

Contents

<i>Preface</i>	vii
<i>Acknowledgments</i>	ix
Brief history of the field and experimental techniques	1
1. The birth of molecular electronics	3
1.1 Why molecular electronics?	5
1.2 A brief history of molecular electronics	6
1.3 Scope and structure of the book	14
2. Fabrication of metallic atomic-size contacts	19
2.1 Introduction	19
2.2 Techniques involving the scanning electron microscope (STM)	19
2.3 Methods using atomic force microscopes (AFM)	21
2.4 Contacts between macroscopic wires	22
2.5 Transmission electron microscope	23
2.6 Mechanically controllable break-junctions (MCBJ)	24
2.7 Electromigration technique	31
2.8 Electrochemical methods	35
2.9 Recent developments	37
2.10 Electronic transport measurements	38
2.11 Exercises	43

3.	Contacting single molecules: Experimental techniques	45
3.1	Introduction	45
3.2	Molecules for molecular electronics	46
3.2.1	Hydrocarbons	47
3.2.2	All carbon materials	50
3.2.3	DNA and DNA derivatives	51
3.2.4	Metal-molecule contacts: anchoring groups	52
3.2.5	Conclusions: molecular functionalities	52
3.3	Deposition of molecules	53
3.4	Contacting single molecules	55
3.4.1	Electromigration technique	56
3.4.2	Molecular contacts using the transmission electron microscope	58
3.4.3	Gold nanoparticle dumbbells	59
3.4.4	Scanning probe techniques	60
3.4.5	Mechanically controllable break-junctions (MCBJs)	64
3.5	Contacting molecular ensembles	66
3.5.1	Nanopores	66
3.5.2	Shadow masks	68
3.5.3	Conductive polymer electrodes	69
3.5.4	Microtransfer printing	70
3.5.5	Gold nanoparticle arrays	71
3.6	Exercises	73

Theoretical background **75**

4.	The scattering approach to phase-coherent transport in nanocontacts	77
4.1	Introduction	77
4.2	From mesoscopic conductors to atomic-scale junctions	79
4.3	Conductance is transmission: Heuristic derivation of the Landauer formula	81
4.4	Penetration of a potential barrier: Tunnel effect	83
4.5	The scattering matrix	88
4.5.1	Definition and properties of the scattering matrix	88
4.5.2	Combining scattering matrices	91
4.6	Multichannel Landauer formula	92

4.6.1	Conductance quantization in 2DEG: Landauer formula at work	97
4.7	Shot noise	99
4.8	Thermal transport and thermoelectric phenomena	104
4.9	Limitations of the scattering approach	106
4.10	Exercises	107
5.	Introduction to Green's function techniques for systems in equilibrium	111
5.1	The Schrödinger and Heisenberg pictures	112
5.2	Green's functions of a noninteracting electron system	113
5.3	Application to tight-binding Hamiltonians	118
5.3.1	Example 1: A hydrogen molecule	118
5.3.2	Example 2: Semi-infinite linear chain	122
5.3.3	Example 3: A single level coupled to electrodes	124
5.4	Green's functions in time domain	128
5.4.1	The Lehmann representation	131
5.4.2	Relation to observables	134
5.4.3	Equation of motion method	136
5.5	Exercises	139
6.	Green's functions and Feynman diagrams	143
6.1	The interaction picture	144
6.2	The time-evolution operator	146
6.3	Perturbative expansion of causal Green's functions	148
6.4	Wick's theorem	149
6.5	Feynman diagrams	151
6.5.1	Feynman diagrams for the electron-electron interaction	152
6.5.2	Feynman diagrams for an external potential	157
6.6	Feynman diagrams in energy space	158
6.7	Electronic self-energy and Dyson's equation	162
6.8	Self-consistent diagrammatic theory: The Hartree-Fock approximation	167
6.9	The Anderson model and the Kondo effect	170
6.9.1	Friedel sum rule	171
6.9.2	Perturbative analysis	173
6.10	Final remarks	175

6.11	Exercises	176
7.	Nonequilibrium Green's functions formalism	179
7.1	The Keldysh formalism	180
7.2	Diagrammatic expansion in the Keldysh formalism	184
7.3	Basic relations and equations in the Keldysh formalism .	186
7.3.1	Relations between the Green's functions	186
7.3.2	The triangular representation	187
7.3.3	Unperturbed Keldysh-Green's functions	189
7.3.4	Some comments on the notation	191
7.4	Application of Keldysh formalism to simple transport problems	191
7.4.1	Electrical current through a metallic atomic contact	193
7.4.2	Shot noise in an atomic contact	199
7.4.3	Current through a resonant level	200
7.5	Exercises	202
8.	Formulas of the electrical current: Exploiting the Keldysh formalism	205
8.1	Elastic current: Microscopic derivation of the Landauer formula	205
8.1.1	An example: back to the resonant tunneling model	211
8.1.2	Nonorthogonal basis sets	212
8.1.3	Spin-dependent elastic transport	213
8.2	Current through an interacting atomic-scale junction . . .	215
8.2.1	Electron-phonon interaction in the resonant tun- neling model	217
8.2.2	The Meir-Wingreen formula	222
8.3	Time-dependent transport in nanoscale junctions	224
8.3.1	Photon-assisted resonant tunneling	231
8.4	Exercises	233
9.	Electronic structure I: Tight-binding approach	237
9.1	Basics of the tight-binding approach	237
9.2	The extended Hückel method	241
9.3	Matrix elements in solid state approaches	242
9.3.1	Two-center matrix elements	244
9.4	Slater-Koster two-center approximation	246

9.5	Some illustrative examples	247
9.5.1	Example 1: A benzene molecule	248
9.5.2	Example 2: Energy bands in line, square and cubic Bravais lattices	250
9.5.3	Example 3: Energy bands of graphene	252
9.6	The NRL tight-binding method	253
9.7	The tight-binding approach in molecular electronics	257
9.7.1	Some comments on the practical implementation of the tight-binding approach	258
9.7.2	Tight-binding simulations of atomic-scale trans- port junctions	259
9.8	Exercises	260
10.	Electronic structure II: Density functional theory	263
10.1	Elementary quantum mechanics	264
10.1.1	The Schrödinger equation	264
10.1.2	The variational principle for the ground state	265
10.1.3	The Hartree-Fock approximation	266
10.2	Early density functional theories	268
10.3	The Hohenberg-Kohn theorems	269
10.4	The Kohn-Sham approach	271
10.5	The exchange-correlation functionals	273
10.5.1	LDA approximation	273
10.5.2	The generalized gradient approximation	275
10.5.3	Hybrid functionals	277
10.6	The basic machinery of DFT	277
10.6.1	The LCAO Ansatz in the Kohn-Sham equations	278
10.6.2	Basis sets	280
10.7	DFT performance	282
10.8	DFT in molecular electronics	284
10.8.1	Combining DFT with NEGF techniques	285
10.8.2	Pluses and minuses of DFT-NEGF-based methods	291
10.9	Exercises	292

Metallic atomic-size contacts **293**

11.	The conductance of a single atom	295
11.1	Landauer approach to conductance: brief reminder	296

11.2	Conductance of atomic-scale contacts	297
11.3	Conductance histograms	300
11.4	Determining the conduction channels	304
11.5	The chemical nature of the conduction channels of one-atom contacts	308
11.6	Some further issues	316
11.7	Conductance fluctuations	319
11.8	Atomic chains: Parity oscillations in the conductance . . .	322
11.9	Concluding remarks	331
11.10	Exercises	332
12.	Spin-dependent transport in ferromagnetic atomic contacts	335
12.1	Conductance of ferromagnetic atomic contacts	336
12.2	Magnetoresistance of ferromagnetic atomic contacts . . .	343
12.3	Anisotropic magnetoresistance in atomic contacts	347
12.4	Concluding remarks and open problems	353
Transport through molecular junctions		355
13.	Coherent transport through molecular junctions I: Basic concepts	357
13.1	Identifying the transport mechanism in single-molecule junctions	359
13.2	Some lessons from the resonant tunneling model	364
13.2.1	Shape of the I-V curves	366
13.2.2	Molecular contacts as tunnel junctions	368
13.2.3	Temperature dependence of the current	369
13.2.4	Symmetry of the I-V curves	371
13.2.5	The resonant tunneling model at work	373
13.3	A two-level model	374
13.4	Length dependence of the conductance	377
13.5	Role of conjugation in π -electron systems	381
13.6	Fano resonances	382
13.7	Negative differential resistance	385
13.8	Final remarks	388
13.9	Exercises	389

14. Coherent transport through molecular junctions II: Test-bed molecules	391
14.1 Coherent transport through some test-bed molecules . . .	392
14.1.1 Benzenedithiol: how everything started	392
14.1.2 Conductance of alkanedithiol molecular junctions: A reference system	395
14.1.3 The smallest molecular junction: Hydrogen bridges	401
14.1.4 Highly conductive benzene junctions	405
14.2 Metal-molecule contact: The role of anchoring groups . .	408
14.3 Tuning chemically the conductance: The role of side-groups	412
14.4 Controlled STM-based single-molecule experiments	416
14.5 Conclusions and open problems	420
15. Single-molecule transistors: Coulomb blockade and Kondo physics	423
15.1 Introduction	423
15.2 Charging effects in transport through nanoscale devices .	425
15.3 Single-molecule three-terminal devices	429
15.4 Coulomb blockade theory: Constant interaction model . .	432
15.4.1 Formulation of the problem	432
15.4.2 Periodicity of the Coulomb blockade oscillations .	435
15.4.3 Qualitative discussion of the transport characteristics	436
15.4.4 Amplitudes and line shapes: Rate equations . . .	439
15.5 Towards a theory of Coulomb blockade in molecular tran- sistors	445
15.5.1 Many-body master equations	447
15.5.2 A simple example: The Anderson model	449
15.6 Intermediate coupling: Cotunneling and Kondo effect . .	451
15.6.1 Elastic and inelastic cotunneling	451
15.6.2 Kondo effect	453
15.7 Single-molecule transistors: Experimental results	456
15.8 Exercises	468
16. Vibrationally-induced inelastic current I: Experiment	473
16.1 Introduction	473

16.2	Inelastic electron tunneling spectroscopy (IETS)	475
16.3	Highly conductive junctions: Point-contact spectroscopy (PCS)	483
16.4	Crossover between PCS and IETS	490
16.5	Resonant inelastic electron tunneling spectroscopy (RIETS)	493
16.6	Summary of vibrational signatures	499
17.	Vibrationally-induced inelastic current II: Theory	501
17.1	Weak electron-phonon coupling regime	501
17.1.1	Single-phonon model	502
17.1.2	Ab initio description of inelastic currents	512
17.2	Intermediate electron-phonon coupling regime	520
17.3	Strong electron-phonon coupling regime	524
17.3.1	Coulomb blockade regime	524
17.3.2	Interplay of Kondo physics and vibronic effects	532
17.4	Concluding remarks and open problems	534
17.5	Exercises	535
18.	The hopping regime and transport through DNA molecules	537
18.1	Signatures of the hopping regime	538
18.2	Hopping transport in molecular junctions: Experimental examples	541
18.3	DNA-based molecular junctions	546
18.4	Exercises	552
19.	Beyond electrical conductance: Shot noise and thermal transport	553
19.1	Shot noise in atomic and molecular junctions	554
19.2	Heating and heat conduction	560
19.2.1	General considerations	561
19.2.2	Thermal conductance	562
19.2.3	Heating and junction temperature	565
19.3	Thermoelectricity in molecular junctions	569
20.	Optical properties of current-carrying molecular junctions	579

20.1	Surface-enhanced Raman spectroscopy of molecular junctions	580
20.2	Transport mechanisms in irradiated molecular junctions .	583
20.3	Theory of photon-assisted tunneling	585
20.3.1	Basic theory	586
20.3.2	Theory of PAT in atomic contacts	590
20.3.3	Theory of PAT in molecular junctions	592
20.4	Experiments on radiation-induced transport in atomic and molecular junctions	594
20.5	Resonant current amplification and other transport phenomena in ac driven molecular junctions	601
20.6	Fluorescence from current-carrying molecular junctions .	604
20.7	Molecular optoelectronic devices	608
20.8	Final remarks	613
20.9	Exercises	614
21.	What is missing in this book?	617

Appendixes 621

Appendix A	Second Quantization	623
A.1	Harmonic oscillator and phonons	624
A.1.1	Review of simple harmonic oscillator quantization	624
A.1.2	1D harmonic chain	626
A.2	Second quantization for fermions	628
A.2.1	Many-body wave function in second quantization	628
A.2.2	Creation and annihilation operators	630
A.2.3	Operators in second quantization	632
A.2.4	Some special Hamiltonians	634
A.3	Second quantization for bosons	637
A.4	Exercises	638

<i>Bibliography</i>	639
---------------------	-----

<i>Index</i>	699
--------------	-----