

NANOSTRUCTURES

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Summary

When one or more of the dimensions of a solid are reduced sufficiently in size, its physico-chemical behavior departs significantly from that of the bulk state. With reduction in size, different and often new electrical, mechanical, chemical, magnetic and optical properties emerge. The resulting structure is a low-dimensional structure. The typical dimensions are usually in the range of a few nanometers. The confinement of particles in a low-dimensional structure leads to a dramatic change in their behavior and to the manifestation of novel size-dependent effects which usually fall into the category of quantum size effects.

Nanostructures are low-dimensional structures. Quantum size effects appear in their

electrical, thermal, magnetic and optical properties, depending on the dimensionality, and offer a rich palette of phenomena to be technological exploited. Several old techniques have been improved and several new techniques have been devised to fabricate and characterize nanostructures.

1. Introduction

Low-dimensional structures exhibit properties that are different from those of the miniature versions of bulk structures. Although the value of the minimum size needed to obtain new properties depends on many factors for a specific material, the value usually falls in the range of a few nanometers. For this reason, a nanostructure can be described as having at least one dimension in the range of few nanometers and displaying new physico-chemical properties not shown by the same material in bulk. Thus, nanostructures constitute a bridge between molecules and bulk materials. Suitable control of the properties and response of nanostructures can lead to new devices and technologies. Accordingly, nanoscience and nanotechnology primarily deal with the synthesis, characterization, exploration and exploitation of nanostructured materials.

In the following section, the basic properties of low-dimensional structures and nanostructures are described. Concepts are presented rigorously but not in depth, since the aim is to provide the tools required to describe and understand the performance of low-dimensional structures, with an eye towards particular applications in such different fields as microelectronics and optoelectronics or medicine. For an in-depth and rigorous discussion of these structures, the reader is encouraged to refer to specific textbooks and review articles, several of which are referenced at the end of this chapter, as well as to other entries in this encyclopedia.

In Section 3, the reduction of the extent of a solid in one or more dimensions is shown to lead to a dramatic alteration of its overall behavior, thereby yielding new electrical, magnetic, optical and thermal properties. The fundamental electronic and vibrational excitations of a nanostructure become quantized, and these excitations determine many of the most important properties of nanostructured materials. This makes nanostructures a subject of both fundamental and practical interest, since their physico-chemical properties can be tailored by controlling their size and shape on the nanometer scale.

Finally, Section 4 deals with available techniques for the growth and characterization of nanoparticles and nanostructures.

2. Low-dimensional Structures

As sizes approach the atomic scale, the relevant physical laws change from the classical to the quantum -mechanical laws of physics. Physical behavior at the nanometer scale is accurately predicted by quantum mechanics, as represented by the Schrödinger equation, which therefore provides a quantitative understanding of the properties of low-dimensional structures.

In the Schrödinger description of quantum mechanics, a particle (electron, hole, exciton, etc.) or physical system (i.e., an atom, ...) is described by a wavefunction $\psi(\vec{r}, t)$, which depends on the variables describing the degrees of freedom of the system, and is interpreted as the probability amplitude of finding a particle at spatial location $\vec{r} = (x, y, z)$ and time t . Thus, while the state of motion of a particle in classical mechanics is specified by the particle's position and velocity, in quantum mechanics the state of motion is specified by the particle's wavefunction, which contains all the information that may be obtained about the particle. Thus, in quantum mechanics, the idea of a trajectory must be eliminated in favor of a more subtle description in terms of quantum states and wavefunctions.

The wavefunction of an uncharged particle with no spin satisfies the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right) \psi(\vec{r}, t) = i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t}, \quad (2.1)$$

where $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator, m is the mass of the particle, \hbar is the reduced Planck constant, and $V(\vec{r}, t)$ is the spatiotemporally varying potential influencing the particle's motion. The Hamiltonian $H(\vec{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t)$ is implicit in this non-relativistic equation. The first part of the Hamiltonian corresponds to the kinetic energy, the second to potential energy. The Hamiltonian thus describes the total energy of the system. As with the force in Newton's second law, the exact form of the Hamiltonian is not provided by the Schrödinger equation and must be independently formulated from the physical properties of a given system.

For many real-world systems, the potential does not depend on time, i.e. $V(\vec{r}, t) = V(\vec{r})$. Then, the dependence on time and spatial coordinates of $\psi(\vec{r}, t)$ can be separated as

$$\psi(\vec{r}, t) = e^{-iEt/\hbar} \psi(\vec{r}) \quad (2.2)$$

where $\psi(\vec{r})$ is a function of space only, and E is the energy of the system of interest. On using this representation of the wavefunction in the Schrödinger Eq. (2.1), the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \psi(\vec{r}) = E\psi(\vec{r}) \quad (2.3)$$

is obtained. Equation (2.3) is analogous in wave mechanics to Hamilton's formulation of classical mechanics for time-independent potentials, i.e., conservative systems.

Low-dimensional systems are usually classified according to the number of reduced dimensions. More precisely, the dimensionality refers to the number of degrees of freedom in the momentum. Accordingly, depending on the dimensions of the system, different cases can be distinguished:

- Three-dimensional (3D) system or bulk system: No quantization of the particle motion occurs, i.e., the particle is free.
- Two-dimensional (2D) system or quantum well: Quantization of the particle motion occurs in one direction, while the particle motion is free in the other two directions.
- One-dimensional (1D) system or quantum wire: Quantization occurs in two directions, leading to free movement along only one direction.
- Zero-dimensional (0D) system or quantum dot (sometimes called "quantum box"): Quantization occurs in all three directions.

In the following subsections, two-, one-, and zero-dimensional systems are discussed and solutions to the Schrödinger equation are given in terms of eigenfunctions and eigenenergies which define the physical behavior of the considered systems.

2.1. Two-dimensional Structures: Quantum Wells

In two-dimensional structures, particles are confined to a thin sheet of thickness L_z along the z axis by infinite potential barriers that create a quantum well (Figure 1). The particles cannot escape from the quantum well $0 \leq z \leq L_z$ and lose no energy on colliding with its walls $z=0$ and $z=L_z$. In real systems, confinement can be due to electrostatic potentials (generated by external electrodes, doping, strain, impurities, etc.), the presence of interfaces between different materials (e.g., in core-shell nanocrystals), the presence of surfaces (e.g., semiconductor nanocrystals), or a combination of these. Motion of the particles in the two other directions (i.e., in the xy plane) inside the quantum well is free.

A one-dimensional potential profile for electrons can be physically implemented by using two heterojunctions. Figure 1 (right) shows the most comprehensively studied quantum-well structure to date. It consists of a layer of GaAs inserted between two $\text{Al}_u\text{Ga}_{1-u}\text{As}$ ($0 \leq u \leq 1$) barrier layers. The energy difference between the valence band and conduction band in a semiconductor is called the bandgap. The layer of GaAs is a quantum well because the barrier layers are made of a material with a larger bandgap than GaAs. By adjusting the aluminum content of the barrier layers and the thickness of the GaAs layer at the time of growth, quantum wells with electronic properties tailored to the user's specifications can be created. This practice is referred to as quantum engineering.

The infinitely deep one-dimensional potential well is the simplest confinement potential to treat in quantum mechanics. In classical mechanics, the solution to the problem is trivial, since the particle will move in a straight line always at the same speed until it reflects from a wall at an equal but opposite angle. However, in order to find the quantum-mechanical solution many fundamental concepts need to be introduced.

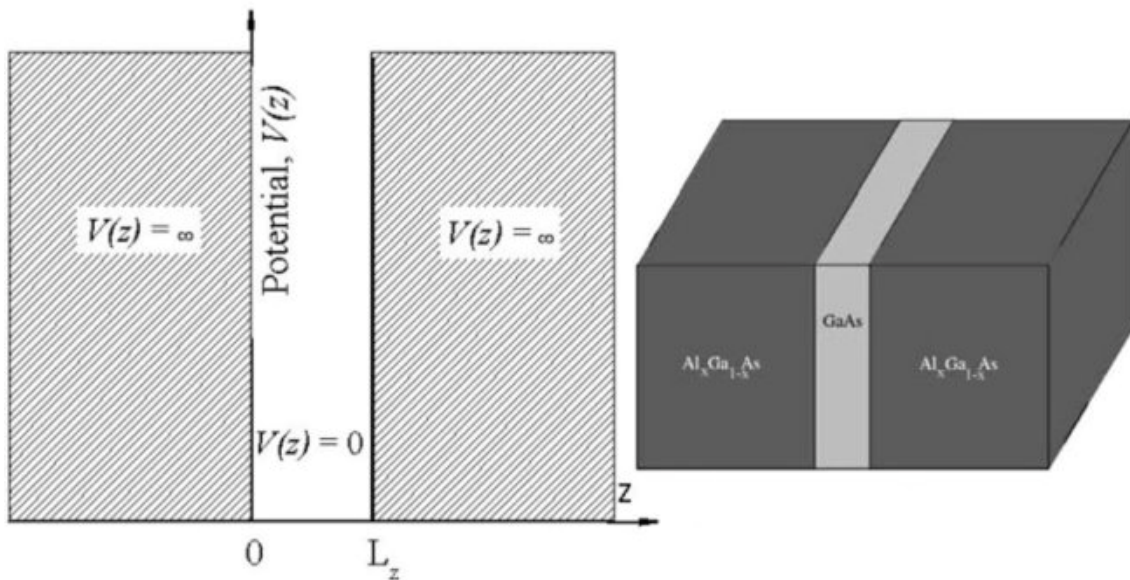


Figure 1. (left) Two-dimensional structure represented by infinite potential barriers that create a quantum well. (right) GaAs quantum well inserted between two $\text{Al}_x\text{Ga}_{1-x}\text{As}$ barrier layers.

On restricting analysis to an infinitely deep, one-dimensional potential well aligned along the z axis (Figure 1) of the form

$$V(z) = \begin{cases} 0, & 0 < z < L_z \\ \infty, & z \leq 0 \text{ or } z \geq L_z \end{cases} \quad (2.4)$$

the time-independent Schrödinger equation can be written as

$$-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \psi(z) + V(z)\psi(z) = E\psi(z). \quad (2.5)$$

Outside the chosen potential well, the potential is infinite; hence, the only possible solution is $\psi(z) = 0$, $z \leq 0$ or $z \geq L_z$, which in turn implies that all values of the energy E are allowed. Within the infinitely deep potential well, the Schrödinger equation simplifies to

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(z)}{dz^2} = E\psi(z), \quad 0 < z < L_z \quad (2.6)$$

Taking into account the appropriate boundary conditions, the solutions of this equation are infinitely many in number. These solutions, called eigenfunctions, may be written down as

$$\psi_{n_z}(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_z\pi z}{L_z}\right), \quad 0 < z < L_z, \quad n_z = 1, 2, 3, \dots \quad (2.7)$$

Note that the index $n_z = 0$ is ruled out since in this case $\psi(z) = 0$ for all $z \in (-\infty, \infty)$, corresponding to the case where there is no particle in the infinitely deep potential well. Negative values of n are also neglected, since they merely change the sign of the sine function. The complete solution is a superposition of all eigenfunctions and is given by the sum

$$\psi(z) = \sum_{n_z=1}^{\infty} A_n \psi_{n_z}(z), \quad 0 < z < L_z, \quad (2.8)$$

where A_n are the coefficients of expansion. The determination of the values of these coefficients lies outside the scope of this chapter.

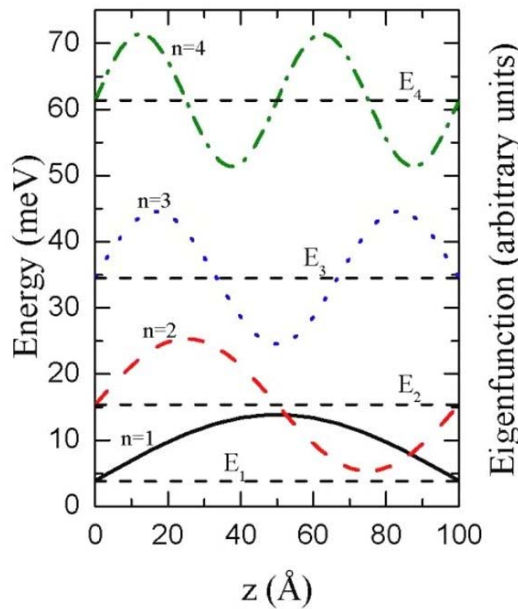


Figure 2. First four eigenfunctions (solid line) and eigenenergies (dashed line) of an electron confined to a 100 Å-thick infinitely deep potential well of Si. An eigenfunction-eigenenergy pair constitutes a quantum state. Computer codes from P. Harrison were used for the calculations.

Figure 2 shows the first four eigenfunctions (2.7) of the Schrödinger Eq. (2.6) for an electron in a 100 Å-thick, infinitely deep potential well of Si. The effective mass of the electron in Si is $m^* = 0.98m_0$, m_0 being the electron rest mass. Although the eigenfunctions were determined for a low-dimensional Si structure, the discussion can be extended to any other material such as GaAs, since eigenfunctions will show a qualitatively similar behavior. Figure 2 shows that the chance $|\psi_{n_z}(z)|^2$ of an electron obeying the n th eigenfunction being found at a specific value of z in the infinitely deep potential well is not uniform. There are certain locations (antinodes) in the potential well where the electron might be found most easily, but there are also locations (nodes) where the probability of finding the electron is zero. This result contrasts sharply with the predictions of classical mechanics where in the probability of finding an electron is the same for all z inside the infinitely deep potential well.

Each eigenfunction may be taken to describe a confined state. The eigenenergy of the n th eigenfunction is given by

$$E_{n_z} = \frac{\hbar^2}{2m} \left(\frac{n_z \pi}{L_z} \right)^2, \quad n_z = 1, 2, 3, \dots \quad (2.9)$$

An eigenfunction-eigenenergy pair constitutes a quantum state labeled by the principal quantum number n_z .

Quantum size effects are apparent for reduced size. Thus, a particle confined to an infinitely deep potential well has only specific (discrete) energy levels and the zero-energy level is not one of them. The lowest possible energy level of the particle is usually called the zero-point energy or confinement energy, which can be understood in terms of the Heisenberg uncertainty principle as follows. Because the particle is constrained within a finite region, the variability in its position has an upper bound. As the variability in the particle's momentum cannot then be zero due to the uncertainty principle, the particle must contain some energy that increases as the width L_z of the infinitely deep potential well decreases. Figure 2 also shows the first four energy levels (eigenenergies) of an electron confined to a 100 Å-thick, infinitely deep potential well of Si.

The infinitely deep potential well is of great interest since it describes qualitatively the behavior of real systems and has served as a platform for developing the physics of two-dimensional structures. In the more realistic case of a potential well of finite depth, wherein a particle is confined to a well with finite-potential wells, the results are comparable to those of infinitely deep potentials. However, unlike the infinite-potential well, there is a probability associated with the particle being found outside the finite-potential well. The quantum-mechanical interpretation is unlike the classical interpretation, where if the total energy of the particle is less than potential-energy barrier of the walls it cannot be found outside the box. In the quantum interpretation,

there is a probability of the particle being outside the box even when the energy of the particle is less than the potential energy barrier of the walls.

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Biographical Sketches

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Distinguished Alumnus in 2007. He won the PSES Outstanding Research Award (1996), the PSES Premier Research Award (2008), and the PSES Outstanding Advising Award (2006). Penn State gave him the 2006 Faculty Scholar Medal in Engineering. His research won two Nano 50 Awards from Nanotech Briefs. He is a Fellow of the Optical Society of America, SPIE, and the Institute of Physics (UK). He is also a Professional Fellow of the Institute of Nanotechnology. He has expertise in the following fields: wave-material interaction, isotropic chiral materials, anisotropic and bianisotropic materials, negative phase-velocity materials, structurally chiral materials, sculptured thin films, carbon nanotubes, nanomodeling, and fractals.

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