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From Theory to Application

Edited by Günter Schmid

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Library of Congress Card No.: applied for
A catalogue record for this book is available from the British Library.
Bibliographic information published by Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at http://dnb.ddb.de

Printed in the Federal Republic of Germany.
Printed on acid-free paper.

Typesetting Asco Typesetters, Hong Kong
Printing betz-druck gmbh, Darmstadt
Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN 3-527-30507-6

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1

General Introduction

Günter Schmid

In 1994 the book entitled “Clusters and Colloids – from Theory to Applications” was published with the goal of summarizing the state of the art in the field of metal clusters and colloids. Nine years ago, interest was mainly focused on synthetic and structural aspects. Theoretical considerations were limited to small molecule-like organometallic clusters. The very first hints of important novel electronic properties of nanosized particles stimulated further activity. Practical applications could be foreseen – at least if the will was there.

Nine years of worldwide revolutionary developments in nanoscience, combining physics, chemistry, material science, theory and even biosciences, have brought us to another level of understanding. “Nanotechnology” became a key word of public interest, since even politicians and economists realized the social power of nanotechnological developments. Nanotechnology is called the technology of the next century, coming after microtechnology. Nanotechnology unfortunately also became a catchword for people with ambitions in science fiction. Such people threaten us with visions of horror, as when self-replicating machines will destroy mankind. Nevertheless, nanoscience, and consequently nanotechnology, is going to initiate a technological impact that can probably not be compared with any other technical development up to the present time, since it will concern all aspects of human life, ranging from novel building materials to medicine. Of course, it is sometimes difficult to distinguish between vision and reality. However, nanotechnology has already become part of our daily lives, even if we do not recognize this. The most revolutionary consequences can be expected if the most valuable properties of nanoparticles, their electronic properties, are exploited. These are of a fascinating nature and will bring about a real technological revolution. Meanwhile, we know the most important basic facts about nanoparticles and so can predict future applications based on their novel properties.

This book does not, of course, deal with any kind of unsubstantiated visions, in either a positive or a negative sense. It reports strictly on the present state of scientific development, which is impressive enough for any kind of science fiction to be quite unnecessary.

Semiconductor and metal nanoparticles occupy the center of scientific interest because of their unique electronic nature: they follow quantum mechanical rules instead of the laws of classical physics which govern bulk materials. Therefore, small molecular clusters, mainly of the organometallic type, are not considered further. It is also no longer helpful to strictly distinguish clusters from colloids. In general, we call compounds of interest nanoparticles, which implies that predominantly they do not exhibit classical bulk properties, while, on the other hand, differing from molecules in so far as they in some way represent pieces of matter related to the bulk material they originate from.

Consequently the first chapter of this book is called ''Quantum Dots'', as it deals with those very special properties of matter in the nanosize regime. The understanding of quantum-confined electrons in very small particles is the basis for the understanding of properties which will be described in following chapters.

Although the principal synthetic routes to nanoparticles of semiconductor or metallic nature have been well known for some decades, some novel developments seem worth reporting here, and for reasons of completeness classical procedures will at least briefly be reconsidered. Syntheses of semiconductor nanoparticles of II–VI, III–V and Ib–VI types will be followed by routes to metal nanoparticles.

The science of nanoparticles during the last decade is characterized by, among other things, the enormous efforts which have been made to organize nanoparticles in three and two dimensions, and to some extent one dimension. Three-dimensional organization of atoms, ions, or molecules is a well-known natural process, called crystallization. Three-dimensional organization of nanoparticles is, however, not always a simple matter, since, with some exceptions, particles of a few up to some dozens of nanometers in size usually do not possess exactly the same number of atoms or, consequently, the same shape. Classically, only identical species were believed to form crystals. Then we learned that particles of similar but not identical size and shape may be able to organize three-, even two-dimensionally. These aspects become important, as we shall see, in applications of nanoparticles in future nanoelectronic or magnetic devices, for instance in relation to storage problems. This is why the organization of semiconductor and metal nanoparticles will be discussed in detail.

The chapter on the various properties of nanoparticles is of central importance in this book. With the parallel development of analytical tools, highly sophisticated intrinsic properties of all kinds of nanoparticles became visible. Optical, electronic, and magnetic properties of nanoparticles open up a novel world with immense implications for future developments.

As already mentioned, biomaterials became part of nanoscience after we learned to use biomolecules as tools to combine inorganic nanoparticles. DNA and proteins developed into valuable materials of manifold excellent utility. The combination of inorganic and biochemical building blocks led to a wide variety of novel hybrid systems with unexpected properties. This field of nanoscience is still at the very beginning and is expected to develop very fast in the near future.

Just like its predecessor, ''Clusters and Colloids'', this book will need a successor in a couple of years, because of the extremely rapid development of nanoscience.

Therefore, it should be stated that this book simply gives an insight into our current, short-lived knowledge of important aspects of nanoscience.

This brings us to those parts of nanoscience that will not be considered here, because they would overstep the limits of this book too much. Thus, we will not consider the rapidly growing field of nanorods and nanowires. Also, nanosized biological and supramolecular aspects will not be discussed, except in some special cases relating to quantum dots. Nanostructured surfaces will also not be explicitly treated, except those resulting from decoration with nanoparticles. Indeed, these are considerable restrictions. However, it is not the purpose of this work to serve as an encyclopedia. Rather it is an attempt to describe one important part of nanoscience that may play a decisive role in future nanotechnology.

2

Quantum Dots

Wolfgang Johann Parak, Liberato Manna, Friedrich Christian Simmel, Daniele Gerion, and Paul Alivisatos

2.1

Introduction and Outline

In the last decade, new directions of modern research, broadly defined as ''nanoscale science and technology'', have emerged [1, 2]. These new trends involve the ability to fabricate, characterize, and manipulate artificial structures, whose features are controlled at the nanometer level. They embrace areas of research as diverse as engineering, physics, chemistry, materials science, and molecular biology. Research in this direction has been triggered by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties with a resolution close to the atomic level. Strongly connected to such technological advances are the pioneering studies that have revealed new physical properties of matter at a level intermediate between atomic/molecular and bulk.

Materials science and technology is a field that is evolving at a very fast pace and is currently giving the most significant contributions to nanoscale research. It is driven by the desire to fabricate materials with novel or improved properties. Such properties can be, for instance, strength, electrical and thermal conductivity, optical response, elasticity, or wear resistance. Research is also evolving toward materials that are designed to perform more complex and efficient tasks. Examples include materials that bring about a higher rate of decomposition of pollutants, a selective and sensitive response toward a given biomolecule, an improved conversion of light into current, or more efficient energy storage. For such and more complex tasks to be realized, novel materials have to be based on several components whose spatial organization is engineered at the molecular level. This class of materials can be defined as ''nano-composites''. They are made of assembled nanosized objects or molecules. Their macroscopic behavior arises from the combination of the novel properties of the individual building blocks and their mutual interaction.

In electronics, the design and the assembly of functional materials and devices based on nanoscale building blocks can be seen as the natural, inevitable evolution of the trend toward miniaturization. The microelectronics industry, for instance, is fabricating integrated circuits and storage media whose basic units are approaching the size of few tens of nanometers. For computers, "smaller" means higher computational power at lower cost and with higher portability. However, this race toward higher performance is driving current silicon-based electronics to the limits of its capability [3–6]. The design of each new generation of smaller and faster devices involves more sophisticated and expensive processing steps, and requires the solution of new sets of problems, such as heat dissipation and device failure. If the trend toward further miniaturization persists, silicon technology will soon reach limits at which these problems become insurmountable. In addition to this, scientists have found that device characteristics in very small components are strongly altered by quantum mechanical effects. In many cases, these effects will undermine the classical principles on which most of today's electronic components are based. For these reasons, alternative materials and approaches are currently being explored for novel electronic components in which the laws of quantum mechanics regulate their functioning in a predictable way. Perhaps in the near future a new generation of computers will rely on fundamental processing units that are made only of a few atoms.

Fortunately, the advent of new methods for the controlled production of nanoscale materials has provided new tools that can be adapted for this purpose. New terms such as nanotubes, nanowires, and quantum dots are now common jargon of scientific publications. These objects are among the smallest man-made units that display physical and chemical properties which make them promising candidates as fundamental building blocks for novel transistors. The advantages envisaged here are higher device versatility, faster switching speed, lower power dissipation, and the possibility of packing many more transistors on a single chip. Prototypes of these new single nano-transistors are nowadays fabricated and studied in research laboratories and are far from commercialization. How millions of such components could be arranged and interconnected in complex architectures and at low cost still remains a formidable problem to be solved.

With a completely different objective, the pharmaceutical and biomedical industries try to synthesize large supramolecular assemblies and artificial devices that mimic the complex mechanisms of nature or that can be potentially used for more efficient diagnoses and better cures for diseases. Examples in this direction are nanocapsules such as liposomes, embodying drugs that can be selectively released in living organs, or bioconjugate assemblies of biomolecules and magnetic (or fluorescent) nanoparticles that may provide faster and more selective analysis of biotissues. These prototype systems may one day evolve into more complex nanomachines with highly sophisticated functional features able to carry out complicated tasks at the cellular level in a living body.

This chapter is not meant as a survey of the present state and future developments of nanoscale science and technology, and the list of examples mentioned above is far from being complete. Nanoscience and nanotechnology will definitely have a strong impact on our lives in many disparate areas. We can mention, as the most significant examples, information technology and the telecommunications industry, materials science and engineering, medicine. In this introductory chapter, we want to stress the point that any development in nanoscience necessarily requires an understanding of the physical laws that govern matter at the nanoscale and of how the interplay of the various physical properties of a nanoscopic system translates into some novel behavior or into a new physical property. In this sense, the chapter will serve as an overview of basic physical rules governing nanoscale materials, with a particular emphasis on quantum dots, including their various physical realizations and their possible applications. Quantum dots are the ultimate example of a solid in which all dimensions shrink down to a few nanometers. Moreover, semiconductor quantum dots are probably the most studied nanoscale systems.

The outline of this chapter is as follows. In Section 2.2 we try to explain with a few examples why the behavior of nanoscale materials can be remarkably different from that of bulk materials and from their atomic counterparts, and how quantum mechanics can help us in rationalizing this. Following this discussion, we give a definition of a ''quantum dot''. In Section 2.3 we follow a bottom-up approach and give the simplified picture of a solid as being a very large molecule, where the energy levels of the individual atomic components have merged into bands. The electronic structure of a quantum dot, being intermediate between that of the two extreme cases of single atoms and bulk material, will then be an easier concept to grasp. In Section 2.4 we use the model of a free-electron gas and the concept of quantum confinement to explain what happens to a solid when its dimensions shrink one by one. This leads us to a more accurate definition of quantum well, quantum wire, and quantum dot. In Section 2.5 we examine in more detail the electronic structure of quantum dots, although we try to keep the discussion at a simple level. Section 2.6 is a brief overview of the most popular methods used to fabricate quantum dots. Different methods lead to different varieties of quantum dots, which can be suited for specific applications. In Section 2.7 we discuss the optical properties of quantum dots. As they are quite unique for this class of materials, the optical properties are probably the most important reason why the research on quantum dots has exploded in the last decade. The discussion here will be focused more on colloidal nanocrystal quantum dots. Electrical and transport properties are nonetheless extremely relevant, as is described in Section 2.8, since, for instance, the addition or subtraction of a charge from a quantum dot leads to dramatic modification of its electronic structure and of the way the dot will handle a further addition or subtraction of a charge. This can be of fundamental importance for future applications in electronics.

2.2
Nanoscale Materials and Quantum Mechanics

2.2.1
Nanoscale Materials as Intermediate between Atomic and Bulk Matter

Nanoscale materials frequently show behavior which is intermediate between that of a macroscopic solid and that of an atomic or molecular system. Consider, for instance, the case of an inorganic crystal composed of few atoms. Its properties will be different from those of a single atom, but we cannot imagine that they will be the same as those of a bulk solid. The number of atoms on the crystal's surface, for instance, is a significant fraction of the total number of atoms, and therefore will have a large influence on the overall properties of the crystal. We can easily imagine that this crystal might have a higher chemical reactivity than the corresponding bulk solid and that it will probably melt at lower temperatures. Consider now the example of a carbon nanotube, which can be thought of as a sheet of graphite wrapped in such a way that the carbon atoms on one edge of the sheet are covalently bound to the atoms on the opposite edge of the sheet. Unlike its individual components, a carbon nanotube is chemically extremely stable because the valences of all its carbon atoms are saturated. Moreover, we would guess that carbon nanotubes can be good conductors because electrons can freely move along these tiny, wire-like structures. Once again, we see that such nanoscopic objects can have properties which do not belong to the realm of their larger (bulk) or smaller (atoms) counterparts. However, there are many additional properties specific to such systems which cannot easily be grasped by simple reasoning. These properties are related to the sometimes counterintuitive behavior that charge carriers (electrons and holes) can exhibit when they are forced to dwell in such structures. These properties can only be explained by the laws of quantum mechanics.

2.2.2
Quantum Mechanics

A fundamental aspect of quantum mechanics is the particle-wave duality, introduced by De Broglie, according to which any particle can be associated with a matter wave whose wavelength is inversely proportional to the particle's linear momentum. Whenever the size of a physical system becomes comparable to the wavelength of the particles that interact with such a system, the behavior of the particles is best described by the rules of quantum mechanics [7]. All the information we need about the particle is obtained by solving its Schrödinger equation. The solutions of this equation represent the possible physical states in which the system can be found. Fortunately, quantum mechanics is not required to describe the movement of objects in the macroscopic world. The wavelength associated with a macroscopic object is in fact much smaller than the object's size, and therefore the trajectory of such an object can be excellently derived using the principles of classical mechanics. Things change, for instance, in the case of electrons orbiting around a nucleus, since their associated wavelength is of the same order of magnitude as the electron-nucleus distance.

We can use the concept of particle-wave duality to give a simple explanation of the behavior of carriers in a semiconductor nanocrystal. In a bulk inorganic semiconductor, conduction band electrons (and valence band holes) are free to move throughout the crystal, and their motion can be described satisfactorily by a linear combination of plane waves whose wavelength is generally of the order of nanometers. This means that, whenever the size of a semiconductor solid becomes comparable to these wavelengths, a free carrier confined in this structure will behave as a particle in a potential box [8]. The solutions of the Schrödinger equation in such case are standing waves confined in the potential well, and the energies associated with two distinct wavefunctions are, in general, different and discontinuous. This means that the particle energies cannot take on any arbitrary value, and the system exhibits a discrete energy level spectrum. Transitions between any two levels are seen as discrete peaks in the optical spectra, for instance. The system is then also referred to as ''quantum confined''. If all the dimensions of a semiconductor crystal shrink down to a few nanometers, the resulting system is called a ''quantum dot'' and will be the subject of our discussion throughout this chapter. The main point here is that in order to rationalize (or predict) the physical properties of nanoscale materials, such as their electrical and thermal conductivity or their absorption and emission spectra, we need first to determine their energy level structure.

For quantum-confined systems such as quantum dots, the calculation of the energy structure is traditionally carried out using two alternative approaches. One approach has just been outlined above. We take a bulk solid and we study the evolution of its band structure as its dimensions shrink down to a few nanometers. This method will be described in more detail later (Section 2.4). Alternatively, we can start from the individual electronic states of single isolated atoms as shown in Section 2.3 and then study how the energy levels evolve as atoms come closer and start interacting with each other.

2.3
From Atoms to Molecules and Quantum Dots

From the point of view of a chemist, the basic building blocks of matter are atomic nuclei and electrons. In an atom, electrons orbit around the single nucleus, and the number of electrons depends on the element. In the simplest case of the hydrogen atom, one electron orbits around one proton. The electronic states of the hydrogen atom can be calculated analytically [9, 10]. As soon as more than one electron is involved, however, the calculation of the energy levels becomes more complicated, since, in addition to the interaction between the nucleus and the electron, now also electron-electron interactions have to be taken into account. Although the energy states of many-electron atoms can no longer be derived analytically, approximations such as the Hartree-Fock method exist [10]. Each electron can be ascribed to an individual orbit, called an atomic orbital (AO), with an associated discrete energy level. Depending on the angular moment of the orbit, AOs can have spherical (*s*-orbital), club-like (*p*-orbital) or a more complicated (*d*-, *f*-orbitals) shape. The eight valence electrons of a neon atom, for example, occupy one *s*- and three *p*-orbitals around the nucleus, one spin up and one spin down per orbit [10], where the energy level of the *s*-orbital is lower than that of the *p*-orbitals. In accordance with the rules of quantum mechanics, the energy levels are discrete.

The next bigger structure, obtained from the combination of several atoms, is

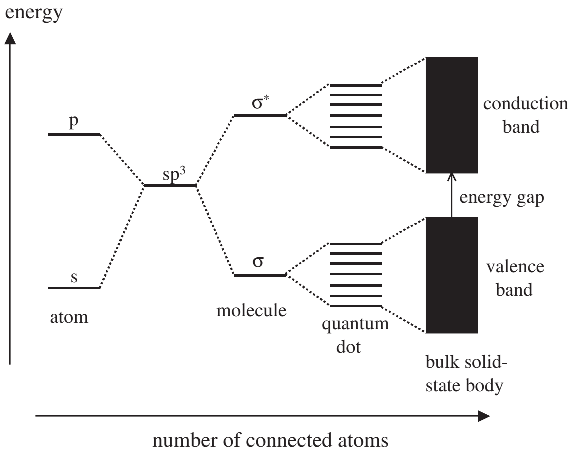

Fig. 2-1 Electronic energy levels depending on the number of bound atoms. By binding more and more atoms together, the discrete energy levels of the atomic orbitals merge into energy bands (here shown for a semiconducting material) [16]. Therefore semiconducting nanocrystals (quantum dots) can be regarded as a hybrid between small molecules and bulk material.

the molecule. Now electrons orbit collectively around more than one nucleus. In a molecule, electrons that are responsible for the covalent bonds between individual atoms can no longer be ascribed to one individual atom, but they are "shared". In methane (CH_4), for instance, each of the four sp^3 atomic orbitals of the central carbon atom is linearly combined with the *s* orbital of a hydrogen atom to form a bonding (σ) and an anti-bonding (σ^*) orbital, respectively [9]. Since these orbitals are "shared" between the atoms, they are called molecular orbitals (MO, see Figure 2-1). Only the lowest energy (bonding) orbitals are occupied, and this explains the relative stability of methane [10]. Using the same principle, it is possible to derive the electronic structure of more complex systems such as large molecules or atomic clusters. When combining atoms to form a molecule, we start from discrete energy levels of the atomic orbitals and we still end up obtaining discrete levels for the molecular orbitals [9].

When the size of a polyatomic system becomes progressively larger, the calculation of its electronic structure in terms of combinations of atomic orbitals becomes unfeasible [11–13]. However, simplifications arise if the system under study is a periodic, infinite crystal. The electronic structure of crystalline solids can be in fact described in terms of periodic combinations of atomic orbitals (Bloch functions) [14, 15]. In this model, perfect translational symmetry of the crystal structure is assumed, and contributions from the surface of the crystal are neglected by assuming an infinite solid (periodic boundary conditions). Electrons are described as a superposition of plane waves extended throughout the solid. As opposed to the case of atoms and molecules, the energy structure of a solid no longer consists of discrete energy levels, but rather of broad energy bands [14, 15], as sketched in Figure 2-1. Every band can be filled only with a limited amount of charge carriers.

In very small crystals of nanometer dimensions, so called nanocrystals, the assumptions of translational symmetry and infinite size of the crystal are no longer valid, and thus these systems cannot be described with the same model used for a bulk solid. We can imagine indeed that the electronic structure of a nanocrystal should be something intermediate between the discrete levels of an atomic system and the band structure of a bulk solid. This can be evidenced from Figure 2-1: the energy levels of a nanocrystal are discrete, their density is much larger, and their spacing is smaller than for the corresponding levels of one atom or a small atomic cluster. Because of their discrete energy levels, such structures are called also quantum dots. The concept of energy bands and band gap can still be used. Highest occupied atomic levels of the atomic (or ionic) species interact with each other to form the valence band of the nanocrystal. Similarly, lowest unoccupied levels combine to form the conduction band of the nanocrystal. The energy gap between the valence and conduction bands results in the band gap of the nanocrystal. As an example, consider a metallic quantum dot. Its level spacing at the Fermi level is roughly proportional to $\sim E_F/N$, where N is the number of electrons in the quantum dot. Given that E_F is a few eV and that N is close to 1 per atom, the band gap of a metallic quantum dot becomes observable only at very low temperatures. Conversely, in the case of semiconductor quantum dots, the band gap is larger and its effects can be observed at room temperature. The size-tunable fluorescence emission of CdSe quantum dots in the visible region of the spectrum is for instance a very explanatory illustration of the presence of a size-dependent band gap.

2.4
Shrinking Bulk Material to a Quantum Dot

In this chapter we will use the concept of quantum confinement of carriers in a solid to derive a more detailed description of the electronic band structure in a low-dimensional solid. This description, although more elaborate than the one just given above, is indeed more powerful and will underline the general physics of a solid when its dimensions shrink one by one down to few nanometers. We will start first with an elementary model of the behavior of electrons in a bulk solid. This model will then be adapted to the case of confined carriers.

2.4.1
Three-Dimensional Systems (Bulk Material)

We now consider the case of a three-dimensional solid of size d_x, d_y, d_z, containing N free electrons. "Free" means that these electrons are delocalized and thus not bound to individual atoms. Furthermore, we will make the assumption that the interactions between the electrons, as well as the interactions between the electrons and the crystal potential, can be neglected as a first approximation. Such a model system is called "free-electron gas" [14, 15].

Astonishingly, this oversimplified model still captures many of the physical aspects of real systems. From more complicated theories it has been learnt that many of the expressions and conclusions from the free-electron model remain valid as a first approximation even when one takes electron-crystal and electron-electron interactions into account. In many cases it is sufficient to replace the free-electron mass m by an "effective" mass m^*, which implicitly contains the corrections for the interactions. To keep the story simple, we proceed with the free-electron picture. In the free-electron model, each electron in the solid moves with a velocity $\vec{v} = (v_x, v_y, v_z)$. The energy of an individual electron is then just its kinetic energy:

$$E = \frac{1}{2} m \vec{v}^2 = \frac{1}{2} m ({v_x}^2 + {v_y}^2 + {v_z}^2) \tag{1}$$

According to Pauli's exclusion principle, each electron must be in a unique quantum state. Since electrons can have two spin orientations ($m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$), only two electrons with opposite spins can have the same velocity $\vec{v}$. This case is analogous to the Bohr model of atoms, in which each orbital can be occupied by two electrons at maximum. In solid-state physics, the wavevector $\vec{k} = (k_x, k_y, k_z)$ of a particle is more frequently used instead of its velocity to describe the particle's state. Its absolute value $k = |\vec{k}|$ is the wavenumber. The wavevector $\vec{k}$ is directly proportional to the linear momentum $\vec{p}$ and thus also to the velocity $\vec{v}$ of the electron:

$$\vec{p} = m\vec{v} = \frac{h}{2\pi} \vec{k} \tag{2}$$

The scaling constant is the Planck constant h, and the wavenumber is related to the wavelength λ associated with the electron through the De Broglie relation [14, 15]:

$$\pm k = |\vec{k}| = \pm \frac{2\pi}{\lambda} \tag{3}$$

The wavelengths λ associated with the electrons traveling in a solid are typically of the order of nanometers[1], much smaller than the dimensions of an ordinary solid.

The calculation of the energy states for a bulk crystal is based on the assumption of periodic boundary conditions. Periodic boundary conditions are a mathematical trick to "simulate" an infinite ($d \rightarrow \infty$) solid. This assumption implies that the conditions at opposite borders of the solid are identical. In this way, an electron that is close to the border does not really "feel" the border. In other words, the electrons at the borders "behave" exactly as if they were in the bulk. This con-

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[1] In fact, the wavelength depends on the electron density. The wavelength for electrons in metals is typically around 10 nm; in semiconductors it may vary between 10 nm and 1 µm.

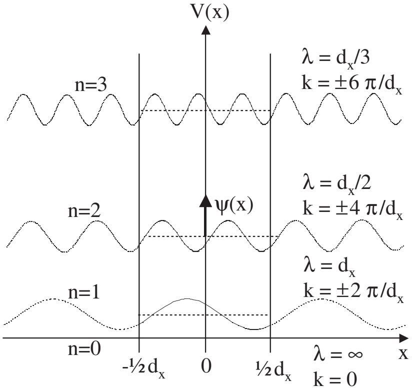

Fig. 2-2 Periodic boundary conditions (only drawn for the x-dimension) for a free-electron gas in a solid with thickness d. The idea of periodic boundary conditions is to mathematically "simulate" an infinite solid. Infinite extension is similar to an object without any borders. This means that a particle close to the "border" must not be affected by the border, but "behaves" exactly as it were in the bulk. This can be realized by using a wavefunction $\psi(x)$ that is periodic within the thickness d of the solid. Any electron that leaves the solid from its right boundary would reenter under exactly the same conditions on its left side. For the electron the borders are quasi-nonexistent. The probability density $|\psi(x)|^2$ is the probability that an electron is at the position x in the solid. Different states for the electrons ($n = 0, 1, 2, \ldots$) have different wavefunctions. λ is the De Broglie wavelength of the electrons and k is their corresponding wavenumber. A "real" bulk solid can be approximated by an infinite solid ($d \to \infty$) and its electronic states in k-space are quasi-continuously distributed: $\Delta k = 2\pi/d_x \to 0$.

dition can be realized mathematically by imposing the following condition to the electron wavefunctions: $\psi(x, y, z) = \psi(x + d_x, y, z)$, $\psi(x, y, z) = \psi(x, y + d_y, z)$, and $\psi(x, y, z) = \psi(x, y, z + d_z)$. In other words, the wavefunctions must be periodic with a period equal to the whole extension of the solid [15, 17]. The solution of the stationary Schrödinger equation under such boundary conditions can be factorized into the product of three independent functions $\psi(x, y, z) = \psi(x)\psi(y)\psi(z) = A \exp(ik_x x) \exp(ik_y y) \exp(ik_z z)$. Each function describes a free electron moving along one Cartesian coordinate. In the argument of the functions, $k_{x,y,z}$ is equal to $\pm n\Delta k = \pm n 2\pi/d_{x,y,z}$ and n is an integer [14, 15, 17]. These solutions are waves that propagate along the negative and the positive direction, for $k_{x,y,z} > 0$ and $k_{x,y,z} < 0$, respectively. An important consequence of the periodic boundary conditions is that all the possible electronic states in the $\vec{k}$ space are equally distributed. There is an easy way of visualizing this distribution in the ideal case of a one-dimensional free-electron gas: there are two electrons $\left(m_s = \pm\frac{1}{2}\right)$ in the state $k_x = 0$ $(v_x = 0)$, two electrons in the state $k_x = +\Delta k$ $(v_x = +\Delta v)$, two electrons in the state $k_x = -\Delta k$ $(v_x = \Delta v)$, two electrons in the state $k_x = +2\Delta k$ $(v_x = +2\Delta v)$, and so on.

For a three-dimensional bulk material we can follow an analogous scheme. Two electrons $\left(m_s = \pm\frac{1}{2}\right)$ can occupy each of the states $(k_x, k_y, k_z) = (\pm n_x \Delta k, \pm n_y \Delta k,$

$\pm n_z \Delta k$), again with $n_{x,y,z}$ being an integer. A sketch of this distribution is shown in Figure 2-3. We can easily visualize the occupied states in $\vec{k}$-space because all these states are included into a sphere whose radius is the wavenumber associated with the highest energy electrons. At the ground state, at 0 K, the radius of the sphere is the Fermi wavenumber k_F (Fermi velocity v_F). The Fermi energy $E_F \propto k_F{}^2$ is the energy of the last occupied electronic state. All electronic states with an energy $E \leq E_F$ are occupied, whereas all electronic states with higher energy $E > E_F$ are empty. In a solid, the allowed wave numbers are separated by $\Delta k = \pm n 2\pi / d_{x,y,z}$. In a bulk material $d_{x,y,z}$ is large, and so Δk is very small. Then the sphere of states is filled quasi-continuously [15].

We need now to introduce the useful concept of the density of states $D_{3d}(k)$, which is the number of states per unit interval of wavenumbers. From this definition, $D_{3d}(k)\Delta k$ is the number of electrons in the solid with a wavenumber between k and $k + \Delta k$. If we know the density of states in a solid we can calculate, for instance, the total number of electrons having wavenumbers less than a given $k_{\max}$, which we will call $N(k_{\max})$. Obviously, $N(k_{\max})$ is equal to $\int_0^{k_{\max}} D_{3d}(k)\,\mathrm{d}k$. In the ground state of the solid, all electrons have wavenumbers $k \leq k_F$, where k_F is the Fermi wavenumber. Since in a bulk solid the states are homogeneously distributed in $\vec{k}$-space, we know that the number of states between k and $k + \Delta k$ is proportional to $k^2 \Delta k$ (Figure 2-3). This can be visualized in the following way. The volume in three-dimensional $\vec{k}$-space varies with k^3. If we only want to count the number of states with a wavenumber between k and $k + \Delta k$, we need to determine the volume of a spherical shell with radius k and thickness Δk. This volume is proportional to product of the surface of the sphere (which varies as k^2) with the thickness of the shell (which is Δk). $D_{3d}(k)\Delta k$ is thus proportional to $k^2 \Delta k$, and in the limit when Δk approaches zero, we can write:

$$D_{3d}(k) = \frac{dN(k)}{dk} \propto k^2 \tag{4}$$

Instead of knowing the density of states in a given interval of wavenumbers it is more useful to know the number of electrons that have energies between E and $E + \Delta E$. From Eqs. (1) and (2) we know that $E(k)$ is proportional to k^2, and thus $k \propto \sqrt{E}$. Consequently, $\mathrm{d}k/\mathrm{d}E \propto 1/\sqrt{E}$. By using Eq. (4), we obtain for the density of states for a three-dimensional electron gas [17]:

$$D_{3d}(E) = \frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{\mathrm{d}N(k)}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}E} \propto E \cdot 1/\sqrt{E} \propto \sqrt{E} \tag{5}$$

This can be seen schematically in Figure 2-3. With Eq. (5) we conclude our simple description of a bulk solid. The possible states in which an electron can be found are quasi-continuous. The density of states varies with the square root of the energy. More details about the free-electron gas model and more refined descriptions of electrons in solids can be found in any solid state physics textbook [14].

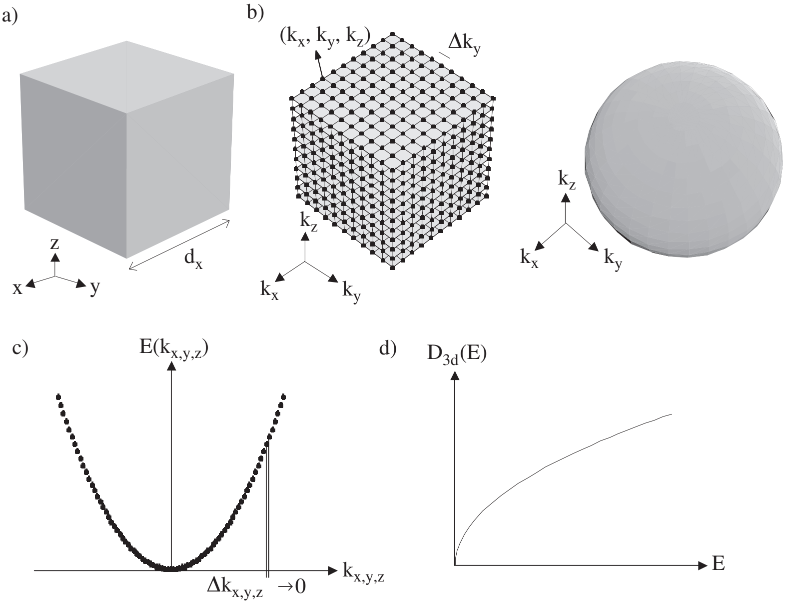

Fig. 2-3 Electrons in a three-dimensional bulk solid [15]. (a) Such a solid can be modeled as an infinite crystal along all three dimensions x, y, z. (b) The assumption of periodic boundary conditions yields standing waves as solutions for the Schrödinger equation for free electrons. The associated wavenumbers (k_x, k_y, k_z) are periodically distributed in the reciprocal k-space [17]. Each of the dots shown in the figure represents a possible electronic state (k_x, k_y, k_z). Each state in k-space can be only occupied by two electrons. In a large solid the spacing $\Delta k_{x,y,z}$ between individual electron states is very small, and therefore the k-space is quasi-continuously filled with states. A sphere with radius k_F includes all states with $k = ({k_x}^2 + {k_y}^2 + {k_z}^2)^{1/2} < k_F$. In the ground state, at 0 K, all states with $k < k_F$ are occupied by two electrons, and the other states are empty. Since the k-space is homogeneously filled with states, the number of states within a certain volume varies with k^3. (c) Dispersion relation for free electrons in a three-dimensional solid. The energy of free electrons varies with the square of the wavenumber, and its dependence on k is described by a parabola. For a bulk solid the allowed states are quasi-continuously distributed and the distance between two adjacent states (here shown as points) in k-space is very small. (d) Density of states D_{3d} for free electrons in a three-dimensional system. The allowed energies are quasi-continuous and their density varies with the square root of the energy $E^{1/2}$.

2.4.2
Two-Dimensional Systems

We now consider a solid that is fully extended along the x- and y-directions, but whose thickness along the z-direction (d_z) is only a few nm (see Figure 2-5). Free electrons can still move freely in the x-y plane. However, movement in the z-direction is now restricted. Such a system is called a 2-dimensional electron gas (2DEG) [18]. As mentioned in Section 2.2, when one or more dimensions of a solid become smaller than the De Broglie wavelength associated with the free charge carriers, an additional contribution of energy is required to confine the component of the motion of the carriers along this dimension. In addition, the movement of electrons along such a direction becomes quantized. This situation is shown in Figure 2-4. No electron can leave the solid, and electrons that move in the z-direction are trapped in a "box". Mathematically this is described by infinitely high potential wells at the border $z = \pm\frac{1}{2}d_z$.

The solutions for the particle-in-a-box situation can be obtained by solving the one-dimensional Schrödinger equation for an electron in a potential $V(z)$, which is zero within the box but infinite at the borders. As can be seen in Figure 2-4, the solutions are stationary waves with energies[2] $E_{nz} = \hbar^2{k_z}^2/2m = h^2{k_z}^2/8\pi^2m = h^2{n_z}^2/8m{d_z}^2$, $n_z = 1, 2, \ldots$ [9, 17]. This is similar to states $k_z = n_z\Delta k_z$ with $\Delta k_z = \pi/d_z$. Again, each of these states can be occupied at maximum by two electrons.

Let us compare the states in the k-space for three- and two dimensional materials (Figures 2-3 and 2-5). For a two-dimensional solid that is extended in the x-y-plane only discrete values are allowed for k_z. The thinner the solid in the z-direction, the larger is the spacing Δk_z between these allowed states. On the other hand, the distribution of states in the k_x-k_y plane remains quasi-continuous. Therefore one can describe the possible states in the k-space as planes parallel to the k_x- and k_y-axes, with a separation Δk_z between the planes in the k_z-direction. We can number the

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[2] The particle-in-a-box approach (Figure 2-4) looks similar to the case of the periodic boundary conditions (Figure 2-2). There are indeed important differences between the two cases. Periodic boundary conditions "emulate" an infinite solid. A quantum mechanical treatment of this problem yields propagating waves that are periodic within the solid. Such waves can be seen as the superposition of plane waves. For an idealized one-dimensional solid, with boundaries fixed at $x = \pm d/2$, a combination of plane waves can be, for instance, $\psi(x) = A \cdot \exp(ikx) + B \cdot \exp(-ikx)$ with $k = n2\pi/d$. Written in another way, the solutions are of the type $\exp(ikx)$, with $k = \pm n2\pi/d$. The solutions for $k = +n2\pi/d$ and $k = -n2\pi/d$ are linearly independent. The waves $\exp(+in2\pi x/d)$ propagate to the right, the waves $\exp(-in2\pi x/d)$ to the left side of the solid. Neither wave feels the boundaries. Since $\exp(ikx) = \cos(kx) + i\sin(kx)$ and $\exp(-ikx) = \cos(kx) - i\sin(kx)$, we also can write $\psi(x) = C \cdot \sin(kx) + D \cdot \cos(kx)$ with $k = n2\pi/d$ as solutions. The only constraint here is that the wavefunction must be periodic throughout the solid. The state with wavenumber $k = 0$ is a solution, since $C \cdot \sin(0) + D \cdot \cos(0) = D \neq 0$. Therefore the state with the lowest kinetic energy is $E \propto k^2 = 0$ for $k = 0$. The individual states in k-space are very close to each other because $\Delta k = 2\pi/d$ tends to 0 when d increases. On the other hand, the particle-in-a-box model describes the case in which the motion of the electrons is confined along one or more directions. Outside the box the probability of finding an electron is zero. For a one-dimensional problem the solutions are standing waves of the type $\psi(x) = A \cdot \sin(kx)$ with $k = n\pi/d$. There is only one solution of this type. The function $\psi(x) = B \cdot \sin(-kx)$ can be written as $\psi(x) = -B \cdot \sin(kx)$ and therefore is still of the type $\psi(x) = A \cdot \sin(kx)$. Because of the boundary conditions $\psi(x = \pm d/2) = 0$ there is no solution of the type $\psi(x) = B \cdot \cos(kx)$. Since the standing wave is confined to the box, there is only the solution $k = +n\pi/d > 0$. For a small box the energy states are far apart from each other in k-space, and the distribution of states and energies is discrete. An important difference with respect to the extended solid is the occurrence of a finite zero-point energy [9]. There is no solution for $k = 0$, since $\psi(0) = A \cdot \sin(0) = 0$. Therefore the energy of the lowest possible state ($n = 1$) is equal to $E = h^2/8md^2$, i.e. $k = \pi/d$. This energy is called zero-point energy and is a purely quantum mechanical effect. It can be understood as the energy that is required to "confine" the electron inside the box. For a large box the zero-point energy tends to zero. However, for small boxes this energy becomes significant as it varies with the square of the reciprocal of the box size d^2.

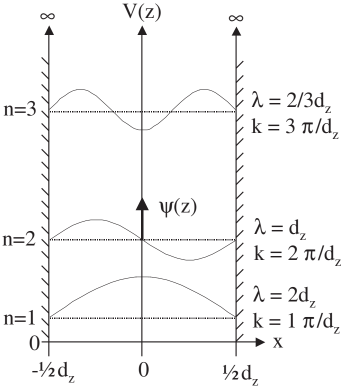

Fig. 2-4 Particle-in-a-box model for a free electron moving along in the *z*-axis. The movement of electrons in the *z*-direction is limited to a "box" with thickness *d*: since electrons cannot "leave" the solid (the box), their potential energy $V(x)$ is zero within the solid, but is infinite at its borders. The probability density $|\psi(z)|^2$ is the probability that an electron is located at position *x* in the solid. Different states for the electrons $(n = 1, 2, \dots)$ differ in their wavefunction.

individual planes with n_z. Since within one plane the number of states is quasi-continuous, the number of states is proportional to the area of the plane. This means that the number of states is proportional to $k^2 = k_x{}^2 + k_y{}^2$. The number of states in a ring with radius k and thickness Δk is therefore proportional to $k \cdot \Delta k$. Integration over all rings yields the total area of the plane in k-space. Here, in contrast to the case of a three-dimensional solid, the density of states varies linearly with k:

$$D_{2\mathrm{d}}(k) = \frac{\mathrm{d}N(k)}{\mathrm{d}k} \propto k \tag{6}$$

In the ground state, all states with $k \le k_\mathrm{F}$ are occupied by two electrons. We now want to know how many states exist for electrons that have energies between E and $E + \Delta E$. From Eqs. (1) and (2) we know the relation between k and E: $E(k) \propto k^2$ and thus $k \propto \sqrt{E}$ and $\mathrm{d}k/\mathrm{d}E \propto 1/\sqrt{E}$. By using Eq. (6) we obtain the density of states for a 2-dimensional electron gas, see also Figure 2-5 [17].

$$D_{2\mathrm{d}}(E) = \frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{\mathrm{d}N(k)}{\mathrm{d}k}\,\frac{\mathrm{d}k}{\mathrm{d}E} \propto \sqrt{E} \cdot 1/\sqrt{E} \propto 1 \tag{7}$$

The density of electronic states in a two-dimensional solid is therefore remarkably different from the three-dimensional case. The spacing between the allowed energy levels in the bands increases, because fewer levels are now present. As soon as one dimension is reduced to nanometer size, dramatic changes due to quantum confinement occur, as, for example, the non-negligible zero-point energy. In two-

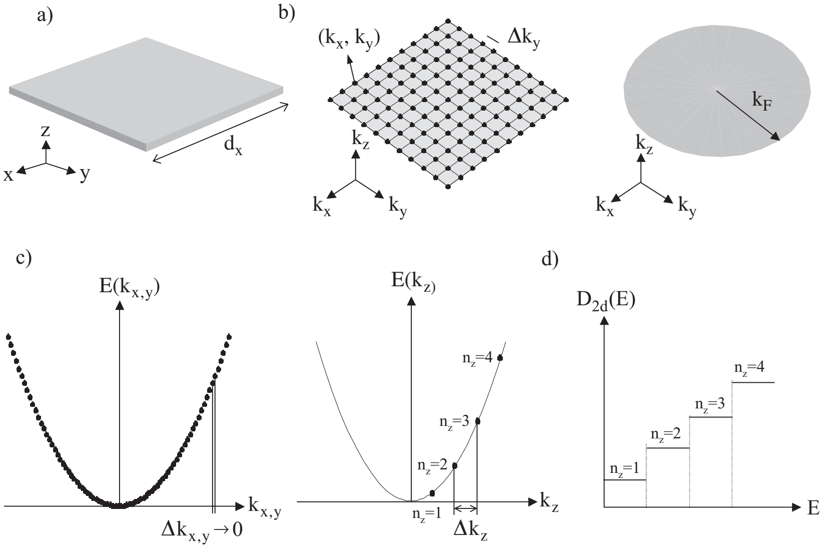

Fig. 2-5 Electrons in a two-dimensional system. (a) A two-dimensional solid is (almost) infinitely extended in two dimensions (here x, y), but is very thin along the third dimension (here denoted as z), which is comparable to the De Broglie wavelength of a free electron ($d_z \rightarrow \lambda$.). (b) Electrons can still move freely along the x- and y-directions. The wavefunctions along such directions can be found again by assuming periodic boundary conditions. k_x and k_y states are quasi-continuously distributed in k-space. The movement of electrons in the z-direction is restricted and electrons are confined to a ''box''. Only certain quantized states are allowed along this direction. For a discrete k_z-state, the distribution of states in three-dimensional k-space can be described as a series of planes parallel to the k_x- and k_y-axes. For each discrete k_z-state, there is a separate plane parallel to the k_x and to the k_y-axes. Here only one of those planes is shown. The k_x- and k_y-states within one plane are quasi-continuous, since $\Delta k_{x,y} = 2\pi/d_{x,y} \rightarrow 0$. The distance between two planes for two separate k_z-states is large, since $\Delta k_z = \pi/d_z \gg 0$. For each k_z-value the k_x- and k_y states are homogeneously distributed on the k_x-k_y-plane [17]. The number of states within this plane is therefore proportional to the area of a disk around $k_x = k_y = 0$. This means that the number of states for a certain wavenumber varies with k^2. In the ground state all states with $k \leq k_F$ are occupied with two electrons, while the remaining states are empty. (c) Free electrons have a parabolic dispersion relation ($E(k) \propto k^2$). The energy levels $E(k_x)$ and $E(k_y)$ for the electron motion along the x- and the y-directions are quasi-continuous (they are shown here as circles). The wavefunction $\psi(z)$ at the border of a small ''box'' must be zero, leading to standing waves inside the box. This constraint causes discrete energy levels $E(k_z)$ for the motion along the z-direction. Electrons can only occupy such discrete states ($n_{z1}, n_{z2}, \ldots$, shown here as circles). The position of the energy levels now changes with the thickness of the solid in the z-direction, or in other words with the size of the ''box''. (d) Density of states for a two-dimensional electron gas. If electrons are confined in one direction (z) but can move freely in the other two directions (x, y), the density of states for a given k_z-state ($n_z = 1, 2, \ldots.$) does not depend on the energy E.

dimensional materials the energy spectrum is still quasi-continuous, but the density of states now is a step function [17, 19].

The quantum-mechanical behavior of electrons in a two-dimensional solid is the origin of many important physical effects. With recent progress in nanoscience and technology, the fabrication of two-dimensional structures has become routine. 2D systems are usually formed at interfaces between different materials or in layered systems in which some of the layers may be only a few nanometers thick. Structures like this can be grown, for example, by successive deposition of the individual layers by molecular beam epitaxy. In such geometry, charge carriers (electrons and holes) can move freely parallel to the semiconductor layer, but their movement perpendicular to the interface is restricted. The study of these nanostructures led to the discovery of remarkable 2-dimensional quantized effects, such as the Integer and the Fractional Quantum Hall Effect [20–23].

2.4.3
One-Dimensional Systems (Quantum Wires)

Let us now consider the case in which the solid also shrinks along a second (y) dimension. Now electrons can only move freely in the x-direction, and their motion along the y- and z-axes is restricted by the borders of the solid (see Figure 2-6). Such a system is called a quantum wire or – when electrons are the charge carriers – a one-dimensional electron system (1DES). The charge carriers and the

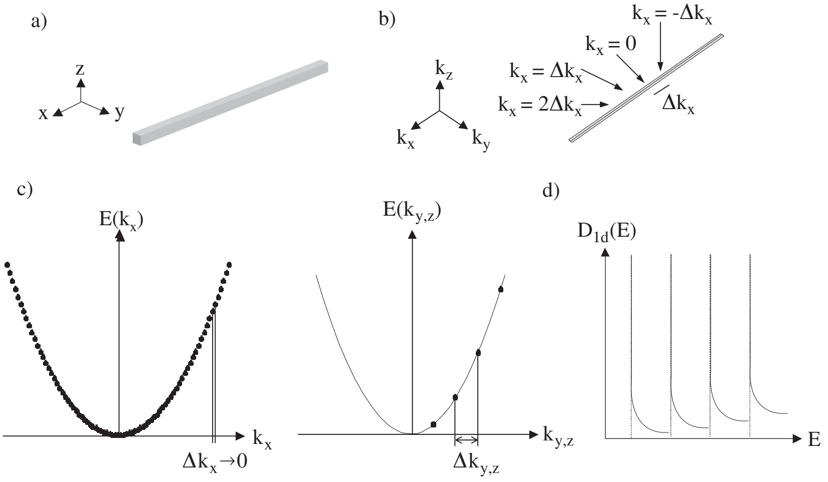

Fig. 2-6 (a) One-dimensional solid. (b) The allowed (k_x, k_y, k_z)-states can be visualized as lines parallel to the k_x-axes in the three-dimensional k-space. In this figure only one line is shows as an example. Within each line, the distribution of states is quasi-continuous, since $\Delta k_x \to 0$. The arrangement of the individual lines is discrete, since only certain discrete k_y- and k_z-states are allowed. (c) This can also be seen in the dispersion relations. Along the k_x-axes the energy band $E(k_x, k_y, k_z)$ is quasi-continuous, but along the k_y- and k_z-axes only certain energies exist. (d) The density of states within one line along the k_x-axes is proportional to $E^{-1/2}$. Each of the hyperbolas shown in the D_{1d}-diagram corresponds to an individual (k_y, k_z)-state.