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Lecture Notes in Chemistry

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Nicolaos Demetrios Epiotis

Unified Valence Bond Theory of Electronic Structure Applications

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PROLOGUE

A senior undergraduate and a doctoral candidate, a high school teacher and a university professor, an industrial researcher and an academician, in short, every chemist can, more or less, provide a believable explanation of an isolated chemical phenomenon. With the same facility, chemists can use different models to rationalize different facts in different areas of chemistry. Indeed, it is often said that a "good man" is the one who can judiciously choose the right model for the right problem. In recent years, the increased sophistication of laboratory instrumentation and the advent of the computer in the everyday life of the scientist have generated multitudes of new facts and have caused a great proliferation of conceptual models in chemistry. The present status can be summarized as follows: There are many theories for many problems but not one theory for all problems, where by "theory" we mean a conceptual framework for the comprehension, rationalization, and prediction of chemical and physical phenomena whether occuring in the laboratory or reproduced (or simulated) by explicit computations.

Some years ago, I sought a solution to the problem stated above. That is to say, I searched for a quantum mechanical formalism which can provide the basis for a general theory of chemistry. The result was the development of the MOVB theory which has been described in a previous monograph along with the reasons why I believe that this is the best way to approach chemistry in a self-consistent manner. The original work was entitled "Unified Valence Bond Theory of Electronic Structure". In it, I stated that "our present 'understanding' of chemistry has been often illusory". This work is an "across chemistry" application of the qualitative VB and MOVB theory presented in the original monograph and it constitutes a defense of the utilization of the term "Unified" and a justification of

the assertion just mentioned. For, I now show that one and the same set of concepts can be applied to organic and inorganic problems, ground and excited states, normal and "hypervalent" molecules, static stereochemistry and reaction stereoselection, the design of "strange" molecules, etc., in a way that has never been accomplished before by any single (non-numerical) theoretical model. In doing so, I reveal common denominators of apparently unrelated problems, I show that certain problems long thought to be related are not so, I compare the predictions of VB theory with those of crude monodeterminantal MO models, and, in general, I demonstrate that the way in which electrons "behave" is very different from what I myself used to think a decade ago. Since chemists think and argue by analogy, MOVB theory, by virtue of annihilating conceptual interdisciplinary barriers, opens new vistas, it suggests new experiments and new computations, and it defines new problems for investigation. Thus, in a certain sense, the original monograph can be re-titled "Qualitative VB Theory - How to Derive It" and this one "Qualitative VB Theory - How to Apply It". Of course, from the standpoint of the practicing chemist, this second volume will be much more entertaining than the first one as it contains chemical applications in its entirety. Indeed, the reader who thinks that all important concepts of chemistry have been discovered and their implications have been understood will be surprised to find in this work a multitude of new ideas: The principle of configuration aromaticity, the notion of weak and strong overlap binding, the concept of electronic anticooperativity and sigma-pi hybridization, the idea of coulomb polarization, etc. In short, this book is good reading for anyone who believes that "small molecule" chemistry is a saturated field wherein everything has already been discovered.

Qualitative FO-PMO theory, as commonly practiced today, is an approximate form of HMO theory. The latter is a crude approximation of SCF-MO theory which is only an approximation of SCF-MO-CI theory. The conceptual superstructure of chemistry is presently based largely on FO-PMO and HMO theory. Even high level SCF-MO-CI computations are nowadays analyzed by using HMO concepts! This work asks the reader to make the intellectual commitment to retrain his thinking at the level of SCF-MO-CI theory, i.e., at the level of VB and MOVB theory. This is not an easy task! The author hopes, however, that even a casual reading of this work, based on the original monograph published a year ago, will provide sufficient incentive for every chemist to take this bold step. For after all, at some point in the future, this will become inevitable, assuming that human intellectual curiosity will continue to exist even in an age when computers may start doing the thinking for us humans.

A word about the organization of the material. The book is divided into two parts for the sole purpose of underscoring the two fundamental aspects of qualitative MOVB theory: its conceptual power and its formal correctness. The various chapters are arranged in such away so that the previous concept leads to the development of the next one. In addition, apparently unrelated topics are discussed in consecutive chapters so that the common denominator is exposed. For, after all, it is not only the individual applications but the over all cohesion of this work which qualifies it as a new theory of chemistry as a whole, where the term "new" means that, aside from the fact that this treatise is based on the Schrödinger equation, the MO and VB recipes of constructing the electronic wavefunction, and the variation and perturbation methods of solving the Schrödinger equation, the theoretical formalism, the ensuing concepts, and the resulting applications contained in this work have, to a very large extent, no precedent.

Because of this, I have an unorthodox suggestion for the "busy" and/or "impatient" reader who wants to find out immediately whether there are good reasons for learning a new chemical language as the author suggests: First read this opus in reverse, starting with the Epilogue of the second volume and ending with the Prologue of the first volume. Thus, having seen why I have claimed that our understanding of chemistry has often been illusory, read it in the proper order always trying to compare what we espouse to the standard MO theory practices of today.

This work has been made possible by the contributions of many people to whom I am grateful. First, I would like to mention the many researchers whose work provided the necessary checks of the approach espoused here. For it is true that I frequently found myself wavering in the application of the same MOVB concepts I developed only to find reassurance and guidance by the experimental and theoretical literature. Mr. Hugh Eaton, Ms. Angela Diamond, Ms. Barbara Lau, and Dr. James Larson carried out several test computations, some of which are included in this work. The Department of Chemistry provided the needed logistical support and Mrs. Martha Kady was the miraculous "secretary-artist-editor" without whom this work could never be produced in the relatively short period of one year. Ms. Linda Daniel was the precious companion who supported me during this undertaking. Finally, Dr. F. L. Boschke and the Editors of this series are the ones responsible for making this work available to the international community of chemists. In closing, I add that the theory described in this and the companion monograph was conceived, tested, refined, and applied without any grant support from private or federal U.S. agencies.

Nicolaos D. Epiotis

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