

A Chemist's Guide to Valence Bond Theory

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PREFACE

This monograph was written to fill the missing niche of a textbook that teaches Valence Bond (VB) theory. The theory that once charted the mental map of chemists has been abandoned since the mid 1960s for reasons that are discussed in Chapter 1. As a result, the knowledge of VB theory and its teaching became gradually more scarce, and was effectively eliminated from the teaching curriculum in many places in the chemical community. Nevertheless, a few elements of the theory somehow survived as the *Lingua Franca* of chemists mostly due to the use of the Lewis bonding paradigm and the post Lewis concepts of hybridization and resonance. But there is much more to VB theory than these concepts and ideas. Since its revival in the 1980s, VB theory has been enjoying a renaissance that is characterized by the development of a growing number of *ab initio* methods that can be applied to chemical problems of bonding and reactivity. Alongside these methodology developments, there has been a surge of new post-Pauling models and concepts that have rendered VB theory useful again as a central theory in chemistry; especially productive concepts arose by importing insights from MO theory and making the VB approach more portable and easier to apply. Following a recent review article by the two authors¹ and two essays on VB theory and its relation to MO theory,^{2,3} we felt that the time has come to write a textbook dedicated to VB theory, its application and special insights.

The monograph is aimed at a non-expert audience and designed as a tutorial material for teachers and students who would like to teach and use VB theory, but who otherwise have basic knowledge of quantum chemistry. As such, the primary focus of this textbook is the qualitative insight of the theory and the way to apply it to problems of bonding and reactivity in the ground and excited states of molecules. Almost every chapter contains

problem sets followed by answers. These provide the teachers, students and interested readers with an opportunity to practice the art of VB theory. We shall be indebted to readers/teachers/students for comments and more suggestions, which can be incorporated into subsequent editions of this book that we hope, will follow.

Another focus of the book is the description of the main methods and programs available today for *ab initio* VB calculations, and how actually one may plan and run VB calculations. In this sense, the book provides a snapshot of the current VB capabilities in 2007. Regrettably, much important work had to be left out. The readers interested in technical and theoretical development aspects of VB theory may wish to consult two other monographs.^{4,5}

The two authors owe a debt of gratitude to colleagues and friends who read the chapters and provided useful comments and insights. In particular we acknowledge Dr Benoit Braida, Professor Narahary Sastry, Professor Hendrik Zipse, Professor François Volatron, and Dr Hajime Hirao for the many comments and careful reading of earlier drafts. François Volatron actually solved all the problem sets and checked the equations of Chapter 3 – the equations are in much better shape thanks to his careful screening. Hajime Hirao went over the entire book in search for glitches. Needless to say, none of these gentlemen should be held responsible for the content of the book.

In addition we are thankful to all our coworkers and students during the years of collaboration (1981 - present). Especially intense collaborations with Professor Addy Pross and Professor Wei Wu are acknowledged. Professor Wei Wu and Professor Joop van Lenthe are especially thanked for making their programs (XMVB and TURTLE) available to us. In fact, Professor Wei Wu has been kind enough to give us unlimited

access to his XMVB code during the work on this book. Dr David Danovich is thanked for producing all the inputs and outputs in this book and for keeping alive the VB computational know-how at the Hebrew University throughout the years from 1992 onwards.

Finally, any readers, teachers or students who wish to comments on aspects of the content, problems-sets and or answer-sets, are welcome to do so by contacting the authors directly by e-mail (sason@yfaat.ch.huji.ac.il and philippe.hiberty@lcp.u-psud.fr).

References

1. S. Shaik, P.C. Hiberty, *Reviews in Computational Chemistry*, **20**, 1 (2004). Valence Bond, Its History, Fundamentals and Applications: A Primer.
2. S. Shaik, P.C. Hiberty, *Helv. Chem. Acta* **86**, 1063 (2003). Myth and Reality in the Attitude Toward Valence-Bond (VB) Theory: Are Its ‘Failures’ Real?”
3. R. Hoffmann, S. Shaik, P.C. Hiberty, *Acc. Chem. Res.* **36**, 750 (2003). Conversation on VB vs. MO Theory: A Never Ending Rivalry?
4. G. A. Gallup, *Valence Bond Methods*, Cambridge University Press: Cambridge, 2002.
5. R. McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd Edition, Academic Press, New York, 1992.

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