A Survey of Recent Developments in Ab Initio Valence Bond Theory*

PHILIPPE C. HIBERTY,[1] **SASON SHAIK**[2,3]
[1]*Laboratoire de Chimie Physique, Groupe de Chimie Théorique, Université de Paris-Sud, 91405 Orsay Cédex, France*
[2]*Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel*
[3]*Lise-Minerva Center for Computational Chemistry, The Hebrew University, Jerusalem 91904, Israel*

Received 20 February 2006; Revision 17 March 2006; Accepted 18 March 2006
DOI 10.1002/jcc.20478

Abstract: Starting from the 1980s and onwards, Valence Bond theory has been enjoying renaissance that is characterized by the development of a growing number of *ab initio* methods, and by many applications to chemical reactivity and to the central paradigms of chemistry. Owing the increase of computational power of modern computers and to significant advances in the methodology, valence bond theory begins to offer a sound and attractive alternative to Molecular Orbital theory. This review aims at summarizing the most important developments of *ab initio* valence bond methods during the last two or three decades, and is primarily devoted to a description of what the various methods can actually achieve within their specific scopes and limitations. Key available softwares are surveyed.

© 2006 Wiley Periodicals, Inc. J Comput Chem 28: 137–151, 2007

Key words: valence bond; spin-coupled; breathing orbitals; bloc-localized wave function; CASVB; VBSCF; SCF-MI; VBCI; VBPCM; BOVB; resonance energy

Introduction

The origin of Valence bond (VB) theory dates back to the landmark 1927 paper of Heitler and London.[1] Put in a current language, their idea, which described the bonding in the H_2 molecule in terms of the pairing of the two electrons in the two atomic orbitals into a singlet state, appeared as the quantum mechanical formulation of Lewis's electron-pair bonding. The generalization to polyatomic molecules, which is at the heart of the VB method, was later achieved by Pauling,[2] Slater,[3] Wheland,[4] Eyring and Polanyi[5] and their coworkers, and led to novel and fundamental concepts, such as hybridization, resonance, electronegativity, etc; concepts which rationalized large amounts of data by means of a few guidelines. VB theory was immediately adopted by chemists, who discovered a model that was close to the traditional notion of valence that viewed molecules as ensembles of atoms held together by local bonds. Difficulties started to accumulate, however, with the first few endeavors to assess the qualitative concepts by means of actual numerical calculations. The early attempts were severely hampered by the considerable difficulty of carrying out VB calculations with sufficient accuracy, needed to assess the merit of these VB concepts. As no really accurate VB calculations were possible, except for very small molecules, most workers had to resort to many approximations. Thus there arose a series of generalizations and conclusions that were based upon results of somewhat uncertain accuracy. In due course, Molecular Orbital (MO) theory gradually gained the upper hand, at least in part, because of its easier implementation into working computer codes. The situation got more and more in favor of MO theory as user-friendly MO-based *ab initio* codes became available. By contrast, the nonorthogonal orbital treatment required by VB theory has been for a very long time an insurmountable computational problem.

As computers became more powerful and computations of large molecules, what chemists call "real" molecules, became increasingly more feasible with the orthogonal MO formalism, MO-based theories became popular, starting from the late1960s onward, while at the same time, the technical difficulties in the computational implementation of the VB approach held VB theory back. However, despite this overwhelming dominance of MO theory in computational chemistry, chemists continued to use the language of VB theory and the associated concepts of Lewis structures, local bonds, hybridization, curved arrows, reso-

---

Correspondence to: P. C. Hiberty; e-mail: philippe.hiberty@lcp.u-psud.fr

*Dedicated to Professor Warren J. Hehre, a pioneer in quantum chemistry.

Contract/grant support: Israel Science Foundation (ISF) (S. Shaik).

nance and so on, to rationalize chemical reactivity and to design new molecules, new reactions, etc. Interestingly, the dynamics community never abandoned VB theory and maintained an uninterrupted chain of VB usage from the early days to the present. Thus, Eyring wrote many papers showing the use of VB theory for obtaining potential energy surfaces for kinetics. In the 1960s and 1970s a lot of work has been going in the dynamics community based on VB ideas, for example the popular diatomics-in-molecules theory[6,7] and the bond-energy-bond-order method[8] were both primarily VB-based theories.[9]

The predominance of MO-based methods over VB appeared to be firmly established up to the late 1970s. However, starting from the 1980s and onwards, VB theory began to rise from its ashes, to dispel many myths about its alleged "failures" and to offer a sound and attractive alternative to MO theory. This renaissance originates in several causes. First, the exponential increase of the computational power of modern computers allows *ab initio* VB calculations to be performed, in which overlap integrals are explicitly considered and all one- and two-electron integrals are precisely evaluated. Second, significant advances have been made by a few groups[10–23] to overcome the computational difficulty associated with the non-orthogonality in the VB method, often called the "$N!$ problem." It might interest the reader that this characterization, the "$N!$ problem," is a misnomer, since the difficulty due to non-orthogonality *does not* imply that the computational effort required to perform a non-orthogonal configuration interaction scales as $N!$, N being the number of electrons. In actual modern implementations,[24] the calculation of hamiltonian matrix elements between non-orthogonal determinants scales as N^4. Among the methodological contributions that brought VB to the modern era, one may cite the Prosser and Hagstrom method of evaluating matrix elements,[10] the generalized Slater-Condon rules,[16] the spin free VB method,[18,19] the left coset decomposition algorithm[20,21] and the paired-permanent-determinant approach.[22,23] Lastly, a third reason for the VB renaissance is the appearance of new VB methods (vide infra), each with its specific field of application: calculation of diabatic states, weak interactions free of basis-set superposition errors, assessment of hybridization, quantification of resonance energies, etc. The growing number of such quantitative applications shows that VB theory is slowly recovering its role as a computational method tailor-made for chemistry, and is able to offer clear interpretation of the wave function. In this context, it is timely to review the modern VB type computational methods that have appeared during the last two or three decades. This review is restricted to *ab initio* methods; a complementary review of applications of VB theory has just appeared.[25] While the methodological improvements would deserve a review themselves, this paper skips the technical aspects and is primarily devoted to a description of what the various methods can actually achieve within their specific scopes and limitations.

The Localized vs Semi-Localized Alternative

Although all *ab initio* VB methods deal with non-orthogonal orbitals that have a strongly local character, the degree of localization of these orbitals varies from one method to the other. As such, some caution has to be exercised in the interpretation of the wave functions of the different VB methods. We shall illustrate the various definitions with the example of a two-electron single bond between two fragments A and B, which in turn, may or may not be polyatomic.

Localized Orbitals

In the "pure" VB method orbitals are strictly localized on a single atom. As these orbitals are allowed to hybridize from the atomic orbitals (AOs) of a given atomic center, it is customary to use the descriptive term "hybrid atomic orbitals," or HAOs. The advantage of the "pure" VB method is that it allows a clear distinction between covalent structure (A and B each bear a singly occupied orbital) and ionic ones (one fragment orbital is doubly occupied, the other is empty). In this framework, the accurate description of the A—B bond requires taking into account the covalent and ionic VB structures, as in eq. (1) (dropping normalization constants):

$$\Psi_{VB} = C_1(|\chi_a\overline{\chi}_b| - |\overline{\chi}_a\chi_b|) + C_2|\chi_a\overline{\chi}_a| + C_3|\chi_b\overline{\chi}_b|. \qquad (1)$$

Here, χ_a and χ_b are HAOs, the first VB structure represents the purely covalent bond (noted A•—•B in what follows), and the two remaining ones represent the A^-B^+ and A^+B^- ionic structures, respectively. As such, Ψ_{VB} takes care of the left-right electron correlation of the A—B bond.

In case the fragments A and B are polyatomic (e.g. $H_3C—CH_3$) and only the A—B bond is being described in a VB manner, the orbitals χ_a and χ_b in eq. (1) may be fragment orbitals (FOs) that have tails on the adjacent atoms (e.g., the Hs of a given CH_3 group), but remain localized in the sense that an orbital of fragment A has no coefficient on B, and *vice versa*. In such a case, the description of the A—B bond will still require explicit consideration of ionic and covalent components as in eq. (1), and the so-defined FOs will be considered throughout the text as a particular case of localized orbitals.

Semi-Localized Orbitals

An inconvenience of using strictly localized orbitals is the exponential growth of the number of VB structures as a function of the number of bonds, such that the description of many bonds in the "pure" VB manner becomes cumbersome and intractable. To resolve this problem, Coulson and Fischer[26] proposed an elegant way of implicitly incorporating the covalent and ionic components into a single VB structure of a formally covalent form. They used slightly delocalized orbitals as exemplified for the A–B bond in eq. (2), dropping the normalization constants:

$$\Psi_{CF} = |\varphi_l\overline{\varphi}_r| - |\overline{\varphi}_l\varphi_r|; \varphi_l = \chi_a + \varepsilon\chi_b,\ \varphi_r = \chi_b + \varepsilon'\chi_a. \qquad (2)$$

Here each orbital, φ_l or φ_r, is mainly localized on a single center but involves a small tail on the other center, so that the expansion of the Coulson–Fischer wave function Ψ_{CF} [eq. (3)]

in AO determinants is in fact equivalent to Ψ_{VB} in eq. (1), provided the coefficients ε and ε' are properly optimized.

$$\Psi_{CF} = (1+\varepsilon\varepsilon')(|\chi_a\overline{\chi}_b| - |\overline{\chi}_a\chi_b|) + \varepsilon'|\chi_a\overline{\chi}_a| + \varepsilon|\chi_b\overline{\chi}_b|. \quad (3)$$

The Coulson–Fischer orbitals can be generalized in the following two ways for a polyatomic molecule:

a. One may allow the orbitals to delocalize freely over the entire molecule, and write the wave function either as a single, and formally covalent VB structure (known as the perfect-pairing approximation, to be discussed later), or as a linear combination of several VB structures that represent all the possible pairing schemes between a given number of electrons and orbitals (e.g. 14 possible pairing schemes for a single configuration of methane with eight electrons in eight orbitals). The orbitals defined this way are called "overlap-enhanced orbitals" (OEOs). Most of the time, the OEOs appear to be fairly localized, but nevertheless, the shape of these orbitals, or their degree of delocalization, is an important feature to be taken into account when one interprets the wave function in terms of Lewis structures.
b. In a more restrictive definition of the CF orbitals, each orbital is allowed to delocalize only onto the atom with which it is bonded in the VB structure under consideration; such orbitals are called "bond-distorted orbitals" (BDOs).

The BDOs have the advantage of allowing an unambiguous correspondence between the mathematical expression of a VB structure and the associated Lewis structure. *On the other hand, neither OEOs nor BDOs allow the distinction to be made between the covalent and ionic components of the bonds.*

As will be seen later, both localized and semi-localized approaches have their specific advantages and inconveniences. Localized orbitals provide a very clear understanding of the nature of chemical bonding, but the number of VB structures that are necessary to take into account may be large if many bonds have to be described in a VB manner. Regarding semi-localized orbitals, both OEOs and BDOs options provide extremely compact wave functions, but in so doing obscure the classical interpretation of covalent and ionic structures. This fundamental difference between methods using localized orbitals and those using semi-delocalized ones will define two distinct categories of VB methods in what follows.

Methods Using Semi-Localized Orbitals

The Generalized Valence Bond Method

The Generalized Valence Bond (GVB) method was the earliest important generalization of the Coulson–Fischer idea to polyatomic molecules.[27–30] The method uses OEOs that are free to delocalize over the whole molecule during orbital optimization. Despite its general formulation, the GVB method is generally used in its restricted form, referred to as GVB–SOPP, which introduces two simplifications. The first one is the perfect-pairing (PP) approximation, in which only one VB structure is generated in the calculation. The wave function may then be expressed in the simple form of eq. (4), as a product of so-called "geminal" two-electron functions, which take the form of a singlet-coupled GVB pair (φ_{ia},φ_{ib}). Each geminal function is associated with a particular bond or lone pair.

$$\Psi_{GVB} = |(|\varphi_{1a}\overline{\varphi}_{1b} - \overline{\varphi}_{1a}\varphi_{1b}|)(|\varphi_{2a}\overline{\varphi}_{2b} - \overline{\varphi}_{2a}\varphi_{2b}|) \cdots (|\varphi_{na}\overline{\varphi}_{nb} - \overline{\varphi}_{na}\varphi_{nb}|)|. \quad (4)$$

The second simplification, which is introduced for computational convenience, is the *strong orthogonality* (SO) constraint, by which all the orbitals in eq. (4) are required to be orthogonal to each other unless they are singlet paired, i.e.,

$$\langle\varphi_{ia}|\varphi_{ib}\rangle \neq 0 \quad (5a)$$

$$\langle\varphi_i|\varphi_j\rangle = 0 \quad \text{otherwise.} \quad (5b)$$

This strong orthogonality constraint, while being a restriction, is usually not a serious one, since it applies to orbitals that are not expected to overlap significantly. On the other hand, the orbitals that are coupled together in the same GVB pair display, of course, a strong overlap.

For further mathematical convenience, each geminal function in eq. (4) can be rewritten, by simple orbital rotation, as an expansion in terms of natural orbitals, in eq. (6):

$$|\varphi_{ia}\overline{\varphi}_{ib}| - |\overline{\varphi}_{ia}\varphi_{ib}| = C_i|\phi_i\overline{\phi}_i| + C_i^*|\phi_i^*\overline{\phi}_i^*|. \quad (6)$$

This alternative form of the geminal contains two closed-shell terms. The natural orbitals ϕ_i and ϕ_i^*, in eq. (6), have the shapes of localized MOs, respectively bonding and antibonding, which are orthogonal to each other. The natural orbitals are connected to the GVB pairs by the simple transformation below:

$$\varphi_{ia} = \frac{\phi_i + \lambda\phi_i^*}{(1+\lambda^2)^{1/2}}, \quad \varphi_{ib} = \frac{\phi_i - \lambda\phi_i^*}{(1+\lambda^2)^{1/2}}, \quad \lambda^2 = -\frac{C_i^*}{C_i}. \quad (7)$$

The great computational advantage of using natural orbitals, rather than GVB pairs, in the effective equations that are to be solved for self-consistency, is that *all* orbitals are now orthogonal to each other. A GVB–PP calculation is thus nothing else, but a special case of a truncated MCSCF calculation, with all the advantages brought by the MO representation. In addition, the transformed GVB–PP wave function has the VB advantage of interpretability as a collection of two electron bonds, in a manner close to the chemist's conception of molecules. Of course, it is straightforward to include a "core" of doubly occupied orthonormal orbitals, like the set of σ MOs for conjugated molecules.

As long as the molecule being considered consists of clearly separated local bonds and is in its equlibrium geometry,[31,32] the perfect-pairing and strong-orthogonality restrictions result in considerable computer time-saving, with no great loss of accuracy. On the other hand, it is clear that these restrictions would be inappropriate for delocalized electronic systems like benzene, whose description requires the above methods beyond the PP approximation, i.e., by inclusion of all possible pairing schemes. Another impressive advantage of the GVB–PP method is that the orbital optimization may be done using a Fock (one-electron) operator, which greatly facilitates direct SCF procedure and exploitation of symmetry.

Since the GVB wave function takes care of the left-right electron correlation for each local bond, it incorporates a good deal of non-dynamical correlation and can serve as a basis for calculations of dynamic correlation. This has been done by Carter and Goddard in their "Correlation-Consistent Configuration Interaction" (CCCI) method,[33] which starts from a GVB–SOPP wave function and incorporates a small set of single and double excitations that are chosen so as to include all the electronic correlation involving the orbitals that change significantly during bond breakage or formation. The method that was aimed at providing accurate bond dissociation energies using simple wave functions, proved to be successful for dissociation of single and double bonds.[33] Another method based on the GVB–SOPP wave function as a starting point, is the GVB–MP2 method of Friesner and Messmer,[34–37] who showed that the computational effort required for this method scales to no more than the third power of the size of the system, while that for the coupled-cluster and complete-active space MO-based methods scales as the seventh or higher power in the system size.

The Spin-Coupled Valence Bond Method

The Spin-Coupled (SC) method, developed by Gerratt and coworkers,[38–43] differs from the GVB–SOPP method in the sense that it removes the orthogonality and perfect-pairing restrictions. The method still relies on a single-configuration type, but all the modes of spin-pairing are included in the wave functions and the orbitals are allowed to overlap freely with each other. Both orbitals and coefficients of the various spin-pairing modes are optimized simultaneously. Thus no constraints are imposed on the spin-coupling schemes nor on the shapes of the orbitals, which are determined by the variational principle alone. As such, the SC method represents the ultimate level of accuracy compatible with the orbital approximation that describes the molecule as a single configuration with fixed orbital occupancies.

The SC wave function provides a correlated but single-particle interpretable description of electrons in molecules. The shapes of the SC orbitals, and their variations with nuclear geometry, provide direct insight into the spatial arrangements of the electronic clouds, the hybridization of the atoms, and the processes of bond making and bond breaking throughout the course of a reaction. The spin-coupling coefficients furnish a quantitative description of the relative importance of the different modes of spin-coupling. It is clear that the degree of delocalization of the SC orbitals is a crucial parameter for the achievement of an unambiguous association of a spin coupling form with a specific Lewis structure; the more localized the orbitals, the easier the interpretation of the wave function in terms of traditional chemical concepts. Although this is not *a priori* guaranteed, a typical outcome of SC calculations is a set of OEOs mostly localized on atoms, but distorted (in other words slightly delocalized) towards all neighboring atoms, and especially so in the direction of bonds in the classical Lewis structure. The number of dominant spin-coupling modes remains generally very small; for molecules like e.g., methane the SC wave function is dominated by the GVB–PP structure,[44] which is the chemist's classical structure, while for e.g., benzene, the wave function is dominated by two major Kekulé structures and three less important Dewar structures,[45] etc.

Both GVB and SC methods take care of the left-right electron correlation in molecules, but do not include the totality of the "non-dynamical" correlation that is accounted for in a CASSCF calculation that involves all valence orbitals in the active space. This is because GVB and SC do not treat properly the various local ionic situations, which are found to have equal weights, while CASSCF would differentiate, for example, the weights of two local adjacent ionic forms $+-/-+$ and $+-/+-$. Nevertheless, the GVB and SC methods provide, as a rule, energies that are much closer to CASSCF quality than to that of Hartree–Fock.

Like GVB, the SC method also provides a wave function that can serve as an appropriate basis for subsequent configuration (CI) interaction and inclusion of dynamic correlation. Subsequent CI on the SC wave function is performed in the spin-coupled valence bond (SCVB) method, which is an extension of the SC method. At the simplest level, the CI includes all the configurations that can possibly be generated by distributing the electrons within the set of the active orbitals that were optimized in the preliminary SC calculation; both covalent and "ionic" type configurations are considered. A higher level of SCVB theory includes additional excitations, e.g. from the orbitals of the core, if any (for example excitations from the σ orbitals when the SC orbitals are only those of π type), or to orbitals that are virtual in the one-configuration calculation. To preserve the valence bond character of the wave function, the virtual orbitals have to be as much localized as possible. This condition is met in the SCVB method,[41] in which each occupied orbital of the ground configuration is constructed to correspond to a stack of virtual orbitals localized in the same region of space, by means of an effective operator representing the field created by the remaining occupied orbitals. Subsequently, starting from the ground state SC configuration and/or from other appropriate reference configurations, additional configurations may be generated by replacing one or more occupied orbitals with virtual orbitals. The usual strategy is to consider only "vertical" excitations, i.e. those within individual stacks, to low-lying orbitals, plus associated ionic configurations. The final energy value is determined by nonorthogonal CI in the so generated configuration space. From experience, the excited configurations generally bring very little stabilization as far as ground states are concerned; this is easily explained by the fact that the orbitals are optimized precisely so as to concentrate all the important physical effects in the reference single configuration. On the other hand, excited configurations are important for satisfactory state ordering and electronic transition energies to excited state.[46]

Recently, an improved SCVB method, called SCVB*, has been devised, aiming at yielding a more compact wave function without lost of accuracy.[47] This is done by optimizing the virtual orbitals that are used to construct the excited configuration for the CI. These virtual orbitals are determined by augmenting the converged SC wave function with all double vertical excitations into the virtuals, and optimizing the latter with respect to the energy of the overall wave function, using a second order perturbation approximation. Ultimately, the SC occupied orbitals and the optimized virtuals are used to construct the final variational SCVB* wave function that includes singly-excited and doubly-excited configurations.[40]

The CASVB Methods

The underlying principle of these methods is the observation that a SC wave function is generally close to the CASSCF wave function that has the same number of electrons and orbitals in its active space. Since a CASSCF calculation is faster than a direct SC calculation, owing to the advantages associated with orbital orthogonality in CASSCF, it is interesting to extract an approximate SC wave function (or another type of VB function, e.g. multiconfigurational) from a CASSCF wave function. The conversion from one wave function to the other relies on the fact that CASSCF wave functions are invariant to linear transformations of the active orbitals. Two different procedures, based on this same basic principle, have been independently developed by different groups, and share the same name, "CASVB."

In the CASVB method of Thorsteinsson,[48–51] one transforms the canonical CASSCF orbitals so that the wave function (which is kept unchanged in this process) involves a dominant component of "modern VB" type, Ψ_{VB}, which is chosen in advance and may be single- or multiconfiguration, as in eq. (8):

$$\Psi_{CAS} = S_{VB}\Psi_{VB} + (1 - S_{VB}^2)\Psi_{VB}^{\perp}. \tag{8}$$

Here $\Psi_{VB}^{\perp}$ is the orthogonal complement of Ψ_{VB} to the CASSCF wave function, and S_{VB} is the overlap between Ψ_{CAS} and Ψ_{VB}. To ensure that the obtained VB function is as close as possible to the starting CASSCF one, an obvious procedure is to transform the orbitals so as to maximize the overlap S_{VB}. An alternative is to minimize the energy of the VB function Ψ_{VB}. This latter procedure is however more expensive than the first one. As both methods generally yield similar sets of orbitals, the method of S_{VB} maximization tends to be preferred.[51]

The CASVB method of Hirao et al.[52,53] differs from the previous one in the requirement that after the transformation of the CASSCF canonical orbitals, the final CASVB wave function is strictly equivalent to the starting CASSCF wave function. The price of this strict equivalence is that the orbitals that are used to construct the VB structures remain more or less of the delocalized MO type, however these VB-type MOs are localized as much as possible following various localization procedures. Two methods are proposed: the first one is a method where the VB structures are constructed from orthogonal localized orbitals (LMOs),[52] while the second uses non-orthogonal localized MOs.[53] As is well known, orthogonal LMOs have important tails on neighboring atoms, and are consequently not so atomic-like. Moreover, the use of orthogonalized LMOs spuriously increases the weights of ionic structures, and this nonphysical effect makes the CASVB wave function difficult to interpret. This led the originators of the method to prefer the non-orthogonal LMO description. In this latter case, the non-orthogonal LMOs are obtained by Ruedenberg's localization procedure[54,55] that yields quasi-atomic CASSCF MOs that have maximum overlap with the AOs of the free atoms. On the other hand, in the CASVB with orthogonal LMO's, Boy's localization procedure is used.[56] This CASVB method bears close relationship to the localization procedure of CASSCF that leads to VB-like information.[57,58]

The Generalized Resonating Valence Bond Method

Multiconfigurational extensions of the GVB method have been specifically devised for delocalized electronic systems, like benzene, whose qualitative description *requires* the use of two, or more, resonance structures, and for which the one-configuration VB approximation is not appropriate. This situation is widespread, including a wide variety of open-shell electronic states, as for example allyl radical and its analogs, pentadienyl anion and its analogs, transition states of chemical reactions, core-ionized diatoms, n-π* excited molecules containing two equivalent carbonyl groups, n-ionized molecules having equivalent remote lone pairs, etc. In the general case, one-configuration methods will yield poor energies for a delocalized system that requires at least two structures (e.g. transition state of a reaction) relative to parts of the potential surface that are well described by a single VB structure (e.g. reactants or products). In some of these species, e.g., core-ionized diatoms, the use of a single configuration method leads to the so-called "symmetry dilemma."[59] The symmetry dilemma was analyzed in VB terms by McLean,[60] and shown to arise from a competition between two effects. One is the familiar resonance effect by which a mixture of two resonance structures is lower in energy than either one taken separately. The second is the so-called "orbital size effect," whereby a specific VB structure gains stabilization if it can have its particular set of optimal orbitals. The two effects cannot be simultaneously taken into account in any one-configuration theory, be it of VB or MO type, because such calculations employ a single set of orbitals. In the (most frequent) case when the orbital size effect is more important than the resonance effect, the wave function will take more or less the form of one particular VB structure leading thereby to a nonphysical symmetry-breaking of the wave function.

A simple remedy for the above cases in the VB framework consists of allowing different orbitals for different VB structures in the course of the orbital optimization. In this line, Jackels and Davidson[61] eliminated the symmetry-breaking problem in the NO_2 radical by using a symmetry-adapted combination of two symmetry-broken Hartree–Fock wavefunction, by means of a 2 × 2 non-orthogonal CI.

Voter and Goddard employed the same idea in the GVB method.[62–65] Considering an electronic state involving the superposition of two possible VB structures **A** and **B** (the generalization to multiple terms is trivial), the total wave function is written as a linear combination of two symmetry-broken sub-wavefunctions Ψ^A and Ψ^B of GVB type, one for each VB structure:

$$\Psi = C_A \Psi^A + C_B \Psi^B. \tag{9}$$

Of course, Ψ^A and Ψ^B are non-orthogonal, and the calculation of the energy of Ψ requires the evaluation of the Hamiltonian matrix element between the sub-wavefunctions.

In a preliminary version of the method,[62] called Resonating-Generalized Valence Bond (R-GVB), each symmetry-broken sub-wavefunction is optimized separately, and the orbitals are not reoptimized in the presence of resonance between the wavefunctions. This may lead to underestimation of the resonance energy since the orbital optimization only takes care of the orbital-size effect. To remedy this defect, Voter and Goddard subsequently improved their method by allowing the sub-wavefunctions to be optimized in the presence of each other, leading to the final Generalized Resonating Valence Bond method (GRVB).[64,65] The quality of such a simple wave function and the usefulness of the method can be appreciated by the results of the difficult test case of the HF + D → H + FD exchange reaction. In a basis set of double-zeta + polarization quality, a GRVB yields a barrier of 47.7 kcal/mol, in very good agreement with higher-level calculations using the same basis set. By contrast, a simple one-configuration GVB calculation leads to a much higher barrier of 69.5 kcal/mol.[64]

The Generalized Multistructural Method

The generalized multistructural (GMS) method[66] can be considered as an extension of the R-GVB and GRVB methods. Like these latter methods, it describes an electronic state in terms of a linear combination of sub-wavefunctions that are non-orthogonal to each other. However, the sub-wavefunctions are not restricted to be of the GVB type, but may assume any type of correlated functions (GVB, GVB + CI, CASSCF, CASSCF + CI, etc.) or even uncorrelated functions of Hartree–Fock or ROHF type. In principle, the sub-wavefunctions can be optimized in the presence of each other (as in a GRVB calculation), but in actual applications the simpler procedure of separate optimization (as in R-GVB) has usually been used. A subsequent non-orthogonal CI is then performed to determine the coefficients of the sub-wavefunctions and the final energy of the electronic state. As in the R-GVB and GRVB methods, the Hamiltonian matrix elements between the various sub-wavefunctions are computed using a biorthogonal procedure.

It is noted that, for a system that is qualitatively described as two equivalent VB structures, the GMS method allows to add, to the total wave function, one symmetry-adapted function in addition to the two localized sub-wavefunctions. For example, for the calculation of the helium dimer cation $(\mathrm{He})_2{}^+$, the total wavefunction was taken to be a combination of two localized forms, of the types HeHe^+ and $\mathrm{He}^+\mathrm{He}$, plus a symmetry-adapted Hartree–Fock wave function of the type $(\mathrm{He}\therefore\mathrm{He})^+$, with doubly occupied σ and singly occupied σ^* orbitals.[67] As the latter structure implicitly contains the two first ones, the wavefunction begins with a redundancy. Indeed the third structure proved to have only a minor effect in the actual calculation.[68]

The GMS method has been applied to a number of electronic systems that exhibit symmetry-breaking at the Hartree–Fock level,[68–71] including core-hole states[68,69] and n→π^* excited states.[70] The method yielded transition energies and ionization potentials in good agreement with experiment, from simple wave functions. It has also been applied, like the GRVB method,[65] to compute resonance energies in organic chemistry.[72] In such a case, the resonance energy is taken as the difference between the ground state energy and the energy of the lowest localized sub-wavefunction. It must however be kept in mind that, in the framework of the GRVB and GMS methods, a sub-wavefunction is not totally localized, and as such it includes some resonance relative to the truly localized reference state. This problem is common to all the methods that use not purely localized atomic functions. In all these methods, the calculated resonance energies are lower bounds of the true values. Of course, this also leads to undesirable strong dependence of the resonance energies on the method, which is not the case in the above described "pure" VB method that rely on pure atomic functions.

Multiconfiguration VB Methods with Optimized Orbitals

The Biorthogonal Valence Bond method of McDouall[73–76] is a multiconfiguration VB method that reduces the non-orthogonality difficulty by the introduction of a second (dual) orbital basis that is related to the primary set by the property of biorthogonality. The wavefunction, Ψ, is expressed as a linear combination of VB structures that are constructed from a set of orbitals $\{\phi\}$ that is subdivided into three categories: a core of doubly occupied orbitals, a valence set of non-orthogonal orbitals with variable occupancies, and a set of virtual orbitals. The core orbitals and virtual orbitals are orthogonal amongst themselves and to all other orbitals. From this set, a dual set $\{\tilde{\phi}\}$ is constructed that is related to the primary basis by the property of biorthogonality, eq. (10), leading to a second valence bond function $\tilde{\Psi}$ expressed in the dual set.

$$\langle \tilde{\phi}_p | \phi_q \rangle = \delta_{pq}. \tag{10}$$

Subsequently, the calculation of the total energy is performed by evaluating $\langle \tilde{\Psi} | \mathrm{H} | \Psi \rangle$ instead of $\langle \Psi | \mathrm{H} | \Psi \rangle$, thus benefiting from all the computational advantages associated to the orthogonality of the orbitals. The orbitals and the coefficients of the VB structures are optimized simultaneously, by a super-CI technique. The orbitals are allowed to delocalize freely as in the SC method.

The biorthogonal procedure is equivalent to an exact resolution of the non-orthogonal secular equations if Ψ involves a complete configuration expansion in the valence space, in which case the biorthogonal scheme is equivalent to performing a valence-CASSCF calculation. On the other hand, if the expansion is truncated, the procedure is only approximate and lacks a variational bound on the energy functional. This drawback, however, is not expected to be severe if the most important VB structures are included in the expansion.[75] This can be achieved, for example, if the selection of the VB structures is done in the spirit as the CCCI procedure of Carter and Goddard.[33] In such a case, the calculated energy lies in-between the SC and CASSCF result, and sometimes very close to the later. Thus, the biorthogonal valence bond wavefunction of methane, with only 129 configuration state functions (CSFs), yield an energy only 5 mh above that of a CASSCF calculation in the same basis set, involving 1764 CSFs.[76]

Another multiconfiguration VB method that involves orbital optimization was devised by McWeeny,[77] based on the spin-free approach.[19] Like the biorthogonal method, this method divides the global space of basis functions into three subspaces: doubly occupied core orbitals, non-orthogonal valence orbitals and virtual orbitals. Valence orbitals are made orthogonal to the core set, and virtual orbitals are orthogonal to both core and valence sets. By comparison to the SC method, the essential extension is the admission of ionic structures into the set of VB structures; subsequently, the structural coefficients and orbitals are simultaneously optimized to yield the final wave function and energy. The resulting orbitals are of the OEO type, since they are allowed to delocalize freely in the course of optimization. The method optimizes the virtual orbitals and core orbitals separately, but self-consistency is ensured by means of an iterative group-by-group optimization, until a further cycle gives no appreciable improvement.

McWeeny's method has been further improved[78] by extending the notion of "groups" beyond a mere core-valence separation. In this method, the molecule is viewed as a collection of interacting groups, each with its many-electron wave function that can be of any desired type (VB, MO-SCF, MCSCF). Each group wavefunction is optimized individually in a step-by-step process (orbital and structure coefficients), thus greatly reducing the number of electrons in the optimization process relative to an all-including standard calculation. Then, the whole wavefunction is finally optimized to take the interactions between groups into account, by means of a rigid rotation algorithm. For example, in the benzene molecule, the 42 electrons are divided into 14 groups: a group of 12 carbon-core electrons, 6 groups of C—H bonds and 6 groups of C—C σ-bonds (all represented as GVB pairs), and a group of 6 π-electrons. The methods allows up to 14 electrons to be treated in each group.[78]

The VBSCF method of van Lenthe and Balint-Kurti[79,80] is another multipurpose multiconfiguration VB method with simultaneous optimization of orbitals and structure coefficients. However, as this method is designed to deal with localized orbitals, we will postpone its description to a subsequent section.

VB Methods Specifically Devised for Weak Interactions

Interaction energies involved in weakly interacting systems (e.g. van der Waals attraction, hydrogen-bond, etc) are often of the same order of magnitude as the basis set superposition error (BSSE). In this context, the SCF-MI method (Self consistent Field for Molecular Interactions)[81–84] aims at avoiding the BSSE in an *a priori* fashion. As this *ab initio* method deals with non-orthogonal orbitals, it can be considered as a VB-type method. The basic principle consists of partitioning the full basis set of orbitals into subsets each centered on a given fragment. The molecular orbitals are then optimized in a Hartree–Fock way, with the restriction that each orbital is expanded only on its own fragment, thus avoiding the BSSE right at the outset. The MOs of a given fragment are orthogonal amongst themselves, but the orbitals of different fragments have finite overlaps.

This Hartree–Fock-like zeroth-order wave-function serves as a basis for either perturbation theory or configuration interaction approaches to account for electron correlation, leading to the MO–VB method.[85–90] The MO–VB wavefunction is a non-orthogonal CI expansion resulting from single and selected double excitations from the SCF-MI determinant into a set of optimal virtual orbitals. The optimal virtual orbitals are generated as follows.

For each pair of occupied SCF-MI orbitals located on two different fragments, a pair of virtual orbitals is determined by minimizing the energy of a CI wavefunction involving the zeroth-order SCF-MI wavefunction and a doubly-excited configuration made of simultaneous single excitations localized on each monomer. Just like the occupied orbitals, the virtual orbitals are constrained by expansion in the partitioned basis sets located on their respective fragment. Of course, during the optimization, two virtual orbitals belonging to different fragments are kept non-orthogonal. Finally, the optimized virtual orbitals are employed to generate an MO–VB wavefunction involving all the local (intrafragment) single excitations and double excitations resulting from simultaneous single excitations on two different fragments, thus taking care of the dispersion forces.

The MO–VB scheme can be further improved by extending the optimization of the virtual orbitals up to saturation. Once a pair of virtual orbitals has been determined by the above procedure, a new pair is optimized by expanding it into the orthogonal complement space to the previously determined space. The whole procedure can be repeated *n* times, thus generating, for each pair of occupied orbitals, *n* optimized virtual orbital pairs; the contribution of a given pair to the total energy is expected to decrease, up to saturation, i.e. the full use of the SCF-MI virtual orbital space. However the contributions to the interacting energy usually converge well before saturation is reached in practical applications, typically after three iterations.[90]

Owing to the strictly partitioned nature of the basis set of orbitals, charge-transfer is not formally included in the above approaches. Therefore, the SCF-MI method is more appropriate for conventional weak hydrogen bonds than for charge-assisted or resonance-assisted hydrogen bonds. However, thanks to the tails of the functions centered on fragment A which extend in the space of fragment B, and vice versa, it is expected that some electronic transfer is not strictly forbidden, due to the non-orthogonality of the MO's of the different fragment, if the basis set is sufficiently large.

The Block-Localized Wavefunction Method

The basic strategy and mathematical formulations of the block-localized wavefunction (BLW) method[91–95] is essentially identical to the SCF-MI method described in the preceding section. In both cases, the molecule or interacting system is partitioned in subgroups, and each localized molecular orbital is expanded in terms of primitive orbitals belonging to only one subgroup. The molecular orbitals belonging to the same subgroup are constrained to be mutually orthogonal, while those belonging to different subgroups are free to overlap. However, while the SCF-MI method is intended to eliminate the BSSE in van der Waals complexes, the BLW method is primarily aimed at evaluating the electronic delocalization and charge transfer effects among molecules Thus, the block-localized wave function is constructed so as to represent a diabatic state that can serve as a non-delocalized reference against which the energy of the fully delocalized wave function can be compared.

Although the theory behind BLW is more general, a typical application of the method is the energy calculation of a specific resonance structure in the context of resonance theory. As a resonance structure is, by definition, composed of local bonds plus core and lone pairs, a bond between atoms A and B will be represented as a bonding MO strictly localized on the A and B centers, a lone pair will be an atomic orbital localized on a single center, etc. With these restrictions on orbital extension, the self-consistent-field solution can be decomposed to coupled Roothaan-like equations each of which corresponds to a block. The final block-localized wave function is optimized at the constrained Hartree–Fock level and is expressed by a Slater determinant. Consequently, the energy difference between the Hartree–Fock wave function, where all electrons are free to delocalize in the whole system, and the block-localized wave function, where electrons are confined to specific zones of the system, is defined generally as the electron delocalization energy. We note that the BLW method is reminiscent of Kollmar's method of constructing a reference Kekulé structure for conjugated molecules, by describing the double bond using localized π MOs taken, e.g., from an SCF calculation on ethylene.[96] However, the BLW method is more general and has the advantage that it fully optimizes the block-localized MOs for self-consistency in the molecule under study.

The BLW method can be considered as an extension of the Orbital Deletion Procedure (ODP),[97–101] a simpler method which can only be applied to carbocations[98–101] and boranes.[100] The ODP consists of representing a resonance structure displaying an electronic vacancy (Lewis acid character) by deleting the primitive basis functions corresponding to the empty site before launching the SCF calculations. As a typical example, the ODP has been applied to calculate the resonance energy of the allyl cation.[101]

As an extension of the BLW method, the Molecular-Orbital-Valence Bond method[102] (MOVB, not to be confused with the MO–VB method of Raimondi and coworkers,[85–90] described above, which carries the same acronym) allows to calculate the electronic coupling energy resulting from the mixing of two, or more, diabatic states. The diabatic states are first calculated by the BLW method, then a non-orthogonal configuration interaction Hamiltonian is constructed using these diabatic states as the basis functions. Although the MO coefficients for each resonance configuration might in principle be reoptimized in the MOVB CI calculations, in practical applications only the configuration coefficients are variationally optimized. Thus, MOVB is a mixed molecular orbital and valence bond method, since it makes use of a Hartree–Fock description for the covalent bonds, while being able to calculate diabatic states.

One interesting potential application of the MOVB method is the study of a chemical reaction in terms of interacting resonance structures, e.g. the configurations representing the reactant and product diabatic states, respectively, plus other configurations if necessary, as in the Valence Bond State Crossing Diagram (VBSCD) model.[103,104] Importantly, solvent effects can be incorporated in the MOVB method. Thus, the MOVB method has been used to model the proton transfer between ammonium ion and ammonia in water,[102] as well as a solvated S_N2 reaction,[105] using Monte Carlo simulations.

Pure VB Methods that Use Localized Orbitals

This section describes those VB methods that possess the facility to constrain the orbitals of the VB structures to be strictly localized hybrid atomic orbitals (HAOs) on a single center or fragment during the optimization process. In such a case, the wave function would be composed of classical type VB structures that clearly distinguish between the covalent and ionic components of the bonds, as in eq. (1) above. For example, if the VB structures of the trifluoride anion, F_3^-, are constructed with HAOs, the corresponding wave function is a resonating combination of six VB structures, illustrated below:

$$\Psi(\text{HAOs}) = \text{F}\cdot\!\!-\!\text{F}\text{F}^- \leftrightarrow \text{F}^-\text{F}\cdot\!\!-\!\text{F} \leftrightarrow \text{F}^+\text{F}^-\text{F}^- \leftrightarrow \text{F}^-\text{F}^+\text{F}^- \\ \leftrightarrow \text{F}^-\text{F}^-\text{F}^+ \leftrightarrow \text{F}\cdot\ \text{F}^-\text{F}\cdot \qquad (11)$$

On the other hand, if OEOs are employed, only two formally "covalent" VB structures would be needed. While these "structures" can be labeled as F—F F⁻ and F⁻ F—F, as shown in eq. (12),

$$\Psi(\text{OEOs}) = \text{F} - \text{F}\ \text{F}^- \leftrightarrow \text{F}^-\ \text{F} - \text{F} \qquad (12)$$

the two structures implicitly involve the six classical structures constructed with HAOs [eq. (11)], as discussed above. As can be seen, defining VB structures with HAOs yields a less compact wavefunction compared with the one based on OEOs. As a balance, the HAO-based VB representation has the advantage having strict one-to-one correspondence between the mathematical VB functions and the classical VB structures that they represent. Furthermore, distinguishing ionic from covalent VB structures, as in the HAO-based representation, allows one to calculate the resonance energies arising from the covalent–ionic mixing, or to highlight the special role of a particular VB structure (e.g. the last one in eq. (11) for F_3^-,[106] or as in a VB Configuration Mixing Diagram[103]). These features are common to the VBSCF, BOVB and VBCI methods (see below), and their use has resulted in some new qualitative concepts.[106–108] Moreover, owing to the use of strictly localized active orbitals, these methods are suitable for calculating clearly defined diabatic states that are required to retain the physical content of a given asymptotic state, at any point of a reaction coordinate, without collapsing to the ground state by virtue of uncontrolled orbital optimization.[25,109,110]

The Valence Bond Self Consistent Field Method

The valence bond self consistent field (VBSCF) has been devised by van Lenthe and Balint-Kurti,[79,80] and was further modified by van Lenthe,[111,112] who also developed an efficient implementation.[24] Basically, the VBSCF method is a multi-configuration SCF method that allows for the use of non-orthogonal orbitals. The wave function is given as a linear combination of valence bond structures, Φ_K, without any restrictions put upon the number of configurations, the orbital occupation numbers and the number of spin-functions per configuration [eq. (13)].

$$\Psi = \sum_K C_K \Phi_K. \tag{13}$$

Both the orbitals and coefficients of VB structures are optimized simultaneously, by means of a Super CI algorithm.[113,114] It is well known that the bottleneck of this algorithm is the evaluation of the non-orthogonal matrix elements, however a number of improvements for speeding up this evaluation have been proposed. Thus, orthogonalization of orbitals is automatically invoked, wherever this procedure leaves the wave function unaltered, and is exploited in the algorithm by generalizing the Slater-Condon rules to cases where not all orbitals are orthogonal.[16] Moreover, the Super CI algorithm is combined with an approximated Newton-Raphson scheme, with Direct Inversion of Iterative Subspace (DIIS) to speed up convergence.[112]

The VBSCF method permits complete flexibility in the definition of the orbitals used for constructing the VB structures, Φ_K. The orbitals can be allowed to delocalize freely during the orbital optimization (resulting in OEOs), thereby performing GVB or SCVB calculations. The orbitals can also be defined by pairs that are allowed to delocalize on only two centers (BDOs), or they can be defined as strictly localized on a single center or fragment (HAOs). Only when applied with BDOs or HAOs, would the VBSCF method be suitable for the calculation of diabatic states. Note that, while all the VB structures Φ_K differ from each other by their orbital occupancies, they still share the same set of orbitals. If a complete set of VB structures (covalent and ionic) is generated for a given electronic system, the resulting VBSCF wave function would be equivalent to a full-valence CASSCF wave function and thereby accounting for all the non-dynamic electronic correlation.

The Breathing-Orbital Valence Method

The breathing-orbital valence (BOVB) method[115–119] was devised with the aim of computing diabatic or adiabatic states with wave functions that combine the properties of compactness, unambiguous interpretability in terms of structural formulas and accuracy of the calculated energies. The following features have to be fulfilled to retain interpretability and achieve reasonably good accuracy for the BOVB method: (i) the VB structures have to be constructed with HAOs, which means that covalent and ionic forms are explicitly considered; (ii) all the VB structures that are relevant to the electronic system being computed are generated; (iii) the coefficients and orbitals of the VB structures are optimized simultaneously. An important specificity of the BOVB method is that the orbitals are variationally optimized with the freedom to be different for different VB structures. Thus, *the different VB structures are not optimized separately but in the presence of each other,* so that the orbital optimization not only lowers the energies of each individual VB structure but also maximizes the resonance energy resulting from their mixing.

Since the BOVB wave function takes a classical VB form, its implementation is not practical for the VB description of large electronic systems, because a large number of VB structures would have to be generated in such a case. As such, the usual way of applying BOVB is to describe with it only those orbitals and electrons that undergo significant changes during the process, like bond breaking and/or formation; the remaining orbitals and electrons are described as doubly occupied MOs. However, even though the "spectator electrons" reside in doubly occupied MOs, these orbitals too are allowed to optimize freely, but are otherwise left uncorrelated.

The difference between the BOVB and VBSCF wave function can be illustrated on the simple example of the description of the A—B bond, where A and B are two polyelectronic fragments. Including the two HAOs that are involved in the bond in the active space, and the adjacent orbitals and electrons in the spectator space, the VBSCF wave function reads:

$$\Psi_{VBSCF} = C_1(|\Phi\overline{\Phi}\chi_a\overline{\chi}_b| - |\Phi\overline{\Phi}\overline{\chi}_a\chi_b|) + C_2|\Phi\overline{\Phi}\chi_a\overline{\chi}_a| + C_3|\Phi\overline{\Phi}\chi_b\overline{\chi}_b| \tag{14}$$

where χ_a and χ_b are the active orbitals, common to all the structures, and Φ is a generic term that represents the product of spectator orbitals. On the other hand, the BOVB wave function takes the following form:

$$\Psi_{BOVB} = B_1(|\Phi\overline{\Phi}\chi_a\overline{\chi}_b| - |\Phi\overline{\Phi}\overline{\chi}_a\chi_b|) + B_2|\Phi'\overline{\Phi'}\chi'_a\,\overline{\chi}'_a| + B_3|\Phi''\overline{\Phi''}\chi''_b\,\overline{\chi}''_b|. \tag{15}$$

Physically, one expects the χ_a' and χ_b'' orbitals to be more diffuse than χ_a and χ_b, since the former are doubly occupied while the later are only singly occupied. Similarly, the spectator orbitals, in the different structures, should have different sizes and shapes depending on whether they reside on cationic, neutral or ionic fragments. Thus, both the active and spectator orbitals can be viewed as instantaneously following the charge fluctuation by rearranging in size and shape, hence the name "Breathing-Orbital." This instantaneous adaptation brings some dynamic correlation that is missing at the VBSCF, GVB, SC and CASSCF levels, and results in better accuracy, as shown in benchmark calculation of bond dissociation energies and reaction barriers.[117,118] The relationship between the effect of breathing orbitals and dynamic correlation is particularly well illustrated in three-electron bonds, where all the electronic correlation is of dynamic nature.[119]

The BOVB method has several levels of accuracy. At the most basic level, referred to as L-BOVB, all orbitals are strictly localized on their respective fragments. One way of improving the energetic is to increase the number of degrees of freedom by permitting the inactive orbitals to be delocalized. This option, which does not alter the interpretability of the wave function, accounts better for the nonbonding interactions between the fragments and is referred to as D-BOVB. Another improvement can be achieved by incorporating radial electron correlation in the active orbitals of the ionic structures, by allowing the doubly orbitals to split into two singly occupied orbitals that are spin-paired. This option carries the label ”S“ (for split), leading to the SL-BOVB and SD-BOVB levels of calculation, the latter being the most accurate one.

The Valence Bond Configuration Interaction Method

In the same spirit as BOVB, the valence bond configuration interaction (VBCI) method[118,120,121] aims at retaining the conceptual clarity of the classical VBSCF method, while improving the energetic aspect by introducing further electron correlation. This is achieved by augmenting the VBSCF calculation with subsequent configuration interaction, and then condensing the final CI space into a minimal number of VB structures.

In a first step, all the fundamental VB structures are involved, and a VBSCF wave function is calculated and taken as a zeroth-order wave function.

$$\Psi^{VBSCF} = \sum_K C_K^{SCF} \Phi_K^0. \tag{16}$$

As in the original VBSCF method, the occupied orbitals that constitute the Φ_K^0 VB structures may be constrained to be block-localized. The blocks can be defined as atoms, fragments, a pair of atoms, etc., depending on whether HAOs, BDOs, or other type of orbitals are required for the particular application. Then, for each occupied orbital in the VBSCF wave function, a projector is used to define a set of virtual orbitals, each being strictly localized on precisely the same block as the corresponding occupied orbital. These virtual orbitals are used to create excited VB structures in the following way: Given a fundamental VB structure Φ_K^0, an excited VB structure Φ_K^i is built by replacing one or more occupied orbital(s) by the same number of virtual orbitals located on the same block. This way, the excited VB structure Φ_K^i retains the same electronic pairing pattern and charge distribution as Φ_K^0. In other words, both Φ_K^0 and Φ_K^i describe the same "classical" VB structure. A subsequent VBCI calculation will involve all the fundamental and excited VB structures in eq. (17):

$$\Psi^{VBCI} = \sum_K \sum_i C_{Ki} \Phi_K^i \tag{17}$$

where the coefficients C_{Ki} and the final energy are determined by solving the secular equations without further orbital optimization.

The CI space can be truncated following the usual CI methodology. The starting point always involves single excitations, i.e. VBCIS. This can be followed by VBCISD, VBCISDT, etc., where D stands for double and T for triple excitations. Practical experience with the method shows that going beyond double excitation is usually not necessary.[118] The method was also augmented by second order perturbation theoretic (PT2) treatment, so that the role of higher excitation can be taken into account; for example, VBCISPT2 accounts for doubles using PT2, etc.

Since the virtual orbitals conserve the nature of the fundamental VB structures, the entire VBCI wave function can be rewritten in a compact form,

$$\Psi^{VBCI} = \sum_K C_K^{CI} \Phi_K^{CI} \tag{18}$$

where the VB structure Φ_K^{CI} is of the form of eq. (19),

$$\Phi_K^{CI} = \sum_i C'_{Ki} \Phi_K^i \tag{19}$$

which collects all the VB functions that belong to the same structure in terms of spin-pairing and charge distribution.

A Valence Bond Method with Polarizable Continuum Model

The valence bond method with polarizable continuum model (VBPCM) method[122] aims at including the solute–solvent interactions in the VB calculations. It uses the same continuum solvation model as the standard PCM model implemented in current *ab initio* quantum chemistry packages, where the solvent is represented as a homogeneous medium, characterized by a dielectric constant, and polarizable by the charge distribution of the solute. The interaction between the solute charges and the polarized electric field of the solvent is taken into account through an interaction potential that is embedded in the Hamiltonian and determined by a self-consistent reaction field (SCRF) procedure.

In its actual implementation, the VBPCM method is based on the VBSCF method (vide supra). Thus, the wave function is expressed in the usual manner as a linear combination of VB structures, eq. (13), but now, these VB structures are optimized and interacting with one another in the presence of a polarizing field of the solvent, by a self-consistent procedure. Within this model, the interaction between solute and solvent is represented by an interaction potential, $V_{R,}$ which is treated as a perturbation term to the Hamiltonian H° of the solute molecule in vacuum. The Schrödinger equation for the VB wave function now reads:

$$(H^0 + V_R)\Psi^{VBPCM} = E\Psi^{VBPCM}. \tag{20}$$

Equation (20) is solved iteratively; the interaction potential V_R for the *i*th iteration is given as a function of electronic density of the (*i*-1)th iteration and is expressed in the form of one-electronic matrix elements that are computed by a standard PCM procedure. The detailed procedures are as follows:

1. A VBSCF procedure in a vacuum is performed (vide supra), and the electron density is computed.
2. Given the electron density from step 1, effective one-electron integrals are obtained by a standard PCM subroutine.
3. A standard VBSCF calculation is carried out with the effective one-electron integrals obtained from step 2. The electron density is computed with the newly optimized VB wave function.
4. Steps 2 and 3 are repeated until the energy difference between the two iterations reaches a given threshold.

By performing the above procedures, the solvent effect is taken into account at the VBSCF level, whereby the orbitals and structural coefficients are optimized till self-consistency is achieved. Like VBSCF, the VBPCM method is suitable for diabatic states, which are calculated with the same solvent field as the one for the adiabatic state. Thus, it has the ability to compute the energy profile of the full state as well as that of individual VB structures throughout the course of a reaction, and in so doing to reveal the individual effects of solvent on the different constituents of the wave function. In this spirit, it has been used to perform a quantitative VBSCD analysis of a reaction that exhibits a marked solvent effect, the S_N2 reaction $Cl^- + CH_3Cl \rightarrow CH_3Cl + Cl^-$.[122]

The VBPCM procedure is not, in principle, restricted to the VBSCF method; it has the potential ability to be implemented to more sophisticated methods like BOVB, VBCI or other methods.

Concluding Remarks and Prospective

Indeed, as demonstrated in this review, VB theory enjoys a renaissance that is marked by a surge of new and relatively efficient computational methods with moderate to good accuracies. Many VB methods exist at the moment with many names and many different functions. This plethora of acronyms for VB methods starts to resemble that which accompanied the ascent of MO theory. While this may sound like good news, certainly it is also a call for systematization much like what Pople and coworkers enforced on computational MO terminology. This has not been attempted yet in VB theory. Nonetheless, at the moment the important point is that the advent of many good VB programs has caused a surge of applications of VB theory to problems ranging from bonding in main group elements to transition metals, conjugated systems, aromatic and antiaromatic species, and even excited states and full pathways of chemical reactions; sometimes even with good accuracy. For example, a recent calculation of the barrier for the identity hydrogen exchange reaction, $H + H–H' \rightarrow H–H + H'$, by Song et al.[118] shows that it is possible to calculate the reaction barrier accurately with just eight classical VB structures! This accuracy will only increase with time. VB theory is coming of age. Applications are many, and the present authors have themselves published quite a few reviews and monographs.[103,104,117,123–126] A recent review summarizes some of these applications as well as those by others.[25]

However, the pride of VB practitioners has never been, and will probably never be, on the ability of the theory to compute huge molecules with linear scaling algorithms and obtain accurate energies that will compete with high MO-CI or density functional methods. VB fans have traditionally prided themselves in the insight that the theory generates into chemical problems. The VB wave function being constructed from localized building blocks provides insight into chemical phenomena that involve "change," be this a change in bonding of two atoms or fragments, or a chemical change as in a chemical reactions, or still a change due to electron reorganization as in an excited state or chemistry thereof. Since this kind of insight was not emphasized in this review, this is perhaps a good point to mention the topical and general VB insight into chemical problems. Below we briefly mention some of these insights without pretence of creating an exhaustive list.

A few general qualitative models based on post-Pauling VB theory started to appear in the late 1970s and early 1980s. Among these models we count also semiempirical approaches based, e.g., on Heisenberg and Hubbard Hamiltonians,[127–130] as well as Hückel VB methods,[131–133] which can handle well ground and excited states of molecules. As amply demonstrated, these approaches provide a great deal of qualitative insight.[128] Without any numerical computations, these methods can be used to deduce qualitative rules, regarding the spin multiplicity of the ground states of polyenes (especially for diradicals), the spin distribution in free radicals and triplet states, differences in bond lengths, and relative stabilities of isomers.

A general model for the origins of chemical reactivity was proposed in 1981, based on crossing and avoided crossing of VB configurations and states.[134] A special feature of the models is the bridging between VB and MO insights in a manner that incorporates the role of orbital symmetry,[131,134] and allows one to derive selection rules in cases where one electron MO theory is not able to do, such as radical reactions, etc. Subsequently, the model has been generalized for a variety of reaction mechanisms,[103,123,135] and used to shed new light on the problems of aromaticity/antiaromaticity and delocalization in isoelectronic series.[136]

VB ideas have also contributed to the revival of theories for photochemical reactivity. Early VB calculations[137] revealed a possible general mechanism for the course of photochemical reactions. Subsequently, Michl[138] articulated this VB-based mechanism into a general photochemical model that highlighted the importance of "funnels" as the potential energy features that mediate the excited state species back into the ground state. Recent work by Bernardi et al.[139], Robb et al.[140] showed that these "funnels" are conical intersections that can be predicted by simple VB arguments, and computed at a high level of sophistication. Similar applications of VB theory to deduce the structure of conical intersections in photoreactions were done by other groups.[25,104,141,142]

VB theory enables a very straightforward account of environmental effects, such as those imparted by solvents and/or protein pockets. The solvent effect is exerted through the ionic VB configurations and leads to polarization of charge and to changes of potential energy surface via covalent–ionic VB curve crossings. A major contribution to the field was made by Warshel who introduced the empirical VB (EVB) method,[143] which was coupled to a molecular mechanics (MM) method to yield the QM(VB)/MM method for the study of enzymatic reaction mechanisms.[144] The facility of coupling solvent models with VB calculations or modeling was demonstrated for classical reactions of physical organic chemistry, such as S_N2 and S_N1, etc.[145,146]

VB theory provides a great deal of insights into bonding in odd-electron systems, specifically on one-electron and three-electron bonds,[25,147–149] into multiple bonding patterns especially in heavier analogs of carbon, e.g., why is the Si=Si bond weaker than the single Si—Si bond, etc.[150–153] In fact, VB theory gives rise to new bonding paradigms. One such paradigm is called "charge-shift bonding" and concerns two-electron bonds which are neither covalent nor ionic but with bonding energy that is dominated by the covalent-ionic resonance interaction; for example F—F and O—O are charge-shift bonds.[107,154] Another paradigm is the "ferromagnetic-bonding" that occurs in high-spin clusters, e.g., $^{n+1}Li_n$, $^{n+1}Cu_n$, etc. that are devoid of an electron pairs but have significant bond energy that can reach as much as 19 kcal/mol per atom.[155,156]

Relatively little amount of VB work exists for transition metal complexes and bioinorganic molecules.[157,158] For obvious reasons, the field is usually limited to empirical VB-type methods, and qualitative arguments. One of the present authors (SS) has applied VB ideas to gain insight into the electronic structure and reactivity of the active species of the enzyme cytochrome P450[159] and to structural features of the active species of the enzyme horseradish peroxidase.[160] Extensive work has been done by Firman and Landis[161] who introduced the VAL-BOND method that predicts with great simplicity the structures of transition metal complexes using Pauling's ideas of orbital hybridization. A recent monograph of Weinhold and Landis[162] applies the ideas of natural resonance theory (NRT) to a variety of transition metal species. Clearly, VB theory is likely to provide to this booming field much more insight than at present.

Finally, much of the future acceptance of VB theory by the chemical community depends on the ability of VB practitioner to harness the insights of MO theory and combine them with the special features of VB theories, and create thereby more portable theories. Some attempts along this line were made by the authors of this review in the formulation of a general theory of reactivity.[25,103,104,123,131,134] Another important bridge are the methods that map MO-based wave functions to VB wave functions and provide thereby much insight into the calculation that rely on intractable MO–CI wave function, e.g., offer a good deal of interpretive insight. Among these mapping procedures we note the various methods for projecting MO-based wave functions onto a valence bond basis,[163–167] and the CASVB methods.[48–53]

Acknowledgments

The authors are indebted to Profs J. H. van Lenthe, W. Wu, D. L. Cooper, Y. Mo, M. Raimondi, J. Li, and R. McWeeny for their very helpful comments.

Appendix: Some Available VB Softwares

Other than the GVB method that is implemented in many packages by now, here are brief descriptions of the main VB softwares we are aware of and with which we had some experience to varying degrees.

The TURTLE Software

TURTLE is a general software[168] that is designed to perform multistructure VB calculations. It can execute either non-orthogonal CI, or non-orthogonal MCSCF calculations with simultaneous optimization of orbitals and coefficients of VB structures. Complete freedom is given to the user to deal with HAOs, BDOs, or OEOs, so that calculations of the VBSCF, SCVB, GMS, BLW, or BOVB can be performed. Currently, TURTLE involves analytical gradients to optimize the energies of individual VB structures or multistructure electronic states with respect to the nuclear coordinates.[169] A parallel version has been developed and implemented using the message-passing interface (MPI), for the sake of making the software portable. Owing to the structure of the SuperCI optimization method, over 99% of the program could be parallelized.[170]

The XMVB Software

The XMVB software[171] is based on the paired-permanent-determinant algorithm of spin-free VB theory and conventional Slater determinant expansion methods, which ensure the efficiency for different systems. The program enables to perform the VBSCF, SCVB, GMS, BLW, BOVB, and VBCI calculations with optimized orbitals defined in any form according to requirements. Particularly, the three pure VB methods, VBSCF, BOVB, and VBCI, described in the section *Pure VB Methods that Use Localized Orbitals*, are implemented as standard methods in the package and can be easily performed by specifying keywords in the input file. XMVB is a stand-alone program, but for flexibility, it can be interfaced to most QM softwares, e.g., GAUSSIAN, GAMESS-US, etc. In addition, it is also feasible to combine XMVB with *ab initio* MO packages to perform hybrid valence bond method calculations, such as VB–DFT, VBPCM, etc. The parallel version of XMVB, based on the Message Passing Interface, is also available.[172]

The CRUNCH Software

The CRUNCH (Computational Resource for Understanding Chemistry) has been written originally in Fortran by Gallup,[173] and recently translated into C.[174] This program can perform multiconfiguration valence bond calculations with fixed orbitals, plus a number of MO-based calculations like RHF, ROHF, UHF (+MP2), Orthogonal CI, and MCSCF.

The VB2000 Software

VB2000[78,175] is an *ab initio* VB package calculations based on the "Algebrant Algorithm."[176] It has also a general implementation of the Group Function (GF) Theory, in which a large molecule is described in terms of its constituent parts of physically identifiable "electron groups"[77] (see the section *Multiconfiguration VB Methods with Optimized Orbitals*). VB2000 can be used for performing non-orthogonal CI, multi-structure VB with optimized orbitals, as well as SCVB, GVB and CASVB calculations in the spirit of Hirao's method[52,53] (see *The CASVB Methods*).

Implementations of VB Methods in Standard Ab Initio Softwares

- VB2000 can be used as a plug-in module for GAMESS(US)[177] and Gaussian98/03[178] so that some of the functionalities of GAMESS and Gaussian can be used for calculating VB wave functions. GAMESS also provides interface (option) for the access of VB2000 module. The Windows version of GAMESS (WinGAMESS) has VB2000 module compiled in, i.e. WinGAMESS is VB2000 ready, although it requires a license to use VB2000 legally.

- TURTLE is implemented in the GAMESS-UK program.[179]
- The CASVB method of Thorsteinsson and coworkers.[48,49] is incorporated in the MOLPRO[180] and in the MOLCAS[181] packages. In addition to the features of the original CASVB method mentioned in section *The CASVB Methods*, the CASVB code also permits fully variational VB calculations, which can be single- or multiconfigurational.
- The BLW and SCF-MI methods are implemented in the GAMESS-US package.[177]

References

1. Heitler, W.; London, F. Z Phys 1927, 44, 455.
2. Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
3. Slater, J. C. Phys Rev 1930, 35, 509.
4. Wheland, G. W. Resonance in Organic Chemistry; Wiley: New York, 1955.
5. Eyring, H.; Polanyi, M. Z Phys Chem 1931, B12, 279.
6. Ellison, F. O. J Am Chem Soc 1963, 85, 3540.
7. Kuntz, P. J. In Models of Theoretical Bonding; Maksic, Z. B., Ed.; Springer-Verlag: Berlin-Heidelberg, 1990; pp. 321–376.
8. Johnston, H. S.; Parr, H. C. J Am Chem Soc 1963, 85, 2544.
9. Truhlar, D. G.; Wyatt, R. E. Adv Chem Phys 1977, 36, 141.
10. Prosser, F.; Hagstrom, S. Int J Quant Chem 1968, 2, 89.
11. Gerratt, J. Adv Atom Mol Phys 1971, 7, 141.
12. Gallup, G. A. Int J Quant Chem 1972, 6, 761, 899.
13. Raimondi, M.; Simonetta, M.; Tantardini, G. F. Comp Phys Rep 1975, 2, 171.
14. Raimondi, M.; Campion, W.; Karplus, M. Mol Phys 1977, 34, 1483.
15. Gallup, G. A.; Vance, R. L.; Collins, J. R.; Norbeck, J. M. Adv Quant Chem 1982, 16, 229.
16. Verbeek, J.; van Lenthe, J. H. Int J Quant Chem 1991, 40, 201.
17. Verbeek, J.; van Lenthe, J. H. J Mol Struct (Theochem) 1991, 229, 115.
18. Li, X.; Zhang, Q. Int J Quant Chem 1989, 36, 599.
19. McWeeny, R. Int J Quant Chem 1988, 34, 25.
20. Li, J.; Wu, W. Theor Chim Acta 1994, 89, 105.
21. Li, J. Theor Chim Acta 1996, 93, 35.
22. Wu, W.; Wu, A.; Mo, Y.; Zhang, Q. Sci China B; 1996, 39, 35 (english edition).
23. Wu, W.; Wu, A.; Mo, Y.; Lin, M.; Zhang, Q. Int J Quant Chem 1998, 67, 287.
24. Verbeek, J., PhD Thesis, Utrecht University, 1990.
25. Shaik, S.; Hiberty, P. C. Rev Comp Chem 2004, 20, 1.
26. Coulson, C. A.; Fischer, I. Phil Mag 1949, 40, 386.
27. Goddard, W. A., III. Phys Rev 1967, 157, 81.
28. Ladner, R. C.; Goddard, W. A., III. J Chem Phys 1969, 51, 1073.
29. Bobrowicz, F. W.; Goddard, W. A., III. In Methods of Electronic Structure Theory, Vol. 4; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; pp. 79–126.
30. Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. Acc Chem Res 1973, 6, 368.
31. Hiberty, P. C.; Cooper, D. L. J Mol Struct (Theochem) 1988, 169, 437.
32. Schultz, P. A.; Messmer, R. P. J Am Chem Soc 1993, 115, 10938.
33. Carter, E. A.; Goddard, W. A., III. J Chem Phys 1988, 88, 3132.
34. Murphy, R. B.; Messmer, R. P. Chem Phys Lett 1991, 183, 443.
35. Murphy, R. B.; Friesner, R. A. Chem Phys Lett 1998, 288, 24.
36. Murphy, R. B.; Pollard, W. T.; Friesner, R. A. J Chem Phys 1997, 106, 5073.
37. Murphy, R. B.; Beachy, M. D.; Friesner, R. A.; Ringnalda, M. N. J Chem Phys 1995, 103, 1481.
38. Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. J Chem Phys 1992, 97, 7637.
39. Cooper, D. L.; Gerratt, J.; Raimondi, M.; Sironi, M.; Thorsteinsson, T. Theor Chim Acta 1993, 85, 261.
40. Sironi, M.; Raimondi, M.; Martinazzo, R.; Gianturco, F. A. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 261–277.
41. Cooper, D. L.; Gerratt, J.; Raimondi, M. Int Rev Phys Chem 1988, 7, 59.
42. Cooper, D. L.; Gerratt, J.; Raimondi, M. In Valence Bond Theory and Chemical Structure; Klein, D. J.; Trinajstic, N., Eds.; Elsevier: Amsterdam, 1990; p. 287.
43. Cooper, D. L.; Gerratt, J.; Raimondi, M. In Topics in Current Chemistry, Vol. 153; Gutman, I.; Cyvin, S. J., Eds.; 1990; p. 41.
44. Penotti, F.; Cooper, D. L.; Gerratt, J.; Raimondi, M. J Mol Struct (Theochem) 1988, 169, 421.
45. Cooper, D. L.; Gerratt, J.; Raimondi, M. Nature 1986, 323, 699.
46. da Silva, E. C.; Gerratt, J.; Cooper, D. L.; Raimondi, M. J Chem Phys 1994, 101, 3866.
47. Raimondi, M.; Sironi, M.; Gerratt, J.; Cooper, D. L. Int J Quant Chem 1996, 60, 225.
48. Thorsteinsson, T.; Cooper, D. L.; Gerratt, J.; Karadakov, P. B.; Raimondi, R. Theor Chim Acta 1996, 93, 343.
49. Cooper, D. L.; Thorsteinsson, T.; Gerratt, J. Adv Quant Chem 1998, 32, 51.
50. Thorsteinsson, T.; Cooper, D. L. Theor Chim Acta 1996, 94, 233.
51. Cooper, D. L.; Karadakov, P. B.; Thorsteinsson, T. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 41–53.
52. Hirao, K.; Nakano, H.; Nakayama, K.; Dupuis, M. J Chem Phys 1996, 105, 9227.
53. Hirao, K.; Nakano, H.; Nakayama, K. Int J Quant Chem 1998, 66, 157.
54. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. Chem Phys 1982, 71, 41.
55. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M. Chem Phys 1982, 71, 51.
56. Foster, J. M.; Boys, S. F. Rev Mod Phys 1960, 32, 300.
57. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. Chem Phys 1982, 71, 65.
58. Schmidt, M. W.; Gordon, M. S. Annu Rev Phys Chem 1998, 49, 233.
59. Löwdin, P. O. Rev Mod Phys 1963, 35, 496.
60. McLean, A. D.; Lengsfield, B. H., III; Pacansky, J.; Ellinger, Y. J Chem Phys 1985, 83, 3567.
61. Jackels, C. F.; Davidson, E. R. J Chem Phys 1976, 64, 2908.
62. Voter, A. F.; Goddard, W. A., III. Chem Phys 1981, 57, 253.
63. Perry, J. K.; Goddard, W. A., III; Ohanessian, G. J Chem Phys 1992, 97, 7560.
64. Voter, A. F.; Goddard, W. A., III. J Chem Phys 1981, 75, 3638.
65. Voter, A. F.; Goddard, W. A., III. J Am Chem Soc 1986, 108, 2830.
66. Hollauer, E.; Nascimento, M. A. C. J Chem Phys 1993, 99, 1207.
67. Hollauer, E.; Nascimento, M. A. C. Chem Phys Lett 1991, 184, 470.
68. Eustatiu, I. G.; Tyliszczak, T.; Hitchcock, A. P.; Turci, C. C.; Rocha, A. B.; Bielschowsky, C. E. Phys Rev A 2000, 61, 042505.
69. Bielschowsky, C. E.; Rocha, A. B. J Chem Phys 2000, 113, 7971.
70. Barbosa, A. G. H.; Nascimento, M. A. C. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 117–142.
71. Hollauer, E.; Nascimento, M. A. C. Chem Phys 1993, 177, 79.

72. Neto, J. D. D.; Nascimento, M. A. C. J. Phys Chem 1996, 100, 15105.
73. McDouall, J. J. W. Theor Chim Acta 1992, 83, 339.
74. McDouall, J. J. W. Theor Chim Acta 1993, 85, 395.
75. Malcom, N. O. J.; McDouall, J. J. W. J Comp Chem 1994, 15, 1357.
76. McDouall, J. J. W. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 227–259.
77. McWeeny, R. Int J Quant Chem 1999, 74, 87.
78. Li, J.; McWeeny, R. Int J Quant Chem 2002, 89, 208.
79. van Lenthe, J. H.; Balint-Kurti, G. G. Chem Phys Lett 1980, 76, 138.
80. van Lenthe, J. H.; Balint-Kurti, G. G. J Chem Phys 1983, 78, 5699.
81. Gianinetti, E.; Raimondi, M.; Tornaghi, E. Int J Quant Chem 1996, 60, 157.
82. Famulari, N.; Gianinetti, E.; Raimondi, M.; Sironi, M. Int J Quant Chem 1998, 69, 151.
83. Famulari, A.; Gianinetti, E.; Raimondi, M.; Sironi, M. Theor Chem Acc 1998, 99, 358.
84. Gianinetti, E.; Vandoni, I.; Famulari, A.; Raimondi, M. Adv Quant Chem 1998, 31, 251.
85. Famulari, A.; Specchio, R.; Sironi, M.; Raimondi, M. J Chem Phys 1998, 108, 3296.
86. Raimondi, M.; Famulari, A.; Gianinetti, E.; Sironi, M.; Specchio, R.; Vandoni, I. Adv Quant Chem 1999, 32, 263.
87. Specchio, R.; Famulari, A.; Sironi, M.; Raimondi, M. J Chem Phys 1999, 111, 6204.
88. Specchio, R.; Famulari, A.; Martinazzo, R.; Raimondi, M. J Chem Phys 2000, 113, 6724.
89. Raimondi, M.; Famulari, A.; Specchio, R.; Sironi, M.; Moroni, F.; Gianinetti, E. J Mol Struct (Theochem) 2001, 573, 25.
90. Calderoni, G.; Cargnoni, F.; Famulari, A.; Raimondi, M. J Phys Chem A 2002, 106, 5521.
91. Mo, Y.; Peyerimhoff, S. D. J Chem Phys 1998, 109, 1687.
92. Mo, Y.; Zhang, Y.; Gao, J. J Am Chem Soc 1999, 121, 5737.
93. Mo, Y.; Gao, J.; Peyerimhoff, S. D. J Chem Phys 2000, 112, 5530.
94. Mo, Y. J Chem Phys 2003, 119, 1300.
95. Mo, Y.; Song, L.; Wu, W.; Zhang, Q. J Am Chem Soc 2004, 126, 3974.
96. Kollmar, H. J Am Chem Soc 1979, 101, 4832.
97. Mo, Y.; Lin, Z. J Chem Phys 1996, 105, 1046.
98. Mo, Y.; Jiao, H.; Lin, Z.; Schleyer, P. v. R. Chem Phys Lett 1998, 289, 383.
99. Mo, Y.; Wu, W.; Zhang, Q. J Chem Phys 2003, 119, 6448.
100. Mo, Y.; Jiao, H.; Schleyer, P. v. R. J Org Chem 2004, 69, 3493.
101. Mo, Y. J Org Chem 2004, 69, 5563.
102. Mo, Y.; Gao, J. J Phys Chem A 2000, 104, 3012.
103. Shaik, S.; Shurki, A. Angew Chem Int Ed Engl 1999, 38, 586.
104. Shaik, S.; Hiberty, P. C. In Theory and Applications of Computational Chemistry: The first 40 years; Dykstra, C. E.; Kim, K. S.; Frenking, G.; Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; pp. 635–668.
105. Mo, Y.; Gao, J. J Comp Chem 2000, 21, 1458.
106. Braïda, B.; Hiberty, P. C. J Am Chem Soc 2004, 126, 14890.
107. Shaik, S.; Danovich, D.; Silvi, B.; Lauvergnat, D. L.; Hiberty, P. C. Chem Eur J 2005, 11, 6358.
108. Hiberty, P. C.; Megret, C.; Song, L.; Wu, W.; Shaik, S. J Am Chem Soc 2006, 128, 2836.
109. Shaik, S.; Wu, W.; Dong, K.; Song, L.; Hiberty, P. C. J Phys Chem A 2001, 105, 8226.
110. Su, P.; Song, L.; Wu, W.; Hiberty, P. C.; Shaik, S. J Am Chem Soc 2004, 126, 13539.
111. van Lenthe, J. H.; Verbeek, J. J Mol Struct (Theochem) 1991, 229, 115.
112. van Lenthe, J. H.; Verbeek, J.; Pulay, P. Mol Phys 1991, 73, 1159.
113. Grein, F.; Chang, T. C. Chem Phys Lett 1971, 12, 44.
114. Banerjee, A.; Grein, F. Int J Quant Chem 1976, 10, 123.
115. Hiberty, P. C.; Flament, J. P.; Noizet, E. Chem Phys Lett 1992, 189, 259.
116. Hiberty, P. C.; Humbel, S.; van Lenthe, J. H.; Byrman, C. P. J Chem Phys 1994, 101, 5969.
117. Hiberty, P. C.; Shaik, S. Theor Chem Acc 2002, 108, 255.
118. Song, L.; Wu, W.; Hiberty, P. C.; Danovich, D.; Shaik, S. Chem Eur J 2003, 9, 4540.
119. Hiberty, P. C.; Humbel, S.; Archirel, P. J Phys Chem 1994, 98, 11697.
120. Wu, W.; Song, L.; Cao, Z.; Zhang, Q.; Shaik, S. J Phys Chem A 2002, 106, 2721.
121. Song, L.; Wu, W.; Zhang, Q.; Shaik, S. J Comp Chem 2004, 25, 472.
122. Song, L.; Wu, W.; Zhang, Q.; Shaik, S. J Phys Chem A 2004, 108, 6017.
123. Shaik, S. S.; Hiberty, P. C. In Theoretical Models of Chemical Bonding, Vol. 4, Maksic, Z. B., Ed.; Springer-Verlag: Berlin-Heidelberg, 1991; pp. 269–322.
124. Hiberty, P. C. In Modern Electronic Structure Theory and Applications in Organic Chemistry; Davidson, E. R., Ed.; World Scientific: River Edge, NJ, 1997; pp. 289–367.
125. Hiberty, P. C. J Mol Struct (Theochem) 1998, 451, 237.
126. Shaik, S.; Schlegel, H. B.; Wolfe, S. Theoretical Aspects of Physical Organic Chemistry: The SN2 Mechanism; Wiley: New York, 1992.
127. Klein, D. J. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 447–502.
128. Malrieu, J. P. In Models of Theoretical Bonding; Maksic, Z. B., Ed.; Springer-Verlag: Berlin-Heidelberg, 1990; pp. 108–136.
129. Matsen, F. A. Acc Chem Res 1978, 11, 387.
130. Ramasesha, S.; Soos, Z. G. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 635–697.
131. Shaik, S. In New Theoretical Concepts for Understanding Organic Reactions; Bertran, J.; Csizmadia, I. G., Eds.; Kluwer: Boston, 1989; pp. 165–217. NATO ASI Series, C267.
132. Wu, W.; Zhong, S. J.; Shaik, S. Chem Phys Lett 1998, 292, 7.
133. Epiotis, N. D.; Larson, J. R.; Eaton, H. L. Lect Notes Chem 1982, 29, 1.
134. Shaik, S. S. J Am Chem Soc 1981, 103, 3692.
135. Pross, A. Theoretical and Physical Principles of Organic Reactivity; Wiley: New York, 1995; pp. 83–124, 235–290.
136. Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. Chem Rev 2001, 101, 1501.
137. van der Lugt, A.; Oosterhoff, L. J. J Am Chem Soc 1969, 91, 6042.
138. Michl, J. Top Curr Chem 1974, 46, 1.
139. Bernardi, F.; Olivucci, M.; Robb, M. Isr J Chem 1993, 33, 265.
140. Robb, M. A.; Garavelli, M.; Olivucci, M.; Bernardi, F. Rev Comp Chem 2000, 15, 87.
141. Shaik, S.; Reddy, A. C. J Chem Soc Faraday Trans 1994, 90, 1631.
142. Zilberg, S.; Haas, Y. Chem Eur J 1999, 5, 1755.
143. Warshel, A.; Weiss, R. M. J Am Chem Soc 1980, 102, 6218.
144. Warshel, A.; Russell, S. T. Q Rev Biophys 1984, 17, 282.
145. Kim, H. J.; Hynes, J. T. J Am Chem Soc 1992, 114, 10508.
146. Shaik, S. J Am Chem Soc 1984, 106, 1227.
147. Hiberty, P. C.; Humbel, S.; Danovich, D.; Shaik, S. J Am Chem Soc 1995, 117, 9003.
148. Braïda, B.; Hiberty, P. C. J Phys Chem A 2000, 104, 4628.
149. Braïda, B.; Lauvergnat, D.; Hiberty, P. C. J Chem Phys 2001, 115, 90.

150. Carter, E. C.; Goddard, W. A., III. J Phys Chem 1986, 90, 998.
151. Trinquier, G.; Malrieu, J. P. J Am Chem Soc 1987, 109, 5303.
152. Karni, M.; Apeloig, Y. J Am Chem Soc 1990, 112, 8589.
153. Danovich, D.; Ogliaro, F.; Karni, M.; Apeloig, Y.; Cooper, D. L.; Shaik, S. Angew Chem Int Ed Engl 2001, 40, 4023.
154. Shaik, S.; Maître, P.; Sini, G.; Hiberty, P. C. J Am Chem Soc 1992, 114, 7861.
155. de Visser, S. P.; Danovich, D.; Wu, W.; Shaik, S. J Phys Chem A 2002, 106, 4961.
156. Danovich, D.; Wu, W.; Shaik, S. J Am Chem Soc 1999, 121, 3165.
157. Ohanessian, G.; Goddard, W. A., III. Acc Chem Res 1990, 23, 386.
158. Galbraith, J. M.; Shurki, A.; Shaik, S. J Phys Chem A 2000, 104, 1262.
159. Shaik, S.; de Visser, S. P.; Kumar, D.; Altun, A.; Thiel, W. Chem Rev 2005, 105, 2279.
160. Derat, E.; Cohen, S.; Shaik, S.; Altun, A.; Thiel, W. J Am Chem Soc 2005, 127, 13611.
161. Firman, T. K.; Landis, C. R. J Am Chem Soc 2001, 123, 1178.
162. Weinhold, F.; Landis, C. Valency and Bonding; Cambridge University Press: New York, NY, 2005.
163. Hiberty, P. C.; Leforestier, C. J Am Chem Soc 1978, 100, 2012.
164. Bachler, V. Theor Chem Acc 1997, 96, 223.
165. Bachler, V. J Comp Chem 2004, 25, 343.
166. Karafiloglou, P.; Malrieu, J. P. Chem Phys 1986, 104, 383.
167. Karafiloglou, P.; Akrivos, P. Chem Phys 1988, 127, 41.
168. Verbeek, J.; Langenberg, J. H.; Byrman, C. P.; Dijkstra, F.; van Lenthe, J. H. TURTLE—A gradient VB/VBSCF program (1998–2004), Theoretical Chemistry Group, Utrecht University, Utrecht. See van Lenthe, J. H.; Dijkstra, F.; Havenith, R. W. A. In Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, 2002; pp. 79–116.
169. Dijkstra, F.; van Lenthe, J. H. J Chem Phys 2000, 113, 2100.
170. Dijkstra, F.; van Lenthe, J. H. J Comp Chem 2001, 22, 665.
171. Song, L.; Wu, W.; Mo, Y.; Zhang, Q. XMVB-01: An ab initio Nonorthogonal Valence Bond Program, Xiamen University, Xiamen, China, 2003. Available at http://ctc.xmu.edu.cn/xmvb/.
172. Song, L.; Mo, Y.; Zhang, Q.; Wu, W. J Comp Chem 2005, 26, 514.
173. Gallup, G. A. Valence Bond Methods; Cambridge University Press: Cambridge, 2002.
174. See the website: http://phy-ggallup.unl.edu/crunch/.
175. Li, J.; Duke, B.; McWeeny, R. VB2000 Version 1.8, SciNet Technologies: San Diego, CA, 2005. Available at www.scinetec.com/.
176. Li, J.; Pauncz, R. Int J Quant Chem 1997, 62, 245.
177. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J Comp Chem 1993, 14, 1347. Available at www.msg.ameslab.gov/GAMESS/GAMESS.html
178. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02, Gaussian, Inc.: Wallingford CT, 2004. Available at www.gaussian.com/.
179. GAMESS-UK is a package of ab initio programs written by Guest, M. F.; van Lenthe, J. H.; Kendrick, J.; Schöffel, K.; Sherwood, P.; Harrison, R. J. with contributions from Amos, R. D.; Buenker, R. J.; Dupuis, M.; Handy, N. C.; Hillier, I. H.; Knowles, P. J.; Bonacic-Koutecky, V.; von Niessen, W.; Saunders, V. R.; Stone, A. The package is derived from the original GAMESS code due to Dupuis, M.; Spangler, D.; Wendoloski, J. NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS), 1980. See: Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J. Mol Phys 2005, 103, 719. Latest version available at www.cfs.dl.ac.uk/gamess-uk/index.shtml.
180. MOLPRO is a package of ab initio programs written by Werner, H.-J.; Knowles, P. J.; Schütz, M.; Lindh, R.; Celani, P.; Korona, T.; Rauhut, G.; Manby, F. R.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklaß, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. Available at www.molpro.net/.
181. MOLCAS Version 5.4, Andersson, K.; Barysz, M.; Bernhardsson, A.; Blomberg, M. R. A.; Cooper, D. L.; Fülscher, M. P.; de Graaf, C.; Hess, B. A.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Nakajima, T.; Neogrády, P.; Olsen, J.; Roos, B. O.; Schimmelpfennig, B.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Stålring, J.; Thorsteinsson, T.; Veryazov, V.; Widmark, P.-O. Lund University, Sweden (2002).