CONTENTS

OPTICAL DEPHASING OF IONS AND MOLECULES IN CRYSTALS 1
By J. L. Skinner and D. Hsu

QUASI-TWO-DIMENSIONAL PHASE TRANSITIONS IN PARAFFINS 45
By J. Naghizadeh

CORRELATION EFFECTS IN THE IONIZATION OF MOLECULES: BREAKDOWN OF THE MOLECULAR ORBITAL PICTURE 115
By L. S. Cederbaum; W. Domcke, J. Schirmer, and W. von Niessen

SEMICLASSICAL CALCULATION OF QUANTUM MECHANICAL WAVEFUNCTIONS 161
By J. B. Delos

CORRELATION FUNCTIONS IN SUBCRITICAL FLUID 215
By John Kerins, L. E. Scriven, and H. Ted Davis

AUTHOR INDEX 281

SUBJECT INDEX 293

OPTICAL DEPHASING OF IONS AND MOLECULES IN CRYSTALS

J. L. SKINNER AND D. HSU

Department of Chemistry, Columbia University, New York, New York 10027

CONTENTS

I. Introduction 1
II. Experimental Overview 3
III. Theoretical Overview: A Historical Perspective 4
IV. Nonperturbative Theory 6
V. Coupling to Acoustic Phonons 14
VI. Coupling to Optical Phonons 19
VII. Coupling to Pseudolocal Phonons 23
VIII. Comparison With Experiment: Acoustic Phonons 31
A. 1,3-Diazaazulene in Naphthalene 31
B. Cr^{3+} in Al_2O_3 (Ruby) 34
C. Additional Remarks 36
IX. Comparison With Experiment: Pseudolocal Phonons 37
A. 3,4,6,7-Dibenzopyrene in *n*-Octane 37
B. Pentacene in Benzoic Acid 39
C. Additional Remarks 40
X. Conclusion 40
References 41

QUASI-TWO-DIMENSIONAL PHASE TRANSITIONS IN PARAFFINS

J. NAGHIZADEH†

Fachrichtung Theoretische Physik, Universität des Saarlandes, 6600 Saarbrücken, Federal Republic of Germany

CONTENTS

I. Introduction 46
II. Potential of Interaction 47
A. Single Chain 48
B. Salem Potential 51
C. Orientational Energy 54
III. Motion of the Chain 55
A. Infrared Spectra 56
B. Equations of Motion ot the Chain 57
1. Generalized Coordinates 57
2. Mass Tensor and Normal Modes 59
3. Torsional Specific Heat 61
C. Conformational Transitions 62
IV. Phase Transitions 67
A. Melting Transition 69
B. Rotator Transition 71
C. Other Transitions 73
1. Transition V → IV 75
2. Transition IV → III 75
3. Transition III → II 76
4. Liquid–Liquid Transition 76
V. Theory of Phase Transitions 77
A. Intralayer Melting Transition 79
1. Ising Theory 80
2. Dislocation Loops 83
3. Chain Folding 86
B. Theory of Rotator Transition 90
C. Theory of Other Transitions 93
1. Surface Melting Transition 93

† Present address: Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

2. V → IV Transition 93
3. IV → II Transition 94
D. Classification of Transitions 95
VI. Cycloparaffins and Phospholipids 97
A. Cycloparaffins 97
B. Phospholipids 100
Appendix A. Dislocations 103
Appendix B. Elastic Constants of Paraffins 108
References 110

CORRELATION EFFECTS IN THE IONIZATION OF MOLECULES: BREAKDOWN OF THE MOLECULAR ORBITAL PICTURE

L. S. CEDERBAUM, W. DOMCKE, J. SCHIRMER, AND W. VON NIESSEN‡

Lehrstuhl für Theoretische Chemie
Institut für Physikalische Chemie
Universität Heidelberg
D-6900 Heidelberg, West Germany

CONTENTS

I. Introduction 115
II. Outline of Theory 119
A. Ionization Spectrum 119
B. Computational Aspects and Results 126
III. Correlation Effects in the Ionization of Molecules 129
A. Representative Examples 129
B. Discussion 143
IV. Other Effects and Outlook 148
References 154

SEMICLASSICAL CALCULATION OF QUANTUM MECHANICAL WAVEFUNCTIONS

J. B. DELOS

Department of Physics,
College of William and Mary,
Williamsburg, Virginia 23185

CONTENTS

I. Introduction 162
II. Classical Trajectories and the Lagrange Manifold 165
A. Hamilton–Jacobi Equation and the Field of Trajectories 165
B. Lagrange Manifold 167
C. Transport Equation and the Classical Density 170
III. Local Formal Asymptotic Solution to the Schroedinger Equation 171
IV. Momentum Space and Mixed Spaces 172
A. Introductory Remarks 172
B. Definition and Essential Properties of Lagrange Manifolds 175
C. Classical Functions for General Representations 178
D. Wavefunctions in Momentum Space and in Mixed Spaces 180
1. Formal Asymptotic Solution of the Schroedinger Equation 180
2. Validity of the Asymptotic Expansion 183
V. Global Formal Asymptotic Solutions 185
A. Local Approximations in Configuration Space 186
B. Joining Semiclassical Functions Using the Stationary Phase Approximation 187
C. Maslov Index 190
D. Canonical Formula for the Wavefunction 194
E. Caustics and Catastrophes 197
VI. Conclusion 198
Appendix A. Formulas Related to Section II 200
A. Solution to the Hamilton–Jacobi Equation 200
B. The Manifold Is Lagrangian 202
C. Solution to the Transport Equation 202
Appendix B. Formulas Related to Section IV 204
A. Hamilton–Jacobi Equation in Mixed Spaces 204
B. Density Function in Mixed Spaces 206
C. Formal Asymptotic Expansion of $\tilde{\Psi}(p_\alpha, q_\beta)$ 208
Appendix C. Summary of Terminology 211
References 212

CORRELATION FUNCTIONS IN SUBCRITICAL FLUID

JOHN KERINS, L. E. SCRIVEN, and H. TED DAVIS

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

CONTENTS

I.	Introduction	215
II.	Background	221
III.	Method of Solution	225
IV.	High Temperature	234
V.	Low Temperature	242
	A. PY Case	243
	B. HNC Case	250
	C. BGYK Case	255
VI.	Summary of Results	262
VII.	Discussion	264
Appendix A		270
Appendix B		273
References		275