Discovering Chemistry with Natural Bond Orbitals

Perhaps the key concept in chemistry is bonding. Over the years, many scientists have contributed to our understanding of the chemical bond, and many different models have been put forward. With the huge progress in computational methods, one might expect that these theories would have been put on a firmer footing. In fact, modern electronic structure calculations do not in themselves return any form of bonding pattern—they merely return an energy (and an electronic wavefunction) for a given configuration of the nuclei making up the system of interest. Some people argue that chemical bonding is an ill-defined concept, whose time has passed. This argument does make some sense: it is possible to think about some problems in chemistry based only on potential energy surfaces, and not needing to worry about whether a given pair of atoms is "bonded" or not (or what this might mean) can be remarkably liberating.

However, for most chemists for most of the time, models of bonding remain very much indispensable. And theory can be persuaded to yield insight into bonding, by carrying out various analyses of the energy, or the wavefunction, thereby providing an interpretation in terms of traditional—or new—concepts of bonding. One of the most popular methods is the Natural Bond Orbital (NBO) approach introduced by Foster and Weinhold in 1980,[1] and subsequently much developed and extended. *Discovering Chemistry with Natural Bond Orbitals* is the second book written by Professor Weinhold, and his colleague Clark Landis, that is aimed at providing an overview of the method and its capabilities. While the earlier book, *Valency and Bonding*,[2] aims to be a comprehensive treatise with a full description of the theory and of applications, the present book is more of an extended manual, wishing to show people how to get the best out of the NBO method and program in a didactic and user-friendly way.

Most probably, almost all scientists who use computational electronic structure methods will have carried out NBO calculations, or at least encountered the method in other people's work. For example, one of the most reliable and widely used ways to compute atomic partial charges, natural population analysis, is based on NBOs. But many aspects of NBO analysis are used much more seldom than others, in part, no doubt, due to a lack of appreciation of what they can deliver. So a book such as this one has a large potential market. There is relatively little about the theoretical basis used to generate NBOs (though enough to get a general idea), with the focus being on applications, and how to carry them out. Full input is provided for many systems, as well as detailed discussion of the associated output and its interpretation. The topics covered provide a good balance between more elementary and more advanced, and include the basics of NBOs and atomic charges, less traditional bonding such as three-center two-electron bonds and transition metals, Lewis resonance structures, steric effects, nuclear magnetic resonance and electron spin resonance spectroscopies, intermolecular interactions, reactivity, and excited states. The book also discusses the different way in which NBO calculations can be performed (e.g. various versions of NBO are bundled with several popular electronic structure codes but it can also be used as a separate program). Also, each chapter contains a generous number of practical exercises and problems.

Readers with a general interest in chemical bonding – from relative beginners to experts—will gain a lot from thinking through the different analyses and examples covered in this book. I certainly did. This area of theoretical chemistry sometimes seems to generate a lot of passion, with proponents of different analysis techniques full of praise for their own method, and of disdain for others. The present book is rather low on this form of partisanship, so that even people who do not intend to use the NBO method will find something to learn from. Nevertheless, the main users will clearly be computational chemists—novices or experts—seeking to improve their NBO skills. Much support for such users is already available through the comprehensive NBO website,[3] but there is even more material in the book, and many users will find it helpful to have all the documentation and explanation collected and systematically arranged.

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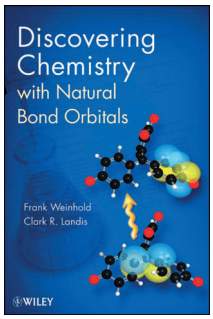
[1] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211 – 7218.
[2] F. Weinhold, C. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005**.
[3] At http://www.chem.wisc.edu/~nbo5/index.htm.



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