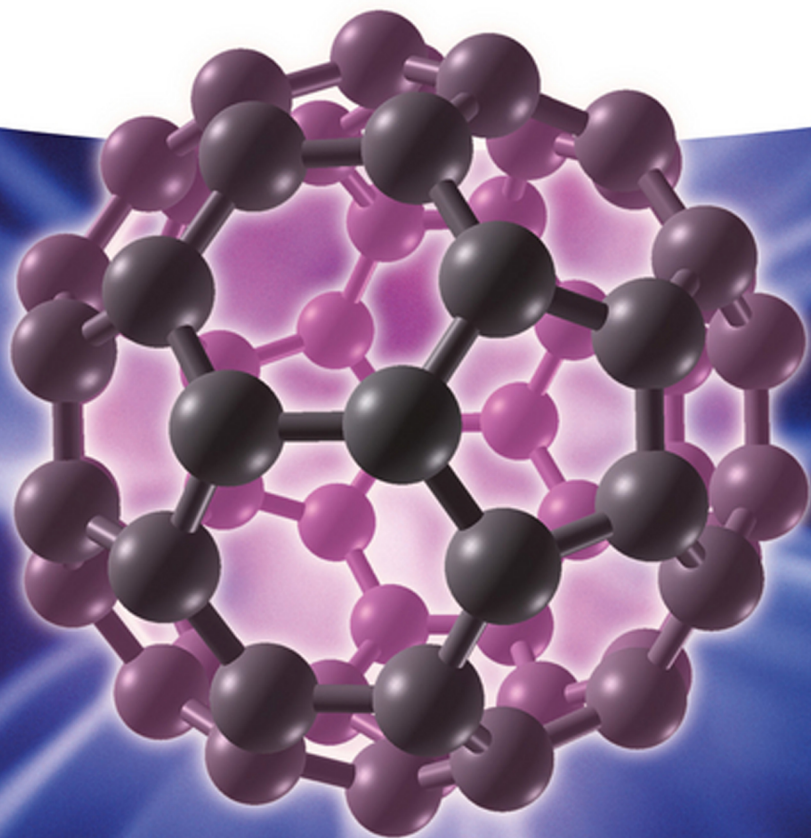


Edward L. Wolf

Nanophysics and Nanotechnology

An Introduction to Modern Concepts
in Nanoscience

Third Edition



Edward L. Wolf

Nanophysics and Nanotechnology

Related Titles

Fujita, S., Suzuki, A.

Electrical Conduction in Graphene and Nanotubes

2013

Print ISBN: 978-3-527-41151-1; also available
in electronic formats

ISBN: 978-3-527-67666-8

Marder, M.P.

Condensed Matter Physics, Second Edition

2nd Edition

2011

Print ISBN: 978-0-470-61798-4; also available
in electronic formats

Dinh, P.M., Reinhard, P., Suraud, E.

An Introduction to Cluster Science

2014

Print ISBN: 978-3-527-41118-4; also available
in electronic formats

Edward L. Wolf

Nanophysics and Nanotechnology

An Introduction to Modern Concepts in Nanoscience

Third Edition

WILEY-VCH
Verlag GmbH & Co. KGaA

Author

Prof. Edward L. Wolf

New York University Polytechnic School
of Engineering
Six Metrotech Center
314 Rogers Hall
Brooklyn NY 11201
USA

Cover

Assembling a ring of 48 Fe atoms on a
(111) Cu surface with an STM. The diam-
eter of the ring is 14.3 nm.

All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2015 Wiley-VCH Verlag GmbH & Co.
KGaA, Boschstr. 12, 69469 Weinheim,
Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-41324-9

ePDF ISBN: 978-3-527-68418-2

ePub ISBN: 978-3-527-68416-8

Mobi ISBN: 978-3-527-68417-5

Cover Design Grafik-Design Schulz,
Fußgönheim, Germany

Typesetting SPi Global, Chennai, India

Printing and Binding Markono Print
Media Pte Ltd, Singapore

Printed on acid-free paper

To

Carol, Doug, Dave, Ben

And

Phill, Dan, Mehdi, Michael

Contents

Preface *XV*

Glossary of abbreviations *XVII*

1	Introduction	<i>1</i>
1.1	Nanometers, Micrometers, and Millimeters	<i>3</i>
1.1.1	Plenty of Room at the Bottom	<i>4</i>
1.1.2	Scaling the Xylophone	<i>4</i>
1.1.3	Reliability of Concepts and Approximate Parameter Values Down to About $L = 10$ nm (100 Atoms)	<i>5</i>
1.1.4	Nanophysics Built into the Properties of Bulk Matter	<i>6</i>
1.2	Moore's Law	<i>7</i>
1.3	Esaki's Quantum Tunneling Diode	<i>9</i>
1.4	QDs of Many Colors	<i>10</i>
1.5	GMR and TMR 100–1000 Gb Hard Drive “Read Heads”	<i>11</i>
1.6	Accelerometers in Your Car	<i>14</i>
1.7	Nanopore Filters	<i>15</i>
1.8	Nanoscale Elements in Traditional Technologies	<i>15</i>
	References	<i>16</i>
2	Systematics of Making Things Smaller, Pre-quantum	<i>17</i>
2.1	Mechanical Frequencies Increase in Small Systems	<i>17</i>
2.2	Scaling Relations Illustrated by a Simple Harmonic Oscillator	<i>20</i>
2.3	Scaling Relations Illustrated by Simple Circuit Elements	<i>21</i>
2.4	Thermal Time Constants and Temperature Differences Decrease	<i>22</i>
2.5	Viscous Forces Become Dominant for Small Particles in Fluid Media	<i>22</i>
2.6	Frictional Forces Can Disappear in Symmetric Molecular Scale Systems	<i>24</i>
	References	<i>26</i>

3	What Are Limits to Smallness?	27
3.1	Particle (Quantum) Nature of Matter: Photons, Electrons, Atoms, and Molecules	27
3.2	Biological Examples of Nanomotors and Nanodevices	28
3.2.1	Linear Spring Motors	29
3.2.2	Linear Engines on Tracks	30
3.2.3	Rotary Motors	33
3.2.4	Ion Channels, the Nanotransistors of Biology	36
3.2.4.1	Ca ⁺⁺ -Gated Potassium Channel	37
3.2.4.2	Voltage-Gated Potassium Channel	37
3.3	How Small Can You Make it?	38
3.3.1	What Are the Methods for Making Small Objects?	39
3.3.2	How Can You See What You Want to Make?	39
3.3.3	How Can You Connect it to the Outside World?	42
3.3.4	If You Cannot See it or Connect to it, Can You Make it Self-Assemble and Work on its Own?	42
3.3.5	Approaches to Assembly of Small Three-Dimensional Objects	42
3.3.5.1	Variable Thickness Electroplating	43
3.3.5.2	Lithography onto Curved Surfaces	43
3.3.5.3	Optical Tweezers	43
3.3.5.4	Arrays of Optical Traps	45
3.3.6	Use of DNA Strands in Guiding Self-Assembly of Nanometer-Sized Structures	46
	References	48
4	Quantum Nature of the Nanoworld	51
4.1	Bohr's Model of Nuclear Atom	52
4.1.1	Quantization of Angular Momentum	52
4.1.2	Extensions of Bohr's Model	53
4.2	Particle–Wave Nature of Light and Matter, DeBroglie Formulas $\lambda = h/p, E = h\nu$	54
4.3	Wavefunction Ψ for Electron, Probability Density $\Psi^*\Psi$, Traveling and Standing Waves	55
4.4	Maxwell's Equations; E and B as Wavefunctions for Photons, Optical Fiber Modes	59
4.5	The Heisenberg Uncertainty Principle	60
4.6	Schrodinger Equation, Quantum States and Energies, Barrier Tunneling	61
4.6.1	Schrodinger Equations in One Dimension	62
4.6.1.1	Time-Dependent Equation	62
4.6.1.2	Time-Independent Equation	63
4.6.2	The Trapped Particle in One Dimension	63
4.6.2.1	Linear Combinations of Solutions	64
4.6.2.2	Expectation Values	64
4.6.2.3	Two-Particle Wavefunction	65

4.6.3	Reflection and Tunneling at a Potential Step	65
4.6.3.1	Case 1: $E > U_0$	66
4.6.3.2	Case 2: $E < U_0$	66
4.6.4	Penetration of a Barrier, Escape Time from a Well, Resonant Tunneling Diode	67
4.6.5	Trapped Particles in Two and Three Dimensions: Quantum Dot	68
4.6.5.1	Electrons Trapped in a 2D Box	69
4.6.5.2	Electrons in a 3D “Quantum Dot”	70
4.6.6	2D Bands and Quantum Wires	71
4.6.6.1	2D Band	71
4.6.6.2	Quantum Wire	71
4.6.7	The Simple Harmonic Oscillator	72
4.6.8	Schrodinger Equation in Spherical Polar Coordinates	73
4.7	The Hydrogen Atom, One-Electron Atoms, Excitons	74
4.7.1	Magnetic Moments	78
4.7.2	Magnetization and Magnetic Susceptibility	79
4.7.3	Positronium and Excitons	80
4.8	Fermions, Bosons, and Occupation Rules	81
	References	81
5	Quantum Consequences for the Macroworld	83
5.1	Chemical Table of the Elements	83
5.2	Nanosymmetry, Diatoms, and Ferromagnets	84
5.2.1	Indistinguishable Particles and Their Exchange	84
5.2.1.1	Fermions	85
5.2.1.2	Bosons	85
5.2.1.3	Orbital and Spin Components of Wavefunctions	85
5.2.2	The Hydrogen Molecule, Dihydrogen: The Covalent Bond	86
5.2.2.1	Covalent Bonding and Covalent AntiBonding, Purely Nanophysical Effects	87
5.2.2.2	Ferromagnetism, a Purely Nanophysical Effect	87
5.3	More Purely Nanophysical Forces: van der Waals, Casimir, and Hydrogen Bonding	88
5.3.1	The Polar and van der Waals Fluctuation Forces	89
5.3.1.1	Electric Polarizability of Neutral Atoms and Molecules	89
5.3.1.2	Dipolar Fluctuations of Neutral and Symmetric Atoms	90
5.3.2	The Casimir Force	92
5.3.3	The Hydrogen Bond	96
5.4	Metals as Boxes of Free Electrons: Fermi Level, DOS, Dimensionality	97
5.4.1	Electronic Conduction, Resistivity, Mean Free Path, Hall Effect, Magnetoresistance	100
5.5	Periodic Structures (e.g., Si, GaAs, InSb, Cu): Kronig–Penney Model for Electron Bands and Gaps	101

5.6	Electron Bands and Conduction in Semiconductors and Insulators; Localization versus Delocalization	107
5.7	Hydrogenic Donors and Acceptors	110
5.7.1	Carrier Concentrations in Semiconductors, Metallic Doping	112
5.7.2	PN Junction, Electrical Diode $I(V)$ Characteristic, Injection Laser	116
5.7.2.1	Radiative Recombination and Emission of Light	117
5.7.2.2	PN Junction Injection Laser	118
5.7.2.3	Increasing Radiative Efficiency η	119
5.7.2.4	Single-Nanowire Electrically Driven Laser	119
5.8	More about Ferromagnetism, the Nanophysical Basis of Disk Memory	121
5.9	Surfaces are Different; Schottky Barrier Thickness $W = [2\epsilon\epsilon_0 V_B / eN_D]^{1/2}$	124
5.10	Ferroelectrics, Piezoelectrics, and Pyroelectrics: Recent Applications to Advancing Nanotechnology	126
5.10.1	Piezoelectric Materials	126
5.10.2	Ultrasonic Initiation of Bubbles, by a Negative Pressure	127
5.10.3	Ferroelectrics and Pyroelectrics	127
5.10.4	A Nanotechnological (Pyroelectric) Compact Source of Neutrons	128
5.10.5	Electric Field Ionization of Deuterium (Hydrogen)	129
5.10.6	An Unexpected High-Temperature Nanoenvironment	131
5.10.7	Collapse of Ultrasonically Produced Bubbles in Dense Liquids	131
	References	134
6	Self-Assembled Nanostructures in Nature and Industry	137
6.1	Carbon Atom $^{12}\text{C } 1s^2 2p^4$ (0.07 nm)	138
6.2	Methane (CH_4), Ethane (C_2H_6), and Octane (C_8H_{18})	139
6.3	Ethylene (C_2H_4), Benzene (C_6H_6), and Acetylene (C_2H_2)	140
6.4	C_{60} Buckyball (~ 0.5 nm)	140
6.5	C_∞ Nanotube (~ 0.5 nm)	141
6.5.1	Si Nanowire (~ 5 nm)	144
6.6	InAs Quantum Dot (~ 5 nm)	145
6.7	AgBr Nanocrystal (0.1–2 μm)	146
6.8	Fe_3O_4 Magnetite and Fe_3S_4 Greigite Nanoparticles in Magnetotactic Bacteria	147
6.9	Self-Assembled Monolayers on Au and Other Smooth Surfaces	149
	References	151
7	Physics-Based Experimental Approaches to Nanofabrication and Nanotechnology	153
7.1	Silicon Technology: The INTEL-IBM Approach to Nanotechnology	154
7.1.1	Patterning, Masks, and Photolithography	154

7.1.1.1	Patterning Deposition Masks	154
7.1.1.2	Masking Layers to Limit Etching	155
7.1.2	Etching Silicon	155
7.1.2.1	Wet Etches	155
7.1.2.2	Dry Etches	156
7.1.3	Defining Highly Conducting Electrode Regions	156
7.1.4	Methods of Deposition of Metal and Insulating Films	156
7.1.4.1	Evaporation	156
7.1.4.2	Sputtering	157
7.1.4.3	Chemical Vapor Deposition	157
7.1.4.4	Laser Ablation	157
7.1.4.5	Molecular Beam Epitaxy	157
7.1.4.6	Ion Implantation	158
7.2	Lateral Resolution (Linewidths) Limited by Wavelength of Light, Now 65 nm	158
7.2.1	Optical and X-Ray Lithography	158
7.2.2	Electron-Beam Lithography	159
7.3	Sacrificial Layers, Suspended Bridges, Single-Electron Transistors	160
7.4	What Is the Future of Silicon Computer Technology?	162
7.5	Heat Dissipation and the RSFQ Technology	163
7.6	Scanning Probe (Machine) Methods: One Atom at a Time	167
7.7	STM as Prototype Molecular Assembler	169
7.7.1	Moving Au Atoms, Making Surface Molecules	169
7.7.2	Assembling Organic Molecules with an STM	172
7.8	Atomic Force Microscope Arrays	173
7.8.1	Cantilever Arrays by Photolithography	173
7.8.2	Nanofabrication with an AFM	174
7.8.3	Imaging a Single Electron Spin by a Magnetic Resonance AFM	175
7.9	Fundamental Questions: Rates, Accuracy, and More	177
7.10	Nanophotonics and Nanoplasmonics	178
	References	181
8	Quantum Technologies Based on Magnetism, Electron and Nuclear Spin, and Superconductivity	183
8.1	Spin as an Element of “Quantum Computing”	183
8.2	The Stern–Gerlach Experiment: Observation of Spin-1/2; Angular Momentum of the Electron	186
8.3	Two Nuclear Spin Effects: MRI (Magnetic Resonance Imaging) and the “21.1 cm Line”	187
8.4	Electron Spin 1/2; as a Qubit for a Quantum Computer: Quantum Superposition, Coherence	190
8.5	Hard and Soft Ferromagnets	193
8.6	The Origins of GMR (Giant Magnetoresistance): Spin-Dependent Scattering of Electrons	194

8.7	The GMR Spin Valve, a Nanophysical Magnetoresistance Sensor	197
8.8	The Tunnel Valve, a Better (TMR) Nanophysical Magnetic Field Sensor	198
8.9	Magnetic Random Access Memory	200
8.9.1	Magnetic Tunnel Junction MRAM Arrays	200
8.9.2	Hybrid Ferromagnet–Semiconductor Nonvolatile Hall Effect Gate Devices	200
8.10	Spin Injection: The Johnson–Silsbee Effect	203
8.10.1	Apparent Spin Injection from a Ferromagnet into a Carbon Nanotube	203
8.11	Magnetic Logic Devices: A Majority Universal Logic Gate	203
8.12	Superconductors and the Superconducting (Magnetic) Flux Quantum	206
8.13	Josephson Effect and the Superconducting Quantum Interference Device (SQUID)	211
8.14	Superconducting (RSFQ) Logic/Memory Computer Elements	214
8.14.1	The Single Flux Quantum Voltage Pulse	215
8.14.2	Analog-to-Digital Conversion (ADC) Using RSFQ Logic	217
	References	217
9	Silicon Nanoelectronics and Beyond	219
9.1	Electron Interference Devices with Coherent Electrons	220
9.1.1	Ballistic Electron Transport in Stubbed Quantum Waveguides: Experiment and Theory	222
9.1.2	Well-Defined Quantum Interference Effects in Carbon Nanotubes	223
9.2	Carbon Nanotube Sensors and Dense Nonvolatile Random Access Memories	226
9.2.1	A Carbon Nanotube Sensor of Polar Molecules, Making Use of the Inherently Large Electric Fields	227
9.2.2	Carbon Nanotube Cross-Bar Arrays for Ultradense Ultrafast Nonvolatile Random Access Memory	228
9.3	Resonant Tunneling Diodes, Tunneling Hot Electron Transistors	232
9.4	Double-Well Potential Charge Qubits	233
9.4.1	Silicon-Based Quantum Computer Qubits	238
9.5	Single Electron Transistors	239
9.5.1	RFSET, a Useful Proven Research Tool	242
9.5.2	Readout of the Charge Qubit, with Subelectron Charge Resolution	242
9.5.3	A Comparison of SET and RTD Behaviors	244
9.6	Experimental Approaches to the Double-Well Charge Qubit	245
9.6.1	Coupling of Two-Charge Qubits in a Solid-State (Superconducting) Context	249

9.7	Ion Trap on a GaAs Chip, Pointing to a New Qubit	253
9.8	Quantum Computing by Quantum Annealing with Artificial Spins	254
	References	255
10	Nanophysics and Nanotechnology of Graphene	257
10.1	Graphene: Record-Breaking Physical and Electrical Properties	257
10.2	Consequences of One-Atom Thickness: Softness and Adherence	258
10.3	Impermeability of Single-Layer Graphene	258
10.4	Synthesis by Chemical Vapor Deposition and Direct Reaction	260
10.5	Application to Flexible, Conducting, and Transparent Electrodes	262
10.6	Potential Application to Computer Logic Devices, Extending Moore's Law	264
10.7	Applications of Graphene within Silicon Technology	266
	References	268
11	Looking into the Future	271
11.1	Drexler's Mechanical (Molecular) Axle and Bearing	271
11.1.1	Smalley's Refutation of Machine Assembly	272
11.1.2	van der Waals Forces for Frictionless Bearings?	274
11.2	The Concept of the Molecular Assembler is Flawed	275
11.3	Could Molecular Machines Revolutionize Technology or Even Self-Replicate to Threaten Terrestrial Life?	276
11.4	The Prospect of Radical Abundance by a Breakthrough in Nanoengineering	277
11.5	What about Genetic Engineering and Robotics?	278
11.6	Possible Social and Ethical Implications of Biotechnology and Synthetic Biology	281
11.7	Is there a Posthuman Future as Envisioned by Fukuyama?	282
	References	284
	Some Useful Constants	285
	Exercises	287
	Index	297

Preface

Nanophysics, in this nonspecialist textbook, deals with physical effects at the nanometer and subnanometer scales; particularly aspects of importance to the *smallest size scales of any possible technology*.

“Nanophysics” thus includes physical laws applicable from the 100 nm scale down to the subatomic, sub-0.1 nm, scale. This includes “quantum mechanics” as advanced by the theoretical physicist Erwin Schrodinger, about 1925; “mesoscale physics,” with more diverse and recent origins; and the physics of the atomic nucleus, on the 10^{-15} m (fm) scale. From a pedagogical point of view, the 1 nm scale requires the concepts of “quantum mechanics” (sometimes here described as “nanophysics”), which, once introduced, are key to understanding behavior down to the femtometer scale of the atomic nucleus.

The third edition includes new material on nanophotonics and nanoplasmonics, and also nanoimprint lithography (Chapter 7), a new section on the quantum annealing computer in Chapter 9, and an entirely new Chapter 10 on graphene. The textbook remains up-to-date also on “nanoelectronics,” from magnetic and quantum points of view, and also relating to the possibilities for “quantum computing” as an extension of the existing successful silicon technology. The new Chapter 8 entitled “Quantum technologies based on magnetism, electron spin, superconductivity,” is followed by the new Chapter 9 titled “Silicon nanoelectronics and beyond.” New electronics-related applications of carbon nanotubes are included. Sections have been added on superconductivity: a concrete example of quantum coherence, and to help understand devices of the “rapid single flux quantum” (RSFQ) computer logic (already mentioned in the original Chapter 7), notable for low power dissipation and fast operation. The original Chapter 8 (“Looking into the Future”) becomes the new Chapter 11.

Additional material has been added (in Chapters 4 and 5, primarily), giving concepts needed for the most important new areas, including the absolutely most recent advances in nanotechnology. The basic ideas of ferromagnetic interactions and quantum computing, now included, are central to any quantum- or magnetic-based technology. The new edition is more self-contained, with the addition of a short list of useful constants and a glossary.

A criterion in choice of new material (many astonishing developments have occurred since the 2004 publication of the first edition of this textbook) has been

the author's view of what may be important in the development of nanotechnology. For this reason, nuclear physics is now touched on (briefly), in connection with proposals to use the "nuclear spin $1/2$ " as the "qubit" of information in a "quantum computer"; and with a recent small-scale experiment demonstrating neutron generation (via a standard "nuclear fusion reaction"), which exploits nanotechnology for its success.

Another essential and relevant aspect of fundamental physics, the "exchange interaction of identical particles," has already been incorporated, as essential to a basic understanding of covalent bonds, ferromagnetism (essential to computer disk drive nanotechnology), and, more recently, to proposals for a "charge qubit" for a quantum computer. This topic (the exchange interaction) is of importance beyond being the basis for covalent bonds in organic chemistry.

From the beginning, this textbook was intended as an introduction to the phenomena and laws of nature applicable on such tiny size scales (without excluding the nuclear, femtometer, size scale) for those who have taken college mathematics and physics, but who have not necessarily studied atomic physics or nuclear physics. Primarily, the reader will need facility with numbers, and an interest in new ideas.

The Exercises have been conceived more as self-learning aids for the interested reader, than as formal problems. Some new material, especially in regard to field ionization by tips, and aspects of the collapse of ultrasonically induced bubbles in dense liquids, appears now in the Exercises, not to clutter the text for the more general reader.

It is hoped that interested readers can find stimulating, even profitable, new ideas in this (still rather slim) textbook. For details, they can use the copious and absolutely current references that are included.

The author is indebted to his colleagues at Wiley-VCH, Ms Ulrike Werner and Stefanie Volk, for their help in preparing the Third Edition. He also thanks his colleagues at New York University Polytechnic School of Engineering, particularly Prof. Lorcan Folan and Ms DeShane Lyew, for their help. He also adds that Mr Malhar Desai and Cornell Anthony have been extremely helpful in preparing the final manuscript. The author thanks his wife Carol for help in many ways in continuous support of the book projects.

New York
March, 2015

Edward L. Wolf

Glossary of Abbreviations

A	Adenosine; one of the four bases in RNA; one of the four bases in the DNA double helix (joins with T)
ABM	Anti-Ballistic Missile (treaty); suggested as a prototype for limits on robots
ADC	Analog-to-digital converter
AFM	Atomic force microscope
amu	Atomic mass unit (u); defined as 1/12 of mass of carbon-12 (^{12}C): $u = 1.661 \times 10^{-27} \text{ kg}$
ATP	Adenosine triphosphate; biological energy source, leading to ADP, adenosine diphosphate
Bar	One atmosphere, 101.3 kPa
BCS	Bardeen, Cooper, Schrieffer (theory); basic accepted theory of superconductivity
BOX	Buried oxide layer; in Si, used to reduce capacitances in FET devices (see SOI)
C	Cytosine; one of the four bases in RNA: one of the four bases in the DNA double helix (joins with G)
CIP	Current in plane; geometry for spin valve type of GMR magnetic field sensor
CMOL	CMOS/nanowire/molecular hybrid; proposed computer logic
CMOS	Complementary metal oxide semiconductor; computer logic
CPP	Current perpendicular to plane; geometry in TMR (tunnel valve) magnetic sensor
CPU	Central processing unit; in computer
CVD	Chemical vapor deposition; a rapid means of depositing layers in semiconductor
D	Debye; unit of electric dipole moment: $1 \text{ D} = 3.3 \times 10^{-30} \text{ C m}$
DMF	Dimethylformamide; a polar molecule
DNA	Deoxyribonucleic acid; polymer, forms single and double helices; latter hydrogen bonded by bases C, G, A, T, encoding information for assembly of proteins
DNT	Dinitrotoluene; an explosive ingredient; a polar molecule, potentially detectable

DOS	Density of states; usually stated per unit energy per unit volume, for electrons
DRAM	Dynamic random access memory
dsDNA	Double-strand DNA
E_F	Fermi energy
E_g	Energy gap of a semiconductor, typically in electron volts
ESR	Electron spin resonance
eV	Electronvolt; $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$
fcc	Face-centered cubic
FET	Field effect transistor
fm	Femtometer; 10^{-15} m , size scale of the atomic nucleus
FQHE	Fractional quantum Hall effect
G	Guanine; one of the four bases in RNA; one of the four bases in the DNA double helix (joins with C)
GMR	Giant magnetoresistance; basis of “spin valve” CIP hard drive <i>B</i> -field sensor
hcp	Hexagonal close packed
HEMT	High-electron-mobility transistor
HTS	High-temperature superconductor
JJ	Josephson tunnel junction
laser	Light amplification by stimulated emission of radiation
mJ	Millijoule; possible energy unit for small systems
MBE	Molecular beam epitaxy; a method for depositing atomically perfect crystal layers
MEMS	Micro-electro-mechanical system
meV	Millielectronvolts; thousandth of an electronvolt
MeV	Megaelectronvolts; million electronvolts
MFM	Magnetic force microscope
MOSFET	Metal oxide semiconductor field effect transistor; basic switch in electronics
MRAM	Magnetic random access memory
MRFM	Magnetic resonance force microscope
MRI	Magnetic resonance imaging; use of proton (spin) magnetic resonance to map locations of water molecules in living specimens
MWNT	Multiwall (carbon) nanotube
NEMS	Nano-electro-mechanical system
NMR	Nuclear magnetic resonance
NW	Nanowire
PMMA	Polymethylmethacrylate; used as a photoresist in silicon technology
PN junction	Junction between P (positively doped) and N (negatively doped) semiconductors; rectifier, element of transistor, and voltage-variable capacitor
Py	Permalloy; a high-permeability Ni–Fe ferromagnet

PZT	Lead zirconate titanate; piezoelectric used in sonar, SPM, and SBSL transducers
QCA	Quantum cellular automata
QD	Quantum dot; a three-dimensionally small object, “artificial atom”
QED	Quantum electrodynamics; interaction of radiation with matter, leading, for example, to small change in g -factor of electron spin from 2.0 to 2.0023
QHE	Quantum Hall effect
QPC	Quantum point contact
radar	Radio detection and ranging
RAM	Random access memory
recA	Protein of prototypical bacterium <i>E. coli</i> used in DNA assembly of nanostructures
RFSET	Radio frequency single electron transistor
RNA	Ribonucleic acid; polymer, similar to DNA, but uses base U instead of base T; evolutionary precursor of DNA, retains central roles in protein synthesis
RNAP	RNA polymerase; enzyme that transcribes DNA template into messenger RNA
RSFQ	Rapid single flux quantum; form of superconducting computer logic
RTD	Resonant tunneling diode; plus related forms (e.g., TBRTD) of transistor and logic
SBSL	Single-bubble sonoluminescence
SEM	Scanning electron microscope
SET	Single electron transistor
SFQ	Single flux quantum
SHO	Simple harmonic oscillator
SOI	Silicon on insulator; sometimes implemented on single-crystal Si by implanting a deep layer of oxygen, followed by annealing to produce quartz insulator (see BOX)
sonar	Sound navigation and ranging; in modern forms uses piezoelectric transducers for sound generation underwater
SPM	Scanning probe microscope
SQUID	Superconducting quantum interference detector
ssDNA	Single-strand DNA
STM	Scanning tunneling microscope
SWNT	Single-wall (carbon) nanotube
T	Thymine; not present in RNA; one of the four bases in the DNA double helix (joins with A)
TBRTD	Triple-barrier resonant tunneling diode (see RTD)
TEM	Transmission electron microscope
TMR	Tunnel magnetoresistance; basis of “tunnel valve” CPP magnetic field sensor

TPa	Terapascal; $1 \text{ TPa} = 10^{12} \text{ N m}^{-2}$; possible value of Young's modulus
u	Atomic mass unit (amu); defined as 1/12 of mass of carbon-12 (^{12}C): $1 \text{ u} = 1.661 \times 10^{-27} \text{ kg}$
U	Uracil; one of the four bases (replacing T) in RNA (joins with A); not present in DNA
2DEG	Two-dimensional electron gas

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 2×10^{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 4×10^{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 8×10^{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}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 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 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

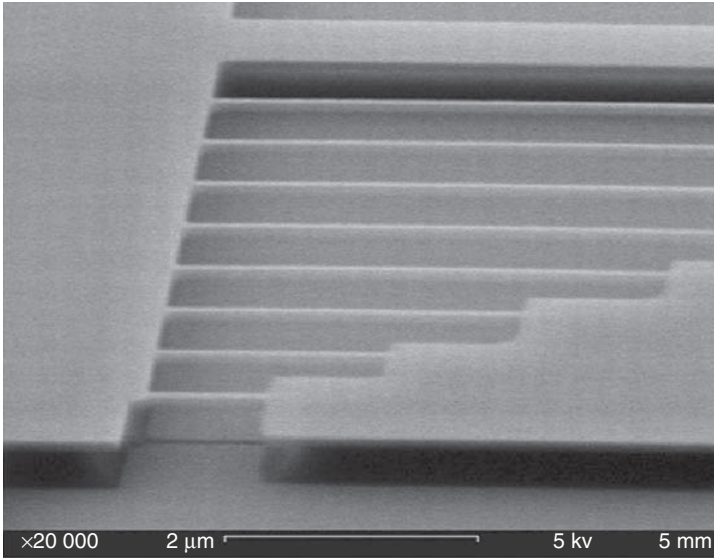


Figure 1.1 Silicon nanowires in a harp-like array. Due to the clamping of the single-crystal silicon bars at each end and the lack of applied tension, the situation is more like an array of xylophone keys. The resonant

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 2×10^{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 ρ , thermal conductivity K , relative magnetic and dielectric susceptibilities κ and ϵ , Fermi energy E_F and work function ϕ 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 6.45×10^{16} per inch².

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 inch² or 10^{11} per inch². 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

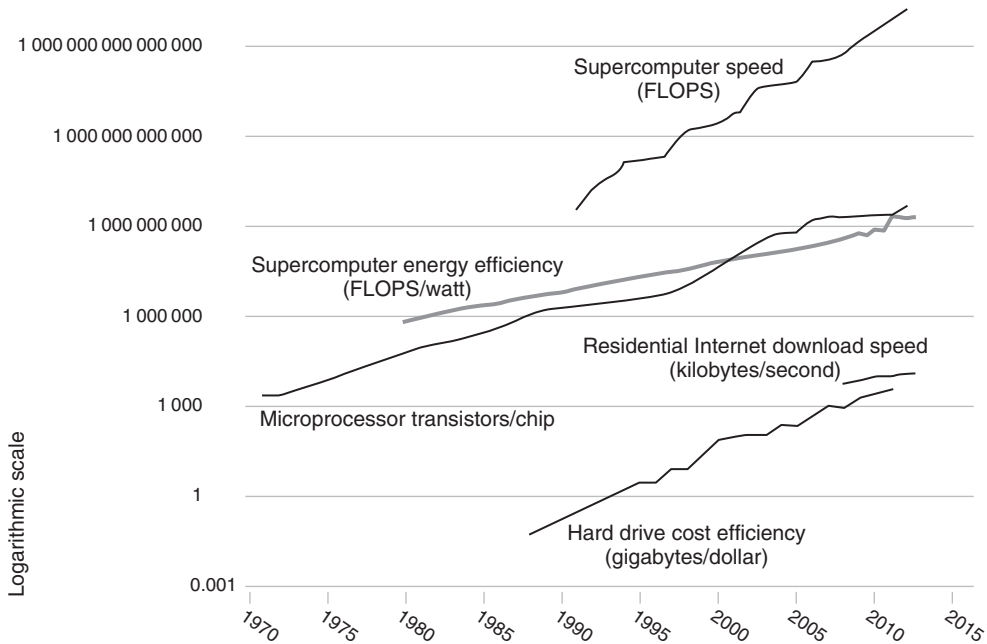


Figure 1.2 Moore's law [6]. The number of transistors in successive generations of computer chips has risen exponentially, doubling every 1.5 years or so. Gordon Moore, cofounder of Intel, Inc., predicted this growth pattern in 1965, when a silicon chip contained only 30 transistors. The number of dynamic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