

PART ONE

THE CONCEPTUAL POWER
OF
MOLECULAR ORBITAL - VALENCE BOND (MOV B)
THEORY

INTRODUCTION

The bond diagrammatic representation of molecules is the foundation of MOVb theory. To a certain extent, this kind of representation is analogous to the one on which "resonance theory" is based and this fact can be projected by a comparison of the various ways in which MOVb theory depicts a species made up of three core and two ligand MO's which define two subsystems containing a total of six electrons and the ways in which "resonance theory" (i.e., qualitative VB theory) depicts a six-electron-six-AO species such as the pi system of $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{O}$. The different pictorial representations are shown in Scheme 1 so that the analogies are made evident. First of all, the total MOVb diagrammatic representation of the 6/5 species is obtained by a linear combination of three complete bond diagrams, as in A1, which describe the optimal linear combination of all MOVb Configuration Wavefunctions (CW's). By the same token, a total VB diagrammatic representation of the 6/6 species can be obtained by writing a "dot structure", as in B1, and taking this to mean the optimal linear combination of all VB CW's. Next, we can approximate the MOVb wavefunction of the 6/5 species by one complete (or detailed) bond diagram (A2). No simple VB representation analogy can be given in this case. Alternatively, we can approximate the MOVb wavefunction by a linear combination of compact bond diagrams, as in A3, in the way described before. These compact bond diagrams have common CW's and they also exclude a set of extrinsic CW's which must necessarily be added in quantitative as well as in some qualitative applications of MOVb theory. The VB analogue in this case is the hybrid representation of the 6/6 species by a set of "important" VB CW's, as in B2. Finally, we can obtain a compact representation of the 6/5 species by simply eliminating all compact bond diagrams except the one "containing" the dominant CW or CW's, as in A4. Correspondingly, we can obtain a compact representation of the 6/6 species by eliminating all but the CW which makes

the major contribution to the VB resonance hybrid, as in B3. Henceforth, we shall use the letter Θ to symbolize a total MOVV wavefunction, Ψ_i to symbolize a complete bond diagram, Ξ_i to denote a compact bond diagram, and Ω_i to denote a subsystem and the associated wavefunction. In this work, we shall make frequent use of the approximate MOVV representation, as this is adequate for the treatment of most problems of interest, and we shall always differentiate between complete and compact MOVV bond diagrams, explicitly or implicitly. Furthermore, we shall use the convention of assigning charges to the core and the ligand by reference to the perfect pairing CW of the total system. We shall revert to the total representation only when the problem demands so.

Some notable aspects of the MOVV representations are the following:

a. The MOVV differ from the conventional VB representations to the extent that MOVV diagrams represent a collection of MOVV CW's while the familiar VB resonance structures represent individual VB CW's.

b. A species having only one subsystem can be fully represented by a single detailed bond diagram. A species having more than one subsystem can be fully represented only by a linear combination of detailed bond diagrams. The reason is that a single detailed bond diagram fully accounts for interfragmental bond "correlation" while a detailed set of complete bond diagrams is required for the reproduction of intrafragmental correlation. At the limit of tight core-ligand binding, higher energy detailed bond diagrams play a small role and can be neglected.

c. The Ψ_i 's as well as the Ξ_i 's are resonance bond diagrams.

d. Neither total nor approximate MOVV wavefunctions can be reproduced by monodeterminantal SCF-MO theory. The total MOVV wavefunction can be obtained by complete SCF-MO-CI theory and the approximate MOVV wavefunction by SCF-MO-CI

<p>A1 TOTAL REPRESENTATION</p> <p>Subsystem 1 $\left[\begin{array}{ccc} + \cdots + & - \cdots - & \# \cdots \# \\ & \leftrightarrow & \leftrightarrow \end{array} \right.$</p> <p>Subsystem 2 $\left[\begin{array}{ccc} + \cdots + & \# \cdots \# & - \cdots - \\ \# \psi_1 & \# \psi_2 & + \psi_3 \end{array} \right.$</p>	<p>B1</p> <p style="text-align: center;">6e</p> $\overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{C}} - \overset{\cdot\cdot}{\text{O}}$
<p>A2 APPROXIMATE REPRESENTATION</p> <p>$\begin{array}{c} + \cdots + \\ + \cdots + \\ \# \psi_1 \end{array}$</p> <p style="text-align: right;">← Complete or Detailed Bond Diagram</p>	
<p>A3 APPROXIMATE HYBRID REPRESENTATION</p> <p>$\begin{array}{cc} + \cdots + & + \cdots + \\ & \text{~~~~~} \\ + \cdots + & \# \cdots + \\ \# \epsilon_1 & + \epsilon_2 \end{array}$</p>	<p>B2</p> $\begin{array}{ccccccc} \text{C} & = & \text{C} & - & \text{C} & = & \text{C} & - & \text{C} & = & \text{O} \\ & & & & & & \updownarrow & & & & \\ + & & & & & & & & & & - \\ \text{C} & - & \text{C} & = & \text{C} & - & \text{C} & = & \text{C} & - & \text{O} \\ & & & & & & \updownarrow & & & & \\ & & & & & & \text{etc.} & & & & \end{array}$
<p>A4 COMPACT REPRESENTATION</p> <p>$\begin{array}{c} + \cdots + \\ + \cdots + \\ \# \epsilon_1 \end{array}$</p> <p style="text-align: right;">← Compact Bond Diagram</p>	<p>B3</p> $\text{C} = \text{C} - \text{C} = \text{C} - \text{C} = \text{O}$
<p>SIX ELECTRONS IN FIVE MO's (6/5)</p>	<p>SIX ELECTRONS IN SIX AO's (6/6)</p>

theory with a truncated configuration basis which does not permit intrafragmental "correlation". These aspects will be better projected by actual examples as this series of articles unfolds.

e. A version of approximate MOVb theory which is ideally suitable for analyzing (ground or excited) chemical stereoselection is the Independent Bond Model, described in the original monograph, according to which a given species can be viewed as the product of MOVb subsystem wavefunctions with its total energy being a simple sum of subsystem energies.

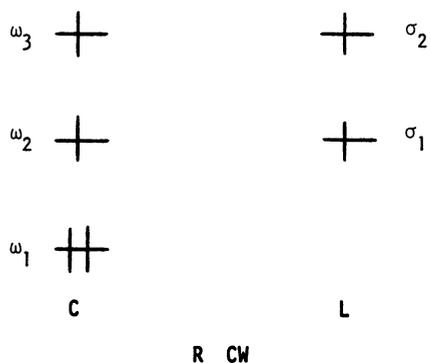
With this background, we can now outline a general MOVb theory of chemical bonding which can be routinely implemented by following these steps:

a. A molecule or complex is divided into a core fragment (C) and a fragment which contains all ligands (L).

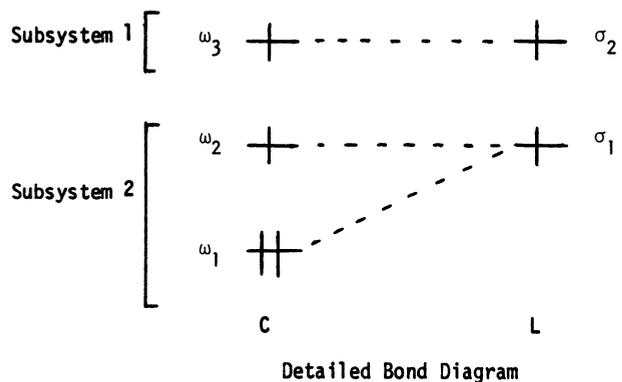
b. A bond diagram is constructed for every assumed geometry of the molecule or complex by following these steps:

1) The core and ligand symmetry adapted orbitals are generated either from first principles or by explicit computation.

2) The electrons are arranged in the core and ligand orbitals in a way which generates the reference, "perfect pairing" (R) CW subject to the symmetry constraints imposed by the geometry in question. This is the open shell CW which places core and ligand electron pairs in the lowest energy orbitals of core and ligand subject to the requirement that it generates the maximum number of core-ligand bonds through spin pairing. For example, the R CW of a six-electron-five-orbital system where the lowest two core (ω_1 and ω_2) and the lowest ligand (σ_1) orbitals are of one symmetry type and the highest core (ω_3) and ligand (σ_2) orbitals are of a different symmetry type is written as follows:



3) The detailed bond diagram for the geometry in question is constructed by adding dashed lines to the drawing of the R CW in order to denote all possible CW's which can be generated by the implied electron shifts under the imposed symmetry constraints. For example, the detailed bond diagram corresponding to the previous case becomes:



Each detailed bond diagram is a pictorial approximate representation of the optimal MOVb wavefunction of the system in question. In addition, it shows explicitly the number and types of independent "many electron-many center" bonds which join the core and the ligand fragments. For the reader's convenience, the symmetry of each orbital is specified either by the formal point group label or by the letters S (symmetric) and A (antisymmetric) which define the behavior of the orbital upon performance of an obvious symmetry operation (e.g., rotation about an axis, reflection through a plane, etc.).

In dealing with detailed bond diagrams, it must be kept in mind that, because of the way in which the R CW is defined and the way in which the detailed bond diagram is constructed, neither the "parent" R CW is necessarily the lowest energy CW nor the principal compact bond diagram (Ξ_1 in Scheme 1) is necessarily the one directly reflected by the detailed bond diagram as written, although in most problems of interest this is indeed the case. However, neither of these semantic difficulties is an obstacle to the qualitative application of MOVb theory. **Consistent with the above stated philosophy, we assign formal charges to C and L by reference to the perfect pairing CW projected by the bond diagram as written.** Thus, for example, we have written C and L underneath the bond diagram shown above because we assumed that neutral C has four electrons and neutral L two electrons. Had neutral C had three and neutral L also three electrons, we would have written C⁻ and L⁺ underneath the bond diagram, keeping always in mind that these are formal charges with the real ones being

determined by all CW's which make up the MOVb wavefunction. Obviously, the formal charge distribution will tend to be a good approximation of the real charge distribution as the perfect pairing CW tends to make a dominant contribution to the total MOVb wave function. Finally, we assume that the lowest and highest energy orbitals of a diatomic core play no significant role insofar as electron delocalization is concerned. This assumption is valid in most problems tackled in this monograph.

c. Each independent "many electron-many center" bond is alternatively called a subsystem. Different subsystems do not interact in a one-electron sense and, in dealing with the stereochemistry of ground state closed shell systems, their bi-electronic interaction can often be neglected. In such an event, the energy change of a composite system is equal to the sum of the energy changes of the individual subsystems.

d. Core and ligand orbital symmetry dictates three different types of subsystem bonding: D bonding which permits electrons to descend to low lying orbitals, U bonding which confines some of the electrons to high lying orbitals, and H bonding which represents a hybrid of D and U bonding sometimes involving conservation of spatial orbital overlap (H' bonding) and other times reduction of spatial orbital overlap (H'' bonding). Finally, N and N' bonding represent two different types of simple two electron-two orbital bonding with the prime denoting impairment of spatial orbital overlap.

e. The result of a structural change on each subsystem is spelled out in the form of an equation. For example, if the structural modification changes an $(\omega, \sigma/2)$ subsystem bonding from N- to N'-type, we write: $N(\omega, \sigma/2) \rightarrow N'(\omega, \sigma/2)$.

f. The critical subsystem conversion(s) is(are) singled out. This becomes necessary because the energetics of some subsystems may or may not change as a result of a structural modification.

g. A conclusion regarding the effect of a modification, i.e., stabilizing or destabilizing, is reached from appraisal of the critical subsystem conversions according to the following delocalization rules:

1) Hybridization Rule: H bonding becomes increasingly favorable relative to D bonding as primary CT occurs in a direction which prevents overlap repulsion and fosters secondary delocalization.

2) Deexcitation Rule: H bonding becomes increasingly favorable relative to U bonding as primary CT occurs in a direction which turns off secondary delocalization.

These rules can be restated in an alternative language:

1) H bonding becomes increasingly more favorable relative to D bonding as V-type CW's attain low energy.

2) H bonding becomes increasingly favorable relative to U bonding as I-type CW's attain low energy.

It ought to be emphasized that these general rules are applicable to actual chemical problems only when the structural variation under scrutiny affects the promotional energies of the interacting CW's but leaves the overlap interaction terms relatively unchanged. When the latter condition is not adequately met, exceptions are expected which, in toto, may define a new chemical concept.

In tailoring VB theory to an operationally useful tool for the practicing chemist, we are less interested in detail and more interested in immediate application which can inspire new experiments or computations. To this extent, one may alternatively use the compact MOVb theory of chemical bonding which can be implemented by following these steps:

a. In comparing two isomers, one constructs the compact MOVB diagram (Ξ_1 in Scheme 1) for each one of them and determines the type of bonding imposed by core and ligand orbital symmetry in each case recalling that there are three bonding "flavors": D bonding which permits electrons to descend to low lying orbitals, U bonding which confines some of the electrons to high lying orbitals, and H bonding which represents a hybrid of D and U bonding accompanied by impairment of core-ligand spatial overlap, at least in most cases of interest. Loss of spatial overlap is indicated by affixing a dagger superscript to the appropriate letter, most often H. The letter (U, H[†], and D) assignment is always made in a relative sense and the selection rules are: D is always better than H[†] and U bonding but H[†] may be superior or inferior to U bonding depending on whether deexcitation is more important than loss of spatial overlap or vice versa. This latter principle constitutes the quantum mechanical rationalization of stereochemical diversity in nature.

b. If the compact bond diagrams of two different isomers belong to the same bond type (e.g., both involve D-bonding, to a first approximation), one proceeds to examine the consequences of the principal direction of interfragmental Charge Transfer (CT) in each of the core-ligand bonds of the two isomers. The way in which primary and secondary CT differentially affect two isomers has been extensively discussed in the original work.¹⁵ This last procedure effectively amounts to a one-to-one energetic comparison of the compact bond diagrams (Ξ_1 's) the linear combinations of which constitute the approximate hybrid bond diagrammatic representations of the two species.

c. When there are core and/or ligand orbital degeneracies, the two compact bond diagrams may differ in that one of them describes stronger core-ligand spatial overlap while core and ligand excitation remains constant. In such an event, we say that the conversion of one isomer to the other involves rebonding

symbolized in any one of the following three ways: $U \rightarrow U^\ddagger$, $D \rightarrow D^\ddagger$, or, $N \rightarrow N'$.

The selection rule is now that the isomer with the impaired core-ligand spatial overlap (U^\ddagger , D^\ddagger , or, N' bonding) is the more unstable one.

d. In (a)-(c), it has been assumed that the two bond diagrams described the same number of core-ligand bonds. If this is not the case, the isomer having the maximum number of core-ligand bonds is the more stable one, at least in the vast majority of cases.

In Part One of this work, we will use the MOVb bond diagrammatic method in order to tackle problems, most of which lie "within" monodeterminantal MO theory, in order to demonstrate the conceptual power of MOVb theory.