

Atoms in Valence Bond. Method, implementation and application

Atomen in Valence Bond. Methode, uitvoering en
toepassing

(met een samenvatting in het Nederlands)

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Dla mojej ukochanej,
jedynej,
dla mojej Sary.

Contents

1	Introduction	7
2	Valence Bond theory	17
3	Atoms in Valence Bond	25
3.1	Electronic configurations of the atoms	26
3.1.1	One electron wave functions	27
3.1.2	N electron wave functions	28
3.1.3	Orbital occupation expressions of atomic states . . .	30
3.2	Real and Complex wave functions	32
4	Implementing Atoms in VB	35
5	Capturing molecules within AiVB	43
5.1	Methane – CH_4	44
5.2	Ammonia – NH_3	46
5.3	Water – H_2O	48
5.4	Hydroxyl radical – OH	51
5.5	Final conclusions, thoughts and outlook.	54

6	Spin Coupling and Resonance	59
6.1	Introduction	60
6.1.1	Other resonance energy definitions	63
6.1.2	Block Localized Wave function approach	64
6.2	Method	66
6.3	Calculations	70
6.3.1	Results and discussion	71
6.4	Conclusions	75
6.5	Acknowledgements	75
7	A Comparison of Approaches to Estimate the Resonance Energy	81
7.1	Introduction	82
7.2	BLW versus VB	83
7.3	Calculations	86
7.4	Results and Discussion	87
7.4.1	Benzene	87
7.4.2	Basis set dependence	88
7.5	Conclusions	91
7.6	Acknowledgements	91
7.7	How to properly...	92
	Appendix A Complementary information on the results	99
	Appendix B The leading term method	105

CHAPTER 1

Introduction

The end of the XIXth century gave all the reasons for satisfaction with the current state of Physics. It had been divided into particles and electromagnetic waves theories described by simple Isaac Newton's equations and James Clerk Maxwell's equations, respectively. The crisis in classical Physics came with the problems describing the microscopic bodies. The relatively "small" issues and meaningful details, concerning black-body radiation, strange photoelectric effect and mysterious atomic and molecular spectra were left unanswered by the classical Physics. The beginning of the XXth century though, brought answers to these bugging questions. The 14th of December 1900, can be taken as the beginning of the "old quant theory", when Max Planck presented the results of his work on black-body radiation effect. Later on in 1905 Albert Einstein solved the problem of the photoelectric effect and in 1914 Niels Bohr presented his vision of the atom and with a striking accuracy he was able to reproduce the hydrogen spectrum. Work of de Broglie between the years 1923 and 1925 showed the wave-particle duality of every particle (not just photons). His work has been followed by Erwin Schrödinger when, in 1926, he presented his wave

equation which laid the foundations to the wave mechanics (now known as quantum mechanics) used until today.

Quantum mechanics is the basis for the description of phenomena occurring in nature. It explains the phenomena on an atomic scale while due to the atomic or molecular interactions, provides information about the properties of the macroscopic bodies, which we can observe directly with our senses. The newly established formalism of quantum mechanics has been quickly adopted and utilized, with success, in chemistry and physics. Its main idea was the introduction of the wave function Φ , which describes quantum mechanical state of the system under consideration. In general, the wave function $\Phi(\mathbf{x}, t)$ depends on the coordinates (\mathbf{x}) and time (t) and is a solution to the Schrödinger equation, which is an equivalent of the equation of motion in classical mechanics

$$i\frac{h}{2\pi}\frac{\partial}{\partial t}\Phi(\mathbf{x}, t) = \hat{H}\Phi(\mathbf{x}, t), \quad (1.1)$$

where \hat{H} is the energy operator called Hamiltonian, an equivalent to the Hamilton function from the classical mechanics and h is Planck's constant. By restricting the problems to those not depending on time, which are of interest in this work, the wave function Φ can be written as $\Phi(\mathbf{x}, t) = \Psi(\mathbf{x})\Theta(t)$, with $\Psi(\mathbf{x})$ being the solution to the stationary Schrödinger equation, which then takes a form

$$\hat{H}\Psi(\mathbf{x}) = \mathcal{E}\Psi(\mathbf{x}), \quad (1.2)$$

where \mathcal{E} is the eigen value of the Hamiltonian \hat{H} .

Equation 1.2 may seem very easy to solve, at first glance. In practice, the wave function will depend on variables determining the spatial configuration of the system which turns equation 1.2 into a differential equation in many variables. Analytical solutions to this equation are limited to just a few systems like harmonic and Morse oscillators and the hydrogen atom. For the vast majority of problems there are no analytical, explicit solutions, thus approximated solutions have to be found. This uncertainty

might suggest, that quantum chemistry is not a trustworthy tool to understand the physical phenomena. On the contrary, quantum chemistry has many great achievements and successes in the past decades, both in the quantitative and the qualitative description of nature.

From its very beginning, quantum chemistry developed two different, yet equivalent, approaches to describe the electronic structure of molecules in chemistry, namely Molecular Orbital theory (MO) and Valence Bond theory (VB). While they are both applied within the Born-Oppenheimer approximation, they differ in their basic design of the starting wave function Ψ . MO theory has a spectroscopic origin and its wave function is based on delocalized molecular orbitals. Its character however contradicts the general chemical feeling and concept that molecules are composed of atomic fragments (functional groups), which to some extent remain the same from molecule to molecule, e.g. the MOs of propane and butane are quite different from each other, although both molecules contain CH_3 and CH_2 building blocks.

In contrast to MO theory, the VB theory is all about combining atoms to form molecules. A 1916 brilliant publication of Gilbert N. Lewis [1] is considered as an initial force which led to the classical VB formulation. The paper introduced the "rule of eight" (later on known as octet rule) and electron pair bonding concepts and even more importantly, a revolutionary symbol for electron pairing, the colon (:), e.g. H:H . With these concepts and tools, still being taught at the high school or basic university chemistry level, he was able to draw electronic structures for a vast number of molecules involving single, double and triple bonds. This tremendously popular idea of Lewis had a very strong chemical support, which turned research towards understanding the mechanisms behind the electron pair bond. The later developments and studies by Heitler and London led to a paper [2] in which they proposed that the bonding in H_2 comes from the quantum mechanical "resonance" interaction which is due to the two electrons that are allowed to interchange their positions between the two atoms as shown on Figure 1.1.

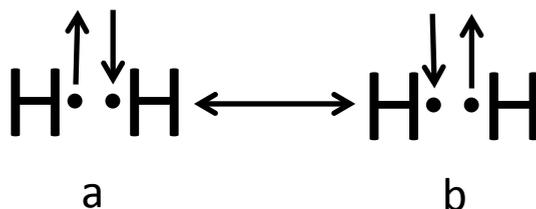


Figure 1.1: Heitler-London's wave function for H_2 . Arrows up and down represent the α and β spins. The $\alpha\beta - \beta\alpha$ interaction describes a chemical bond.

Their approach laid the foundation for the development of the classical Valence Bond theory. Linus Pauling and John C. Slater picked it up, in 1931, where Heitler-London left it and successfully and effectively developed a general quantum chemical theory for polyatomic molecules. Moreover, in the same year they introduced the famous concept of hybridization and a picture of a resonating benzene structures [3–7]. Two years later Pauling brought many improvements and simplifications in the classical VB theory [18] and applied it to more complex compounds. Thanks to Pauling's vision and more simplistic approach in terms of chemically important concepts, the VB theory became popular and was successfully applied in a qualitative way by many. The classical VB theory developed by him was basically the quantum chemical version of Lewis' theory of valence. These aspects still form part of the beauty of the Valence Bond theory, that it is possible to intuitively picture the wave function as a combination of chemically meaningful structures. These things made the VB theory so popular in the 1930s-1950s and brought the theory to its revival since the 1980s.

Pauling applied his simplified VB theory to all known structural chemistry problems of that time and Wheland solved various organic chemistry problems. The easy application and formulation of the problem within this VB theory gained special attention within the organic chemistry world which holds to this day with the modern Valence Bond theory. The methane molecule CH_4 is the basis of all organic compounds. Its

geometry resembles perfectly a tetrahedron and has been well established for decades before any sophisticated experimental techniques for structural examination had been available. The geometry of methane, at the high school or university level of organic chemistry, is explained with help of hybridization and electron promotion concepts, the latter being taken for granted. The question of the main contributing state of a given atom in a particular molecule is often posed, yet no Valence Bond tool is currently available to provide a straightforward answer. The, sometimes abstract, VB structures give no real, chemically important information, for an average user, about the atoms in the molecules and their contributions to the bonding.

The Valence Bond Self Consistent Field method (VBSCF) [8, 9], developed at the Utrecht group of Theoretical Chemistry, has grown in to a general VB purpose program, TURTLE [10], that is now embedded into GAMESS-UK [11]. VBSCF uses a linear combination of spin-adapted VB structures as its wave function. The structures are built as a linear combination of Slater determinants. The orbitals that build one structure are allowed to be mutually nonorthogonal; the orbitals of different structures may also be mutually nonorthogonal. Many of the orbitals in each structure can be chosen to be mutually orthogonal, without posing extra restrictions on the VBSCF wave function. This is for example true for the so-called inactive orbitals that are doubly occupied in all Slater determinants of a structure. Which of the remaining orbitals are allowed to be nonorthogonal and which are forced to be orthogonal is defined by the user. In general, less restrictions on orthogonality implies more computer-time needed for the calculations. The real bottleneck in the VBSCF calculations is computation of hamiltonian matrix elements between Slater-determinants that are expressed in terms of mutually nonorthogonal orbitals. The nonorthogonality of orbitals causes the program to be relatively slow, hence its name TURTLE. The VBSCF program was initially developed by J. Verbeek and J.H. van Lenthe [12] and optimized/extended by a number of PhD students in the group of Van Lenthe [13–16].

Clearly, the aim of the VBSCF approach is not to reach high computational efficiency. A major advantage over more common approaches, which are usually based on a single orthonormal set of orbitals, is that the resulting VBSCF wave function can be written in a compact form. Furthermore, the VBSCF results are close to the chemist's intuition. For example, the weight of each structure can be given a chemical interpretation. Bonding is described by the pairing of spins. Resonance energies may be calculated, for example by comparing the total energy with that of the structure of lowest energy. In contrast, in the more common multi-configuration approaches, like CASSCF (complete active space SCF), the wave functions are expressed in terms of Slater-determinants that are all built from one single orthonormal molecular orbital (MO) set. In CASSCF this MO set is divided into three sub-sets: the inactive set with MOs that are doubly occupied in all Slater-determinants of the wave function; a virtual set that is unoccupied in all Slater-determinants; and finally an active set that is occupied by those electrons that are not in the doubly occupied MOs of the inactive set. The CASSCF wave function contains all possible distributions of these "active" electrons over the active MOs. The CASSCF wave function is invariant with respect to unitary transformations within the set of inactive orbitals, it is also invariant with respect to such transformations within the active orbitals, be it that the weights of the various Slater-determinants change under such transformations. This makes the interpretation of orbitals and weights in a CASSCF wave function less straightforward than the weights and orbitals in a VBSCF wave function. Careful studies have shown, that it is in many cases possible to choose for a particular problem a CASSCF approach and a VBSCF approach that have approximately the same variational space, see e.g. Dijkstra and van Lenthe [17]. Advantages of the CASSCF approach are computational efficiency and simplicity in terms of molecular orbital spaces; advantages of the VBSCF approach are compact wave functions in terms of chemical structures, whose weights can also be given a clear chemical interpretation.

The author's main goal was to develop a new and innovative approach,

within the existing Valence Bond framework, to build and analyze the molecular VB wave function in terms of atoms and their atomic states, in a very user-friendly environment. The entry point for this development process was the work by van Lenthe and Balint-Kurti [8,9] in which they analyzed the possible atomic states of oxygen in hydroxyl radical molecule (OH) for different O-H distances and confronted the resulting dissociation curve with that of Hartree-Fock theory. Their principal idea was to build various VB structures of OH from real, oxygen and hydrogen, atoms, by selecting different atomic states for each, a similar idea that was tried to be grasped before within the Atoms In Molecules (AIM) concept due to Moffit [19]. A new approach to this concept and its possible implementation within an existing VB framework, was presented. Its development started with a brief and basic literature overview of the AIM concept [19–23] and the work of Balint-Kurti and van Lenthe [8,9]. Then a working framework of the program was written to handle a ground state oxygen in the hydroxyl radical, and later on expanded to handle the excited states of oxygen and its projections. After validations and tests the program has been expanded to handle different *sp*-block atoms and applied to a wider range of molecules. The resulting AiVB approach is completely new, addresses questions which have not so far been posed in the literature and touches new aspects of wave function analysis.

The content of this work can be divided into two distinctive parts. The first part will present the Atoms in Valence Bond approach, a completely new concept in Valence Bond theory, while the second part will introduce and compare different, yet well established approaches to estimate the resonance and delocalization energy. The first part consisting of three stages, is collected in five chapters. Stage one (chapter **2**) will introduce a short, historical development review and the basic formalism of the Valence Bond theory. Stage two (chapters **3** and **4**) shall present the ideas and the necessary theoretical tools needed when developing the AiVB approach. It will also describe the specific implementation of the AiVB approach within TURTLE [10]. The last stage (chapter **5**) gathers results and their

discussion, of AiVB calculations performed on various, widely used and thoroughly studied molecules. Moreover, it addresses certain aspects of the AiVB which can still be improved. The second part of this work is gathered in two chapters, separately published in two scientific journals. Both chapters contain key aspects and points in a very heated discussion, that took place some time ago, over the difference between delocalization and resonance energy and between various definitions of the resonance energy.

References

- [1] G. N. Lewis, *J. Am. Chem. Soc.* **38** (1916) 762
- [2] W. Heitler, F. London, *Z. Phys.* **44** (1927) 455
- [3] J. C. Slater, *Phys. Rev.* **38** (1931) 1109
- [4] J. C. Slater, *Phys. Rev.* **37** (1931) 481
- [5] J. C. Slater, *Phys. Rev.* **41** (1932) 255
- [6] L. Pauling, *J. Am. Chem. Soc.* **53** (1931) 1367
- [7] L. Pauling, *J. Am. Chem. Soc.* **53** (1931) 3225
- [8] J. H. van Lenthe, G. G. Balint-Kurti, *Chem. Phys. Lett.* **76** (1980) 138
- [9] J. H. van Lenthe, G. G. Balint-Kurti, *J. Chem. Phys.* **78** (1983) 5699
- [10] J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, J. Engelberts, M. L. Zielinski, Z. Rashid, J. H. van Lenthe, *TURTLE: Ab-Initio VB/VBCF Program*, Utrecht, 1988-2012
- [11] M. F. Guest, I. J. Bush, H. J. J. van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A. Havenith, J. Kendrick, *Mol. Phys.* **103** (2005) 719

-
- [12] J. Verbeek, *Nonorthogonal Orbitals in Ab Initio Many-Electron Wave functions.*, Ph. D. Thesis, Utrecht University (1990)
- [13] C. P. Byrman, *Nonorthogonal Orbitals in Chemistry.*, Ph. D. Thesis, Utrecht University (1995)
- [14] F. Dijkstra, *Valence Bond Theory. Implementation and use of analytical gradients.*, Ph. D. Thesis, Utrecht University (2000)
- [15] M. L. Zielinski, *Atoms in Valence Bond. Method, Implementation and Application.*, Ph. D. Thesis, Utrecht University (2012)
- [16] Z. Rashid, work in progress, Ph. D. Thesis, Utrecht University (2013)
- [17] F. Dijkstra, J. H. van Lenthe, *Int. J. Quant. Chem.* **74** (1999) 213
- [18] L. Pauling, G. W. Wheland, *J. Chem. Phys.* **1** (1933) 362
- [19] W. Moffitt, *Proc. Roy. Soc. A* **210** (1951) 245
- [20] A. C. Hurley, *Proc. Phys. Soc. (London)* **A69** (1956) 49
- [21] T. Arai, *Rev. Mod. Phys.* **32** (1960) 370
- [22] G. G. Balint-Kurti, M. Karplus, *J. Chem. Phys.* **50** (1969) 478
- [23] R. F. W. Bader, *Atoms in molecules : A Quantum Theory.* Clarendon Press, Oxford, (1993)
- [24] M. L. Zielinski, J. H. van Lenthe, *J. Phys. Chem. A* **112** (2008) 13197
- [25] M. L. Zielinski, R. W. A. Havenith, L. W. Jenneskens, J. H. van Lenthe, *Theo. Chem. Acc.* **127** (2010) 19

CHAPTER 2

Valence Bond theory

The early beginnings of Valence Bond theory can be seen in 1916 and in the paper by Lewis [1], predating even the new quantum mechanics. This formed the ideological basis for later developments and generalizations. The earliest and the simplest formulation of VB wave function was given by Heitler [2] and London [3] for the H_2 molecule and is known as the "Heitler-London" (HL) function

$$\Phi_{HL} = \left(1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)\right) [\alpha\beta - \beta\alpha], \quad (2.1)$$

where $1s_a$ and $1s_b$ are atomic orbitals of hydrogen atom a and b , and indices 1 and 2 are numbering the electrons. We also introduced the shorthand notation $[\alpha\beta - \beta\alpha]$ for the two electron spin function $[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$. However, the original HL wave function combines only the covalent structures of H_2 , thus leaving room for its improvement by including ionic structures

$$\begin{aligned} \Phi_{HL+ion} &= c_1 \left(1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)\right) [\alpha\beta - \beta\alpha] \\ &+ c_2 \left(1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)\right) [\alpha\beta - \beta\alpha]. \end{aligned} \quad (2.2)$$

It has been discovered unfortunately, that even for the simple systems like hydrocarbons, the most important contributions can come from the ionic structures, and the rapidly growing number of ionic structures that must be included increases with the size of the system, thus obscuring the original clarity and compactness of the VB theory.

In 1933 another milestone in Valence Bond theory was set by Linus Pauling. In his memorable paper [4] from that year, Pauling set up the benzene problem essentially in the same way as Hückel did in his approach [5–7]. On the basis of assumptions and simplifications from the Hückel approach, he was able to treat the benzene molecule with the relatively simple Slater method [8] for formulating the secular equation, combined with Rumer’s diagrammatic method [14] and rules following from that [10] for finding the matrix elements. His approach made the calculations more feasible, to such extent that they were not restricted to just benzene and a few other simple molecules, but could be easily applied to naphthalene and other conjugated aromatic systems.

In 1949 Coulson and Fisher [11] proposed a significant improvement to the HL-type of wave function for H_2 , introducing distorted atomic orbitals, since then known as the "Coulson-Fischer" (CF) type wave function

$$\Psi_{CF} = (\phi_a\phi_b + \phi_b\phi_a) [\alpha\beta - \beta\alpha], \quad (2.3)$$

$$\phi_a = 1s_a(1) + c1s_b(1), \quad (2.4)$$

$$\phi_b = 1s_b(2) + c1s_a(2). \quad (2.5)$$

The constant c in equations (2.4) and (2.5) is relatively small, however this extra degree of freedom for atomic orbitals allows them to take the optimum shape, and eliminates the need for ionic structures in the case of H_2 .

Our own implementation of Valence Bond theory is called a Valence Bond Self Consistent Field [12,13] method, after Multi-Configurational Self Consistent Field method. The similarity is easily seen for which VBSCF can be, in general, regarded as a non-orthogonal implementation of the

MCSCF method. In general, the molecular VBSCF wave function is a linear combination of VB structures

$$\Psi_{VB} = \sum_i C_i \Phi_i, \quad (2.6)$$

and each structure Φ_i in (2.6) is an antisymmetrized product of one-electron (atomic) orbitals and N-electron spin eigen-function $\Theta(N, S, M_S; i)$ with eigenvalues S and M_S for S^2 and S_z , respectively

$$\Phi_i = \hat{A} \varphi_1 \varphi_2 \dots \varphi_N \Theta(N, S, M_S; i), \quad (2.7)$$

where \hat{A} is the antisymmetrizer.

Application of Rumer's diagrammatic method [14] determines the description of the single bond within the Valence Bond theory. In general, a single bond in a molecule is described by two orbitals, ϕ_1 of atom 1 and ϕ_2 of atom 2, coupled to a singlet, which can be written in the functional form

$$\Psi_{12} = \mathcal{N}(|\varphi_1 \bar{\varphi}_2| - |\bar{\varphi}_1 \varphi_2|), \quad (2.8)$$

where φ_i represents orbital ϕ_i multiplied by an α spin function, $\bar{\varphi}_j$ an orbital ϕ_j multiplied by a β spin function and \mathcal{N} is a normalization constant. This description can be easily extended to describe many single bonds of molecules within the VB framework, e.g. the three π bonds of benzene (Figure 2.1a) are effectively described as an antisymmetrized product of three different functional forms from (2.8)

$$\Psi_{12,34,56} = \mathcal{N} \hat{A} (|\varphi_1 \bar{\varphi}_2| - |\bar{\varphi}_1 \varphi_2|) (|\varphi_3 \bar{\varphi}_4| - |\bar{\varphi}_3 \varphi_4|) (|\varphi_5 \bar{\varphi}_6| - |\bar{\varphi}_5 \varphi_6|). \quad (2.9)$$

The complex mathematical aspects of the VB theory, presented above in equations 2.8 and 2.9, that can be simply visualized with the help of Rumer diagrams (Figure 2.2a), may further be easily related to the real chemical bonds within the molecule (Figure 2.1a) in a way that appeals to every chemist. Moreover, every chemist can easily draw Lewis-type of structures that represent his given chemical system and then easily translate that

to Rumer diagrams which effectively lay the grounds for prospective VB calculations.

The non-orthogonality of the atomic orbitals causes the VB structures to be non-orthogonal to each other. Hence, the square of the coefficient can not anymore be linked with the importance of the given VB structure. However, the relative importance of the given VB structure may be assessed using a weight, that can be computed and assigned to each VB structure. The most popular way to calculate the weight, with which given VB structure takes part in the VB wave function, for non-orthogonal structures, is the one suggested by Chirgwin and Coulson [15]

$$w_k^{CC} = C_k \sum_l S_{kl} C_l, \quad (2.10)$$

where w_k^{CC} is the Chirgwin-Coulson weight for the k th VB structure, C_k and C_l are the coefficients of the k th and l th structure respectively and S_{kl} is the overlap between structures k th and l th. The Chirgwin-Coulson weights add up to one, however nothing prevents them from taking negative values. Another, yet less popular, weight formulation was proposed by Gallup and Norbeck [16], based on the inverse overlap matrix

$$w_k^{GN} = \frac{N_{GN} C_k^2}{(S^{-1})_{kk}}; \quad N_{GN} = \frac{1}{\sum_k C_k^2 / (S^{-1})_{kk}}, \quad (2.11)$$

where w_k^{GN} is the Gallup-Norbeck weight of the k th structure, C_k is the coefficient of the k th structure, S_{kk}^{-1} is a kk th element of the inversed overlap matrix and N_{GN} is the normalization constant. The Gallup-Norbeck weights also add up to one, but more importantly, are positive.

Depending on the orbital occupation scheme, the starting VB structures can be either covalent (Figure 2.1a) or ionic (Figure 2.1b). In this VBSCF approach it is possible to optimize the orbitals φ_j from 2.7 and the structure coefficients C_i from 2.6 (VBSCF employing distorted orbitals¹) or just the structure coefficients (VB Configuration Interaction). The spin

¹first introduced by Coulson and Fischer for the H₂ case [11]

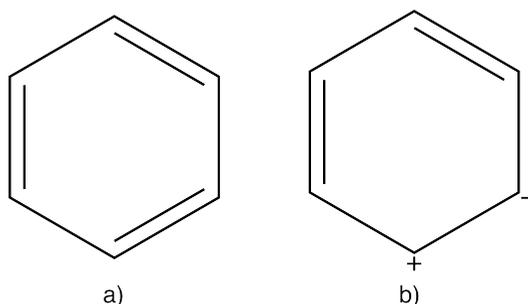


Figure 2.1: *The covalent (Kekulé) A) and ionic B) VB structures of Benzene.*

functions in the VB structures, are mostly generated and visualized, using either the Rumer diagrammatic method [14] (Figure 2.2a) or the Kotani (branching diagrams) method [17] (Figure 2.2b). The Rumer spin functions for the VBSCF approach, as implemented in GAMESS-UK [18], are generated using, the most suitable for computer implementations, leading term method [19]. A simple relationship between the Rumer spin functions, constructed using the leading term method, and the Kotani spin functions was found by Simonetta et al. [19]. The latter can be easily obtained by applying the Schmidt orthogonalization procedure to the former.

Perhaps, the biggest drawback of the VB methods in general is the non-orthogonality of the one-electron atomic orbitals describing each VB structure and its very own wave function that is multi-determinant. The number of determinants describing the entire VB wave function, grows rapidly with the number of bonds (2^n with n being equal to the number of bonds). This problem may be, however, partly overcome by treating either the interesting parts of the molecule or just the interesting bonds, with VB and the rest using MO description. The approach to treat only the interesting bonds, inside the molecule, with VB is very often used in the case of flat, aromatic compounds like benzene, where the core and σ orbitals are described using MO and only the π bonds are described using VB, vide Figure 2.1a and equation 2.9. Such limitations can significantly reduce the number of determinants and therefore the computational ef-

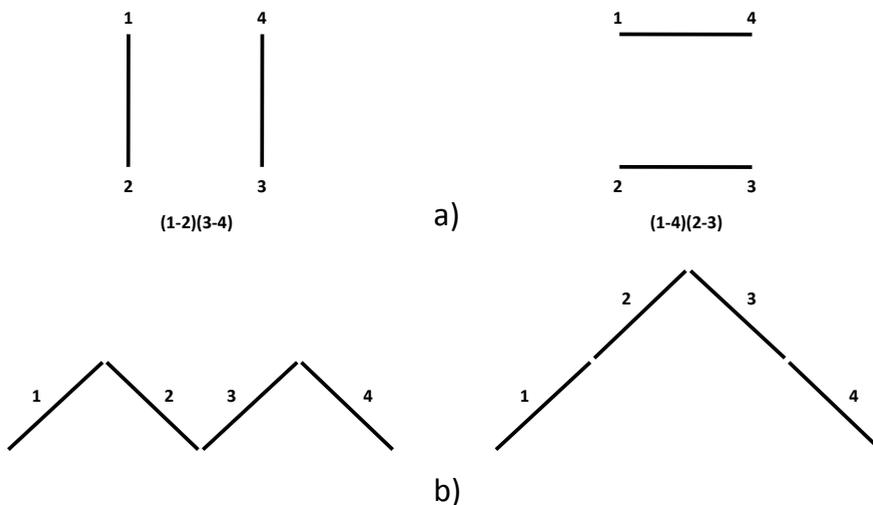


Figure 2.2: Spin-function representation for 4 electrons, with Rumer A) and branching B) diagrams.

fort. The problems with the non-orthogonality of the atomic orbitals arise when the interactions between the determinants need to be calculated. In general, such interactions are calculated using the Löwdin's formula [20]. The most time-consuming part during these calculations, and often the most time-consuming step in the entire VB calculations, is the computation of the cofactors² that appear in numbers in the Löwdin's formula. However, specially derived techniques by Prosser and Hagstrom [21, 22], that were later further developed by Verbeek and van Lenthe [23, 24], significantly reduced the size of the problem and made the calculations even more feasible. For more detailed discussion on this topic I suggest the PhD dissertation by J. Verbeek [25].

The clarity and interpretability of the standard VB wave function is undoubtedly due to the simple relation than can be made between Lewis-type of structure and the Rumer diagram. However, if one wants to describe

²sub-determinant of the overlap matrix reduced by the appropriate columns and rows

realistically the atoms in the molecule, it is rather important to go beyond the simple description of the VB structure.

References

- [1] G. N. Lewis, *J. Am. Chem. Soc.* **38** (1916) 762
- [2] W. Heitler, F. London, *Z. Phys.* **44** (1927) 455
- [3] F. London, *Z. Phys.* **46** (1928) 455
- [4] L. Pauling, G. W. Wheland, *J. Chem. Phys.* **1** (1933) 362
- [5] E. Hückel, *Z. Phys.* **70** (1931) 204
- [6] E. Hückel, *Z. Phys.* **72** (1931) 310
- [7] E. Hückel, *Z. Phys.* **76** (1932) 628
- [8] J. C. Slater, *Phys. Rev.* **38** (1931) 1109
- [9] R. Pauncz, *Spin Eigenfunctions - Construction and Use*, Plenum Press, New York and London, (1979) 77
- [10] L. Pauling, *J. Chem. Phys.* **1** (1933) 280
- [11] C. A. Coulson, I. Fischer, *Philos. Mag.* **40** (1949) 386
- [12] J. H. van Lenthe, G. G. Balint-Kurti, *Chem. Phys. Lett.* **76** (1980) 138
- [13] J. H. van Lenthe, G. G. Balint-Kurti, *J. Chem. Phys.* **78** (1983) 5699
- [14] G. Rumer, *Gottinger Nachr.* **3** (1932) 337
- [15] B. H. Chirgwin, C. A. Coulson, *Proc. R. Soc. London, Ser. A* **201** (1950) 196
- [16] G. A. Gallup, J. M. Norbeck, *Chem. Phys. Lett.* **21** (1973) 495

-
- [17] M. Kotani, A. Amemyia, E. Ishiguro, T. Kimura, *Tables of Molecular Integrals*, Maruzen, Tokyo, (1963)
- [18] M. F. Guest, I. J. Bush, H. J. J. van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A. Havenith, J. Kendrick, *Mol. Phys.* **103** (2005) 719
- [19] M. Simonetta, E. Gianinetti, I. Vandoni, *J. Chem. Phys.* **48** (1968) 1579
- [20] P. O. Löwdin, *Phys. Rev.* **97** (1955) 1474
- [21] F. Prosser, S. Hagstrom, *Int. J. Quant. Chem.* **2** (1968) 89
- [22] F. Prosser, S. Hagstrom, *J. Chem. Phys.* **48** (1968) 4807
- [23] J. Verbeek, J. H. van Lenthe, *Int. J. Quant. Chem.* **40** (1991) 201
- [24] J. Verbeek, J. H. van Lenthe, *J. Mol. Struct. (Theochem)* **229** (1991) 115
- [25] J. Verbeek, *Nonorthogonal Orbitals in Ab Initio Many-Electron Wave functions*, Ph. D. Thesis, Utrecht University (1990)

CHAPTER 3

Atoms in Valence Bond

The Atoms in Valence Bond concept is aimed at understanding the molecular wave function in terms of proper atoms, by generating the molecular VB structures, atom by atom, from proper atomic wave functions (Figure 3.1)

$$\Phi = \hat{A} \prod \psi_{atom}. \quad (3.1)$$

There were many attempts to capture this idea, e.g. that by Moffit and his followers [1–4]. Especially the Quantum Theory of Atoms in Molecules (QTAIM) developed by Bader [5] has become, in the past decades, the theory which addresses the problems regarding chemical systems that can hardly be handled by any other model or theory in Chemistry. The QTAIM theory is among the earliest to recognize the importance and a critical role of electron density in explaining and understanding the experimental observations of chemistry. It connects the fundamental concepts of chemistry like chemical structure, chemical bonding, transferability of func-

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tional groups, and chemical reactivity with the topology of the electron-density distributions. However the difference between those mentioned above and the AiVB approach comes from the very different ansatz.

The procedure to build the molecular AiVB wave function is not arbitrary, and is carried out by specifying the atomic states of the atoms in the different atomic AiVB structures (Figure 3.1). For now we restrict ourselves to atomic orbitals from atomic Hartree-Fock calculations, but this is not a fundamental restriction. All possible projections of the atomic state, for each of the atoms, have to be included as separate VB structures. The AiVB approach extends the standard concept of VB structure, which is limited to a single spin-function in (2.9), in order to realistically describe the atoms in their atomic states. The AiVB structure assumes a more general form

$$\Phi_i = \mathcal{N} \sum_j c_j \Delta_j, \quad (3.2)$$

where now it is a sum of N-electron Slater determinants. The c_j is a fixed expansion coefficient, that is not optimized variationally and \mathcal{N} is the normalization constant. The AiVB structures Φ_i have the good quantum numbers S and M_S of the molecule considered. The Φ_i will have different orbitals for each Slater determinant, however this does not always apply to the spin function. The compactness in many cases might be lost due to this extension, but it is inevitable if a proper description of the atomic states of the atoms is required.

3.1 Electronic configurations of the atoms

In order to understand the AiVB molecular wave function in terms of proper atoms, it is imperative to employ proper atomic wave functions. A proper atomic wave function can be understood as an arrangement of the electrons in the atom, generally referred to as an atomic state or as an orbital occupation scheme and spin coupling scheme, which describes the distribution of the electrons over the atomic orbitals, and is defined

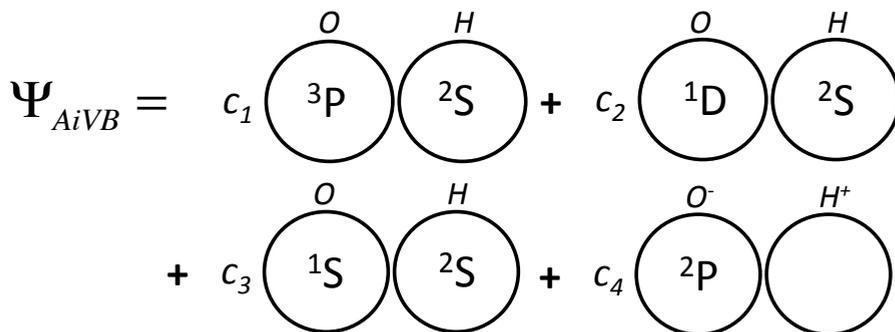


Figure 3.1: A conceptual Atoms in Valence Bond wave function for hydroxyl radical (OH).

by the L , M_L , S and M_S quantum numbers. Their energy depend on L and S only and the corresponding Russel-Saunders term is symbolically written as ^{2S+1}L . The AiVB approach so far has been limited to s and p atomic orbitals and naturally p type orbitals are complex, thus making the whole proper atomic wave functions complex. Since modern *ab initio* methods like VB employ real basis sets during their computation, and there is no 1-to-1 mapping between complex and real atomic orbitals, the atomic states have to be translated into configurations expressed in the real atomic orbitals.

3.1.1 One electron wave functions

An atomic orbital with orbital angular momentum quantum numbers l and m can be written as a radial function $f_{n,l}(r)$ times a spherical harmonic $Y_{lm}(\theta, \phi)$

$$\phi_{n,l,m}(\mathbf{r}) = f_{n,l}(r)Y_{lm}(\theta, \phi), \quad (3.3)$$

where $\mathbf{r} = (x, y, z)$ are the Cartesian coordinates of the electron, which are related to spherical coordinates through $x = r \cos \phi \sin \theta$, $y = r \sin \phi \sin \theta$, and $z = r \cos \theta$. To define the transformation to real wave functions it is

convenient to use regular harmonics

$$R_{lm}(\mathbf{r}) = r^l C_{lm}(\theta, \phi) = r^l \sqrt{\frac{2l+1}{4\pi}} Y_{lm}(\theta, \phi). \quad (3.4)$$

The complex conjugate of a regular harmonic satisfying the Condon and Shortley phase convention [6] is given by

$$R_{lm}(\theta, \phi)^* = (-1)^m R_{l,-m}(\theta, \phi) \quad (3.5)$$

and so for $m = 0$ they are real. For $m > 0$ we define real regular harmonics $R_{lm,c}$ and $R_{lm,s}$ through

$$R_{lm,c} = \frac{1}{\sqrt{2}} [(-1)^m R_{lm} + R_{l,-m}] \quad (3.6)$$

$$iR_{lm,s} = \frac{1}{\sqrt{2}} [(-1)^m R_{lm} - R_{l,-m}] \quad (3.7)$$

Real atomic s and p orbitals, ignoring their radial parts, are given by

$$s \equiv R_{0,0} = 1 \quad (3.8)$$

$$p_x \equiv R_{1,1,c} = x \quad (3.9)$$

$$p_y \equiv R_{1,1,s} = y \quad (3.10)$$

$$p_z \equiv R_{1,0} = z = p_0. \quad (3.11)$$

The $l = 1$ complex orbitals are

$$p_+ \equiv R_{1,1} = \frac{p_x + ip_y}{\sqrt{2}} \quad (3.12)$$

$$p_- \equiv R_{1,-1} = \frac{p_x - ip_y}{\sqrt{2}}. \quad (3.13)$$

For complex conjugation we find $p_+^* = -p_-$.

3.1.2 N electron wave functions

For a p^2 electronic configuration, states with total orbital angular momentum L are given by

$$|p^2; LM\rangle = \sum_{m=-1}^1 \sum_{m'=1}^1 p_m p_{m'} \langle 1, m, 1, m' | L, M \rangle, \quad (3.14)$$

where the factors $\langle 1, m, 1, m' | L, M \rangle$ are Clebsch-Gordan coefficients [7]. They are only nonzero for $m + m' = M$. Complex conjugation gives

$$|p^2; LM\rangle^* = \sum_{m=-1}^1 \sum_{m'=1}^1 p_m^* p_{m'}^* \langle 1, m, 1, m' | L, M \rangle \quad (3.15)$$

$$= \sum_{m=-1}^1 \sum_{m'=1}^1 (-1)^{m+m'} p_{-m} p_{-m'} \langle 1, m, 1, m' | L, M \rangle \quad (3.16)$$

$$= (-1)^M \sum_{m=-1}^1 \sum_{m'=1}^1 p_m p_{m'} \langle 1, -m, 1, -m' | L, M \rangle \quad (3.17)$$

$$= (-1)^{L+M} \sum_{m=-1}^1 \sum_{m'=1}^1 p_m p_{m'} \langle 1, m, 1, m' | L, -M \rangle \quad (3.18)$$

$$= (-1)^{L+M} |p^2; L, -M\rangle, \quad (3.19)$$

where we used

$$\langle l_1 m_1 l_2 m_2 | LM \rangle = (-1)^{l_1+l_2-L} \langle l_1, -m_1 l_2, -m_2 | L, -M \rangle. \quad (3.20)$$

For an N electron configuration with atomic orbital angular momenta (l_1, l_2, \dots, l_N) we derive in a similar way

$$|(l_1, \dots, l_N); LM\rangle^* = (-1)^{L+M+\sum_i l_i} |(l_1, \dots, l_N); L, -M\rangle, \quad (3.21)$$

so real N -electron wave functions $|LM, c\rangle$ and $|LM, s\rangle$ can be constructed for $M > 0$ by

$$|LM; c\rangle = \frac{1}{\sqrt{2}} \left[(-1)^{L+M+\sum_i l_i} |LM\rangle + |L, -M\rangle \right] \quad (3.22)$$

$$i|LM; s\rangle = \frac{1}{\sqrt{2}} \left[(-1)^{L+M+\sum_i l_i} |LM\rangle - |L, -M\rangle \right] \quad (3.23)$$

For $M = 0$ we define

$$|L, 0; c\rangle = |L, 0\rangle, \quad \text{when } (L + \sum_i l_i) \text{ is even} \quad (3.24)$$

$$i|L, 0; s\rangle = |L, 0\rangle, \quad \text{when } (L + \sum_i l_i) \text{ is odd.} \quad (3.25)$$

3.1.3 Orbital occupation expressions of atomic states

The automatic transformation procedure, if any, which would translate the atomic state into configuration expressed in the real atomic orbitals, is undoubtedly complicated, thus all spectroscopically allowed atomic states are manually translated and supplied in the program. Table 3.1 presents expressions for all the spectroscopically allowed atomic states expressed in terms of real atomic orbitals. Configurations of the highest possible value of M_S for the given atomic state, are presented only. Moreover, the closed shell parts have for clarity, been omitted from the Slater determinants presented in this table. The notation of the atomic states, used throughout the table 3.1 is $|(p^N)^{2S+1}L; L, M_L, s/c\rangle$.

Table 3.1: *Orbital occupations of atomic states expressed with real atomic spin orbitals.*

atomic state	orbital occupation of atomic states
$ (s^1)^2S; 0, 0, c\rangle$	$ s $
$ (s^2)^1S; 0, 0, c\rangle$	$ s\bar{s} $
$ (p^1)^2P; 1, 1, c\rangle$	$ p_x $
$ (p^1)^2P; 1, 1, s\rangle$	$ p_y $
$ (p^1)^2P; 1, 0, c\rangle$	$ p_z $
$ (s^1p^3)^5S; 0, 0, c\rangle$	$ s p_x p_y p_z $
$ (p^2)^3P; 1, 1, c\rangle$	$- p_x p_z $
$ (p^2)^3P; 1, 1, s\rangle$	$- p_y p_z $
$ (p^2)^3P; 1, 0, c\rangle$	$ p_x p_y $
$ (p^2)^1D; 2, 2, c\rangle$	$ p_x \bar{p}_x - p_y \bar{p}_y $
$ (p^2)^1D; 2, 2, s\rangle$	$ p_x \bar{p}_y - \bar{p}_x p_y $
$ (p^2)^1D; 2, 1, c\rangle$	$ p_x \bar{p}_z - \bar{p}_x p_z $
$ (p^2)^1D; 2, 1, s\rangle$	$ p_y \bar{p}_z - \bar{p}_y p_z $
$ (p^2)^1D; 2, 0, c\rangle$	$ p_x \bar{p}_x + p_y \bar{p}_y - 2 p_z \bar{p}_z $
$ (p^2)^1S; 0, 0, c\rangle$	$ p_x \bar{p}_x + p_y \bar{p}_y + p_z \bar{p}_z $
$ (p^3)^4S; 0, 0, c\rangle$	$ p_x p_y p_z $
$ (p^3)^2D; 2, 2, c\rangle$	$ p_x \bar{p}_x p_z - p_y \bar{p}_y p_z $

Table 3.1: *continued*

$ (p^3)^2D; 2, 2, s\rangle$	$ p_x \bar{p}_y p_z - \bar{p}_x p_y p_z $
$ (p^3)^2D; 2, 1, c\rangle$	$ p_x p_y \bar{p}_y - p_x p_z \bar{p}_z $
$ (p^3)^2D; 2, 1, s\rangle$	$ p_x \bar{p}_x p_y - p_y p_z \bar{p}_z $
$ (p^3)^2D; 2, 0, c\rangle$	$ p_x \bar{p}_y p_z + \bar{p}_x p_y p_z $ $- 2 p_x p_y \bar{p}_z $
$ (p^3)^2P; 1, 1, c\rangle$	$ p_x p_z \bar{p}_z + p_x p_y \bar{p}_y $
$ (p^3)^2P; 1, 1, s\rangle$	$ p_y p_z \bar{p}_z + p_x \bar{p}_x p_y $
$ (p^3)^2P; 1, 0, c\rangle$	$ p_x \bar{p}_x p_z + p_y \bar{p}_y p_z $
$ (p^4)^3P; 1, 1, c\rangle$	$ p_x p_y \bar{p}_y p_z $
$ (p^4)^3P; 1, 1, s\rangle$	$ p_x \bar{p}_x p_y p_z $
$ (p^4)^3P; 1, 0, c\rangle$	$ p_x p_y p_z \bar{p}_z $
$ (p^4)^1D; 2, 2, c\rangle$	$ p_x \bar{p}_x p_z \bar{p}_z - p_y \bar{p}_y p_z \bar{p}_z $
$ (p^4)^1D; 2, 2, s\rangle$	$ p_x \bar{p}_y p_z \bar{p}_z - \bar{p}_x p_y p_z \bar{p}_z $
$ (p^4)^1D; 2, 1, c\rangle$	$ p_x p_y \bar{p}_y \bar{p}_z - \bar{p}_x p_y \bar{p}_y p_z $
$ (p^4)^1D; 2, 1, s\rangle$	$ p_x \bar{p}_x p_y \bar{p}_z - p_x \bar{p}_x \bar{p}_y p_z $
$ (p^4)^1D; 2, 0, c\rangle$	$ p_x \bar{p}_x p_z \bar{p}_z + p_y \bar{p}_y p_z \bar{p}_z $ $- 2 p_x \bar{p}_x p_y \bar{p}_y $
$ (p^4)^1S; 0, 0, c\rangle$	$ p_x \bar{p}_x p_y \bar{p}_y + p_x \bar{p}_x p_z \bar{p}_z $ $+ p_y \bar{p}_y p_z \bar{p}_z $
$ (p^5)^2P; 1, 1, c\rangle$	$ p_x p_y \bar{p}_y p_z \bar{p}_z $
$ (p^5)^2P; 1, 1, s\rangle$	$ p_x \bar{p}_x p_y p_z \bar{p}_z $
$ (p^5)^2P; 1, 0, c\rangle$	$ p_x \bar{p}_x p_y \bar{p}_y p_z $
$ (p^6)^1S; 0, 0, c\rangle$	$ p_x \bar{p}_x p_y \bar{p}_y p_z \bar{p}_z $

3.2 Real and Complex wave functions for atomic states

The application of the above equations for the translation from the complex to real atomic orbitals can be shown based on the 3P atomic state $|p^2; 11\rangle$

$$|p^2; 11\rangle = |p_+ p_0|. \quad (3.26)$$

Substituting the regular harmonics expressions from (3.11) and (3.12) into (3.26) gives

$$|p^2; 11\rangle = \left| \left(-\frac{1}{\sqrt{2}} \right) (p_x + ip_y) p_z \right| \quad (3.27)$$

and performing simple rearrangements, leads to

$$|p^2; 11\rangle = -\frac{1}{\sqrt{2}} (|p_x p_z| + i|p_y p_z|). \quad (3.28)$$

Similar reasoning and transformations can be performed for the $|p^2; 1 -1\rangle$ part required in (3.22) and (3.23)

$$|p^2; 1 -1\rangle = |p_0 p_-| = \frac{1}{\sqrt{2}} (|p_z p_x| - i|p_y p_z|). \quad (3.29)$$

Substituting both (3.28) and (3.29) to (3.22) and (3.23) yields

$$\begin{aligned} |p^2; 11, c\rangle &= \frac{1}{\sqrt{2}} \left\{ (-1)^4 \left[-\frac{1}{\sqrt{2}} (|p_x p_z| + i|p_y p_z|) \right. \right. \\ &\quad \left. \left. + \frac{1}{\sqrt{2}} (|p_z p_x| - i|p_y p_z|) \right] \right\} \\ &= -|p_x p_z| \end{aligned} \quad (3.30)$$

$$\begin{aligned} i|p^2; 11, s\rangle &= \frac{1}{\sqrt{2}} \left\{ (-1)^4 \left[-\frac{1}{\sqrt{2}} (|p_x p_z| + i|p_y p_z|) \right. \right. \\ &\quad \left. \left. - \frac{1}{\sqrt{2}} (|p_z p_x| - i|p_y p_z|) \right] \right\} \\ &= -|p_y p_z|, \end{aligned} \quad (3.31)$$

thus obtaining the desired atomic state 3P configuration, for $M_L = 1$ and a maximal value of M_S , expressed in real atomic orbitals.

Exactly the same reasoning can be employed to $|(p^2) {}^3P; 10\rangle$. First, the shift down $-L_-$ (shift up $+L_+$) operator has to be applied at the $|(p^2) {}^3p; 11\rangle$ ($|(p^2) {}^3P; 1 -1\rangle$) function

$$\begin{aligned} L_- |p^2; 11\rangle &= L_- |p_+ p_0| \\ &= \sqrt{2} (|p_0 p_0| + |p_+ p_-|) \\ &= \sqrt{2} |p_+ p_-|. \end{aligned} \tag{3.32}$$

Again, substituting expressions in (3.32) with those from (3.12) and (3.13) yields, after performing simple rearrangements,

$$|p^2; 10, c\rangle = i\sqrt{2} |p_x p_y|. \tag{3.33}$$

This straightforward process can be continued for every possible atomic state there is for sp -block atoms, leading to a set of atomic states expressed in real atomic orbitals.

References

- [1] W. Moffitt, *Proc. Roy. Soc. A* **210** (1951) 245
- [2] A. C. Hurley, *Proc. Phys. Soc. (London)* **A69** (1956) 49
- [3] T. Arai, *Rev. Mod. Phys.* **32** (1960) 370
- [4] G. G. Balint-Kurti, M. Karplus, *J. Chem. Phys.* **50** (1969) 478
- [5] R. F. W. Bader, *Atoms in molecules : A Quantum Theory*, Clarendon Press, Oxford, (1993)
- [6] E. U. Condon, G. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, England (1951)
- [7] R. N. Zare, *Angular Momentum*, John Wiley, New York, US (1988)

CHAPTER 4

Implementing Atoms in VB

The translation of the atomic terms into configurations expressed in real atomic orbitals is the very first step before the wave function build-up procedure can even start. The whole process is very complex and much more detailed than the simplified Figure 4.1 shows. Since the AiVB approach is a part of the TURTLE [1] *ab initio* VBSCF program, its implementation is specific and according to the TURTLE requirements, therefore the forthcoming steps (Figure 4.1 A, B, C, D, E and F) could be completely different in other *ab initio* VB programs. The implementation is explained using an AiVB calculation for the hydroxyl radical (OH) molecule, with single atomic states of oxygen (1D) and hydrogen (2S). The choice of the oxygen atomic state is based on the fact, that the example will cover most features of the implementation and will exhibit its flexibility in covering various tricky, technical aspects.

The build up process starts with a declaration as to which particular atomic states of the given atoms should be considered, e.g. oxygen in a 1D state and hydrogen in a 2S state (cf. Table 3.1 for atomic terms configurations). Defining and controlling the molecules, atom by atom, from the

input level for AiVB calculations has been done in a very straightforward way. Thus, for the case considered here as an example, the TURTLE input line for AiVB calculations, defining the OH molecule, boils down to

```
AIVB
CONF
  O 1D
  H 2S
END.
```

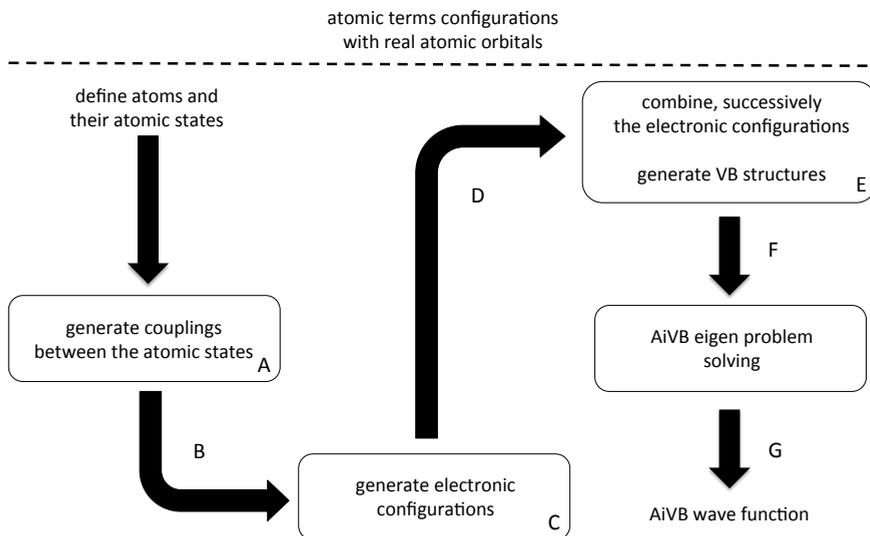


Figure 4.1: *An Atoms in Valence Bond approach step-by-step process scheme.*

The 1D state of Oxygen is determined by two $|(p^4)^1D, 22\rangle$ sub-states, two $|(p^4)^1D, 21\rangle$ sub-states and one $|(p^4)^1D, 20\rangle$ sub-state. Each can be

represented symbolically as

$$\begin{aligned}
 |(p^4)^1D; 2, 2, c\rangle &= \chi_1 - \chi_2, \\
 |(p^4)^1D; 2, 2, s\rangle &= \chi_3 - \chi_4, \\
 |(p^4)^1D; 2, 1, c\rangle &= \chi_5 - \chi_6, \\
 |(p^4)^1D; 2, 1, s\rangle &= \chi_7 - \chi_8, \\
 |(p^4)^1D; 2, 0, c\rangle &= \chi_9 + \chi_{10} - 2\chi_{11},
 \end{aligned}$$

whereas the 2S of hydrogen is simply a $|(s^1)^2S; 00\rangle = \chi_{12}$, and the χ s refer to the different configurations determining the give atomic state (see Table 3.1). In principle, all possible couplings have to be considered (Figure 4.1, A), giving as a result five possible VB structures (Ξ_i)

$$\begin{aligned}
 \Xi_1 &= |(p^4)^1D; 2, 2, c\rangle \otimes |(s^1)^2S; 00\rangle, \\
 \Xi_2 &= |(p^4)^1D; 2, 2, s\rangle \otimes |(s^1)^2S; 00\rangle, \\
 \Xi_3 &= |(p^4)^1D; 2, 1, c\rangle \otimes |(s^1)^2S; 00\rangle, \\
 \Xi_4 &= |(p^4)^1D; 2, 1, s\rangle \otimes |(s^1)^2S; 00\rangle, \\
 \Xi_5 &= |(p^4)^1D; 2, 0, c\rangle \otimes |(s^1)^2S; 00\rangle.
 \end{aligned}$$

At step B (Figure 4.1), each VB structure Ξ_i is defined as

$$\begin{aligned}
 \Xi_1 &= (\chi_1 - \chi_2) \otimes \chi_{12} = \chi_1 \otimes \chi_{12} - \chi_2 \otimes \chi_{12} = X_{1,1} - X_{1,2}, \\
 \Xi_2 &= (\chi_3 - \chi_4) \otimes \chi_{12} = \chi_3 \otimes \chi_{12} - \chi_4 \otimes \chi_{12} = X_{2,1} - X_{2,2}, \\
 \Xi_3 &= (\chi_5 - \chi_6) \otimes \chi_{12} = \chi_5 \otimes \chi_{12} - \chi_6 \otimes \chi_{12} = X_{3,1} - X_{3,2}, \\
 \Xi_4 &= (\chi_7 - \chi_8) \otimes \chi_{12} = \chi_7 \otimes \chi_{12} - \chi_8 \otimes \chi_{12} = X_{4,1} - X_{4,2}, \\
 \Xi_5 &= (\chi_9 + \chi_{10} - 2\chi_{11}) \otimes \chi_{12} = \chi_9 \otimes \chi_{12} + \chi_{10} \otimes \chi_{12} - 2\chi_{11} \otimes \chi_{12} \\
 &= X_{5,1} + X_{5,2} - 2X_{5,3},
 \end{aligned}$$

where $X_{i,j}$ form a set of data required in step C (Figure 4.1).

In the following step (C), each $X_{i,j}$ depends only on one configuration per atom (χ_i) and is considered separately. Thus, for pure convenience, each of the $X_{i,j}$ is transformed into an electron configuration, where each

number represents a given atomic orbital in that particular atom

$$\text{oxygen} \quad : \quad 1 = 1s; 2 = 2s; 3 = 2p_x; 4 = 2p_y; 5 = 2p_z,$$

$$\text{hydrogen} \quad : \quad 6 = 1s,$$

$$\begin{aligned} X_{1,1} &= \hat{A}\chi_1 \otimes \chi_{12} = \hat{A}|1s \bar{1}s \ 2s \ \bar{2}s \ 2p_x \ \bar{2p}_x \ 2p_z \ \bar{2p}_z| \otimes |1s|, \\ &= \mathcal{N}(N_O + N_H) | 1 \bar{1} \ 2 \ \bar{2} \ 3 \ \bar{3} \ 5 \ \bar{5} \ 6 |, \end{aligned} \quad (4.1)$$

$$X_{1,2} = \mathcal{N}(N_O + N_H) | 1 \bar{1} \ 2 \ \bar{2} \ 4 \ \bar{4} \ 5 \ \bar{5} \ 6 |, \quad (4.2)$$

and where electron (atomic state) configuration per atom (χ_i) holds. In equations 4.1 and 4.2, $\mathcal{N}(N_O + N_H)$ is a normalization constant, that depends on the total number of electrons in the system considered. At the D point of the whole starting wave function build-up process, each of the $X_{i,j}$ is expressed as an electron configuration of the whole molecule. The generated set of $X_{i,j}$ determines a starting point for the upcoming step E. At this stage, each VB structure Ξ_i is defined as

$$\begin{aligned} \Xi_1 &= X_{1,1} - X_{1,2} = | 1 \bar{1} \ 2 \ \bar{2} \ 3 \ \bar{3} \ 5 \ \bar{5} \ 6 | - | 1 \bar{1} \ 2 \ \bar{2} \ 4 \ \bar{4} \ 5 \ \bar{5} \ 6 |, \\ \Xi_2 &= X_{2,1} - X_{2,2} = | 1 \bar{1} \ 2 \ \bar{2} \ 3 \ \bar{4} \ 5 \ \bar{5} \ 6 | - | 1 \bar{1} \ 2 \ \bar{2} \ \bar{3} \ 4 \ 5 \ \bar{5} \ 6 |, \\ \Xi_3 &= X_{3,1} - X_{3,2} = | 1 \bar{1} \ 2 \ \bar{2} \ 3 \ 4 \ \bar{4} \ 5 \ \bar{6} | - | 1 \bar{1} \ 2 \ \bar{2} \ \bar{3} \ 4 \ \bar{4} \ 5 \ 6 |, \\ \Xi_4 &= X_{4,1} - X_{4,2} = | 1 \bar{1} \ 2 \ \bar{2} \ 3 \ \bar{3} \ 4 \ \bar{5} \ 6 | - | 1 \bar{1} \ 2 \ \bar{2} \ \bar{3} \ \bar{3} \ 4 \ 5 \ 6 |, \\ \Xi_5 &= X_{5,1} + X_{5,2} - 2X_{5,3} = | 1 \bar{1} \ 2 \ \bar{2} \ 3 \ \bar{3} \ 5 \ \bar{5} \ 6 | + | 1 \bar{1} \ 2 \ \bar{2} \ 4 \ \bar{4} \ 5 \ \bar{5} \ 6 | \\ &\quad - 2| 1 \bar{1} \ 2 \ \bar{2} \ 3 \ \bar{3} \ 4 \ \bar{4} \ 6 |. \end{aligned}$$

At step E, each of the $X_{i,j}$ has to be re-expressed in a format understandable to TURTLE, then combined together to form AiVB structures (Ξ_i) which then will form the starting AiVB wave function (Figure 4.1, F). The re-expressing process covers two certain steps: mark and store the singly occupied orbitals and generate the spin functions. First, each $X_{i,j}$ has to be analyzed and its singly occupied orbitals recognized. Next, the orbital numbers ($\nu_{i,j}(1)$), their ordering positions in $X_{i,j}$ ($\nu_{i,j}(2)$) and their spins ($\nu_{i,j}(3)$) are stored, for TURTLE, as the ν vector

$$\nu_{1,1}(1) = \nu_{1,2}(1) = 6 \quad (\text{the only singly occupied orbital in } X_{1,1})$$

$$\begin{aligned}
\nu_{1,1}(2) &= \nu_{1,2}(2) = 9 && \text{(the position in } X_{1,1} \text{ of that singly occupied} \\
&&& \text{orbital)} \\
\nu_{1,1}(3) &= \nu_{1,2}(3) = 1 && \text{(the spin of that singly occupied orbital,} \\
&&& \text{1 for } \alpha, \text{ 0 for } \beta) \\
\nu_{2,1}(1) &= \{3, 4, 6\} && \nu_{2,2}(1) = \{3, 4, 6\} \\
\nu_{2,1}(2) &= \{5, 6, 9\} && \nu_{2,2}(2) = \{5, 6, 9\} \\
\nu_{2,1}(3) &= \{1, 0, 1\} && \nu_{2,2}(3) = \{0, 1, 1\} \\
\nu_{3,1}(1) &= \{3, 5, 6\} && \nu_{3,2}(1) = \{3, 5, 6\} \\
\nu_{3,1}(2) &= \{5, 8, 9\} && \nu_{3,2}(2) = \{5, 8, 9\} \\
\nu_{3,1}(3) &= \{1, 0, 1\} && \nu_{3,2}(3) = \{0, 1, 1\} \\
\nu_{4,1}(1) &= \{4, 5, 6\} && \nu_{4,2}(1) = \{4, 5, 6\} \\
\nu_{4,1}(2) &= \{7, 8, 9\} && \nu_{4,2}(2) = \{7, 8, 9\} \\
\nu_{4,1}(3) &= \{1, 0, 1\} && \nu_{4,2}(3) = \{0, 1, 1\} \\
\nu_{5,1}(1) &= \nu_{5,2}(1) = \nu_{5,3}(1) = 6 \\
\nu_{5,1}(2) &= \nu_{5,2}(2) = \nu_{5,3}(2) = 9 \\
\nu_{5,1}(3) &= \nu_{5,2}(3) = \nu_{5,3}(3) = 1
\end{aligned}$$

The available set of data is now used in another step, where the spin functions are generated. Using the leading term method [2], that is implemented by default in TURTLE¹, a full set of linearly independent Rumer spin functions [3] is generated and Schmidt-orthogonalized [2] to obtain Kotani (branching diagrams) spin functions [4]. The two starting, singly occupied orbitals, that are stored in the $\nu_{i,j}(1)$ vector for Ξ_2 , Ξ_3 and Ξ_4 , are spin-bound by the transformation procedure from complex to real atomic orbitals described in chapter 3.1 and 3.2 (cf. Table (3.1)). Therefore, only the last electron in that set, bound to $1s$ orbital of the hydrogen, has the freedom of the spin. Hence, only the branching diagram, that match the desired spin pattern of the spin-bound orbitals, stored in $\nu_{i,j}(3)$ vector, is

¹A description, explanation and simple example of the leading-term algorithm can be found in the Appendix B

used for that AiVB structure. In general case, in molecules, that involve more spin unbound orbitals (namely $1s$ of hydrogens), i.e. in methane or ammonia, all branching diagrams with all possible spin couplings of the $1s$ orbitals of hydrogens coupled to the desired multiplicity of the molecule considered, are included as separate AiVB structures.

The above procedure, to seek for and match the corresponding branching diagrams, is applied to every $X_{i,j}$. At the end of step E each $X_{i,j}$ have an assigned branching diagram and is expressed in a block format $|\alpha\alpha\alpha\dots\beta\beta\beta\dots|$, e.g.

$$\begin{aligned}
 X_{1,1} &= \chi_1 \otimes \chi_{12} = | 6 \ 1 \ 2 \ 3 \ 5 \ \bar{1} \ \bar{2} \ \bar{3} \ \bar{5} |, \\
 X_{1,2} &= \chi_2 \otimes \chi_{12} = | 6 \ 1 \ 2 \ 4 \ 5 \ \bar{1} \ \bar{2} \ \bar{4} \ \bar{5} |, \\
 X_{2,1} &= \chi_3 \otimes \chi_{12} = | 6 \ 3 \ 1 \ 2 \ 5 \ \bar{4} \ \bar{1} \ \bar{2} \ \bar{5} |, \\
 X_{2,2} &= \chi_4 \otimes \chi_{12} = | 6 \ 4 \ 1 \ 2 \ 5 \ \bar{3} \ \bar{1} \ \bar{2} \ \bar{5} |, \\
 X_{3,1} &= \chi_5 \otimes \chi_{12} = | 6 \ 3 \ 1 \ 2 \ 4 \ \bar{5} \ \bar{1} \ \bar{2} \ \bar{4} |, \\
 X_{3,2} &= \chi_6 \otimes \chi_{12} = | 6 \ 5 \ 1 \ 2 \ 4 \ \bar{3} \ \bar{1} \ \bar{2} \ \bar{4} |, \\
 X_{4,1} &= \chi_7 \otimes \chi_{12} = | 6 \ 4 \ 1 \ 2 \ 3 \ \bar{5} \ \bar{1} \ \bar{2} \ \bar{3} |, \\
 X_{4,2} &= \chi_8 \otimes \chi_{12} = | 6 \ 5 \ 1 \ 2 \ 3 \ \bar{4} \ \bar{1} \ \bar{2} \ \bar{3} |, \\
 X_{5,1} &= \chi_9 \otimes \chi_{12} = | 6 \ 1 \ 2 \ 3 \ 5 \ \bar{1} \ \bar{2} \ \bar{3} \ \bar{5} |, \\
 X_{5,2} &= \chi_{10} \otimes \chi_{12} = | 6 \ 1 \ 2 \ 4 \ 5 \ \bar{1} \ \bar{2} \ \bar{4} \ \bar{5} |, \\
 X_{5,3} &= \chi_{11} \otimes \chi_{12} = | 6 \ 1 \ 2 \ 3 \ 4 \ \bar{1} \ \bar{2} \ \bar{3} \ \bar{4} |.
 \end{aligned}$$

Later on, the AiVB structures Ξ_i are created by combining the re-expressed $X_{i,j}$ s

$$\begin{aligned}
 \Xi_1 &= X_{1,1} - X_{1,2} = | 6 \ 1 \ 2 \ 3 \ 5 \ \bar{1} \ \bar{2} \ \bar{3} \ \bar{5} | - | 6 \ 1 \ 2 \ 4 \ 5 \ \bar{1} \ \bar{2} \ \bar{4} \ \bar{5} |, \\
 \Xi_2 &= X_{2,1} - X_{2,2} = | 6 \ 3 \ 1 \ 2 \ 5 \ \bar{4} \ \bar{1} \ \bar{2} \ \bar{5} | - | 6 \ 4 \ 1 \ 2 \ 5 \ \bar{3} \ \bar{1} \ \bar{2} \ \bar{5} |, \\
 \Xi_3 &= X_{3,1} - X_{3,2} = | 6 \ 3 \ 1 \ 2 \ 4 \ \bar{5} \ \bar{1} \ \bar{2} \ \bar{4} | - | 6 \ 5 \ 1 \ 2 \ 4 \ \bar{3} \ \bar{1} \ \bar{2} \ \bar{4} |, \\
 \Xi_4 &= X_{4,1} - X_{4,2} = | 6 \ 4 \ 1 \ 2 \ 3 \ \bar{5} \ \bar{1} \ \bar{2} \ \bar{3} | - | 6 \ 5 \ 1 \ 2 \ 3 \ \bar{4} \ \bar{1} \ \bar{2} \ \bar{3} |, \\
 \Xi_5 &= X_{5,1} + X_{5,2} - 2X_{5,3} = | 6 \ 1 \ 2 \ 3 \ 5 \ \bar{1} \ \bar{2} \ \bar{3} \ \bar{5} | + | 6 \ 1 \ 2 \ 4 \ 5 \ \bar{1} \ \bar{2} \ \bar{4} \ \bar{5} | \\
 &\quad - 2| 6 \ 1 \ 2 \ 3 \ 4 \ \bar{1} \ \bar{2} \ \bar{3} \ \bar{4} |,
 \end{aligned}$$

forming the starting AiVB wave function (Figure 4.1, F). The AiVB procedure stops at this point and the formed starting AiVB wave function is used as input for the subsequent subroutines of the VB/VBSCF program. At the end of the whole VB/VBSCF program (Figure 4.1, G), the final AiVB wave function is defined in terms of the AiVB structures Ξ_i and their weights (contributions) to the bonding in the molecule under consideration.

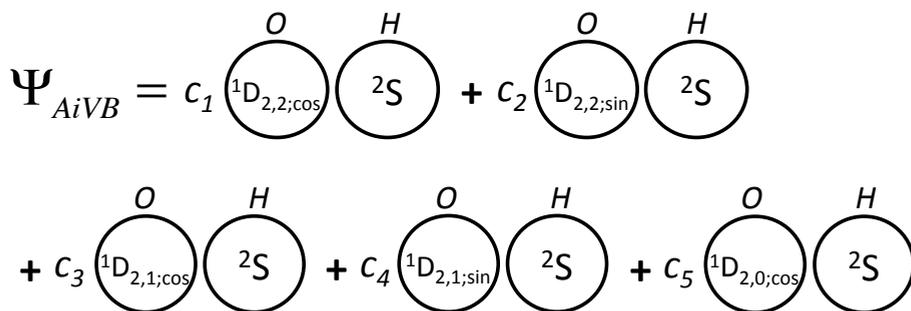


Figure 4.2: An AiVB wave function for case of OH.

It is however very important to note, that in the majority of cases the $X_{i,j}$ can have more singly occupied orbitals than presented in the example here, therefore increasing the number of determinants in the AiVB wave function. The rapid growth of the determinants describing the AiVB wave function and increasing number of the AiVB structures itself, is a very good example of how an AiVB calculation can become complex and get out of hand. On the other hand, the use of molecular point group symmetry may help to limit the number of structures Ξ_i in a AiVB wave function. For the calculations described in this thesis molecular symmetry has only been used to check the outcomes.

References

- [1] J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, J. Engelberts, M. L. Zielinski, Z. Rashid, J. H. van Lenthe, *TURTLE: Ab-Initio VB/VBCF Program*, Utrecht, 1988-2012
- [2] M. Simonetta, E. Gianinetti, I. Vandoni, *J. Chem. Phys.* **48** (1968) 1579
- [3] G. Rumer, *Göttinger Nachr.* **3** (1932) 337
- [4] M. Kotani, A. Amemyia, E. Ishiguro, T. Kimura, *Tables of Molecular Integrals*, Maruzen, Tokyo, (1963)

CHAPTER 5

Capturing molecules within AiVB

The first Atoms in Valence Bond test results were reported already in [1] and are also included in this chapter. The AiVB calculations were carried out for the methane (CH_4), ammonia (NH_3) and water (H_2O) molecules and for the OH radical, using the *ab initio* program TURTLE [2], which has been integrated into the GAMESS-UK [3] package. The geometries of the molecules used during the calculations, were optimized at the MP2/cc-pvtz level and are listed in Table 5.1. All AiVB calculations were carried out with the 6-31G [4] basis set and with VB-local (all orbitals remain localized on the parent atoms) orbital optimization models [5]. No equivalence restrictions were enforced on orbitals and the calculations converged with the Brillouin states' mixing coefficients lower than 10^{-6} . The weights of the AiVB structures are calculated based on the "inverse-overlap" definition due to Gallup-Norbeck [6]

$$w_k = \frac{N_{GN} C_k^2}{(S^{-1})_{kk}}; \quad N_{GN} = \frac{1}{\sum_k C_k^2 / (S^{-1})_{kk}}, \quad (5.1)$$

where w_k is the weight of the k th structure, C_k is that k th structure coefficient, S_{kk}^{-1} is a kk th element of the inversed overlap matrix and N_{GN} is the normalization constant. Complementary information about the results of this Chapter is given in Appendix A.

Table 5.1: Geometries of the considered molecules (lengths in Å), optimized at the MP2/cc-pvtz level.

molecule	methane	ammonia	water	hydroxyl radical
X-H _{<i>n</i>}	CH ₄	NH ₃	H ₂ O	OH
bond length (X-H)	1,0843	1,0088	0,9410	0,9509
angle (H-X-H)	109,5	106,3	105,5	

5.1 Methane – CH₄

The starting wave function of methane for Atoms in Valence Bond calculations is a combination of three different carbon atomic states, namely ³P, ¹D and ⁵S (an electron promotion of one 2s electron to the unoccupied 2p orbital, yields the 2s2p³ configuration). Each of the hydrogens is in its ground, ²S, state. The resulting mixture of above atomic states gave 20 AiVB structures, described with over 300 determinants, that come up for the starting CH₄ AiVB wave function, reported in Table 5.2. The 1s, 2s and xyz (abbreviation for 2p_x2p_y2p_z notation) orbitals are on the carbon, while h₁, h₂, h₃ and h₄ are the 1s orbitals of the four hydrogens. The AiVB approach gives us opportunity to answer questions like, which atomic state of the carbon would contribute the most to the bonding within the methane molecule. The AiVB calculations in this setup are in a position to answer that question. The carbon of the methane molecule has been put at the (0, 0, 0) XYZ coordinates and the remaining hydrogens put in the corners of tetrahedral.

Table 5.2: *The starting AiVB structures of methane.*

constituent atomic states	orbital occupation scheme
$C(^5S) \otimes 4x H(^2S)$	$1s^2 2sxyzh_1h_2h_3h_4$
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 xzh_1h_2h_3h_4$ $1s^2 2s^2 yzh_1h_2h_3h_4$ $1s^2 2s^2 xyh_1h_2h_3h_4$
$C(^1D) \otimes 4x H(^2S)$	$1s^2 2s^2 (x^2 - y^2)h_1h_2h_3h_4$ $1s^2 2s^2 (x\bar{y} - \bar{x}y)h_1h_2h_3h_4$ $1s^2 2s^2 (x\bar{z} - \bar{x}z)h_1h_2h_3h_4$ $1s^2 2s^2 (y\bar{z} - \bar{y}z)h_1h_2h_3h_4$ $1s^2 2s^2 \left((x^2 + y^2) - 2z^2 \right)$ $h_1h_2h_3h_4$

Results and discussion

Table 5.3: *The final weights of AiVB structures for methane. E_{tot} in hartree.*

contributing AiVB structures	multi-structure AiVB local weight
$C(^5S) \otimes 4x H(^2S)$ $1s^2 2sxyzh_1h_2h_3h_4$	0.939902
$C(^3P) \otimes 4x H(^2S)$ $1s^2 2s^2 xyh_1h_2h_3h_4$	0.013924
$C(^1D) \otimes 4x H(^2S)$ $1s^2 2s^2 \left((x^2 + y^2) - 2z^2 \right)$ $h_1h_2h_3h_4$	0.036663
$C(^1D) \otimes 4x H(^2S)$ $1s^2 2s^2 (x^2 - y^2)h_1h_2h_3h_4$	0.009511
	E_{tot} -39.987379

Table 5.3 reports the coefficients and weights of the final methane AiVB structures. These results clearly show the major role of carbons 5S state, contributing more than 90% to the bonding. This state corresponds to the sp^3 configuration of carbon within the methane molecule, which is the assumed and well established, by organic chemists, configuration of carbon

within all saturated organic compounds. The remaining states of carbon, ³P and ¹D, however mixed in small degree with the ⁵S as well. This ⁵S state represents the well known concept in organic chemistry of electron promotion assumed for carbon atom in the organic compounds.

The dissociation of the methane molecule, with hydrogens placed 7Å away from the carbon, exhibits another significant feature of the AiVB approach. Results for this many-structure AiVB calculation show 100% contribution from the ground, ³P, state of the carbon, which is what is to be expected.

5.2 Ammonia – NH₃

Table 5.4: *The starting AiVB structures of ammonia.*

constituent atomic states	orbital occupation scheme
N(⁴ S) ⊗ 3x H(² S)	1s ² 2s ² xyzh ₁ h ₂ h ₃
N(² D) ⊗ 3x H(² S)	1s ² 2s ² (x ² - y ²)zh ₁ h ₂ h ₃
	1s ² 2s ² (x \bar{y} - $\bar{x}y$)zh ₁ h ₂ h ₃
	1s ² 2s ² x(y ² - z ²)h ₁ h ₂ h ₃
	1s ² 2s ² (x ² y - yz ²)h ₁ h ₂ h ₃
	1s ² (2s ² (x \bar{y} + $\bar{x}y$)z - 2(2s ² xy \bar{z}))h ₁ h ₂ h ₃
N(² P) ⊗ 3x H(² S)	1s ² 2s ² x(z ² + y ²)h ₁ h ₂ h ₃
	1s ² 2s ² y(z ² + x ²)h ₁ h ₂ h ₃
	1s ² 2s ² z(x ² + y ²)h ₁ h ₂ h ₃

A very similar approach, to that of methane, can be taken in the case of ammonia. Its starting AiVB wave function was built from combination of three different atomic states of nitrogen (either ⁴S, ²D or ²P) coupled with three hydrogens, each in its ground, ²S state. This yields a set of 17 starting AiVB structures, described with over 200 determinants, reported in Table 5.4. The 1s, 2s and xyz (abbreviation for 2p_x2p_y2p_z notation)

orbitals are on the nitrogen, while h_1 , h_2 and h_3 are the $1s$ orbitals of the three hydrogens. The ionic states of nitrogen were neglected deliberately to allow a direct comparison with the methane calculation. The nitrogen of the ammonia molecule has been put at the origin of the coordinate system with one of the hydrogens being placed on the Z axis.

Just as for methane, the ammonia molecule has been investigated in the direction of, which atomic state of nitrogen contributes the most to the bonding in the ammonia molecule.

Results and discussion

Table 5.5: *The final weights of AiVB structures for ammonia. E_{tot} in hartree.*

contributing AiVB structures		multi-structure AiVB local weight
$N(^4S) \otimes 3x H(^2S)$	$1s^2 2s^2 x y z h_1 h_2 h_3$	0,736732
$N(^2D) \otimes 3x H(^2S)$	$1s^2 2s^2 (x^2 y - y z^2) h_1 h_2 h_3$	0,145297
$N(^2D) \otimes 3x H(^2S)$	$1s^2 2s^2 (x \bar{y} - \bar{x} y) z h_1 h_2 h_3$	0,117970
E_{tot}		-56,020667

The final weights and coefficients of Atoms in Valence Bond calculations performed for ammonia are reported in Table 5.5. The scenario here is similar to that of methane, as ammonias most contributing structure is that with nitrogen in 4S state, corresponding to a $2s^2 2p^3$ orbital occupation scheme. This state contributes almost 74% to the bonding within the ammonia molecule. The mixed-in contributions from two 2D sub-states of nitrogen sum up to approximately 26%. This contribution is considerable and rather manifests the lone-pair of nitrogen effect and the geometry deviation of ammonia from the perfect tetrahedron.

Hypothetically, structures where nitrogen is either N^- or N^{3-} , might make small contributions reflecting the small polarity of the N-H bonds.

The many-structure AiVB calculation for a dissociated ammonia (with hydrogens at 7\AA from the nitrogen) exhibits, again, the same feature as in

case of methane, where the only atomic state of nitrogen, contributing to the bonding in ammonia, is its ⁴S ground state.

5.3 Water – H₂O

Table 5.6: *The starting AiVB structures of water.*

constituent atomic states	orbital occupation scheme
O(³ P) ⊗ 2x H(² S)	1s ² 2s ² y ² xzh ₁ h ₂ 1s ² 2s ² x ² yzh ₁ h ₂ 1s ² 2s ² z ² xyh ₁ h ₂
O(¹ D) ⊗ 2x H(² S)	1s ² 2s ² (x ² - y ²)z ² h ₁ h ₂ 1s ² 2s ² (x \bar{y} - $\bar{x}y$)z ² h ₁ h ₂ 1s ² 2s ² (xy ² \bar{z} - $\bar{x}y^2z$)h ₁ h ₂ 1s ² 2s ² x ² (y \bar{z} - $\bar{y}z$)h ₁ h ₂ 1s ² (2s ² (x ² + y ²)z ² - 2(2s ² x ² y ²))h ₁ h ₂
O(¹ S) ⊗ 2x H(² S)	1s ² 2s ² x ² y ² h ₁ h ₂
O ²⁻ (¹ S) ⊗ 2x H ²⁺	1s ² 2s ² x ² y ² z ²
O ⁻ (² P) ⊗ H(² S) ⊗ H ⁺	1s ² 2s ² xy ² z ² h ₁ 1s ² 2s ² yx ² z ² h ₁ 1s ² 2s ² zx ² y ² h ₁
O ⁻ (² P) ⊗ H ⁺ ⊗ H(² S)	1s ² 2s ² xy ² z ² h ₂ 1s ² 2s ² yx ² z ² h ₂ 1s ² 2s ² zx ² y ² h ₂
O ²⁺ (¹ D) ⊗ 2x H ²⁻ (¹ S)	1s ² 2s ² (x ² - y ²)h ₁ ² h ₂ ² 1s ² 2s ² (x \bar{y} - $\bar{x}y$)h ₁ ² h ₂ ² 1s ² 2s ² (x \bar{z} - $\bar{x}z$)h ₁ ² h ₂ ² 1s ² 2s ² (y \bar{z} - $\bar{y}z$)h ₁ ² h ₂ ² 1s ² (2s ² (x ² + y ²) - 2(2s ² z ²))h ₁ ² h ₂ ²
O ²⁺ (¹ S) ⊗ 2x H ²⁻ (¹ S)	1s ² 2s ² z ² h ₁ ² h ₂ ²
O ⁺ (² D) ⊗ H ⁻ (¹ S) ⊗ H(² S)	1s ² 2s ² (x ² - y ²)zh ₁ ² h ₂ 1s ² 2s ² (x \bar{y} - $\bar{x}y$)zh ₁ ² h ₂

Table 5.6: *continued*

	$1s^2 2s^2 x(y^2 - z^2) h_1^2 h_2$
	$1s^2 2s^2 (x^2 y - yz^2) h_1^2 h_2$
	$1s^2 \left(2s^2 (\bar{x}\bar{y} + \bar{x}\bar{y})z - \right.$
	$\left. 2(2s^2 xy\bar{z}) \right) h_1^2 h_2$
$O^+(^2P) \otimes H^-(^1S) \otimes H(^2S)$	$1s^2 2s^2 x(z^2 + y^2) h_1^2 h_2$
	$1s^2 2s^2 y(z^2 + x^2) h_1^2 h_2$
	$1s^2 2s^2 (x^2 + y^2) z h_1^2 h_2$

The water molecule is very peculiar due to the oxygen atom. The vast variety of atomic states of oxygen and oxygen anions, makes it a very interesting and intriguing study case and puts this problem in a different perspective than those of methane and ammonia. The starting AiVB wave function is a combination of structures built by mixing three different atomic states of O (3P , 1D and 1S) with the 2S of hydrogen, one atomic state of O^{2-} (1S) with hydrogens without electrons, one state of O^- (2P) with one hydrogen in 2S and the other without an electron (this combination is also interchanged giving another set of structures), two of O^{2+} (1D and 1S) with hydrogens in 1S states and two of O^+ (2D and 2P) with hydrogens in 1S and 2S states. This huge mix yields a round number of 30 starting AiVB structures, which are reported in Table 5.6. The $1s$, $2s$ and $2xyz$ (abbreviation for $2p_x 2p_y 2p_z$ notation) orbitals are on the oxygen, while h_1 and h_2 are the $1s$ orbitals of two hydrogens. The water molecule has been set in a XZ plane with hydrogens being equally distanced from both axes.

Results and discussion

Table 5.7: *The final weights of AiVB structures for water. E_{tot} in hartree.*

contributing AiVB structures		multi-structure AiVB local weight
$O(^3P) \otimes 2x H(^2S)$	$1s^2 2s^2 y^2 xz h_1 h_2$	0,349447
$O(^1D) \otimes 2x H(^2S)$	$1s^2 2s^2 (xy^2 \bar{z} - \bar{x}y^2 z) h_1 h_2$	0,086288
$O^{2-}(^1S) \otimes 2x H^{2+}$	$1s^2 2s^2 x^2 y^2 z^2$	0,039708
$O^-(^2P) \otimes H(^2S) \otimes H^+$	$1s^2 2s^2 xy^2 z^2 h_1$	0,262062
$O^-(^2P) \otimes H(^2S) \otimes H^+$	$1s^2 2s^2 zx^2 y^2 h_1$	0,000219
$O^-(^2P) \otimes H^+ \otimes H(^2S)$	$1s^2 2s^2 xy^2 z^2 h_2$	0,000221
$O^-(^2P) \otimes H^+ \otimes H(^2S)$	$1s^2 2s^2 zx^2 y^2 h_2$	0,262055
E_{tot}		-76,015433

The results of the complex and numerically sensitive AiVB-local calculations for water are reported in Table 5.7. The final weights and structure coefficients are presented along with the total energy.

It is perhaps very important to mention that the total energy of AiVB-local water calculations ($-76,015433$ hartree), as set up as here, is lower than the total energy from Hartree-Fock calculations (-75.983644 hartree). This is more of a positive side effect of this AiVB calculation, since the explanation here is parallel with what is observed in a MCSCF or CI type of calculation. There, the lowering in total energy is observed with the expansion of the configuration space (more structures and determinants describing the system). The AiVB calculations here are rather complex, comprising 30 structures built from more than 100 determinants, with comparison to only one determinant describing the water molecule in HF calculations. Hence, it is to be expected that the total AiVB energy converges lower than its HF counterpart.

The biggest contribution to the bonding comes from the ionic structures of oxygen (O^-), with 56%. The slight deviations (10^{-4}) between the weights of structures 4 and 7 and those of 5 and 6 in Table 5.7 are due to

the converging criterion of the Brillouin theorem. It is set throughout all AiVB calculations at 10^{-6} which effectively sets the convergence criterion for the weights at around $10^{-4} - 10^{-5}$. The remaining contributions come from the covalent structures (almost 35% from a ground ^3P state of oxygen). Therefore it is safe to say that the OH bond character is ionic rather than covalent.

Again, the many-structure AiVB calculation for a dissociated water (hydrogens at 7\AA from the oxygen) shows that the only AiVB structure contributing, is that with oxygen in its ^3P ground state.

5.4 Hydroxyl radical – OH

The hydroxyl radical (OH) is the only example which Atoms in Valence Bond results can be validated and compared with existing literature data. Therefore the standard multi-structure AiVB-local and -delocal calculations were supplemented with the AiVB-local calculations done in a special basis set. The basis set was chosen to be the same as the one used in [8], of double-zeta plus polarization quality and made out of gaussian type orbitals. The double-zeta part of the basis was taken from tables of van Duijneveldt [9]. A set of d orbitals (spherical harmonics) on oxygen and a set of p orbitals on hydrogen, both with exponents 1.0, were added to the basis set to provide polarization functions. The O-H bond length for the supplemental calculations is set to 1.85 bohr just as is in [8] and the convergence criterion was set less severe with the Brillouin states' mixing coefficients lower than 10^{-4} . The starting AiVB wave function used in the calculations was built from the structures constructed from the wave functions of the neutral atoms and ions in their different electronic configurations. The combination of O with H, O^- with H^+ and O^+ with H^- gave a round number of 20 AiVB structures for the calculations, all reported in Table 5.8. The goal was to set up the starting AiVB wave function as close to the reference VBSCF wave function in [8] as possible. Since their starting wave function was set up manually, it consisted of some extra

ionic structures¹ improving a description of H^- or O^- , therefore being not entirely in line with ours, however still containing all the most important structures, that AiVB calculations have. The hydroxyl radical diatomic molecule has been put along the Z axis.

Table 5.8: *The starting AiVB structures of the hydroxyl radical.*

constituent atomic states	orbital occupation scheme
$\text{O}(^3\text{P}) \otimes \text{H}(^2\text{S})$	$1s^2 2s^2 y^2 xz h$
	$1s^2 2s^2 x^2 yz h$
	$1s^2 2s^2 z^2 xy h$
$\text{O}(^1\text{D}) \otimes \text{H}(^2\text{S})$	$1s^2 2s^2 (x^2 - y^2) z^2 h$
	$1s^2 2s^2 (x\bar{y} - \bar{x}y) z^2 h$
	$1s^2 2s^2 (xy^2\bar{z} - \bar{x}y^2z) h$
	$1s^2 2s^2 x^2 (y\bar{z} - \bar{y}z) h$
	$1s^2 2s^2 (x^2 z^2 + y^2 z^2 - 2x^2 y^2) h$
$\text{O}(^1\text{S}) \otimes \text{H}(^2\text{S})$	$1s^2 2s^2 x^2 y^2 h$
$\text{O}^+(^2\text{D}) \otimes \text{H}^-(^1\text{S})$	$1s^2 2s^2 (x^2 - y^2) z h^2$
	$1s^2 2s^2 (x\bar{y} - \bar{x}y) z h^2$
	$1s^2 2s^2 x (y^2 - z^2) h^2$
	$1s^2 2s^2 (x^2 y - yz^2) h^2$
	$1s^2 2s^2 (x\bar{y}z + \bar{x}yz - 2xy\bar{z}) h^2$
$\text{O}^+(^2\text{P}) \otimes \text{H}^-(^1\text{S})$	$1s^2 2s^2 (z^2 + y^2) x h^2$
	$1s^2 2s^2 (z^2 + x^2) y h^2$
	$1s^2 2s^2 (x^2 + y^2) z h^2$
$\text{O}^-(^2\text{P}) \otimes \text{H}^+$	$1s^2 2s^2 xy^2 z^2$
	$1s^2 2s^2 x^2 yz^2$
	$1s^2 2s^2 x^2 y^2 z$

¹see [8], chapter III.C for more details

Results and discussion

Table 5.9: *The final weights of AiVB structures for hydroxyl radical. E_{tot} in hartree.*

contributing AiVB structures		multi-structure AiVB local weight
$O(^3P) \otimes H(^2S)$	$1s^2 2s^2 y^2 xz h$	0,577805
$O(^1D) \otimes H(^2S)$	$1s^2 2s^2 (xy^2 \bar{z} - \bar{x}y^2 z) h$	0,131468
$O^-(^2P) \otimes H^+$	$1s^2 2s^2 xy^2 z^2$	0,290727
E_{tot}		-75,378653

Tables 5.9 and 5.10 report weights and coefficients of the AiVB structures composing the AiVB wave function for hydroxyl radical, OH. From the coefficients it is clear that the major contribution to the bonding arises from the two covalent structures of OH (3P and 1D of oxygen mixed with 2S of hydrogen) and from the ionic structure O^-H^+ . The AiVB coefficients in Table 5.10 are in a very good agreement with the literature data of almost 30 years ago [8] and the contributing states (and their projections) to the VB wave function, in both cases, match as well. The visible difference between the structures coefficients of $O^+(^2D) \otimes H^-(^1S)$ can be attributed to the extra ionic structures in the reference VBSCF wave function. All of these interact with the main, five structures causing the structure coefficient deviations with respect to those of AiVB, whereas in the case of the AiVB calculation the main contributing structures do not interact with any of the remaining one. Unfortunately, this behaviour and its different aspects cannot be studied further due to data that are missing from the original publication, e.g. orbitals overlap integrals to study the weights.

Furthermore, we can even say that total energy (E_{tot}) matches. The Hartree-Fock calculations have converged at the total energy values of $-75,361860$ hartree and of $-75,401661$ hartree in the case of standard (6-31G [4] basis set) and supplemental (double zeta due to van Duijneveldt + polarization functions) calculations respectively. In both cases AiVB total

energies are lower than HF total energy, which is a similar effect to the one observed in the case of the water AiVB calculations, where the expansion of configuration space lowers the energy. The OH AiVB calculations may seem a bit less complex than those for water, although still comprising of 20 structures built from 43 determinants, considerably more than the HF calculations. Moreover, the ionic structures are included, as for water, also lowering the energy. To sum up, the hydroxyl radicals bond has more covalent character, but the oxygen anion (O^-) is nonetheless quite important.

Dissociating the hydroxyl radical molecule (hydrogen moved 7\AA away from the oxygen) proves, that the covalent structure of OH, with both atoms in their ground states (3P of oxygen), provides a full description on its own at large nuclear distances.

Table 5.10: Comparison of the Atoms in Valence Bond structures coefficients and total energies (E_{tot} , hartree) of OH with the literature data.

contributing AiVB structures		multi-structure AiVB local coefficient	Balint-Kurti & van Lenthe ^a coefficient
$O(^3P) \otimes H(^2S)$	$1s^2 2s^2 y^2 xzh$	-0,5717	-0,5442
$O(^1D) \otimes H(^2S)$	$1s^2 2s^2 (xy^2 \bar{z} - \bar{x}y^2 z)h$	0,2669	0,2535
$O^+(^2D) \otimes H^-(^1S)$	$1s^2 2s^2 x(y^2 - z^2)h^2$	-0,0667	0,0803
$O^+(^2P) \otimes H^-(^1S)$	$1s^2 2s^2 (z^2 + y^2)xh^2$	-0,0321	-0,0447
$O^-(^2P) \otimes H^+$	$1s^2 2s^2 xy^2 z^2$	-0,3384	0,3399
E_{tot}		-75,4204(51)	-75,4202(25)

^a for more details see [8]

5.5 Final conclusions, thoughts and outlook.

The Atoms in Valence Bond concept [1], as implemented for TURTLE [2] at this moment, is a self contained, working and validated approach to

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build and analyze the molecular VB wave function in terms of atoms. Its basic assumptions of no preconceptions and of restrictions of the starting chemical picture, makes it truly an *ab initio* type of VB calculations, something which did not exist until this time in the Valence Bond theory. Strengths and weaknesses of Valence Bond theory are best summarized in [10] by Murrell and co. " *Valence bond theory relies on chemical intuition for finding suitable valence structures. In some respect, this may seem as an advantage, that chemical experience can be directly introduced into a quantum-chemical calculation. In another respect, however, it is a weakness because it assumes some knowledge of the answer at the start. If chemical intuition is wrong, the VB calculation is wrong. The most valuable calculations are often those whose results refute intuition. In contrast, molecular orbital theory does not make any assumption about the way orbitals are paired in a molecule.*" In this light, AiVB brings a completely new quality, it does not make any assumption about the way orbitals are paired in a molecule and does not require any chemical intuition nor knowledge of the answer at the start.

The computational study, using Atoms in Valence Bond approach, of the model molecules presented in this chapter has exhibited a completely new character of Valence Bond calculations and has shown some interesting results. The AiVB study of methane molecule has reassured us that the high-school concept of electron promotion is not entirely artificial. The *ab initio* AiVB result shows that methane is most stable when carbon has one 2s electron promoted to the empty 2p orbital. Following the results further, a complex AiVB analysis shows a picture of water having more ionic, rather than covalent, character of its O-H bonds. Another conclusion explained with an *ab initio* Atoms in Valence Bond calculation, that is being explained in high school with help of electronegativity.

Regardless, there is still scope for improvements and implementation of new features into it. As it is mentioned in Chapter 3, the current implementation of AiVB is limited to *s* and *p* type atomic orbitals only, hence only molecules built from *sp*-block atoms can be investigated. Ex-

panding the AiVB approach with the d -block atoms is possible, although not necessary. There are 46 possible and spectroscopically allowed atomic states within the d -block atoms, ranging from singlets to sextets and from S states to even I state for d^5 atoms. The complexity of states like F, G, H or I is very hard to guess, but based on the complexity of the present implementation and its limited number of excited states, calculations with such states would result in unrealistic and most likely unfeasible sizes. It is however a challenge for AiVB to expand towards the d -block in the future and this challenge should not be disregarded because of the aforementioned problems. The use of molecular point group symmetry could help to limit the number of structures.

Finally, the atomic orbitals employed throughout the AiVB calculations come from atomic Hartree-Fock calculations and are, indeed, the same for each atomic state of the considered system. Moreover, the atomic orbitals are averaged over the lowest states of the atoms. It would be a very attractive approach to improve the AiVB results by introducing different atomic orbitals for different atomic states. Although a preliminary, working implementation of this feature is already available, the resulting complexity of the calculations combined with very demanding hardware requirements necessitate the exercise of great care and further validation. Such an implementation would be interesting to see applied i.e for the water molecule with O^- -type of structures, where the orbitals for structures with O^- should be more diffused than those of structures with neutral O.

References

- [1] M. L. Zielinski, J. H. van Lenthe, *Chem. Phys. Lett.* **500** (2010) 155
- [2] J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, J. Engelberts, M. L. Zielinski, Z. Rashid, J. H. van Lenthe, *TURTLE: Ab-Initio VB/VBCF Program*, Utrecht, 1988-2012

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- [3] M. F. Guest, I. J. Bush, H. J. J. van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A. Havenith, J. Kendrick, *Mol. Phys.* **103** (2005) 719
- [4] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **56** (1972) 2256
- [5] J. H. van Lenthe, G. G. Balint-Kurti, *Chem. Phys. Lett.* **76** (1980) 138
- [6] G. A. Gallup, J. M. Norbeck, *Chem. Phys. Lett.* **21** (1973) 495
- [7] O. G. Stradella, H. O. Villar, E. A. Castro, *Theoret. Chim. Acta (Berl.)* **70** (1986) 67
- [8] J. H. van Lenthe, G. G. Balint-Kurti, *J. Chem. Phys.* **78** (1983) 5699
- [9] F. B. van Duijneveldt, *IBM Technical Report RJ 945* (1971)
- [10] J. N. Murrell, S. F. A. Kettle, J. M. Tedder, *The Chemical Bond*, John Wiley & Sons, (1985)

CHAPTER 6

Spin Coupling and Resonance

Abstract

The Resonating Block Localized Wave function (RBLW) method is introduced, a resonating modification of the Block Localized Wave functions introduced by Mo et al. [1] This approach allows the evaluation of resonance energies following Pauling's recipe. The method is tested on two model molecules, hexagonal H_6 and benzene. Calculations have been done with (local) and without local restrictions (delocal). Resonance energies for both molecules have been obtained for each type of calculation, in agreement with Pauling's concept. From a comparison of the resonance energies obtained from RBLW and standard Valence Bond calculations, the Resonating Block Localized Wave functions are shown to yield resonance energies close to standard delocalized Valence Bond calculations.

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6.1 Introduction

In the early years of Quantum Mechanics and its applications to Chemistry, scientists concluded that the resonance between two Kekulé structures of benzene, led to its hexagonal symmetry and great stability. This was deemed to be an indisputable fact. Tremendous work during the past decades has, however undermined that belief. For example, in a series of papers [2–10], Shaik *et al.* stated, that the π system of benzene in fact favors a distorted geometry with localized bonds, with the σ system forcing the molecule to be symmetrical. Since the XIX-th century, when Kekulé derived his famous benzene structures [11] (Figure 6.1) until now, the Re-

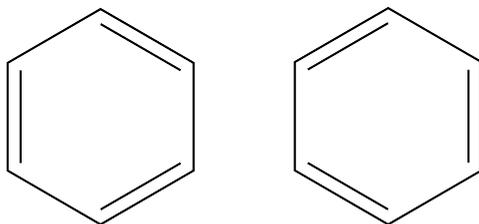


Figure 6.1: *Two possible Kekulé structures of benzene.*

sonance Theory and the Electronic Delocalization of aromatic species has been a source of great confusion among chemists. Even after all these years, with basic concepts like delocalization and Resonance Energy (RE) deeply rooted in the minds of everyone involved, chemists still seek an improvement to the resonance picture [12–17]. In order to understand where this confusion might come from, we first have to understand the basic concept of Pauling’s Resonance Energy (PRE) introduced in the ’30s of XXth century [18], which was a basis for all future development in this area. In this memorable paper, Pauling sets up the benzene problem in essentially the same way as Hückel did in his approach [19–21]. With all the assumptions and simplifications coming from the Hückel approach, he was able to treat the benzene molecule with the relatively simple Slater method [22] for formulating secular equation, combined with Rumer’s diagrammatic

method [23] and rules following from that [24] for finding the matrix elements. The fundamental historical interpretation of the Resonance Energy (PRE) was then defined by Pauling as the difference between the energy of the benzene molecule described with five, resonating Kekulé and Dewar structures and the energy of a single Kekulé structure (Figure 6.2)

$$E_{PRE} = E_{5 \text{ res. struc.}} - E_{1 \text{ Kekule}}. \quad (6.1)$$

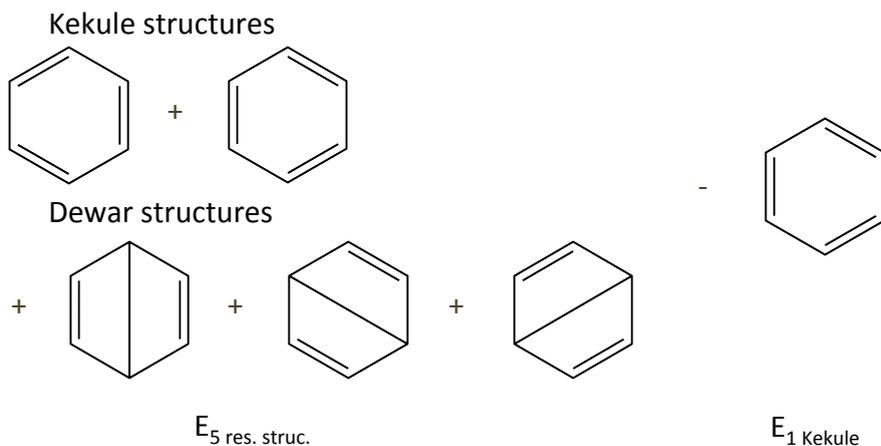


Figure 6.2: Pauling's Resonance Energy definition for benzene.

Based on those calculations, he estimated the resonance energy and predicted quite accurately the contributions of the Kekulé and Dewar structures to the overall energy. No orbital optimization was performed and all energies were calculated with the same set of orbitals.

The introduction of the principal concept of resonance energy by Pauling was not the only important feature of that paper. By application of Rumer's diagrammatic method, the calculations became more feasible, to such an extent that they were not restricted anymore to just benzene and a few other simple aromatic compounds, but could be easily applied to naphthalene and bigger conjugated aromatic systems. Moreover, the utilization of Rumer's method had very important impact on how a single

bond has been described within Valence Bond theory. In the general case, a single bond in a molecule, is described by two orbitals, ϕ_1 of atom 1 and ϕ_2 of atom 2, coupled to a singlet, which can be written in the functional form:

$$\Psi_{12} = N(|\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|), \quad (6.2)$$

where φ_i represents orbital ϕ_i multiplied by an α spin function and $\bar{\varphi}_j$ an orbital ϕ_j multiplied by a β spin function. Extending this idea to the description of a molecule with more than one bond, for example the π -bonds in a single benzene Kekulé structure (Figure 6.3), we find that the resulting $\Psi_{12,34,56}$ function is simply an antisymmetrized product of the three functions in (6.2):

$$\Psi_{12,34,56} = N\hat{A}(|\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|)(|\varphi_3\bar{\varphi}_4| - |\bar{\varphi}_3\varphi_4|)(|\varphi_5\bar{\varphi}_6| - |\bar{\varphi}_5\varphi_6|). \quad (6.3)$$

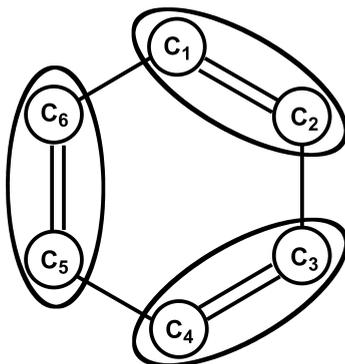


Figure 6.3: π -bond description with highlighted hybrid-like subgroups in the case of benzene Kekulé structure.

The spin-coupling scheme arising from function (6.3) is of special importance in the Valence Bond (VB) method, since one can describe the whole molecule and its covalent bonds, by generating all possible functions of the form (6.3). Because we are interested only in an independent set of these functions, special non-crossing rules are available [23], that can ensure the selection of a proper subset of functions. In all VB methods,

which have been developed over the years, like Generalized Valence Bond (GVB) [25,26], Valence Bond Self Consistent Field (VBSCF) [27,28], Spin-Coupled Valence Bond (SCVB) [29], or Complete Active Space Valence Bond (CASVB) [30–32], spin-coupling is a, sometimes implicit [33, 34], inseparable part.

6.1.1 Other resonance energy definitions

Moving from the early Heitler-London approach [35], in which the Pauling's Resonance Energy was defined, to the modern VB approach, we face difficulties arising from orbital optimization [43,55,56]. Since orbital optimization is required to ensure a consistent answer which does not depend on the start, the original concept is no longer valid, because we would obtain different orbitals for resonating benzene and for one Kekulé benzene structure. Many inconsistencies arose around this, which might be the cause of all the confusion. Thus, many different resonance energy definitions were introduced over the years. In the modern VB approach, Pauling's resonance energy can be defined as a difference between total energy and the energy of the most stable single structure, from the same calculations. We emphasize here the concept "same calculations", which implies that both energies have to be obtained with the same set of orbitals, like in the original idea of Pauling. If one does allow the orbitals to distort, one obtains the Vertical Resonance Energy (VRE) [12,36], which is the energy difference between the molecule lacking resonance, i.e. one Kekulé benzene structure, and that same molecule described by resonating structures, i.e. resonating benzene (Figure 6.4a). The orbitals are optimized but the geometry is kept the same. Perhaps the limit of this approach is reached by employing "breathing orbitals" [15,16]. Finally also the geometry may be optimized yielding the Theoretical Resonance Energy (TRE) [13,42]. Now the geometries of the molecule lacking resonance (1,3,5-cyclohexatriene) and of the molecule with resonance (resonating benzene) are optimized without any constraints, thus giving, for example, different bond lengths for single and double bonds for the former [43] (Figure 6.4b). In all the

models discussed so far the spin-coupling defines the bond as in eq.(6.2).

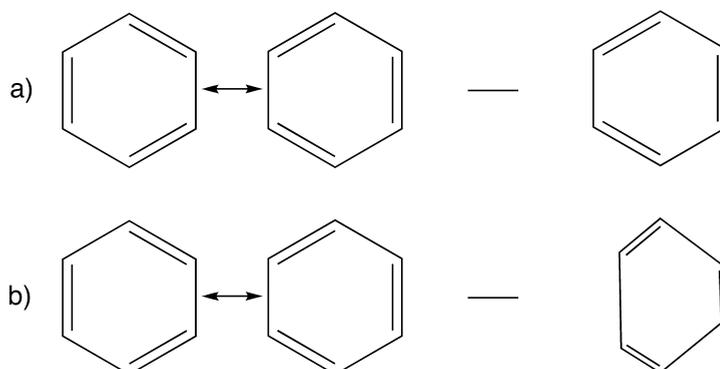


Figure 6.4: Vertical a) and Theoretical b) Resonance Energy definitions in the case of benzene.

6.1.2 Block Localized Wave function approach

Resonance energy is in general an energy difference between the real system described by all possible resonating structures, and its most stable structure. One would thus expect problems defining this concept within the Molecular Orbital (MO) framework, since usually in MO calculations all molecular orbitals are delocalized over the whole system. The first who tried to overcome this problem were Mulliken and Parr [36]. They evaluated the energy of a single Kekulé benzene structure, simply by replacing the three delocalized π MOs in benzene with three non resonating ethylene-like π MOs. Later a similar approach has been used by Daudey et al. [37] and Kollmar [38], who also considered the electronic relaxation of the σ frame, and by Glendening et al. [39]. The delocalized nature of MOs still made those developments impractical, even though the post-SCF analyses such as the Natural Bond Order (NBO) [40, 41] method by Weinhold et al. was able to estimate the delocalization energy. Trying to combine the best of both VB and MO worlds, Mo *et. al.* introduced the Block Localized Wave function method (BLW) [1, 44]. The BLW approach divides all

basis functions into subgroups. All MOs then, are expanded in terms of the basis functions in only one of the subgroups. Full orthogonality of orbitals within given subgroup is imposed, while those belonging to different subgroups are obviously nonorthogonal to each other. The implication of such an approach is, that each bond is described now by one, doubly occupied orbital, and the whole molecular wave function is only one, close shell determinant. This leads to the situation where no explicit spin-coupling between singly occupied orbitals is in use anymore. Considering now the single Kekulé benzene structure from Figure 6.3 and its π bonds only, each ellipse around a π bond represents a given subgroup – a doubly occupied hybrid-like orbital. From the standard hybrid definition [45] we know, that a hybrid is an orbital, localized on one atom, and defined as a linear combination of atomic orbitals belonging to that atom. Now in the case of the BLW approach, each π bond from the considered example in Figure 6.3, is a doubly occupied orbital, or, in fact, a doubly occupied hybrid, but localized over two atomic centers, so it is a linear combination of atomic orbitals belonging to both atoms. Now, assuming that Θ_{ij} represents a hybrid molecular orbital localized over carbon atoms i and j , the whole π system from Figure 6.3 can be described as:

$$\Psi = |\Theta_{12}\bar{\Theta}_{12}\Theta_{34}\bar{\Theta}_{34}\Theta_{56}\bar{\Theta}_{56}|, \quad (6.4)$$

where Θ_{ij} is a linear combination of atomic orbitals, φ_i belonging to atom i and φ_j belonging to atom j :

$$\Theta_{ij} = b_1\varphi_i + b_2\varphi_j, \quad (6.5)$$

and $\bar{\Theta}_{ij}$ represents the same hybrid with opposite spin.

Mo *et. al.* have defined the resonance energy within BLW approach as a difference between the total Hartree-Fock energy of a given molecule and an energy of molecule described within the Block Localized Wave function approach (Figure 6.5a):

$$E_{res-blw} = E_{HF} - E_{BLW}. \quad (6.6)$$

Apart from the mentioned Resonance Energy definitions, which are the most important, and widely used ones, there are many others, which we have not mentioned because this paragraph is not meant to be an exhaustive literature overview on resonance energy definitions.

6.2 Method

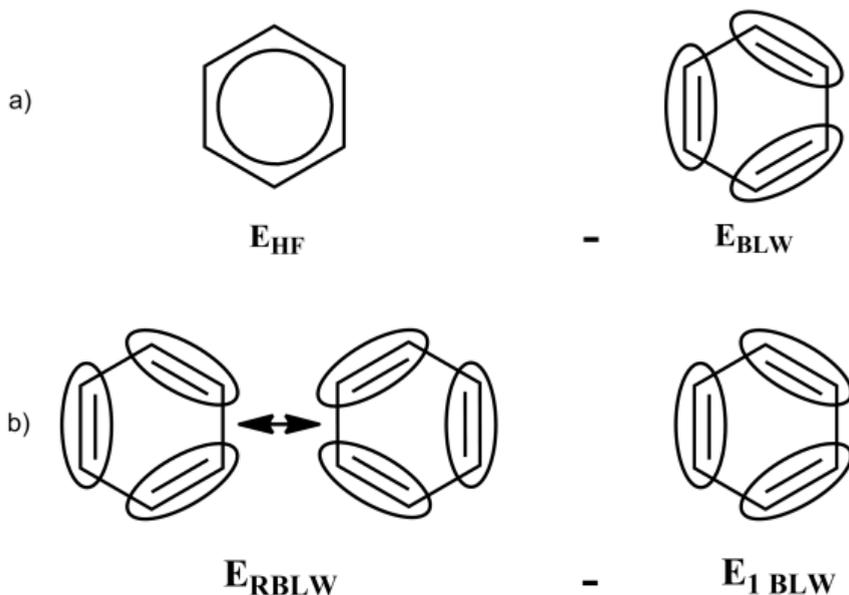


Figure 6.5: Resonance energy definitions within Block Localized Wave function a) and Resonating BLW approach b).

Looking at Valence Bond theory, one can conclude that from its very beginning, VB is based on two major aspects: nonorthogonality and spin-coupling. Since removing the nonorthogonality of orbitals would cause a lack of interaction between the atoms, and removing spin-coupling of the singly occupied orbitals, as another crucial ingredient in Valence Bond calculations, is readily possible, we felt inclined to expand the BLW idea even further.

We believe that Mo's definition of resonance energy, based on Block Localized Wave functions, is heavily basis set dependent [46], *vide infra*, and no explicit resonance is actually present in the wave functions considered. Since the omission of spin-coupling of the singly occupied orbitals in VB calculations seems interesting, we decided to expand the BLW idea into the Resonating Block Localized Wave function approach (RBLW), where we let two, or possibly more, Block Localized Wave functions resonate with each other, just like different structures in standard Valence Bond calculations resonate. By considering two resonating BLW, we can define the resonance energy in agreement with Pauling's concept, just as we define it in standard Valence Bond with spin-coupling. The resonance energy definition, in the case of benzene, in the RBLW approach is defined then as the energy difference between benzene described with both resonating Kekulé-like BLW E_{RBLW} and one, most stable BLW $E_{1\ BLW}$, where both energies come from calculations with the same orbitals (Figure 6.5b), namely the set that is optimized for both resonating, Kekulé-like BLW:

$$E_{res-rblw} = E_{RBLW} - E_{1\ BLW}. \quad (6.7)$$

A consequence of this is that our standard VB approach is affected. As previously mentioned, a bond in BLW approach is described by one, doubly occupied orbital which, in fact, is a doubly occupied hybrid-like block, localized over two atomic centers. Each hybrid-like block is expanded as a linear combination of atomic orbitals belonging to atoms over which given block is localized. By allowing two Kekulé-like block localized wave functions from Figure 6.6a to resonate, a situation is created where two hybrids, of the two Block Localized Wave functions share the same atomic orbitals, a situation not intended in an original hybrid definition. This means that the system is severely over determined, and new orbital schemes had to be devised.

Consider a standard Valence Bond calculation including spin-coupling and an arbitrary wave function $\Psi_0 = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3|$. Then, in the orbital optimization, orbital ϕ_1 can be changed by adding infinitesimal small (δ_{14})

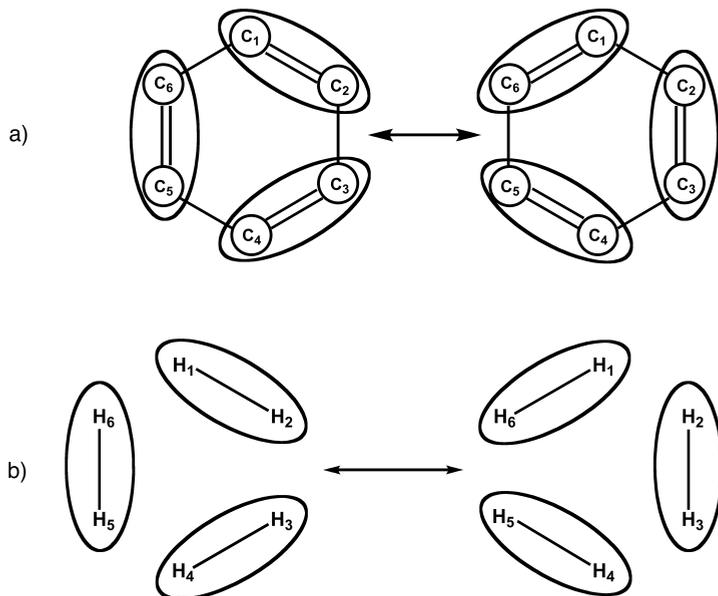


Figure 6.6: Resonating Block Localized Wave functions in the case of benzene a) and hexagonal H_6 b).

part of orbital ϕ_4 :

$$\phi_1 \longrightarrow \phi_1 + \delta_{14}\phi_4. \quad (6.8)$$

Such an orbital change has an impact on Ψ_0 :

$$\Psi_0 = |(\phi_1 + \delta_{14}\phi_4)\overline{(\phi_1 + \delta_{14}\phi_4)}\phi_2\bar{\phi}_2\phi_3|, \quad (6.9)$$

which after simple mathematical perations and neglecting terms with δ_{14}^2 leads to:

$$\Psi_0 = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3| + \delta_{14}C_{1\rightarrow 4}|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3|. \quad (6.10)$$

Operator $C_{1\rightarrow 4}$ is the unnormalized excitation operator which, in this case, replaces orbital ϕ_1 with orbital ϕ_4 , once for α spin and once for β spin per Slater determinant. In general, each $C_{i\rightarrow j}$ operator generates a singly excited Brillouin state Ψ_{ij} , and each of these Brillouin states corresponds to an orbital change. When all possible singly excited Brillouin states Ψ_{ij}

are generated, a Super CI wave function can be created:

$$\Psi_{Super\ CI} = b_0\Psi_0 + \sum_i^n \sum_j^m b_{ij}\Psi_{ij}, \quad (6.11)$$

where i runs over n occupied orbitals, and j runs over m virtual orbitals. If hybrid restrictions are imposed on orbitals, only excitations within given local subgroups are treated, and all other are being discarded. The variational coefficients b_{ij} from eq. (6.11) are being obtained by solving the secular equation

$$(\mathbf{H} - E\mathbf{S})\mathbf{b} = 0, \quad (6.12)$$

and are subsequently used to make improved orbitals. In (6.12), \mathbf{H} and \mathbf{S} are the Hamiltonian and metric matrices in the basis of singly excited states, E is the lowest eigenvalue and \mathbf{b} is the corresponding eigenvector. Upon successful convergence, when the orbitals are optimal, and Ψ_0 coincides with $\Psi_{Super\ CI}$, the coefficients b_{ij} are equal to zero and the generalized Brillouin Theorem is satisfied

$$\langle \Psi_0 | \hat{H} - E_0 | \Psi_{ij} \rangle = 0. \quad (6.13)$$

In practice, molecular orbitals are being mixed with virtual orbitals. The latter are generated from the doubly occupied orbitals, as an orthogonal complement to them

$$1 - \mathbf{c} \cdot \mathbf{c}^\dagger, \quad (6.14)$$

where \mathbf{c} is a matrix containing vectors of occupied orbitals, and $\mathbf{c} \cdot \mathbf{c}^\dagger$ is a projection operator. In this set the (partial) singly occupied are included. For standard Valence Bond calculations we generate one set of virtual orbitals, common for all structures. But now, since different hybrids in the two different Block Localized Wave functions share part of their basis functions, we had to generate separate virtuals for each hybrid-like block, and perform excitations only within the blocks [48]. Of course, in the cases considered, the occupied orbitals are completely equivalent. However due to the overlap of the orbitals and the extreme linear dependency in the

optimization process, even a slight numerical discrepancy can result in the loss of this equivalence. Thus we applied equivalence restrictions [47] to ensure that the orbitals stay equivalent. Setting up these conditions means, in fact, adding all equivalent Brillouin states Ψ_{ij} , and using the resulting mixing coefficient b_{ij} from (6.11) for all the excitations concerned.

An interesting feature of the general hybrid definition, we introduced, is that there are no restrictions on the number of atomic centers over which a given hybrid-like block can be localized. This can be used to aid convergence. In the calculations without local restrictions for hexagonal H_6 and benzene molecules, multi-center hybrid-like blocks, localized over the whole molecule were used to ensure the equivalence of the orbitals.

6.3 Calculations

All VB calculations were performed using the *ab initio* program TURTLE [48], which has been integrated into the GAMESS-UK [49] package. Geometries of the model molecules considered in this paper were optimized in GAMESS-UK using Density Functional Theory [50] with the B3LYP [51] functional in a 6-31G** [52] basis set and are presented in Table 6.1. All VB and RBLW calculations were performed with 6-31G [53] and TZVP(Ahlrichs) [54], basis sets. Throughout all calculations, only Kekulé-like structures were included in the description of hexagonal H_6 and Benzene, since the three Dewar structures contribute only about 6-7% [55, 56] each in case of benzene and they would obscure the view of the resonance of the former structures. For the benzene calculations, the σ orbitals were included in optimization and the $1s$ orbitals of the carbons were kept as frozen core.

Table 6.1: Geometries of the considered molecules (bond lengths in Å).

Molecule	CC1	CC2	HC	Molecule	HH1	HH2
Benzene	1.397	1.397	1.087	H_6 cycled	0.740	0.740

6.3.1 Results and discussion

Hexagonal H_6

In the case of H_6 , a hexagonal arrangement with a fixed H-H bond length of 0.74\AA has been used. The total energies from the Resonating Block Localized Wave function (E_{RBLW}), standard Valence Bond (E_{VB}) calculations, and the energies of the most stable structures from RBLW ($E_{RBLW\ struc}$), VB ($E_{VB\ struc}$) calculations and Hartree-Fock energies (E_{HF}) for 6-31G [53] and tzvp [54] basis sets are presented in Table 6.2. Both types of VB calculation have been done with (local) and without any local restrictions on the orbitals (delocal). We have to emphasize here that local restrictions differ when considering RBLW or VB calculations. In the case of the RBLW method with local restrictions, we are dealing with hybrid-like blocks, localized over two atomic centers. In case of the standard VB calculations, the well known hybrid definition is used, where each hybrid is localized only on one atom [45]. In the delocal calculations, we start from the end-result of the local calculations and no restrictions are used. The orbitals are free to delocalize over the whole molecule. In the case of the RBLW calculations, special care was taken to ensure the equivalence of the orbitals.

Table 6.2: Hexagonal H_6 total energies (hartree).

basis set	6-31G	6-31G	tzvp	tzvp
method	local	delocal	local	delocal
E_{HF}	-3.068967	-3.068967	-3.097497	-3.097497
E_{RBLW}	-2.956032	-3.071512	-2.986240	-3.099904 [†]
$E_{RBLW\ struc}$	-2.764622	-3.025661	-2.812897	-3.054957 [†]
E_{VB}	-2.906863	-3.106965	-2.977412	-3.133662
$E_{VB\ struc}$	-2.774565	-3.052446	-2.865810	-3.081974

[†] Generalized Brillouin Theorem converged at 10^{-4}

Resonance energies according to Pauling from RBLW ($E_{RBLW\ res}$) and VB ($E_{VB\ res}$) calculations are presented in Table 6.3. As expected, both

Kekulé-like structures (Figure 6.6b), have the same weight. Considering the total energies from Hartree-Fock, RBLW and standard VB calculations in the 6-31G [53] basis set with local restrictions (cf. Table 6.3), we can conclude that all "VB" energies are higher than Hartree-Fock energy. The delocalization of the orbitals in the MO calculation provides a better description, due to the complete delocalization, whereas the local restrictions imposed on orbitals in both types of VB calculations, stop them from tailing onto neighboring atoms. We can observe the same effect when moving to bigger basis sets. The total energies obtained from local RBLW calculations are always lower than total energies obtained from local VB calculations, which is due to hybrid-like blocks being localized over two atomic centers in the case of RBLW method as opposed to one atomic center hybrids in the local VB approach.

Table 6.3: *Hexagonal H_6 resonance energies (kcal/mol).*

basis set	method	$E_{RBLW\ res}$	$E_{VB\ res}$
6-31G	local	120.11	83.02
6-31G	delocal	28.77	34.21
tzvp	local	108.78	70.03
tzvp	delocal	28.21 [†]	32.44

[†] Generalized Brillouin Theorem converged at 10^{-4}

Considering now proper RBLW and VB calculations, without any local restrictions (delocal), and comparing their total energies with the Hartree-Fock energy, in the 6-31G [53] basis set (cf. Table 6.2), we see that both VB calculations give lower energies than the Hartree-Fock calculations. For the RBLW calculations it was checked that the Generalized Brillouin Theorem was satisfied without any restrictions after convergence to ensure that the equivalence restrictions did not actually constrain our calculations. The RBLW delocal calculations result in higher energies than standard delocal VB calculations, due to the fact that the BLW functions are Hartree-Fock like, whereas the VB includes electron correlation. Unfortunately, for

the RBLW delocal calculations in the tzvp [54] basis set, the Generalized Brillouin Theorem has converged only to 10^{-4} .

Comparing resonance energies obtained from delocal calculations with the RBLW method (28.77 kcal/mol) and the standard VB method (34.21 kcal/mol) in the 6-31G [53] basis set, and in a bigger basis set, 28.21 kcal/mol and 32.44 kcal/mol for RBLW and VB respectively, we notice that the resonance energies from both calculations behave and are quite similar and rather basis set independent. In contrast to this, the behavior of resonance energies from calculations with local restrictions suggest a heavy basis set dependency [43].

From the definition of hybrids in RBLW method, where two neighboring hybrid-like blocks (each coming from two separate Block Localized Wave functions) overlap, we can expect much bigger overlaps than between two hybrids in standard Valence Bond calculations. That is indeed the case, as the overlap between the RBLW orbitals H1H2 and H6H1 (Figure 6.6b) is approximately 0.84, compared to 0.59 between the orbitals on H1 and H2, both in delocal calculations

Benzene

Table 6.4: *Benzene total energies (hartree).*

basis set	6-31G	6-31G	tzvp	tzvp
method	local	delocal	local	delocal
E_{HF}	-230.623206	-230.623206	-230.769906	-230.769906
E_{RBLW}	-230.564082	-230.626666	-230.696877	-
$E_{RBLW\ struc}$	-230.486581	-230.597931	-230.620422	-
E_{VB}	-230.542991	-230.692657	-230.672199	-230.834378
$E_{VB\ struc}$	-230.499684	-230.660998	-230.627816	-230.803434

We can follow the same reasoning when considering the benzene molecule. From the calculations we obtained the same weights for both Kekulé-like Block Localized Wave functions (Figure 6.6a), as expected. Comparing

the total energies of Hartree-Fock, RBLW and VB delocal calculations in the 6-31G [53] basis set (cf. Table 6.4), again shows that delocal calculations of both VB types give lower total energies than Hartree-Fock calculations. Unfortunately the total energy for RBLW delocal calculations in the tzvp [54] basis set is not available yet, due to program restrictions. Comparison of the total energies from RBLW and VB local calculations in the 6-31G [53] basis set with the Hartree-Fock energy (cf. Table 6.4) also confirms that local calculations of both VB types give higher total energies than Hartree-Fock calculations.

The resonance energies (see Table 6.5) obtained within RBLW (18.03 kcal/mol) and VB (19.87 kcal/mol) (delocal, 6-31G [53]) are almost equal, as was also observed in the case of hexagonal H_6 . As RBLW calculations utilize separate sets of orbitals for hybrid-like blocks per resonating Block Localized Wave function, we might expect resonance energy obtained from RBLW delocal calculations to be close to the one obtained from Breathing Orbital Valence Bond (BOVB) method (-44.13 kcal/mol [43]). However, resonance energies from RBLW delocal calculations are close to those of delocal VB, which might be due to fact that the "breathing" effect in RBLW is compensated for by the extra correlation in normal VB. Resonance energies obtained from RBLW and VB local calculations in the 6-31G basis set [53], 48.63 kcal/mol versus 27.18 kcal/mol, again show large differences between those two types of calculations. Repeating these calculations in a tzvp [54] basis set confirms the results from H_6 , that the resonance energy obtained from both types of VB calculations with local restrictions, is not very basis set dependent.

The overlap of the RBLW orbitals C1C2 (cf. Figure 6.6a) is 0.68, substantially larger than that of the VB orbitals C1 and C2 at 0.53, suggesting that the RBLW orbitals do resemble breathing orbitals [43].

Table 6.5: *Benzene resonance energies (kcal/mol).*

basis set	method	$E_{RBLW\ res}$	$E_{VB\ res}$
6-31G	local	48.63	27.18
6-31G	delocal	18.03	19.87
tzvp	local	47.98	27.85
tzvp	delocal	-	19.42

6.4 Conclusions

Our calculations for the Resonating Block Localized Wave function method show, that removing spin-coupling between singly occupied orbitals, as one of the two crucial ingredients for Valence Bond calculations, is possible and yields perfectly consistent results. Resonance energies obtained from RBLW delocal calculations converge to values obtained by standard VB. Thus by removing spin-coupling and having only resonating closed shell determinants, normal resonance is obtained.

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References

- [1] Y. Mo, S. D. Peyerimhoff, *J. Chem. Phys.* **109** (1998) 1687
- [2] S. S. Shaik, P. C. Hiberty, *J. Am. Chem. Soc.* **107** (1985) 3089
- [3] S. S. Shaik, P. C. Hiberty, J. M. Lefour, G. J. Ohanessian, *J. Am. Chem. Soc.* **109** (1987) 363
- [4] S. S. Shaik, P. C. Hiberty, G. J. Ohanessian, J. M. Lefour, *J. Phys. Chem.* **107** (1988) 3089
- [5] P. C. Hiberty, D. Danovich, A. Shurki, S. S. Shaik, *J. Am. Chem. Soc.* **117** (1994) 7760
- [6] S. S. Shaik, S. Zilberg, Y. Haas, *Acc. Chem. Res.* **29** (1996) 211
- [7] S. S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *J. Am. Chem. Soc.* **118** (1996) 666
- [8] S. S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *J. Mol. Struct. Theochem.* **398/399** (1997) 155
- [9] J. A. Parkhill, K. Lawler, M. Head-Gordon, *J. Chem. Phys.* **130** (2009) 084101
- [10] D. W. Small, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **13** (2011) 19285
- [11] A. Kekulé, *Bull. Soc. Chim. Fr.* **3** (1865) 98
- [12] R. S. Mulliken, *J. Chem. Phys.* **19** (1951) 1271
- [13] M. J. S. Dewar, C. de Llano, *J. Am. Chem. Soc.* **91** (1969) 789
- [14] Y. Mo, W. Wu, Q. Zhang, *J. Phys. Chem.* **98** (1994) 10048
- [15] P. C. Hiberty, S. Humbel, C. P. Byrman, J. H. van Lenthe, *J. Chem. Phys.* **101** (1994) 5969

- [16] P. C. Hiberty, *J. Mol. Struct. Theochem* **35** (1997) 398
- [17] Y. Mo, P. von R. Schleyer, *Chem. Eur. J.* **12** (2006) 2009
- [18] L. Pauling, G. W. Wheland, *J. Chem. Phys.* **1** (1933) 362
- [19] E. Hückel, *Z. Phys.* **70** (1931) 204
- [20] E. Hückel, *Z. Phys.* **72** (1931) 310
- [21] E. Hückel, *Z. Phys.* **76** (1932) 628
- [22] J. C. Slater, *Phys. Rev.* **38** (1931) 1109
- [23] R. Pauncz, *Spin Eigenfunctions - Construction and Use*.
Plenum Press, New York and London, (1979) 77
- [24] L. Pauling, *J. Chem. Phys.* **1** (1933) 280
- [25] W. J. Hunt, P. J. Hay, W. A. Goddard III, *J. Chem. Phys.* **57** (1972)
738
- [26] W. A. Goddard III, L. B. Harding, *Annu. Rev. Phys. Chem.* **29**
(1978) 363
- [27] J. H. van Lenthe, G. G. Balint-Kurti, *Chem. Phys. Lett.* **76** (1980)
138
- [28] J. H. van Lenthe, G. G. Balint-Kurti, *J. Chem. Phys.* **76** (1981) 5699
- [29] D. L. Cooper, J. Gerratt, M. Raimondi, *Nature* **323** (1987) 699
- [30] T. Thorsteinsson, D. L. Cooper, J. Gerratt, P. B. Karadakov, M. Raimondi, *Theor. Chim. Acta* **93** (1996) 343
- [31] T. Thorsteinsson, D. L. Cooper, *Theor. Chim. Acta* **94** (1996) 233
- [32] K. Hirao, M. Dupuis, H. Nakano, K. Nakayama, *J. Chem. Phys.* **105**
(1996) 9227

- [33] G. A. Gallup, R. C. Vance, J. R. Collins, J. M. Norbeck, *Adv. Quantum Chem.* **16** (1982) 229
- [34] G. A. Gallup, *Valence Bond Theory and Chemical Structure*, Amsterdam, (1990) 229
- [35] W. Heitler, F. London, *Z. Phys.* **44** (1927) 455
- [36] R. S. Mulliken, R. G. Parr, *J. Chem. Phys.* **19** (1951) 1271
- [37] J. P. Daudey, G. Trinqueier, J. C. Barthelat, J. P. Malrieu, *Tetrahedron* **36** (1980) 3399
- [38] H. Kollmar, *J. Am. Chem. Soc.* **101** (1979) 4832
- [39] E. D. Glendening, R. Faust, A. Streitwieser, K. P. C. Vollhardt, F. Weinhold, *Tetrahedron* **115** (1993) 952
- [40] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **102** (1980) 7211
- [41] A. E. Reed, L. A. Curtis, F. Weinhold, *Chem. Rev.* **88** (1988) 899
- [42] Y. Mo, W. Wu, Q. Zhang, *J. Phys. Chem.* **98** (1994) 10048
- [43] J. H. van Lenthe, R. W. A. Havenith, F. Dijkstra, L. W. Jenneskens, *Chem. Phys. Lett.* **361** (2002) 203
- [44] Y. Mo, *J. Chem. Phys.* **119** (2003) 1300
- [45] L. Pauling, *J. Am. Chem. Soc.* **53** (1931) 1367
- [46] M. L. Zielinski, R. W. A. Havenith, L. W. Jenneskens, J. H. van Lenthe, *Theo. Chem. Acc.* **127** (2010) 19
- [47] D. R. Yarkony, H. F. Schaefer III, C. F. Bender, *J. Chem. Phys.* **64** (1976) 981
- [48] J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, J. Engelberts, M. L. Zielinski, Z. Rashid, J. H. van Lenthe, *TURTLE: Ab-Initio VB/VBCF Program*, Utrecht, 1988-2012

-
- [49] M. F. Guest, I. J. Bush, H. J. J. van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A. Havenith, J. Kendrick, *Mol. Phys.* **103** (2005) 719
- [50] P. Hohenberg, W. Kohn, *Phys. Rev.* **136** (1964) B864
- [51] A. D. Becke, *J. Chem. Phys.* **98** (1993) 5648
- [52] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **77** (1982) 3654
- [53] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **56** (1972) 2257
- [54] R. Ahlrichs, P. R. Taylor, *J. Chem. Phys.* **78** (1981) 315
- [55] D. L. Cooper, J. Gerratt, M. Raimondi, *M. Adv. Chem. Phys.* **323** (1986) 699
- [56] F. Dijkstra, J. H. van Lenthe, *Int. J. Quantum Chem.* **74** (1999) 213

CHAPTER 7

A Comparison of Approaches to Estimate the Resonance Energy

Abstract

We discuss *ab initio* approaches to calculate the energy lowering (stabilization) due to aromaticity. We compare the valence bond method and the block localized wave function approaches to calculate the resonance energy. We conclude that the valence bond approach employs a Pauling-Wheland resonance energy and that the block localized approach employs a delocalization criterion. The latter are shown to be more basis set dependent in a series of illustrative calculations.

Reprinted with kind permission from Springer Science+Business Media: Theoretical Chemistry Accounts, "A Comparison of Approaches to Estimate the Resonance Energy", 127, 2010, 19, Marcin Zielinski, Remco W. A. Havenith, Leonardus W. Jenneskens and Joop H. van Lenthe.

7.1 Introduction

The extra energetic stabilization of aromatic compounds, e.g. benzene, compared to their non-aromatic counterparts is a subject of considerable interest in chemistry. Many approaches for its calculation have been suggested in the literature, both empirical [1–3] and employing *ab initio* quantum chemistry [4–8]. Historically, Pauling and Wheland [9] have defined the resonance energy of an aromatic compound as the difference in energy between the resonating multi structure valence bond wave function and the lowest contributing structure. This definition has been widely used in VB calculations [5–8]. Pauling and Sherman [10] have also published another way to calculate the resonance energy from thermochemical data. These can be obtained by using a hypothetical, non-aromatic molecule 1,3,5-cyclohexatriene in a relaxed, D_{3h} symmetry and compare it to the real benzene. It is also possible to mimic the thermochemical approach computationally, by calculating the parts of a molecule (non-aromatic counterpart) and the whole (real molecule). That has been defined in Valence Bond as a Theoretical Resonance Energy (TRE) [7] and defines it as the energy difference between the resonating, multi-structure VB wave function used for the description of benzene (real molecule) and the single structure VB wave function that describes its non-aromatic counterpart 1,3,5-cyclohexatriene in a relaxed D_{3h} symmetry. In contrast, in the Block Localized Wave function (BLW) [11–13] approach the resonance energy is defined as the energy that is gained by delocalization. It is computed as the difference between the energy of the BLW (non-aromatic counterpart with orbital constraints) and the HF energy (without orbital restrictions). This implies that in the BLW approach the delocalization energy is calculated using a BLW wave function (non-aromatic counterpart), to calculate the energy of the fictional non-delocalized molecular wave function and that this is compared to the energy calculated using the Hartree-Fock wave function representing the real delocalized molecular wave function. Of course other methods like DFT could be used as well for BLW, instead of Hartree-

Fock [14, 15]. In any case, the hypothetical molecules are only accessible computationally by restricting the variational space in which the wave function is expanded or by use of fixed (non-optimized) orbitals. Pauling and Wheland [9] comment on the Pauling and Sherman [10] approach, in their paper: the resonance energy calculated by Pauling and Sherman is not strictly comparable with that found by the present method.

The proposed Pauling-Wheland and Pauling-Sherman approaches are two completely different ways to consider the extra stabilization energies of aromatic compounds, which are often rather loosely mixed [11, 13], but not strictly comparable, due to the different basic approaches. When comparing a non-aromatic system, like three ethene molecules, with its aromatic counterpart benzene, both effects may be invoked to explain the extra stabilization (*vide infra*).

In this chapter, we study and compare the basis set dependence of both approaches. Benzene is the archetype of aromatic molecules, and its aromatic stabilization is still a matter of dispute [7, 11, 13]. To illustrate our considerations we compare the resonance energies, obtained using the BLW approach and the VB approach using different orbital models *ie.* VB-local and VB-delocal [6-8]. The interpretation of the results obtained is discussed.

To illustrate the basis set dependence of the results, we performed calculations on H_6 in a benzene arrangement. For this system a wide range of basis sets of increasing size may be used. We present both BLW and VB results and show that especially the former shows a significant basis-set dependence, as do the VB-local results. In contrast, the VB calculations without restrictions on the one-electron space (VB-delocal) are shown to be remarkably independent of the one-electron basis.

7.2 BLW versus VB

In the VB picture the extra stabilization is brought about by the mixing of different Valence Bond structures, *e.g.* in the case of benzene the mixing

of primarily the two Kekulé structures (Figure 7.1).

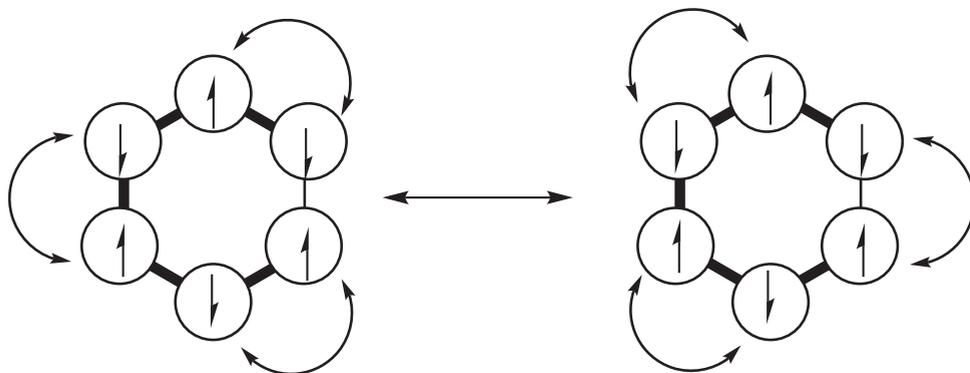


Figure 7.1: *Schematic representation of the resonance, according to VB, in benzene.*

In the BLW approach the energy of the most stable resonance structure is calculated in a way, where the primitive basis functions are partitioned into several subgroups and each block localized orbital is expanded in only one subgroup. The energy of the real molecule is evaluated using the Hartree-Fock method (Figure 7.2). Consequently, the energy difference between the HF wave function, where all electrons are free to delocalize over the whole system, and the BLW, where electrons are confined to specific zones of the system, can be defined generally as the electron delocalization energy [11,13,16,17]. Note the similarity between the BLW approach and the calculation of the resonance energy of benzene using Hückel theory, where the resonance energy is defined as the energy difference between three doubly occupied ethene bonds and the "true" Hückel benzene energy.

There is however a parallel between the ways the delocalization energy and the resonance energy are calculated. Both the BLW and the VB approach rely on a restriction of the variational space, in order to define the subunits for which the energies are calculated, that are subsequently compared to that of the real system.

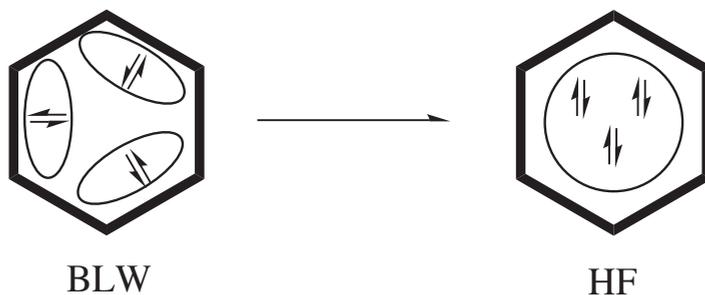


Figure 7.2: *Schematic representation of the BLW approach for benzene.*

In the BLW approach the orbital space available to each subunit is restricted to the orbitals of that subunit, i.e. the atomic orbitals of the bonding atoms. This BLW approach suffers from a dependence on the one-electron basis, as it is used to define the restriction. The same applies to our strictly atomic (VB-local) model (vide infra) [18]. These orbital restrictions are untenable in the limit of a complete basis set [7], which for sake of argument may be chosen to be centred on just one atom of the subunit. In that case the calculated delocalization energy will be zero as both the subunit and the molecule share the same basis. The delocalization energy for the other subunits in the molecule will defy calculation, as no orbitals are available to describe its wave function. Of course part of the basis may be assigned to each subunit, and then the result will depend on the choices made. Thus the calculation of the delocalization energy is by design dependent on the chosen partition of the one-electron basis set.

The VB approach suffers from no such dependence on the one-electron basis. Even in the limit of a complete one-atom basis the resonance energy will be retained. This does not imply that it does not depend on the basis set at all as it still has the normal dependence on the basis any calculation has. However, as the restriction used to determine the resonance energy now is at the many-electron level, an extension of the reference model beyond a simple VB model will give n-electron basis dependent results. As a consequence the limit of a full CI (full VB) description of one structure

will be identical to the description of the real molecule, resulting in zero resonance energy in this case. Thus any definition of resonance energy or delocalization energy will depend on a restriction of the variational space. Still other choices have been made in the literature to describe 1,3,5-cyclohexatriene and benzene, in order to estimate the extra stabilization of benzene [19,20].

Whatever model is chosen for the description of the molecule and its localized counterpart, it is imperative that the answers obtained are not too heavily dependent on the chosen one-electron basis set. The different electron space restrictions in case of BLW (one-electron basis) and VB (n-electron basis) determines the difference between the delocalization and resonance energies and should not be mixed [11,13].

The resonance energies are all evaluated at one geometry, usually the geometry of the real molecule, and are referred to in the literature, either as the vertical resonance energy (VRE) [21], as in Block Localized Wave Function approach or as the Pauling-Wheland resonance energy (PRE) within our VBSCF method.

7.3 Calculations

All calculations were performed with TURTLE [22], as implemented in GAMESS-UK [23]. All VB calculations have a multi-structure character and all the energies are obtained with the same orbital set. For comparison, various basis sets were used for benzene BLW and VB calculations, in order of increasing number of orbitals 6-31G [24] (66 AOs), 6-311+G** [25] (174 AOs), aug-cc-pVTZ [26] (474 AOs) and aug-cc-pVQZ [26] (954 AOs). Two different orbital models were used for the VB calculations, 1) the strictly atomic model (VB-local), in which the p_π -orbitals are restricted to remain localized on one atom, and 2) the delocal model (VB-delocal), where the p_π -orbitals are not restricted at all. The VB wave functions of benzene consisted of the two Kekulé structures and the three Dewar structures. The benzene geometry used throughout all BLW and VB calculations was

optimized at the RHF/6-311+G** [25] level with the R_{C-C} bond lengths equal to 1.386 Å, and applied to both the real molecules and their non-aromatic counterparts. All σ -orbitals of benzene were kept frozen during the BLW and VB calculations, and were taken from a preceding RHF calculation.

In the case of H_6 we used a hexagonal arrangement with a fixed H-H bond length of 0.74 Å. The basis sets used, were, in order of increasing number of orbitals, 6-31G [24] (12 σ AOs), 6-311++G** [25] (36 σ AOs), aug-cc-pVTZ [26] (108 σ AOs) and a specially engineered ANO type basis ANO-3s2p1d1f1g [27] (156 σ AOs).

7.4 Results and Discussion

7.4.1 Benzene

Table 7.1 reports the vertical resonance energies (VRE) as obtained using the BLW description vs. Hartree-Fock benzene [11–13], and the Pauling-Wheland resonance energies (PRE) using the VB by multi-structure (Kekulé + Dewar) calculations, with different orbital optimization models [7, 8].

The BLW VRE is significantly higher than the VB PRE ones. Apparently, this is due to the heavy restriction imposed on the one-structure calculation. The BLW one-structure has an energy (E_{BLW-1}) that is even higher than the VB-local ($E_{VB-local-1}$). The VB-delocal calculations give the lowest total energies for both benzene, and the single structure. The interpretation of the different wave functions is straightforward: the BLW corresponds to a Hartree-Fock-like description of both compounds, while the Valence Bond delocal wave functions include static correlation, and resemble MCSCF wave functions for both compounds.

A comprehensive overview of different approaches to calculating the resonance energy has been given in Ref. [13] and compares various values obtained for benzene. Our reported PREs of benzene (Table 7.1) differ significantly from some of these literature values. Note however, that the very different nature of all the techniques, reported there, prohibits a strict

comparison. The PREs of benzene from the VB-delocal calculations, suggest an extra stabilization of approximately 20 kcal/mol for benzene with respect to the single Kekulé structure description. In the delocal model, the one-structure description can be interpreted chemically as a (closed) polyene like reference: delocalization of the atomic orbitals to neighboring atoms still occurs. This interpretation is further corroborated by the results of geometry optimization of benzene using a single-structure wave function: alternating bond lengths of 1.369 Å and 1.433 Å are obtained [7], which are close to the bond lengths found in for example 1,3-butadiene.

Table 7.1: *Block Localized Wave Function (VRE, kcal/mol) and Valence Bond Resonance Energies (PRE, kcal/mol) for benzene (D_{6h} symmetry), together with the total energies (E_{RHF} , $E_{VB-model}$, hartree) and one-structure energies (E_{BLW-1} , $E_{VB-model-1}$, hartree).*

Basis set	6-31G	6-311+G**	aug-cc-pVTZ	aug-cc-pVQZ
E_{RHF}	-230.624421	-230.756773	-230.635030	-230.679033
E_{BLW-1}	-230.485802	-230.603970	-230.501065	-230.560824
$E_{VRE(BLW)}^a$	86.99	95.89	84.06	74.18
$E_{VB-local}$	-230.544124	-230.658278	-230.573139	-230.651415
$E_{VB-local-1}$	-230.494868	-230.607478	-230.522119	-230.599634
$E_{PRE(VB-local)}^b$	30.91	31.88	32.01	32.49
$E_{VB-delocal}$	-230.692571	-230.819761	-230.698438	-230.742042
$E_{VB-delocal-1}$	-230.659917	-230.787820	-230.666453	-230.710071
$E_{PRE(VB-delocal)}^b$	20.49	20.04	20.07	20.06

^a Defined as $VRE = E_{BLW-1} - E_{HF}$.

^b Defined as $PRE = E_{VB-model-1} - E_{VB-model}$.

7.4.2 Basis set dependence

To study the basis set dependence of the various resonance energies, we have calculated the resonance energies for hexagonal H_6 . In principle, restrictions on the one-electron basis vanish for a complete basis set, and even a one-center basis set expansion would suffice to describe a molecule.

Thus, the completeness of the one-electron basis can be probed by the calculation of the energy of H_2 where the basis set is expanded on only one hydrogen atom. In Table 7.2, the energies of H_2 are presented for different basis sets. For the biggest basis the error in the one-center description of H_2 is only ca. 13 kcal/mol. The better the one-center expansion for H_2 is, the smaller is the difference in energy between a one- and two-centre basis set expansion. In the limit of a complete set, that is when the Hartree-Fock limit is reached for the one-center expansion on H_2 , this difference will be zero.

We present the resonance energies for hexagonal H_6 in Table 7.3. The ANO basis set [27] was engineered in such a way that it would give a reasonable description of the H_2 molecule with the basis set expanded on only one hydrogen atom. If the bonding would be recovered using this basis set and the one-center expansion in H_2 , the basis would also recover the bonding in H_6 while the restrictions of the BLW wave function are in effect, hence, the use of this basis set exemplifies the convergence of the BLW energy to the HF energy in case of large (complete) basis sets. The BLW values show a similar dependence on the chosen basis set as we found in the H_2 one-center expansion case. In the limit of a complete one-electron basis set, the BLW wave function has to converge to the RHF benzene solution, with the (undesirable) result that the resonance energy approaches zero!

The VB-local resonance energies show a matching behavior, though they do not approach zero. Ultimately they have to converge to the results obtained by the VB delocal approach instead. The only approach yielding consistent resonance energies over the whole range of basis sets is the VB delocal approach. The delocal VB resonance energies are indeed remarkably basis independent. The VB-delocal model will still give a non-zero (Pauling-Wheland) resonance energy in the limit, as the required spin-couplings schemes to get the benzene wave function are absent in the one-structure wave function.

The basis dependence is already obvious from the differences between

Table 7.2: *The RHF energy (hartree) of H_2 normal (2-center) and with the basis set centered on only one hydrogen atom (1-center), its difference (delocalization energy, kcal/mol).*

Basis set	6-31G	6-311++G**	aug-cc-pVTZ	ANO-3s2p1d1f1g
H_2 one-centre	-0.882030	-0.968449	-1.068027	-1.111538
Two-centre	-1.126755	-1.132492	-1.133069	-1.132155
E_{deloc}	153.57	102.94	40.81	12.94

Table 7.3: *The RHF energy of hexagonal H_6 (hartree), the BLW energy (hartree) and the resonance energy of H_6 (kcal/mol), calculated with various basis sets. For comparison Valence Bond (two-structure) results are given, calculated on VB-local and VB-delocal levels. All basis sets consist of cartesian gaussians.*

Basis set	6-31G	6-311++G**	aug-cc-pVTZ	ANO-3s2p1d1f1g
H_6 E_{RHF}	-3.068967	-3.096080	-3.098831	-3.096138
E_{BLW}	-2.770030	-2.869046	-2.979454	-3.024724
E_{deloc}	187.59	142.47	74.91	44.81
H_6 $E_{VB-local}$	-2.906863	-2.987603	-3.071606	-3.074902
$E_{res(VB-local)}$	83.02	68.51	60.77	40.91
H_6 $E_{VB-delocal}$	-3.106965	-3.132358	-3.135363	-3.132652
$E_{res(VB-delocal)}$	34.21	32.51	32.58	32.60

BLW and RHF energies. The former changes in the first decimal when the basis is changed, whereas the latter changes only in the second or third decimal place. As the difference between them defines the delocalization energy, its dependence on the basis is obvious.

7.5 Conclusions

The delocalization, resonance energy obtained using the BLW approach is determined by the incompleteness of the chosen one-electron basis set, and consequently will be one-electron basis set dependent. The highlighted extreme cases of ANO basis set for H_2 one- centre and H_6 or the aug-cc-pVQZ for benzene, though not used very often in VB calculations, show the expected problem of reduction of the resonance energy, due to the fact that the applied orbital restrictions become meaningless in the case of a near complete basis set. Therefore, different models used to describe this reference will give different results. The VB-delocal (vertical) resonance energies are almost independent of the basis set. However, employing a realistic basis set and "as long as the atomic characteristics are well retained in the basis functions", the BLW will generate stable results [13]. We infer, that the resonance energy definition using the BLW approach [11,13] does not seem compatible with the Pauling and Wheland concept [9] and should be actually referred to as a delocalization energy.

7.6 Acknowledgements

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7.7 How to properly compute the resonance energy within the ab initio valence bond theory.

Mo, Hiberty and Schleyer [28] (MHS hereafter) have presented various approaches to calculate the resonance energy and came to many conclusions and findings including a computational way of calculating the resonance energy with the Block Localized Wave function method [11, 12] (BLW), finding the compression energy (ΔE_c) or lack of any significant basis set dependency in the BLW resonance energy definition.

MHS often refers [13, 28] to various, calculated values of resonance energy (above 80kcal/mol), estimated using "sophisticated analyses of experimental and computational data". It is however important to realize first that resonance energy is not an observable property, and thus there is no way to define this property unequivocally using quantum mechanics. That means that slightly different definitions and interpretations of these definitions may lead to completely different results and conclusions, but nature does not provide a mechanism to decide which is right or wrong. In our method, we try to adhere as strictly as possible to the Pauling and Wheland [9] definition using modern Valence Bond techniques.

Secondly, we stress the difference between the Pauling-Wheland's resonance energy (PRE) and the Vertical resonance energy (VRE), while MHS call Pauling-Wheland a VRE method. We do not understand this and refer rather to the original definition, in the original paper[9]. We considered the VRE before as well [7,29]. The Pauling-Wheland's concept of the resonance energy, in the case of the benzene, is "the extra energy of the molecule resulting from resonance among the five independent structures", which in other words mean an energy difference between the multi-structure (e.g. two Kekulé and three Dewar structures in the case of benzene) resonating VB wave function and the energy calculated for the most stable structure (Kekulé structure), both coming from the very same calculations. In the case of VRE, both energies come from separate calculations. The authors

This paragraph is based on a reply [31] to a comment by Mo et al [28].

repeatedly say [11, 13, 28] that the Pauling-Wheland's resonance energy is the Vertical resonance energy, hence misinterpreting our VBSCF PRE results. Moreover, any reference to the relation between the VRE and the Adiabatic (Theoretical) Resonance Energy (ARE/TRE) is purely artificial and not the subject of our publication. For that we refer to our previous article [7].

Another way to calculate the resonance energy is a Pauling-Sherman recipe [10] where the resonance energy is calculated from thermochemical data. However, we are willing to concede, that the BLW approach does not employ the Pauling-Sherman [10] recipe, but it definitely does not Pauling-Wheland either.

Going further in that direction, according to MHS, the delocalization energy and the resonance energy is the same. We realize that this misunderstanding is widespread, but we think the discussion should be about the resonance. As stated many times, we use the Pauling-Wheland's definition [9]. This is an n -electron (correlation) effect, whereas the delocalization is an one-electron effect. They may point in the same direction, but they are not the same. MHS use a (de)localization approach in the BLW method, which determines their definition of the resonance energy. It is possible to use real resonance with BLW functions, as some of us have demonstrated [29] and the resulting Pauling-Wheland's resonance energy is almost like our VBSCF PRE. They call their resonance energy, misleadingly the Pauling-Wheland resonance energy, though without a reference, which is even more confusing.

MHS state in their paper that atoms are defined by basis sets [28]. However, this is not real; plane wave basis sets are equally capable of describing atoms and molecules, and this does not negate the concept of atoms, as it is the VB orbitals that should exhibit the atomic character. We realize that employing big-sized basis sets makes the identification more cumbersome, but identifying basis sets with atoms is not based on theory. The idea of possible infinite basis sets, one center or otherwise, is at the heart of *ab initio* quantum chemistry.

Furthermore, it is clear that MHS missed the difference between a one-electron basis set and a n-electron basis set: the former are one-electron functions, such as atomic orbitals or molecular orbitals, whereas the latter are n-electron functions, such as determinants, configuration state functions or structures. Deficiencies in one set can never be remedied by expansion of the other set. The fact that MHS say that correlation is unimportant shows that they miss the point. Resonance in the Pauling-Wheland definition is correlation. The fact that MHS consider correlation a minor correction to basically a Hartree-Fock function indicates that their theory is a one-electron (Hartree-Fock or DFT) theory. The explicitly correlated basis functions [30] to which MHS refer, are two-electron functions, and we have not used them yet in our VB methodology.

The results reported in [31] are the *ab initio* Valence Bond results. Perhaps the "sophisticated analysis of experimental and computational data" produces something that is not the resonance energy. Our results match those of Cooper et al. [32] as they should do because both Spin Coupled VB [8] and VBSCF [18, 33] are in essence the same. They are related to resonance, since they are calculated from a wave function with resonance. The experimental results definitely do not contain explicit resonance and the computational results of MHS [28] probably not either, since they surely do not include Cooper et al. and only quote Mo himself. So, our calculations do not agree with Mo's calculations and that was, we thought, rather obvious.

Using the VB local method, the real benzene molecule is poorly described, but it has the advantage of allowing some interpretation, though it is not as obvious as it might seem due to the arbitrary assignment of basis functions to atomic orbitals. If we employ the delocal model (the spin-coupled model) the wave function is much better, as it now includes the ionic structures but the PRE is even smaller. To get the largest (but we are not aiming for that) resonance energy we can do a full π -CI (one can still use VB, but an orthogonal calculation gives the same answer) and include a Kekulé structure with local atomic orbitals. Then the Resonance

Energy is $E_{kekule\ atomic}$ (-230.480868 Hartree) - $E_{full\ \pi-CI}$ (-230.709822 Hartree), which is 143.7 kcal/mole, all in the same basis (6-31G). So we can get any number we like between 20 and 143 kcal/mol, but as we said, we are not aiming for that.

Compression energy of the hypothetical 1,3,5-cyclohexatriene was also calculated by some of us [7] and represented in the thermocycle for benzene. The authors remark that VRE of benzene must be at least 30 kcal/mole larger than its ARE is not valid. Since "optimal" or "rigid" 1,3,5-cyclohexatriene is a hypothetical system, the calculated compression energy depends on the way, one captures this system in computro. In our CPL paper we used VB and we find consistent results for PRE, VRE and TRE. The compression energy of 1,3,5-cyclohexatriene calculated with BLW method cannot be compared with the one calculated with the VB method as the two approaches are totally different.

Unfortunately, MHS have missed the main point of our paper [31]: in order to calculate a resonance energy, the energy of an, even in computro, non-existing reference molecule has to be calculated. This is only possible by posing limits on the expansion space of the real molecule. This can be done in several ways, each with their own advantages and disadvantages. One way is to limit the one-electron space (limiting the expansion freedom of the orbitals in the calculation) leading to the BLW approach [11, 12] and results in a delocalization energy comparable to the Hückel method, the other way is to limit the n-electron space (limiting the number of determinants (structures) in which the wave function is expanded), resulting in a resonance energy according to the Pauling-Wheland definition. The disadvantage of restricting the freedom of the orbitals (one-electron space) is that enlarging the basis set leads necessarily to a delocalization energy of zero, whereas in the same limit of a complete one-electron basis set, the resonance energy calculated using the VB method (where the number of structures is limited) converges to a finite, non-zero limit. The only reason we did our H_6 case is that we tried to approach a limit, like we use to do in *ab initio* Quantum Chemistry. The basis set dependence of the BLW

method is thus clearly different from the VB behaviour. MHS cannot be in disagreement with this statement, because they also admit that they prefer to restrict the BLW calculations to medium-sized basis sets.

It is important to note that both methods have their place in computational chemistry, and that neither can be either qualified as being right or wrong. We actually used the BLW concept and showed [29] that, if properly optimized, the doubly occupied BLW functions can take the place of the singlet coupled singly occupied orbitals in a really resonating set of structures. The use of large basis sets does not pose a problem, as it is the VB orbitals, that should be analyzed. The restriction to medium sized basis sets does not allow the standard quantum chemical approach to employ as big basis as possible to test the stability of the answers when increasing the basis. In the past this testing has revealed real artifacts [34, 35] and we should not be afraid to go there.

References

- [1] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, W. E. Vaughan, *J. Am. Chem. Soc.* **58** (1936) 146
- [2] M. J. S. Dewar, C. De Llano, *J. Am. Chem. Soc.* **91** (1969) 789
- [3] S. W. Slayden, J. F. Liebmann, *Chem. Rev.* **101** (2001) 1541
- [4] S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *Chem. Rev.* **101** (2001) 1501
- [5] G. F. Tantardini, M. Raimondi, M. Simonetta, *J. Am. Chem. Soc.* **99** (1977) 2913
- [6] F. Dijkstra, J. H. van Lenthe, R. W. A. Havenith, L. W. Jenneskens, *Int. J. Quantum Chem.* **91** (2003) 566
- [7] J. H. van Lenthe, R. W. A. Havenith, F. Dijkstra, L. W. Jenneskens, *Chem. Phys. Lett.* **361** (2002) 203

-
- [8] D. L. Cooper, J. Gerratt, M. Raimondi, *Chem. Phys. Lett.* **323** (1986) 699
- [9] L. Pauling, G. W. Wheland, *J. Chem. Phys.* **1** (1933) 362
- [10] L. Pauling, J. Sherman, *J. Chem. Phys.* **1** (1933) 606
- [11] Y. Mo, P. v. R. Schleyer, *Chem. Eur. J.* **12** (2006) 2009
- [12] Y. Mo, S. D. Peyerimhoff, *J. Chem. Phys.* **109** (1998) 1678
- [13] Y. Mo, *J. Phys. Chem. A* **113** (2009) 5163
- [14] Y. Mo, *J. Phys. Chem. A* **119** (2003) 1300
- [15] Y. Mo, L. Song, Y. Lin, *J. Phys. Chem. A* **111** (2007) 8291
- [16] R. C. Kerber, *J. Chem. Edu.* **83** (2006) 223
- [17] D. G. Truhlar, *J. Chem. Edu.* **84** (2007) 781
- [18] J. H. van Lenthe, G. G. Balint-Kurti, *J. Chem. Phys.* **78** (1983) 5699
- [19] P. C. Hiberty, C. P. Byrman, J. H. van Lenthe, *J. Chem. Phys.* **101** (1994) 5969
- [20] P. C. Hiberty, *THEOCHEM.* **35** (1997) 398
- [21] Y. Mo, W. Wu, Q. Zhang, *J. Phys. Chem.* **98** (1994) 10048
- [22] J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, J. Engelberts, M. L. Zielinski, Z. Rashid, J. H. van Lenthe, *TURTLE: Ab-Initio VB/VBCF Program*, Utrecht, 1988-2012
- [23] M. F. Guest, I. J. Bush, H. J. J. van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A. Havenith, J. Kendrick, *Mol. Phys.* **103** (2005) 719
- [24] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **56** (1972) 2256

-
- [25] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **72** (1980) 650
- [26] T. H. Dunning Jr., *J. Chem. Phys.* **90** (1989) 1007
- [27] R. W. A. Havenith, Specially designed ANO -type basis, geared to be as complete as possible, without causing linear dependencies. Details are available upon request (2007)
- [28] Y. Mo, P. C. Hiberty, P. v. R. Schleyer, *Theo. Chem. Acc.* **127** (2010) 27
- [29] M. L. Zielinski, J. H. van Lenthe, *J. Phys. Chem. A* **112** (2008) 13197
- [30] W. Klopper, F. R. Manby, S. Ten-No, E. F. Valeev, *Rev. Phys. Chem.* **25** (2006) 427
- [31] M. L. Zielinski, R. W. A. Havenith, L. W. Jenneskens, J. H. van Lenthe, *Theo. Chem. Acc.* **127** (2010) 19
- [32] D. L. Cooper, J. Gerratt, M. Raimondi, *Topics in Curr. Chem.* **153** (1990) 41
- [33] J. H. van Lenthe, G. G. Balint-Kurti, *Chem. Phys. Lett.* **76** (1980) 138
- [34] B. J. Ransil, *J. Chem. Phys.* **34** (1960) 2109
- [35] N. R. Kestner, *J. Chem. Phys.* **48** (1968) 252

APPENDIX A

Complementary information on the results

As explained in Chapter **3**, the compactness of the Atoms in Valence Bond wave function might be lost due to a different AiVB structures definition. Moreover, the Atoms in Valence Bond Self Consistent Field (AiVBSCF) process becomes very complex when the systems are defined with many structures and the complexity grows very rapidly with the increasing number of AiVB structures (increasing number of determinants). Both of these difficulties can cause numerical instabilities during the AiVBSCF process which then influences the convergence of the whole AiVB calculation.

The AiVB calculations presented in this book (Chapter **5**) were supported with convergence aiding techniques like DIIS (Direct Inversion of Iterative Space) [1] to help and improve the convergence. Even then, achieving it at the minimum desirable level was difficult and time consuming.

Results reported in this appendix (Tables A.1, A.2, A.3 and A.4) are intermediate and were used as a starting point to obtain those reported in Chapter **5**. The procedure to obtain the final results was to dismiss the

lowest contributing structures from the intermediate AiVB wave function. The sum of the weights of the most contributing structures was taken as a dismissal threshold and was set to minimum 0.95. The AiVB structures, which sum of their weights was approximately 0.95, were used for the final AiVB calculations and the remaining ones were dismissed.

Based on this threshold, the methane AiVB structures taken for the final AiVB calculation (their weight sum equal 0,951307) were structures #1, #7, #15 and #16, whereas for ammonia those were structures #1, #5 and #8 (0,969175), structures #1, #6, #10, #11, #13, #14 and #16 for water (0,964165) and structures #1, #6 and #18 for hydroxyl radical (0,994). Removing #6 from the hydroxyl radical set would result with the weights sum being too low, thus giving a too poor description of the system. In each case, the relative error, due to the dismissal, between the full set and the final set was not bigger than 5%.

Tables A.1 and A.2 contain an extra column describing the remaining spin coupling scheme of the remaining hydrogens in the system with the spin configuration of the spin-bound atom as a starting point, i.e. the total branching diagram for structure #2 in Table A.1 is $\alpha\alpha(\text{O})\beta\beta\alpha\beta(4x \text{ H})$.

References

- [1] P. Pulay, *J. Comp. Chem.* **3** (1982) 556

Table A.1: *The final coefficients and weights of AiVB structures for methane. E_{tot} in hartree.*

contributing AiVB structures		hydrogen's spin coupling	multi-structure weight	AiVB local coefficient
$C(^5S) \otimes 4x H(^2S)$	$1s^2 2sxyzh_1 h_2 h_3 h_4$		0.906507	-0.622159
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 xzh_1 h_2 h_3 h_4$	$\beta\beta\alpha\beta$	0.008804	0.136247
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 yzh_1 h_2 h_3 h_4$	$\beta\beta\alpha\beta$	0.008804	-0.136247
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 xzh_1 h_2 h_3 h_4$	$\beta\alpha\beta\beta$	0.003143	0.078662
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 yzh_1 h_2 h_3 h_4$	$\beta\alpha\beta\beta$	0.003143	0.078662
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 xyh_1 h_2 h_3 h_4$	$\beta\alpha\beta\beta$	0.014736	-0.174487
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 xzh_1 h_2 h_3 h_4$	$\alpha\beta\beta\beta$	0.006071	-0.111245
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 yzh_1 h_2 h_3 h_4$	$\alpha\beta\beta\beta$	0.006071	-0.111245
$C(^3P) \otimes 4x H(^2S)$	$1s^2 2s^2 xyh_1 h_2 h_3 h_4$	$\alpha\beta\beta\beta$	0.007679	-0.123381
$C(^1D) \otimes 4x H(^2S)$	$1s^2 2s^2 (x^2 - y^2) h_1 h_2 h_3 h_4$	$\alpha\beta\alpha\beta$	0.004978	0.147761
$C(^1D) \otimes 4x H(^2S)$	$1s^2 2s^2 \left((x^2 + y^2) - 2z^2 \right) h_1 h_2 h_3 h_4$	$\alpha\beta\alpha\beta$	0.015231	0.263000
$C(^1D) \otimes 4x H(^2S)$	$1s^2 2s^2 (x^2 - y^2) h_1 h_2 h_3 h_4$	$\alpha\alpha\beta\beta$	0.014833	-0.255930
E_{tot}			-40.0151593	

Table A.2: *The final coefficients and weights of AiVB structures for ammonia. E_{tot} in hartree.*

contributing AiVB structures		hydrogen's spin coupling	multi-structure AiVB local weight coefficient	
$N(^4S) \otimes H_3 (^2S)$	$1s^2 2s^2 xyz h_1 h_2 h_3$		0.789122	1.041822
$N(^2D) \otimes H_3 (^2S)$	$1s^2 2s^2 (x^2 - y^2) z h_1 h_2 h_3$	$\beta\alpha\beta$	0.000017	0.008103
$N(^2D) \otimes H_3 (^2S)$	$1s^2 2s^2 x (y^2 - z^2) h_1 h_2 h_3$	$\beta\alpha\beta$	0.000003	-0.003036
$N(^2D) \otimes H_3 (^2S)$	$1s^2 2s^2 (x^2 y - y z^2) h_1 h_2 h_3$	$\beta\alpha\beta$	0.077889	0.565656
$N(^2D) \otimes H_3 (^2S)$	$1s^2 \left(2s^2 (x\bar{y} + \bar{x}y) z - \right.$ $\left. 2(2s^2 xy\bar{z}) \right) h_1 h_2 h_3$	$\beta\alpha\beta$	0.006242	-0.206186
$N(^2D) \otimes H_3 (^2S)$	$1s^2 2s^2 (x\bar{y} - \bar{x}y) z h_1 h_2 h_3$	$\alpha\beta\beta$	0.102164	-0.453585
$N(^2D) \otimes H_3 (^2S)$	$1s^2 2s^2 x (y^2 - z^2) h_1 h_2 h_3$	$\alpha\beta\beta$	0.000009	0.005297
$N(^2D) \otimes H_3 (^2S)$	$1s^2 \left(2s^2 (x\bar{y} + \bar{x}y) z - \right.$ $\left. 2(2s^2 xy\bar{z}) \right) h_1 h_2 h_3$	$\alpha\beta\beta$	0.013849	0.357126
$N(^2P) \otimes H_3 (^2S)$	$1s^2 2s^2 y (z^2 + x^2) h_1 h_2 h_3$	$\beta\alpha\beta$	0.010705	-0.198519
$N(^2P) \otimes H_3 (^2S)$	$1s^2 2s^2 x (z^2 + y^2) h_1 h_2 h_3$	$\alpha\beta\beta$	0.000001	-0.001369
E_{tot}			-56.036696	

Table A.3: The final coefficients and weights of AiVB structures for water. E_{tot} in hartree.

contributing AiVB structures	multi-structure	
	weight	AiVB local coefficient
$O(^3P) \otimes 2x H(^2S)$	$1s^2 2s^2 y^2 xz h_1 h_2$	0,220558 0,344984
$O(^1D) \otimes 2x H(^2S)$	$1s^2 2s^2 (x^2 - y^2) z^2 h_1 h_2$	0,006624 -0,068206
$O(^1D) \otimes 2x H(^2S)$	$1s^2 2s^2 (xy^2 \bar{z} - \bar{x}y^2 z) h_1 h_2$	0,063834 0,215741
$O(^1D) \otimes 2x H(^2S)$	$1s^2 \left(2s^2 (x^2 + y^2) z^2 - 2(2s^2 x^2 y^2) \right) h_1 h_2$	0,002090 -0,034774
$O(^1S) \otimes 2x H(^2S)$	$1s^2 2s^2 x^2 y^2 h_1 h_2$	0,022694 0,133796
$O^{2-}(^1S) \otimes 2x H^{2+}$	$1s^2 2s^2 x^2 y^2 z^2$	0,036045 -0,183052
$O^{-(^2P)} \otimes H(^2S) \otimes H^+$	$1s^2 2s^2 xy^2 z^2 h_1$	0,260676 0,435238
$O^{-(^2P)} \otimes H(^2S) \otimes H^+$	$1s^2 2s^2 zx^2 y^2 h_1$	0,065317 0,188054
$O^{-(^2P)} \otimes H^+ \otimes H(^2S)$	$1s^2 2s^2 xy^2 z^2 h_2$	0,062399 -0,183945
$O^{-(^2P)} \otimes H^+ \otimes H(^2S)$	$1s^2 2s^2 zx^2 y^2 h_2$	0,255336 -0,432170
$O^{2+}(^1D) \otimes 2x H(^1S)$	$1s^2 2s^2 (x^2 - y^2) h_1^2 h_2^2$	0,000033 -0,004936
$O^{2+}(^1D) \otimes 2x H(^1S)$	$1s^2 2s^2 (x\bar{z} - \bar{x}z) h_1^2 h_2^2$	0,000027 -0,005741
$O^{2+}(^1D) \otimes 2x H(^1S)$	$1s^2 \left(2s^2 (x^2 + y^2) - 2(2s^2 z^2) \right) h_1^2 h_2^2$	0,000104 -0,007346
$O^{2+}(^1S) \otimes 2x H^{2-}(^1S)$	$1s^2 2s^2 z^2 h_1^2 h_2^2$	0,000099 0,009473
$O^+(^2D) \otimes H^-(^1S) \otimes H(^2S)$	$1s^2 2s^2 (x^2 - y^2) zh_1^2 h_2$	0,003011 0,045433
$O^+(^2D) \otimes H^-(^1S) \otimes H(^2S)$	$1s^2 2s^2 x(y^2 - z^2) h_1^2 h_2$	0,000120 0,009810
$O^+(^2P) \otimes H^-(^1S) \otimes H(^2S)$	$1s^2 2s^2 x(z^2 + y^2) h_1^2 h_2$	0,000920 0,027109
$O^+(^2P) \otimes H^-(^1S) \otimes H(^2S)$	$1s^2 2s^2 (x^2 + y^2) zh_1^2 h_2$	0,000113 -0,008818
E_{tot}		-76,017392

Table A.4: *The final coefficients and weights of AiVB structures for hydroxyl radical. E_{tot} in hartree.*

struc. #	Constituent atomic states	multi-struc	
		AiVB local	
		Weight	Struc. coeff.
$O(^3P) \otimes H(^2S)$	$1s^2 2s^2 y^2 xzh$	0,500920	0,563218
$O(^1D) \otimes H(^2S)$	$1s^2 2s^2 (xy^2 \bar{z} - \bar{x}y^2 z)h$	0,151119	-0,267434
$O^+(^2D) \otimes H^-(^1S)$	$1s^2 2s^2 x(y^2 - z^2)h^2$	0,005244	-0,056578
$O^+(^2P) \otimes H^-(^1S)$	$1s^2 2s^2 (z^2 + y^2)xh^2$	0,000975	-0,024394
$O^-(^2P) \otimes H^+$	$1s^2 2s^2 xy^2 z^2$	0,341742	-0,427180
	E_{tot}	-75,379239	

APPENDIX B

The leading term method

The leading term method [1], by default implemented in TURTLE [2], is the first configuration of the given rumer diagram [3] and in general is a linear combination of primitive functions, that can easily be derived from the given leading term. The procedure to generate the leading terms for N electrons with S total spin is straightforward and is as follows

(1) create the first leading term from $\frac{1}{2}N - S$ of $(\alpha\beta)$'s and from $2S$ of α 's

$$\frac{1}{2}N - S \quad 2S \\ (\alpha\beta)\dots(\alpha\beta)\alpha\dots\alpha \tag{B.1}$$

(2) make a new leading term from the previous leading term, by (reading from left to right) shifting one place to the right the first β which is followed by an α

(3) bring all the β 's that precede the shifted one to the position they held in the first leading term (B.1)

(4) the last leading term should be made from $\frac{1}{2}N + S$ α 's and from

$\frac{1}{2}N - S$ β 's

$$\alpha\alpha\dots\alpha\beta\beta\dots\beta. \quad (\text{B.2})$$

Taking as an example the case considered in the Chapter 4

(a) $\nu_{2,1}(1) = \{3, 4, 6\}$ = three singly occupied orbitals ($N = 3$ and $S = 1/2$)

(b) the starting leading term is $\alpha\beta\alpha$

(c) the remaining leading term is $\alpha\alpha\beta$

(d) the $\nu_{2,1}(3)$ ($101 = \alpha\beta\alpha$) match the first leading term $\alpha\beta\alpha$

The primitive spin functions are generated from this leading term, by interchanging all $\alpha\beta$ pairs in all possible combinations. Following the example above

(e) the two primitive spin functions that can be generated from this leading term are $\alpha\beta\alpha$ and $\beta\alpha\alpha$

To elaborate the generation of the primitive spin functions on a more general example, let us assume the leading term is

$$\text{leading term} = \alpha\beta\alpha\beta, \quad (\text{B.3})$$

then the generated primitive spin function are

$$\alpha\beta\alpha\beta, \quad \beta\alpha\alpha\beta, \quad \alpha\beta\beta\alpha, \quad \beta\alpha\beta\alpha. \quad (\text{B.4})$$

References

- [1] M. Simonetta, E. Gianinetti, I. Vandoni, *J. Chem. Phys.* **48** (1968) 1579
- [2] J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, J. Engelberts, M. L. Zielinski, Z. Rashid, J. H. van Lenthe, *TURTLE: Ab-Initio VB/VBCF Program*, Utrecht, 1988-2012
- [3] G. Rumer, *Gottinger Nachr.* **3** (1932) 337

Summary

Since the late 1970s and early 1980s, we have witnessed the rebirth of the old Valence Bond (VB) theory. The long forgotten theory was based on a very simple idea, to recognize atoms within the molecule considered. However, over the period of modern VB developments, that idea has been somewhat obscured.

Chapter I of this thesis first briefly goes through the very beginnings of quantum mechanics history. It touches the beginnings of applied quantum mechanics in chemistry that lead to quantum chemistry development and describes in short its basic foundations. Then chapter I introduces two leading methods for description of the electronic structure, Molecular Orbital theory (MO) and Valence Bond theory, compares them both and points to their basic differences. After that, history and development of classical Valence Bond theory is presented which ends with a brief comparison between a modern MO approach (CASSCF) and our VB approach (VBSCF).

Where in chapter I covered merely the basics of Valence Bond theory, **chapter II** introduces the formalism and the necessary theoretical tools to understand VB.

One of the main chapters of this thesis, except for the results, **chapter III**, covers the basic ideas and theoretical formalism behind the Atoms in Valence Bond approach. This approach is based on the notion to build a molecular VB wave function from proper atomic wave functions. Each AiVB structure then is built from atoms, that can exist in any atomic state, specified earlier. The importance of the given, atomic state that contributes to the molecular bonding is based only on the variational principle during the SCF procedure. Moreover, the end of the chapter III covers an exemplary transformation procedure of complex atomic wave functions into configurations expressed with real atomic orbitals.

In **chapter IV** of the thesis, the entire implementation of Atoms in Valence Bond within TURTLE, a VB/VBSCF program, is explained. The implementation process covers the most important stages in the entire pro-

cedure that leads to building the molecular AiVB wave function. Moreover, it also explains the importance of some data arrays that are used throughout the process.

The Atoms in Valence Bond method has been tested on some testing molecules, like methane, ammonia, water and hydroxyl radical. The results of these complex AiVB calculations and their discussion are covered in **chapter V**. Some important conclusions are drawn from the calculations for methane and water. The ground state of methane has at its equilibrium geometry a dominant contribution from the 5S state of the carbon atom. The methane AiVB structure with carbon in that state, contributes more than 93% to the bonding. Moreover, based on the AiVB calculations, the bond character of the water molecule has been proven to be more ionic rather than covalent.

The two final chapters cover several key points about the difference between the resonance energy and delocalization energy. They review various resonance energy definitions like Pauling's Resonance Energy, Vertical Resonance Energy, Theoretical/Adiabatical Resonance Energy. Moreover, dependencies of the above on the chosen basis set and the number of VB structures included in the calculations is studied.

In **Chapter VI** the Resonating Block Localized Wave function (RBLW) method is introduced, a resonating modification of the Block Localized Wave function approach (BLW) that has been described in the literature. The RBLW approach allows for the evaluation of resonance energies following Pauling's recipe. The method is tested on a model molecule, hexagonal H_6 , and on benzene. Calculations were done with (local) and without (delocal) restrictions on the delocalization of orbitals. From a comparison of the resonance energies obtained from RBLW and standard VB calculations, the Resonating Block Localized Wave functions are shown to yield resonance energies close to standard delocalized VB calculations.

In **Chapter VII** we discuss ab initio approaches to calculate the energy stabilization due to aromaticity. We compare the valence bond method and the block localized wave function approaches to calculate the resonance

energy. We conclude that the VB approach employs a Pauling-Wheland resonance energy and that the BLW approach employs in fact a delocalization criterion. In a series of calculations on benzene, the hydrogen molecule and hexagonal H_6 , the BLW results are shown to be very basis set dependent.

Samenvatting

Eind jaren 70, begin jaren 80 zien we een wedergeboorte van de oude Valence Bond (VB) theorie. Deze al lang vergeten theorie was gebaseerd op een erg simpel idee, nl. om atomen te onderscheiden in een molecuul. Dit idee is echter verloren gegaan tijdens de moderne VB ontwikkelingen.

Hoofdstuk I van dit proefschrift gaat eerst kort over het begin van de Quantummechanica. In dit hoofdstuk wordt het begin van de toegepaste Quantummechanica in de chemie aangestipt, wat geleid heeft tot de ontwikkeling van de Quantumchemie; de fundamentele worden kort beschreven. Vervolgens introduceert het twee belangrijke methoden voor het beschrijven van de elektronenstructuur, de Moleculaire Orbital (MO) theorie en de Valence Bond theorie. Het vergelijkt ze en wijst op de fundamentele verschillen. Dan wordt de geschiedenis en de ontwikkeling van de klassieke Valence Bond theorie gegeven, wat eindigt met een korte vergelijking van moderne MO (CASSCF) en moderne VB (Valence Bond Self Consistent Field – VBSCF).

Waar hoofdstuk I voornamelijk de basis van de Valence Bond theorie behandelde, introduceert **hoofdstuk II** het formalisme en de benodigde gereedschappen om VB te begrijpen.

Een van de belangrijkste hoofdstukken van dit proefschrift, buiten de resultaten, **hoofdstuk III**, behandelt de ideeën en het theoretische formalisme achter de "Atomen in Valence Bond" aanpak. Deze aanpak vindt zijn oorsprong in het idee dat een moleculaire VB golf functie opgebouwd wordt uit nette atomaire golf functies. Elke A_i VB structuur wordt gebouwd uit atomen, die elk in een atomaire toestand zijn, zoals eerder gespecificeerd. Hoe groot het belang is van elke atomaire toestand, die deelneemt aan de moleculaire binding, is bepaald gedurende de SCF procedure, enkel door het variatie principe. Het eind van hoofdstuk III beschrijft als voorbeeld, de transformatie van de complexe (zuiver imaginaire) atomaire golf functie naar configuraties met reële atomaire orbitals.

In **hoofdstuk IV** van het proefschrift wordt de gehele implementatie van "Atoms in Valence Bond" in TURTLE, het VB/VBSCF programma

beschreven. Het implementatie- proces omvat de belangrijkste stadia in de gehele procedure, die resulteert in de moleculaire AiVB golffunctie. Bovendien beschrijft het sommige belangrijke data-arrays, die gedurende het hele proces gebruikt zijn.

De "Atoms in Valence Bond" methode is getest op enkele proef-moleculen, zoals Methaan, Ammonia, Water en het hydroxyl radicaal. De resultaten van deze complexe AiVB berekeningen en de discussie staan in **hoofdstuk V**. In de discussie staan enkele belangrijke conclusies over de berekeningen aan Methaan en Water. In Methaan blijkt het koolstof atoom in een 5S atomaire toestand te zitten. De methaan AiVB structuur met dat koolstof atoom draagt voor meer dan 93% bij aan de golffunctie. Gebaseerd op de AiVB berekeningen blijkt water meer ionisch dan covalent te zijn.

De twee laatste hoofdstukken behandelen een aantal aspecten van de verschillen tussen de resonantie-energie en de delocalisatie-energie. Ze geven een overzicht van verschillende definities zoals Pauling's Resonantie Energie, de Verticale Resonantie Energie en de Theoretische/Adiabatische Resonantie Energie. Bovendien wordt de afhankelijkheid onderzocht van deze berekende grootheden met betrekking tot de basisset en het aantal VB structuren gebruikt in de berekeningen.

In **Hoofdstuk VI** wordt de Resonating Block Localized Wave function (RBLW) methode geïntroduceerd, een resonerende modificatie van de al bestaande Block Localized Wave function (BLW) benadering. Met de RBLW aanpak is het mogelijk resonantie energieën te bepalen volgens Pauling's recept. De methode is uitgetest op een model-molecuul, hexagonal H_6 , en op benzeen. De berekeningen zijn gedaan met (local) en zonder (de-local) beperkingen op de delocalisatie van orbitalen. Uit vergelijking van de resonantie-energieën verkregen uit RBLW en standaard VB berekeningen blijkt dat Resonating Block Localized Wave functions resonantie energieën opleveren die dicht bij die uit standaard (gedelocaliseerde) VB berekeningen liggen.

In **Hoofdstuk VII** worden ab initio aanpakken beschreven om de

energie stabilisatie ten gevolge van aromaticiteit te berekenen. De VB en de BLVB aanpakken om de resonantie energie te berekenen worden vergeleken. We concluderen dat de VB aanpak overeen komt met de Pauling-Wheland resonantie energie en dat in de BLW aanpak in feite een delocalisatie criterium gebruikt wordt. Met een serie berekeningen aan benzeen, het waterstof molecuul en hexagonaal H_6 , wordt aangetoond dat de BLW resultaten bovendien sterk basisset-afhankelijk zijn.

List of publications

Marcin Zielinski and Joop H. van Lenthe

"Spin Coupling and Resonance"

J. Phys. Chem. A **112** (2008) 13197

Marcin Zielinski, Remco W. A. Havenith,

Leonardus W. Jenneskens and Joop H. van Lenthe

"A Comparison of Approaches to Estimate the Resonance Energy"

Theor. Chem. Acc. **127** (2010) 19

Marcin Zielinski and Joop H. van Lenthe

"Atoms in Valence Bond - AiVB. Synopsis and test results"

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Curriculum Vitae

Marcin Łukasz Zieliński was born on the 8th of September 1981 in Toruń, in an old and beautiful medieval city located at the north central part of Poland. In 2001 he graduated from Chemical High School with his diploma work receiving special honors.

Few months later, in October 2001, after completing final high school exams, he stepped into the academic world beginning his 5 years long journey with Theoretical and Computational Chemistry at Nicolaus Copernicus University in Toruń. He received his BSc in Chemometrics in September 2004. Before he graduated, he had a chance of visiting the Utrecht group of Theoretical Chemistry in August 2006 meeting Joop H. van Lenthe and his Valence Bond world. In September 2006 he finally graduated with the MSc degree in Theoretical and Computational Chemistry and joined the Utrecht group in December 2006 where he started studying for his Ph.D. degree under the supervision of Joop H. van Lenthe. If he only knew what was coming...

His work involved almost entirely the Valence Bond theory. He has been part of some spectacular heated discussions in the journals about the resonance and delocalization energies and also around the Block Localized Wave function (BLW) approach. However, his work at the Theoretical Chemistry group of Utrecht University will be remembered by developing the Atoms in Valence Bond approach.

He took part in many winter and summer schools, conferences and workshops during his Ph.D. studies, giving many lectures and presenting many posters. Also, he was a member of the Debye AIO Committee, a committee representing interests of every Ph.D. student and post-doc within the Debye Institute for Nanomaterials Science.

Since May 2011 he works as an advisor at the Supercomputing group at SARA, Amsterdam where he was appointed at a permanent position as of May 2012.

