

CONTENTS

1	Introduction to conjugated polymers	
2	τ -electron theories of conjugated polymers	7
2.1	Introduction	7
2.2	The many body Hamiltonian	7
2.3	The Born-Oppenheimer approximation	8
2.4	Second quantization of the Born-Oppenheimer Hamiltonian	10
2.5	sp^n hybridization	11
2.5.1	sp hybridization	12
2.5.2	sp^2 hybridization	12
2.5.3	sp^3 hybridization	14
2.5.4	Remarks	14
2.6	τ -electron models	15
2.7	Electron-phonon coupling	17
2.7.1	The nuclear-nuclear potential, $V_n(\{u_n\})$	18
2.8	Summary of τ -electron models	19
2.8.1	The Hückel model	19
2.8.2	The Su-Schrieffer-Heeger model	20
2.8.3	The Pariser-Parr-Pople model	20
2.9	Symmetries and quantum numbers	21
2.9.1	Spatial symmetries	22
2.9.2	Particle-hole symmetry	22
2.9.3	Quantum numbers	24
2.9.4	State labels	24
3	Noninteracting electrons	26
3.1	Introduction	26
3.2	The noninteracting (Hückel) Hamiltonian	26
3.3	Undimerized chains	26
3.3.1	Cyclic chains	26
3.3.2	Linear chains	29
3.4	Dimerized chains	29
3.4.1	Cyclic chains	30
3.4.2	Linear chains	32
3.5	The ground state and particle-hole excitations	32
3.5.1	The band, charge, and spin gaps	34
3.6	Symmetries	35
3.6.1	Particle-hole symmetry and particle-hole parity	35
3.6.2	Linear chains and inversion symmetry	37

4	Electron-lattice coupling I: Noninteracting electrons	39
4.1	Introduction	39
4.2	The Peierls model	39
4.3	The dimerized ground state	41
4.3.1	The Hückel ' $4n + 2$ ' rule	43
4.4	Self-consistent equations for $\{\mathbf{A}_n\}$	43
4.5	Solitons	45
4.5.1	Odd-site chains	45
4.5.2	Even-site chains	47
4.6	Soliton-antisoliton pair production	49
4.7	Polarons	52
4.8	Nondegenerate systems	52
4.9	The continuum limit of the Su-Schrieffer-Heeger model	55
4.10	Dynamics of the Su-Schrieffer-Heeger model	57
4.11	Self-trapping	57
4.12	Concluding remarks	58
5	Interacting electrons	59
5.1	Introduction	59
5.1.1	Broken symmetries	59
5.1.2	Undimerized chains	60
5.1.3	Dimerized chains	62
5.2	The weak-coupling limit	64
5.2.1	Undimerized chains	64
5.2.2	Dimerized chains	64
5.3	The strong-coupling limit	65
5.3.1	Low-energy dimerized Heisenberg antiferromagnet	65
5.3.2	High-energy spinless fermion model	66
5.4	The phase diagram of the undoped Pariser-Parr-Pople model	69
5.5	The valence bond method	69
6	Excitons in conjugated polymers	73
6.1	Introduction	73
6.2	The weak-coupling limit	74
6.2.1	The effective-particle model	74
6.2.2	Solutions of the effective-particle model	79
6.2.3	Comparisons to the numerical calculations	79
6.2.4	Refinements of the theory	85
6.3	The strong-coupling limit	86
6.3.1	The effective-particle model	87
6.3	The intermediate-coupling regime	90
6.5	Concluding remarks	92

7	Electron-lattice coupling II: Interacting electrons	95
7.1	Introduction	95
7.2	The Pariser-Parr-Pople-Peierls model	96
7.3	Dimerization and optical gaps	97
7.4	Excited states and soliton structures	101
7.4.1	$1^1B_u^-$ state	102
7.4.2	$1^3B_u^+$ state	104
7.4.3	$2^1A_g^+$ state	105
7.5	Polarons	107
7.6	Extrinsic dimerization	108
7.7	Self-trapping	110
7.8	Concluding remarks	111
8	Optical processes in conjugated polymers	113
8.1	Introduction	113
8.2	Linear optical processes	114
8.3	Evaluation of the transition dipole moments	115
8.3.1	The Franck-Condon principle	115
8.3.2	Electronic selection rules	118
8.3.3	Franck-Condon factors	119
8.3.4	Electronic dipole moments: Application of the exciton model	121
8.4	Nonlinear optical processes	123
8.4.1	The essential states mechanism	124
8.4.2	Third order harmonic generation	125
8.4.3	Electroabsorption	126
8.5	Size-dependencies of $\chi^{(n)}$	130
9	Electronic processes in conjugated polymers	131
9.1	Introduction	131
9.2	Exciton transfer	131
9.2.1	Exciton transfer integral	132
9.2.2	Coherent transfer	134
9.2.3	Incoherent transfer	138
9.2.4	The density matrix approach	140
9.3	Excited molecular complexes	141
9.3.1	Excimers	141
9.3.2	Exciplexes	142
9.4	Screening of intramolecular states	143
9.5	Electron transfer	148
9.5.1	Unimolecular electron transfer	148
9.5.2	Bimolecular electron transfer	151
9.6	The singlet exciton yield in light emitting polymers	154
9.6.1	Introduction	154
9.6.2	Basic model and the rate equations	156

9.6.3	Derivation of the intermolecular interconversion rate	159
9.6.4	Estimate of the interconversion rates	167
9.6.5	Discussion and conclusions	169
10	Linear polyenes and trans-polyacetylene	171
10.1	Introduction	171
10.2	Predictions from the Pariser-Parr-Pople-Peierls model	174
10.2.1	Transition energies	174
10.2.2	Soliton structures	176
10.2.3	Adiabatic potential energy curves	178
10.3	Quantum phonons	180
10.3.1	Results and discussion	182
10.4	Character of the excited states of trans-polyacetylene	185
10.5	Other theoretical approaches	185
11	Light emitting polymers	187
11.1	Introduction	187
11.2	Poly(para-phenylene)	192
11.2.1	Benzene	192
11.2.2	Biphenyl	196
11.2.3	Oligo and poly(<i>para</i> -phenylenes)	200
11.3	Poly(<i>para</i> -phenylene vinylene)	207
11.3.1	Stilbene	207
11.3.2	Oligo arid poly(<i>para</i> -phenylene vinylenes)	207
11.4	Other theoretical approaches	209
11.5	The excited states of light emitting polymers	212
11.6	Electron-lattice coupling	213
11.6.1	Noninteracting limit	214
11.6.2	Interacting limit	218
11.7	Concluding remarks	221
A	Dirac bra-ket operator representation of one-particle Hamiltonians	223
A.1	The Hückel Hamiltonian	223
A.2	The exciton transfer Hamiltonian	224
B	Particle-hole symmetry and average occupation number	226
C	Single-particle eigensolutions of a periodic polymer chain	227
C.1	Dimerized chain	228
C.2	poly(<i>para</i> -phenylene)	229
D	Derivation of the effective-particle Schrodinger equation	

E Hydrogenic solutions of the effective-particle exciton models	234
E.1 The weak-coupling limit	234
E.1.1 Odd parity, even n solutions	235
E.1.2 Even parity, odd n solutions	236
E.1.3 Numerical results	236
E.2 The strong-coupling limit	236
F Evaluation of the electronic transition dipole moments	238
F.1 The weak-coupling limit	238
F.1.1 Transitions between the ground state and an excited state	239
F.1.2 Transitions between excited states	240
F.2 The strong-coupling limit	241
F.2.1 Transitions between the ground state and an excited state	241
F.2.2 Transitions between excited states	241
G Valence-bond description of benzene	242
H Density Matrix Renormalization Group method	245
H.1 Introduction to the real-space method	245
H.1.1 Infinite algorithm method	245
H.1.2 Rotation and truncation of the basis	247
H.1.3 Symmetries and excited states	247
H.1.4 Finite algorithm method	248
H.1.5 Application to linear polyenes	248
H.2 Local Hilbert space truncation	249
References	251
Index	259