Excited States in Quantum Chemistry

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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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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 Öhrn 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 ἑκάστου διὰ σμικρότητα οὐδὲν ὁρώμενον ὑφ' ἡμῶν, ξυναθροισθέντων δὲ πολλῶν τοὺς ὄγκους αὐτῶν ὁρᾶσθαι. καὶ δὴ καὶ τὸ τῶν ἀναλογιῶν περί τε τὰ πλήθη καὶ τὰς κινήσεις καὶ τὰς ἄλλας δυνάμεις, πανταχῇ τὸν θεόν, ὅπηπερ ἡ τῆς ἀνάγκης ἑκοῦσα πειστεῖά τε φύσις ὑπεῖκε, ταύτῃ πάντῃ δι' ἀκριβείας ἀποτελεσθεισῶν ὑπ' αὐτοῦ ξυνηρμόσθαι ταῦτα ἀνὰ λόγον.

ΤΙΜΑΙΟΣ

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