Lecture Notes in Chemistry
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N.D. Epiotis

With J.R. Larson and H.L. Eaton

Unified Valence Bond Theory of Electronic Structure

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In the last fifty years, computational chemistry has made impressive strides. Hückel MO computations were rapidly succeeded by semiempirical monodeterminantal Self Consistent Field (SCF) MO calculations which now give way to high quality ab initio calculations of the poly-determinantal SCF-MO and Generalized VB variety. By contrast, no analogous progress has been made in the area of the qualitative theory of chemical bonding. In fact, more than a half-century after the exposition of Hückel MO theory the conceptual superstructure of chemistry is still founded on it. This is made glaringly evident by the fact that highly sophisticated computations are still interpreted with primitive Hückel MO theory, despite the fact that most chemists are well aware of its formal deficiencies. The current popularity of qualitative MO theory among experimentalists is not the result of formal advances but rather the consequence of stimulating application of old MO theoretical concepts. This work attemps to improve this situation by outlining a qualitative theory of chemical bonding which operates at a high level of theoretical sophistication. It was first presented at the NATO Advanced Study Institute on "Topics in Theoretical Organic Chemistry" in Gargnano, Italy, in June 1979, and in other international meetings and conferences, colloquia, and informal gatherings in the period of time following the Gargnano meeting. It was also presented in a seminar given at the University of Washington in October 1980. It can be said that this work is the result of the natural evolution of the type of thinking introduced many years ago in an article published in Angewandte Chemie and then pursued further in a series of papers and a monograph entitled "Theory of Organic Reactions" published by Springer-Verlag. It represents our total abandonment of MO theory as an interpretative and predictive tool and a call for a shift to sound, as opposed to intuitive, VB theory.

In developing a new conceptual approach one ultimately has to come to grips with presentation, so to speak, problems. In submitting this work to public scrutiny, we recognize two such problems. The first one has to do with the fact that the theory we are attempting to popularize is essentially a VB-type theory and, in an age of MO theory dominance, VB theoretical principles are hardly familiar to most chemists. We have tried to counteract this problem by being as explicit as possible in developing the theory while trying to simplify things at the same time. The second problem has to do with the understandable skepticism with which new ideas are met. The reader may legitimately ask: Is it worth the time mastering a new "language" when there is no guarantee that the allegedly new approach accomplishes much more than previous methods? We have tried to deal with this understandable sentiment by including a motivational section in which we outline the reasons why we believe that the time is ripe for a major change in the way we think about chemical bonding. However, the compelling argument in favor of adopting the "language" which we propose is actually embodied in a series of papers which follow this publication and in which we apply the newly developed theory to diverse problems in a way which makes evident that our previous "understanding" of chemistry has been often illusory.

The last statement needs some amplification. In the course of this presentation and, much more so, in following papers we will discover that previous interpretations based on qualitative MO theory of the Frontier Orbital One-Electron Perturbation MO type were either deficient or incorrect. As former practitioners of such a brand of qualitative theory, we can state that it was exactly these failures which led us to the development of the theory outlined in this article. In fact, the involvement of this author with quantum chemistry has been the direct result of the stimulating influence of the Frontier Orbital idea of Fukui and the conservation of MO symmetry idea of Woodward and Hoffmann.

Thus, we shall point out failures of qualitative MO theoretical models cognizant of the evolutionary nature of science and appreciative of the past contributions of brilliant investigators which actually brought us to the threshold on which we step now.

Finally, I wish to mention the fact that the work described here has been carried out without the support of private or Federal U.S. agencies and express my appreciation for the assistance provided during different times by Dr. James Larson and Mr. Hugh Eaton.

Nicolaos D. Epiotis

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Introduction

"Supression of details may yield results more interesting than a full treatment. More importantly, it may suggest new concepts. Pure quantum mechanics alone, in all its details, cannot supply a definition of, e.g., an acid or a base or a double bond." These statements are attributed to E. Schrödinger and they constitute one of the earliest realizations of the necessity of interplay between "quantitative" and "qualitative" quantum theory.[1] In the former case, a preoccupation with the physical significance of mathematical expressions is secondary to obtaining a numerical answer which can be compared with the result of an experiment. Indeed, the mathematical structure of quantum mechanics itself is the actual model. By contrast, "qualitative" theory attempts, through computational tests and reference to experimental facts, to simplify the rigorous equations of "quantitative" theory so that some approximate physical model, which can be routinely applied to chemical problems without the need of explicit calculations, finally emerges. It then follows that, while "quantitative" theory can be elaborated on an ab initio level, "qualitative" theory is always empirical and rests on fundamental assumptions. A better "quantitative" calculation can aid the development of a better "qualitative" physical model, and vice versa. Ultimately, one hopes that the two different theoretical approaches will yield results which are in harmony between them as well as with the results of experimental studies.

We have been interested in the "quantitative" theory-"qualitative" theory-experiment triptych for about a decade during which time we have explored different theoretical frameworks and viewpoints in a variety of structure and reactivity problems.[2,3] About three years ago, our original enthusiasm and confidence in the qualitative approach began to diminish as an alarmingly large number of experimental and computational results at odds with expectations

based on current qualitative theory began to appear with increasing frequency in the literature. These new facts were added to an already impressive list of "exceptions" to well known rules of qualitative theory ultimately producing a solid body of evidence which we could no longer dismiss casually or rationalize in any reasonable and self consistent manner. Immediately, disturbing questions were raised: Are the successes of qualitative theory nothing but happy coincidences? Have we developed heuristic concepts which, though frequently useful in predicting and rationalizing some (but not all) chemical trends, are based on an illusory understanding of chemical bonding? Have we been overly impressed by simplicity and have we been unwilling to tackle problems at the proper level of theory?

The above concerns have been shared by other investigators in the past and they have been expressed in the chemical literature in implicit and explicit forms. For example, a recent monograph by Schaefer[4] reviews results of ab initio computations of "small" and "medium" size molecules which are not always in keeping with ordinary expectations based upon our present day qualitative understanding of chemical bonding. In addition, the mere fact that practically every theoretical interpretation of even the simplest stereochemical trend has been and still is controversial attests to a rather unclear, if not inadequate, understanding of the nature of the chemical bond. Thus, the factors responsible for the angular shapes of the simple triatomics H_2O and H_2S are still under scrutiny.[5] The origin of the rotational barrier in ethane is still being debated.[6] The intuitively unexpected preference of a large number of molecules for a "crowded" geometry, e.g., the greater stability of cis relative to trans-1,2-difluoroethylene, continues to provoke spirited discussions.[7] The list of

current controversies related to interpretations of well established experimental facts continues <u>ad infinitum</u>. Indeed, one is tempted to adopt the posture that nature is too complicated and chemical and physical trends arise as a result of an indecipherable combination of multitudes of competing factors!

The purpose of this series of papers is to present a general qualitative model of chemical bonding founded principally on Valence Bond (VB) theory as an alternative to current qualitative Molecular Orbital (MO) theoretical models. In proposing a rebuilding of the conceptual superstructure of chemistry, we must provide ample evidence of the shortcomings of the MO method and spell out exactly how we plan to improve on it. This is done in the following section.

A. The Formal and Conceptual Difficulties of MO Theory

Quantum chemistry, as practiced today by most theoreticians, relies upon the Schrödinger equation, mathematical methods for its approximate solution, most notably the variational method[8] and the Rayleigh-Schrödinger and Brillouin-Wigner perturbation methods,[9] and the MO[10] and VB[11] recipes for the construction of the antisymmetrized molecular wavefunction.[12] It is not inaccurate to say that the vast majority of chemists have been nurtured with MO and VB theory, with the latter yielding decisively to the former in popularity in the last fifteen years or so. Accordingly, our first task is to survey briefly the various brands of MO theory and identify the formal and conceptual difficulties which hinder their application to chemical problems.

We can distinguish three different levels of MO theory:

a) Hückel MO (HMO) theory which encompasses a multitude of equivalent or related theoretical frameworks and their approximate versions. The character-istic features of the various HMO approaches are touched upon briefly below.

1. Pi HMO theory.[13] This is the conventional HMO theory for pi conjuyated systems.

2. Extended Hückel MO (EHMO) theory.[14] This represents the generalization of pi HMO theory to pi as well as sigma orbitals and all valence electrons.[15] The well-known Mulliken-Walsh model of molecular structure[16] can be viewed as nothing but a diagrammatic representation of EHMO theory applied to molecular

structure problems. Similarly, the analysis of the stereochemistry of peri-
cyclic reactions via one-electron MO or state correlation diagrams espoused by
Woodward and Hoffmann as well as by Longuet-Higgins and Abrahamson[17] is founded
on EHMO theory.

3. One-electron Perturbation MO (PMO) theory.[18] Under conditions which make
the use of Perturbation Theory (PT) valid, one-electron PMO is equivalent to HMO
theory. Its approximate version is the one-electron Frontier Orbital (FO) PMO
model.[19] In this model, only the FO orbitals of two or more arbitrarily defined
interacting fragments and the electrons which they contain are considered and PT
is implemented only up to second order in energy. Currently, the FO-PMO model
is the most popular qualitative theoretical tool.[20]

4. The one-electron Second Order Jahn-Teller (SOJT) model.[21] This is
equivalent to a one-electron FO-PMO theory of molecular distortion. We now
continue with higher level theoretical approaches.

b) Semiempirical[22a-c] and ab initio[23] monodeterminantal Hartree-Fock Self
Consistent Field (SCF) MO theory, henceforth referred to as SCF-MO theory.

c) Semiempirical[22d] and ab initio[23b] polydeterminantal SCF-MO theory,
henceforth referred to as SCF-MO Configuration Interaction (CI) theory. With
this overview of MO theory in mind, it is not an exaggeration to say that the
conceptual superstructure of organic chemistry is founded on HMO theory, with
the term "HMO theory" being inclusive of all complete and approximate one-
electron theories and models.

What is the reason behind the extreme and undeniable popularity of HMO

theory and related qualitative theoretical models? The answer is straight-

forward: HMO theory is simple enough to be comprehended by the practicing

chemist who does not strive to become a theoretical expert, yet hopes to become

sufficiently knowledgeable in theory so that he can grasp and apply simple

quantum chemical concepts and carry out explicit quantum chemical calculations

with so called "canned" computer programs.[24] An undeniable impetus to this

tendency has been provided by the apparent successes of qualitative HMO theory

in the form of the HMO theory of pi conjugated systems,[13b,25] the Woodward-

Hoffmann rules for pericyclic reactions,[26] the FO-PMO model of molecular struc-

ture and reactivity,[20] etc. Perhaps there is no better illustration of the

dominant influence of HMO theory on chemistry as a whole other than the fact

that, in an age when sophisticated quantum chemical computations are reported in

the literature with an ever increasing frequency, their interpretation is still

performed by falling back on concepts founded on HMO theory, such as

"aromaticity",[27] "hyperconjugation",[28] etc.! Indeed, we can say that HMO theory

"touches" to a smaller or greater extent every chemist, whether theoretician or

experimentalist.

Simplicity is the virtue of HMO theory. What are its drawbacks? These are

numerous and they can be categorized into formal and conceptual drawbacks. The

formal limitations of HMO theory are well known.[29] At this level of theory, the

following interactions are _explicitly_ neglected:

a) "Classical" interelectronic coulomb repulsion.

b) "Classical" internuclear coulomb repulsion.

c) "Classical" coulomb attraction between an electron on one center and

   nuclei of different centers.

If we symbolize AO's by lower case letters, e.g., r,s,t,u, etc., and nuclei by capital letters, e.g., A,B, etc., the three approximations stated above can be articulated in mathematical language as follows:[30]

$$< rs \mid \frac{1}{r_{12}} \mid tu > = 0 \tag{1}$$

$$\frac{Z_A Z_B}{r_{AB}} = 0 \tag{2}$$

$$< t_A \mid \frac{Z_B}{r_{1B}} \mid t_A > = 0 \tag{3}$$

Z_A is the effective nuclear charge of A. A special brand of HMO theory is HMO theory with neglect of AO overlap, i.e.,

$$< t \mid u > = 0 \tag{4}$$

Parametrization effectively introduces some component of these effects in an implicit manner but it cannot remove the basic deficiencies of the method.

At this point, we open a parenthesis in order to specify the meaning of "classical", "semiclassical", and "nonclassical". "Classical" terms are potential and kinetic energy terms which have a counterpart in classical physics. Specifically, "classical" potential energy terms arise as a result of the interaction of electrons and nuclei in all possible ways and in a manner consistent with Coulomb's Law. Similarly, "classical" kinetic energy terms arise as a result of the motion of electrons and nuclei in a manner consistent with expectations based on classical kinematics. The "classical" terms describe interactions of "local" particle distributions, e.g., the attraction of an electron in one AO by a nucleus of some other atom. "Semiclassical" terms are analogous to "classical" terms, the only difference being that they describe interactions of "overlap" particle distributions, e.g., the attraction of an electron contained in two overlapping AO's by the nuclei of the two corresponding atoms and/or the nuclei of other atoms. Finally, "nonclassical" terms