

## 1

## Introduction

Technology has to do with the application of scientific knowledge to the economic (profitable) production of goods and services. This textbook is concerned with the size or scale of working machines and devices in different forms of technology. It is particularly concerned with the smallest devices that are possible, and equally with the appropriate laws of nanometer-scale physics: “nanophysics,” which are available to accurately predict behavior of matter on this invisible scale. Physical behavior at the nanometer scale is predicted accurately by quantum mechanics, represented by Schrodinger’s equation. Schrodinger’s equation provides a quantitative understanding of the structure and properties of atoms. Chemical matter, molecules, and even the cells of biology, being made of atoms, are therefore, in principle, accurately described (given enough computing power) by this well-tested formulation of nanophysics.

There are often advantages in making devices smaller, as in modern semiconductor electronics. What are the limits to miniaturization and how small a device can be made? Any device must be composed of atoms, whose sizes are of the order of 0.1 nm. Here, the term “nanotechnology” will be associated with human-designed working devices in which some essential element(s), produced in a controlled fashion, have sizes of 0.1 nm to thousands of nanometers, or, 1 Å to 1 μm. There is thus an overlap with “microtechnology” at the micrometer-size scale. Microelectronics is the most advanced present technology, apart from biology, whose complex operating units are on a scale as small as micrometers.

Even though the literature of nanotechnology may refer to nanoscale machines, even “self-replicating machines built at the atomic level” [1], it is admitted that an “assembler breakthrough” [2] will be required for this to happen, and no nanoscale machines presently exist. In fact, scarcely any micrometer-scale machines exist either, and it seems that the smallest mechanical machines readily available in a wide variety of forms are really on the millimeter scale, as in conventional wrist-watches. (To avoid confusion, note that the prefix “micro” is sometimes applied, but never in this textbook, to larger scale techniques guided by optical microscopy, such as “microsurgery.”)

The reader may correctly infer that nanotechnology is presently more concept than fact, although it is certainly a media and funding reality. The fact that the

concept has great potential for technology is the message to read from the funding and media attention to this topic.

The idea of the limiting size scale of a miniaturized technology is fundamentally interesting for several reasons. As sizes approach the atomic scale, the relevant physical laws change from classical to quantum-mechanical laws of nanophysics. The changes in behavior from classical, to “mesoscopic,” to atomic scale, are broadly understood in contemporary physics, but the details in specific cases are complex and need to be worked out. While the changes from classical physics to nanophysics may mean that some existing devices will fail, the same changes open up possibilities for the invention of new devices.

A primary interest in the concept of nanotechnology comes from its connections with biology. The smallest forms of life, bacteria, cells, and the active components of living cells of biology, have sizes in the nanometer range. In fact, it may turn out that the only possibility for a viable complex nanotechnology is that represented by biology. Certainly, the present understanding of molecular biology has been seen as an existence proof for “nanotechnology” by its pioneers and enthusiasts. In molecular biology, the “self-replicating machines at the atomic level” are guided by DNA, replicated by RNA, specific molecules are “assembled” by enzymes, and cells are replete with molecular-scale motors, of which kinesin is one example. Ion channels, which allow (or block) specific ions (e.g., potassium or calcium) to enter a cell through its lipid wall, seem to be exquisitely engineered molecular-scale devices where distinct conformations of protein molecules define an open channel versus a closed channel.

Biological sensors, such as the rods and cones of the retina and the nanoscale magnets found in magnetotactic bacteria, appear to operate at the quantum limit of sensitivity. Understanding the operation of these sensors doubtlessly requires application of nanophysics. One might say that Darwinian evolution, a matter of odds of survival, has mastered the laws of quantum nanophysics, which are famously probabilistic in their nature. Understanding the role of quantum nanophysics entailed in the molecular building blocks of nature may inform the design of artificial sensors, motors, and perhaps much more, with expected advances in experimental and engineering techniques for nanotechnology.

In the improbable event that engineering, in the traditional sense, of molecular-scale machines becomes possible, the most optimistic observers note that these invisible machines could be engineered to match the size or scale of the molecules of biology. Medical nanomachines might then be possible, which could be directed to correct defects in cells, to kill dangerous cells, such as cancer cells, or even, most fancifully, to repair cell damage present after thawing of biological tissue, frozen as a means of preservation [3].

This textbook is intended to provide a guide to the ideas and physical concepts that allow an understanding of the changes that occur as the size scale shrinks toward the atomic scale. Our point of view is that a general introduction to the concepts of nanophysics will add greatly to the ability of students and professionals whose undergraduate training has been in engineering or applied science, to contribute in the various areas of nanotechnology. The broadly applicable concepts

of nanophysics are worth study, as they do not become obsolete with inevitable changes in the forefront of technology.

## 1.1

### Nanometers, Micrometers, and Millimeters

A nanometer,  $10^{-9}$  m, is about 10 times the size of the smallest atoms, such as hydrogen and carbon, while a micron is barely larger than the wavelength of visible light, thus invisible to the human eye. A millimeter, the size of a pinhead, is roughly the smallest size available in present-day machines. The range of scales from millimeters to nanometers is one million, which is also about the range of scales in present-day mechanical technology, from the largest skyscrapers to the smallest conventional mechanical machine parts. The vast opportunity for making new machines, spanning almost six orders of magnitude from 1 mm to 1 nm, is one take on Richard Feynman's famous statement [4]: "there is plenty of room at the bottom." If  $L$  is taken as the typical length, 0.1 nm for an atom, perhaps 2 m for a human, this scale range in  $L$  would be  $2 \times 10^{10}$ . If the same scale range were to apply to an area, 0.1 nm by 0.1 nm versus  $2 \text{ m} \times 2 \text{ m}$ , the scale range for area  $L^2$  is  $4 \times 10^{20}$ . Since the volume  $L^3$  is enclosed by sides  $L$ , we can see that the number of atoms of size 0.1 nm in a  $(2 \text{ m})^3$  volume is about  $8 \times 10^{30}$ . Recalling that Avogadro's number  $N_A = 6.022 \times 10^{23}$  is the number of atoms in a gram mole, supposing that the atoms were  $^{12}\text{C}$ , molar mass 12 g; then the mass enclosed in the  $(2 \text{ m})^3$  volume would be  $15.9 \times 10^4 \text{ kg}$ , corresponding to a density  $1.99 \times 10^4 \text{ kg m}^{-3}$  ( $19.9 \text{ g cc}^{-1}$ ). (This is about 20 times the density of water, and higher than the densities of elemental carbon in its diamond and graphitic forms (which are 3.51 and  $2.25 \text{ g cc}^{-1}$ , respectively), because the equivalent size  $L$  of a carbon atom in these elemental forms slightly exceeds 0.1 nm.)

A primary working tool of the nanotechnologist is facility in scaling the magnitudes of various properties of interest, as the length scale  $L$  shrinks, for example, from 1 mm to 1 nm.

Clearly, the number of atoms in a device scales as  $L^3$ . If a transistor on a micron scale contains  $10^{12}$  atoms, then on a nanometer scale,  $L'/L = 10^{-3}$  it will contain 1000 atoms, likely too few to preserve its function!

Normally, we think of scaling as an isotropic scale reduction in three dimensions. However, scaling can be thought of usefully when applied only to one or two dimensions, scaling a cube to a two-dimensional (2D) sheet of thickness  $a$  or to a one-dimensional (1D) tube or "nanowire" of cross-sectional area  $a^2$ . The term "zero-dimensional" is used to describe an object small in all three dimensions, having volume  $a^3$ . In electronics, a zero-dimensional object (a nanometer sized cube  $a^3$  of semiconductor) is called a "quantum dot" (QD) or "artificial atom" because its electronic states are few, sharply separated in energy, and thus resemble those of an atom.

As we see, a QD also typically has so small a radius  $a$ , with correspondingly small electrical capacitance  $C = 4\pi\epsilon\epsilon_0 a$  (where  $\epsilon\epsilon_0$  is the dielectric constant of

the medium in which the QD is immersed), that the electrical charging energy  $U = Q^2/2C$  is “large.” (In many situations, a “large” energy is one that exceeds the thermal excitation energy,  $k_B T$ , for  $T = 300$  K, basically room temperature. Here,  $T$  is the absolute Kelvin temperature and  $k_B$  is the Boltzmann’s constant,  $1.38 \times 10^{-23} \text{ J K}^{-1}$ .) In this situation, a change in the charge  $Q$  on the QD by even one electron charge  $e$  may effectively, by the “large” change in  $U$ , switch off the possibility of the QD being part of the path of flow for an external current.

This is the basic idea of the “single electron transistor.” The role of the QD in this application resembles the role of the grid in the vacuum triode, but only one extra electron change of charge on the “grid” turns the device off. To make a device of this sort work at room temperature requires that the QD be tiny, only a few nanometers in size.

### 1.1.1

#### Plenty of Room at the Bottom

Think of reducing the scale of working devices and machines from 1 mm to 1 nm, six orders of magnitude! Over most of this scaling range, perhaps the first five orders of magnitude, down to 10 nm (100 Å), the laws of classical Newtonian physics may well suffice to describe changes in behavior. This classical range of scaling is so large, and the changes in magnitudes of important physical properties, such as resonant frequencies, are so great, that completely different applications may appear.

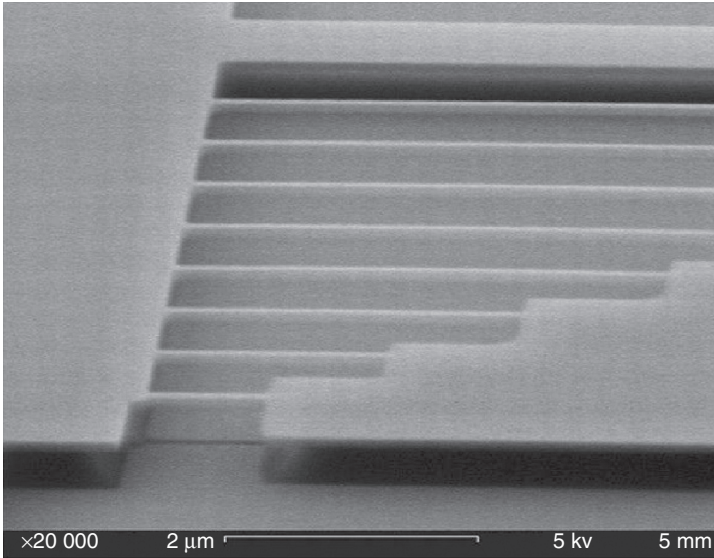
### 1.1.2

#### Scaling the Xylophone

The familiar xylophone produces musical sounds when its keys (a linear array of rectangular bars of dimensions  $a \times b \times c$ , with progressively longer key lengths  $c$  producing lower audio frequencies) are struck by a mallet and go into transverse vibration perpendicular to the smallest,  $a$ , dimension. The traditional “middle C” in music corresponds to 256 Hz. If the size scale of the xylophone key is reduced to the micrometer scale, as has recently been achieved, using the semiconductor technology, and the mallet is replaced by electromagnetic excitation, the same transverse mechanical oscillations occur, and are measured to approach the gigahertz ( $10^9$  Hz) range [5]!

The measured frequencies of the micrometer-scale xylophone keys are still accurately described by the laws of classical physics. (In fact, the oscillators that have been successfully miniaturized, see Figure 1.1, differ slightly from xylophone keys, in that they are clamped at both ends, rather than being loosely suspended. Very similar equations are known to apply in this case.) Oscillators whose frequencies approach the gigahertz range have completely different applications than those in the musical audio range!

Could such elements be used in new devices to replace Klystrons and Gunn oscillators, conventional sources of gigahertz radiation? If means could be found



**Figure 1.1** Silicon nanowires in a harp-like array. Due to the clamping of the single-crystal silicon bars at each end and the lack of applied tension, the situation is more like an array of xylophone keys. The resonant

frequency of the wire of  $2\ \mu\text{m}$  length is about 400 MHz. After reprinted with permission from Ref. [5], Copyright 1999. American Institute of Physics.

to fabricate “xylophone keys” scaling down from the micrometer scale to the nanometer scale, classical physics would presumably apply almost down to the molecular scale. The limiting vibration frequencies would be those of diatomic molecules, which lie in the range  $10^{13}$ – $10^{14}$  Hz. For comparison, the frequency of light used in fiber-optic communication is about  $2 \times 10^{14}$  Hz.

### 1.1.3

#### Reliability of Concepts and Approximate Parameter Values Down to About $L = 10\ \text{nm}$ (100 Atoms)

The large extent of the “classical” range of scaling, from 1 mm down to perhaps 10 nm, is related to the stability (constancy) of the basic microscopic properties of condensed matter (conventional building and engineering materials) almost down to the scale  $L$  of 10 nm or 100 atoms in line, or a million atoms per cube.

Typical microscopic properties of condensed matter are interatomic spacing, mass density, bulk speed of sound  $v_s$ , Young’s modulus  $Y$ , bulk modulus  $B$ , cohesive energy  $U_o$ , electrical resistivity  $\rho$ , thermal conductivity  $K$ , relative magnetic and dielectric susceptibilities  $\kappa$  and  $\epsilon$ , Fermi energy  $E_F$  and work function  $\phi$  of a metal, and bandgap of a semiconductor or insulator,  $E_g$ . A timely example in which bulk properties are retained down to nanometer sample sizes is afforded by the CdSe “QD” fluorescent markers, which are described below.

## 1.1.4

**Nanophysics Built into the Properties of Bulk Matter**

Even if we can describe the size scale of 1 mm to 10 nm as one of “classical scaling,” before distinctly size-related anomalies are strongly apparent, a nanotechnologist must appreciate that many properties of bulk condensed matter already require concepts of nanophysics for their understanding. This might seem obvious, in that atoms themselves are completely nanophysical in their structure and behavior!

Beyond this, however, the basic modern understanding of semiconductors, involving energy bands, forbidden gaps, and effective masses  $m^*$  for free electrons and free holes, is based on nanophysics in the form of Schrodinger’s equation as applied to a periodic structure.

Periodicity, a repeated unit cell of dimensions  $a \times b \times c$  (in three dimensions), profoundly alters the way an electron (or a “hole,” which is the inherently positively charged in the absence of an electron) moves in a solid. As we discuss more completely in the following, ranges (bands) of energy of the free carrier exist for which the carrier will pass through the periodic solid with no scattering at all, much in the same way that an electromagnetic wave will propagate without attenuation in the passband of a transmission line. In energy ranges between the allowed bands, gaps appear, where no moving carriers are possible, in analogy to the lack of signal transmission in the stopband frequency range of a transmission line.

Therefore, the “classical” range of scaling as mentioned earlier is one in which the consequences of periodicity for the motions of electrons and holes (wildly “nonclassical,” if referred to Newton’s laws, for example) are unchanged. In practice, the properties of a regular array of 100 atoms on a side, a nanocrystal containing only a million atoms, is still large enough to be accurately described by the methods of solid-state physics. If the material is crystalline, the properties of a sample of  $10^6$  atoms are likely to be an approximate guide to the properties of a bulk sample. To extrapolate the bulk properties from a 100-atom-per-side simulation may not be too far off.

It is probably clear that a basic understanding of the ideas, and also the fabrication methods, of semiconductor physics is likely to be a useful tool for the scientist or engineer who works in nanotechnology. Almost all devices in the Micro-Electro-Mechanical Systems category, including accelerometers, related angular rotation sensors, and more, are presently fabricated using the semiconductor microtechnology.

The second, and more challenging, question for the nanotechnologist is to understand and hopefully to exploit those changes in physical behavior that occur at the end of the classical scaling range. The “end of the scaling” is the size scale of atoms and molecules, where nanophysics is the proven conceptual replacement of the laws of classical physics. Modern physics, which includes quantum mechanics as a description of matter on a nanometer scale, is a fully developed and proven subject whose application to real situations is limited only by modeling and computational competence.

In the modern era, simulations and approximate solutions increasingly facilitate the application of nanophysics to almost any problem of interest. Many central problems are already (adequately, or more than adequately) solved in the extensive literature of theoretical chemistry, biophysics, condensed matter physics, and semiconductor device physics. The practical problem is to find the relevant work, and, frequently, to convert the notation and units systems to apply the results to the problem at hand.

It is worth saying that information has no inherent (i.e., zero) size. The density of information that can be stored is limited only by the coding element, be it a bead on an abacus, a magnetized region on a hard disk, a charge on a complementary metal oxide semiconductor capacitor, a nanoscale indentation on a plastic recording surface, the presence or absence of a particular atom at a specified location, or the presence of an “up” or “down” electronic or nuclear spin (magnetic moment) on a density of atoms in condensed matter,  $(0.1 \text{ nm})^{-3} = 10^{30} \text{ m}^{-3} = 10^{24} \text{ cm}^{-3}$ . If these coding elements are on a surface, then the limiting density is  $(0.1 \text{ nm})^{-2} = 10^{20} \text{ m}^{-2}$ , or  $6.45 \times 10^{16}$  per inch<sup>2</sup>.

The principal limitation may be the physical size of the reading element, which historically would be a coil of wire (solenoid) in the case of the magnetic bit. The limiting density of information in the presently advancing technology of magnetic computer hard disk drives is about 100 Gb per inch<sup>2</sup> or  $10^{11}$  per inch<sup>2</sup>. It appears that nonmagnetic technologies, perhaps based on arrays of atomic force microscope tips writing onto a plastic film such as polymethylmethacrylate, may eventually overtake the magnetic technology.

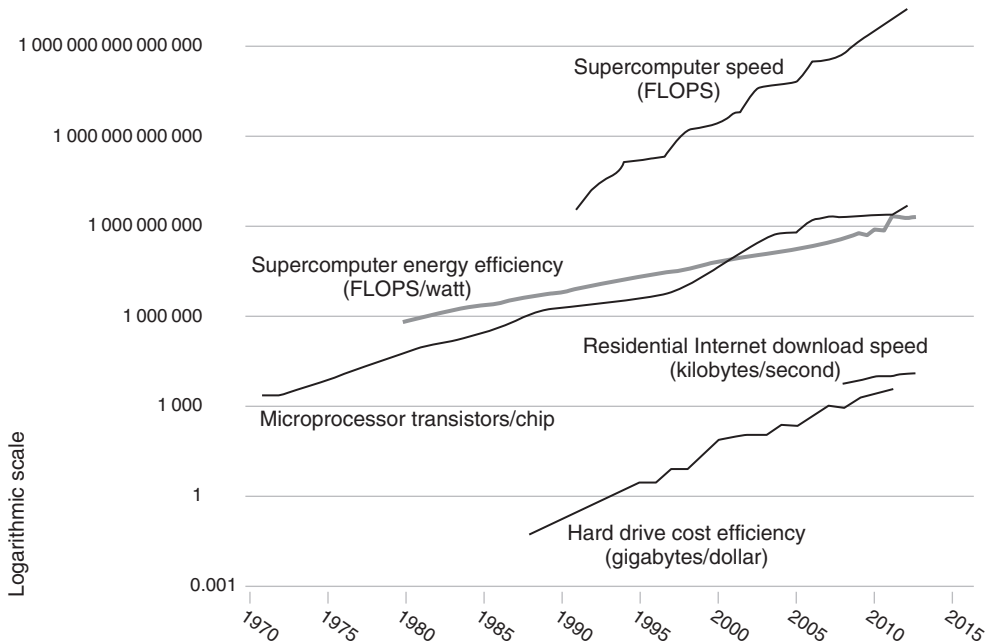
## 1.2

### Moore's Law

The computer chip is certainly one of the preeminent accomplishments of twentieth-century technology, making vastly expanded computational speed available in smaller size and at lower cost. Computers and e-mail communication are almost universally available in modern society. Perhaps the most revolutionary results of computer technology are the universal availability of e-mail to the informed and at least minimally endowed, and magnificent search engines such as Google. Without an unexpected return to the past, which might roll back this major human progress, it seems rationally that computers have ushered in a new era of information, connectedness, and enlightenment in human existence.

Moore's empirical law, illustrated in several forms in Figure 1.2, is based on the observation of Moore that the number of microprocessor transistors per chip doubles every 1.5 years, an exponential growth pattern. As shown in Figure 1.2, several related performance measures (top to bottom), supercomputer speed, supercomputer energy efficiency, residential Internet download speed, and hard drive cost, also suggest exponential growth. In general, the empirical rule summarizes the “economy of scale” in getting the same function by making the working elements





**Figure 1.2** Moore's law [6]. The number of transistors in successive generations of computer chips has risen exponentially, doubling every 1.5 years or so. Gordon Moore, cofounder of Intel, Inc., predicted this growth pattern in 1965, when a silicon chip contained only 30 transistors. The number of dynamic random access memory (DRAM) cells follows a similar

growth pattern. The growth is largely due to continuing reduction in the size of key elements in the devices, to less than 45 nm, with improvements in optical photolithography. Clock speeds have similarly increased, presently around 2 GHz. For a summary, see [7]. Reprinted with permission from Ref. [6].

ever smaller. (It turns out, as we see, that smaller means faster, characteristically enhancing the advantage in miniaturization). In the ancient abacus, bead positions represent binary numbers, with information recorded on a scale of perhaps 1 bit [(0,1) or (yes/no)] per centimeter square. In silicon microelectronic technology, an easily produced memory cell size of  $1\ \mu\text{m}$  corresponds to  $10^{12}$  bits per centimeter square ( $1\ \text{Tb cm}^{-2}$ ). Equally important is the continually reducing size of the magnetic disk memory element (and of the corresponding read/write sensor head) making possible the  $\sim 1000\ \text{Gb}$  disk memories of contemporary laptop computers. The continuing improvements in performance (reductions in size of the performing elements), empirically summarized by Moore's law (a doubling of performance every 1.5 years, or so), arise from corresponding reductions in the size scale of the computer chip, aided by the advertising-related market demand.

The vast improvements from the abacus to the Pentium and Core i7 chips exemplify the promise of nanotechnology. Please note that this is all still in the range



of “classical scaling”! The computer experts are absolutely sure that nanophysical effects are so far negligible.

The semiconductor industry, having produced a blockbuster performance over decades, transforming advanced society and suitably enriching its players and stockholders, is concerned about its next act!

The next act in the semiconductor industry, if a second act indeed shows up, must deal with the nanophysical rules. Any new technology, if such is feasible, will have to compete with a base of universally available applied computation, at unimaginably low costs. If terahertz-speed computers with 8 Gb randomly accessible memories and 1000 Gb hard drives, indeed become a commodity, what can compete with that? Silicon technology is a hard act to follow.

Nanotechnology, taken literally, also represents the physically possible limit of such improvements. The limit of technology is also evident, since the smallest possible interconnecting wire on the chip must be at least 100 atoms across! Moore's law empirically has characterized the semiconductor industry's success in providing faster computers of increasing sophistication and continually falling price. Success has been obtained with a larger number of transistors per chip made possible by finer scales of the wiring and active components on the silicon chips. There is a challenge to the continuation of this trend (Moore's law) from the economic reality of steeply increasing plant cost (to realize reduced linewidths and smaller transistors).

The fundamental challenge to the continuation of this trend (Moore's law) from the change of physical behavior as the atomic size limit is approached is a central topic in this textbook.

### 1.3

#### Esaki's Quantum Tunneling Diode

The tunneling effect is basic in quantum mechanics, a fundamental consequence of the probabilistic wave function as a measure of the location of a particle. Unlike a tennis ball, a tiny electron may penetrate a barrier. This effect was first exploited in semiconductor technology by Leo Esaki, who discovered that the current–voltage ( $I/V$ ) curves of semiconductor p–n junction rectifier diodes (when the barrier was made very thin, by increasing the dopant concentrations) became anomalous, and in fact double-valued. The forward bias  $I$  versus  $V$  plot, normally a rising exponential  $\exp(eV/kT)$ , was preceded by a distinct “current hump” starting at zero bias and extending to  $V = 50$  mV or so. Between the region of the “hump” and the onset of the conventional exponential current rise, there was a region of negative slope,  $dI/dV < 0$ !

The planar junction between an  $N$ -type region and a  $P$ -type region in a semiconductor such as Si contains a “depletion region” separating conductive regions filled with free electrons on the  $N$ -side and free holes on the  $P$ -side. It is a useful nontrivial exercise in semiconductor physics to show that the width  $W$  of the depletion region is

$$W = \left[ \frac{2\epsilon\epsilon_0 V_B (N_D + N_A)}{e(N_D N_A)} \right]^{1/2}, \quad (1.1)$$

where  $\epsilon\epsilon_0$  is the dielectric constant,  $e$  the electron charge,  $V_B$  in Volts is the shift in the bands across the junction, and  $N_D$  and  $N_A$ , respectively, are the concentrations of donor and acceptor impurities.

The change in electrical behavior (the negative resistance range) resulting from the electron tunneling (in the thin depletion region limit) made possible an entirely new effect, an oscillation, at an extremely high frequency! (As often happens with the continuing advance of technology, this pioneering device has been largely supplanted as an oscillator by the Gunn diode, which is easier to manufacture.)

The Esaki tunnel diode is perhaps the first example in which the appearance of quantum physics at the limit of a small size led to a new device. In our terminology, the depletion layer tunneling barrier is 2D, with only one small dimension, the depletion layer thickness  $W$ . The Esaki diode falls into our classification as an element of nanotechnology, since the controlled small barrier  $W$  is only a few nanometers in thickness.

#### 1.4

##### QDs of Many Colors

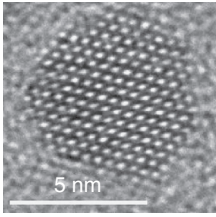
QDs of CdSe and similar semiconductors are grown in carefully controlled solution precipitation with controlled sizes in the range  $L = 4$  or  $5$  nm. It is found that the wavelength (color) of strong fluorescent light emitted by these QDs under ultraviolet (UV) light illumination depends sensitively on the size  $L$ , see Figure 1.3.

There are enough atoms in this particle to effectively validate the concepts of solid-state physics, which include electron bands, forbidden energy bandgaps, electron and hole effective masses, and more.

Still, the particle is small enough to be called an “artificial atom,” characterized by discrete sharp electron energy states, and discrete sharp absorption, and emission wavelengths for photons.

Transmission electron microscope (TEM) images of such nanocrystals, which may contain only 50 000 atoms, reveal perfectly ordered crystals having the bulk crystal structure and nearly the bulk lattice constant. Quantitative analysis of the light emission process in QDs suggests that the bandgap, effective masses of electrons and holes, and other microscopic material properties are very close to their values in large crystals of the same material. The light emission in all cases comes from radiative recombination of an electron and a hole, created initially by the shorter wavelength illumination (Figure 1.3).

The energy  $E_R$  released in the recombination is given entirely to a photon (the quantum unit of light), according to the relation  $E_R = h\nu = hc/\lambda$ . Here,  $\nu$  and  $\lambda$  are, respectively, the frequency and wavelength of the emitted light,  $c$  is the speed of light  $3 \times 10^8 \text{ m s}^{-1}$ , and  $h$  is Planck's constant  $h = 6.63 \times 10^{-34} \text{ Js} = 4.136 \times 10^{-15} \text{ eVs}$ . The color of the emitted light is controlled by the choice



**Figure 1.3** Transmission electron micrograph (TEM) image of one 5 nm CdSe quantum dot particle. Courtesy Andreas Kornowski, University of Hamburg, Germany.

of  $L$ , since  $E_R = E_G + E_e + E_h$ , where  $E_G$  is the semiconductor bandgap, and the electron and hole confinement energies,  $E_e$  and  $E_h$ , respectively, become larger with decreasing  $L$ .

It is an elementary exercise in nanophysics, which will be demonstrated in Chapter 4, to show that these confinement (blue shift) energies are proportional to  $1/L^2$ . Since these terms increase the energy of the emitted photon, they act to shorten the wavelength of the light relative to that emitted by the bulk semiconductor, an effect referred to as the “blue shift” of light from the QD.

These nanocrystals are used in biological research as markers for certain kinds of cells, as observed under an optical microscope with background UV light illumination.

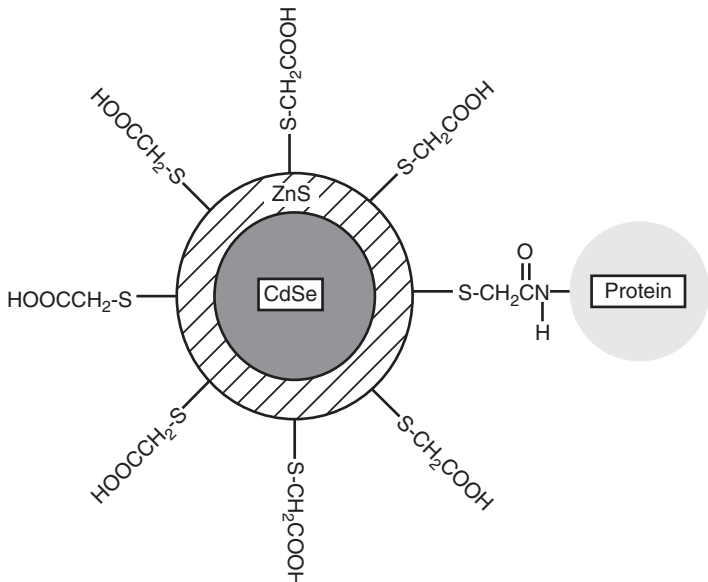
In these applications, the basic semiconductor QD crystal is typically coated with a thin layer to make it impervious to (and soluble in) an aqueous biological environment. A further coating may then be applied, which allows the QD to preferentially bond to a specific biological cell or cell component of interest. Such a coated QD is shown in Figure 1.4 [8]. These authors say that the QDs they use as luminescent labels are 20 times as bright, 100 times as stable against photobleaching, and have emission spectra 3 times sharper than conventional organic dyes, such as rhodamine.

The biological researcher may, for example, see the outer cell surface illuminated in green while the surface of the inner cell nucleus illuminated in red, all under illumination of the whole field with light of a single shorter wavelength.

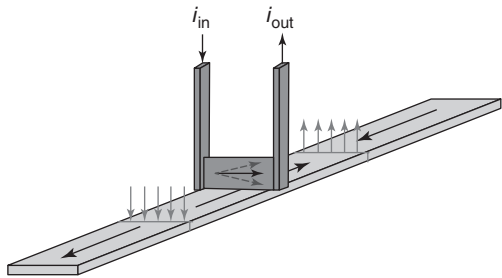
## 1.5

### GMR and TMR 100–1000 Gb Hard Drive “Read Heads”

In modern computers, the hard disk encodes information in the form of a dense array of tiny linear reversible ferromagnetic regions, or bits. The performance of hard drives has been vastly improved since about 1995 with sequential discovery and development of the Giant Magnetoresistance (GMR) and Tunneling Magnetoresistance (TMR) effects, allowing successively smaller assemblies (read heads) to scan the magnetic data. In the GMR devices, the ferromagnetic bits lie parallel to the disk surface, as shown in Figure 1.5. The operation of the GMR reader is a wonderful example of nanophysics, and led to the Nobel Prize in Physics in 2007 to Peter Grunberg and Albert Fert. We here discuss the GMR effect on the basis of its priority and connection with the Nobel Prize. A more detailed discussion,



**Figure 1.4** Schematic of quantum dot with coatings suitable to assure water solubility, for application in biological tissue. This ZnS-capped CdSe quantum dot is covalently coupled to a protein by mercaptoacetic acid. The typical QD core size is 4.2 nm [8]. Reprinted with permission from [8], Copyright 1998 AAAS.



**Figure 1.5** Schematic diagram of the GMR read head, showing two current leads connected by the sensing element, which itself is a conducting copper sheet sandwiched between a pair of hard and soft magnets. Courtesy Prinz, G.A., U.S. Naval Research Laboratory, Washington, DC.

including the tunnel junction TMR reader, adapted to ferromagnetic bits that are perpendicular to the disk surface, and that has allowed 1000 Gb drives, is deferred to Sections 8.2–8.5. The TMR technology is now used in the “cloud computers” that handle vast amounts of information generated by YouTube and Facebook, while even smaller but more expensive “flash memory” cells (used in the familiar USB “thumb drives”) replace the disk memory in some premium applications. The ferromagnetic bits are written onto (and read from) the disk surface, which is uniformly coated with a ferromagnetic film having a small coercive field. This is a “soft” ferromagnet, so that a small imposed magnetic field  $B$  can easily establish

the ferromagnetic magnetization  $M$  along the direction of the applied  $B$  field. Both writing and reading operations are accomplished by the “read head.”

The density of information that can be stored in a magnetic disk is fundamentally limited by the minimum size of a ferromagnetic “domain.” Ferromagnetism is a cooperative nanophysical effect requiring a minimum number of atoms: below this number, the individual atomic magnetic moments remain independent of each other. It is estimated that this “superparamagnetic limit” is on the order of 100 Gb per inch<sup>2</sup>.

The practical limit, however, has historically been the size of the “read head,” as depicted in Figure 1.5, which on the one hand impresses a local magnetic field  $B$  on the local surface region to create the magnetized domain, and then also senses the magnetic field of the magnetic domain so produced. In present technology, the linear bits are about 100 nm in length ( $M$  along the track) and have widths in the range 0.3–1.0  $\mu\text{m}$ . The ferromagnetic domain magnetization  $M$  is parallel or antiparallel to the linear track.

The localized, perpendicular, magnetic fields  $B$  that appear at the junctions between parallel and antiparallel bits are sensed by the read head. The width of the transition region between adjacent bits, in which the localized magnetic field is present, is between 10 and 100 nm. The localized  $B$  fields extend linearly across the track and point upward (or down) from the disk surface, as shown in Figure 1.5.

The state-of-the-art magnetic field sensor is an exquisitely thin sandwich of magnetic and nonmagnetic metals oriented vertically to intercept the fringe  $B$  field between adjacent bits. The total thickness of the sensor sandwich, along the direction of the track, is presently about 80 nm, but it may soon fall to 20 nm. The GMR detector sandwich is composed of a sensing soft ferromagnetic layer of NiFe alloy, a Cu spacer, and a “magnetically hard” Co ferromagnetic film. A sensing current is directed along the sandwich in the direction transverse to the track, and the voltage across the sandwich, which is sensitive to the magnetic field in the plane of the sandwich, is measured. In this read-head sandwich the Cu layer is about 15 atoms in thickness! The sensitivity of this GMR magnetoresistive sensor is presently in the vicinity of 1% per Oersted.

Writing the magnetic bits is accomplished by an integrated component of the “read head” (not shown in Figure 1.5), which generates a surface-localized magnetic field  $B$  parallel or antiparallel to the track. The local surface magnetic field is produced inductively in a closed planar loop, resembling an open-ended box, of thin magnetic film, which is interrupted by a linear gap facing the disk, transverse to the track.

These “read-head” units are fabricated in mass, using methods of the silicon lithographic microtechnology. It is expected that even smaller sensor devices and higher storage densities may be possible with advances in the silicon fabrication technology.

These units, which have had a large economic impact, are a demonstration of nanotechnology in that their closely controlled dimensions are in the nanometer range. The mechanism of greatly enhanced magnetic field sensitivity in the GMR Effect is also fully nanophysical in nature, an example of (probably unexpectedly) better results at the quantum limit of the scaling process.

## 1.6

## Accelerometers in Your Car

Modern cars have airbags that inflate in crashes to protect drivers and passengers from accidents. Micro-electro-mechanical semiconductor acceleration sensors (accelerometers) are located in bumpers, which quickly inflate the airbags. The basic accelerometer is a mass  $m$  attached by a spring of constant  $k$  to the frame of the sensor device, itself secured to the automobile frame. If the car frame (and thus the frame of the sensor device) undergoes a strong acceleration, the spring connecting the mass to the sensor frame will extend or contract, leading to a motion of the mass  $m$  relative to the frame of the sensor device. This deflection is measured, for example, by change in a capacitance, which then triggers expansion of the airbag. This micro-electro-mechanical device is mass produced in an integrated package, including relevant electronics, using the methods of silicon microelectronics.

### Newton's laws of motion

**Newton's laws of motion** describe the position  $x$ , the velocity  $v = dx/dt$ , and the acceleration  $a = d^2x/dt^2$  of a mass  $m$  which may be acted upon by a force  $F$ , according to

$$m d^2x / dt^2 = F. \quad (1.2)$$

Kinematics describes the relationships among  $x$ ,  $v$ ,  $a$ , and  $t$ . As an example, the time-dependent position  $x$  under uniform acceleration  $a$  is

$$x = x_0 + v_0 t + at^2, \quad (1.3)$$

where  $x_0$  and  $v_0$ , respectively, are the position and velocity at  $t = 0$ . Also, if a time-varying acceleration  $a(t)$  is known, and  $x_0 = 0$  and  $v_0 = 0$ , then

$$x(t) = \int \int a(t) dt^2. \quad (1.4)$$

Newton's first law states that in the absence of a force, the mass  $m$  remains at rest if initially so, and if initially in motion continues unchanged in that motion. (These laws are valid only if the coordinate system in which the observations are made is one of uniform motion, and certainly do not apply in an accelerated frame of reference, such as a carousel or a merry-go-round. For most purposes, the earth's surface, although accelerated toward its rotation axis, can be regarded as an "inertial frame of reference," that is, Newton's laws are useful.)

Newton's second law is  $F = ma$ , Eq. (1.2).

The Third Law states that for two masses in contact, the force exerted by the first on the second is equal and opposite to the force exerted by the second on the first.

A more sophisticated version of such an accelerometer, arranged to record accelerations in  $x, y, z$  directions, and equipped with integrating electronics, can be used to record the three-dimensional displacement over time.

These devices are not presently built on a nanometer scale, of course, but are one example of a wide class of microelectronic sensors that could be made on smaller scales as semiconductor technology advances, and if smaller devices are useful.

## 1.7

### Nanopore Filters

The original nanopore (Nuclepore) filters<sup>1)</sup> [9] are sheets of polycarbonate of 6–11  $\mu\text{m}$  thickness with closely spaced arrays of parallel holes running through the sheet. The filters are available with pore sizes rated from 0.015 to 12.0  $\mu\text{m}$  (15–12 000 nm). The holes are made by exposing the polycarbonate sheets to perpendicular flux of ionizing  $\alpha$  particles, which produce linear paths of atomic-scale damage in the polycarbonate. Controlled chemical etching is then employed to establish and enlarge the parallel holes to the desired diameter. This scheme is an example of nanotechnology.

The filters are robust and can have a very substantial throughput, with up to 12% of the area being open. The smallest filters will block passage of bacteria and perhaps even some viruses, and are used in many applications including water filters for hikers.

A second class of filters (Anapore) was later established, formed of alumina grown by anodic oxidation of aluminum metal. These filters are more porous, up to 40%, and are stronger and more temperature resistant than the polycarbonate filters. They have been used, for example, to produce dense arrays of nanowires. Nanowires are obtained using a hot press to force a ductile metal into the pores of the nanopore alumina filter.

## 1.8

### Nanoscale Elements in Traditional Technologies

From the present knowledge of materials, it is understood that the beautiful colors of stained glass windows originate in nanometer-scale metal particles present in the glass. These metal particles have scattering resonances for light of specific wavelengths, depending on the particle size  $L$ . The particle size distribution, in turn, will depend upon the choice of metal impurity, its concentration, and the heat treatment of the glass. When the metallic particles in the glass are illuminated, they preferentially scatter light of particular colors. Neutral density filters

1) These filters are manufactured by Nuclepore Corporation, 7035 Commerce Circle, Pleasanton, CA 94566.



marketed for photographic application also have distributions of small particles embedded in glass.

Carbon black, commonly known as soot, which contains nanometer-sized particles of carbon, was used very early as an additive to the rubber in automobile tires. (As we now know, carbon black contains small amounts of  $^{60}\text{C}$  (Buckminsterfullerene), other fullerenes, and graphitic nanotubes of various types.)

The AgBr and AgI crystals of conventional photography are nanometer-sized single crystals embedded in a thin gelatin matrix. It appears that the fundamental light absorption in these crystals is close to the quantum sensitivity limit. It further appears that the nanoscopic changes in these tiny crystals, which occur upon absorption of one or more light photons, enable them to be turned into larger metallic silver particles in the conventional photographic development process. The conventional photographic negative image is an array of solid silver grains embedded in a gelatin matrix. As such, it is remarkably stable as a record, over decades or more.

The drugs that are very important in everyday life (and are also of huge economic importance), including caffeine, aspirin, and many more, are specific molecules of nanometer size, typically containing fewer than 100 atoms.

Controlled precipitation chemistry, for example, is employed to produce uniform nanometer-sized spheres of polystyrene, which have long been marketed as calibration markers for transmission electron microscopy.

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