

CONTENTS

Introduction. By A. Szent-Györgyi ix

PART I: THEORETICAL

A. Electronic Structure of Proteins and Nucleic Acids

- | | |
|---|-----|
| 1. Electronic structures in quantum biochemistry. By J. I. Fernández-Alonso | 3 |
| 2. Quantum mechanical considerations on some properties of DNA. By T. A. Hoffmann and J. Ladik | 84 |
| 3. Electronic structure and magnetic properties of hemoproteins, particularly of hemoglobins. By Masao Kotani | 159 |
| 4. Magnetic susceptibilities and the chemical bond in hemoproteins. By G. Schoffa | 182 |

PART II: EXPERIMENTAL

B. Influence of Physical Agents on Proteins and Nucleic Acids

- | | |
|--|-----|
| 5. Thermal effects on protein, nucleic acid and viruses. By Ernest C. Pollard | 201 |
| 6. Adsorption of water on solid proteins with special reference to haemoglobin. By D. D. Eley and R. B. Leslie | 238 |
| 7. The effects of ionizing radiations on some fibrous proteins. By R. Braams and G. Van Herpen | 259 |

C. Electrical and Magnetic Properties of Organic Molecular Solids, Proteins and Nucleic Acids

- | | |
|---|-----|
| 8. Electronic conduction in organic molecular solids. By David R. Kearns | 282 |
| 9. The electronic properties of deoxyribonucleic acid. By Pierre Douzou and Charles Sadron | 339 |
| 10. The properties of metal-porphyrin and similar complexes. By P. S. Braterman, R. C. Davies and R. J. P. Williams | 359 |

D. Applications of Spectroscopic Methods

- | | |
|--|-----|
| 11. Prospects for the use of infrared spectroscopy in biology. By J. Lecomte | 408 |
| 12. Infrared spectra of nucleic acids and related compounds. By Takehiko Shimanouchi, Masamichi Tsuboi and Yoshimasa Kyogoku | 435 |

13. The study of specific molecular interactions by nuclear magnetic relaxation methods. <i>By Oleg Jardetzky</i>	499
14. Recent advances in EPR spectroscopy. <i>By Bernard Smaller</i>	532
E. Physico-chemical Mechanisms in Biological Systems	
15. Photoprotection from far ultraviolet effects in cells. <i>By John Jagger</i>	584
16. Some recent developments in the study of paramagnetic species of biological interest. <i>By Anders Ehrenberg</i>	602
17. ESR investigations on different plant systems. <i>By Claude S. Nicolau</i>	628
18. The use of product inhibition and other kinetic methods in the determination of mechanisms of enzyme action. <i>By Charles Walter</i>	645
Author Index	725
Subject Index	739

1

ELECTRONIC STRUCTURES IN QUANTUM BIOCHEMISTRY *

J. I. FERNÁNDEZ-ALONSO, *Faculty of Science
University of Valencia, Valencia, Spain*

CONTENTS

I.	Introduction	4
II.	Fundamental Concepts and Methods of Quantum Mechanics	6
A.	Atomic Orbitals	10
B.	The Chemical Bond	16
C.	Bond Orbitals	18
D.	Bonding and Antibonding Molecular Orbitals	19
F.	Orbitals for Multiple Bonds	20
G.	Localized and Delocalized Bonds	21
H.	Principal Quantum Mechanical Methods	21
I.	Molecular Orbital Theory; LCAO Approximation	22
(1)	Hückel Approximation (HMO)	26
(2)	Mulliken-Wheland Method	28
(3)	Introduction of Heteroatoms and Substituents: Pauling-Wheland Method	30
(4)	Other Naïve Methods	32
(5)	Goeppert-Mayer and Sklar Method	32
(6)	Self-Consistent Molecular Orbital Method (Roothaan's Equations)	33
(7)	Generalized Hückel or "SCF-like LCAO-MO" Method (Semi-empirical Methods)	35
J.	Electronic Indices	38
(1)	Total π -Electron and Delocalization Energies	38
(2)	π -Electron Charges or Densities	40
(3)	Bond Order	41
(4)	Free-Valence Index	42
(5)	Localization Energies	42
(6)	Chemical Reactivity	43
III.	Biochemical Applications	44
A.	Theory of Electron Transfer	45
B.	Electronic Structures of Biomolecules	47
(1)	Purines	47
(2)	Pyrimidines	52

* Translated by Dr. L. C. Cusachs.

(3) Adenine-Thymine and Guanine-Cytosine Pairs	54
(4) Pteridines	55
(5) Basicity of the Aromatic Ring Nitrogens	59
(6) Electronic Structure and Antitumor Activity in Cancer .	60
C. Electronic Interpretation of Some Biocatalyzed Reactions .	61
(1) Electronic Structure of Energy-Rich Bonds	62
(2) Electronic Structure of the Coenzymes DPN and FAD .	67
(3) Electronic Structure of the Transelectronases (Cytochromes)	71
(4) The Pullmans' Theory of Enzymatic Hydrolysis	74
(5) Other Biochemical Processes	77
IV. Conclusions	77
V. Acknowledgements	79
References	79

QUANTUM MECHANICAL CONSIDERATIONS ON SOME PROPERTIES OF DNA

T. A. HOFFMANN, *Research Institute for Telecommunication,
Budapest*, and J. LADIK, *Central Research Institute for
Chemistry of the Hungarian Academy of Sciences, Budapest*

CONTENTS

I. Introduction	84
II. The General Plan of the Quantum Mechanical Treatment of the Electronic Structure of DNA	86
III. The Electronic System of the Single Bases and Their Spectroscopical Properties	90
IV. The Problem of Mutation and the Tautomerism of the Single Bases	103
V. The Electronic Structure of the Base Pairs	108
VI. Interaction Between the Superimposed Bases; Spectroscopical Consequences	116
VII. Genetical Considerations: the Coding Problem	130
VIII. Calculation of the Band Structure of Polynucleotides in the Hückel Approximation	136
IX. Considerations on the Band Structure of Real DNA and Its Conducting Properties	142
X. Working Hypothesis for the Mechanism of DNA Duplication and Tumour Development	148
XI. Acknowledgements	155
References	156

ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF HEMOPROTEINS, PARTICULARLY OF HEMOGLOBINS

MASAO KOTANI, *Department of Physics, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo, Japan*

CONTENTS

I. Introduction	159
II. Energy Levels of Free Atoms and Ions Containing Incomplete Shells	161
III. Magnetic Moment	164
IV. Cubic Ligand Field; Splitting of d Orbitals; High and Low Spin	167
V. Incomplete Quenching of Orbital Magnetic Moment in $(d\epsilon)^5$	170
VI. Analysis of EPR Data on a Ferrihemoglobin Derivative with Low Spin	172
VII. Property of 6S State in Ferrihemoglobin Fluoride	174
VIII. Electronic Structure of Iron in Ferrohemoglobin	177
References	181

4

MAGNETIC SUSCEPTIBILITIES AND THE CHEMICAL BOND IN HEMOPROTEINS

G. SCHOFFA, *Physics Department of the Technische Hochschule,
Karlsruhe*

CONTENTS

I.	Introduction	182
II.	Experimental Approach	184
	A. Magnetic Susceptibility Measurements	184
	B. Visible Absorption Spectra	185
III.	Theoretical Aspects	186
	A. Magnetic Susceptibility and the Chemical Bond	186
	(1) The Valence-Bond Method	188
	(2) The Ligand-Field Theory	190
	(3) The Molecular-Orbital Method	191
	References	197

THERMAL EFFECTS ON PROTEIN, NUCLEIC ACID AND VIRUSES

ERNEST C. POLLARD, *Graduate School Committee on Biophysics,* The Pennsylvania State University, University Park, Pennsylvania*

CONTENTS

I. Introduction	201
II. The Nature of Thermal Action	203
III. Experimental Findings	211
A. Enzyme Reaction Rates	211
B. Enzyme Inactivation	212
C. Denaturation of Proteins	216
D. Denaturation of Nucleic Acids: Melting Out	217
E. Loss of Biological Activity of Nucleic Acids	220
F. The Effect of Heat on Viruses	222
G. The Thermal Expansion of Proteins	224
IV. Theoretical Discussion	225
A. Inactivation	225
B. The Role of Water in the Inactivation Process	227
V. Theoretical Partition Functions for Proteins and DNA	229
VI. Energy of the Hydrogen Bond	232
VII. Loss of Infectivity of Viruses	233
VIII. Conclusion	235
IX. Acknowledgements	235
References	236

ADSORPTION OF WATER ON SOLID PROTEINS WITH SPECIAL REFERENCE TO HAEMOGLOBIN

D. D. ELEY and R. B. LESLIE, *University of Nottingham*

CONTENTS

I. Introduction	238
II. Adsorption Isotherms	240
III. Hysteresis Effects	243
IV. Thermodynamics of Adsorption	244
V. The Experimental Kinetics of Adsorption	247
VI. Interpretation of the Kinetics	249
VII. Conductivity and Adsorbed Water	251
A. The Intrinsic Mechanism	253
B. The Impurity Mechanism	254
References	257

THE EFFECTS OF IONIZING RADIATIONS ON SOME FIBROUS PROTEINS

R. BRAAMS and G. VAN HERPEN, *Department of Radiobiophysics
Physics Laboratory, University of Utrecht, Utrecht, Netherlands*

CONTENTS

I.	Introduction	259
A.	Ionizing Radiation(s)	259
B.	Proteins	261
C.	Radiation Effects on Proteins	262
II.	Studies on Fibrous Proteins	264
A.	Silk	264
(1)	Experimental Results	264
(2)	Discussion	265
B.	Keratins	265
(1)	Experimental Results	266
(2)	Discussion	269
C.	Collagen	270
(1)	Experimental Results	271
(2)	Discussion	274
D.	Myosin	274
(1)	Experimental Results	275
(2)	Discussion	276
III.	General Conclusions	277
IV.	Acknowledgements	278
References	279	

ELECTRONIC CONDUCTION IN ORGANIC MOLECULAR SOLIDS

DAVID R. KEARNS,* *Department of Biology and Research
Laboratory of Electronics,†
Massachusetts Institute of Technology,
Cambridge, Massachusetts*

CONTENTS

I. Introduction	284
II. Preliminary Theoretical Considerations	285
A. Energetics of Charge Carrier Formation	285
(1) Donor-Acceptor Theory	286
(2) Singlet State Theory	287
(3) Triplet State Theory	287
(4) Combined Singlet-Triplet Theory	287
B. Thermal Generation of Carriers	288
C. Photogeneration of Carriers	288
(1) Donor-Acceptor Theory	288
(2) Singlet State Theory	289
(3) Triplet State Theory	289
III. Mobilities	290
A. Experimental Results	290
(1) Pulsed Photoconductivity	290
(2) Space-Charge-Limited Currents	292
(3) Diffusion Techniques	293
B. Theoretical Calculations	293
(1) Band Theory Calculations	293
(2) Tunnelling Calculation	295
(3) Evaluation of V_{ns}	295
C. Comparison of Experiment and Theory	296
(1) Temperature Dependence	296
(2) Anisotropy	297
(3) Pressure Dependence	297

* NAS-NRC Postdoctoral Fellow, 1961-1962. Permanent address: Department of Chemistry, University of California, Riverside, California.

† The work of this laboratory is supported in part by the U.S. Army Signal Corps, the Air Force Office of Scientific Research, and the Office of Naval Research.

IV.	Solid State Ionization Potentials and Electron Affinities	298
A.	Ionization Potentials	298
B.	Electron Affinities	302
C.	Energy of Charge Carrier Formation	303
V.	Dark Electrical Conductivity of Pure Aromatic Molecular Solids	303
A.	Temperature Dependence	304
(1)	Electrode Effects	306
(2)	Non-ohmic Behavior	306
(3)	Impurity Effects	307
B.	The Pre-exponential Factor in the Conductivity Expression	308
VI.	Photoconduction in Pure Aromatic Molecular Solids	310
A.	Sign of the Majority Carrier	311
B.	Spectral Dependence	311
(1)	Surface Cell	311
(2)	Sandwich Cells	312
C.	Non-ohmic Currents	313
D.	Temperature Dependence	316
E.	Intensity Dependence	317
F.	Impurity Effects	318
G.	Additional Measurements	319
VII.	Neutral Free Radicals	319
VIII.	Donor-Acceptor Complexes	320
A.	Homogeneous Complexes	321
(1)	Electrical Properties	321
(a)	Aromatic-Halogen Complexes	321
(b)	Aromatic Amine-Quinone Complexes	321
(c)	Salts	323
(2)	Magnetic Properties	323
(3)	Interpretation of Electrical and Magnetic Properties	324
B.	Lamellar Complexes	326
(1)	Electrical Properties	327
(a)	Liquid Electrode Cell	327
(b)	Condenser Cell	327
(c)	Surface Cells	327
(2)	Polarization Measurements	329
(3)	Electron Spin Resonance Measurements	330
(4)	Absorption Spectra	331
IX.	Summary Comparison of Experiment and Theory	331
A.	Singlet State Theory	331
B.	Triplet State Theory	332
C.	Combined Singlet-Triplet State Theory	333
D.	Donor-Acceptor Theory	333
X.	Acknowledgment	335
	References	335

THE ELECTRONIC PROPERTIES OF DEOXYRIBONUCLEIC ACID

PIERRE DOUZOU and CHARLES SADRON,
*Laboratoire de Biophysique du Muséum National d'Histoire
Naturelle, Paris*

CONTENTS

I. Introduction	339
II. The Molecular Structure of Deoxyribonucleic Acid	341
III. The Study of the Electronic Properties of DNA	346
A. Theoretical Aspects of the Problem of the Interaction of Heterocyclic Bases	346
B. Comparison of the Electronic Properties of DNA and Its Components	347
(1) Studies with Optical Methods	347
(2) Studies with Magnetic Methods	350
(3) Direct Research on Supramolecular Electronic Properties	354
IV. Conclusion	357
References	357

THE PROPERTIES OF METAL-PORPHYRIN AND SIMILAR COMPLEXES

P. S. BRATERMAN, R. C. DAVIES, and R. J. P. WILLIAMS,
Inorganic Chemistry Laboratory, Oxford University, Oxford, England

CONTENTS

I. Introduction	360
II. Properties of Metal Complexes	360
A. The Metal (Octahedral Field)	360
B. Ligand-Field Transitions and the Spectrochemical Series	363
C. The Nephelauxetic Series	364
D. Change of Spin State	365
E. Thermodynamic Factors	366
F. Kinetic Effects	367
G. Charge Transfer Spectra	368
III. The Complexes of Dimethylglyoximate, DMG	369
A. Crystal Structure of DMG Complexes	369
B. Spectra of Complexes of DMG	371
C. Thermodynamic Effects	374
D. High and Low Spin States in Equilibrium	375
IV. The Reactivity of Ligands	376
A. Conjugation with Metals	376
B. The Action of Light	379
C. Summary of Reactivity	379
V. Energy Levels of Ligands	380
A. Spectra of Conjugated Organic Ligands	380
B. The Effect of Substitution in Pyrrole Rings	385
C. Metal Substituents in Phthalocyanines	387
D. Metal Substituents in Porphyrins	389
E. Spectra of Haemin Derivatives—Effects of <i>z</i> -Axis Ligands	394
F. Restrictions upon Ring Conjugation	397
G. The Spectra of Conjugated Chains	398
H. The Corrins	399
VI. Chemical Reactions	402
A. Chemical Reactivity of Ring Chelates	402
B. Reactions of Some Biologically Important Complexes	404
C. Photochemistry of Porphyrin-Like Compounds	404
References	405

PROSPECTS FOR THE USE OF INFRARED SPECTROSCOPY IN BIOLOGY

J. LECOMTE, *Laboratoire des Recherches Physiques de la Sorbonne, Paris*

CONTENTS

I.	Introduction	408
II.	Experimental Technique	409
	A. Detection of Infrared Radiations	409
	B. Sample Preparation	410
III.	Some Applications of Infrared	412
	A. Identifying Substances by Their Infrared Absorption Spectrum	413
	B. Demonstrating Small Structural Differences Between Very Similar Compounds or Isomers	416
	C. Attempts at Determining the Structures of Biological Substances	418
	D. Detecting Inter- or Intramolecular Bonds	423
IV.	Prospect for the Use of Infrared Spectrometry (or Global Infrared) in Biology	427
	A. Experimental Technique	427
	B. Problems Requiring Study	429
	C. Use of Undispersed Infrared Radiations	432
	D. Miscellaneous Applications	432
V.	Conclusion	434

12

INFRARED SPECTRA OF NUCLEIC ACIDS AND RELATED COMPOUNDS

TAKEHIKO SHIMANOUCHI, *Department of Chemistry,
Faculty of Science, University of Tokyo, Bunkyo-ku,
Tokyo, Japan*

MASAMICHI TSUBOI and YOSHIMASA KYOGOKU,
*Faculty of Pharmaceutical Sciences, University of
Tokyo, Bunkyo-ku, Tokyo, Japan*

CONTENTS

I.	Infrared Spectra of Nucleic Acids	436
A.	Introduction	436
B.	General Scope of the Spectra	436
II.	Absorption Bands due to the Base Residues	440
A.	Nucleosides	440
(1)	Cytidine	441
(2)	Adenosine	445
(3)	Uridine	447
(4)	Guanosine	449
(5)	Inosine	451
B.	Mixed Products of Nucleosides	452
C.	Synthetic Polyribonucleotides	454
(1)	Polycytidylic Acid	455
(2)	Polyadenylic Acid	456
(3)	Polyuridylic Acid and Polyinosinic Acid	459
(4)	Complexes of Polynucleotides	460
D.	Nucleic Acids	460
(1)	On the 1710 cm^{-1} Band of Undeuterated Film	460
(2)	On the 1685 cm^{-1} Band of Deuterated Nucleic Acid	463
(3)	Infrared Dichroism of Deoxyribonucleate	467
III.	Absorption Bands due to the Phosphate Groups	467
A.	General Considerations	467
B.	Phosphite Anion	469
C.	Monoalkyl Phosphate Anions	476
D.	Mononucleotides	477
E.	Hypophosphite Anion	478
F.	Dialkylphosphate Anions	484

G. Deoxyribonucleate	489
H. Ribonucleates	492
IV. Absorption Bands due to the Sugar Groups	494
References	496

13

THE STUDY OF SPECIFIC MOLECULAR INTERACTIONS BY NUCLEAR MAGNETIC RELAXATION MEASUREMENTS

OLEG JARDETZKY, *Department of Pharmacology,
Harvard Medical School, Boston, Massachusetts*

CONTENTS

I. Introduction	499
II. Theoretical Foundations	501
A. Basic Definitions	501
B. The Interpretation of Relaxation Times (T_1 and T_2) in Terms of Molecular Events	505
C. Simplifications of the Theory Applicable to High Resolution Proton Magnetic Resonance	511
D. Interpretation of Relaxation Measurements in Terms of Molecular Interactions	515
III. Experimental	518
A. Interactions between Small Molecules	518
B. The Binding of Small Molecules to Macromolecules	523
References	531

RECENT ADVANCES IN EPR SPECTROSCOPY*

BERNARD SMALLER, *Argonne National Laboratory,
Argonne, Illinois*

CONTENTS

I. Introduction	532
II. Theoretical Aspects of Hyperfine Interaction	533
A. Isotropic "Contact" Term	534
B. Anisotropic Dipolar Interaction	540
III. Free Radicals Produced in Organic Single Crystals	541
A. Dicarboxylic Acid and Derivatives	541
B. Amino Acid and Derivatives	546
C. Glycollic Acid and Derivatives	552
IV. Triplet State Studies	553
A. Zero-Field Splittings	554
(1) Experimental Determinations	556
(2) Theoretical Basis	559
B. Hyperfine Structure and Line Widths	562
C. Lifetime Studies	564
D. Energy Transfer Experiments	567
E. Triplet State and Photochemical Processes	576
References	579

PHOTOPROTECTION FROM FAR ULTRAVIOLET EFFECTS IN CELLS

JOHN JAGGER, *Biology Division, Oak Ridge National Laboratory,*
Oak Ridge, Tennessee*

CONTENTS

I.	Introduction	584
A.	Some Definitions	585
B.	Photoreactivation	586
II.	Behavior of Photoprotection	587
A.	Photoprotection in <i>Escherichia coli</i>	587
B.	Photoprotection in Other Organisms	591
C.	Attempts to Photoprotect Subcellular Systems	593
III.	The Chromophore	593
IV.	The Mechanism	595
A.	Direct Effects	595
(1)	Simple Photochemical Alteration	595
(2)	Utilization of Other Molecules	595
B.	Enzyme Involvement	596
C.	Indirect Effects	597
(1)	Alteration of Enzyme Balance	597
(2)	Superimposed Damage	598
D.	Further Experiments	599
V.	General Remarks	600
	References	600

16

SOME RECENT DEVELOPMENTS IN THE STUDY OF PARAMAGNETIC SPECIES OF BIOLOGICAL INTEREST

ANDERS EHRENBERG, *Biokemiska Institutionen,
Medicinska Nobelinstitutet, Karolinska Institutet, Stockholm, Sweden*

CONTENTS

I.	Introduction	602
II.	Experimental Techniques	603
	A. Static Susceptibility	603
	(1) Gouy Balance	603
	(2) Rankine Balance	605
	B. Electron Spin Resonance Spectroscopy	605
	C. Comparison of Methods	607
III.	Enzyme Systems and Components	607
	A. Hemoproteins	607
	(1) General Considerations	607
	(2) Temperature Dependence	609
	(3) Reactions between Ferrihemoproteins and Peroxides.	612
	B. Flavin Free Radicals and Flavoproteins	617
	C. Multicomponent Systems	620
IV.	Radiation-Induced Free Radicals	621
	A. General Considerations	621
	B. Model Systems	622
	C. Living Seeds	623
V.	Concluding Remarks	626
	References	626

ESR INVESTIGATIONS ON DIFFERENT PLANT SYSTEMS

CLAUDE S. NICOLAU, *Centre of Research of the Ministry of Health,
and Institute of Petroleum, Gas and Geology, Bucharest, Rumania*

CONTENTS

I. Introduction	628
II. ESR Investigation of the Mechanism of Photosynthesis in Green Plants	628
III. Non-photosynthetic Plant Material	638
IV. Irradiated Plant Material	640
References	643

THE USE OF PRODUCT INHIBITION AND OTHER KINETIC METHODS IN THE DETERMINATION OF MECHANISMS OF ENZYME ACTION

CHARLES WALTER, *Cardiovascular Research Institute, University
of California Medical Center, San Francisco, California*

CONTENTS

I. Preliminary Considerations	645
II. Single-Substrate, Single-Product Reactions	648
III. More-than-One-Substrate, Single-Product Reactions	653
IV. Reactions in Which More than One Product is Formed by One Substrate	665
V. Reactions of More than One Substrate to Form More than One Product	676
VI. General Comments on the Methods Employed	721
References	723