

Quantum Theory of Polymers as Solids

János J. Ladik

*University of Erlangen-Nuremberg
Erlangen, Federal Republic of Germany*

Plenum Press • New York and London

Contents

Introduction	1	
I. QUANTUM THEORY OF POLYMERIC ELECTRONIC STRUCTURE		
1. Hartree-Fock Crystal-Orbital Theory of Periodic Polymers	9	
1.1. Simple Translation	9	
1.1.1. Block Diagonalization of the Hamiltonian Matrix	9	
1.1.2. Elimination of the Overlap Matrix	13	
1.1.3. Hartree-Fock-Roothaan Crystal-Orbital Formalism	16	
1.2. Combined Symmetry Operation	20	
1.3. Methods to Treat Many-Neighbor Interactions	23	
1.4. Different Orbitals for Different Spin Formalisms	29	
1.5. Relativistic Formulation	34	
1.5.1. Introductory Remarks	34	
1.5.2. Derivation of the Relativistic Hartree-Fock-Roothaan Equations for Molecules and Crystals	35	
1.5.3. Concluding Remarks	44	
References	49	
2. Examples of <i>Ab Initio</i> Calculations on Quasi-One-Dimensional Polymers		53
2.1. Some Polymers Used for the Production of Plastics: Polyethylene and Its Fluoro Derivatives	53	
2.1.1. The Energy-Band Structure of Polyethylene	53	
2.1.2. Band Structures of Fluorinated Polyethylenes	55	
2.2. Highly Conducting Polymers: $(\text{CH})_x$, $(\text{SN})_x$, TCNQ and TTF Stacks	63	

2.2.1.	Hartree-Fock Calculations on <i>cis</i> - and <i>trans</i> -Polyacetylenes (Polyenes)	63
2.2.2.	The Energy-Band Structure of $(SN)_x$	69
2.2.3.	<i>Ab Initio</i> Calculation of Infinite TCNQ and TTF Stacks	72
2.3.	Periodic Biopolymers: Homopolynucleotides and Homopolyptides	74
2.3.1.	Homopolynucleotides	74
2.3.2.	Homopolyptides	81
	References	84
3.	Semiempirical Band-Structure Calculations	89
3.1.	Semiempirical Crystal-Orbital Methods	89
3.1.1.	The Pariser-Parr-Pople Crystal-Orbital Method	89
3.1.2.	Semiempirical All-Valence Electron Crystal-Orbital Schemes	93
3.2.	Applications to Highly Conducting Polymers and Biopolymers	97
3.2.1.	<i>Trans</i> -Polyacetylene	97
3.2.2.	TCNQ and TTF Stacks	99
3.2.3.	Periodic DNA and Protein Models	103
	References	106
4.	The Treatment of Aperiodicity in Polymers	109
4.1.	Elementary Green Function Theory	109
4.1.1.	Solution of Inhomogeneous Differential Equation by Means of Green Functions	109
4.1.2.	Application of Green Functions to the Solution of the Time-Independent Schrödinger Equation	112
4.1.3.	Simple Derivation of the Dyson Equation	115
4.2.	Demonstration of the Effects of Aperiodicity on the Electronic Structure of Polymers	116
4.2.1.	Effect of Side-Chain Disorder on the Electronic Structure of Proteins	117
4.2.2.	Localization of Wave Functions in a Disordered Hydrogen Ring	125
4.3.	Single-Site Coherent Potential Approximation and Its Application to $(SN)_x$ with Hydrogen Impurities	130
4.3.1.	Derivation of the Single-Site CPA Equation	131
4.3.2.	Application of the Single-Site CPA Method to $(SN)_x$ with Hydrogen Impurities	135

4.4.	The Negative Factor Counting (NFC) Technique and Its Application to Aperiodic DNA and Proteins	140
4.4.1.	The Negative Factor Counting Technique in Its One Band (Simple Tight-Binding) Form	140
4.4.2.	The NFC Method in Its <i>Ab Initio</i> (Matrix-Block) Form	143
4.4.3.	Application of the NFC Method to Aperiodic Polypeptides and Polynucleotides	146
4.5.	Investigation of the Localization of the Orbitals in Disordered Chains	162
4.5.1.	Green Matrix Method for the Study of the Localization Properties of the States Belonging to a Disordered Chain	163
4.5.2.	Application to a Model Hamiltonian	166
4.6.	Treatment of a Cluster of Impurities Imbedded in a Periodic Chain	168
4.6.1.	Green Matrix Formulation of the Problem	168
4.6.2.	Application to a Hydrogen Impurity in a Lithium Chain	173
	References	179
5.	Electronic Correlation in Polymers	183
5.1.	Construction of Wannier Functions	184
5.2.	Second-Order Møller-Plesset Many-Body Perturbation Theory for Infinite Systems	191
5.3.	The Electronic Polaron Model and the Quasi-Particle Band Structure of Polymers	199
5.4.	Selected Correlation Energy Calculations on Polymers	205
5.4.1.	Ground-State Energy of an Infinite Metallic Hydrogen Chain	205
5.4.2.	The Quasi-Particle Energy Gap of Alternating <i>trans</i> -Polyacetylene	207
5.4.3.	Correlation Energy and Quasi-Particle Gap in a Cytosine Stack	212
5.5.	Correlation in Polymers with Large Unit Cells	213
5.6.	Remarks on Correlation in Disordered Chains	223
	References	228
6.	Interaction between Polymers	231
6.1.	Perturbation Theoretical Considerations	231
6.2.	The Mutually Consistent Field (MCF) Method	239

6.2.1.	The MCF Method in the Point-Charge Representation of the Potentials	240
6.2.2.	The MCF Method in the Pseudopolarization Tensor Formulation	244
6.3.	Application to DNA-Protein Interactions	248
6.3.1.	Models for B-DNA and Polyglycine and Methods of Calculation	250
6.3.2.	Results of B-DNA-Polyglycine Calculations and Their Discussion	259
References	256
7.	The Effect of Environment on the Band Structure of Polymers	263
7.1.	Generation of an Effective Potential Field of the Environment	263
7.2.	Results for a Cytosine Stack	266
References	267
II.	THEORETICAL CALCULATION OF THE DIFFERENT PHYSICAL PROPERTIES OF POLYMERS	
8.	Excited and Ionized States of Polymers	271
8.1.	Intermediate Exciton Theory with Correlation	271
8.2.	Application of Intermediate Exciton Theory to UV Spectra of Different Polymers	278
8.2.1.	Applications to Polydiacetylenes and to Polyethylenes	278
8.2.2.	Applications to a Cytosine Stack and to Polyglycine	281
8.2.3.	The Exciton Spectrum of Polyglycine and Polyalanine	283
8.3.	Ionized States of Polymers and Their X-Ray Photoelectron Spectra	286
8.3.1.	Theoretical Calculation of the Ionized States of Simple Periodic Polymer Chains	286
8.3.2.	Interpretation of the Photoelectron Spectra of Polymers	288
References	291
9.	Vibrational Spectra and Transport Properties of Polymers.	295
9.1.	Methods for the Calculation of Vibrational Spectra of Polymers	295

9.2.	Phonon Calculations for Selected Ordered and Disordered Polymer Chains	300
9.2.1.	Polymethineimine	300
9.2.2.	Polyethylene	303
9.2.3.	Bent Chain of Hydrogen Fluoride Molecules	304
9.2.4.	Periodic and Nonperiodic Alternating <i>trans</i> -Polyacetylene	311
9.3.	Transport Properties of Polymers	323
9.3.1.	The Theory of Bloch-Type Electric Conduction in Polymers and Its Applications	325
9.3.2.	Calculation of Bloch Conduction for Narrow-Band Polymers.	337
9.3.3.	Theory of Hopping Conduction in Very Narrow Band Polymers and in Disordered Polymers with Applications	346
	References	354

10. Magnetic, Electrical, and Mechanical Properties of Polymers 359

10.1.	Hartree-Fock Equations for Periodic Polymer Chains in a Magnetic Field	359
10.1.1.	Static Magnetic Field	359
10.1.2.	Some General Remarks about the Theory of the Effects of Magnetic Fields on Polymers	368
10.2.	Electric Polarizabilities of Polymers	369
10.2.1.	Theoretical Methods.	369
10.2.2.	Numerical Applications.	372
10.3.	Mechanical Properties of Polymers	374
10.3.1.	Theoretical Considerations	374
10.3.2.	Application to Polyethylene	376
	References	379

11. The Possible Role of Solid-State Physical Properties of Biopolymers in Their Biological Functions 381

11.1.	Mutation and Aging	381
11.1.1.	Theory of Point Mutation	381
11.1.2.	Remarks about Aging	388
11.2.	Carcinogenesis Caused by Chemicals and Different Radiations	389
11.2.1.	Different Biochemical Mechanisms of Oncogene Activation through Chemical Carcinogens	389

11.2.2. Different Long-Range Physical Mechanisms
of Carcinogen Binding to DNA 394

11.2.3. Remarks on the Effect of UV and Particle
Radiation and the Initiation of Carcinogenesis. . 403

References 404

Index 407