

# Excited States in Quantum Chemistry

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**Series C – Mathematical and Physical Sciences**

*Volume 46 – Excited States in Quantum Chemistry*

# Excited States in Quantum Chemistry

Theoretical and Experimental Aspects of the  
Electronic Structure and Properties of the Excited States  
in Atoms, Molecules and Solids

*Proceedings of the NATO Advanced Study Institute  
held at Kos, Greece, June 4–18, 1978*

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**D. Reidel Publishing Company**

Dordrecht : Holland / Boston : U.S.A. / London : England

Published in cooperation with NATO Scientific Affairs Division

Library of Congress Cataloging in Publication Data



NATO Advanced Study Institute, Kos Island, Greece, 1978.

Excited States in Quantum Chemistry

(NATO advanced study institutes series : Series C, Mathematical and physical sciences ; v. 46)

Bibliography: p.

Includes index.

1. Excited state chemistry—Congresses.

I. Nicolaidis, Cleanthes A. II. Beck, Donald R. III. Title. IV. Series.

QD461.5.N36 1978 541'.28 78-24278

ISBN-13: 978-94-009-9904-6 e-ISBN-13: 978-94-009-9902-2

DOI: 10.1007/978-94-009-9902-2

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Published by D. Reidel Publishing Company  
P.O. Box 17, Dordrecht, Holland

Sold and distributed in the U.S.A., Canada, and Mexico  
by D. Reidel Publishing Company, Inc.  
Lincoln Building, 160 Old Derby Street, Hingham, Mass. 02043, U.S.A.

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Softcover reprint of the hardcover 1st edition 1979

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TABLE OF CONTENTS

PREFACE	vii
EXPERIMENTAL STUDIES OF ATOMIC AND MOLECULAR LIFETIMES Indrek Martinson	1
EXCITATION ENERGIES AND TRANSITION MOMENTS FROM THE POLARIZATION PROPAGATOR Jan Linderberg	35
ACCURACY, TIMING AND GENERAL APPLICABILITY OF THE MRD-CI METHOD Robert J. Buenker and Sigrid D. Peyerimhoff	45
CALCULATION OF VIBRATIONAL WAVEFUNCTIONS AND ENERGIES USING MRD-CI TECHNIQUES Robert J. Buenker, Sigrid D. Peyerimhoff, and Miljenko Perić	63
CI CALCULATIONS OF VERTICAL EXCITATION ENERGIES AND OSCILLATOR STRENGTHS FOR RYDBERG AND VALENCE STATES OF MOLECULES S.D. Peyerimhoff and R.J. Buenker	79
THEORY OF THE ELECTRONIC STRUCTURE OF EXCITED STATES IN SMALL SYSTEMS WITH NUMERICAL APPLICATIONS TO ATOMIC STATES Donald R. Beck and Cleanthes A. Nicolaides	105
MANY BODY THEORY OF PHOTOABSORPTION IN ATOMS AND MOLECULES Cleanthes A. Nicolaides and Donald R. Beck	143
ON GREEN'S FUNCTION METHODS FOR THE STUDY OF IONIC STATES IN ATOMS AND MOLECULES W. von Niessen, L.S. Cederbaum, and W. Domcke	183
AUGER ELECTRON SPECTRA FROM FREE ATOMS AND MOLECULES Hans Siegbahn	273
MANY BODY PERTURBATION METHODS FOR THE CALCULATION OF EXCITED STATES Michael A. Robb, Dermot Hegarty, and Sally Prime	297

THE CALCULATION OF ATOMIC AND MOLECULAR ELECTRON BINDING ENERGIES Yngve Öhrn	317
THEORY OF ONE ELECTRON BINDING ENERGIES INCLUDING CORRELATION, RELATIVISTIC AND RADIATIVE EFFECTS: APPLICATION TO FREE ATOMS AND METALS Donald R. Beck and Cleanthes A. Nicolaidis	329
ATOMIC PHOTOIONIZATION CROSS SECTIONS P.L. Altick	361
THEORY OF ATOMIC AND MOLECULAR NON-STATIONARY STATES WITHIN THE COORDINATE ROTATION METHOD Cleanthes A. Nicolaidis and Donald R. Beck	383
USE OF CI METHODS FOR THE STUDY OF MOLECULAR DISSOCIATION PROCESSES IN VARIOUS ELECTRONIC STATES Sigrid D. Peyerimhoff and Robert J. Buenker	403
THE ROLE OF EXCITED STATE IN ORGANIC PHOTOCHEMISTRY Josef Michl	417
EXCITONS IN SOLIDS T.C. Collins	437
ASPECTS OF THE THEORY OF DISORDERED SYSTEMS E.N. Economou	457
EXCITED STATES OF TRANSITION METAL OXIDES A. Barry Kunz	471
ELECTRONIC STRUCTURE AND EXCITED STATES OF POLYMERS J. Ladik	495
THEORY OF SURFACE STATES AND CHEMISORPTION Jaroslav Koutecký	531
INDEX	557

## PREFACE

It is undoubtedly true that much of the progress in the quantum theory of matter is due to the remarkable success of the independent particle model (IPM)--especially in describing ground states. However, the accurate experimental results of the last 10 years or so, on a variety of spectroscopic phenomena and chemical processes which involve the Excited State, and the related failure of the IPM to reproduce accurately--in many cases, even qualitatively--the observed data, have sent to theorists a clear message: There is need to create and/or apply general and useful approaches to the many-electron problem of the excited state which go beyond the IPM, treat electron correlation and relativity and explain or predict all relevant physical or chemical information with consistent accuracy.

This book contains articles devoted mainly to some of the most important new developments in Quantum Chemistry concerning the theoretical foundations and the computational implementation of many-body approaches to the quantitative and detailed understanding of the electronic excited states of atoms, molecules and solids. Furthermore, it contains experimental and phenomenological articles on Photoelectron and Auger spectroscopy, Lifetime measurements and Organic Photochemistry.

In combination or individually, these articles constitute a good description of some current theoretical and experimental work on the electronic structure and spectroscopy of atoms, molecules, polymers, surfaces, metal oxides and amorphous solids. The theoretical models which are reviewed and employed are based on: Configuration Interaction (CI), Green's function and Polarization Propagator techniques, the Relativistic and Non-Relativistic Restricted and Unrestricted Hartree-Fock methods, the Coherent Potential and Random Phase Approximations, Many-Body Perturbation Theory, Cluster expansions of the wave-function, CI in the continuum and the Complex Coordinate Rotation Method.

When it comes to applications of these advanced theories, it becomes clear from the reading of the articles that much

progress is underway in the study of small systems. For example, it is indeed impressive to see the accuracy and efficiency with which several theoretical and experimental approaches produce numbers on valence electron excitation and ionization energies and transition probabilities, core electron binding energies or lifetimes of excited states in a variety of atoms and small molecules. Such accuracy was impossible until very recently. Large and extended systems are of course more difficult to treat quantitatively. There, with few exceptions, the nature and role of the excited state is still "terra incognita", although theory has made considerable advances, especially in the qualitative formulation of the problems and in the formal foundations.

The articles are based on the lectures which were given during the NATO Advanced Study Institute (ASI) on "The Electronic structure and properties of the excited states of atoms, molecules and solids" held on the island of Kos, Greece, June 4-18, 1978. These lectures were addressed to European and American graduate students and active researchers in the fields of Electronic Spectroscopy, Organic and Inorganic Chemistry, Physical and Quantum Chemistry and Solid State Physics. The particular blend of up-to-date reviews and original contributions present in these articles should prove educationally and scientifically valuable to a similar but broader audience.

We close by sincerely thanking the lecturers for their contributions which made the ASI and this book realities.

Special thanks also go to the NATO Scientific Affairs Division, Brussels, for the financial assistance and to Professors Ladik, Linderberg, von Niessen, Peyerimhoff, and Ohrn for their encouragement and advice throughout the period of preparation and organization of the ASI.

Athens, August 1978

C.A. Nicolaides

D.R. Beck

Editors



Ἔστω δὴ κατὰ τὸν ὀρθὸν λόγον καὶ κατὰ τὸν εἰκότα τὸ μὲν τῆς πυραμίδος στερεὸν γεγονὸς εἶδος πυρὸς στοιχεῖον καὶ σπέρμα. τὸ δὲ δεύτερον κατὰ γένεσιν εἴπωμεν ἀέρος, τὸ δὲ τρίτον ὕδατος πάντα οὖν δὴ ταῦτα δεῖ διανοεῖσθαι σμικρὰ οὕτως, ὡς καθ' ἓν ἕκαστον μὲν τοῦ γένους ἕκαστου διὰ σμικρότητα οὐδὲν ὀρώμενον ὑφ' ἡμῶν, ξυναθροισθέντων δὲ πολλῶν τοὺς ὄγκους αὐτῶν ὀραῖσθαι. καὶ δὴ καὶ τὸ τῶν ἀναλογιῶν περὶ τε τὰ πλήθη καὶ τὰς κινήσεις καὶ τὰς ἄλλας δυνάμεις, πανταχῆ τὸν θεόν, ὅπηπερ ἢ τῆς ἀνάγκης ἐκούσα πεισθεῖσά τε φύσις ὑπέικε, ταύτη πάντη δι' ἀκριβείας ἀποτελεσθεισῶν ὑπ' αὐτοῦ ξυνηρμόσθαι ταῦτα ἀνά λόγον.

TIMAIOS

Thus, in accordance with the right account and the probable, that solid which has taken the form of a pyramid shall be the element and seed of fire; the second in order of generation we shall affirm to be air, and the third water. Now one must conceive all these to be so small that none of them, when taken singly each in its several kind, is seen by us, but when many are collected together their masses are seen. And, moreover, as regards the numerical proportions which govern their masses and motions and their other qualities, we must conceive that God realized these everywhere with exactness, in so far as the nature of Necessity submitted voluntarily or under persuasion, and thus ordered all in harmonious proportion.

TIMAEUS  
PLATO