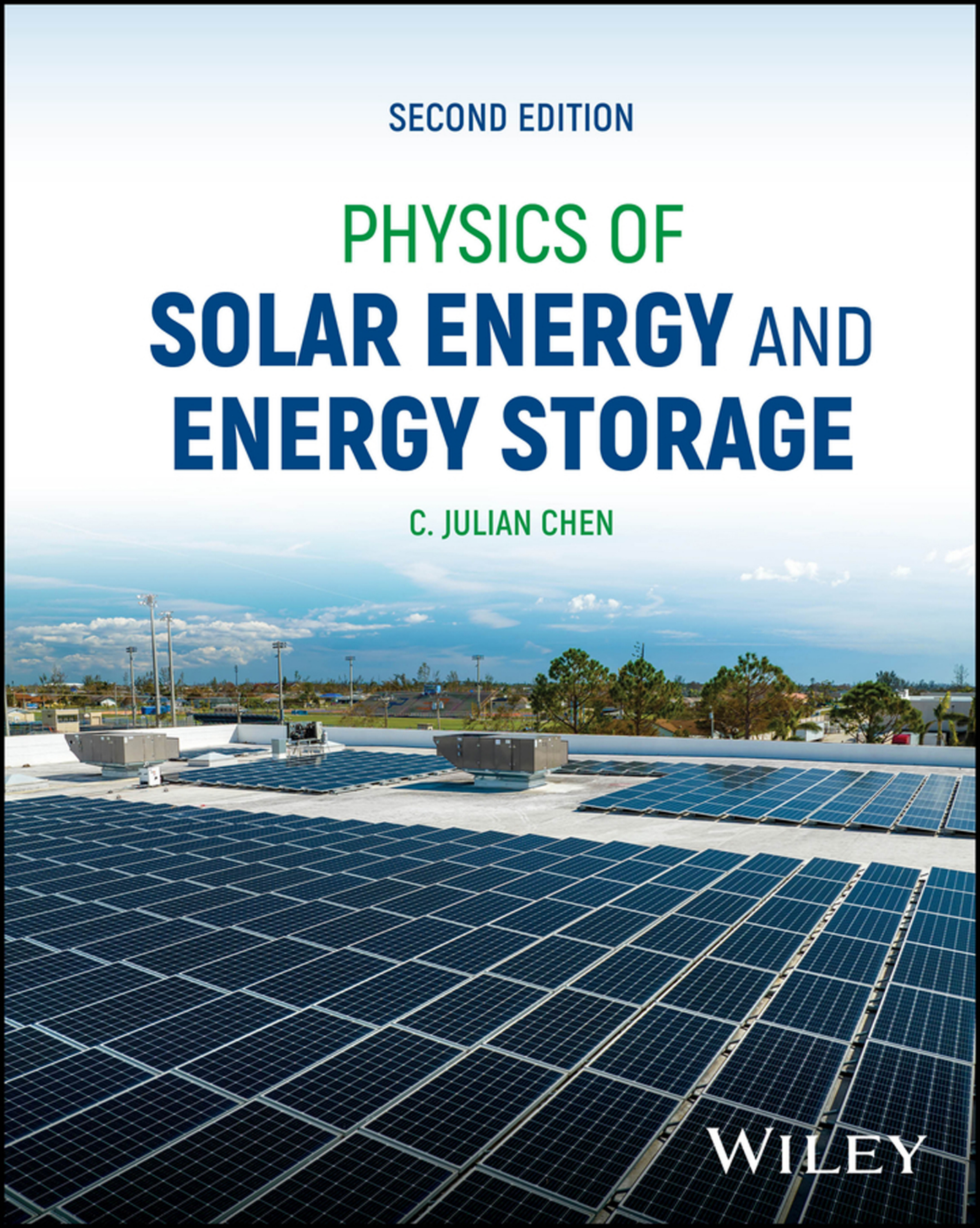
SECOND EDITION

PHYSICS OF SOLAR ENERGY AND ENERGY STORAGE

C. JULIAN CHEN



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Physics of Solar Energy and Energy Storage

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Second Edition

C. Julian Chen

Columbia University

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Contents

List of Figures xiii
List of Tables xix
Preface to the Second Edition xxi
Preface to the First Edition xxiii

Chapter 1: Introduction 1

1.1 Shaping a More Livable World 1
1.1.1 Fossil Fuels and Beyond 2
1.1.2 The Paris Agreement 4
1.1.3 Phasing Out Coal-Generated Power 5
1.1.4 Phasing Out ICE Vehicles 6
1.1.5 Economics of Renewable Energy 7

1.2 Solar Energy 9

1.3 Solar Photovoltaics 12
1.3.1 Birth of Modern Solar Cells 12
1.3.2 Basic Terms and Concepts on Solar Cells 14
1.3.3 Types of Solar Cells 15

1.4 A Rechargeable Battery Primer 16
1.4.1 Whittingham's Initial Invention 17
1.4.2 Goodenough's Improved Cathode 18
1.4.3 Yoshino's Improved Anode 19
1.4.4 Current Status 20

1.5 Other Renewable Energy Resources 21
1.5.1 Hydroelectric Power 21
1.5.2 Wind Power 23
1.5.3 Biomass and Bioenergy 26
1.5.4 Shallow Geothermal Energy 31
1.5.5 Deep Geothermal Energy 32
1.5.6 Tidal Energy 34

Chapter 2: Nature of Solar Radiation 37

2.1 Light as Electromagnetic Waves 37
2.1.1 Maxwell's Equations 38
2.1.2 Vector Potential and Scalar Potential 39
2.1.3 Electromagnetic Waves 40
2.1.4 Plane Waves and Polarization 41
2.1.5 Sinusoidal Waves 42

2.2 Interface Phenomena 43
2.2.1 Relative Dielectric Constant and Refractive Index 43

2.2.2 Energy Balance and Poynting Vector . . . 45
2.2.3 Fresnel Formulas . . . 46
2.2.4 Optics of metals . . . 48
2.3 Blackbody Radiation . . . 51
2.3.1 Rayleigh–Jeans Law . . . 52
2.3.2 Planck Formula and Stefan–Boltzmann's Law . . . 55
2.4 Photoelectric Effect and Concept of Photons . . . 58
2.4.1 Einstein's Theory of Photons . . . 59
2.4.2 Millikan's Experimental Verification . . . 61
2.4.3 Electron as a Field . . . 61
2.5 Einstein's Derivation of Blackbody Formula . . . 63

Chapter 3: Origin of Solar Energy 67

3.1 Basic Parameters of the Sun . . . 68
3.1.1 Distance . . . 68
3.1.2 Mass . . . 68
3.1.3 Radius . . . 68
3.1.4 Emission Power . . . 69
3.1.5 Surface Temperature . . . 69
3.1.6 Composition . . . 70
3.2 Kelvin–Helmholtz Time Scale . . . 70
3.3 Energy Source of the Sun . . . 72
3.3.1 The $p-p$ Chain . . . 73
3.3.2 Carbon Chain . . . 74
3.3.3 Internal Structure of the Sun . . . 74

Chapter 4: Tracking Sunlight 77

4.1 Rotation of Earth: Latitude and Longitude . . . 77
4.2 Celestial Sphere . . . 78
4.2.1 Coordinate Transformation: Cartesian Coordinates . . . 80
4.2.2 Coordinate Transformation: Spherical Trigonometry . . . 82
4.3 Treatment in Solar Time . . . 84
4.3.1 Obliquity and Declination of the Sun . . . 84
4.3.2 Sunrise and Sunset Time . . . 86
4.3.3 Direct Solar Radiation on an Arbitrary Surface . . . 87
4.3.4 Direct Daily Solar Radiation Energy . . . 88
4.3.5 The 24 Solar Terms . . . 92
4.4 Treatment in Standard Time . . . 94
4.4.1 Sidereal Time and Solar Time . . . 94

4.4.2 Right Ascension of the Sun . . . 95
4.4.3 Time Difference Originated from Obliquity . . . 96
4.4.4 Aphelion and Perihelion . . . 98
4.4.5 Time Difference Originated from Eccentricity . . . 98
4.4.6 Equation of Time . . . 99
4.4.7 Declination of the Sun . . . 102
4.4.8 Analemma . . . 102

Chapter 5: Interaction of Sunlight with Earth 105

5.1 Interaction of Radiation with Matter . . . 105
5.1.1 Absorptivity, Reflectivity, and Transmittivity . . . 105
5.1.2 Emissivity and Kirchhoff's Law . . . 106
5.1.3 Bouguer–Lambert–Beer's Law . . . 106

5.2 Interaction of Sunlight with Atmosphere . . . 108
5.2.1 AM1.5 Reference Solar Spectral Irradiance . . . 109
5.2.2 Annual Insolation Map . . . 110

5.3 Penetration of Solar Energy into Earth . . . 111

Chapter 6: Thermodynamics of Solar Energy 117

6.1 Definitions . . . 117

6.2 First Law of Thermodynamics . . . 118

6.3 Second Law of Thermodynamics . . . 121
6.3.1 Carnot Cycle . . . 121
6.3.2 Thermodynamic Temperature . . . 124
6.3.3 Entropy . . . 125

6.4 Thermodynamic Functions . . . 125
6.4.1 Free Energy . . . 126
6.4.2 Enthalpy . . . 126
6.4.3 Gibbs Free Energy . . . 127
6.4.4 Chemical Potential . . . 127

6.5 Ideal Gas . . . 127

6.6 Ground Source Heat Pump and Air Conditioning . . . 131
6.6.1 Theory . . . 131
6.6.2 Coefficient of Performance . . . 133
6.6.3 Vapor-Compression Heat Pump and Refrigerator . . . 133
6.6.4 Ground Heat Exchanger . . . 136

Chapter 7: A Quantum Mechanics Primer **139**

7.1 The Static Schrödinger Equation 140
7.1.1 Wavefunctions in a One-Dimensional Potential Well 142
7.1.2 The Bra-and-Ket Notations 144
7.1.3 The Harmonic Oscillator 146
7.1.4 The Hydrogen Atom 151
7.1.5 The Stern–Gerlach Experiment 159
7.1.6 Nomenclature of Atomic States 160
7.1.7 Degeneracy and Wavefunction Hybridization 160

7.2 Many-Electron Systems 163
7.2.1 The Self-Consistent Field (SCF) Method 164
7.2.2 Slater Determinates and the Hartree-Fock Method 165
7.2.3 Density-Functional Theory (DFT) 165
7.2.4 HOMO and LUMO 166

7.3 The Chemical Bond 169
7.3.1 Bonding Energy and Antibonding Energy 169
7.3.2 The Hydrogen Molecular Ion 170
7.3.3 Types of Chemical Bonds 171

7.4 The Solid State 174
7.4.1 Bloch Waves and Energy Bands 174
7.4.2 Effective Mass 177
7.4.3 Conductor, Semiconductor, and Insulator 177
7.4.4 Semiconductors 179
7.4.5 The Band Structure of Silicon 180

7.5 The Dynamic Schrödinger Equation 181
7.5.1 A Heuristic Derivation 181
7.5.2 Reduction to Static Schrödinger's Equation 184
7.5.3 Meaning of the Time-Dependent Phase Factor 184
7.5.4 Interaction with Radiation 185

Chapter 8: *pn*-Junctions **189**

8.1 Semiconductors 189
8.1.1 Electrons and Holes 189
8.1.2 *p*-Type and *n*-Type Semiconductors 191

8.2 Formation of a *pn*-Junction 194

8.3 Analysis of *pn*-Junctions 198
8.3.1 Effect of Bias Voltage 199
8.3.2 Lifetime of Excess Minority Carriers 199
8.3.3 Junction Current 200
8.3.4 Shockley Equation 201

8.4 Light-Emitting Diodes for Illumination 202
8.4.1 Invention of the Blue LED 203
8.4.2 The Working Principle 204
8.4.3 Wavelength Engineering 206
8.4.4 The Freestanding GaN Substrate 208
8.4.5 A Brief Sketch of History 208

Chapter 9: Semiconductor Solar Cells 211

9.1 Basic Concepts 211
9.1.1 Generating Electric Power 214
9.1.2 Solar Cell Equation 215
9.1.3 Maximum Power and Fill Factor 215

9.2 The Shockley–Queisser Limit 217
9.2.1 Ultimate Efficiency 218
9.2.2 Role of Recombination Time 220
9.2.3 Detailed-Balance Treatment 220
9.2.4 Nominal Efficiency 223
9.2.5 Shockley–Queisser Efficiency Limit 223
9.2.6 Efficiency Limit for AM1.5 Radiation 224

9.3 Nonradiative Recombination Processes 225
9.3.1 Auger Recombination 227
9.3.2 Trap-State Recombination 227
9.3.3 Surface-State Recombination 228

9.4 Antireflection Coatings 228
9.4.1 Matrix Method 229
9.4.2 Single-Layer Antireflection Coating 231
9.4.3 Double-Layer Antireflection Coatings 233

9.5 Crystalline Silicon Solar Cells 234
9.5.1 Production of Pure Silicon 235
9.5.2 Solar Cell Design and Processing 236
9.5.3 Module Fabrication 237

9.6 Thin-Film Solar Cells 238
9.6.1 CdTe Solar Cells 238
9.6.2 CIGS Solar Cells 239
9.6.3 Amorphous Silicon Thin-Film Solar Cells 240

9.7 Tandem Solar Cells 241

Chapter 10: Solar Photochemistry **245**

10.1 Physics of Photosynthesis 245
10.1.1 Chlorophyll 246
10.1.2 ATP: Universal Energy Currency of Life 248
10.1.3 NADPH and $NADP^+$ 248
10.1.4 Calvin Cycle 249
10.1.5 C4 Plants versus C3 Plants 250
10.1.6 Chloroplast 250
10.1.7 Efficiency of Photosynthesis 251

10.2 Artificial Photosynthesis 253

10.3 Genetically Engineered Algae 253

10.4 Dye-Sensitized Solar Cells 253

10.5 Bilayer Organic Solar Cells 256

Chapter 11: Solar Thermal Energy **259**

11.1 Early Solar Thermal Applications 259

11.2 Solar Heat Collectors 262
11.2.1 Selective Absorption Surface 262
11.2.2 Flat-Plate Collectors 266
11.2.3 All-Glass Vacuum-Tube Collectors 268
11.2.4 Thermosiphon Solar Heat Collectors 269
11.2.5 High-Pressure Vacuum Tube Collectors 271

11.3 Solar Water Heaters 271

11.4 Solar Thermal Power Systems 272
11.4.1 Parabolic Trough Concentrator 273
11.4.2 Central Receiver with Heliostats 274
11.4.3 Paraboloidal Dish Concentrator with Stirling Engine 274

Chapter 12: Physical Energy Storage **278**

12.1 Pumped Hydro Storage 278

12.2 Sensible Heat Energy Storage 279
12.2.1 Water 281
12.2.2 Solid Sensible Heat Storage Materials 282
12.2.3 Synthetic Oil in Packed Beds 283

12.3 Phase Transition Thermal Storage 283
12.3.1 Water–Ice Systems 284
12.3.2 Paraffin Wax and Other Organic Materials 286
12.3.3 Salt Hydrates 286

Chapter 13: Rechargeable Batteries 288

13.1 An Electrochemistry Primer 288
13.1.1 Basic Terms and Definitions 288
13.1.2 Oxidation State 290
13.1.3 Standard Oxidation-Reduction Potentials 291

13.2 Lithium-Ion Batteries 292
13.2.1 Benefit to Humankind 292
13.2.2 Intercalation of Metal Ions 294
13.2.3 The Cathode Materials 296
13.2.4 The Anode Materials 299
13.2.5 Electrolytes 300
13.2.6 The Separator 301
13.2.7 Packaging 302
13.2.8 Mineral Resource of Lithium 305

13.3 Sodium-Ion Batteries 306
13.3.1 The Cathode Materials 307
13.3.2 The Anode Materials 309
13.3.3 Rest of the System 310

13.4 Traditional Rechargeable Batteries 310
13.4.1 Lead–Acid Batteries 310
13.4.2 Nickel Metal Hydride Batteries 311

Chapter 14: Building with Sunshine 313

14.1 Early Solar Architecture 314
14.1.1 Ancient Solar Architecture 314
14.1.2 Holistic Architecture in Rural China 314

14.2 Building Materials 315
14.2.1 Thermal Resistance 316
14.2.2 Specific Thermal Resistance 316
14.2.3 Heat Transfer Coefficient: The U-Value 317
14.2.4 Thermal Mass 318
14.2.5 Glazing 318

14.3 Example of Holistic Design 320

Appendix A: Energy Unit Conversion **325**

Appendix B: Spherical Trigonometry **327**
B.1 Spherical Triangle . . . 327
B.2 Cosine Formula . . . 328
B.3 Sine Formula . . . 329
B.4 Formula C . . . 331

Appendix C: Vector Analysis and Determinants **333**
C.1 Vector Analysis . . . 333
C.2 Determinants . . . 334

Appendix D: Real Spherical Harmonics **336**
D.1 The Spherical Coordinate System . . . 336
D.2 Spherical Harmonics . . . 337

Appendix E: Complex Numbers **341**
E.1 Definition of Complex Numbers . . . 341
E.2 The Euler Formula . . . 342

Appendix F: Statistics of Particles **343**
F.1 Maxwell–Boltzmann Statistics . . . 344
F.2 Fermi–Dirac Statistics . . . 345
F.3 Bose–Einstein Statistics . . . 346

Appendix G: Measurement in Quantum Mechanics **347**
G.1 The Measurement Postulate . . . 347
G.2 Experiments in Position Detection . . . 349
G.3 Tomographic Imaging of Wavefunctions . . . 351
G.4 Einstein's Opinion on Quantum Mechanics . . . 353
G.5 A Modern View of Schrödinger's Cat . . . 353
G.6 A Natural Presentation of Quantum Mechanics . . . 354

Bibliography **357**
Index **365**

List of Figures

1.1 Energy consumption by sectors . . . 2
1.2 History of fossil-fuels consumption . . . 3
1.3 Deepwater Horizon oil rig explosion . . . 4
1.4 Volume and percentage of coal-generated electricity . . . 5
1.5 Phasing out coal electricity in the United States . . . 6
1.6 Cost decline of installed solar PV systems . . . 7
1.7 Cost of various energy resources . . . 8
1.8 Annual solar energy arriving at surface of Earth . . . 9
1.9 World energy consumption . . . 10
1.10 Sources of electricity: history and forecast . . . 11
1.11 Selenium solar cell and silicon solar cell . . . 12
1.12 Inventors of silicon solar cells . . . 13
1.13 Average price of solar panels: 1975–2021 . . . 13
1.14 Maximum power and fill factor . . . 14
1.15 Volume and types of solar cells: 2011–2021 . . . 15
1.16 Winners of the 2019 Nobel Prize in Chemistry . . . 16
1.17 The first lithium-ion rechargeable battery of Stanley Whittingham . . . 17
1.18 Improved Li-ion battery cathode materials of John Goodenough . . . 18
1.19 Improved Li-ion battery anode materials of Akira Yoshino . . . 19
1.20 The expansion of Li-ion rechargeable battery market . . . 20
1.21 Percentage of electricity generation from hydropower in various countries 21
1.22 Itaipu hydropower station at border of Brazil and Paraguay . . . 22
1.23 Derivation of Betz theorem of wind turbine . . . 23
1.24 Efficiency of wind turbine . . . 24
1.25 Wind turbines in Copenhagen . . . 25
1.26 Costa Pinto Production Plant of sugar ethanol . . . 27
1.27 Annual production of ethanol in Brazil . . . 28
1.28 Production process of biodiesel . . . 29
1.29 Oil palm fruit . . . 30
1.30 Wild oil palms in Africa . . . 30
1.31 Shallow geothermal energy . . . 31
1.32 Deep geothermal energy . . . 32
1.33 Regions for deep geothermal energy extraction . . . 33
1.34 Nesjavellir geothermal power station, Iceland . . . 33
1.35 The Rance Tidal Power Station, France . . . 34

2.1 James Clerk Maxwell . . . 37
2.2 Electromagnetic wave . . . 42
2.3 Derivation of Fresnel formulas . . . 47
2.4 Blackbody radiation . . . 52

2.5 Blackbody spectral irradiance . . . 56
2.6 Lenard's apparatus for studying photoelectric effect . . . 58
2.7 Louis de Broglie . . . 62
2.8 Einstein's derivation of blackbody radiation formula . . . 64
2.9 Wavelengths of visible lights . . . 66

3.1 Luminosity of the Sun . . . 67
3.2 Sir William Thomson . . . 70
3.3 The Kelvin–Helmholtz model . . . 71
3.4 Hans Albrecht Bethe . . . 73
3.5 Internal structure of the Sun . . . 75

4.1 The night sky . . . 77
4.2 Latitude and longitude . . . 78
4.3 Celestial sphere and coordinate transformation . . . 79
4.4 Coordinate transformation in Cartesian coordinates . . . 81
4.5 Obliquity and the seasons . . . 85
4.6 Apparent motion of the Sun . . . 86
4.7 Daily solar radiation energy on a vertical surface facing south . . . 89
4.8 Daily solar radiation energy on a horizontal surface . . . 90
4.9 Daily solar radiation energy on a latitude-tilt surface . . . 91
4.10 Daily solar radiation energy on a surface with tracking . . . 92
4.11 Sidereal time and solar time . . . 95
4.12 Obliquity and equation of time . . . 96
4.13 Eccentricity of Earth's orbit: Kepler's laws . . . 99
4.14 Equation of time . . . 100
4.15 The analemma: the apparent motion of the Sun . . . 101

5.1 Absorptivity, reflectivity, and transmittivity . . . 105
5.2 Emissivity and absorptivity . . . 106
5.3 Bouguer–Lambert–Beer's law . . . 107
5.4 Attenuation of sunlight at azimuth θ . . . 108
5.5 Interaction of sunlight with atmosphere . . . 109
5.6 AM0 and AM1.5 solar radiation spectra . . . 110
5.7 Insolation map of the world . . . 111
5.8 Derivation of the heat-conduction equation . . . 112
5.9 Penetration of solar energy into Earth . . . 114

6.1 Joule's experiment . . . 120
6.2 Carnot cycle . . . 122
6.3 Reverse Carnot cycle . . . 123
6.4 Carnot cycle with ideal gas as the system . . . 130
6.5 Ground source heat pump . . . 132
6.6 Ground source heat pump: cooling mode . . . 134

6.7 Ground source heat pump: heating mode . . . 135
6.8 Heat-exchange configurations for ground source heat pumps . . . 136
6.9 Vertical well in a heat pump system . . . 137

7.1 Austrian banknote with a portrait of Schrödinger . . . 140
7.2 Wavefunctions in a one-dimensional potential well . . . 142
7.3 Energy levels in a one-dimensional potential well . . . 143
7.4 Energy levels and wavefunctions of a harmonic oscillator . . . 150
7.5 Hydrogen atom in spherical polar coordinates . . . 151
7.6 Wavefunction of ground-state hydrogen atom . . . 153
7.7 Wavefunctions of excited-states of hydrogen atom . . . 155
7.8 Hydrogen wavefunctions . . . 157
7.9 Schematics of Stern-Gerlach experiment . . . 159
7.10 Hybrid $sp1$ wavefunctions . . . 161
7.11 Hybrid $sp2$ wavefunctions . . . 161
7.12 Hybrid $sp3$ wavefunctions . . . 162
7.13 Scanning tunneling microscope . . . 166
7.14 HOMO of pentacene imaged by STM . . . 167
7.15 LUMO of pentacene imaged by STM . . . 168
7.16 Concept of chemical bond . . . 169
7.17 Accuracy of the perturbation treatment of hydrogen molecular ion . . . 171
7.18 Wavefunctions outside the atomic core . . . 172
7.19 Molecular orbitals built from two s-type AOs . . . 172
7.20 The $p\sigma$ and $p\sigma^*$ MOs . . . 173
7.21 The $p\pi$ and $p\pi^*$ MOs . . . 173
7.22 Chemical bonds of seven first-row elements . . . 174
7.23 Bloch wavefunctions . . . 175
7.24 Reciprocal space and the first Brillouin zone . . . 177
7.25 Conductor, semiconductor, and insulator . . . 178
7.26 Direct semiconductors and indirect semiconductors . . . 179
7.27 Band gaps of a number of semiconductors . . . 180
7.28 Formation of energy bands in crystalline silicon . . . 181
7.29 Condition of energy conservation . . . 187

8.1 Intrinsic semiconductors: Free electrons and holes . . . 190
8.2 The n-type semiconductor . . . 191
8.3 The p-type semiconductor . . . 192
8.4 Unit cell in crystalline silicon . . . 193
8.5 Roles of doners and acceptors in silicon . . . 193
8.6 Formation of a pn-junction . . . 195
8.7 The depletion model of pn-junction . . . 196
8.8 Effect of bias in a pn-junction . . . 198
8.9 Current-voltage behavior of a pn-junction . . . 201
8.10 Evolution of the efficiency of light sources . . . 202

8.11 Nobelists for the invention of blue-light LED . . . 203
8.12 The relation between driving voltage and bandgap . . . 205
8.13 Two main methods to produce white light from LEDs . . . 206
8.14 Generating white light by blue luminescence and yellow phosphorescence . 207
8.15 Wavelength and lattice constant for $In_xGa_{1-x}N$ . . . 207
8.16 Blue-light LED fabricated on a GaN substrate . . . 208
8.17 The first blue-light LED built in 1972 . . . 209

9.1 Interaction of radiation with semiconductors . . . 212
9.2 Direct and indirect semiconductors . . . 212
9.3 Absorption spectra of some semiconductors commonly used for solar cells 213
9.4 Generating voltage and current by the electron–hole pairs . . . 214
9.5 Equivalent circuit of solar cell . . . 215
9.6 Generation of an electron–hole pair . . . 218
9.7 Ultimate efficiency of solar cells . . . 219
9.8 A simplified optical model of semiconductors . . . 221
9.9 Efficiency limit of solar cells . . . 224
9.10 Efficiency limit of solar cells for AM1.5 solar radiation . . . 225
9.11 The Auger recombination process . . . 226
9.12 Two-step recombination processes . . . 227
9.13 Antireflection coatings . . . 228
9.14 Matrix method for antireflection coatings . . . 230
9.15 Choice of materials for SLAR coatings . . . 232
9.16 Wavelength range of antireflection coatings . . . 234
9.17 Typical high-efficiency silicon solar cell . . . 236
9.18 Cross section of typical solar module . . . 237
9.19 Monocrystalline solar module and polycrystalline solar module . . . 238
9.20 Typical structure of CdTe thin film solar cell . . . 239
9.21 Typical structure of CIGS thin-film solar cell . . . 240
9.22 CIGS solar cell integrated circuit . . . 240
9.23 Multijunction tandem solar cell . . . 241
9.24 Working principle of multijunction tandem solar cells . . . 242

10.1 Chlorophyll . . . 246
10.2 Absorption spectra of chlorophyll *a* . . . 247
10.3 ATP and ADP . . . 248
10.4 NADPH and $NADP^+$ . . . 249
10.5 Key steps in the Calvin cycle . . . 250
10.6 Chloroplast . . . 251
10.7 Efficiency of photosynthesis . . . 252
10.8 Structure of dye-sensitized solar cell . . . 254
10.9 The N3 ruthenium dye and photocurrent spectrum . . . 255
10.10 Bilayer organic solar cell . . . 256
10.11 CuPc and its absorption spectrum . . . 257

11.1 A 3000-years old solar igniter . . . 259
11.2 Hot box of Horace de Saussure . . . 260
11.3 Adams solar oven . . . 261
11.4 Cast-iron solar oven . . . 261
11.5 Spectral power density of solar radiation and hot bodies . . . 263
11.6 Reflectance curve for cermet selective-absorbing surface . . . 265
11.7 Flat-plate solar heat collector . . . 266
11.8 Transmittance of window glass . . . 267
11.9 Evacuated-tube solar thermal collector . . . 269
11.10 Thermosiphon solar heat collector . . . 270
11.11 High-pressure vacuum tube collector . . . 271
11.12 Solar water heater with thermosiphon collectors . . . 272
11.13 Aerial photo of SEGS system . . . 273
11.14 Solar power plant with central receiver . . . 274
11.15 Stirling engine . . . 275
11.16 Working principle of Stirling engine . . . 275
11.17 Focusing property of a parabola . . . 276
11.18 Kyoto box . . . 277

12.1 The Nant de Drance pumped hydro storage plant . . . 279
12.2 Water in an insulating tank . . . 281
12.3 Rock-bed thermal energy storage system . . . 283
12.4 Ice Bear energy storage system . . . 285
12.5 A typical domestic hot water tank . . . 287

13.1 Electrochemistry of rechargeable batteries . . . 289
13.2 Setup for measuring standard potential . . . 291
13.3 Electrochemical processes in a Li ion cell . . . 292
13.4 Production and demand for lithium-ion batteries . . . 293
13.5 Energy density and specific energy of Li-ion batteries . . . 294
13.6 Ball-and-stick model of lithium cobalt oxide . . . 296
13.7 Share of different cathode materials of Li-ion batteries in 2022 . . . 297
13.8 A ball-and-stick model of the phosphate polyanion . . . 298
13.9 Lithium iron phosphate and iron phosphate . . . 298
13.10 Structure of LiC_6 . . . 299
13.11 Organic solvents in Li-ion batteries . . . 300
13.12 Structure of lithium hexafluorophosphate . . . 301
13.13 An electron microscopy image of a separator for Li-ion battery . . . 302
13.14 Stacking of electrodes, separators, and current collectors . . . 302
13.15 Cylindrical lithium-ion battery . . . 303
13.16 Prismatic lithium-ion battery . . . 304
13.17 Elemental abundance in the earth's crust . . . 305
13.18 Variation of the price of lithium carbonate . . . 305
13.19 Number of research papers on Ni-ion battery . . . 306

13.20 Sodium ion rechargeable battery . . . 307
13.21 Ferrocyanide anion and Prussian blue . . . 308
13.22 The falling-cards model of hard carbon . . . 309

14.1 Traditional peasant house in rural northern China . . . 315
14.2 Effect of glazing on insulation . . . 318
14.3 Design of a solar house: First floor . . . 320
14.4 Design of a solar house: Second floor . . . 321
14.5 External view of the solar house . . . 322
14.6 Internal view of the solar house . . . 323
14.7 Calculation of eaves . . . 324

B.1 The spherical triangle . . . 328
B.2 Derivation of cosine formula . . . 329

D.1 Laplace operator in spherical coordinates . . . 336

G.1 Electron in the wavefunction of hydrogen atom . . . 348
G.2 Double-slit experiment with single-photon detectors . . . 349
G.3 Building-up of the interference pattern . . . 350
G.4 Creating a Wilson-chamber track by a plane wave . . . 351
G.5 Tomographic image of a nitrogen molecule . . . 352
G.6 Tomographic image of carbon dioxide . . . 352
G.7 Schrödinger's cat scan . . . 354

List of Tables

1.1 Inventions in energy conversion 1
1.2 Consumption of fossil fuels, in EJ 3
1.3 Production cost of solar PV electricity 8
1.4 Proved resources of various fossil fuels 10
1.5 Regional hydroelectric power potential and output 22
1.6 Basic data of bioenergy 26
1.7 Yield of biofuel from different crops 29

2.1 Quantities in Maxwell's equations 38
2.2 Dielectric constant and refractive indices 44
2.3 Skin depths of several metals in nanometers 49
2.4 Absorptivity of several metals in % 51
2.5 Blackbody radiation at different temperatures 57
2.6 Stopping voltage for photocurrent 59

3.1 Chemical composition of the Sun 69

4.1 Notations in positional astronomy 80
4.2 Average daily solar radiation on various surfaces 92
4.3 The 24 solar terms 93
4.4 Cardinal points in years 2024 through 2030, in GMT 97

5.1 Thermal property of earth 113

6.1 Ground source heat pumps in selected countries 131

7.1 Wavefunctions of the harmonic oscillator 149
7.2 Wavefunctions of the hydrogen atom in Bohr radius a_0 158
7.3 Nomenclature of atomic states 160

9.1 Properties of common solar-cell materials 213

10.1 Power density of photosynthesis 252

11.1 Selective absorbing surfaces 265
11.2 Typical parameters of flat-plate solar heat collectors 268

12.1 Thermal properties of commonly used materials 280
12.2 Thermal properties of solid materials 282
12.3 Commonly used phase-change materials 284

13.1 Standard potentials at 25 °C 291
13.2 Comparison of rechargeable batteries 293
13.3 Intercalation voltage of electrode materials 295
13.4 Properties of organic solvents for Li-ion batteries 300
13.5 Cylindrical lithium ion batteries 303
13.6 Prismatic lithium-ion batteries 304

14.1 Specific thermal resistance 316
14.2 Typical R-values of wall insulation materials 317

A.1 Energy and power units 325

D.1 Spherical harmonics 339

Preface to the Second Edition

Twelve years have elapsed since the publication of the first edition of Physics of Solar Energy. During the one dozen years, dramatic changes have emerged in solar energy and related fields. A new edition is needed to reflect those advances.

First, from 2010 to 2022, the price of solar panels has dropped from $2 per watt to $0.2 per watt, a full order of magnitude. The cost reduction made solar electricity the least expensive of all energy sources in most places on the Earth. In the future, solely based on economics, solar energy will become a main source of energy.

Second, around 2010, lithium-ion rechargeable battery was almost exclusively applied to portable electronics, such as laptop computers, cellular phones, digital cameras, hand-held tools, etc. In 2020s, lithium-ion battery has been massively applied to automobiles and utility-scale energy storage. Because solar radiation is intermittent, to make solar energy the main source, energy storage is a necessity. Lithium-ion battery is the most versatile energy storage device. Logically, the 2019 Nobel Prize for chemistry was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino for their contributions to the development of the lithium-ion battery. The Nobel Prize press release concluded with "It can also store significant amounts of energy from solar and wind power, making possible a fossil fuel-free society."

Third, around 2010, light-emitting diodes (LED) accounted for less than 1% of the illumination market. In 2022, it grew to more than 50%. It is expected to reach almost 100% in 2025. As a reverse process of solar cells, LED is also based on a semiconductor *pn*-junction. The efficiency of LED lights is more than 10 folds higher than that incandescent light, and its lifetime is more than 10 times longer. Logically, the 2014 Nobel Prize in Physics was awarded to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura "for the invention of efficient blue light-emitting diodes which has enabled bright, long-lasting, and energy-saving white light sources".

Last but not the least, in 2015, the United Nations Framework Convention on Climate Change (UNFCCC) held the 21st Conference of the Parties in Paris, where a legally binding international treaty on climate change was reached by 196 parties, known as the "Paris Agreement". Accordingly, all countries or regions signed up to that treaty should propose and implement their nationally determined contributions to reduce their greenhouse gas emissions in order to limit the increase of global average temperature following the goals of the Paris Agreement. The implementation of the above technological advances becomes a globally coordinated endeavor.

To reflect those advances, in the second edition of the book, several new sections are added, including Section 1.1 entitled *Shaping a More Livable World*, Section 1.4 entitled *A Rechargeable-Battery Primer*, and Section 8.4 entitled *Light-Emitting Diodes for Illumination*. Because of the importance and richness of contents, a new Chapter *Rechargeable Batteries* is added. Accordingly, the title of the second edition of the book is changed to *Physics of Solar Energy and Energy Storage*.

Besides adding new contents, in view of the recent advances in fundamental physics, the presentation is also modernized. The common theoretical basis for solar cells, LEDs,

and rechargeable batteries is *quantum mechanics*. It is the centerpiece of modern physics. In the first edition, essential quantum mechanics was presented in Chapter 7 and Appendix C. It follows the traditional formulation based on Hilbert space, where the dynamic variables of point particles are represented by Hermitian operators. The crown jewelry of the traditional formulation, Wolfgang Pauli's 1925 algebraic solution of the hydrogen atom problem, was presented in detail because of its mathematical beauty. Nevertheless, my teaching experience showed that the traditional formulation of quantum mechanics was difficult to understand, and not useful to explain solid-state physics and chemistry, as related to solar energy and energy storage.

The 2023 Nobel Prize in Physics elables a natural view of wavefuncions, the central concept in quantum mechanics. Using attosecond light pulses, atomic and molecular wavefunctions, also called as orbitals, were imaged experimentally in real space [74, 43]. It showed that Schrödinger's wavefunction is a physical field, the same as electromagnetic fields. Teaching quantum mechanics becomes much easier. The confusing and paradoxical concepts such as Hilbert space, von Neumann axioms, complex operators, uncertainty relations, Born statistical rule, and wave-particle duality, are eliminated. All wavefunctions are real and they never collapse. Complex number is an optional mathematical tool for time-dependent phenomena, same as in electromagnetics. In Chapter 7, *A Quantum Mechanics Primer*, a conceptually and logically consistent elementary quantum mechanics is presented at a sophomore level for all natural scientists and engineers. It is the foundation for the understanding of atomic physics, molecular physics, solid-state physics, chemistry, molecular biology, including the interaction of radiation with atomic systems. More mathematical details of Section 7.3, The Chemical Bond, can be found in Chapter 4 of the third edition of Introduction to Scanning Tunneling Microscopy, Oxford University Press 2021, entitled Atomic Forces. In Appendix G, entitled Quantum Measurement in Light of Experiments, some basic concepts concerning the understanding of quantum mechanics are presented.

In Spring 2009, I started to teach a graduate-level course Physics of Solar Energy at Columbia University. I sincerely thank Professors Irving Herman, Cevdet Noyan, and Richard Osgood for assistance to establish the new course. The first edition of this book was based on the lecture notes of that course. I especially thank Marina Zamalin, the Associate Dean of Online Education of the School of Engineering and Applied Science, to establish a Columbia Video Network (CVN) course. I sincerely thank Professor Marc Spiegelman for assistance to establish an updated course, Physics of Solar Energy and Energy Storage, for the Fall semester 2023 and on. For 14 consecutive years, the Physics of Solar Energy course has attended by several hundreds of students, mostly graduates. I heartily thank their valuable feedback to improve the course.

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August 2023

Preface to the First Edition

One of the greatest challenges facing mankind in the twenty-first century is energy. Starting with the industrial revolution in the 18th century, fossil fuels such as coal, petroleum, and natural gas have been the main energy resources for everything vital for human society: from steam engines to Otto and diesel engines, from electricity to heating and cooling of buildings, from cooking and hot-water making, from lighting to various electric and electronic gadgets, as well as for most of the transportation means. However, fossil fuel resources as stored solar energy accumulated during hundreds of millions of years are being rapidly depleted by excessive exploration. In addition, the burning of fossil fuels has caused and is causing damage to the environment of Earth.

It is understandable that alternative or renewable energy resources, other than fossil fuels, have been studied and utilized. Hydropower, a derivative of solar energy, currently supplies about 2% of the world's energy consumption. The technology has matured, and the available resources are already heavily explored. Wind energy, also a derivative of solar energy, is being utilized rapidly. The resource of such highly intermittent energy is also limited. Nuclear energy is not renewable. The mineral resource of uranium is limited. The problems of accident prevention and nuclear waste management are still unresolved.

The most abundant energy resource available to human society is solar energy. At 4×10^6 EJ/year, it is ten thousand times the energy consumption of the world in 2007. For example, if 50% of the sunlight shining on the state of New Mexico is converted into useful energy, it can satisfy all the energy needs of the United States.

The utilization of solar energy is as old as human history. However, to date, among various types of renewable energy resources, solar energy is the least utilized. Currently, it only supplies about 0.1% of the world's energy consumption, or 0.00001% of the available solar radiation. Nevertheless, as a result of intensive research and development, the utilization of solar energy, especially solar photovoltaics, is enjoying an amazingly rapid progress. Therefore, it is reasonable to expect that in the latter half of the 21st century solar energy will become the main source of energy, surpassing all fossil fuel energy resources.

Similar to other fields of technology, the first step to achieve success in solar energy utilization is to have a good understanding of its basic science. Three years ago, Columbia University launched a master's degree program in solar energy science and engineering. I was asked to give a graduate-level course on the physics of solar energy. In the spring semester of 2009, when the first course was launched, 46 students registered. Columbia's CVN (Columbia Video Network) decided to record the lectures and distribute them to outside students. Because of the high demand, the lectures series for regular students repeated for two more semesters, and the CVN course on the physics of solar energy was repeated for seven consecutive semesters. This book is a compilation of lecture notes.

The basic design of the book is as follows. The first chapter summarizes the energy problem and compares various types of renewable energy resources, including

hydropower and wind energy, with solar energy. Chapter 2, "Nature of Solar Radiation," presents the electromagnetic wave theory of Maxwell as well as the photon theory of Einstein. Understanding of blackbody radiation is crucial to the understanding of solar radiation, which is described in detail. Chapter 3, "Origin of Solar Energy," summarizes the astrophysics of solar energy, including the basic parameters and structure of the Sun. The gravitational contraction theory of Lord Kelvin and the nuclear fusion theory of Hans Bethe for the origin of stellar energy are presented. Chapter 4, "Tracking Sunlight," is a self-contained but elementary treatment of the positional astronomy of the Sun for nonastronomy majors. It includes an elementary derivation of the coordinate transformation formulas. It also includes a transparent derivation of the equation of time, the difference between solar time and civil time, as the basis for tracking sunlight based on time as we know it. This chapter is supplemented with a brief summary of spherical trigonometry in Appendix B. The accumulated daily direct solar radiation on various types of surfaces over a year is analyzed with graphics. Chapter 5, "Interaction of Sunlight with Earth," presents both the effect of the atmosphere and the storage of solar energy in the ground, the basis for the so-called shallow geothermal energy. A simplified model for scattered or diffuse sunlight is presented. Chapter 6, "Thermodynamics of Solar Energy," starts with a summary of the basics of thermodynamics followed by several problems of the application of solar energy, including basics of heat pump and refrigeration. Chapters 7–10 deal with basic physics of solar photovoltaics and solar photochemistry. Chapter 7, "Quantum Transition," presents basic concepts of quantum mechanics in Dirac's format, with examples of organic molecules and semiconductors, with a full derivation of the golden rule and the principle of detailed balance. Chapter 8 is dedicated to the essential concept in solar cells, the *pn*-junction. Chapter 9 deals with semiconductor solar cells, including a full derivation of the Shockley–Queisser limit, with descriptions of the detailed structures of crystalline, thin-film, and tandem solar cells. Chapter 10, "Solar Photochemistry," presents an analysis of photosynthesis in plants as well as research in artificial photosynthesis. Various organic solar cells are described, including dye-sensitized solar cells and bilayer organic solar cells. Chapter 11 deals with solar thermal applications, including solar water heaters and solar thermal electricity generators. The vacuum tube collector and the thermosiphon solar heat collectors are emphasized. Concentration solar energy is also presented, with four types of optical concentrators: trough, parabolic dish, heliostat, and especially the compact linear Fresnel concentrator. Chapter 12 deals with energy storage, including sensible and phase-change thermal energy storage systems and rechargeable batteries, especially lithium–ion batteries. The last chapter, "Building with Sunshine," introduces architectural principles of solar energy utilization together with civil engineering elements.

Experience in teaching the course has shown me that the student backgrounds are highly diversified, including physics, chemistry, electrical engineering, mechanical engineering, chemical engineering, architecture, civil engineering, environmental science, materials science, aerospace engineering, economy, and finance. Although it is a senior undergraduate and beginning graduate-level course, it must accommodate a broad spectrum of student backgrounds. Therefore, necessary scientific background knowledge is

part of the course. The book is designed with this in mind. For example, background knowledge in positional astronomy, thermodynamics, and quantum mechanics is included. For students who have already taken these courses, the background material serves as a quick review and as a reference for the terminology and symbols used in this book. The presentation of the background science is for the purpose of solar energy utilization only, along a "fast track." For example, quantum mechanics is presented using an "empirical" approach, starting from direct perception of quantum states by a scanning tunneling microscope; thus, the quantum states are not merely a mathematical tool but a perceptible reality. The scanning tunneling microscope is also an important tool in the research for novel devices in solar energy conversion.

At an insert of the book, a gallery of color graphics and photographs is constructed and compiled. It serves as a visual introduction to the mostly mathematical presentation of the materials, which is useful for intuitive understanding of the concepts.

During the course of giving lectures and writing the lecture notes, I have encountered many unexpected difficulties. Solar energy is a multidisciplinary topic. The subject fields comprise astronomy, thermodynamics, quantum mechanics, solid-state physics, organic chemistry, solid-state electronics, environmental science, mechanical engineering, architecture, and civil engineering. As a unified textbook and reference book, a complete and consistent set of terminology and symbols must be designed which should be as consistent as possible with the established terminology and symbols of the individual fields, but yet be concise and self-consistent. A list of symbols is included toward the end of the book.

I sincerely thank Professors Irving Herman, Richard Osgood, and Vijay Modi for helping me setting up the solar energy course. I am especially grateful to many business executives and researchers in the field of solar energy who provided valuable information: Steve O'Rourke, then Managing Director and Research Analyst of Deutsch Bank, currently Chief Strategy Officer of MEMC Electronics, for detailed analysis of solar photovoltaic industry. John Breckenridge, Managing Director of investment bank Good Energies, for information on renewable energy investment in the world. Robert David de Azevedo, Executive Director of Brazilian American Chamber of Commerce, for information and contacts of renewable energy in Brazil. Loury A. Eldada, Chief Technology Officer of HelioVolt, for manufacture technology of CIGS thin-film solar cells. Ioannis Kymissis, a colleague professor at Columbia University, for two guest lectures in the Solar Energy Course about organic solar cells. Section 10.5 is basically based on literature suggested by him. Vasili Fthenakis, also a colleague professor at Columbia University, for valuable information about economy and environment issues of solar cells. John Perlin, a well-known solar energy historian, for kindly sending me electronic versions of his two books. George Kitzmiller, owner of Miami Pluming and Solar Heating Company, for showing me a number of 80-years-old solar hot water heaters still working in Miami. Margaret O'Donoghue Castillo, President of American Institute of Architects, for introducing me to the geothermal heating and cooling system in AIA, New York City. Mitchell Thomashaw, President of Union College, Maine, for letting me eyewitness the history of solar energy in the United States through brokering the donation of a Carter-era White House solar panel to the Solar Energy Museum in

Dézhōu, China. Academician Hé Zuòxiū, a prominent advocate of renewable energy, for helping me establish contacts in renewable-energy research and industry in China. Lǐ Shēnshēng, Professor Emeritus of Beijing Normal Institute, for kindly gifted me an autographed copy of his out-of-print book Tàiyángnéng Wùlǐxué. Published in 1996, it is probably the first book about the physics of solar energy in any language. Mr. Huáng Míng, founder and CEO of Himin Solar Energy Group and Vice President of International Solar Energy Association, for many inspiring discussions and a visit to Himin Corp, including an impressive production line for vacuum tube solar collectors. Professor Huáng Xuéjié, a long-time researcher of lithium rechargeable batteries and the founder of Phylion Battery Co., for many discussions about electric cars and a tour to the production lines of Phylion. Mire Ma, Vice President of Yingli Green Energy Group, for valuable information and a tour to the entire manufacturing process of solar-grade silicon, solar cells and solar modules. Last but not least, the book could not be written without the patience and support of my wife Liching.

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April 2011

Chapter 1

Introduction

1.1 Shaping a More Livable World

The progress of human civilization depends critically on the utilization of energy. The modern industrial revolution is intimately associated with the generation and conversion of energy, as evidenced by the sequence of inventions that greatly improved the living conditions of human society, see Table 1.1.

In the 18th century, the invention and improvement of steam engine not only drove up the modern industry, but also revolutionized transportation, especially trains and steamboats. The invention of light bulbs by Thomas Edison in 1878 started the era of centralized generation and transmission of electrical power. The steam turbine was invented. After the invention of the internal combustion engines (ICE), including the Otto engine (gasoline engine) and the Diesel engine, the efficiency is increased to more than 20%. And The ICE is significantly lighter than the steam engine. Transportation was revolutionized. Petroleum-based liquid fuels took central stage.

In the 20th century, the worldwide industrialization made an explosive expansion of energy generation and conversion. The invention of airplanes and the widespread application of electricity accelerates that trend. Figure. 1.1 shows the annual consumption of energy in different sectors, the data of 2015 in the United States. The total energy consumption is 102.9 EJ. The largest sector of energy consumption is electricity,

Table 1.1: Inventions in energy conversion

Year	Invention	Inventor
1712	Original steam engine	Thomas Newcomen
1764	Improved steam engine	James Watt
1807	Steam boat	Robert Fulton
1814	Steam locomotive	George Stephenson
1861	Gaseline engine	Nicolaus Otto
1884	Steam turbine	Charles Parsons
1898	Diesel engine	Rudolph Diesel

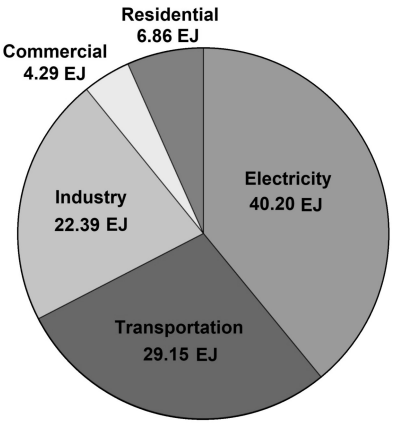

Figure 1.1 Energy consumption by sectors. The energy consumption in the United States in 2015 by sectors. The total energy consumption is 102.9 EJ. Therefore, the number in EJ is also approximately the percentage for different sectors. The largest consumer is electricity, accounts about 40%. The second largest consumer is transportation, accounts for about 29%. Residential and commercial consumption accounts for about 10%.

accounts almost 40%. The second largest is transportation, roughly 28%. Residential and commercial consumption account for about 10%.

1.1.1 Fossil Fuels and Beyond

In the early years of industrial revolution, up to late 19th century, coal was the main source of energy. For example, in 1750, Britian was producing 5.2 million tons of coal per year. By 1850, it was producing 62.5 million tons per year, more than 10 times greater than 1750. The efficiency of steam engine is much less than 10%. Currently, coal is still the main source of electrical energy in the world. Especially in many third-world countries, coal is the dominating source of electricity. In advanced industrialized countries, natural gas started to replace coal to become the main source of electrical power generation. After the invention of the internal combustion engines in late 19th century, an explosive growth of petroleum derivatives is seen.

Currently, fossil fuels are still the main source of energy, including coal, petroleum, and natural gas. Figure 1.2 shows the global consumption of fossil fuels from 1800 to 2021. The numbers are shown in Table 1.2. The surge of coal burning in early 21st century is because third-world countries like China and India are in an early stage of industrialization, and coal is indispensable. Nevertheless, the reliance in fossil fuels creates many problems detrimental to human civilization. Here is a short list.

1. The distribution of fossil fuel resource is extremely uneven over the world. According to a recent report by United Nations, about 80 percent of the global population lives in countries that are net importers of fossil fuels – that is about six billion people who are dependent on fossil fuels from other countries, which makes then vulnerable to geopolitical shocks and crises.

2. The burning of fossil fuels generates pollutions detrimental to environment and public health. One example is nitrogen oxides (NO_x). Because air contains about