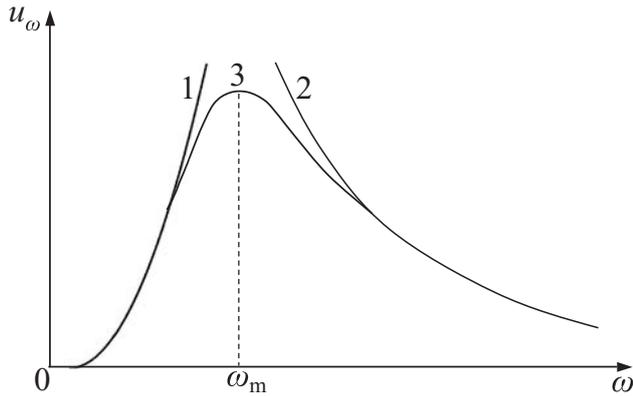


Figure 2.3 The dependences of the spectral density of blackbody radiation on frequency. Curve 1 corresponds to the Rayleigh–Jeans law, curve 2 to Wien’s radiation law, and curve 3 to experimental data.

where $\langle \varepsilon_\omega \rangle$ is the average energy, which corresponds to one standing wave with frequency ω and generally does not depend on temperature and frequency.

2.1.3 The classical limit. The Rayleigh–Jeans law

Let us define the density of energy of an ensemble of standing waves, which exist inside of a cavity at a temperature T . From the energy point of view each standing wave can be considered as a harmonic oscillator with one degree of freedom. According to the classical point of view for a standing wave the average thermal energy is

$$\langle \varepsilon_\omega \rangle = k_B T. \quad (2.14)$$

This is because the same average kinetic and potential energy corresponds to one-dimensional motion of the particle. Therefore, the total thermal energy is equal to

$$\langle \varepsilon_\omega \rangle = 2 \frac{k_B T}{2}. \quad (2.15)$$

The classical expression for the average thermal energy of each oscillator does not depend on the oscillation’s frequency. Therefore for blackbody thermal radiation at temperature T we obtain the following expression for the spectral density, u_ω :

$$u_\omega(T) = \frac{\omega^2}{\pi^2 c^3} k_B T, \quad (2.16)$$

which is called the *Rayleigh–Jeans law*. This fits the experimental data sufficiently well in the region of low frequencies (waves with long wavelengths) (see Fig. 2.3, curve 1). However, with increasing frequency the discrepancy between the experimental data and expression (2.16) increases significantly (see Fig. 2.3,

curve 3). The failure of the classical approach to describe correctly the experimental results is seen especially clearly when you calculate the total energy of blackbody radiation, i.e., the energy of standing waves in the cavity in the entire frequency interval:

$$u(T) = \int_0^{\infty} u_{\omega}(T) d\omega = \frac{k_B T}{\pi^2 c^3} \int_0^{\infty} \omega^2 d\omega. \quad (2.17)$$

The integral of Eq. (2.17) diverges and $u(T) \rightarrow \infty$, which contradicts the simple fact that the total energy radiated by a heated body is finite. The divergence of $u(T)$ to infinity is known in physics as the *ultraviolet catastrophe*.

2.1.4 Energy quanta and Planck's equation

The main difference between the classical approach to the blackbody radiation problem and the quantum approach (which was suggested by Max Planck in 1900) is in the calculation of the average energy of thermal radiation. According to the hypothesis suggested by Planck, the radiation is not emitted and absorbed continuously by a heated body, but rather is emitted and absorbed in finite portions of energy with the minimal portion for a given frequency defined as

$$\varepsilon = h\nu \quad (2.18)$$

or

$$\varepsilon = \hbar\omega, \quad (2.19)$$

where $h = 6.62 \times 10^{-34}$ [J s], which was later called *Planck's constant*. Very often instead of Eq. (2.18) the equation (2.19) is used with the constant, \hbar , which is called the *reduced Planck constant*:

$$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34} \text{ J s}. \quad (2.20)$$

Planck postulated that the possible energy states which can have wave oscillators (standing waves) in the cavity are given by the equation

$$\varepsilon_n = n\hbar\omega, \quad (2.21)$$

where n is an arbitrary integer number known as the *quantum number*. All wave oscillators at a given temperature are in different energy states.

According to classical concepts, the probability that in the state of thermodynamical equilibrium at temperature T the wave oscillator will have energy ε_n is defined by the expression

$$P_n = C e^{-\varepsilon_n/(k_B T)}. \quad (2.22)$$

The constant C is determined from the condition that the total probability must be equal to unity, i.e.,

$$\sum_{n=0}^{\infty} P_n = C \sum_{n=0}^{\infty} e^{-\varepsilon_n/(k_B T)} = 1, \quad (2.23)$$

where we obtain

$$C = \left(\sum_{n=0}^{\infty} e^{-\varepsilon_n/(k_B T)} \right)^{-1}. \quad (2.24)$$

Taking into account the above-mentioned expressions, the average energy of a wave oscillator has to be calculated as

$$\langle \varepsilon_\omega \rangle = \sum_{n=0}^{\infty} P_n \varepsilon_n = \frac{\sum_{n=0}^{\infty} n \hbar \omega e^{-n \hbar \omega / (k_B T)}}{\sum_{n=0}^{\infty} e^{-n \hbar \omega / (k_B T)}}. \quad (2.25)$$

After carrying out simple calculations (see Example 2.1), we obtain for the average energy one of the most important relationships in physics:

$$\langle \varepsilon_\omega \rangle = \frac{\hbar \omega}{e^{\hbar \omega / (k_B T)} - 1}. \quad (2.26)$$

On substituting this expression into Eq. (2.13) we obtain the well-known *Planck formula for the spectral density of blackbody radiation*:

$$u_\omega(T) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / (k_B T)} - 1}. \quad (2.27)$$

Equation (2.27) is in complete agreement with experimental data over the entire spectral range of blackbody radiation (see Fig. 2.3, curve 3). In the limiting case of low frequencies ($\hbar \omega \ll k_B T$, $e^{\hbar \omega / (k_B T)} \approx 1 + \hbar \omega / (k_B T)$) this formula approaches the Rayleigh–Jeans law: $u_\omega \sim \omega^2$ (see Eq. (2.16)), which was obtained on the basis of classical concepts. In the region of high frequencies ($\hbar \omega \gg k_B T$) expression (2.27) approaches the experimentally established radiation law of Wilhelm Wien, according to which the spectral density of energy, $u_\omega(T)$, exponentially decreases with increasing radiation frequency (see Fig. 2.3, curve 2).

Example 2.1. Using the expression for the average energy of a wave oscillator, Eq. (2.25), derive Eq. (2.26) and Planck's formula, Eq. (2.27).

Reasoning. Let us write Eq. (2.25) in the following form:

$$\langle \varepsilon_\omega \rangle = \hbar \omega \frac{\sum_{n=0}^{\infty} n e^{-n\gamma}}{\sum_{n=0}^{\infty} e^{-n\gamma}}, \quad (2.28)$$

where we introduced

$$\gamma = \frac{\hbar \omega}{k_B T}. \quad (2.29)$$

The sum in the denominator of Eq. (2.28) represents a geometric progression:

$$F(\gamma) = \sum_{n=0}^{\infty} e^{-n\gamma} = \frac{1}{1 - e^{-\gamma}}. \quad (2.30)$$

After differentiating two different expressions for the function $F(\gamma)$ in Eq. (2.30) and equating them, we will obtain for the numerator in Eq. (2.28)

$$\frac{dF}{d\gamma} = \frac{d}{d\gamma} \left(\sum_{n=0}^{\infty} e^{-n\gamma} \right) = - \sum_{n=0}^{\infty} n e^{-n\gamma}, \quad (2.31)$$

$$\frac{dF}{d\gamma} = \frac{d}{d\gamma} \left(\frac{1}{1 - e^{-\gamma}} \right) = - \frac{e^{-\gamma}}{(1 - e^{-\gamma})^2}, \quad (2.32)$$

$$\sum_{n=0}^{\infty} n e^{-n\gamma} = \frac{e^{-\gamma}}{(1 - e^{-\gamma})^2}. \quad (2.33)$$

After the substitution of Eqs. (2.30) and (2.33) into the initial expression (2.28), we obtain for the average energy of a wave oscillator

$$\langle \varepsilon_{\omega} \rangle = \hbar\omega \frac{e^{-\gamma}}{1 - e^{-\gamma}} = \frac{\hbar\omega}{e^{\gamma} - 1} = \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1}, \quad (2.34)$$

which coincides with Eq. (2.26). On combining Eqs. (2.13) and (2.34) we obtain Planck's formula (2.27).

2.1.5 Photon gas

Using Planck's ideas, Einstein suggested that the quantum properties of electromagnetic radiation (light) become apparent not only in the emission and absorption of radiation by materials, but also during the propagation of electromagnetic radiation. According to his hypothesis, radiation can be imagined in the form of a gas, which consists of particles called *photons*. The photons possess energy defined as

$$\varepsilon_{\text{ph}} = \hbar\omega = \frac{2\pi\hbar c}{\lambda}. \quad (2.35)$$

The photons move in vacuum with the speed of light, c , and they cannot stay at rest at any time. If a photon “stops” after some inelastic collision with a surface or after a collision with another particle, it simply disappears, giving its energy to the object with which it collided.

For a photon, as for any other real particle, we can define a mass. A photon's mass at rest must be equal to zero because a photon has speed equal to c and only particles with mass equal to zero can move at the speed of light. Using the relation between a relativistic particle's energy and its mass, m_{ph} , we can write

$$m_{\text{ph}} c^2 = \hbar\omega, \quad (2.36)$$

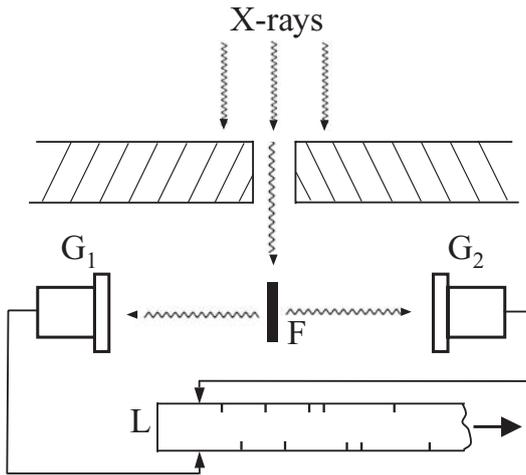


Figure 2.4 The scheme of Bethe's experiment for photon registration. By F we denote metallic foil, G_1 and G_2 are detectors of photons, and L is a registration device.

or

$$m_{\text{ph}} = \frac{\hbar\omega}{c^2}. \quad (2.37)$$

The photon, which has mass and speed, must also have a momentum, the magnitude of which is defined as

$$p_{\text{ph}} = m_{\text{ph}}c = \frac{\hbar\omega}{c} = \frac{2\pi\hbar}{\lambda}. \quad (2.38)$$

For a photon considered as a particle and for electromagnetic radiation, whose quantum is a photon, the directions of propagation coincide and can be defined by a wavevector \mathbf{k} , whose modulus is equal to $k = |\mathbf{k}| = 2\pi/\lambda$, i.e.,

$$\mathbf{p}_{\text{ph}} = \hbar\mathbf{k} \quad (2.39)$$

(compare this with Eqs. (2.38) and (2.4)). The first direct proof of the existence of a photon as a particle was provided by the experiment carried out by Hans Bethe: a metallic foil, F , was exposed to weak X-rays, and it became itself the source of secondary radiation (see Fig. 2.4). If the radiation were propagating in the form of spherical waves, then two independent counters, G_1 and G_2 , placed at the opposite sides of the metallic foil, F , would simultaneously detect the arrival of waves of secondary radiation. However, when one of the counters detected a signal the other did not show that the signal had arrived, although the number of detections of each counter was practically the same. This can be explained only by the assumption that the radiation from the foil propagated in the form of separate quanta, which were detected by one or the other counter but not by both.

Thus, blackbody radiation can be represented in the form of a photon gas, which fills up the cavity. The particles of this gas – photons – propagate with equal probability along all directions, just like molecules at thermal equilibrium.