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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 "corpuscules" – 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

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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 Röhrer 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.

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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 $\mathrm{mm\,s^{-1}}$.

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.

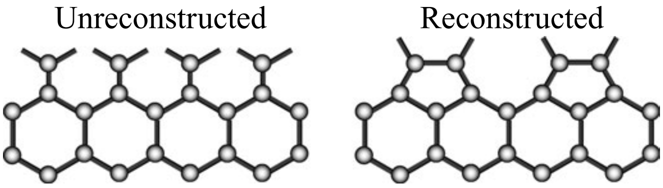

Figure 1.1 Reconstruction of Si surface.

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 ($\sim$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

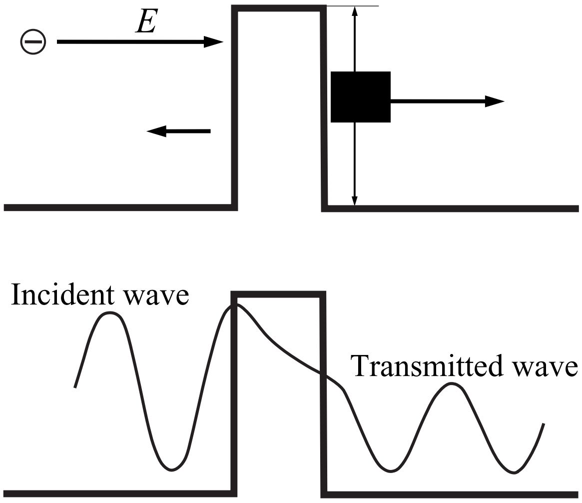

Figure 1.2 An electron with energy E tunneling through the potential barrier $U_0 (U_0 > E)$.

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

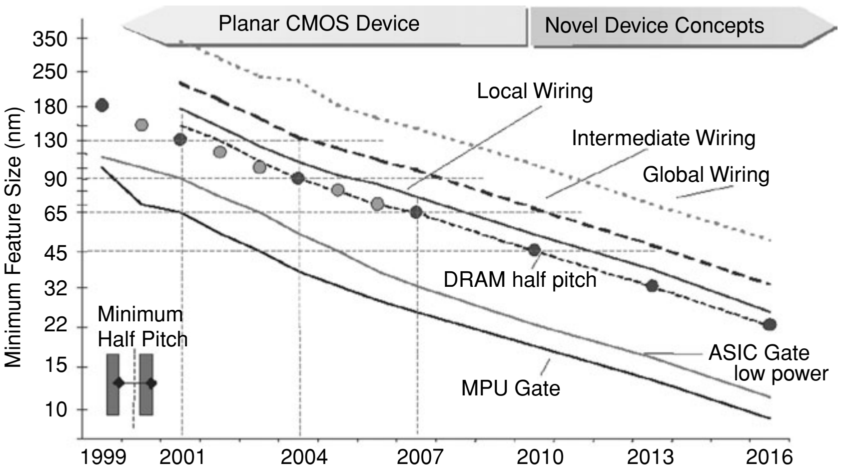

Figure 1.3 Technology nodes and minimum feature sizes from the ITRS 2002 Roadmap: MPU, microprocessing unit; ASIC, application-specific integrated circuit.

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.

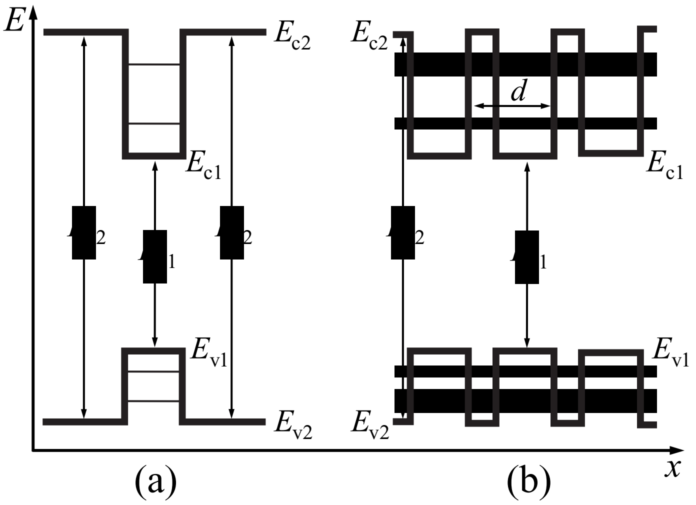

Figure 1.4 The energy bandstructure of a semiconductor quantum well (a) and a type-I heterostructure superlattice (b): E_{g1} and E_{g2} are the bandgaps, E_{c1} and E_{c2} are the bottoms of the conduction bands, and E_{v1} and E_{v2} are the tops of the valence bands of narrow-bandgap and wide-bandgap 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/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. 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/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ 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 $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ (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 $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. 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 $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As/GaSb}_{1-y}\mathrm{As}_y$.

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 nth shell can be calculated using the following formula:

$$N_n = 10n^2 + 2. \tag{1.1}$$