

Table of Contents

1	General Basis for Computations and Theoretical Models	1
1.1	Ab initio One-Particle Theories for the Ground State	1
1.1.1	Non-interacting N Electron System	2
1.1.2	The Hartree Approximation	3
1.1.3	The Hartree-Fock Approximation	5
1.1.4	Correlations and Exchange-Correlation Hole	6
1.1.5	Local Density Approaches	10
1.2	Quasi-particles and Excitons	13
1.2.1	One-Particle Eigenvalues	14
1.2.2	The Exchange-Correlation Hole and Static Screening	15
1.2.3	Dynamically Screened Interactions	16
1.2.4	The GW Approximation	21
1.2.5	Excitons	26
1.2.6	Towards a More Quantitative Theory	28
1.2.7	Time-Dependent Density Functional Theory (TDDFT)	29
1.3	Semi-empirical Methods	31
1.3.1	The Empirical Tight Binding Method	32
1.3.2	The Empirical Pseudopotential Method	39
1.3.3	The $\mathbf{k} \cdot \mathbf{p}$ Description and Effective Masses	43
2	Quantum Confined Systems	47
2.1	Quantum Confinement and Its Consequences	47
2.1.1	Idealized Quantum Wells	47
2.1.2	Idealized Quantum Wires	51
2.1.3	Idealized Cubic Quantum Dots	52
2.1.4	Artificial Atoms: Case of Spherical Wells	53
2.1.5	Electronic Structure from Bulk to Quantum Dots	54
2.2	Computational Techniques	56
2.2.1	$\mathbf{k} \cdot \mathbf{p}$ Method and Envelope Function Approximation	57
2.2.2	Tight Binding and Empirical Pseudopotential Methods	60
2.2.3	Density Functional Theory	63
2.3	Comparison Between Different Methods	64
2.4	Energy Gap of Semiconductor Nanocrystals	67
2.5	Confined States in Semiconductor Nanocrystals	69

2.5.1	Electron States in Direct Gap Semiconductors	69
2.5.2	Electron States in Indirect Gap Semiconductors	70
2.5.3	Hole States	72
2.6	Confinement in Disordered and Amorphous Systems	74
3	Dielectric Properties	77
3.1	Macroscopic Approach: The Classical Electrostatic Theory . . .	78
3.1.1	Bases of the Macroscopic Electrostatic Theory of Dielectrics	78
3.1.2	Coulomb Interactions in a Dielectric Quantum Well . . .	80
3.1.3	Coulomb Interactions in Dielectric Quantum Dots	83
3.2	Quantum Mechanics of Carriers in Dielectrics: Simplified Treatments	84
3.2.1	Dielectric Effects in Single-Particle Problems	84
3.2.2	Dielectric Effects in Many-Particle Problems	86
3.3	Microscopic Calculations of Screening Properties	90
3.3.1	General Formulation in Linear-Response Theory	90
3.3.2	Random-Phase Approximation	91
3.3.3	Beyond the Random-Phase Approximation	93
3.3.4	From Microscopic to Macroscopic Dielectric Function for the Bulk Crystal	93
3.4	Concept of Dielectric Constant for Nanostructures	94
3.4.1	The Importance of Surface Polarization Charges	94
3.4.2	Dielectric Screening in Quantum Wells	95
3.4.3	Dielectric Screening in Quantum Dots	96
3.4.4	General Arguments on the Dielectric Response in Nanostructures	97
3.4.5	Conclusions	100
3.5	Charging of a Nanostructure	100
3.5.1	Case of a Quantum Dot	100
3.5.2	Case of a Quantum Well	103
4	Quasi-particles and Excitons	105
4.1	Basic Considerations	105
4.2	Excitons in the Envelope Function Approximation	108
4.2.1	Theory of Bulk Excitons	108
4.2.2	Excitons in Quantum Wells	109
4.2.3	Exciton Binding Energy in Limiting Situations	110
4.2.4	The Influence of Dielectric Mismatch	111
4.3	Excitons in More Refined Semi-empirical Approaches	112
4.3.1	General Discussion	112
4.3.2	Excitons in Nanocrystals of Direct Gap Semiconductors	114
4.3.3	Excitons in Si Nanocrystals	116

4.3.4	Screening of the Electron–Hole Interaction and Configuration Interaction	120
4.4	Quantitative Treatment of Quasi-particles	121
4.4.1	General Arguments	122
4.4.2	Tight Binding GW Calculations	123
4.4.3	Conclusions	126
4.5	Quantitative Treatment of Excitons	129
4.5.1	Numerical Calculations	129
4.5.2	Interpretation of the Results	131
4.5.3	Comparison with Experiments	132
4.6	Charging Effects and Multi-excitons	133
4.6.1	Charging Effects: Single Particle Tunneling Through Semiconductor Quantum Dots	133
4.6.2	Multi-excitons	138
4.7	Conclusion	140
5	Optical Properties and Radiative Processes	141
5.1	General Formulation	141
5.1.1	Optical Absorption and Stimulated Emission	141
5.1.2	Luminescence	148
5.1.3	Nanostructures in Optical Cavities and Photonic Crystals	149
5.1.4	Calculation of the Optical Matrix Elements	150
5.2	Electron–Phonon Coupling and Optical Line-Shape	151
5.2.1	Normal Coordinates	152
5.2.2	Calculation of Phonons in Nanostructures	153
5.2.3	Configuration Coordinate Diagram	154
5.2.4	General Expression for the Optical Transition Probabilities	156
5.2.5	Calculation of the Coupling Parameters	161
5.2.6	Fröhlich Coupling: Optical Modes	162
5.2.7	Coupling to Acoustic Modes	169
5.2.8	The Importance of Non-adiabatic Transitions	172
5.3	Optical Properties of Heterostructures and Nanostructures of Direct Gap Semiconductors	174
5.3.1	Interband Transitions	175
5.3.2	Intraband Transitions	181
5.3.3	The Importance of Electron–Phonon Coupling	184
5.4	Optical Properties of Si and Ge Nanocrystals	185
5.4.1	Interband Transitions	186
5.4.2	Intraband Transitions	191

6	Defects and Impurities	195
6.1	Hydrogenic Donors	195
6.1.1	Envelope Function Approximation	195
6.1.2	Tight Binding Self-Consistent Treatment	197
6.2	Deep Level Defects in Nanostructures	200
6.3	Surface Defects: Si Dangling Bonds	205
6.3.1	Review of the Properties of Si Dangling Bonds	205
6.3.2	Si Dangling Bonds at the Surface of Crystallites	207
6.3.3	Dangling Bond Defects in III–V and II–VI Semiconductor Nanocrystals	208
6.4	Surface Defects: Self-Trapped Excitons	210
6.5	Oxygen Related Defects at Si–SiO ₂ Interfaces	214
7	Non-radiative and Relaxation Processes	219
7.1	Multi-phonon Capture at Point Defects	219
7.2	Auger Recombination	225
7.2.1	Theoretical Calculation	225
7.2.2	Experimental Evidence for Auger Recombination	230
7.3	Hot Carrier Relaxation: Existence of a Phonon Bottleneck	233
8	Transport	235
8.1	Description of the Systems and of the Boundary Conditions ..	236
8.2	Weak Coupling Limit	237
8.2.1	Perturbation Theory	237
8.2.2	Orthodox Theory of Tunneling	239
8.3	Beyond Perturbation Theory	245
8.3.1	Elastic Scattering Formalism	245
8.3.2	Calculation of the Green’s Functions	249
8.4	Electron–Electron Interactions Beyond the Orthodox Theory ..	253
8.4.1	Self-Consistent Mean-Field Calculations	253
8.4.2	The Self-Consistent Potential Profile	255
8.4.3	The Coulomb Blockade Effect	258
8.5	Transport in Networks of Nanostructures	263
8.5.1	Tunneling Between Nanostructures	263
8.5.2	Hopping Conductivity	266
8.5.3	Coherent Potential Approximation	268
8.5.4	Example of a Network of Silicon Nanocrystals	270
A	Matrix Elements of the Renormalizing Potential	273
B	Macroscopic Averages in Maxwell’s Equations	277
C	Polarization Correction	279
	References	281
	Index	299