



# CONTENTS

## OPTIMIZATION AND CHARACTERIZATION OF A MULTICONFIGURATIONAL SELF-CONSISTENT FIELD (MCSCF) STATE

*By Jeppe Olsen, Danny L. Yeager, and Poul Jørgensen*

1

## TWO-PHOTON SPECTROSCOPY OF PERTURBED BENZENES

*By Lionel Goodman and Richard P. Rava*

177

## INHOMOGENEOUS RELATIVISTIC ELECTRON SYSTEMS: A DENSITY FUNCTIONAL FORMALISM

*By M. V. Ramana and A. K. Rajagopal*

231

## POLARITON AND SURFACE EXCITON STATE EFFECTS IN THE PHOTODYNAMICS OF ORGANIC MOLECULAR CRYSTALS

*By J. M. Turlet, Ph. Kottis, and M. R. Philpott*

303

## AUTHOR INDEX

469

## SUBJECT INDEX

479



# **OPTIMIZATION AND CHARACTERIZATION OF A MULTICONFIGURATIONAL SELF-CONSISTENT FIELD (MCSCF) STATE**

**JEPPE OLSEN AND DANNY L. YEAGER**

*Chemistry Department  
Texas A & M University  
College Station, Texas*

**AND**

**POUL JØRGENSEN**

*Chemistry Department  
Aarhus University  
Aarhus, Denmark*

## **CONTENTS**

I.	Introduction	2
II.	MCSCF Optimization Using Exponential Unitary Operators	6
	A. Unitary Transformations of the Multiconfigurational Hartree–Fock State	6
	B. Variations in the Total Energy	8
III.	The Newton–Raphson Iterative Function	10
	A. The Linear Newton–Raphson Iterative Function	11
	B. The Nonlinear Newton–Raphson Iterative Function	14
	C. Implementation of the Nonlinear Newton–Raphson Approach	21
	D. Matrix Elements in a Nonlinear Newton–Raphson Approach	23
IV.	Characterization of an MCSCF State	25
	A. $n$ th State of the CI Using the MCSCF Configuration State Functions (CSFs)	27
	B. Eigenvalues of the Hessian	28
	C. Excitation Energies in the Multiconfigurational Time-Dependent Hartree–Fock Approximation	30
	D. Stability Condition for a Multiconfigurational Hartree–Fock State	32

V.	Calculations with the Newton-Raphson Approach	34
A.	Step Size and Sign Control in the Newton-Raphson Approach	35
B.	Small Hessian Eigenvalues	40
C.	Step Size and Sign Controlled Nonlinear Newton-Raphson Calculations	41
D.	Initial Guess of Orbitals and States	62
E.	Conditions for Improved Iterative Methods	65
VI.	Generalized and Fixed Hessian Approaches	66
A.	The Generalized Newton-Raphson Perturbative Approach	66
B.	The Linear Fixed Hessian Approach	67
C.	Optimal Use of Fixed Hessian Approaches	69
D.	Numerical Results	72
VII.	Update Methods	78
A.	Broyden Unsymmetric Rank-1 Update and Its Symmetrization	79
B.	The Broyden Family (DFP and BFGS Updates)	82
C.	A Variational Approach to Update Procedures	86
D.	Inverse Updates	87
E.	Convergence Characteristics of Hessian Update Methods	88
F.	Numerical Results	90
G.	Other Applications of Update Methods	100
VIII.	Cubic Contributions in MCSCF Optimization	101
A.	Theory	101
B.	Numerical Results	107
C.	Summary and Conclusions	112
IX.	Effective Implementation and Combination of MCSCF Procedures	114
A.	Simplifications of Transformations	116
B.	Effective Treatment of Large CI Expansions	121
C.	Combination and Overview of Methods	126
D.	Higher (Infinite) Order Procedures	134
X.	Summary and Conclusions	141
Appendix A.	Redundant Variables	143
Appendix B.	The First Partial Derivative of the Total Energy	145
Appendix C.	Formulas for $(\mathbf{P}'^T \mathbf{F}(0))$ and $(\mathbf{P}'^T \mathbf{G}(0) \mathbf{P}')$	151
Appendix D.	Eigenvalues of the Full Hessian and the Reduced Hessian Matrix	156
Appendix E.	Construction of Cubic Contributions for the Iterative Cubic and Perturbative (Chebyshev) Cubic Procedures	158
Appendix F.	Two-Electron Integral Transformations in MCSCF	164
References		173





# TWO-PHOTON SPECTROSCOPY OF PERTURBED BENZENES

LIONEL GOODMAN AND RICHARD P. RAVA\*

*Department of Chemistry  
Rutgers University  
New Brunswick, New Jersey*

## CONTENTS

I.	Introduction	177
II.	Two-Photon Spectrum of the Parent $^1B_{2u} \leftarrow ^1A_{1g}$ Benzene Transition	179
III.	Mass Perturbations	180
	A. Harmonic Mode Scrambling	181
	B. Duschinsky Rotation	188
IV.	Two-Photon $L_b$ Spectra of Toluene and Fluorobenzene	191
V.	Regularities in the Two-Photon Spectra of Perturbed Benzenes	192
VI.	The Perturbation Approach to Perturbed Benzene	194
VII.	Vibronic Mechanisms in the Benzene Two-Photon Spectrum	198
	A. The $B_{2u}$ State	198
	B. The $B_{1u}$ State	200
VIII.	Electrostatic Effects on the Two-Photon Spectrum	201
	A. The $L_b$ State	201
	B. The $L_a$ State	209
IX.	Two-Photon $L_b$ Spectra of Monosubstituted Benzenes	211
X.	Polysubstitution	216
XI.	Phenylacetylene, Benzonitrile, and Styrene	220
XII.	Conclusions	224
XIII.	Frequently used Abbreviations and Symbols	225
	References	228



# INHOMOGENEOUS RELATIVISTIC ELECTRON SYSTEMS: A DENSITY-FUNCTIONAL FORMALISM\*

M. V. RAMANA AND A. K. RAJAGOPAL

*Department of Physics and Astronomy  
Louisiana State University  
Baton Rouge, Louisiana*

## CONTENTS

I.	Introduction	232
A.	Notations, Orders of Magnitude, and the Need for Relativistic Treatment	232
B.	Survey of Earlier Work for Relativistic Many-Electron Systems	234
C.	The Density-Functional Formalism in Relativistic Systems	237
D.	Spin-Density-Functional Formalism in Relativistic Systems	238
E.	A Note on Renormalization	239
II.	Formal Theory	240
A.	Density-Functional Theory for the Inhomogeneous Relativistic Electron System	240
B.	The Relativistic Electron Gas	243
C.	The Calculation of Exchange-Correlation Energy	255
III.	Some Numerical Calculations	258
A.	Numerical Calculation of the Correlation Energies	258
B.	A Self-Consistent Atomic Calculation for Mercury and Fermium	265
IV.	Spin-Density Theory	273
A.	Relativistic Spin-Density-Functional Formalism	273
B.	Exchange Energy in a Homogeneous Spin-Polarized Electron Gas	279
C.	Effective Exchange Potentials of the Relativistic Spin-Density-Functional Theory	282
V.	Summary, Conclusions, and Remarks	288
Appendix A.	Equivalence of the Expressions for the Dielectric Constant Given by Various Authors	290
Appendix B.	Approximations for Correlation Energy	294
Appendix C.	Local Approximation for the Breit Interaction	296
Appendix D.	Explicit Expressions for $E_x^{(c)}$ and $E_x^{(tr)}$ for the Polarized Case	297
Addendum		298
References		299

\*Based on the Doctoral Dissertation of M.V.R., submitted to the Department of Physics and Astronomy, Louisiana State University, Baton Rouge, La. (1981). Present address: Department of Physics, University of West Virginia, Morgantown, W. Va.



# POLARITON AND SURFACE EXCITON STATE EFFECTS IN THE PHOTODYNAMICS OF ORGANIC MOLECULAR CRYSTALS

J. M. TURLET AND PH. KOTTIS

*Centre de Physique Moléculaire Optique et Hertzienne  
Université de Bordeaux I and CNRS Talence, France*

AND

M. R. PHILPOTT

*IBM Research Laboratory San Jose, California*

## CONTENTS

I.	Introduction	304
II.	Bulk and Surface Excitons in Molecular Crystals	305
A.	Molecular Crystals and Frenkel Excitons	306
B.	Effect of Exciton-Photon Coupling	314
C.	Surface and Subsurface Excitons	315
D.	Principal Theoretical and Experimental Results Obtained on the First Singlet Transition of Anthracene	320
E.	Subject of the Present Work	325
III.	Polaritons in "Infinite" Crystals	327
A.	Introduction	327
B.	Semiclassical Theory of the Polariton	328
C.	Application of the Semiclassical Theory to Crystalline Anthracene	340
D.	Quantum Theory of the Polariton	359
IV.	Experimental Methods	372
A.	The Anthracene Crystal	372
B.	Low-Temperature Techniques	376
C.	Apparatus	378
V.	Experimental Reflectivity and Fluorescence Studies of the Photodynamic Properties of Crystalline Anthracene	381
A.	Introduction	381
B.	b-Polarized Reflectivity Spectrum	385
C.	Influence of Surface Modifications on the E  b Reflectivity Spectrum	390

D.	a-Polarized Reflectivity Spectrum	396
E.	Fluorescence Studies of the Region of I and II	398
VI.	Theoretical Model of the Reflectivity of a Semi-Infinite and a Finite Crystal	406
A.	Theory of the Reflectivity of a Semi-infinite Crystal	406
B.	Reflectivity of a Semi-infinite Crystal	409
C.	Reflectivity of a Finite Crystal	412
VII.	Interpretation and Generalization	422
A.	Discussion and Interpretation of Our Observations on Anthracene	422
B.	Generalization of Our Observations	433
VIII.	New Developments: Exciton Surface Polaritons	437
A.	Basic Principles on Exciton Surface Polaritons	438
B.	Experimental Excitation and Detection of Surface Polaritons	448
C.	Study of Exciton Surface Polaritons on Anthracene Crystal	451
Conclusion and Prospects		455
Appendix		460
Bibliography		461

