VBSCF Methods

Classical Chemical Concepts and Beyond

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VBSCF Methods
Classical Chemical Concepts and Beyond

VBSCF Methoden
Klassieke Chemische Concepten en Verder

(met een samenvatting in het Nederlands)

وِی بِی اَیس سِی اَیف طریقہ ہائے کار
کلاسیکی کیمیائی تصوّرات و ما بعد

(اردو خلاصے کے ساتھ)

Proefschrift

ter verkrijging van de graad van doctor aan de Universiteit Utrecht op gezag van de rector magnificus prof. dr. G. J. van der Zwaan, ingevolge het besluit van het college voor promoties in het openbaar te verdedigen op maandag 21 januari 2013 des ochtends te 10.30 uur

door

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geboren op 8 juli 1983 te Pakpattan, Pakistan

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… be joyous only for an increase in knowledge or in good works,

for they are your two companions …

Imam Al-Ghazali

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CHAPTER 1

AN OVERVIEW OF THE THESIS

Soon after the discovery of the electron, both chemists and physicists started developing the concept of bonding between atoms in terms of valence electrons but the electronic structure of even the simplest molecules remained an unsolved mystery until the development of quantum mechanics. Heitler and London[1] took the challenge and, by using quantum mechanics, showed for the first time how atoms combine to form molecules. Their approach laid the foundations of Valence Bond (VB) theory. At about the same time Hund,[2--4] Mulliken[5] and Leonard-Jones[6] developed another approach called Molecular Orbital (MO) theory. For a long time, the VB method used to be the popular approach for the electronic structure of molecules. With the advent of electronic computers, the MO methods became prominent while the VB methods slowly "left the stage" because of the difficulties involved in the computational implementation and applications due to the nonorthogonality of the orbitals. However, the classical VB theory left behind "a rich legacy of useful concepts and of theoretical methods"[7] which not only attract chemists but also physicists.[8,9] This is one of the reasons that the past three decades have seen a re-emergence of the VB methods in a powerful *ab initio* form.[10--16] Moreover, recent advances in computer technology have made it possible to use these methods to study almost the same range of molecules that are accessible by higher level MO methods.

One of the most general forms of modern VB approaches is the Valence Bond Self-Consistent Field (VBSCF) method and its efficient implementation in the TURTLE program due to van Lenthe and co-workers.[15--17] The author became involved with these methods with the aim of further developing the VBSCF methodology and its applications to solve chemical problems. The main focus has been on making the orbital optimisation procedure more efficient and the implementation more user friendly like automatic generation of the VB wave functions in terms of chemically significant configurations. Some important developments are summarised in this thesis.

Some aspects of *ab initio* electronic structure theory are discussed briefly in chapter 2. In chapter 3 a procedure to construct VB wave functions in terms of some chemically meaningful configurations (the Kekulé valence structures) is described along with the results of some actual calculations. In chapter 4 a second-order VBSCF method for simultaneous optimisation of orbitals and CI coefficients is presented, based on a Newton-Raphson scheme. The convergence behaviour of this method is analysed using different test cases and its efficiency is compared with the Super-CI method. A discussion on the efficiency of different algorithms for orbital optimisation in VBSCF methods is presented in chapter 5. In the last chapter the VBSCF method is applied to calculate resonance energies of cyclic conjugated systems using two orbital models. The resonance is considered an important measure of aromaticity. It is shown that resonance energies calculated with fully optimised orbitals, while retaining the intuitive chemical picture of VB structures, are more reliable than those obtained by strictly atomic but otherwise optimised orbitals.

References

1. Heitler, W.; London, F. *Z. Physik* **1927**, *44*, 455--472.
2. Hund, F. *Z. Physik* **1927**, *40*, 742--764.
3. Hund, F. *Z. Physik* **1927**, *42*, 93--120.
4. Hund, F. *Z. Physik* **1928**, *51*, 759--795.
5. Mulliken, R. S. *Phys. Rev.* **1928**, *32*, 186--222.
6. Lennard-Jones, J. E. *Trans. Faraday Soc.* **1929**, *25*, 668--686.
7. McWeeny, R. *Spins in Chemistry*; Dover Publications: New York, **2004**.
8. Anderson, P. *Materials Research Bulletin* **1973**, *8*, 153 -- 160.
9. *Theoretical and Computational Chemistry: Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10.
10. Hunt, W. J.; Hay, P. J.; Goddard, W. A. *J. Chem. Phys.* **1972**, *57*, 738--748.
11. Moss, B. J.; Bobrowicz, F. W.; III, W. A. G. *J. Chem. Phys.* **1975**, *63*, 4632--4639.
12. Gerratt, J.; Raimondi, M. *Proc. R. Soc.* **1980**, *A371*, 525--552.
13. Cooper, D. L.; Gerratt, J.; Raimondi, M. Modern Valence Bond Theory. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 319--397.
14. Gallup, G. A. *Valence Bond Methods: Theory and Applications*; Cambridge University Press: Cambridge, **2002**.
15. van Lenthe, J. H.; Balint-Kurti, G. G. *Chem. Phys. Lett.* **1980**, *76*, 138--142.

16. van Lenthe, J. H.; Balint-Kurti, G. G. *J. Chem. Phys.* **1983**, *78*, 5699--5713.
17. van Lenthe, J. H.; Dijkstra, F.; Havenith, R. W. A. TURTLE - A gradient VBSCF Program Theory and Studies of Aromaticity. In *Theoretical and Computational Chemistry: Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10, pp 79--116.

CHAPTER 2

A BRIEF INTRODUCTION TO ELECTRONIC STRUCTURE METHODS

Ab initio quantum chemistry has become a powerful tool to study the electronic structure and properties of molecules. According to quantum mechanics all possible information about the electronic structure and other observable properties of a molecule, in its stationary state, can be derived completely from a wave function $\Psi(q)$ which is obtained by solving the time-independent Schrödinger wave equation.[1–3]

$$\hat{\mathscr{H}}\Psi(q) = E\Psi(q) \tag{2.1}$$

where $\hat{\mathscr{H}}$ is the Hamiltonian operator, E is the eigenvalue of this operator (i.e., the total energy of the system) and q represents the space and spin variables of the wave function. Neglecting the spin-orbit interactions and other relativistic effects and adopting the "clamped nuclei" or Born-Oppenheimer approximation,[4,5] the Hamiltonian for a system of M nuclei and N electrons (in atomic units) is given by:

$$\hat{\mathscr{H}} = -\sum_{i}\frac{1}{2}\nabla_i^2 + \sum_{A}\sum_{B>A}\frac{Z_A Z_B}{\mathbf{R}_{AB}} + \sum_{i}\sum_{j>i}\frac{1}{\mathbf{r}_{ij}} - \sum_{A}\sum_{i}\frac{Z_A}{\mathbf{R}_{Ai}} \tag{2.2}$$

where A and B refer to nuclei with atomic numbers Z_A and Z_B, respectively and $\mathbf{R}_{AB}$ is the distance between them, i and j refer to electrons, $\mathbf{r}_{ij}$ is the distance between electron i and j, $\mathbf{R}_{Ai}$ represents the distance between electron i and nucleus A. ∇_i^2 is the Laplacian operator which involves differentiation with respect to the coordinates of ith electron. The first term in Eq. (2.2) is the kinetic energy operator for electrons. The second and third terms are the potential energies due to nuclear-nuclear and electron-electron repulsions, respectively and the last term is the electron-nuclear attraction.

The time-independent Schrödinger wave equation (Eq. (2.1)) can be solved analytically for only a few systems, for example, the hydrogen atom, H_2^+, He^+, etc. The "exact" solution for a system with more than one electron is impossible. However, by using a number of approximations, it is possible to find accurate solutions for *many*-electron systems. The Schrödinger wave equation is central in all *ab initio* quantum mechanical methods. The aim of these methods is to solve this equation for a system of N-electrons in atoms, molecules or solids and these methods are usually called electronic structure methods.

2.1 One- and N-electron Basis Approximation

The most commonly used approach to solve the electronic Schrödinger equation for molecules is the orbital method. In this method the one-electron wave functions, i.e., the molecular orbitals (MOs), are constructed from a linear combination of one-particle basis functions. The antisymmetrised products of these MOs are then used to build the N-electron wave functions.

In principle an MO can be expanded in terms of hydrogen-like atomic orbitals, exponential or gaussian functions, plane waves, etc. However, two type of atom-centred basis functions are more commonly used in the electronic structure methods, namely the Slater Type Orbitals (proposed by Zener[6] and Slater[7]) and Gaussian Type Orbitals (after Boys[8] and McWeeny[9]). These basis functions are also called atomic orbitals (AOs), although they are not solutions to an atomic Schrödinger wave equation in general. The Slater type orbitals have the $e^{-\zeta r}$ form where ζ is called orbital exponent which can have any positive values and r is the electron-nucleus distance. Due to this exponential relationship with the nucleus-electron distance, the STOs mimics the hydrogen-like orbitals and show excellent behaviour in the near and far regions of the atomic nucleus. For polyatomic molecules, however, the solution of Eq. (2.1) requires multi-centred (two, three and four centred) two-electron integrals for which the STOs have complicated analytical solutions. This factor makes the choice of STOs computationally expensive.

To make *ab initio* calculations faster and feasible for large systems, the use of Gaussian type orbitals (GTOs) was proposed which have the $e^{-\zeta r^2}$ form. Compared to STOs, Gaussian functions are inferior in approximating an orbital. However, a linear combination of several Gaussians can be taken to approximate an STO. Since the product of two Gaussian functions centred at two nuclei is an another Gaussian centred at a third point, the evaluation of multi-centred two electron integrals is much cheaper than with STOs. This factor makes GTOs a preferred choice for performing *ab initio* calculations.

The total N-electron wave function, constructed from MOs, must be anti-symmetric with respect to the exchange of coordinates of two electrons (Pauli's principle[10]). This antisymmetry requirement can be achieved by writing the wave function in the form of determinants, usually called Slater determinants.[11] When a Slater determinant, or a linear combination of a few symmetry adapted Slater determinants, is an eigenfunction of the N-electrons' spin operators $\hat{\mathbf{S}}^2$ and $\hat{\mathbf{S}}_z$ for a given system it is called a configuration state function (CSF) or simply a configuration. If the one-electron functions form a *complete* set and N-electrons wave functions are expanded in a *complete* N-electron basis (all possible CSFs), the exact solution of Eq. (2.1) can be found. However, a complete one-particle basis requires that the unknown MOs are expanded in an infinite number of one-particle basis functions which is not feasible. In practice the MOs are expanded in a basis set of finite size. So even when the N-electron basis is complete in the given one-electron space, it is still an approximation because of the incomplete one-electron basis set. Thus, both the size and the quality of the basis set affect the accuracy of a solution. Furthermore, the number of CSFs grows factorially with the number of electrons and the size of the basis set. This puts further restrictions on the choice of the N-electron space and more approximations have to be made to make calculations possible for reasonably large systems.

2.2 Hartree-Fock Method

The simplest approach to solve the electronic Schrödinger equation is the Hartree-Fock method[12--16] where the N-electron wave function is approximated by a single Slater determinant (a single CSF). For a normalised wave function, the energy is then calculated as an expectation value of the Hamiltonian:

$$E = \langle \Psi_{HF} | \hat{\mathscr{H}} | \Psi_{HF} \rangle \tag{2.3}$$

where Ψ_{HF} is the single determinant Hartree-Fock wave function composed of spin-orbitals, ϕ. Using the Hamiltonian given in Eq. (2.2) the above energy expression becomes:

$$E = \sum_i h_{ii} + \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}) + V_{NN} \tag{2.4}$$

where

$$h_{ii} = \langle \phi_i(1) | -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{\mathbf{R}_{A1}} | \phi_i(1) \rangle \tag{2.5}$$

describes the kinetic energy of electron 1 and its attraction to all the nuclei,

$$J_{ij} = \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | \phi_i(1) \phi_j(2) \rangle \tag{2.6}$$

and

$$K_{ij} = \langle \phi_i(1)\phi_j(2)|\frac{1}{r_{12}}|\phi_j(1)\phi_i(2)\rangle \tag{2.7}$$

are the coulomb and the exchange interactions and V_{NN} is the potential energy due to the nucleus-nucleus interaction.

Starting with an initial guess, the orbitals in the Ψ_{HF} are determined using the variational principle[17] so that the energy expectation value in Eq. (2.4) becomes a minimum or at least stationary. The variation in the orbitals is subjected to the constraint that they remain orthonormal. The minimisation of the energy with respect to change in the orbitals leads to the following Hartree-Fock equations:

$$\hat{F}(i)\phi_j(i) = \epsilon_j \phi_j(i) \tag{2.8}$$

where $\hat{F}(i)$ is an effective one-electron operator, called the Fock operator and is written as:

$$\hat{F}(i) = \hat{h}(i) + \sum_j (\hat{J}_j(i) - \hat{K}_j(i)) \tag{2.9}$$

Since the Fock operator is dependent on the orbitals, the Hartree-Fock equations (Eq. (2.8)) are solved iteratively in a way called self-consistent field (SCF) method. The Hartree-Fock integro-differential equations can be solved using numerical methods.[16,18] However, these methods are limited to only atoms and some small (usually diatomic) molecules due to the computational difficulties involved. In the commonly used method, the unknown molecular orbitals are expanded in terms of known basis functions.[19,20]

$$\phi_j = \sum_\mu c_{\mu j} \chi_\mu \tag{2.10}$$

and the coefficients of expansion c_μ are determined using the variational principle. The resulting equations, called Hartree-Fock-Roothaan-Hall equations, have the following form:

$$\hat{F} \sum_\mu c_{\mu j} \chi_\mu = \epsilon_j \sum_\mu c_{\mu j} \chi_\mu \tag{2.11}$$

which, after left multiplying with a basis function and integrating, can be written in matrix form as:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{2.12}$$

The **F** in Eq. (2.12) is called the Fock matrix, the **S** is the overlap matrix between the basis functions, **C** is the matrix of coefficients and $\boldsymbol{\varepsilon}$ is the matrix of orbital energies. The basis functions used to expand the MOs are not orthogonal, however, a linear combination can be chosen such that this new set forms an orthogonal basis. With this choice the new overlap matrix $\mathbf{S}'$ becomes a unit matrix and the expression in Eq. (2.12) is reduced to eigenvalue equation:

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\varepsilon} \tag{2.13}$$

In Eqs. (2.8) and (2.13) the matrix of orbital energies is a diagonal matrix and the resulting MOs are called canonical MOs. According to Koopman's theorem,[21] the orbital energies ϵ_i for canonical MOs are approximately equal to the negative of the ionization energy.

The Hartree-Fock approximation implies that an electron moves in an average potential field created by other electrons, without any instantaneous interaction. It is quite successful in determining the electronic structure and some one-electron properties of most (but not all) molecules near their equilibrium geometries. It can recover more than 99% of the total energy for atomic or molecular systems. However, it can not be used in situations where the electrons undergo rearrangements, as in the formation and dissociation of bonds. In that case this approximation breaks down.

In its most popular form the HF method uses the same set of spatial orbitals for electrons whose spins are paired. For closed-shell systems where all electrons are paired, this form is called restricted HF (RHF) or simply HF and for open-shell systems (where one or more electrons are unpaired) it is called restricted open-shell HF (ROHF). It is also possible to use different spatial orbitals for electrons with different spin in both closed-shell and open-shell systems. This approach is called unrestricted Hartree-Fock (UHF). The UHF wave functions give correct dissociation of atoms or molecular fragments and for open-shell systems at equilibrium geometry, gives slightly lower energies than ROHF. However, a disadvantage of this method is that the wave functions are incorrect as they are not eigenfunctions of the total spin operator $\hat{\mathbf{S}}^2$.

2.3 Electron Correlation Methods

The serious shortcomings of the Hartree-Fock method can be related to its neglect of electron correlation effects. The correlation effects are usually divided into near-degeneracy effects (static correlation) and dynamic correlation.[22] The static correlation is the inadequacy of the Hartree-Fock wave function to describe the situations where several configurations become degenerate or near degenerate. This happens most often when bonds are formed or broken. Dynamic correlation stems from the fact that electrons tend to avoid each other instantaneously, due to the coulomb repulsion. In the Hartree-Fock method the electron-electron interaction is treated in an average way using a single CSF. For a more accurate picture, the instantaneous interaction between the electrons must be taken into account instead of an average interaction. The electronic structure methods which take care of electron correlation are called electron correlation methods.

The correlation energy[23,24] is defined as the difference between the exact non-relativistic energy of the system and the energy of the Hartree-Fock wave function in a complete basis.

2.3.1 Configuration Interaction Methods

In the Configuration Interaction (CI) method,[25,26] the N-electron wave function is expanded as a linear combination of CSFs:

$$\Psi_{CI} = \sum_{i} c_i \Phi_i \tag{2.14}$$

These CFSs are generated by distributing N electrons in the m orbitals in all possible ways. The coefficients c_is of the linear expansion are determined by the variational principle[17] while the orbitals (MO coefficients) are held fixed. When all possible configurations are included in Eq. (2.14) in a given basis set, this approach is called full CI. Full CI gives the "exact" energy of Eq. (2.1) within the given basis set. The difference between the Hartree-Fock energy in a given one-electron basis and the results of a full CI in the same basis is called the *basis set correlation energy*.[24] In the full CI, the number of CSFs grows factorially with the number of electrons and the size of the basis set. The total number of CSFs for a system of N electrons, m basis functions with total spin S is given by Weyl's formula:[27–29]

$$f_{CSF_s}(n, m, S) = \frac{2S+1}{m+1} \begin{pmatrix} m+1 \\ \frac{1}{2}N - S \end{pmatrix} \begin{pmatrix} m+1 \\ \frac{1}{2}N + S + 1 \end{pmatrix} \tag{2.15}$$

For a small system like the C_2 molecule with 12 electrons and 100 orbitals, the number of CSFs is approximately 10^{17}. This makes full CI calculations impossible for all but very small molecules in a small basis. To make the CI calculations practical for large systems, it is necessary to truncate the CI expansion space in some way by ignoring certain CSFs. This gives rise to the truncated versions of full CI which are abbreviated as CIS, CID, CISD, CISDT, CISDTQ, so on where S, D, T, Q, represents singly, doubly, triply, quadruply, excited CSFs. According to the Brillouin theorem,[30] the singly excited CSFs do not interact with the Hartree-Fock wave function through the Hamiltonian. The CID level is, therefore, the smallest truncation which can provide an improved wave function and energy over the Hartree-Fock reference.

An essential requirement in the *ab initio* methods is their *size extensivity*[31] which allows a consistent comparison of the energies of molecules of different sizes. A method that scales linearly, i.e., scales as the exact energy does, with the number of (interacting or non-interacting) particles in the system, is called a size extensive method. *Size consistency*[32] is another required feature in *ab initio* approaches. A method is size consistent if it gives the energy of two or more infinitely separated atomic or molecular fragments equal to the sum of the energies of the isolated fragments. The full CI method is both size extensive and size consistent, however, it is not practical for large systems. A major problem with the truncated CI methods is that they are neither size extensive nor size consistent.

2.3.2 Multi-Configurational Self-Consistent Field Methods

In the multi-configuration self-consistent field (MCSCF) methods[33--39] the wave function is constructed as a linear combination of a limited number of carefully chosen CSFs and both the CI coefficients and the orbitals are optimised by an SCF procedure to yield the lowest energy expectation value. The optimisation of an MCSCF wave function is much more work than optimising only the CI coefficients and several schemes based on the generalized Brillouin theorem[40] (an extended form of Brillouin theorem for MCSCF wave functions), Newton-Raphson method or direct minimisation of the energy have been developed for this purpose (for a review of these methods see Ref. 41 and references therein).

In a special form of the MCSCF method the orbitals (and similarly the electrons) are divided into a set of "inactive" orbitals which remain doubly occupied in all CSFs and an "active" space of variably occupied orbitals. In the active space the CSFs are generated by distributing active electrons among the active orbitals in all possible ways (a full CI in the active space). This method is called a fully optimised reaction space (FORS) method[42--44] or a complete active space SCF (CASSCF) method.[45--48] It is widely used in the situations where near to complete degeneracies play important roles.

To account for both the dynamic and static correlation, a combination of MCSCF and CI approaches has also been developed, called Multireference Configuration Interaction (MR-CI).[38] In the conventional CI usually the HF wave function is taken as a reference while in the MR-CI, the MCSCF (or CASSCF) wave function is taken as reference and then a CI is performed by including all singly and doubly excited CSFs with respect to the reference. This approach is mainly used for small molecules and gives accurate results. However, for large systems it becomes computationally extremely demanding.

2.3.3 Perturbation Theory

The Raleigh-Schrödinger perturbation theory (RS-PT) is another way to obtain corrections to HF wave functions and recover electron correlation effects. In this method the Hamiltonian for the system to be solved is divided into an unperturbed Hamiltonian ($\hat{\mathscr{H}}_0$), for which solutions have already been found, plus a small perturbation ($\hat{V}$).

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \lambda \hat{V} \tag{2.16}$$

where λ is a parameter so that when $\lambda = 0$ there is no perturbation and when $\lambda = 1$ the system is fully perturbed. The unperturbed Hamiltonian has known eigenfunctions and eigenvalues. For small perturbations, the solution for the perturbed system can then be found by expanding the wave function and energy in terms of the following series:

$$\begin{aligned} \Psi &= \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \lambda^3\Psi^{(3)} + \cdots\cdots \\ E &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \cdots\cdots \end{aligned} \tag{2.17}$$

where $\Psi^{(0)}$ is an unperturbed wave function and $E^{(0)}$ is its eigenvalue. The higher terms are the first order, second order, and so on, corrections to the wave function and energy. A special variant of RS-PT is Møller-Plesset (MP) perturbation theory.[49] In this approach the unperturbed Hamiltonian is taken as the sum of one-electron Fock-operators and $\Psi^{(0)}$ is taken to be the Hartree-Fock wave function. The truncation of the series in Eq. (2.17) is denoted as MPn (n = 1, 2, 3 $\cdots$), for example, MP2, MP3, MP4, etc. MP2 is the lowest level required to get an improvement on the HF energy. It is the most economical way to account for the correlation energy. MP2 method is size extensive and in most cases it can recover more than 80-90% of the correlation energy.

In the MPn methods the perturbation is applied to a single determinant HF wave function. When a system has a (nearly-)degenerate ground state, a single configuration is not enough to describe the unperturbed wave function. In that case a proper reference is a multiconfiguration wave function. Such methods have been developed where the MCSCF (CASSCF) wave function is taken as the zeroth order wave function and then the perturbation is applied. These methods are commonly called CASPT2,[50--52] CASPT3,[53] depending on the level of the applied perturbation. These methods are not size extensive in general. However, using appropriate zeroth-order Hamiltonian an exactly size extensive and size consistent form of Multi-reference Møller-Plesset (MRMP) perturbation theory has also been developed.[54,55] The convergence of these approaches is almost of the same quality as MRCI methods but the former are quite less intensive in computational cost.

2.3.4 Coupled Cluster Methods

In the Coupled Cluster (CC) approach[56,57] the wavefunction is expanded from the HF reference as:

$$\Psi_{CC} = e^{\hat{T}} \Phi_0 \tag{2.18}$$

where the operator $e^{\hat{T}}$ is define by Taylor series expansion as:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \cdots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!} \tag{2.19}$$

The cluster operator $\hat{T}$ is defined as:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N \tag{2.20}$$

$\hat{T}_1$, $\hat{T}_2$, $\hat{T}_3$, and so on, are one-particle, two-particle, three-particle, up to N-particle excitation operators. The exponential nature of the cluster operator ensures size extensivity at all levels. When all $\hat{T}_N$ operators are included in the expansion, this method becomes equivalent to the full CI method. However, as mentioned earlier, that is only possible for quite small systems in small basis sets. The CCSD level, where $\hat{T} = \hat{T}_1 + \hat{T}_2$, is commonly used. The CCSDT is the next level which contains the contribution of triple excitations. It gives highly accurate results for correlation energies but is also computationally very demanding. Some approximate forms of CCSDT have been developed among which the CCSD(T)[58,59] is widely used. In CCSD(T) the contribution of the triples is estimated using perturbation theory.

2.4 Valence Bond Methods

In the *ab initio* approaches discussed so far the molecular orbitals (MOs) are expanded as linear combinations of atomic orbitals (LCAO), i.e., the basis functions. These MOs are orthogonal to each other and each MO spans the entire molecule rather than being localised on atoms or in the bonding regions. This approach is called Molecular Orbital (MO) theory[60--64] the simplest of which is the Hartree-Fock method. These delocalised MOs do not give the intuitive picture of a chemist's idea of a bond. They may be transformed to localised orbitals[65--68] without affecting the total wave function, however, there is no unique way to do that.

An alternate approach to find the solutions of the electronic Schrödinger equation for molecular systems is the use of Valence Bond (VB) theory which is closely related to the chemist's idea of molecules as being composed of atoms and held together by chemical bonds. Actually, the idea that atoms combine by sharing their valence electrons to form molecules predates modern quantum mechanics.[69] Heitler and London,[70] using the principles of quantum mechanics, showed for the first time how the sharing of electrons holds the atoms together in a covalent molecule like H_2 thus providing the quantum mechanical basis for this theory. Pauling and Slater introduced the idea of maximum overlap between the orbital and the "changed quantization" (hybridisation) which became very popular among the organic chemists. Further efforts by Heitler and Rumer,[71] Slater,[72] Pauling[73,74] and many others[75] developed the Heitler-London's methods into a general theory of electronic structure which is now known as valence bond theory.

2.4.1 Classical Valence Bond Theory

In the Heitler-London method[70] a bond is described as a singlet-coupled pair of singly occupied orbitals. For example, for the H_2 molecule the $1s_a$ orbital of one hydrogen atom is singlet-coupled to the $1s_b$ orbital of the second hydrogen atom. In the determinantal form the Heitler-London wave function for H_2 molecule can be represented by a linear combination of two Slater determinants as follows:

$$\Phi_{HL} = \mathcal{N}\{|1s_a(1)\overline{1s_b(2)}| - |\overline{1s_a(1)}1s_b(2)|\} \tag{2.21}$$

or

$$\Phi_{HL} = \mathcal{N}\{1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{2.22}$$

where $\mathcal{N}$ is the normalisation constant. The above wave function gives a qualitatively correct picture of bonding. For quantitative results it can be improved by adding more configurations which correspond to ionic structures.

$$\Phi_{ionic} = \mathcal{N}\{1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{2.23}$$

The total VB wave function is then taken as a linear combination of these structures:

$$\Psi_{VB} = c_1\Phi_{HL} + c_2\Phi_{ionic} \tag{2.24}$$

The number of all (ionic and covalent) VB structures for a system can be determined by Eq. (2.15) while the number of covalent structures is given by:

$$f_S^N = \begin{pmatrix} N \\ \frac{1}{2}N + S \end{pmatrix} - \begin{pmatrix} N \\ \frac{1}{2}N + S + 1 \end{pmatrix} \tag{2.25}$$

where N is the number of electrons and S is the total spin of the system.

2.4.2 Coulson-Fisher Approach

In the classical form of the VB method, the atomic orbitals are not allowed to distort freely as the atoms approach each other in a molecule. To compensate this effect, a large number of ionic structures is required. As the number of ionic structures becomes large, the simple predictive power of VB wave functions is obscured. Coulson and Fischer[76] suggested the use of optimal (slightly deformed atomic) orbitals. For the H_2 molecule, a Coulson-Fischer wave function can be represented as:

$$\Psi_{CF} = \mathcal{N}\{\phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{2.26}$$

where ϕ_1 and ϕ_2 are now deformed atomic orbitals:

$$\phi_1 = 1s_a + \lambda 1s_b \qquad \text{and} \qquad \phi_2 = 1s_b + \lambda 1s_a \tag{2.27}$$

where λ is a variationally adjustable parameter. The resulting orbitals are predominantly atomic in character, however, they are slightly delocalised. Since this deformation of the orbitals automatically includes the effect of the ionic structures, an obvious advantage of the Coulson-Fischer approach is that the number of structures in the wave function can be kept to a minimum.

2.4.3 Generalised Valence Bond Method

The first VB method based on the Coulson-Fisher approach is the generalised valence bond (GVB) method.[77--79] In the GVB approach, two nonorthogonal orbitals are used to describe a pair of electrons in a bond. Each pair of electrons in a bond is coupled to a singlet. The singlet coupled pairs of orbitals are then combined to give the total wave function of a system with an overall singlet spin state. This is known as the GVB perfect pairing (GVB-PP) approach. Such two electron two orbital pairs are called *geminal pairs*. These orbitals are optimised variationally. The computation cost is reduced by posing *strong orthogonality* (SO) between different geminal pairs. The SO-GVB-PP is a restricted form of VB where only a single spin-coupling pattern is allowed. In another form called *unrestricted* SO-GVB[80] multiple spin-couplings are allowed for a given number of singly occupied orbitals. The restriction on different pairs to remain orthogonal, while computationally advantageous, leads sometimes to artefacts.[22,81]

2.4.4 Spin-Coupled Valence Bond Method

The spin-coupled valence bond (SCVB) method[82--85] uses a more generalised form of the Coulson-Fisher wave function for molecules. In the SCVB approach, the N electrons which are involved in the bonding are described by N singly occupied nonorthogonal orbitals. These orbitals are then singlet-coupled in all possible ways to give the overall spin S of the system. The general form of an SCVB wave function is:

$$\Psi_{SCVB} = \mathcal{N} \sum_{k=1}^{f_S^N} c_{Sk} \hat{\mathscr{A}} [\phi_1 \phi_2 \phi_3 \cdots \phi_N \Theta_{S,M;k}^N] \tag{2.28}$$

where $\mathcal{N}$ is the normalisation factor, $\hat{\mathcal{A}}$ is an antisymmetriser, $\Theta^N_{S,M;k}$ describes a particular spin-coupling pattern between the orbitals and c_{Sk} is the spin-coupling coefficient. The different spin-coupling modes are generally referred to as VB structures. The total number of these structures, f^N_S is determined by Eq. (2.25). Both the orbitals and the VB coefficients are optimised.

2.4.5 Valence Bond Self-Consistent Field Method

The Valence Bond Self-Consistent Field (VBSCF) method[86--88] is the most general form of the modern VB approaches. Mathematically, it is the nonorthogonal equivalent of MCSCF methods which are based on the generalised Brillouin theorem. In the VBSCF approach the VB wave functions can be constructed using any number of VB structures and any amount of nonorthogonality among the orbitals is allowed. Both the orbitals and VB structure coefficients are optimised. The resulting wave functions are compact and can be easily interpreted in terms of chemical concepts. The orbitals used to build the VB structures may be fully optimised as in the SCVB or they may be restricted to a subspace of the full orbital space, e.g., just on the atoms where they are centred. The expressions for the analytical molecular energy gradients[89,90] and second order response properties[91] have also been developed for the VBSCF wave functions. Recently, a new approach, called Atoms in Valence Bond (AIVB) method[92,93] has been developed within the framework of the VBSCF method. In this approach, instead of the traditional VB structures, the wave function is constructed as a linear combination of all possible atomic states of the different atoms in a molecule. The advantage of this approach is that no preconceptions are required about a system to describe its electronic structure or properties.

References

1. Schrödinger, E. *Ann. Phys.* **1926**, *384*, 361--376.
2. Levine, I. N. *Quantum Chemistry*, 5th ed.; Prentice Hall: New Jersey, **2000**.
3. Atkins, P.; de Paula, J. *Atkins' Physical Chemistry*, 8th ed.; Oxford University Press: Oxford, **2009**.
4. Born, M.; Oppenheimer, R. *Ann. Phys.* **1927**, *389*, 457--484.
5. *Quantum Chemistry: Classic Scientific Papers*; Hettema, H., Ed.; World Scientific, **2000**; Vol. 8.
6. Zener, C. *Phys. Rev.* **1930**, *36*, 51--56.
7. Slater, J. C. *Phys. Rev.* **1930**, *36*, 57--64.
8. Boys, S. F. *Proc. R. Soc. Lond. A* **1950**, *200*, 542--554.
9. McWeeny, R. *Nature* **1950**, *166*, 21--22.
10. Pauli, W., Jr. *Z. Physik* **1925**, *31*, 765--783.

11. Slater, J. C. *Phys. Rev.* **1929**, *34*, 1293--1322.
12. Hartree, D. R. *Proc. Cam. Phil. Soc.* **1928**, *24*, 89--110.
13. Hartree, D. R. *Proc. Cam. Phil. Soc.* **1928**, *24*, 111--132.
14. Hartree, D. R. *Proc. Cam. Phil. Soc.* **1928**, *24*, 426--437.
15. Fock, V. *Z. Physik* **1930**, *61*, 126--148.
16. Hartree, D. R. *The Calculation of Atomic Structures*; Structure of Matter Series; John Wiley & Sons Ltd.: London, **1957**.
17. Ritz, W. *J. Reine Angew. Math.* **1909**, *135*, 1--61.
18. Fischer, C. F. *The Hartree-Fock Method for Atoms: A Numerical Approach*; A Wiley-Interscience Publication; John Wiley & Sons Ltd.: London, **1977**.
19. Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69--89.
20. Hall, G. G. *Proc. R. Soc. London A* **1951**, *205*, 541--552.
21. Koopmans, T. *Physica* **1934**, *1*, 104 -- 113.
22. Jensen, F. *Introduction to Computational Chemistry*, 2nd ed.; John Wiley & Sons, Ltd.: Chichester, England, **2007**.
23. Löwdin, P.-O. Correlation Problem in Many-Electron Quantum Mechanics I. Review of Different Approaches and Discussion of Some Current Ideas. In *Advances in Chemical Physics*; Prigogine, I., Ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, **1959**; Vol. 2, pp 207--322.
24. Szabo, A.; Ostlund, N. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Books on Chemistry Series; Dover Publications, Inc.: New York, **1996**.
25. Shavitt, I. The Method of Configuration Interaction. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum Press: New York, **1977**; pp 189--275.
26. Shavitt, I. *Mol. Phys.* **1998**, *94*, 3--17.
27. Weyl, H. *The Theory of Groups and Quantum Mechanics*; Dover books on advanced mathematics; Dover Publications, Inc.: New York, **1950**.
28. Mulder, J. J. C. *Mol. Phys.* **1966**, *10*, 479--488.
29. Paldus, J. *J. Chem. Phys.* **1974**, *61*, 5321--5330.
30. Mayer, I. *Simple Theorems, Proofs and Derivations in Quantum Chemistry*; Mathematical and Computational Chemistry; Kluwer Academic/Plenum Publishers: New York, **2003**.
31. Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561--581.
32. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1--19.
33. Das, G.; Wahl, A. C. *J. Chem. Phys.* **1972**, *56*, 1769--1775.
34. Wahl, A. C.; Das, G. P. The Multiconfiguration Self-Consistent Field Method. In *Methods of Electronic Structure Theory*; (III), H. F. S., Ed.; Plenum Press: New York, **1977**;

Vol. 3, pp 51--78.

35. Ruttink, P. J. A.; Lenthe, J. H. *Theor. Chem. Acc.* **1977**, *44*, 97--107.
36. Roos, B. O. The Multiconfigurational (MC) SCF Method. In *Methods in Computational Molecular Physics*; Diercksen, G. H. F., Wilson, S., Eds.; NATO ASI Series: Mathematical and Physical Sciences; Kluwer Academic Publishers Group: Dordrecht, Holland, **1983**; pp 161--188.
37. Olsen, J.; Yeager, D. L.; Jørgensen, P. Optimization and Characterization of a Multiconfigurational Self-Consistent Field (MCSCF) State. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons, Inc.: New York, **1983**; pp 1--176.
38. Werner, H.-J. Matrix-Formulated Direct Multiconfiguration And Multiconfiguration Reference Configuration Interaction Methods. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 1--62.
39. Shepard, R. The Multiconfiguration Self-Consistent Field Method. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 63--200.
40. Levy, B.; Berthier, G. *Int. J. Quant. Chem.* **1968**, *2*, 307--319.
41. Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233--366.
42. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. *Chem. Phys.* **1982**, *71*, 41--49.
43. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M. *Chem. Phys.* **1982**, *71*, 51--64.
44. Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. *Chem. Phys.* **1982**, *71*, 65--78.
45. Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157--173.
46. Siegbahn, P. E. M.; Heiberg, A.; Roos, B. O.; Levy, B. *Phys. Scr.* **1980**, *21*, 23--327,.
47. Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384--2396.
48. Roos, B. O. The Complete Active Space Self-Consistent Field Method and its Applications in Electronic Structure Calculations. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 399--445.
49. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618--622.
50. Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483--5488.
51. Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218--1226.
52. Roos, B. O.; Andersson, K. *Chem. Phys. Lett.* **1995**, *245*, 215--223.

53. Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645--661.
54. van Dam, H. J. J.; van Lenthe, J. H.; Pulay, P. *Mol. Phys.* **1998**, *93*, 431--439.
55. van Dam, H. J. J.; van Lenthe, J. H.; Ruttink, P. J. A. *Int. J. Quantum Chem.* **1999**, *72*, 549--558.
56. Coester, F.; Kümmel, H. *Nucl. Phys.* **1960**, *17*, 477--485.
57. Čížek, J. *J. Chem. Phys.* **1966**, *45*, 4256--4266.
58. Purvis III, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910--1918.
59. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479--483.
60. Hund, F. *Z. Physik* **1927**, *40*, 742--764.
61. Mulliken, R. S. *Phys. Rev.* **1928**, *32*, 186--222.
62. Lennard-Jones, J. E. *Trans. Faraday Soc.* **1929**, *25*, 668--686.
63. Coulson, C. A. *Valence*, 2nd ed.; Oxford University Press: London, England, **1961**.
64. Hall, G. G. The Lennard-Jones paper of 1929 and the foundations of Molecular Orbital Theory. In *Advances in Quantum Chemistry*; Per-Olov Löwdin, J. R. S., Zerner, M. C., Eds.; Academic Press, **1991**; Vol. 22, pp 1--6.
65. Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296--299.
66. Edmiston, C.; Ruedenberg, K. *J. Chem. Phys.* **1965**, *43*, S97--S116.
67. von Niessen, W. *J. Chem. Phys.* **1972**, *56*, 4290--4297.
68. Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916--4926.
69. Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762--785.
70. Heitler, W.; London, F. *Z. Physik* **1927**, *44*, 455--472.
71. Heitler, W.; Rumer, G. *Z. Physik* **1931**, *68*, 12--41.
72. Slater, J. C. *Phys. Rev.* **1931**, *37*, 481--489.
73. Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367--1400.
74. Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, **1960**.
75. Gallup, G. A. *Valence Bond Methods: Theory and Applications*; Cambridge University Press: Cambridge, **2002**.
76. Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386--393.
77. Hunt, W. J.; Hay, P. J.; Goddard, W. A. *J. Chem. Phys.* **1972**, *57*, 738--748.
78. Hay, P. J.; Hunt, W. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 8293--8301.
79. Goddard, W. A.; Dunning, T. H.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368--376.
80. Moss, B. J.; Bobrowicz, F. W.; III, W. A. G. *J. Chem. Phys.* **1975**, *63*, 4632--4639.
81. Cooper, D. L.; Gerraatt, J.; Raimondi, M.; Wright, S. C. *Chem. Phys. Lett.* **1987**, *138*,

296--302.

82. Gerratt, J. General Theory of Spin-Coupled Wave Functions for Atoms and Molecules. In *Advances in Atomic and Molecular Physics*; Bates, D., Esterman, I., Eds.; Academic Press, **1971**; Vol. 7, pp 141--221.
83. Gerratt, J.; Raimondi, M. *Proc. R. Soc.* **1980**, *A371*, 525--552.
84. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Farady Symp. Chem. Soc.* **1984**, *19*, 149--163.
85. Cooper, D. L.; Gerratt, J.; Raimondi, M. Modern Valence Bond Theory. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 319--397.
86. van Lenthe, J. H.; Balint-Kurti, G. G. *Chem. Phys. Lett.* **1980**, *76*, 138--142.
87. van Lenthe, J. H.; Balint-Kurti, G. G. *J. Chem. Phys.* **1983**, *78*, 5699--5713.
88. van Lenthe, J. H.; Dijkstra, F.; Havenith, R. W. A. TURTLE - A gradient VBSCF Program Theory and Studies of Aromaticity. In *Theoretical and Computational Chemistry: Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10, pp 79--116.
89. Dijkstra, F.; van Lenthe, J. H. *J. Chem. Phys.* **2000**, *113*, 2100--2108.
90. Dijkstra, F.; van Lenthe, J. H. *Chem. Phys. Lett.* **1999**, *310*, 553--556.
91. Havenith, R. W. A. *Chem. Phys. Lett* **2005**, *414*, 1--5.
92. Zielinski, M. L. *Atoms in Valence Bond Method, Implementation and Application*; Ph. D. Thesis; Utrecht University: Utrecht, The Netherlands, **2012**.
93. Zielinski, M. L.; van Lenthe, J. H. *Chem. Phys. Lett.* **2010**, *500*, 155 --160.

CHAPTER 3

GENERATION OF KEKULÉ VALENCE STRUCTURES AND THE CORRESPONDING VALENCE BOND WAVE FUNCTIONS

Abstract

A general method based on a *recursive* algorithm is presented for generating Kekulé valence structures. This method is applicable for all kinds of (poly)cyclic conjugated systems including fullerenes. The application of the algorithm in generating Valence Bond wave functions, in terms of Kekulé valence structures, is discussed and illustrated in actual Valence Bond calculations. Two types of VBSCF calculations, one involving Kekulé valence structures only and the second one involving all covalent VB structures, were performed for benzene, pentalene, benzocyclobutadiene and naphthalene. Both strictly local and delocalised *p*-orbitals were used in these calculations. Our results show that when the orbitals are restricted to their own atoms, other VB structures (Dewar structures) also have a significant contribution in the VB wave function. When removing this restriction, the other VB structures (Dewar and also the ionic structures) are accommodated in the Kekulé valence structures, automatically. Therefore, at VBSCF delocal level, the ground states of these systems can be described almost quantitatively by considering Kekulé valence structures only at a considerable saving of time.

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3.1 Introduction

Kekulé valence structures have been around for more than a century and these structures have played a key role in understanding the stability of (poly)cyclic conjugated systems.[1--3] *A Kekulé structure is a representation of an aromatic molecular entity (such as benzene), with fixed alternating single and double bonds, in which interactions between multiple bonds are assumed to be absent.*[4] Shown in Figure 3.1 are the two Kekulé valence structures of the benzene molecule.

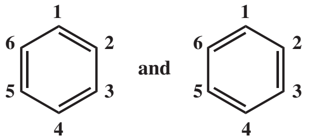


Figure 3.1: The two Kekulé valence structures of the benzene molecule

The number of Kekulé valence structures for a system depends upon the arrangement of the atoms. Different structural isomers, therefore, can have different number of Kekulé valence structures, for example, anthracene and phenanthrene. The former has four and the latter has five Kekulé valence structures. It is not difficult to generate all Kekulé valence structures for smaller (poly)cyclic conjugated systems, however, the problem quickly goes out of hand for bigger molecules as Pauling says, *"A few minutes suffices to draw the four unexcited (Kekulé) structures for anthracene, the five for phenanthrene, or the six for pyrene .... an hour or two might be needed for the 110 structures of tetrabenzoheptacene"*.[5] A lot of work has been done on the enumeration of these structures for different kinds of system and has been discussed in books,[6--8] reviews[9,10] and research articles (for an overview see a *Chem. Rev.* article by M. Randić[10] and the references therein). But very few methods have been reported so far for constructing all Kekulé valence structures for a given system. Randić[11] described an algorithm based on the graph of a molecule to generate Kekulé valence structures for (poly)cyclic conjugated systems. Based on the reduced graph of a molecule, Dzonova-Jerman-Blazic and Trinajstić[12] discussed an elegant algorithm for the enumeration and display of Kekulé valence structures for benzenoids. Cai and co-workers[13] proposed a method for generating Kekulé valence structures and longer range resonance valence structures (Dewar structures) using the adjacency matrix and adjacency bonding array. The adjacency matrix **A** is defined as a square matrix (with dimensions $N \times N$ for an N-atoms system) with the following elements.[14,15]

$$a_{ij} = \begin{cases} 1 & \text{bonded directly are } j \text{ and } i \text{ if} \\ 0 & \text{otherwise} \end{cases}$$

The adjacency matrix is related to the well known Hückel's Hamiltonian matrix.[16] The latter can be converted to adjacency matrix after a suitable scaling (the set of approximations used by Hückel[16] to construct the Hamiltonian matrix and the (0,1) notation was originally introduced by Bloch[17,18]). For the benzene molecule in Figure 3.1 the adjacency matrix is (hydrogens excluded):

$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

where the diagonal of the above matrix represents the atom itself and the off-diagonal non zero entries shows its neighbours. An adjacency bonding array is defined as a connection matrix (with dimensions $N \times 3$, based on the concept that a carbon atom involved in the Kekulé valence structures can have maximum three adjacent atoms) which records the position of the non-zero elements in the adjacency matrix of a molecule. The elements of the adjacency bonding array ($(aba)_{ik}$, $k = 1, 2, 3$) will be:

$$(aba)_{ik} = \begin{cases} j & \text{1 is } a_{ij} \text{ if} \\ 0 & \text{otherwise} \end{cases}$$

The adjacency bonding array for the benzene molecule, based on the above adjacency matrix, will be;

$$\begin{bmatrix} 2 & 6 & 0 \\ 1 & 3 & 0 \\ 2 & 4 & 0 \\ 3 & 5 & 0 \\ 4 & 6 & 0 \\ 1 & 5 & 0 \end{bmatrix}$$

here the first row shows that atom number 2 and 6 are neighbours of atom number 1 and so on. If some of the rows of the adjacency matrix of a system have three non-zero elements (e.g., in case of the adjacency matrix of the naphthalene molecule, excluding hydrogen atoms) the corresponding rows of the adjacency bonding array will have three non-zero entries.

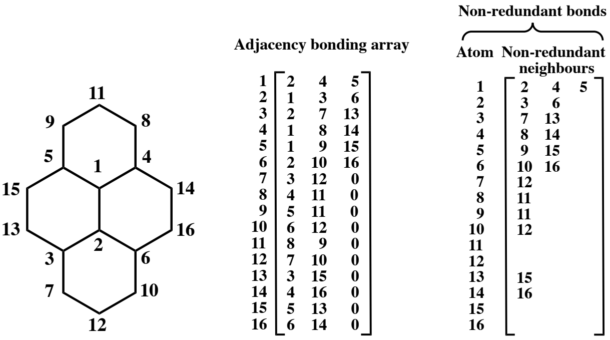
In this chapter a new approach is presented to generate all Kekulé valence structures for a given system. For any kind of system we record the number of all unique (single) bonds and their positions and we call this representation *list of non-redundant bonds*. The idea is similar to that described by Cai and co-workers[13] but in terms of adjacency matrix, we use only the upper triangle (or the transpose of the lower triangle) of this matrix. Our method is very economical in memory and very efficient in computing time. In this method only a one dimensional array of N integers is required to generate all Kekulé valence structures for an N atoms system. Since Kekulé valence structures are central in the *ab initio* Valence Bond based quantum chemical description of aromaticity, our main focus is the generation of a Valence Bond wave function in terms of all Kekulé valence structures for a given (poly)cyclic conjugated system. First, an introduction to the list of non-redundant bonds is presented and, based on this list, the algorithm is described for generating Kekulé valence structures. The implementation of the algorithm is explained and its efficiency is discussed based on selected examples of benzenoids, among which the most complicated case has 206 carbon atoms and has more than 10^{10} Kekulé valence structures, and fullerenes where the most complicated one has 140 carbon atoms and more than 10^{9} Kekulé valence structures. Next, a brief introduction to a Valence Bond (VB) structure and VB wave function is given along with the role of Kekulé valence structures in the *ab initio* VB based calculations. Finally, the results of actual VBSCF calculations on some selected systems are presented.

3.2 Generation of Kekulé Valence Structures

To generate Kekulé valence structures a list of non-redundant bonds is constructed for a given system. For illustration we take the example of pyrene as shown in Figure 3.2. Throughout the rest of this section we will be considering only that part of a molecule which is actually involved in the Kekulé valence structures (i.e., the part of the system where the position of single and double bonds is resonating) and we will call it the skeleton of the system. The hydrogens atoms or other substituents that are not involved in Kekulé valence structures, will be excluded. A bond $x-y$ between two atoms x and y will always be a nearest neighbour bond. We will use N for the total number of atoms or the number of singly occupied p-orbitals that are involved in the Kekulé valence structures. N will always be an even number.

3.2.1 List of Non-redundant Bonds

A list of non-redundant bonds is a representation for all the single bonds in the skeleton along which double bonds can be assigned in any of the Kekulé valence structures for that system. To make this list, the atoms in the skeleton are numbered from 1 to N. The numbering is completely arbitrary and can start wherever one wants. Then in each $x-y$ bond, the higher numbered atom is listed as a neighbour of the lower numbered atom but the lower numbered atom is not listed as a neighbour of the higher numbered atom. Any atom x, therefore, has only those atoms as its neighbours which are higher than x in numbering order. Such neighbours of each atom are called non-redundant neighbours and in the list, each non-redundant neighbour of an atom x represents a bond between atom x and the neighbour atom. As soon



Adjacency bonding array

$$\begin{array}{c} 1\\2\\3\\4\\5\\6\\7\\8\\9\\10\\11\\12\\13\\14\\15\\16 \end{array}\begin{bmatrix} 2 & 4 & 5\\ 1 & 3 & 6\\ 2 & 7 & 13\\ 1 & 8 & 14\\ 1 & 9 & 15\\ 2 & 10 & 16\\ 3 & 12 & 0\\ 4 & 11 & 0\\ 5 & 11 & 0\\ 6 & 12 & 0\\ 8 & 9 & 0\\ 7 & 10 & 0\\ 3 & 15 & 0\\ 4 & 16 & 0\\ 5 & 13 & 0\\ 6 & 14 & 0 \end{bmatrix}$$

Non-redundant bonds

Atom	Non-redundant neighbours		
1	2	4	5
2	3	6	
3	7	13	
4	8	14	
5	9	15	
6	10	16	
7	12		
8	11		
9	11		
10	12		
11			
12			
13	15		
14	16		
15			
16			

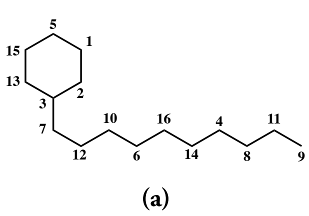
(a) **(b)** **(c)**

Figure 3.2: **(a).** carbon skeleton of the pyrene molecule, **(b).** adjacency bonding array for the skeleton, **(c).** list of non-redundant bonds for the skeleton.

as we have decided which atoms are involved in the Kekulé valence structures, this list can be generated, automatically, from the atomic coordinates of the system by specifying a suitable distance for nearest neighbours. It can also be generated from the adjacency matrix for that system. In the latter case the position of non-zero entries in a row x in the upper triangle of the matrix would be the non-redundant neighbours for atom x. The adjacency bonding array can also be used to construct the list of non-redundant bonds and in that case if the non-zero element in a row x of the adjacency bonding array is higher than x then it will be a non-redundant neighbour of atom x.

Figure 3.2 shows the skeleton of pyrene, the adjacency bonding array and the "list of non-redundant bonds" for it. In the list of non-redundant bonds (Figure 3.2c), for example, atom 1 has three non-redundant neighbours, i.e., 2, 4 and 5, and with atom 1, each of these neighbours represents a bond, i.e., $1-2$, $1-4$ and $1-5$ are non-redundant bonds as we do not consider them again as $2-1$, $4-1$ or $5-1$.

In the skeleton, if there is an atom that has an adjacency of three then there must be another atom which also has an adjacency of three and the total number of such atoms (i.e., atoms having an adjacency of three) must be even. Otherwise the third adjacency of the former atom will be a substituent and we have to exclude this from the skeleton and renumber the remaining part to construct Kekulé valence structures for that system. This situation is explained in Figure 3.3. In Figure 3.3a atom number 3 has three adjacent atoms, i.e., 2, 7 and 13, and there is no other atom with an adjacency of three in this system. To construct the Kekulé valence structures for this system we have to treat atom number 7 and the rest of the tail attached to it, as substituent and then renumber the atoms in the remaining six membered skeleton. Note that the position of the double bonds in the substituent will remain fixed (non-resonating double bonds) and these non-resonating double bonds can be included in each Kekulé valence structure after the Kekulé valence structures are generated. For the



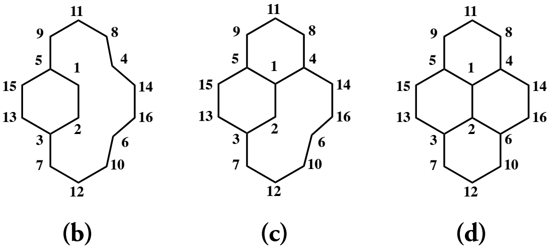


Figure 3.3: Substituents and non-redundant neighbours in the skeleton.

systems shown in Figures 3.3b to 3.3d all atoms can be included in Kekulé valence structures as each of these systems has an even number of those atoms having an adjacency of three and the double bonds will be resonating in the entire system.

As each bond is counted with the lower numbered atom only, for two atoms having an adjacency of three we get only one extra non-redundant bond or neighbour. For monocyclic conjugated hydrocarbons, like 1,3-cyclobutadiene or benzene, the total number of non-redundant bond or neighbours of all the atoms is always equal to the number of atoms (N) in the skeleton. For all polycyclic conjugated hydrocarbons, the total number of non-redundant bonds or neighbours of all atoms can be calculated as $N + nT/2$, where nT is the total number of atoms having an adjacency of three. In the list of non-redundant bonds the first atom always has at least two or at most three non-redundant neighbours, atom number 2 has one up to three and atoms from 3 to N - 3 can have zero up to a maximum of three non-redundant neighbours. Atom N - 2 can have zero up to two, atom N - 1 can have zero or one and the Nth atom cannot have any non-redundant neighbour.

Once this list is generated from any arbitrary numbering, the numbering order of the atoms and the non-redundant neighbours for each atom are fixed. We can not change this order or any neighbour of an atom. This is the base of our algorithm.

3.2.2 Algorithm

Considering all bonds in the list of non-redundant bonds as double bonds, we make all possible combinations of these bonds with the only condition that no atom can be present twice in any combination. Each of these combinations is called a candidate (Kekulé) structure. We begin the procedure with a candidate structure containing no atom or bond (an empty candidate structure). Then starting from atom 1 in the list and going to each next atom one by one in order (the order is important), any of the (double) bonds for each atom can be selected to combine it with the existing candidate structure as long as the above mentioned condition is not violated. On reaching the last atom, in the list of non-redundant bonds, if all atoms have been included in the candidate structure then that candidate structure is a Kekulé valence structure. The algorithm, presented here, to generate candidate structures is

```
recursive procedure generateKekule (kneib, ineib, kekule, N, katom, natom)

integer N, katom, natom  ! N = total number of atoms in the system.
                         ! katom = the atom we have selected from the list.
                         ! natom = no. of atoms stored in candidate structure.
                         ! on first time entering the procedure natom will be zero
integer kneib(N+N/2)     ! kneib(*) contains all non-redundant neighbours.
integer ineib(N)         ! ineib(*) contains number of non-redundant neighbours
                         ! for each atom.
integer kekule(natom+2)  ! kekule(*) is a candidate (kekule) structure. It is an
                         ! array of numbers (atom numbers) that represent the position
                         ! of (double) bonds in a candidate (kekule) structure.
                         ! natom is the number of atoms already stored in this array and
                         ! 2 provides the space for the next two atoms (i.e., a double bond)
                         ! that can be combined with this candidate (kekule) structure.
1:    start of the procedure
      if katom is not present in the candidate (kekule) structure then
         if katom has non-redundant neighbours then
            for all non-redundant neighbours i of katom
            do
               if i is not present in the candidate (kekule) structure then
                  store katom and i as a (double) bond in the candidate (kekule)
                  structure at natom + 1 and natom + 2
                  recursive call generateKekule (kneib, ineib, kekule, N, katom+1, natom+2)
               end if
            end do
         end if
      else (i.e., katom is already present in the candidate (kekule) structure)
         if katom < N (i.e., all atoms have not been included yet in the candidate
            (kekule) structure) then choose the next atom from the list of
            non-redundant bonds as katom (i.e., increment katom by 1)
            go to 1
         else (i.e., katom = N and all atoms have been included in the candidate structure)
            A Kekule structure has been generated.
            Store this Kekule structure and exit the procedure (to go up in recursion(s)).
      end if
      end of the procedure
```

Figure 3.4: A description of the algorithm to generate Kekulé valence structures.

recursive. To combine a (double) bond, with the existing candidate structure, the algorithm calls itself. Starting from the first atom in the list (we call this atom *katom*), the algorithm is described in Figure 3.4.

As the algorithm is recursive, it keeps on calling itself within itself unless the last atom is selected as *katom* from the list of non-redundant bonds. Each time, calling the procedure for the next *katom* means making the next recursion within the loop *i* over the neighbours of current *katom*. In the next recursion, there is again a loop *i* over the neighbours of new *katom* and then there is again a recursive call. When the algorithm reaches the last atom in the recursion, a candidate structure containing a (double) bond for each atom is generated. This structure is stored as a Kekulé valence structure and the algorithm goes up in recursion(s) to make a new candidate structure.

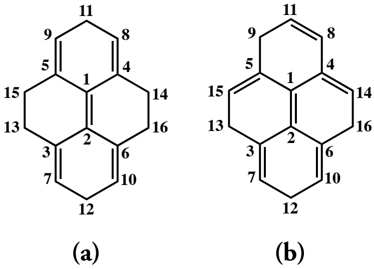


Figure 3.5: Two candidate structures which are not suitable for Kekulé valence structures.

When generating a candidate structure, there may be a situation where all the neighbours of an atom *x* have already been included in a candidate structure and atom *x* itself is left alone. This kind of situation is shown in Figure 3.5. In Figure 3.5a atom number 11 is left alone (only the lowest numbered atom is mentioned here) and now a bond (i.e., a double bond) is not possible for it in this candidate structure. This candidate structure is, therefore, not going to be a part of a Kekulé valence structure. The same is the situation in Figure 3.5b where atom number 9 is left alone. As soon as such an atom is selected as *katom* in the list of non-redundant bonds, i.e., an atom whose neighbours are already present in the candidate structure but that atom itself is not present in it, the algorithm does not go further in combining the rest of the possible bonds with this structure. Instead, it goes up in the recursion(s) in order to generate a different candidate structure. If it gets stuck again somewhere in the same situation as shown in Figure 3.5, it again goes up in the recursion(s). In this way it tries to create every possible candidate structure but finally gives only Kekulé valence structures. The rest of the structures disappear automatically. The non-redundancy of neighbours of each atom in the list of non-redundant bonds and the check to find out if the newly selected *katom* is already present in the candidate (Kekulé) structure, ensure that each Kekulé valence structure will be unique. The last mentioned two factors are also the points where the algorithm gains its efficiency.

3.2.3 Implementation and Efficiency

The algorithm has been implemented in Fortran. The program allocates two integer arrays of size (N+$N/2$) and (N) to store the non-redundant neighbours for all the atoms and their number for each atom, respectively (for monocyclic systems an integer array of size (N) is required to store all non-redundant neighbours). An integer array of size (N) is used to store the candidate structures. As soon as a Kekulé valence structure is generated, the program writes it (if requested) to an output file. For the pyrene molecule in Figure 3.2, the six Kekulé valence structures generated using this algorithm, are presented in Table 3.1. In this representation each atom at odd position forms a double bond to the atom that is immediately to its right. These Kekulé valence structures are graphically shown in Figure 3.6.

Table 3.1: Symbolic representation of the six Kekulé valence structures of pyrene.

Structure	Representation															
1	1	2	3	7	4	14	5	9	6	16	8	11	10	12	13	15
2	1	2	3	13	4	8	5	15	6	10	7	12	9	11	14	16
3	1	4	2	3	5	9	6	10	7	12	8	11	13	15	14	16
4	1	4	2	6	3	7	5	9	8	11	10	12	13	15	14	16
5	1	5	2	3	4	8	6	10	7	12	9	11	13	15	14	16
6	1	5	2	6	3	7	4	8	9	11	10	12	13	15	14	16

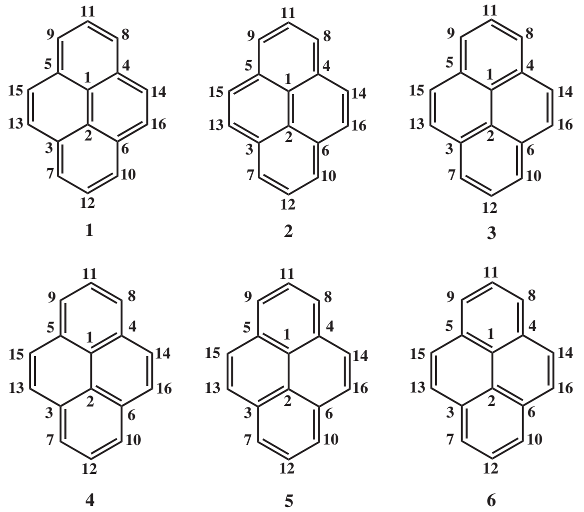


Figure 3.6: Graphical representation of the six Kekulé valence structures of pyrene.

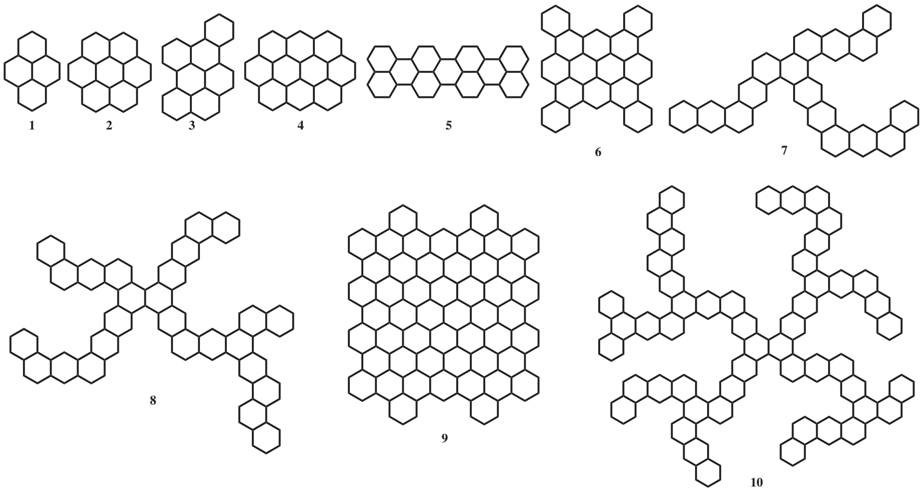


Figure 3.7: Some selected benzenoids for which Kekulé valence structures are generated.

Table 3.2: The number of Kekulé valence structures for molecules **1-10** in Figure 3.7 and computational cost.

Compound	No. of atoms (N)	No. of Kekulé structures	Time (seconds)
1	16	6 *	0.000
2	24	20 *	0.000
3	26	25	0.000
4	32	50 *	0.000
5	40	81 *	0.000
6	48	520	0.003
7	66	1365 *	0.002
8	106	145908	0.324
9	132	125820416 *	803.762
10	206	11983093719	56635.887

*Literature values are availabe. See Refs. 10, 13

Table 3.3: The number of Kekulé valence structures for some Fullerenes and computational cost.*

Fullerene/N	Symmetry Group	No. of Kekulé structures	Time (seconds)
C_{20}	I_h	36	0.000
C_{32}	D_2	184	0.000
C_{60}	I_h	12500 †	0.058
C_{70}	D_{5h}	52168 †	0.324
C_{80}	I_h	140625 †	1.002
C_{80}	D_{5d}	270153	1.854
C_{90}	D_{5h}	1384341	7.275
C_{100}	C_2	4792838	26.154
C_{110}	C_2	19105016	111.003
C_{120}	C_2	90229920	459.907
C_{120}	D_2	97491466	521.936
C_{130}	C_2	420111098	6947.965
C_{140}	I_h	2178836352 †	15314.475
C_{140}	D_2	2181807742	15399.886

*For all fullerenes cartesian coordinates were used to make the list of non-redundant bonds.

†Literature values are availabe. See Refs. 10, 13, 19, 20

To check the efficiency of the program, it has been tested by generating Kekulé valence structures for some selected benzenoids shown in Figure 3.7 and fullerenes. The number of Kekulé valence structures generated and the computing time is given in Tables 3.2 and 3.3. All test were run on a 1.5 GHz Itanium-2 single processor. For all examples the storage of the Kekulé valence structures was turned off to save output file space (for the biggest benzenoid shown in Figure 3.7, about 9 TB of disk space is required to store all Kekulé structures). It is apparent from Tables 3.2 and 3.3 that the algorithm is very efficient and takes a few minutes to generate more than 10^8 and a few hours for more than 10^{10} Kekulé valence structures. For most of these benzenoids and some of the fullerenes, the number of Kekulé valence structures has already been reported in the literature.[10,13,19,20] The number of generated Kekulé valence structures using this algorithm are in line with the literature values. Since the described algorithm tries to assign the double bonds in the candidate structures in every possible way, this guarantees that it will not forget any of the Kekulé structures of a given system.

3.3 Kekulé Valence Structures in Valence Bond Theory

Valence Bond (VB) Theory has special importance for chemists because it directly deals with the structures of the molecular systems that chemists are familiar with. However, other (indirect) methods[21–24] also exist where the localised picture of electrons in the bond regions or lone pairs can be regained after transforming the delocalised molecular orbitals obtained from a calculation based on molecular orbital theory. In VB Theory a bond is described as resulting from the overlap of two orbitals ϕ_1 and ϕ_2 lying on atom 1 and 2, respectively, that are singlet-coupled. Thus a bond is:

$$(\text{bond})_{12} = \mathscr{N}\{|\phi_1\overline{\phi_2}| - |\overline{\phi_1}\phi_2|\} \equiv (1-2) \tag{3.1}$$

where $\mathscr{N}$ is the normalisation constant. A "VB structure" for a system is defined as a multiple of these bonds:

$$\Phi = \hat{\mathscr{A}}\left[(core)(1-2)(3-4)(5-6)......((n-1)-n)\right] \tag{3.2}$$

where *core* represents doubly occupied core orbitals and $\hat{\mathscr{A}}$ is an anti-symmetriser. If the same set of orbitals is used to describe different structures of a system then these structures differ only in their spin part (i.e., the spin coupling pattern of the orbitals). An ionic structure can be defined as having orbital ϕ_i occupied twice or alternatively with two singly occupied orbitals on the same atom that share the same space. The VB wave function for a molecule is then constructed as a linear combination of these VB structures.

$$\Psi_0 = \sum_i c_i \Phi_i \tag{3.3}$$

Each structure (Φ) is a linear combination of Slater determinants and can be expressed as:

$$\Phi = \sum_i \alpha_i \Delta_i \tag{3.4}$$

where Δ_i is an anti-symmetrised product of orbitals.

Table 3.4: The number of Kekulé valence structures vs the total number of VB structures and the number of Slater determinants per structure for some (poly)cyclic conjugated systems.

Molecule	No. of singly occupied p-orbitals	f_S^N	No. of Kekulé valence structures	No. of det./ structure
benzene	6	5	2	8
naphthalene	10	42	3	32
anthracene	14	429	4	128
phenanthrene	14	429	5	128
pyrene	16	1430	6	256
coronene	24	208012	20	4096

The total number of, linearly independent, VB structures with only covalent bonds is obtained by the expression;[25]

$$f_S^N = \binom{N}{\frac{1}{2}N+S} - \binom{N}{\frac{1}{2}N+S+1} \tag{3.5}$$

where N is the number of electrons, S is the overall spin of the system and f_S^N is the number of covalent VB structures. The relative importance of each structure is determined by solving the generalized eigenvalue problem for the structure coefficients:

$$[\mathbf{H} - E\mathbf{S}]\mathbf{c} = 0 \tag{3.6}$$

where **H** is the Hamiltonian matrix and **S** is the overlap matrix.

Rumer's diagram method[26] is widely used to generate VB structures (spin-functions). In this method the orbitals (i.e., the singly occupied orbitals) are singlet coupled in all possible ways as long as the bonds do not intersect. In a Valence Bond description of (poly)cyclic conjugated systems, these VB structures are always related to the Kekulé and Dewar structures. For these systems, the VB structures where all the bonds are between the nearest neighbours, are Kekulé valence structures. Those with one or more long bonds are Dewar structures. Table 3.4 shows the total number of VB structures, f_S^N, and the number of Kekulé valence structures for some (poly)cyclic conjugated systems. It is obvious from the table that the total number of VB structures and the number of Slater determinants increases exponentially with the number of electrons (singly occupied p-orbitals).

Because of the computational cost, *ab initio* VB calculations involving all VB structures, are possible for systems having only a few electrons or singly occupied p-orbitals. However, it was discovered[27,28] that for (poly)cyclic conjugated systems the most important structures are those where the bonds are between the nearest neighbours (i.e., Kekulé valence structures) and their contribution in the VB wave function is more than 80%. The number of Kekulé valence structures for these systems does not grow so fast with the number of electrons or singly occupied p-orbitals. To make *ab initio* VB calculations practical for systems like phenanthrene or pyrene, the ground state wave function can be approximated as a linear combination of Kekulé valence structures (K) only.

$$\Psi_0 = \sum_i c_i K_i \tag{3.7}$$

Equation (6.4) is then solved for the energy eigenvalues (E) and the structure coefficients (c_i) to determine the relative importance of each Kekulé valence structure in the wave function. It is necessary, however, to point out that for systems having twentyfour singly occupied p-orbitals, for example coronene, the *ab initio* VB calculation is not an easy task (beyond the limits of normal desktop computers) because of the large number of determinants involved, even though the number of Kekulé valence structures is not too large (only 20 structures in the case of coronene).

In order to generate a Valence Bond wave function as a linear combination of Kekulé valence structures only, the above algorithm has been implemented in the *ab initio* Valence Bond program TURTLE[29](a VB/VBCI/VBSCF program available as part of GAMESS-UK[30]). In the *ab initio* VB method each singly occupied atomic p-orbital is expanded as a linear combination of Gaussian-type orbitals (GTOs), centred at different atoms:

$$\phi_{\pi_i} = \sum_\mu c_{\mu i} \chi_\mu \tag{3.8}$$

where each χ_μ is a set of contracted primitive Gaussian functions for a given basis. The program uses these localised atomic GTOs to figure out which p-orbital is centred on which atom by checking the orbital coefficients, c_μ. It uses the atomic coordinates to make a list of non-redundant bonds for the atoms involved in the Kekulé valence structures. For each Kekulé valence structure, a corresponding spin-function is generated. The linear combination of these spin-functions is then used as the Valence Bond wave function in *ab initio* VB calculations.

3.4 Test Calculations

VBSCF calculations were performed on benzene, pentalene, benzocyclobutadiene and naphthalene (compounds **1-4** in Figure 3.8). The geometries of the compounds **1-4** (Figure 3.8) were optimised, within the given point group symmetry and without any other constraint, at the Hartree-Fock level using GAMESS-UK.[30] In these calculations a 6-31G

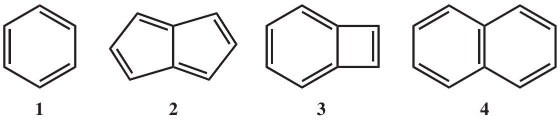


Figure 3.8: Selected systems for VBSCF study (only a single Kekulé valence structure of each system is shown). **1**. benzene (D_{6h}), **2**. pentalene (C_{2h}), **3**. benzocylcobutadiene (C_{2v}), **4**. naphthalene (D_{2h})

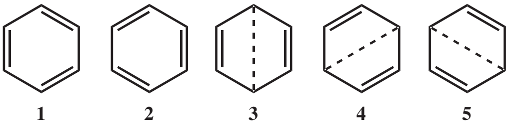


Figure 3.9: Graphical representation of the 5 VB structures of benzene

basis set (after Pople and co-workers[31]) was used. For pentalene only the C_{2h} symmetric structure was considered as earlier results show that the highly symmetrical D_{2h} molecule is not a genuine minimum.[32,33] The Hessian calculations showed that these geometries are genuine minima.

3.4.1 VBSCF Calculations

The *ab initio* VBSCF calculations were performed with the TURTLE[29] program package. In these calculations again the 6-31G basis set was used. For each system, the VB wave function was constructed as a linear combination of all Kekulé valence structures. The initial (doubly occupied) σ-orbitals, for each system, were taken from a preceding restricted Hartree-Fock calculation and for the π-system singly occupied atomic p-orbitals were used. In all the calculations, the σ-orbitals were orthogonal to each other and to the p-orbitals while the p-orbitals were allowed to be nonorthogonal to each other. Both the structure coefficients and the orbitals coefficients (for all σ and π-orbitals) were optimised. In the optimisation procedure two methods were used. In the first method, that we call VB-local, each p-orbital is expanded only in the basis functions which are centred on the same atom and mixing with the basis functions which are centred on different atoms is not allowed. In the second method, called VB-delocal, each p-orbital was allowed to expand arbitrarily, i.e., its tail may lie on the neighbouring atoms or beyond. For comparison, VBSCF calculations on a complete set of covalent VB structures (spin-functions) were also performed for each system. To each structure, a weight was assigned according to the formula:

$$W_i = \mathcal{N}|c_i|^2/(S^{-1})_{ii} \qquad \text{where} \qquad \mathcal{N} = \frac{1}{\sum_j |c_j|^2/(S^{-1})_{jj}} \tag{3.9}$$

after Gallup and Norbeck[34] where W_i and c_i represent, respectively, the weight and the VB

Table 3.5: Results of VBSCF calculation for benzene with 2 Kekulé valence structures. (here and in the following tables E_i = energy of structure i (hartree), W_i = weight of structure i, E_{total} = total energy of the system (hartree), E_{diff} = E_Ψ of the given method - E_Ψ of VB-delocal (kcal/mol)).

Method	$E_1 = E_2$	E_{total}	$W_1 = W_2$	E_{diff} (kcal/mol)
RHF		-230.624474		42.83
VB-local	-230.496517	-230.540678	0.500	95.41
VB-delocal	-230.660858	-230.692726	0.500	0

Table 3.6: Results of VBSCF with 2 Kekulé valence structures, with 175 (covalent + ionic) structures and the full CI (6 electrons in 12 orbitals) calculation for benzene (in these calculations the σ-orbitals taken from a preceding RHF calculation were treated as frozen core).

Method	E_{total} (hartree)	E_{diff} (kcal/mol)
VB-delocal (2 Kekulé structures)	-230.692579	0
VB-local (175 structures)	-230.695052	-1.55
Full CI (in the π-space)	-230.709822	-10.82

coefficient of structure i, $(S^{-1})_{ii}$ is the element of the inverse overlap matrix between the structures and $\mathcal{N}$ is the normalisation constant. With this definition the weight of a contributing structure is always ≥ 0 and the sum of the weights of all the structures in the VB wave function equals 1.

3.4.2 Results and Discussion

Benzene

The benzene molecule can be described with two Kekulé and three Dewar structures (Figure 3.9). The results of the VBSCF calculations with two Kekulé valence structures only are shown in Table 3.5. The contribution of each structure to the VB wave function is 50%. Although the *p*-orbitals in VB-local are optimised they still remain atomic *p*-orbitals because of the local restriction. As a consequence the energy of the VB wave function is higher than the HF wave function. In VB-delocal, the orbitals are free to relax and their symmetrical distortion towards the neighbouring atoms results in an enhanced overlap between the orbitals (stronger bonds) in benzene. The energies of the individual structures and also of the VB wave function, thus, decrease compared to the VB-local energies. Because the orbitals are now allowed to delocalise, the other (ionic and Dewar-)structures are automatically included in the Kekulé valence structures. We, therefore, expect that the two wave functions, the one with only two Kekulé valence structures at VB-delocal level and the other one with all covalent and ionic structures at VB-local level, will have almost the same energy and that is indeed the case (the VB-local wave function containing all covalent and ionic structures for

Table 3.7: Results of VBSCF calculation for benzene with 5 VB structures.*

Method	E_{1-2}	E_{3-5}	E_{total}	W_{1-2}	W_{3-5}	E_{diff}
VB-local	-230.496469	-230.431936	-230.545424	0.3836	0.0776	92.64
VB-delocal	-230.660406	-230.631763	-230.693050	0.4670	0.0219	0

*E_i and E_{total} in hartree, E_{diff} in kcal/mol

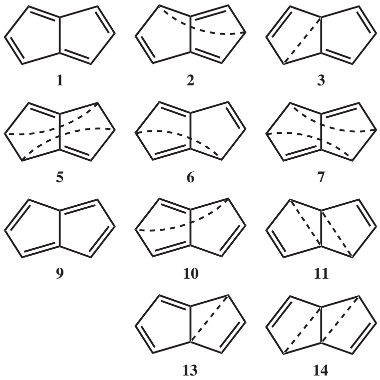


Figure 3.10: Graphical representation of the 14 VB structures of pentalene

benzene gives a lower energy than the two Kekulé valence structure VB-delocal wave function by 1.55 kcal/mol, see Table 3.6). To see how close to the "exact" energy (full CI energy within the π-space) we can get with only two Kekulé valence structures at VB-delocal level, we performed a full CI (in the π-space/6-electrons in 12-orbitals) calculation for benzene. The results are shown in Table 3.6. It can be seen that the difference between the energies of the full CI wave function and the VB wave function with two Kekulé valence structures (at the VB-delocal level) is only 10.82 kcal/mol.

When the three Dewar structures are also included in the VB wave function, the contribution of each Dewar structures in the wave function is almost 8% at VB-local level (see Table 3.7) and the total energy decreases by 0.004746 hartree or 2.98 kcal/mol compared to the VB-local with only Kekulé valence structures. In VB-delocal, however, the involvement of three Dewar structures does not make much difference in the total energy and a difference of only 0.000324 hartree (0.20 kcal/mol) is found which is negligible. Moreover, the total contribution of the three Dewar structures in the wave function is only 7% in VB-delocal.

Pentalene

The pentalene molecule has 8 singly occupied *p*-orbitals and 14 VB structures (Figure 3.10). Only two of them (structure 1 and 9 in Figure 3.10) are Kekulé valence structures. As the molecule has C_{2h} symmetry, the two Kekulé valence structure are not equivalent. One of them (structure 1) has double bonds along the shorter bond lengths while the second one

Table 3.8: Results of VBSCF calculation for pentalene with 2 Kekulé valence structures.*

Method	E_1	E_9	E_{total}	W_1	W_9	E_{diff}
RHF			-306.229649			72.27
VB-local	-306.157948	-306.021966	-306.160810	0.9798	0.0202	115.47
VB-delocal	-306.344124	-306.155291	-306.344816	0.9964	0.0036	0

*E_i and E_{total} in hartree, E_{diff} in kcal/mol

Table 3.9: Results of VBSCF calculation for pentalene with 14 VB structures.*

Structure	E_i (VB-local)	W_i (VB-local)	E_i (VB-delocal)	W_i (VB-delocal)
1	-306.157914	0.8215	-306.343708	0.8782
2	-306.045334	0.0330	-306.250341	0.0201
3	-306.034970	0.0242	-306.247963	0.0178
4	-306.002072	0.0036	-306.167232	0.0016
5	-305.994890	0.0003	-306.228032	0.0000
6	-306.045334	0.0330	-306.250341	0.0201
7	-305.938334	0.0016	-306.161832	0.0010
8	-305.993417	0.0001	-306.151839	0.0000
9	-306.021933	0.0025	-306.141540	0.0001
10	-306.002072	0.0036	-306.167232	0.0016
11	-305.977333	0.0522	-306.207638	0.0412
12	-305.993417	0.0001	-306.151839	0.0000
13	-306.034970	0.0242	-306.247963	0.0178
14	-305.918086	0.0000	-306.155135	0.0002

*E_i in hartree

$E_{VB-delocal}$ = -306.347050 hartree, E_{RHF} = -306.229649 hartree, E_{diff} = 73.67 kcal/mol,

$E_{VB-local}$ = -306.170678 hartree, E_{diff} = 110.68 kcal/mol

(structure 9) has all the double bonds along the longer bonds. The results of the VBSCF calculations, when the wave function is a linear combination of two Kekulé valence structures only, are summarised in Table 3.8. Here, structure 1 contributes almost 98% when the *p*-orbitals are restricted to remain atomic while this contribution goes to more than 99.6% when the restriction is removed. This means that the molecule is almost a single structure (structure 1). The overlap between the orbitals shows that the distortion of orbitals towards the neighbours is non-symmetrical and unlike the *p*-orbitals of benzene, the orbitals of pentalene are distorted more towards the shorter bonds.

When the VB wave function is constructed as linear combination of all 14 structures, structure 1 is, again, the major contributor in the wave function (results in Table 3.9). Structure 11 is second in importance and its contribution is more than 4%. Among the other structures the two symmetry related structures 2 and 6 are next in importance. Structures 5, 8, 9, 12 and 14 are non-contributing structures. The inclusion of 12 Dewar structures res-

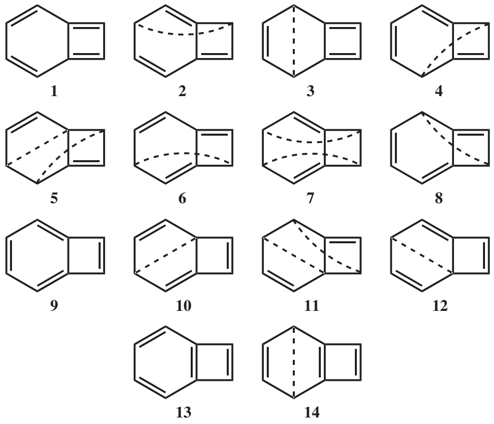


Figure 3.11: Graphical representation of the 14 VB structures of benzocyclobutadiene

Table 3.10: Results of VBSCF calculation for benzocyclobutadiene with 3 Kekulé valence structures.*

Method	E_1	E_9	E_{13}	E_{total}	E_{diff}
RHF				-306.217848	66.31
VB-local	-305.980220	-306.113201	-306.037765	-306.132106	120.12
VB-delocal	-306.125190	-306.316705	-306.207114	-306.323523	0

*E_i and E_{total} in hartree, E_{diff} in kcal/mol

ults in an energy decrease of -0.009868 hartree (-6.19 kcal/mol) in VB-local and -0.002234 (-1.40 kcal/mol) in case of VB-delocal.

Benzocyclobutadiene

The benzocyclobutadiene molecule has three Kekulé valence structures (structure 1, 9 and 13 in Figure 3.11) and 11 Dewar structures. The results of VBSCF calculations, when the VB wave function is a linear combination of the three Kekulé valence structures, are summarised in Tables 3.10 and 3.11. The weight of the structures shows that in VB-local, almost 90% of the VB wave function is composed of only one Kekulé valence structure (structure 9) while structure 13 is the second important structure in the wave function. Structure 1 is the least contributing structure in this case and it accounts for 1.45% of the total wave function. In VB-delocal, structure 9 becomes even closer to the VB wave function and forms 97.5% of it while the contribution of structure 1 is almost zero in this case. These results can be rationalised easily in terms of the 4n+2 rule. Both structures 9 and 13 have three double bonds within the benzene-like six membered ring (benzene-like Kekulé valence structure) while the position of the fourth double bond remains the same in both structures. However, unlike benzene where the two Kekulé structures have equal weights, these two structures of benzocyclobutadiene show totally different weights. It is because in structure 13 of ben-

Table 3.11: Contribution of the Kekulé valence structures to the VB wave function of benzocyclobutadiene.

Method	W_1	W_9	W_{13}
VB-local	0.0145	0.9046	0.0809
VB-delocal	0.0019	0.9746	0.0235

Table 3.12: Results of VBSCF calculation for benzocyclobutadiene with 14 VB structures.*

Structure	E_i (VB-local)	W_i(VB-local)	E_i(VB-delocal)	W_i(VB-delocal)
1	-305.980200	0.0014	-306.112856	0.0002
2	-305.965709	0.0096	-306.141493	0.0032
3	-305.932391	0.0009	-306.122735	0.0061
4	-305.990559	0.0441	-306.216432	0.0310
5	-305.894231	0.0039	-306.141359	0.0012
6	-305.965709	0.0096	-306.141493	0.0032
7	-305.953244	0.0007	-306.201998	0.0004
8	-305.990559	0.0441	-306.216432	0.0310
9	-306.113149	0.5344	-306.316461	0.6632
10	-306.017936	0.0543	-306.242661	0.0465
11	-305.894231	0.0039	-306.141359	0.0012
12	-306.017936	0.0543	-306.242661	0.0465
13	-306.037721	0.1447	-306.192599	0.0982
14	-306.002575	0.0940	-306.233333	0.0678

*E_i in hartree

$E_{VB-delocal}$ = -306.324945 hartree, E_{RHF} = -306.217847 hartree, E_{diff} = 67.20 kcal/mol,

$E_{VB-local}$ = -306.139516 hartree, E_{diff} = 116.36 kcal/mol

zocyclobutadiene a double bond in the benzene-like ring also fully contributes to the four membered ring and makes it a cyclobutadiene-like ring which is an unstable system. This cyclobutadiene-like contribution is absent in structure 9. So the dominance of structure 9 is apparent. In structure 1 the stable benzene-like contribution is absent while it has a contribution of the unstable cyclobutadiene-like ring. Therefore, compared to structures 9 and 13, structure 1 is expected to be the least contributing structure in the VB wave function and that is clearly the case (see Tables 3.10 and 3.11).

The results of the VBSCF calculations when benzocyclobutadiene is described with all 14 covalent structures, are presented in Table 3.12. Here structure 9 is again the most important structure and contributes more than 66% to the wave function. Structure 13 is the second important contributing structure while structure 1 is of least importance. By including 11 Dewar structures in the wave function, a decrease in energy of -0.00741 hartree (-4.65 kcal/mol) and -0.001422 hartree (-0.89 kcal/mol) is found at the VB-local and the VB-delocal level, respectively.

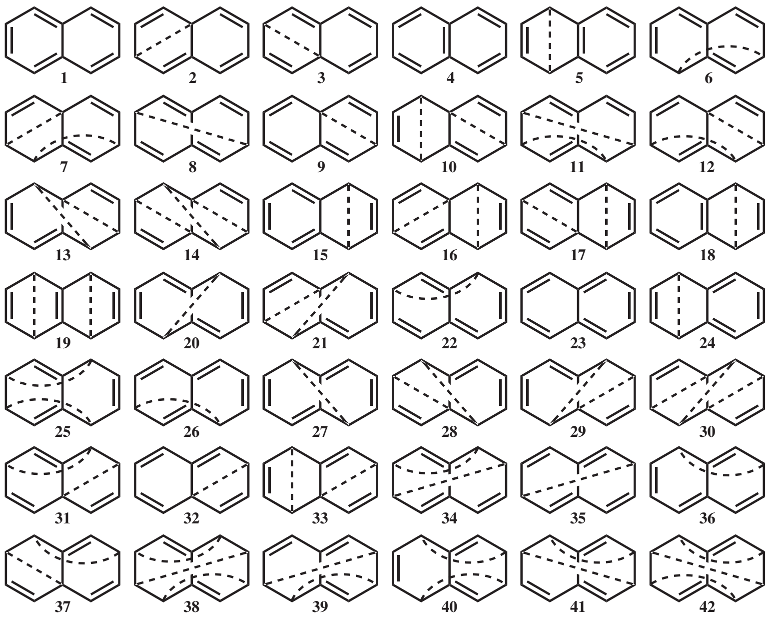


Figure 3.12: Graphical representation of the 42 VB structures of naphthalene

Table 3.13: Results of VBSCF calculation for naphthalene with 3 Kekulé valence structures.*

Method	$E_{1,23}$	E_4	E_{total}	$W_{1,23}$	W_4	E_{diff}
RHF	-	-	-383.222722	-	-	71.65
VB-local	-382.991841	-383.020040	-383.070923	0.2716	0.4567	166.91
VB-delocal	-383.246795	-383.315526	-383.336904	0.1809	0.6382	0

*E_i and E_{total} in hartree, E_{diff} in kcal/mol

Naphthalene

The naphthalene molecule can be described with 42 covalent structures (Figure 3.12). Three of them (structures 1, 4 and 23 in Figure 3.12) are the Kekulé valence structures. The remaining 39 structures are the Dewar structures. The results of VBSCF calculations, when the wave function is constructed as linear combination of the Kekulé valence structures only, are summarised in Table 3.13 which shows that, of the three Kekulé valence structures of naphthalene, structure 4 is the most important structure both at the VB-local and the delocal level because its both rings resemble benzene in the arrangement of double bonds. The other two structures (each with one ring having benzene-like arrangement of double bonds) also have a considerable contribution in the wave function.

Involving 39 Dewar structures along with the 3 Kekulé valence structures in VBSCF calculation results in an energy decrease of -8.76 kcal/mol and -0.96 kcal/mol at VB-local

Table 3.14: Results of the VBSCF calculation for naphthalene with 42 VB structures.*

Structure	E_i (VB-local)	W_i(VB-local)	E_i(VB-delocal)†	W_i(VB-delocal)
1	-382.991793	0.0467	-383.235160	0.0406
2	-382.945211	0.0226	-383.258334	0.0120
3	-382.945211	0.0226	-383.258332	0.0120
4	-383.019825	0.5128	-383.315945	0.7442
5	-382.936885	0.0869	-383.252191	0.0435
6	-382.910902	0.0091	-383.153406	0.0022
7	-382.855841	0.0026	-383.164978	0.0004
8	-382.916832	0.0155	-383.185673	0.0086
9	-382.945211	0.0226	-383.258332	0.0120
10	-382.854006	0.0017	-383.187546	0.0003
11	-382.845129	0.0004	-383.129737	0.0000
12	-382.855841	0.0026	-383.164977	0.0004
13	-382.842985	0.0013	-383.122272	0.0002
14	-382.799190	0.0009	-383.156860	0.0000
15	-382.899059	0.0060	-383.160967	0.0032
16	-382.854006	0.0017	-383.187546	0.0003
17	-382.854006	0.0017	-383.187545	0.0003
18	-382.936885	0.0869	-383.252188	0.0435
19	-382.853506	0.0136	-383.187973	0.0030
20	-382.888201	0.0046	-383.100237	0.0000
21	-382.842985	0.0013	-383.122268	0.0002
22	-382.910902	0.0091	-383.153400	0.0022
23	-382.991793	0.0467	-383.235154	0.0406
24	-382.899059	0.0060	-383.160963	0.0032
25	-382.830724	0.0008	-383.086078	0.0001
26	-382.910902	0.0091	-383.153401	0.0022
27	-382.888201	0.0046	-383.100237	0.0000
28	-382.842985	0.0013	-383.122268	0.0002
29	-382.842985	0.0013	-383.122274	0.0002
30	-382.799190	0.0009	-383.156863	0.0000
31	-382.855841	0.0026	-383.164977	0.0004
32	-382.945211	0.0226	-383.258332	0.0120
33	-382.854006	0.0017	-383.187546	0.0003
34	-382.845129	0.0004	-383.129739	0.0000
35	-382.916832	0.0155	-383.185677	0.0086
36	-382.910902	0.0091	-383.153406	0.0022
37	-382.855841	0.0026	-383.164977	0.0004
38	-382.776101	0.0000	-383.076460	0.0000
39	-382.845129	0.0004	-383.129735	0.0000

continue on the next page

Table 3.14: -- continued from the previous page.

Structure	E_i (VB-local)	W_i(VB-local)	E_i(VB-delocal)	W_i(VB-delocal)
40	-382.830724	0.0008	-383.086081	0.0001
41	-382.845129	0.0004	-383.129733	0.0000
42	-382.776101	0.0000	-383.076459	0.0000

[*] E_i in hartree

[†] The slight difference (at fifth or sixth decimal place) in the energies of some symmetry equivalent structures in VB-delocal is due to the low convergence criterion used.

$E_{VB-delocal}$ = -383.338435 hartree, E_{RHF} = -383.222722 hartree, E_{diff} = 72.61 kcal/mol,
$E_{VB-local}$ = -383.084880 hartree, E_{diff} = 159.11 kcal/mol

and VB-delocal level, respectively. The results are presented in Table 3.14. The weights of the structures show that structure 4 is again the major contributing structure. Among the other structures, 5 and 18 (each with one longer bond) have larger weights compared to the other two Kekulé valence structures (i.e., structures 1 and 23). Each of these structures (i.e., 5, 18, 1 and 23) has one benzene-like contributing ring. The benzene-like contributing ring in structures 5 and 18 is similar to that of structure 4 (the most stable structure) so they get stabilised by their larger overlap with the most stable structure. Therefore, despite of having one longer bond, their weights are still larger both at VB-local and VB-delocal level compared to the two Kekulé valence structures. The total contribution of the three Kekulé valence structures is 60.6% and 82.6% in the wave function at VB-local and VB-delocal level, respectively.

3.5 Conclusion

A new scheme has been presented to record the number and position of bonds which are involved in the Kekulé valence structures for a given system. Based on this, an efficient and economical method (both in memory and time) for generating all Kekulé valence structures for a given system has been devised. The efficiency of the algorithm has been tested by a Kekulé valence structures count for selected cases of small as well as giant conjugated systems. The application of the algorithm for generating a Valence Bond wave function in terms of Kekulé valence structures has been discussed. As a VB wave function is very expensive to calculate, we have shown that for (poly)cyclic conjugated systems, in their ground states, almost quantitative results can be obtained by considering only Kekulé valence structures in *ab initio* VBSCF calculations at the delocal level.

References

1. Clar, E.; Kemp, W.; Stewart, D. G. *Tetrahedron* **1958**, *3*, 325--333.

2. Clar, E.; Macpherson, I. A. *Tetrahedron* **1962**, *18*, 1411--1416.
3. Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London and New York, **1964**; Vol. 1-- 2.
4. Muller, P. *Pure Appl. Chem.* **1994**, *66*, 1077--1184.
5. Pauling, L. *Acta. Cryst.* **1980**, *B36*, 1898--1901.
6. Cyvin, S. J.; Gutman, I. *Kekulé Structures in Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, **1988**.
7. Trinajstić, N. *Chemical Graph Theory*, 2nd ed.; CRC Press : Boca Raton: FL, **1992**.
8. Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, **1989**.
9. Klein, D. J.; Babic, D.; Trinajstić, N. Enumeration in Chemistry. In *A Specialist Periodical Report: Chemical Modelling: Applications and Theory*; Hinchliffe, A. S. R., Ed.; The Royal Society of Chemistry: London, **2002**; Vol. 2, pp 55--95.
10. Randić, M. *Chem. Rev.* **2003**, *103*, 3449--3606.
11. Randić, M. *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 232--243.
12. Dzonova-Jerman-Blazic, B.; Trinajstić, N. *Computers & Chemistry* **1982**, *6*, 121--132.
13. Cai, F.; Shao, H.; Liu, C.; Jiang, Y. *J. Chem. Inf. Model.* **2005**, *45*, 371--378.
14. Chartrand, G. *Graphs As Mathematical Models*; Prindle, Weber & Schmidt: Boston, **1977**; p 218.
15. Haruo, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2332--2339.
16. Hückel, E. *Z. Physik* **1931**, *70*, 204--286.
17. Bloch, F. *Z. Physik* **1929**, *52*, 555--600.
18. Bloch, F. *Z. Physik* **1930**, *61*, 206--219.
19. Randić, M.; Vukičević, D. *Croat. Chem. Acta* **2006**, *79*, 471--481.
20. Klein, D. J.; Zhu, H.; Valenti, R.; Garcia-Bach, M. A. *Int. J. Quantum Chem.* **1997**, *65*, 421--438.
21. Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296--299.
22. Edmiston, C.; Ruedenberg, K. *J. Chem. Phys.* **1965**, *43*, S97--S116.
23. von Niessen, W. *J. Chem. Phys.* **1972**, *56*, 4290--4297.
24. Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916--4926.
25. Simonetta, M.; Gianinetti, E.; Vandoni, I. *J. Chem. Phys.* **1968**, *48*, 1579--1594.
26. Rumer, G. *Nachr. ges. Wiss. Gött. Math. Phys.* **1932**, 337--341.
27. Pauling, L.; Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 362--374.
28. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Nature* **1986**, *323*, 699--701.
29. Verbeek, J.; Langenberg, J. H.; Byrman, C. P.; Dijkstra, F.; Havenith, R. W. A.; Engelberts, J. J.; Zielinski, M. L.; Rashid, Z.; van Lenthe, J. H. **1988--2012**, TURTLE an *ab*

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30. Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J. *Mol. Phys.* **2005**, *103*, 719--747.
31. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257--2261.
32. Nakajima, T.; Yaguchi, Y.; Kaeriyama, R.; Nemoto, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 272--276.
33. Bally, T.; Chai, S.; Neuenschwander, M.; Zhu, Z. *J. Am. Chem. Soc.* **1997**, *119*, 1869--1875.
34. Gallup, G. A.; Norbeck, J. M. *Chem. Phys. Lett.* **1973**, *21*, 495--500.

CHAPTER

4

A QUADRATICALLY CONVERGENT VBSCF METHOD

Abstract

A quadratically convergent Valence Bond Self-Consistent Field method is described where the simultaneous optimisation of orbitals and CI (VB-structure) coefficients is based on a Newton-Raphson scheme. The applicability of the method is demonstrated in actual calculations. The convergence and efficiency is compared with the Super-CI method. A necessary condition to achieve convergence in the Newton-Raphson method is that the Hessian is positive definite. When this is not the case, a combination of the Super-CI and Newton-Raphson methods is shown to be an optimal choice instead of shifting the eigenvalues of the Hessian to make it positive definite. In the combined method, the first few iterations are performed with the Super-CI method and then the Newton-Raphson scheme is switched on based on an internal indicator. This approach is found computationally a more economical choice than using either the Newton-Raphson or Super-CI method alone to perform a full optimisation of the nonorthogonal orbitals.

Zahid Rashid and Joop H. van Lenthe, Submitted to *J. Chem. Phys.* with dedication to the memory of Joseph Gerratt.

4.1 Introduction

The Valence Bond Self-Consistent Field (VBSCF) method[1--3] describes the electronic structure of molecules with a few chemically meaningful configurations (VB structures). This method is a powerful generalisation of analogous MCSCF methods[4--8] which allows the use of nonorthogonal orbitals to construct molecular wave functions. Like in the MCSCF methods, usually a small number of configurations is sufficient to give an accurate description of the electronic structure of molecules. If required, however, all possible configurations within a given "active space" can also by employed which correspond to covalent and ionic VB structures.

Unlike the classical VB theory[9--11] which uses non-optimised atomic orbitals, in the VBSCF method the orbitals and the coefficients of the configurations (in the following referred to as CI coefficients) are optimised according to the variational principle. The nonorthogonality amongst the orbitals presents a major difficulty in the optimisation procedures as compared to the equivalent methods which use orthogonal orbitals. Whereas in MCSCF methods, the most intensive computational step is generally the four index transformation required in each iteration, the case is more complicated in VBSCF method. In the latter, the additional challenge is the evaluation of matrix elements over the Slater determinants. In VBSCF calculations if the basis set (one-electron basis) is not too large, the time required for the four-index transformation is usually a small fraction of that taken in the calculations of matrix elements.

In the orbital optimisation procedure in the VBSCF methods, the orbital changes are derived from the vectors of a "Super-CI" (SCI)[5] matrix consisting of the VBSCF wave function and all singly excited configurations. The iterative procedure of Super-CI is divided into two parts. In the first part the CI coefficients are calculated by solving a linear variation problem in the configuration space. In the second part the orbital optimisation is performed while the CI coefficients are held fixed. The time taken by the first part is usually quite small compared to that required in the orbital optimisation procedure. The convergence behaviour of this method is quite robust and when combined with DIIS[12,13] and level shift[14] it almost always works.[15] However, with the Super-CI method only first-order convergence is achieved.

A second-order (quadratic) convergence behaviour is important for mainly two reasons. First, to calculate the molecular energy gradients or other properties of the molecules (e.g., dipole moment, response properties, etc.), the wave function has to be well converged. If the optimisation procedure is quadratically convergent, only a few iterations are required to reach the optimal solution. Second, the additional efforts required to calculate the second derivative matrix of the energy with respect to the wave function parameters (Hessian matrix) is usually compensated by a substantial reduction in the number of iterations.

In the past few decades, efficient schemes for the second-order MCSCF methods have been developed[7,16–24] (for a review of these methods see Ref. 25 and references therein). For optimisation of nonorthogonal orbitals, however, the progress is less remarkable. For the Spin-Coupled VB method, Gerratt and co-workers[26,27] developed a quadratically convergent method based on a Newton-Raphson scheme. In most of these methods (for orthogonal or nonorthogonal orbitals), usually the quadratic convergence starts close to the minimum. However, it is still important due to the above mentioned reasons. Especially, when calculating potential energy surfaces, the solutions at neighbouring points (the previous step) usually provide very good starting orbitals. The quadratic convergence in that case is achieved from the very beginning and thus improves the efficiency considerably.

In this chapter a quadratically convergent procedure for optimisation of VBSCF wave functions is described. This method is based on a Newton-Raphson scheme where the orbitals and CI-coefficients are optimised simultaneously. The linear equations which define the improved orbitals and CI-coefficients are solved in a single step by inverting the Hessian matrix. Explicit formulae for the orbital gradients and all second derivatives of energy with respect to the change in orbitals, CI-coefficients and coupled orbital-CI coefficients, which appear in the Newton-Raphson method, are presented for a general VBSCF wave function. Since all these second derivatives of energy are required in the Newton-Raphson method to get an overall quadratic convergence, a Newton-Raphson iteration is computationally more expensive than that of the Super-CI. To get convergence in the Newton-Raphson method, an essential requirement is that the second derivative matrix (Hessian) is positive definite. If this is not the case, the Hessian has to be augmented to make it positive definite otherwise the iterative procedure may not converge. When this is done, the Newton-Raphson method usually shows linear convergence at a substantially higher computational cost. In that case, instead of making the Hessian positive definite, we present an alternate approach where the optimisation procedure is started with the Super-CI method and after the first 2-5 iterations switched to the Newton-Raphson method. We show that this approach is computationally more economical than using either the Super-CI or Newton-Raphson method alone.

4.2 VBSCF Wave Functions and Energy Expressions

In the VBSCF method the reference wave function is constructed from a linear combination of valence bond configurations (VB structures) as:

$$\Psi_0 = \sum_i c_i \Phi_i \qquad \text{where} \qquad \langle \Phi_i | \Phi_j \rangle = S_{ij} \neq 0 \tag{4.1}$$

Each Φ in itself is a spin-adapted linear combination of Slater determinants.

$$\Psi_0 = \sum_p c_p \Delta_p \tag{4.2}$$

and each Slater determinant is an antisymmetrised product of spin-orbitals (ϕ's) which are nonorthogonal to each other.

$$\int \phi(1)_i^* \phi_j(2) d\tau = \langle \phi_i | \phi_j \rangle = S_{ij} \tag{4.3}$$

These orbitals are expanded as linear combinations of mutually nonorthogonal basis functions (AOs).

$$\phi_i = \sum_\mu d_{\mu i} \chi_\mu \tag{4.4}$$

For a given set of orbitals and CI coefficients, the energy of the VBSCF wave function is calculated using Löwdin's formula[28] as:

$$\begin{aligned} E_0 &= \langle \Psi_0 | \hat{\mathscr{H}} | \Psi_0 \rangle \\ &= \sum_{ik} h_{ik} \sum_p \sum_q \mathbf{S}_{pq}^{(i,k)} c_p c_q + \sum_{i<j,k<l} \Big(\langle ij|kl \rangle - \langle ij|lk \rangle \Big) \sum_p \sum_q \mathbf{S}_{pq}^{(i,j,k,l)} c_p c_q \end{aligned} \tag{4.5}$$

where

$$h_{ik} = \langle \phi_i(1) | \hat{h} | \phi_k(1) \rangle \tag{4.6}$$

and

$$\langle ij|kl \rangle = \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | \phi_k(1) \phi_l(2) \rangle \tag{4.7}$$

are one- and two-electron integrals over MOs. $\mathbf{S}_{pq}^{(i,k)}$ and $\mathbf{S}_{pq}^{(i,j,k,l)}$ are the first- and second-order cofactors of the overlap matrix. c_p and c_q are the coefficients of the determinants Δ_p and Δ_q, respectively. The indices i and j refer to the occupied orbitals in determinant Δ_p and k, l to the occupied orbitals in Δ_q. Efficient schemes for the rapid evaluation of nonorthogonal matrix elements and cofactors[29--31] have been developed based on the generalisation of Löwdin's formula[28] and Slater-Condon rules.[32,33]

The aim of the optimisation procedure is to minimise the energy of the wave function with respect to orbital rotations and CI coefficients. In the VBSCF method these orbitals may be fully optimised as in the spin-coupled VB approach[26,27,34--36] or they may be restricted to a subspace of the full orbital space, e.g., on the atoms where they are centred. The first approach (full optimisation) is called the VB-delocal method while the latter is called the VB-local method.

4.3 Orbital Optimisation

4.3.1 The Super-CI Method

The Super-CI method for orbital optimisation is well documented.[1,2,5,6,8,15] Here we briefly describe this method again. To optimise the orbitals, consider the effect of an infinitesimal change in an orbital ϕ_i, due to mixing with an other orbital ϕ_j by an amount $\delta\gamma_{ij}$

$$\phi_i \rightarrow \phi_i + \delta\gamma_{ij}\phi_j \tag{4.8}$$

This change in orbital ϕ_i is accompanied by a corresponding change in the the wave function Ψ_0:

$$\Psi_0 \rightarrow \Psi_0 + \delta\gamma_{ij}\Psi_{ij} \tag{4.9}$$

where Ψ_{ij} is called a Brillouin state function which is obtained from the reference function Ψ_0 by replacing the spatial orbital ϕ_i by the orbital ϕ_j, once for α and once for β spin in each determinant of Ψ_0. Thus the Brillouin state Ψ_{ij} may be represented as:

$$\Psi_{ij} = \mathbf{C}_{i\to j}\Psi_0 \tag{4.10}$$

where $\mathbf{C}_{i\to j}$ is an un-normalised excitation operator.[37] The total number of singly excited Brillouin states, n_{Brill} in Eqs. (4.9) and (4.10) depends on the number of active occupied orbitals N and the number of basis functions m and, ignoring the spacial symmetry of the orbitals, is approximately equal to mN. Note that the above definitions are valid for multi-determinantal states without orthogonality restrictions as in the VBSCF method. The excitation operator, therefore, does not have to adhere to the unitary condition, as is the case for orthogonal orbitals. If orthogonality constraints are used, like in the MCSCF methods[5,6] or orthogonal VB, the definition of the Brillouin state includes the unitary condition[4]

$$\Psi_{ij}^{unitary} = (\mathbf{C}_{i\to j} - \mathbf{C}_{j\to i})\Psi_0 \tag{4.11}$$

To find the optimum mixing coefficients $\delta\gamma_{ij}$, which minimise the energy, the wave function is expanded in the space spanned by the reference function Ψ_0 and all the Brillouin state functions Ψ_{ij}.

$$\Psi_{SCI} = b_0\Psi_0 + \sum_{j\neq i} b_{ij}\Psi_{ij} \tag{4.12}$$

The Ψ_{SCI} is called the Super-CI wave function.[5] The coefficients b_0 and b_{ij} are obtained by solving this Super-CI problem which is a linear variation problem in the space of Ψ_0 and all Ψ_{ij}. The b_{ij}'s lower the energy expectation value, they are "absorbed" into the reference function so that Ψ_0 approaches Ψ_{SCI}. This leads to the following orbital transformation:

$$\phi_i' \rightarrow b_0\phi_i + \sum_{j \neq i} b_{ij}\phi_j \tag{4.13}$$

From these new orbitals, ϕ_i', new Brillouin state functions are generated and a new Super-CI problem is solved. This process is repeated until all b_{ij}'s approach zero or at least below a certain threshold and a stationary condition for the energy is achieved.

4.3.2 The Newton-Raphson Method

The Newton-Raphson set of linear equations is derived by expanding the energy of the VBSCF wave function up to second order around the current wave function parameters. Collecting the current wave function parameters in a vector $\mathbf{x}_0$ and the new parameters (which result from the second-order energy expansion) in a vector $\mathbf{x}$ we can write:

$$E^{(2)}(\mathbf{x}) = E_0(\mathbf{x}_0) + \mathbf{g}^{\dagger}(\mathbf{x}-\mathbf{x}_0) + \frac{1}{2}(\mathbf{x}-\mathbf{x}_0)^{\dagger}\mathbf{H}(\mathbf{x}-\mathbf{x}_0) + \cdots \tag{4.14}$$

The stationary condition is given by requiring that the gradient of $E^{(2)}(\mathbf{x})$ in Eq. (4.14) vanishes at $\mathbf{x}$. This leads to the following set of Newton-Raphson equations.

$$\mathbf{H}(\mathbf{x}-\mathbf{x}_0) + \mathbf{g} = 0 \qquad \text{or} \qquad \delta\mathbf{c} = -\mathbf{H}^{-1}.\mathbf{g} \tag{4.15}$$

where $\delta\mathbf{c} = (\mathbf{x}-\mathbf{x}_0)$ is the correction vector for the wave function parameters, $\mathbf{g}$ is the gradient and $\mathbf{H}$ is the Hessian of energy at current parameters $\mathbf{x}_0$.

$$g_i = \left(\frac{\partial E_0}{\partial x_i}\right)_{\mathbf{x}_0} \qquad \text{and} \qquad H_{i,j} = \left(\frac{\partial^2 E_0}{\partial x_i \partial x_j}\right)_{\mathbf{x}_0} \tag{4.16}$$

Equation (4.15) defines the sequence of the Newton-Raphson iterative procedure. If the energy is an exact quadratic function of the wave function parameters, a single iteration is required to reach the optimal solution. In general, however, more iterations are needed because the expansion in Eq. (4.14) also contains terms beyond the second-order. Typically Newton-Raphson method shows quadratic convergence if the initial guess parameters are close to the final solution and the second-order expansion of the energy is a good approximation to the true energy. In that case the norm of the gradient vector is reduced quadratically in each iteration, i.e., if the norm reduces by a factor of 1 in the first iteration, it will decrease by a factor of 2 in the second and a factor of 4 in the third iteration.

To get a quadratic convergence with the Newton-Raphson method, it is necessary that all the wave function parameters are optimised simultaneously.[7] For this we need the orbital and

CI gradients and the orbital, CI and coupled orbital-CI Hessian. When these are calculated, Eq. (4.15) is used to find the corrections to the old parameters.

The VBSCF Gradient and Hessian

Using the definitions of orbital mixings and the Brillouin states given in the Section 4.3.1, the orbital gradient can be calculated by differentiation of E_0 with respect to the orbital mixing coefficients γ_{ij}:[2]

$$\frac{\partial E_0}{\partial \gamma_{ij}} = g_{ij}^{Orb} = 2\langle \Psi_0 | \mathscr{H} - E_0 | \Psi_{ij} \rangle \qquad \text{for} \qquad \langle \Psi_0 | \Psi_0 \rangle = 1 \tag{4.17}$$

The orbital Hessian ($\mathbf{H}^{\mathbf{Orb-Orb}}$) is obtained by differentiating E_0 twice:[2]

$$\begin{aligned}\frac{\partial^2 E_0}{\partial \gamma_{kl} \partial \gamma_{ij}} = H_{ij,kl}^{Orb-Orb} =& 2\langle \Psi_{kl} | \mathscr{H} - E_0 | \Psi_{ij} \rangle + 2\langle \Psi_0 | \mathscr{H} - E_0 | \Psi_{ij,kl} \rangle \\ &- 4\langle \Psi_0 | \mathscr{H} - E_0 | \Psi_{ij} \rangle \langle \Psi_0 | \Psi_{kl} \rangle - 4\langle \Psi_0 | \mathscr{H} - E_0 | \Psi_{kl} \rangle \langle \Psi_0 | \Psi_{ij} \rangle\end{aligned} \tag{4.18}$$

The $\Psi_{ij,kl}$ appearing in the above equation is a doubly excited state which is obtained by applying two excitation operators $\mathbf{C}_{i \rightarrow j}$ and $\mathbf{C}_{k \rightarrow l}$ to the reference wave function. When the orbitals are orthogonal as in the MCSCF methods, the last two terms in Eq. (4.18) disappear while in the Super-CI for orthogonal orbitals[5,6,8] or nonorthogonal orbitals[1,2,15] only the first term in Eq. (4.18) is used as an approximation to the Hessian. The CI part of the gradient is calculated by differentiating E_0 with respect to change in CI coefficients:

$$\frac{\partial E_0}{\partial c_k} = g_{c_k}^{CI} = 2\langle \Psi_0 | \mathscr{H} - E_0 | \Phi_k \rangle = 0 \tag{4.19}$$

The CI gradient is zero because for a given set of orbitals, the CI coefficients are already optimised. The CI part of the Hessian ($\mathbf{H}^{\mathbf{CI-CI}}$) is calculated by differentiating E_0 twice with respect to the CI coefficients:[38]

$$\begin{aligned}\frac{\partial^2 E_0}{\partial c_l \partial c_k} = H_{c_k,c_l}^{CI-CI} =& 2\langle \Phi_l | \mathscr{H} - E_0 | \Phi_k \rangle \\ &- 4\langle \Psi_0 | \mathscr{H} - E_0 | \Phi_k \rangle \langle \Psi_0 | \Phi_l \rangle - 4\langle \Psi_0 | \mathscr{H} - E_0 | \Phi_l \rangle \langle \Psi_0 | \Phi_k \rangle\end{aligned} \tag{4.20}$$

where the last two CI gradient-like terms will disappear. The coupled orbital-CI Hessian ($\mathbf{H}^{\mathbf{Orb-CI}}$) is given as:[38]

$$\begin{aligned}\frac{\partial^2 E_0}{\partial c_k \partial \gamma_{ij}} = H_{ij,c_k}^{Orb-CI} =& 2\langle \Phi_k | \mathscr{H} - E_0 | \Psi_{ij} \rangle + 2\langle \Psi_0 | \mathscr{H} - E_0 | (\Phi_k)_{ij} \rangle \\ & - 4\langle \Psi_0 | \mathscr{H} - E_0 | \Psi_{ij} \rangle \langle \Psi_0 | \Phi_k \rangle - 4\langle \Psi_0 | \mathscr{H} - E_0 | \Phi_k \rangle \langle \Psi_0 | \Psi_{ij} \rangle\end{aligned} \tag{4.21}$$

again the last term in Eq. (4.21) will be zero. Eq. (4.15) for the orbital and CI update coefficients becomes:

$$\begin{bmatrix} \delta \mathbf{c}^{\mathrm{Orb}} \\ \delta \mathbf{c}^{\mathrm{CI}} \end{bmatrix} = - \begin{bmatrix} \mathbf{H}^{\mathrm{Orb-Orb}} & \mathbf{H}^{\mathrm{Orb-CI}} \\ \mathbf{H}^{\mathrm{Orb-CI}\dagger} & \mathbf{H}^{\mathrm{CI-CI}} \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{g}^{\mathrm{Orb}} \\ \mathbf{g}^{\mathrm{CI}} \end{bmatrix} \tag{4.22}$$

Equation (4.22) can be solved in a single step by inverting the Hessian matrix. Alternately, conjugate gradient methods can be used to solve it iteratively. Due to the normalisation condition (i.e., $\langle \Psi | \Psi \rangle = 1$), not all wave function parameter are independent. In other words, if there are N total parameters, N - 1 can be determined independently while the Nth parameter is determined by the independent parameters and the normalisation constraint. This constraint reduces the dimensions of the Hessian matrix by 1. The new orbitals are found by adding the correction to the old vectors while setting one correction parameter equal to 1 for each orbital ϕ_i.

$$\phi_i' \rightarrow c_0 \phi_i + \sum_{j \neq i} c_{ij} \phi_j \qquad \text{(by setting } c_0 = 1\text{)} \tag{4.23}$$

The new orbitals are subsequently re-normalised and the process is then iterated until convergence. For a converged wave function, according to the Brillouin theorem,[4] the interaction between the Ψ_0 and all singly substituted states (i.e., the orbital gradient) will vanish

$$\langle \Psi_0 | \mathscr{H} - E_0 | \Psi_{ij} \rangle = 0 \tag{4.24}$$

The necessary condition for the convergence of the Newton-Raphson scheme is that the Hessian matrix is positive definite. When far away from the solution the Hessian often has many negative or very small eigenvalues and the Eq. (4.22) in that case produces very large values for the orbital corrections in the beginning. When this is the case, the Newton-Raphson method may lead to divergence. To force the iterative procedure to converge, a level shift is necessary which makes the Hessian positive definite and the step vector $\delta \mathbf{c}$ sufficiently small. In that situation (i.e., when the Hessian is not positive definite) we can either use the Super-CI method in the first few iterations (see Section 4.5 for more details) or the so-called "stabilised Newton-Raphson" approach.[26] In the stabilised Newton-Raphson method, the

Hessian matrix is augmented as:

$$\begin{aligned} &\delta\mathbf{c} = -(\mathbf{H} + \lambda\mathbf{I})^{-1}.\mathbf{g} \\ \text{with} \quad &\lambda = -\epsilon_0 + R.\langle \mathbf{g}|\mathbf{g}\rangle \end{aligned} \tag{4.25}$$

where **I** is the unit matrix, ϵ_0 is the largest negative eigenvalue of the Hessian and R is a suitably chosen scalar which ensures that the Hessian is positive definite.

4.4 Test Calculations

The Newton-Raphson method described above has been implemented in the VB program TURTLE[39] which is a part of the GAMESS-UK[40] quantum chemistry package. To test the convergence and efficiency of the method, calculations were performed on N_2, cyclobutadiene, benzene molecules. The cc-pVTZ ((10s,5p,2d,1f/5s,2p,1d) → [4s,3p,2d,1f/3s, 2p,1d]) basis set was used in all the calculations. This is a fairly large basis set and adds more flexibility to the basis functions using *p* and *d* functions on H and *d* and *f* functions on C and N atoms. In the orbital optimisation procedure of the VBSCF method two models are used. In the first model mixing between the orbitals that are centred on different atoms is not considered. This model is called the VB-local method. In the second model, called the VB-delocal method, a full optimisation is performed without any restrictions. Thus, all orbital mixings (i.e., with all singly occupied and all virtuals which are allowed by symmetry) are taken into account. All calculations were run on a single core of intel XEON X7542 2.67GHz machine using the serial version of TURTLE. For all VBSCF calculations a convergence criterion of 1.0×10^{-10} was used for the correction to the VB energy. For the nitrogen molecule at each geometrical step the number of iterations required to get convergence, the maximum component of the orbital gradient vector (g_{max}) after the final iteration and the total cpu time (in seconds) were noted. For cyclobutadiene and benzene, the decrease in g_{max}, the correction to the VB energy and the cpu time were collected after each iteration.

4.4.1 Potential Energy Curves for the N_2 Molecule

For the nitrogen molecule we calculated the potential energy (PE) curves for the singlet ground state of the molecule using the VB-local and VB-delocal methods. A single configuration VB wave function was used in these calculations. In VB-local, the nitrogen $1s, 2s, 2p_x, 2p_y$ and $2p_z$ orbitals were used as starting vectors which were taken from a preceding atomic RHF/cc-pVTZ calculation and all these orbitals were optimised in the VBSCF calculations. The VB-local results are presented in Table 4.1 using the Newton-Raphson and the Super-CI

Table 4.1: Convergence of the second-order VBSCF and Super-CI for PE curve calculations of N_2 using the VB-local method in cc-pVTZ basis.

r_{12} (Å)	**Newton-Raphson**			**Super-CI**			VB Energy (hartree)
	No. Iter.	g_{max}	cpu(s)	No. Iter.	g_{max}	cpu(s)	
0.800	5	9.6E-11	123	10	1.1E-06	134	-108.43872201
1.000	5	1.6E-13	122	9	7.0E-07	124	-108.91415109
1.100	4	1.7E-11	99	8	1.4E-06	107	-108.94327542
1.094*	-	7.1E-14	105	-	1.1E-06	167	-108.94336792
1.200	5	5.6E-13	122	9	6.9E-07	122	-108.92124554
1.400	5	1.5E-13	123	8	4.9E-07	108	-108.83213680
1.600	4	5.0E-14	99	7	7.3E-07	95	-108.75925457
1.800	4	6.3E-14	98	8	2.5E-07	108	-108.72196978
2.000	3	8.5E-13	74	8	2.4E-07	107	-108.70705978
2.200	3	2.3E-13	75	7	6.0E-07	95	-108.70053116
2.400	3	3.4E-13	81	7	2.8E-07	97	-108.69660807
2.600	3	1.8E-12	76	6	5.2E-07	81	-108.69391806
2.800	2	9.5E-12	50	5	1.1E-06	67	-108.69214096
3.000	2	3.5E-12	50	5	8.5E-07	67	-108.69105147
3.500	2	1.4E-12	50	4	4.1E-07	55	-108.68998446
4.000	2	1.8E-12	50	3	3.7E-07	41	-108.68977968
5.000	1	7.3E-12	25	1	4.0E-07	14	-108.68974256
∞	3	1.4E-11	41	7	6.8E-07	51	-108.68974201
	Total cpu(s) = 1463			Total cpu(s) = 1640			

*Geometry from the previous step (1.10 Å) is allowed to relax, r_{12} = 1.09394 Å.

method. The Newton-Raphson method shows excellent convergence in this case. Although, a single Newton-Raphson iteration is computationally more expensive than a Super-CI iteration, the overall results (the total time for the calculation of the curve) show that this cost is overcompensated by a reduction in the number of iterations required in the Newton-Raphson method. In VB-delocal (see Table 4.2) at very compressed geometry (i.e., at 0.80 Å) almost the same number of iterations are need in the Newton-Raphson method as in the Super-CI method. So at that point the Newton-Raphson method is slightly more expensive than the Super-CI method. However, again the total time for the calculation of the curve using the Newton-Raphson method is less than that required using the Super-CI method. Moreover, the wave function is more precisely converged in the Newton-Raphson method than the Super-CI method both in VB-local and VB-delocal.

4.4.2 Cyclobutadiene and Benzene

For the cyclobutadiene and benzene molecules, RHF/cc-pVTZ optimised geometries were used. The VBSCF calculations were performed only on the orbitals of π-symmetry.

Table 4.2: Convergence of the second-order VBSCF and Super-CI for PE curve calculations of N_2 using the VB-delocal method in cc-pVTZ basis.

r_{12} (Å)	Newton-Raphson			Super-CI			VB Energy (hartree)
	No. Iter.	g_{max}	cpu(s)	No. Iter.	g_{max}	cpu(s)	
0.800	11	1.1E-10	244	13	3.5E-07	181	-108.53998519
1.000	5	3.0E-13	126	9	6.0E-07	119	-109.02900261
1.100	5	3.7E-10	132	10	3.2E-07	140	-109.05948651
1.094*	-	3.0E-12	163	-	9.5E-07	181	-109.05959762
1.200	6	4.0E-13	168	12	3.6E-07	190	-109.03550884
1.400	5	1.8E-13	156	14	4.5E-07	251	-108.93427308
1.600	4	4.2E-11	143	13	5.0E-07	258	-108.83977145
1.800	4	1.2E-12	161	10	6.4E-07	214	-108.77631398
2.000	4	1.5E-13	156	8	5.3E-07	171	-108.73853744
2.200	4	2.6E-13	172	7	3.1E-07	162	-108.71689988
2.400	3	3.5E-11	127	6	3.6E-07	139	-108.70465907
2.600	3	6.3E-13	133	5	9.4E-07	115	-108.69784635
2.800	3	4.4E-13	131	5	4.3E-07	116	-108.69411787
3.000	3	2.2E-13	123	5	4.4E-07	109	-108.69209400
3.500	3	1.1E-12	135	4	7.7E-07	91	-108.69026095
4.000	3	1.0E-12	132	5	1.6E-06	94	-108.68989353
5.000	1	7.0E-12	25	1	1.8E-07	14	-108.68974256
∞	0	1.4E-11	1	0	1.4E-11	1	-108.68974201
	Total cpu(s) = 2428			Total cpu(s) = 2546			

*Geometry from the previous step (1.10 Å) is allowed to relax, r_{12} = 1.09357 Å.

For the doubly occupied orbitals of σ-symmetry, RHF-SCF orbitals were used which were kept frozen in the VB calculations. In the VB-local method, singly occupied atomic *p*-orbitals, taken from a preceding atomic Hartree-Fock calculation, were used as an initial guess. All spin-coupling modes between the singly occupied *p*-orbitals were considered in the VB wave function which correspond to 2 configuration state functions or VB structures for cyclobutadiene and 5 for benzene.

In the VB-local calculations for both molecules, the only orbital mixings are between the "singly occupied orbitals and the corresponding virtuals (on the same atom)". The results of the Newton-Raphson and Super-CI iterations are summarised in Tables 4.3 and 4.4. In the Newton-Raphson method the Hessian matrix exhibiteds no negative eigenvalues in any iteration for both molecules and the optimisation procedure goes quadratically from the very beginning. Only 3 iterations are required in this case to minimise the energy correction to less than 1×10^{-10} hartree. With the same initial vectors the Super-CI converges more slowly and takes 5 iteration to decrease the energy correction to a similar value. The time required to perform one Newton-Raphson iteration for both systems is almost the same as that required

Table 4.3: Convergence of the second-order VBSCF method and Super-CI for cyclobutadiene using the VB-local method (2 structures, 4 singly occupied and 12 doubly occupied/frozen orbitals, cc-pVTZ basis).

it.	**Newton-Raphson**			**Super-CI**		
	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)
0	-153.6656878103	6.1E-02	98	-153.6656878103	6.1E-02	96
1	-0.0314269657	2.1E-03	179	-0.0311914562	6.3E-03	177
2	-0.0000469668	2.9E-06	261	-0.0002807006	5.1E-04	259
3	0.0000000000	5.2E-12	341	-0.0000017613	4.4E-05	345
4				-0.0000000143	3.9E-06	425
5				-0.0000000001	3.5E-07	503

Table 4.4: Convergence of the second-order VBSCF method and Super-CI for benzene using the VB-local method (5 structures, 6 singly occupied and 18 doubly occupied/frozen orbitals, cc-pVTZ basis).

it.	**Newton-Raphson**			**Super-CI**		
	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)
0	-230.6598655922	5.9E-02	255	-230.6598655922	5.9E-02	254
1	-0.0335719529	6.1E-04	455	-0.0335161482	2.5E-03	449
2	-0.0000032764	1.2E-07	654	-0.0000588137	1.7E-04	644
3	0.0000000000	2.1E-15	853	-0.0000002657	1.3E-05	838
4				-0.0000000018	1.1E-06	1032
5				0.0000000000	1.0E-07	1226

Table 4.5: Convergence of the second-order VBSCF method and Super-CI for cyclobutadiene using the VB-delocal method (2 structures, 4 singly occupied and 12 doubly occupied/frozen orbitals, cc-pVTZ basis).

it.	**Newton-Raphson**			**Super-CI**		
	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)
0	-153.6971617429	7.0E-02	102	-153.6971617429	7.0E-02	95
1	-0.0553953655	1.9E-02	193	-0.0570020283	2.0E-02	179
2	-0.0039995033	3.5E-03	277	-0.0026079505	7.2E-04	265
3	-0.0002195682	2.8E-04	361	-0.0000069087	2.4E-05	347
4	-0.0000024653	6.0E-06	446	-0.0000000156	2.6E-06	427
5	-0.0000000011	3.1E-09	531	-0.0000000002	4.2E-07	509
6	0.0000000000	1.8E-15	615	0.0000000000	4.0E-08	596

in the Super-CI method. This is because the basis set is quite big compared to the number of active VB orbitals (more precisely the number of Brillouin states, n_{Brill}, see Eqs. (4.9) and (4.10)) so the 4-index transformation is the most expensive part in each iteration of VB-local calculations for these systems. As the Newton-Raphson scheme requires less iterations

Table 4.6: Convergence of the second-order VBSCF method and Super-CI for benzene using the VB-delocal method (5 structures, 6 singly occupied and 18 doubly occupied/frozen orbitals, cc-pVTZ basis).

it.	Newton-Raphson			Super-CI		
	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)
0	-230.6934408216	6.1E-02	265	-230.6934408216	6.1E-02	262
1	-0.1013617755	3.2E-02 (4)*	731	-0.0970436377	4.6E-02	626
2	-0.0373469262	1.2E-02 (4)	1197	-0.0350191849	2.6E-02	971
3	-0.0078561640	3.4E-03 (1)	1662	-0.0139572868	6.9E-03	1333
4	-0.0008452295	4.8E-04 (1)	2146	-0.0014225024	6.4E-04	1694
5	-0.0000472300	7.0E-05 (1)	2630	-0.0000151943	2.0E-05	2055
6	-0.0000012788	2.0E-05	3113	-0.0000006562	9.3E-06	2416
7	-0.0000000752	2.8E-06	3596	-0.0000001620	4.7E-06	2777
8	-0.0000000015	6.3E-08	4060	-0.0000000417	2.4E-06	3138
9	0.0000000000	2.6E-11	4543	-0.0000000108	1.2E-06	3491
10				-0.0000000028	6.3E-07	3850
11				-0.0000000007	3.2E-07	4203
12				-0.0000000002	1.6E-07	4556
13				-0.0000000001	8.4E-08	4910

*Number of negative eigenvalues of the Hessian in the parentheses.

than Super-CI, a considerable time is saved using the former method.

Using the well converged VB-local orbitals as initial guess, the results of full optimisation (VB-delocal) are presented in Tables 4.5 and 4.6. For cyclobutadiene the Hessian matrix is positive definite and quadratic convergence is achieved from the 2nd iteration. However, the Super-CI method is equally good in this case. So the computational time is almost the same in both the Newton-Raphson and Super-CI methods. For the benzene molecule in the starting few iterations, the Hessian matrix has a few negative eigenvalues in the Newton-Raphson method. This is an indication that the starting vectors are not so good and they change a lot in the beginning. To restrict the step size, the Hessian was augmented according to Eq. (4.25) using $R = 1.5$. After the 5th iteration the Hessian becomes positive definite on its own and no further adjustment is required. Although, in case of benzene, the Newton-Raphson method shows quadratic behaviour in the last 4 iterations, it is still computationally less expensive than Super-CI which takes 13 iterations to converge as compared to 9 iterations in the Newton-Raphson method. Also the Newton-Raphson method provides a better converged wave function than the Super-CI method in all these calculations.

It is worth mentioning that the second-order VBSCF method described above is very general and, apart from VB-local and VB-delocal methods, also works for the breathing orbital valence bond (BOVB) method[41,42] and for the optimisation of nonorthogonal orbitals

Table 4.7: Convergence of the Newton-Raphson method combined with Super-CI for cyclobutadiene using the VB-delocal method (2 structures, 4 singly occupied and 12 doubly occupied/frozen orbitals, cc-pVTZ basis).

Super-CI + Newton-Raphson			
it.	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)
0	-153.6971617429	7.0E-02	95
1 (SCI)	-0.0570020283	2.0E-02	178
2 (SCI)	-0.0026079505	7.2E-04	263
3 (NR)	-0.0000069245	3.0E-06	345
4 (NR)	-0.0000000002	2.8E-10	434
5 (NR)	0.0000000000	2.0E-15	521

Table 4.8: Convergence of the Newton-Raphson method combined with Super-CI for benzene using the VB-delocal method (5 structures, 6 singly occupied and 18 doubly occupied/frozen orbitals, cc-pVTZ basis).

Super-CI + Newton-Raphson			
it.	$\Delta E_{(it,it-1)}$ (hartree)	g_{max}	cpu(s)
0	-230.6934408216	6.1E-02	268
1 (SCI)	-0.0970436377	4.6E-02	618
2 (SCI)	-0.0350191889	2.6E-02	969
3 (SCI)	-0.0139572830	6.9E-03	1319
4 (SCI)	-0.0014225024	6.4E-04	1688
5 (NR)	-0.0000160608	9.1E-06	2175
6 (NR)	-0.0000000080	1.2E-08	2662
7 (NR)	-0.0000000000	7.9E-14	3149

with (other) arbitrary restrictions, for example, bond distorted orbitals (where the orbitals are allowed to distort only towards certain centres), block localised wave functions (BLW)[43] and resonating block localised wave functions (RBLW).[44]

4.5 A Combined Super-CI and Newton-Raphson Approach

As has been demonstrated previously[15] the Super-CI and the Newton-Raphson method are very closely related to each other. Our own experience tells us that the Super-CI method is quite good at the start. However, it becomes slow as convergence is approached. On the other hand, the Newton-Raphson method is not so good in the beginning if the Hessian matrix is not positive definite. In that case the Newton-Raphson method shows linear convergence in the starting few iterations at a considerably higher cost compared to Super-CI, due to the requirement to compute the exact Hessian matrix. However, close to the minimum it shows quadratic convergence. In our approach, we combine the advantages of both these methods.

In this combined method, when the initial guess orbitals are far away from the minimum which is usually the case in the VB-delocal method, the optimisation procedure is started with the Super-CI method which produces very good correction vectors in the beginning. As the largest correction vector drops below a certain threshold the Newton-Raphson method is switched on. This approach is used for the optimisation of orbitals for cyclobutadiene and benzene using the VB-delocal method and the results are shown in Tables 4.7 and 4.8. A value of 0.02 for the maximum component of the orbital correction vector (the b_{ij}/b_0 ratio in Eq. (4.13)) was used as switching criterion from the Super-CI to the Newton-Raphson method in these calculations. As can be seen from the results, this strategy considerably improves the efficiency. In case of cyclobutadiene it takes one iteration less than using either Newton-Raphson or Super-CI alone. While for the benzene molecule, the number of iterations is now reduced to 7 instead of 9 in the Newton-Raphson or 13 in the Super-CI method and a considerable time saving is achieved.

4.6 Conclusion

A second-order VBSCF method has been presented based on the Newton-Raphson scheme. Test calculations have shown that this method shows quadratic convergence from the start when the orbital mixings are only between the doubly or singly occupied orbitals and the virtual orbitals. This is usually the case when a restricted optimisation is performed as in the VB-local method. In that case, only 3-5 iterations have been found sufficient to reduce the energy correction to less than 1.0×10^{-10}. When the singly occupied orbitals also mix with each other, the quadratic convergence behaviour was found in the last 4 or 5 iterations. A comparison of the Newton-Raphson method and the Super-CI have shown that the former is more efficient in most of the test calculations presented above. Since a one full iteration is computationally more expensive in the Newton-Raphson method than in the Super-CI, another approach has been presented which combines these two methods. In the combined method the first few iterations were performed with the Super-CI and then the Newton-Raphson method was used. When performing a full optimisation, this approach has been found computationally more economical than using the Newton-Raphson method alone.

References

1. van Lenthe, J. H.; Balint-Kurti, G. G. *Chem. Phys. Lett.* **1980**, *76*, 138--142.
2. van Lenthe, J. H.; Balint-Kurti, G. G. *J. Chem. Phys.* **1983**, *78*, 5699--5713.
3. van Lenthe, J. H.; Dijkstra, F.; Havenith, R. W. A. TURTLE - A gradient VBSCF Program Theory and Studies of Aromaticity. In *Theoretical and Computational Chemistry:*

Valence Bond Theory; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10, pp 79--116.

4. Levy, B.; Berthier, G. *Int. J. Quantum Chem.* **1968**, *2*, 307--319.
5. Grein, F.; Chang, T. C. *Chem. Phys. Lett.* **1971**, *12*, 44--48.
6. Banerjee, A.; Grein, F. *Int. J. Quantum Chem.* **1976**, *10*, 123--134.
7. Chang, T. C.; Schwarz, W. H. E. *Theor. Chim. Acta. (Berl.)* **1977**, *44*, 45--59.
8. Ruttink, P. J. A.; van Lenthe, J. H. *Theor. Chem. Acc.* **1977**, *44*, 97--107.
9. Heitler, W.; London, F. *Z. Physik* **1927**, *44*, 455--472.
10. Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed.; Cornell University Press: New York, **1960**.
11. Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill Book Company, Inc.: New York, **1963**; Vol. 1.
12. Pulay, P. *Chem. Phys. Lett.* **1980**, *73*, 393--398.
13. Hamilton, T. P.; Pulay, P. *J. Chem. Phys.* **1986**, *84*, 5728--5734.
14. Banerjee, A.; Grein, F. *J. Chem. Phys.* **1977**, *66*, 1054--1062.
15. van Lenthe, J. H.; Verbeek, J.; Pulay, P. *Mol. Phys.* **1991**, *73*, 1159--1170.
16. Yaffe, L. G.; Goddard, W. A. *Phys. Rev. A* **1976**, *13*, 1682--1691.
17. Dalgaard, E.; Jørgensen, P. *J. Chem. Phys.* **1978**, *69*, 3833--3844.
18. Dalgaard, E. *Chem. Phys. Lett.* **1979**, *65*, 559 -- 563.
19. Roothaan, C. C. J.; Detrich, J.; Hopper, D. G. *Int. J. Quantum Chem. Symp.* **1979**, *16*, 93--101.
20. Lengsfield III, B. H. *J. Chem. Phys.* **1980**, *73*, 382--390.
21. Werner, H.-J.; Meyer, W. *J. Chem. Phys.* **1980**, *73*, 2342--2356.
22. Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384--2396.
23. Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053--5063.
24. Werner, H.-J. Matrix-Formulated Direct Multiconfiguration And Multiconfiguration Reference Configuration Interaction Methods. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 1--62.
25. Schmidt, M. W.; Gordon, M. S. *Ann. Rev. Phys. Chem.* **1998**, *49*, 233--266.
26. Pyper, N. C.; Gerratt, J. *Proc. R. Soc. Lond. A* **1977**, *355*, 407--439.
27. Gerratt, J.; Raimondi, M. *Proc. R. Soc. Lond. A* **1980**, *371*, 525--552.
28. Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474--1489.
29. Verbeek, J.; van Lenthe, J. H. *J. Mol. Struct. (Theochem)* **1991**, *229*, 115--137.
30. Verbeek, J.; van Lenthe, J. H. *Int. J. Quantum Chem.* **1991**, *40*, 201--210.

31. Dijkstra, F.; van Lenthe, J. H. *Int. J. Quantum Chem.* **1998**, *67*, 77--83.
32. Slater, J. C. *Phys. Rev.* **1929**, *34*, 1293--1322.
33. Condon, E. U. *Phys. Rev.* **1930**, *36*, 1121--1133.
34. Gerratt, J. General Theory of Spin-Coupled Wave Functions for Atoms and Molecules. In *Advances in Atomic and Molecular Physics*; Bates, D., Esterman, I., Eds.; Academic Press, **1971**; Vol. 7, pp 141--221.
35. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Farady Symp. Chem. Soc.* **1984**, *19*, 149--163.
36. Cooper, D. L.; Gerratt, J.; Raimondi, M. Modern Valence Bond Theory. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 319--397.
37. Ruttink, P. J. A. *Theor. Chim. Acta. (Berlin)* **1975**, *36*, 289--296.
38. Havenith, R. W. *Chem. Phys. Lett.* **2005**, *414*, 1--5.
39. Verbeek, J.; Langenberg, J. H.; Byrman, C. P.; Dijkstra, F.; Havenith, R. W. A.; Engelberts, J. J.; Zielinski, M. L.; Rashid, Z.; van Lenthe, J. H. **1988--2012**, TURTLE an *ab initio* VB/VBSCF Program, Theoretical Chemistry Group, Utrecht University, Utrecht.
40. Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J. *Mol. Phys.* **2005**, *103*, 719--747.
41. Hiberty, P. C.; Humbel, S.; Byrman, C. P.; van Lenthe, J. H. *J. Chem. Phys.* **1994**, *101*, 5969--5976.
42. Hiberty, P. *J. Mol. Struct. (THEOCHEM.)* **1997**, *398--399*, 35--43.
43. Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687--1697.
44. Zielinski, M.; van Lenthe, J. H. *J. Phys. Chem. A* **2008**, *112*, 13197--13202.

CHAPTER 5

THE EFFICIENCY OF VBSCF ALGORITHMS

Abstract

The efficiency of two orbital optimisation algorithms in VBSCF methods is discussed. One of these algorithms is based on the approximate Newton-Raphson (aNR) method which employs the orbital gradient and the diagonal of the Super-CI matrix (as an approximation to the orbital Hessian) for the optimisation of nonorthogonal orbitals. The second algorithm uses a Fock matrix to compute a matrix element between two different determinants, which can be used for orbital optimisation. Detailed timings for orbital optimisation in terms of different orbital types in the calculations are presented for both algorithms.

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5.1 Introduction

Modern Valence Bond approaches[1--6] describe the electronic structure of molecules with variationally optimised wave functions. In most of these methods, the VB wave functions are multiconfigurational in form and each configuration is constructed from a set of nonorthogonal orbitals. The Valence Bond Self-Consistent Field (VBSCF) method[4--6] is one of the most general form of these VB methods and offers a complete freedom in the choice of configurations and the amount of nonorthogonality amongst the orbitals. A general VBSCF wave function is constructed as a linear combinations of configurations (usually called VB structures):

$$\Psi_{VBSCF} = \sum_i C_i \Phi_i \tag{5.1}$$

where each configuration is a linear combination of Slater determinants composed of nonorthogonal orbitals. The orbitals and the CI coefficients are determined variationally by an iterative SCF procedure. The optimisation of these wave functions and more specifically the orbitals is a difficult task. The bottleneck in the VBSCF calculations is the evaluation of the Hamiltonian matrix elements between the determinants. Difficulties arise due to the use of nonorthogonal orbitals and a large number of cofactors of the overlap matrices need to be calculated. This problem is absent in the multiconfigurational approaches which use orthogonal orbitals.

In the past, efficient schemes have been developed for the optimisation of VB wave functions based on the Newton-Raphson method[7,8] and the generalised Brillouin theorem as extended to nonorthogonal orbitals.[4--6,9] It is the aim of this chapter to discuss the efficiency of two orbital optimisation approaches in the VBSCF method. One of these is based on an approximation to the exact Newton-Raphson scheme and uses only the orbital gradient and the diagonal elements of the Super-CI matrix to derive orbital changes. In the second approach the Fock matrix is used to calculate the matrix elements required in the orbital optimisation. The computational complexity $\mathcal{O}$ of the major steps involved in the optimisation procedure is described and the most time consuming part in each of these algorithms is discussed in a way that is more or less machine independent. Finally, the results of actual test calculations are presented.

5.2 Orbital Optimisation

When optimising the orbitals various approaches, including the simplest one (simplex),[10] may be used. Most efficient is to employ an exact gradient and either an exact Hessian or some reasonable approximation thereof. For a single determinant wave function with doubly occupied orthogonal orbitals we have the well known Fock matrix,[11] where the off-diagonal elements are the gradients and an approximation to the Hessian may be generated from the diagonal elements. This Fock matrix may be simply obtained by adding the product of the 2-electron super matrix and the density matrix to the one-electron matrix. Since the 2-electron super matrix has n^4 elements (roughly) the computational effort is deemed to be $\mathcal{O}(n^4)$, where n is the number of basis functions.

In the Super-CI method[12,13] or its derivatives one expresses the orbital gradient in terms of Hamiltonian ($\mathcal{H}$) matrix elements between Ψ_0 and the singly excited states, Ψ_{ij} (which we call Brillouin states), where Ψ_{ij} is defined as:

$$\Psi_{ij} = \mathbf{C}_{i\rightarrow j}\Psi_0 \tag{5.2}$$

where $\mathbf{C}_{i\rightarrow j}$ is an operator, that replaces orbital i by orbital j, once for α and once for β spin for each determinant in Ψ_0. This definition is valid for multi-determinantal states without orthogonality restrictions as is the case in the Valence Bond methods. If orthogonality constraints are used, like in the original Super-CI[12,13] the definition of the Brillouin states includes the unitary condition[14]

$$\Psi_{ij}^{unitary} = (\mathbf{C}_{i\rightarrow j} - \mathbf{C}_{j\rightarrow i})\Psi_0 \tag{5.3}$$

Using these definitions the gradient $\mathbf{g}$ for mixing orbital j into orbital i is:[5]

$$g_{ij} = \langle\Psi_0|\mathcal{H} - E_0|\Psi_{ij}\rangle \tag{5.4}$$

The generalised Brillouin theorem[14] is obtained by putting the orbital gradient with the Brillouin state of Eq. (5.2) equal to 0. The orbital Hessian $\mathbf{H}$ is obtained by differentiating the gradient to obtain:[5,15]

$$\begin{aligned} H_{ij,kl} =& 2\langle\Psi_{kl}|\mathcal{H} - E_0|\Psi_{ij}\rangle + 2\langle\Psi_0|\mathcal{H} - E_0|\Psi_{ij,kl}\rangle \\ & - 4\langle\Psi_0|\mathcal{H} - E_0|\Psi_{ij}\rangle\langle\Psi_{kl}|\Psi_0\rangle - 4\langle\Psi_0|\mathcal{H} - E_0|\Psi_{kl}\rangle\langle\Psi_{ij}|\Psi_0\rangle \end{aligned} \tag{5.5}$$

where $\Psi_{ij,kl}$ is analogously a doubly excited state. Only the first term in Eq. (5.5) is used as an approximation to the Hessian in the Super-CI for orthogonal (MCSCF)[12,13] or nonorthogonal (VBSCF)[4,5] calculations.

In the past an approximate scheme was defined, called approximate Newton-Raphson (aNR),[16] where only the orbital gradient and the diagonal of the Super-CI problem is evaluated. Recently a scheme was published,[17] where just the orbital gradient was calculated for a few orbital mixings using transition density matrices. In the following we analyse the computational cost of these approaches.

The number of singly excited states (Brillouin states), which depends on the number of basis functions n and the number of active occupied orbitals N, is approximately equal to nN. In a complete Super-CI calculation we need the interaction between all the Brillouin states $\langle \Psi_{kl} | \mathscr{H} - E_0 | \Psi_{ij} \rangle$, a total of $(nN)^2$ matrix elements. As one matrix element requires $\sim N^4$ operations we estimate a total number of operations of n^2N^6,[18] ignoring the triangle symmetry which is a factor of 2.

Using the Fock matrix method, a gradient for the mixing of two orbitals i and j is calculated which is just one matrix element between Ψ_0 and Ψ_{ij} over the Hamiltonian. An efficient method for the calculation of these matrix elements was developed by Broer and Nieuwpoort[19] and it has been used by Song and co-workers[17] for the optimisation of nonorthogonal orbitals. The computational cost is indeed, as written in the original paper,[19] $\mathscr{O}(n^4)$ per matrix element. As there are of the order of $(n^2/2)$ orbital gradients, the total cost is about $\mathscr{O}(n^6/2)$, really more then suggested in the literature.[17]

The computational complexity of the orbital optimisation procedure can be compared to the complexity of the calculation of the Lagrangian, which is needed for the evaluation of the molecular energy gradients (although in some formulations the Lagrangian is apparently not needed, but then the restrictions on the wave function are not properly taken into account (see Section 5.A)). A very rough guess of the cost for calculating the Lagrangian is of the order of N^6 operations.[18] Thus, when calculating the molecular energy gradients using the VBSCF method, the evaluation of the Lagrangian is computationally less expensive than the orbital optimisation because the latter scales as n^2N^6.

5.3 Results and Discussion

We consider different types of orbitals featuring in the singly excited states to get a more precise estimate of the number of Brillouin states, n_{Brill}. Frozen orbitals (nfrz) are neither excited *from* nor excited *to*. Doubly occupied orbitals (ndoc) are not available to excite *to* as Pauli principle forbids it. The only orbitals available to excite *from* and *to* are the variably occupied ones (nvoc) (including the singly occupieds). Finally exciting *from* an orbital *to* itself produces no Brillouin state. The only virtuals (nvirt) available are the ones of the right symmetry. So we get [(ndoc × nvirt) + nvoc × (nvoc-1 + nvirt)] Brillouin states, ignoring symmetry.

To be able to give a meaning to our estimates and to give actual timings we define some example cases of the benzene molecule in a standard 6-31G basis, with all covalent VB structures.

I. In the first case only the π orbitals are optimised. This means n = 66, N = 6, nfrz = 18, ndoc = 0, nvoc = 6 and nvirt = 6. Here we have ignored 36 virtual orbitals. The only excitations involved are *from* the orbitals of π spatial-symmetry *to* the orbitals of π symmetry and the number of singly excited Brillouin states is: 6 nvoc × ((6 - 1) nvoc + 6 nvirt) = 66 .

II. Alternatively we could consider the case where only nine orbitals are frozen. Then we will have n = 66, N = 6 + 9. We have occupied and virtual orbitals of σ and π symmetry, but we cannot excite from σ *to* π and vice versa. In this case, we have nfrz = 9, ndoc(σ) = 9, nvoc(π) = 6, nvirt(σ) = 36 and nvirt(π) = 6. So the number of Brillouin states is: 9 ndoc × 36 nvirt(σ) + 6 nvoc × (5 nvoc + 6 nvirt(π)) = 324 + 66 = 390.

III. Finally we can destroy the σ-π spacial separation by moving a hydrogen out of the plane. Then we will have nfrz = 9, ndoc = 9, nvoc = 6 and nvirt = 42. The number of Brillouin states then becomes: 9 ndoc × (6 nvoc + 42 nvirt) + 6 nvoc × (5 nvoc + 42 nvirt) = 714.

All these cases can be handled by the VBSCF program TURTLE[6,20] and (presumably) by the XMVB[21,22] program. Either program can employ less properly chosen Brillouin states, if desired. The number of matrix elements that have to be calculated in each optimisation procedures discussed above is dependent on the number of Brillouin states:

(a) In a Super-CI the number of matrix elements is $n_{Brill} \times (n_{Brill} + 1)/2 + 1$.

(b) In a Perturbation calculation (aNR), it is $2 \times n_{Brill} + 1$.

(c) Using the Fock matrix it is $n_{Brill} + 1$ (although an estimate of the Hessian must be made).

In the aNR (or Super-CI) method, an orbital transformation is involved from atomic orbital (AO) basis to the basis of VB orbitals. A 4-index transformation costs $\mathcal{O}((25/24)n^5)$ for all matrix elements.[23] If there are only n_{activ} orbitals, for which we need to calculate the integrals, we estimate a cost of about $\mathcal{O}(n_{activ} \times n^4)$.

The 4-index transformation is performed just once for all matrix elements, so we distribute that cost over all the matrix-elements. For the aNR scheme, this means that we get a cost of

$$\frac{n_{activ} \times n^4}{(2 \times n_{Brill}) + 1} \tag{5.6}$$

which evaluates to $\mathcal{O}(1.71 \times 10^6)$ operations for case I, $\mathcal{O}(1.38 \times 10^6)$ operations for case II and $\mathcal{O}(7.57 \times 10^5)$ operations for case III per matrix element. Note that for Super-CI the cost of the 4-index transformation is even more negligible.

Table 5.1: Timings per iteration (in seconds) for an aNR calculation for the three cases on a 2.67 GHz Xeon (using a single core).

	Case I	**Case II**	**Case III**
No. of Brillouin states	66	390 (152)*	714 (243)*
Matrix elements Ψ_0	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-2}
4-index Ψ_0	2.4×10^{-1}	2.9×10^{-1}	3.4×10^{-1}
Matrix elements orbital-opt.	2.0×10^{-2}	2.6×10^{0}	3.7×10^{0}
4-index orbital-opt.	3.0×10^{-1}	1.1×10^{0}	1.3×10^{0}
Fock matrix construction	4.0×10^{-2}	3.5×10^{-2}	4.5×10^{-2}

*Number of Brillouin states which are treated using a Fock matrix are given in parentheses.

One Brillouin state consists of determinants. In our examples each Brillouin state is built up of 20 determinants. So one Brillouin matrix element consists of 210 matrix elements over the determinants. Each takes $\mathcal{O}(N^4)$ operations, where $N = 6$ for case I or 15 in cases II and III. Hence, for the evaluation of one Brillouin matrix element, we get $\mathcal{O}(210 \times 6^4 = 2.72 \times 10^5)$ operations for case I and $\mathcal{O}(210 \times 15^4 = 1.06 \times 10^7)$ operations for cases II and III.

In the Fock matrix method (Broer-Nieuwpoort method[19]), the cost of calculating one matrix element is $\mathcal{O}(n^4)$. So we have one matrix element at a cost of $\mathcal{O}(66^4 = 1.897 \times 10^7)$ operations. This is considerably more than in the most expensive aNR scheme, and we do not have an estimate of the Hessian yet and we have not considered the back-transformation.

In Table 5.1 we present some timings per iteration (in seconds) for an aNR calculation for the three cases discussed above. For cases II and III we can use standard Fock matrix elements for some of the orbital gradients.[24] So the number of Brillouin states are given for aNR and the number of matrix elements among these which are done with a Fock matrix are given separately in parenthesis. As only one Fock matrix has to be calculated considerable time is saved. From the example cases given above and Table 5.1 it follows that the most time consuming part is generally the calculation of the matrix elements in the orbital optimisation procedure of the VBSCF method.

5.4 Conclusion

The computational costs of different steps has been analysed in detail in the different orbital optimisation schemes for nonorthogonal orbitals in the VBSCF method. It has been found that the Fock matrix method is slightly more expensive than the aNR method, although the former does not involve a 4-index transformation from atomic orbitals to VB orbitals. This is because the calculation of the matrix elements is often more expensive than the 4-index transformation.

APPENDIX

5.A Molecular Energy Gradients in VB and Lagrange Multipliers

When calculating the molecular energy gradients, the constraints in the wave function must be taken into account.[25] In the orthogonal orbital approaches, these are maintaining the orthonormality of the orbitals and configuration state functions (in the multiconfiguration approaches). In Valence Bond methods it is only the normalisation of the total wave function. To calculate the molecular energy gradients using VB, the normalisation restriction:

$$\langle\Psi_0|\Psi_0\rangle = 1 \qquad \text{or} \qquad \langle\Psi_0|\Psi_0\rangle - 1 = 0 \tag{5a}$$

must be incorporated in the energy function. In the method of Lagrange multipliers this constraint is handled by introducing another variable λ, called the Lagrange multiplier. By multiplying the constraint with λ and subtracting it from the object function, which is the energy expectation value, the associated Lagrange function becomes:

$$E = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle - \lambda\big(\langle\Psi_0|\Psi_0\rangle - 1\big) \tag{5b}$$

where λ is determined by requiring that the derivative of E with respect to the wave function variables (orbital and CI coefficients) vanishes. As we have only one restriction, it can be shown that λ is equal to the energy E of the VB wave function.[18] The expression for the molecular energy gradient becomes:

$$\frac{\partial E}{\partial \mathbf{R}} = \frac{\partial}{\partial \mathbf{R}}\Big(\langle\Psi_0|\mathscr{H}|\Psi_0\rangle - E\big(\langle\Psi_0|\Psi_0\rangle - 1\big)\Big) \tag{5c}$$

The change in the one- and two-electron integrals at each geometrical step induces a change in the norm of the wave function which is now incorporated in the above expression. In the gradient expression given in Ref. 17 no such constraint is included.

References

1. Gerratt, J. General Theory of Spin-Coupled Wave Functions for Atoms and Molecules. In *Advances in Atomic and Molecular Physics*; Bates, D., Esterman, I., Eds.; Academic Press, **1971**; Vol. 7, pp 141--221.
2. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Farady Symp. Chem. Soc.* **1984**, *19*, 149--163.
3. Cooper, D. L.; Gerratt, J.; Raimondi, M. Modern Valence Bond Theory. In *Advances in*

Chemical Physics: Ab intio Methods in Quantum Chemistry -II; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 319--397.

4. van Lenthe, J. H.; Balint-Kurti, G. G. *Chem. Phys. Lett.* **1980**, *76*, 138--142.
5. van Lenthe, J. H.; Balint-Kurti, G. G. *J. Chem. Phys.* **1983**, *78*, 5699--5713.
6. van Lenthe, J. H.; Dijkstra, F.; Havenith, R. W. A. TURTLE - A gradient VBSCF Program Theory and Studies of Aromaticity. In *Theoretical and Computational Chemistry: Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10, pp 79--116.
7. Pyper, N. C.; Gerratt, J. *Proc. R. Soc. Lond. A* **1977**, *355*, 407--439.
8. Gerratt, J.; Raimondi, M. *Proc. R. Soc. Lond. A* **1980**, *371*, 525--552.
9. van Lenthe, J. H.; Verbeek, J.; Pulay, P. *Mol. Phys.* **1991**, *73*, 1159--1170.
10. Dantzig, G. B. *Linear Programming and Extensions*; Princeton University Press: Princeton, New York, **1963**.
11. Szabo, A.; Ostlund, N. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Books on Chemistry Series; Dover Publications, Inc.: New York, **1996**.
12. Banerjee, A.; Grein, F. *Int. J. Quant. Chem.* **1976**, *10*, 123--134.
13. Grein, F.; Chang, T. C. *Chem. Phys. Lett.* **1971**, *12*, 44--48.
14. Levy, B.; Berthier, G. *Int. J. Quant. Chem.* **1968**, *2*, 307--319.
15. Chang, T. C.; Schwarz, W. H. E. *Theor. Chem. Acc.: Theory, Computation, and Modeling (Theoretica Chimica Acta)* **1977**, *44*, 45--59.
16. van Lenthe J. H.,; Verbeek, J.; Pulay, P. *Mol. Phys.* **1991**, *73*, 1159--1170.
17. Song, L.; Song, J.; Mo, Y.; Wu, W. *J. Comput. Chem.* **2009**, *30*, 399--406.
18. Dijkstra, F.; van Lenthe, J. H. *J. Chem. Phys.* **2000**, *113*, 2100--2108.
19. Broer, R.; Nieuwpoort, W. C. *Theo. Chim. Acta.* **1988**, *73*, 405--418.
20. Verbeek, J.; Langenberg, J. H.; Byrman, C. P.; Dijkstra, F.; Havenith, R. W. A.; Engelberts, J. J.; Zielinski, M. L.; Rashid, Z.; van Lenthe, J. H. **1988--2012**, TURTLE an *ab initio* VB/VBSCF Program, Theoretical Chemistry Group, Utrecht University, Utrecht.
21. Song, L.; Mo, Y.; Zhang, Q.; Wu, W. *J. Comput. Chem.* **2005**, *26*, 514--521.
22. Song, Y., L.; Mo; Zhang, Q.; Wu, W. **2003**, XMVB: An ab initio Non-orthogonal Valence Bond Program, Xiamen University, Xiamen 361005, China.
23. Saunders, V. R.; van Lenthe, J. H. *Mol. Phys.* **1983**, *48*, 923--954.
24. Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157--173.
25. Pulay, P. Analytical Gradients in *ab intio* Methods. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 241--286.

CHAPTER 6

RESONANCE AND AROMATICITY: AN AB INITIO VBSCF APPROACH

Abstract

Resonance energy is one of the criteria to measure aromaticity. The effect of the use of different orbital models is investigated in the calculated resonance energies of cyclic conjugated hydrocarbons within the frame work of the *ab initio* Valence Bond Self-Consistent Field (VBSCF) method. The VB wave function for each system was constructed using a linear combination of the VB structures (spin-functions) which closely resemble the Kekulé valence structures and two types of orbitals, i.e., strictly atomic (local) and delocalised atomic (delocal) *p*-orbitals, were used to describe the π-system. It is found that the Pauling Wheland resonance energy with nonorthogonal structures decreases while the same with orthogonalised structures and the total mean resonance energy (the sum of the weighted off-diagonal contributions in the Hamiltonian matrix of orthogonalised structures) increase when delocal orbitals are used compared to local *p*-orbitals. Analysis of the interactions between the different structures of a system show that the resonance in the 6π electrons conjugated circuits have the largest contributions to the resonance energy. The VBSCF calculations also show that the extra stability of phenanthrene, a kinked benzenoid, compared to its linear counterpart, anthracene, is a consequence of the resonance in the π system rather than the H−H interaction in the bay region as suggested previously. Finally the empirical parameters for the resonance interactions between different (4n+2) or 4n π electron conjugated circuits, used in the Randić's conjugated circuits theory or Herdon's semi-emprical VB approach, are quantified. These parameters have to be scaled by the structure coefficients (weights) of the contributing structures.

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6.1 Introduction

Aromaticity is one of the most important and fundamental concepts in chemistry.[1--4] It is associated with cyclic electron delocalisation[5,6] that provides extra stability to the molecular systems. There is, however, still much dispute about what aromaticity really is and the notion is as elusive as ever.[1,2,7,8] Because aromaticity is not an observable or directly measurable quantity, it is defined by convention. Several criteria like extra stabilisation (delocalisation and resonance) energy (energetic criterion[9--16]), bond length equalisation (geometric criterion[3,17,18]) and π electron ring currents induced by an external magnetic field (magnetic criterion[6,19--21]) are frequently used as indicators for aromaticity.

The energetic criterion is widely accepted as an index for aromaticity. Various quantum mechanical and experimental schemes have been proposed to determine this extra stabilisation energy due to resonance or delocalisation for mono- and polycyclic conjugated compounds. The first theoretical estimate of the delocalisation energy came from the work by E. Hückel[9--11] (Hückel delocalisation energy). Subsequently, Pauling and Wheland[12--14] used Valence Bond Theory to calculate the resonance energies of conjugated systems (Pauling Wheland resonance energy). Later various other approaches were also put forward to calculate resonance or delocalisation energies. These, among others, include Dewar method,[22] Hess-Schaad method,[23] topological or graph theoretical method,[24--26] Randić conjugated circuits method,[27--30] Herndon semiempirical VB method[31,32] and the block-localised wave function (BLW) method.[33--38] Some of these methods (Dewar method, Hess-Schaad method and BLW method) calculate the extra stabilisation energy as the difference between the energy of the real molecule and a separate real or hypothetical "reference" system lacking resonance and/or cyclic delocalisation. This leads to a Hückel's type description of delocalisation energy (a detailed discussion about the difference between delocalisation energy and the resonance energy can be found elsewhere[39,40]). The choice of the reference system is crucial in these methods and the computed delocalisation energies depend upon the chosen reference.[41] However, in these approaches, no information regarding the importance of the different contributing (Lewis or Kekulé) valence structures is obtained.

Different isodesmic[42] and homodesmotic[43--45] reactions are also frequently used to estimate the extra stabilisation due to the π electrons delocalisation, the so-called Aromatic Stabilisation Energy (ASE).[3,4,46] In this case too, the ASEs depend upon the formulation of the reactions. An example is the ASE value for the benzene molecule which ranges from 20.3 kcal/mol to 74.7 kcal/mol depending upon the reaction scheme and the level of the theory used in the calculation.[3,4,46] The same is the case with the experimental estimates which range from 21 kcal/mol[3] to 65 kcal/mol.[33]

Pauling and Wheland[12--14] used the concept of two Kekulé and three Dewar structures (also the two Kekulé valence structures only) for the benzene molecule to study aromaticity. They employed an approximate form of the VB method which was developed by Heitler and London[47] and the concept of quantum mechanical resonance, developed by Heisenberg[48--50] and later Pauling,[14] was used to measure the aromaticity. In this method the resonance energy arises as a result of the interaction between the structures which contribute to the ground state of a system, for example, the two VB structures for the benzene molecule which correspond to its two Kekulé valence structures. Pauling and Wheland[12--14] defined the resonance energy, which we call the Pauling Wheland resonance energy, as the energy difference between the energy of the multi-structure VB wave function and the energy of the most stable contributing structure in the same calculation. Since the resonance energy in this method arises automatically when two or more structures are involved in the VB wave function coupled with the presence of an intrinsic reference (the structure with the lowest energy in the wave function), a separate reference is not required. Thus the Pauling Wheland approach offers the opportunity to calculate the resonance energy directly as a difference between the total energy of the system and the energy of the most stable contributing structure in the same calculation.

In the *ab initio* form of the VB method the contributing structures are represented as multiples of singlet-coupled pairs of singly occupied orbitals as in Valence Bond Self Consistent Field (VBSCF) method[51--53] and Spin-Coupled VB (SCVB) method.[54--57] The latter method uses the Kotani's branching diagrams method[58] to construct the spin-coupling patterns but at the end of the calculation the spin functions can be transformed to Rumer basis[59] (singlet-coupled pairs of singly occupied orbitals).

A few years ago some of us calculated the resonance energy of benzene[60,61] and naphthalene[62] using the VBSCF approach with fully optimised p-orbitals, and pyrene[63] using a VBCI approach with benzene-optimised atomic p-orbitals. In the VBSCF results for the benzene molecule, it was found that the arbitrariness in the choice of the orbitals (restricted atomic p-orbitals, delocalised p-orbitals and different orbitals for different structures) greatly affects the resonance energy. The purpose of this work is to find whether there is a qualitative trend in the resonance energies of different cyclic conjugated systems, with different VB orbital models, i.e. restricted (local) and delocalised atomic p-orbitals. For this purpose we first treat the well rehearsed system, benzene, the archetypal aromatic compound and then extend the calculations to different (4n+2) and 4n π electrons polycyclic systems. The systems studied include both anthracene and phenanthrene and our VB results present the opportunity to elucidate the role of the π electrons resonance in their stability difference. At last, we quantify the empirical parameters for the resonance interactions between different (4n+2) and 4n conjugated circuits used in the Randić's π electron conjugated circuit theory[27--30] and Herdon's semi-emprical Valence Bond approach.[31,32] These parameters are scaled by the coefficients (weights) of the structures between which these interactions occur.

6.2 Method

6.2.1 Valence Bond Method: Theory

In the *ab initio* VBSCF[51--53] method a bond is described as a singlet-coupled pair of singly occupied orbitals, ϕ_1 and ϕ_2 centred on atom 1 and 2, respectively. Thus a bond is:

$$(\text{bond})_{12} = \mathcal{N}\{|\phi_1\overline{\phi_2}| - |\overline{\phi_1}\phi_2|\} \equiv (1-2) \tag{6.1}$$

where $\mathcal{N}$ is the normalisation constant. A VB structure for a system is defined as a product of all the bonds:

$$\Phi = \hat{\mathscr{A}}\{(core)(1-2)(3-4)(5-6)......((n-1)-n)\} \tag{6.2}$$

where $\hat{\mathscr{A}}$ is an anti-symmetriser and *core* represents the doubly occupied core orbitals. If the same set of orbitals is used to describe different structures of a system then these structures differ only in their spin functions, i.e., the spin coupling mode of the orbitals. An ionic structure can be defined with orbital ϕ_i occupied twice or alternatively with two singly occupied orbitals on the same atom that share the same space.[64] The VB wave function for a molecule is then constructed as a linear combination of these VB structures:

$$\Psi_0 = \sum_i c_i \Phi_i \tag{6.3}$$

In the VBSCF method, the orbitals and the structure coefficients are optimised to get the wave function which minimises energy expectation value. The relative importance of each structure in the wave function is determined by solving the generalised eigenvalue problem for the structure coefficients:

$$[\mathbf{H} - E\mathbf{S}]\mathbf{c} = 0 \tag{6.4}$$

Here **H** is the Hamiltonian matrix and **S** is the overlap matrix between the structures.

To each structure, a weight can be assigned according to the formula:[65]

$$W_i = \mathcal{N}|c_i|^2/(S^{-1})_{ii} \qquad ; \qquad \mathcal{N}^{-1} = \sum_j |c_j|^2/(S^{-1})_{jj} \tag{6.5}$$

where c_i represents the coefficient of structure i, S_{ii}^{-1} is the element of the inverse overlap matrix between the structures and $\mathcal{N}$ is the normalisation constant. The sum of the weights of all the structures in the VB wave function equals 1. The resonance energy of each system is calculated according to Pauling and Wheland's[12--14] definition as:

$$E_{resonance} = E - E_{struc} \tag{6.6}$$

where E is the energy of the VB wave function and E_{struc} is the energy of the structure which has the lowest energy in the wave function. When the E_{struc} is calculated from the Hamiltonian ($\mathbf{H}$) matrix of nonorthogonal structures the calculated resonance energy in Eq. (6.6) is called Pauling-Wheland resonance energy with nonorthogonal structures and we designate it as E_{res} (the abbreviations used for different types of resonance energies are given in Table 6.13). The $\mathbf{H}$ matrix can also be transformed to an orthogonal basis using Löwdin's symmetric orthogonalisation procedure.[66] In that case the structures are changed by changing the space of each structure while the total space remains the same. The energies of the contributing structures are, therefore, raised relative to the total energy of the system. After the orthogonalisation there is no overlap between the structures and these structures can be interpreted as as separate from each other as possible while maintaining the closest resemblance to the original nonorthogonal structures. In this case the use of Eq. (6.6) will give a more negative resonance energy than E_{res}. This resonance energy is called Pauling-Wheland resonance energy with orthogonal structures ($E_{res}^{\perp}$). In the orthogonal $\mathbf{H}$ matrix ($\mathbf{H}^{\perp}$) the total energy is partitioned into the weighted diagonal contribution ($\sum_i c_i^2 H_{ii}^{\perp}$) of the structures and the weighted off-diagonal or resonance contribution ($c_i c_j H_{ij}^{\perp}$) between them:[63]

$$E = \sum_i \sum_j c_i c_j H_{ij}^{\perp} = \sum_i c_i^2 H_{ii}^{\perp} + 2 \sum_{i<j} c_i c_j H_{ij}^{\perp} \tag{6.7}$$

The sum of the off-diagonal contributions is yet another measure of the resonance energy, called the total mean resonance energy ($E_{res}^{\perp m}$) of the system with respect to the weighted mean value of the energy of all structures. The $E_{res}^{\perp m}$ of a system can be equal to or even more negative than the $E_{res}^{\perp}$. If only two symmetrical structures are involved in the VB wave function, e.g., the two VB structures for the benzene molecule which correspond to its two Kekulé valence structures, the energies of the two structures and similarly the structure coefficients will be equal to each other, i.e., $H_{11} = H_{22}$ and $c_1 = c_2$. Eq. (6.7), in that case, becomes $E = H_{11} + H_{12}$ (since the structure coefficients are normalised so $2c_1^2 = 2c_2^2 = 1$) which means that the $E_{res}^{\perp}$ and the $E_{res}^{\perp m}$ will be the same. In other cases, i.e., where two nonsymmetrical or more than two structures are involved, the $E_{res}^{\perp m}$ will be more negative than

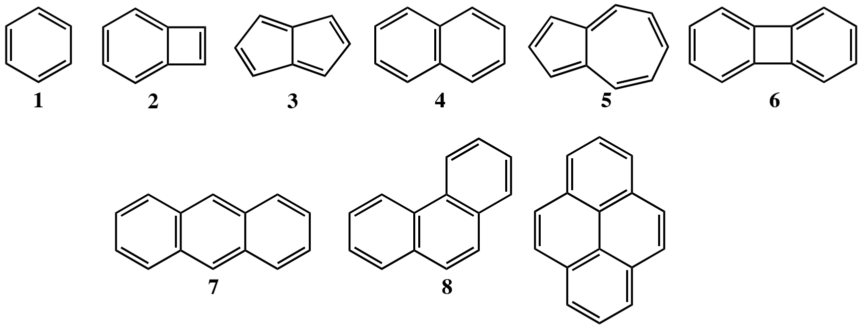

Figure 6.1: Selected systems for VBSCF study (only a single Kekulé valence structure of each system is shown). **1**- benzene (D_{6h}); **2**- benzocyclobutadiene (C_{2v}); **3**- pentalene (C_{2h}); **4**- naphthalene (D_{2h}); **5**- azulene (C_{2v}); **6**- biphenylene (D_{2h}); **7**- anthracene (D_{2h}); **8**- phenanthrene (C_{2v}); **9**- pyrene (D_{2h})

the $E^{\perp}_{res}$. The orthogonalised **H** matrix also enables the analysis of all resonance interactions between different contributing structures of a system. The most important contributions to the resonance energy, in terms of Clar's sextets[67,68] or π electrons conjugated circuits,[27–29] can thus be identified.

6.2.2 Computational Details

All calculations were performed using the 6-31G basis set.[69] The geometries of the compounds **1-9** in Figure 6.1 were optimised, within the given point group symmetry and without any other constraint, at RHF level using GAMESS-UK.[70] The geometries of compounds **1**, **3**, **4**, **7**, **8** and **9** at RHF/6-31G level are in good agreement with B3LYP/6-31G** optimised geometries.[71,72] Also it is expected that the geometry optimisation at higher levels of the theory would not change the Valence Bond picture of these systems. Hessian calculations confirmed that these geometries are genuine minima.

The *ab initio* VBSCF calculation were performed with TURTLE.[73] For each compound, the VB wave function was constructed by a linear combination of those VB structures which correspond to all the Kekulé valence structures of the system. From now on we will call these VB structures the Kekulé valence structures. The (doubly occupied) σ-orbitals were taken from a preceding RHF calculation and, as an initial guess, the π system was described by singly occupied atomic *p*-orbitals. In all the VB calculations, the σ-orbitals were orthogonal to each other and to the *p*-orbitals while the *p*-orbitals were nonorthogonal to each other. Both the *p*-orbitals and the structure coefficients were optimised while the doubly occupied σ-orbitals were frozen.

Two Valence Bond models were used in the orbital optimisation procedure. In the first model, each *p*-orbital is expanded only in the basis functions centred on the same atom and mixing with the basis functions on different atoms is not allowed. We call this model VB-local. The VB-local has an interpretational advantage and the spin-coupling modes (spin functions) can be directly related to the Lewis or the Kekulé valence structures. In the second model, each *p*-orbital is allowed to expand arbitrarily, i.e., its tail may lie on the neighbouring atoms or beyond and this model is called VB-delocal. In VB-local, since the atomic orbitals are not allowed to distort freely in a molecule, a large number of (physically untenable) ionic and long-bond (Dewar) structures are required to compensate for this restriction. However, the real interpretational advantage of VB is lost when all the covalent and ionic structures, for example, 170 ionic and 3 longer-bond structures for **1** or 19362 ionic and 39 longer-bond structures for **4**. We, therefore, considered only Kekulé valence structures in the wave function to compare it with the VB-delocal approach. The VB-delocal level gives an accurate description of cyclic conjugated hydrocarbons in their ground states with only Kekulé valence structures.[74,75]

It has been shown in the past[39] that the VB-delocal resonance energy of benzene (**1**) is practically insensitive to basis set size: both the 6-31G (66 AOs) and the aug-cc-pVQZ (954 AOs) basis set calculations give a resonance energy of 20 ± 0.5 kcal/mol at the VB-delocal level. This insensitivity of the VB-delocal resonance energy with respect to basis set is also expected for other related systems. This means that we can use the the modest 6-31G basis set for the VB calculations, which is computationally advantageous.

6.3 Results and Discussion

6.3.1 The Choice of the Orbitals and the Resonance Energy

The Kekulé valence structures of the molecules **1-9** (Figure 6.1) and their contribution in the VB wave function of each system are shown in Figure 6.2. The total energies of these systems at RHF, VB-local and VB-delocal level and the different resonance energies are presented in Table 6.1.

Before analysing the different resonance energies, we discuss the quality of the VB wave function in the VB-local and the VB-delocal models. In VB-local each *p*-orbital, though optimised, is restricted to remain an atomic *p*-orbital. Due to this restriction the energy of the (multi-determinant) VB wave function is higher than the energy of the (single determinant) Hartree-Fock wave function. Also the bonds (double bonds) described with these restricted *p*-orbitals are too weak in the contributing Kekulé valence structures and the energies of the individual structures remain high in the wave function. In VB-delocal the wave function is much better because the distortion of the orbitals towards the neighbouring atoms results in

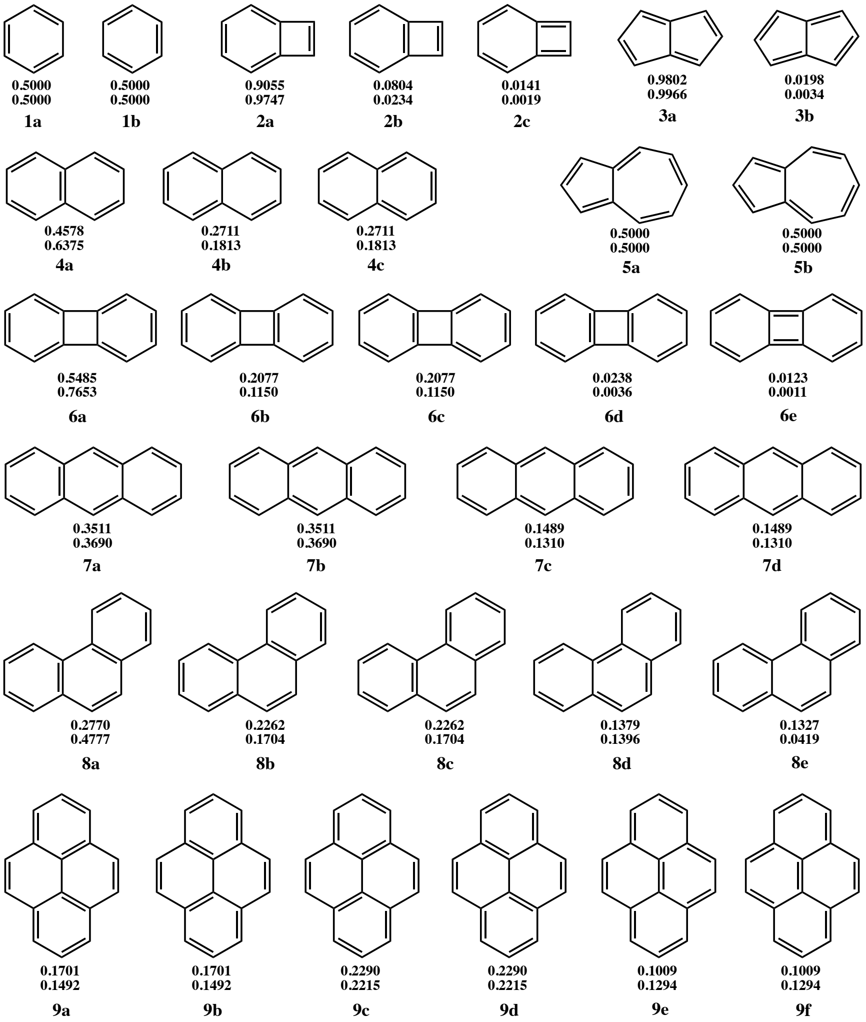

Figure 6.2: The Kekulé valence structures of the molecules **1-9** and their weights in the VB-local (upper value) and VB-delocal (lower value) wave function

an enhanced overlap between the orbitals (stronger bonds). The individual structures, thus, become more stable in VB-delocal compared to those in VB-local. The VB wave function also has a lower energy in VB-delocal than in VB-local (or Hartree-Fock) because of the increased interaction between the structures.

In the VB wave function with nonorthogonal structures, each structure also uses the the space of other structures both in VB-local and VB-delocal. Due to the enhanced overlap between the orbitals in VB-delocal, the overlap between the structures is also increased compared to that in VB-local. This increase in overlap between the structures decreases the energies of the contributing Kekulé structures relative to the total energy. In other words the

Table 6.1: Results of RHF and VBSCF calculations on the molecules **1-9** and their resonance energies (in kcal/mol)

System	Method	E (hartree)	E_{res}	$E^{\perp}_{res}$	$E^{\perp m}_{res}$
1 (benzene)	RHF	-230.624472	-	-	-
	VB-local	-230.540385	-27.74	-44.16	-44.16
	VB-delocal	-230.692578	-19.97	-60.79	-60.79
2 (benzocyclobutadiene)	RHF	-306.217848	-	-	-
	VB-local	-306.131381	-11.80	-26.77	-49.33
	VB-delocal	-306.323242	-4.26	-39.98	-69.46
3 (pentalene)	RHF	-306.229649	-	-	-
	VB-local	-306.159860	-1.77	-5.05	-9.58
	VB-delocal	-306.344285	-0.41	-6.85	-13.04
4 (napthalene)	RHF	-383.222722	-	-	-
	VB-local	-383.070614	-31.90	-61.38	-64.18
	VB-delocal	-383.336654	-13.41	-83.12	-96.36
5 (azulene)	RHF	-383.147289	-	-	-
	VB-local	-383.000007	-14.44	-16.23	-16.23
	VB-delocal	-383.262309	-19.70	-31.81	-31.81
6 (biphenylene)	RHF	-458.847135	-	-	-
	VB-local	-458.670739	-32.43	-62.63	-86.16
	VB-delocal	-458.986715	-14.37	-67.81	-103.93
7 (anthracene)	RHF	-535.812437	-	-	-
	VB-local	-535.595274	-42.26	-71.97	-75.49
	VB-delocal	-535.972929	-26.58	-101.34	-109.82
8 (phenanthrene)	RHF	-535.824583	-	-	-
	VB-local	-535.600939	-49.72	-92.73	-94.81
	VB-delocal	-535.981031	-21.05	-123.55	-140.21
9 (pyrene)	RHF	-611.555552	-	-	-
	VB-local	-611.286993	-62.34	-95.38	-100.87
	VB-delocal	-611.731359	-41.15	-134.18	-141.61

difference between the energy of the most stable Kekulé valence structure and the total energy of the system (i.e., the E_{res}) becomes smaller in VB-delocal compared to that in VB-local. The E_{res} of a system calculated with VB-delocal method is, therefore, generally smaller than that calculated with VB-local method. The E_{res} values at VB-delocal level are in excellent agreement with those reported by Cooper et al.[76–78] (-19.96 to -21.0 kcal/mol for **1** and -18.2 kcal/mol for **4**) with their SCVB approach.

When the structures are transformed to an orthogonal basis, the energies of the contributing Kekulé valence structures are raised and the difference between the total energy and the energy of the most stable Kekulé valence structure increases. The $E^{\perp}_{res}$ is, therefore, larger than the E_{res} both in VB-local and VB-delocal. The effect of the orbital delocalisation (VB-delocal)

Table 6.2: The energies (in hartree) of the Kekulé valence structures of **1-9**. The values in the parentheses are after the Löwdin orthogonalisation

System/Method	VB-local		VB-delocal	
1a, 1b	-230.496173	(-230.470018)	-230.660754	(-230.595707)
2a	-306.112587	(-306.088720)	-306.316451	(-306.259536)
2b	-306.036693	(-305.973298)	-306.206720	(-306.088287)
2c	-305.978477	(-305.922757)	-306.124709	(-306.032501)
3a	-306.157042	(-306.151812)	-306.343631	(-306.333363)
3b	-306.020070	(-306.012359)	-306.153677	(-306.132030)
4a	-383.019784	(-382.972802)	-383.315281	(-383.204187)
4b, 4c	-382.991394	(-382.964411)	-383.246728	(-383.161110)
5a, 5b	-382.976987	(-382.974136)	-383.230910	(-383.211612)
6a	-458.619061	(-458.570936)	-458.963775	(-458.878647)
6b, 6c	-458.576114	(-458.524568)	-458.890860	(-458.754201)
6d	-458.517839	(-458.430062)	-458.803825	(-458.597409)
6e	-458.484216	(-458.432553)	-458.724072	(-458.633006)
7a, 7b	-535.527934	(-535.480588)	-535.930574	(-535.811441)
7c, 7d	-535.488766	(-535.461820)	-535.853096	(-535.768051)
8a	-535.521701	(-535.452288)	-535.947492	(-535.819397)
8b, 8c	-535.504245	(-535.452818)	-535.892883	(-535.750870)
8d	-535.479787	(-535.453160)	-535.853078	(-535.747381)
8e	-535.485941	(-535.433868)	-535.844162	(-535.669941)
9a, 9b	-611.187644	(-611.117732)	-611.665779	(-611.496527)
9c, 9d	-611.186540	(-611.135020)	-611.658929	(-611.517535)
9e, 9f	-611.152670	(-611.125702)	-611.587155	(-611.499568)

on $E_{res}^{\perp}$ is opposite to that on E_{res}. While the E_{res} generally decreases in VB-delocal compared to that in VB-local, the $E_{res}^{\perp}$ increases. This is because the overlap between the structures (in the wave function with nonorthogonal structures) is larger in VB-delocal than in VB-local so orthogonalisation raises the energy of the contributing structures more in VB-delocal than in VB-local relative to the total energy at the same level. The $E_{res}^{\perp m}$ also shows the same trend, i.e., increases when going from VB-local to VB-delocal, because of the increased interactions between the contributing structures.

The E_{res} value of **5** (azulene) shows an opposite trend with delocal orbitals. The reason can be the charge separation in its π-system (calculated dipole moment (μ) at RHF/6-31G = 1.74 D, experimental[79,80] = 0.80−1.08 D) that cannot be adequately described using the VB-local model with only Kekulé valence structures (shown by the low dipole moment, μ calculated at VB-local with two structures is 0.30 D). So the energy of the wave function does not go as down as it would have been if a few ionic structures had been included. Consequently, the energy difference between the total energy and the energy of the single Kekulé valence structure (the E_{res}) is small. In VB-delocal the orbitals are allowed to distort freely and the effects of the ionic structures are automatically included in the space of the Kekulé valence structures. The interaction between the two Kekulé valence structures (the off-diagonal element of the H-matrix) is enhanced (μ at VB-delocal with two structures = 0.85 D) which lowers the total energy of the system and results in the large energy gap between the energy of the single Kekulé structure and the total energy, i.e., the E_{res} value.

The energies of the contributing structures (Table 6.2) in the VB wave function show that the Kekulé valence structures with the maximum number of 6π electron conjugated circuits have the lowest energy in VB-local when the structures are nonorthogonal. This is, however, not the case in VB-delocal or when the structures are transformed to an orthogonal basis in VB-local (see, for example, the energies of the contributing structures of **8** or **9**).

Analysis of the different contributions to the $E_{res}^{\perp m}$ (Tables 6.3 to 6.8) shows that those interactions which lead to the 6π electron conjugated circuits or the Clar's sextets are the most important contributors to the resonance energy. For **1** there is one 6π electron conjugated circuit and this is the only contribution to the $E_{res}^{\perp m}$. Its value increases from -44.16 kcal/mol in VB-local to -60.79 kcal/mol in VB-delocal (Table 6.1). For **2**, **4**, **6-9** the values of the contributions of the 6π electron conjugated circuits range from -9.62 (in **9**) to -30.03 kcal/mol (in **2**) at VB-local and -9.34 (in **6**) to -45.53 kcal/mol (in **2**) at VB-delocal level. The 10π electron conjugated circuits have a small contribution to the resonance energy in the range of 3 kcal/mol to 11 kcal/mol. Interestingly, the contributions of the 4π and the 8π electron circuits in **2** also fall in the range of that of the 10π electron circuits. Tables 6.3 to 6.8 show that the contributions of the different π electron conjugated circuits to the $E_{res}^{\perp m}$ are also dependent upon the choice of the orbitals. However, no clear trend is found in the values of these contributions while going from VB-local to VB-delocal.

The large difference in the contribution of the same type of conjugated circuits (especially the 6π electron conjugated circuits) in different systems can be related to the energy differences of the Kekulé valence structures of a system between which these interactions occur and their weights (the structure coefficients, Eq. (6.3)) in the VB wave function. For example, **1** has only two structures which contribute equally ($c_{1\mathrm{a}} = c_{1\mathrm{b}}$) to the wave function. The interaction between these structures involve resonance in the 6π electron conjugated circuit and the value obtained for the resonance contribution is equal to $H^{\perp}_{(1\mathrm{a},1\mathrm{b})}$ (since the wave function is normalised, the $2c_{1\mathrm{a}}c_{1\mathrm{b}}$ in the second term of Eq. (6.7) is equal to 1). In other cases where two nonsymmetrical or more than two structures are involved, the $2c_ic_j$ is smaller than 1 and the resonance contribution ($H^{\perp}_{ij}$) is scaled down by $2c_ic_j$.

The resonance energies per π electron ($E_{resonance}PE$) for these systems (Table 6.9) show that **1** has the largest values for the $E_{res}PE$, $E_{res}^{\perp}PE$ and $E_{res}^{\perp m}PE$ both at VB-local and VB-

Table 6.3: Contribution of different interactions to the $E_{res}^{\perp m}$ (in kcal/mol) for **2**

Structures	**2a**	**2b**	**2a**	**2b**
	VB-local		VB-delocal	
2b	-30.03		-45.53	
2c	-8.56	-10.73	-14.20	-9.73

Table 6.4: Contribution of different interactions to the $E_{res}^{\perp m}$ (in kcal/mol) for **4**

Structures	**4a**	**4b**	**4a**	**4b**
	VB-local		VB-delocal	
4b	-28.69		-42.41	
4c	-28.69	-6.79	-42.41	-11.54

Table 6.5: Contribution of different interactions to the $E_{res}^{\perp m}$ (in kcal/mol) for **6**

Structures	**6a**	**6b**	**6c**	**6d**
		VB-local		
6b	-27.09			
6c	-27.09	0.49		
6d	-0.03	-10.61	-10.61	
6e	-0.62	-3.18	-3.18	-4.23
		VB-delocal		
6b	-40.28			
6c	-40.28	0.97		
6d	-0.18	-9.34	-9.34	
6e	-0.67	-1.96	-1.96	-0.88

Table 6.6: Contribution of different interactions to the $E_{res}^{\perp m}$ (in kcal/mol) for **7**

Structures	**7a**	**7b**	**7c**
		VB-local	
7b	-26.64		
7c	-5.50	-18.28	
7d	-18.28	-5.50	-1.29
		VB-delocal	
7b	-33.63		
7c	-10.13	-26.00	
7d	-26.00	-10.13	-3.92

delocal levels and, hence, the most aromatic character. For **1**, **4** and **7** (linear benzenoids) the aromatic character decreases in the order **1** > **4** > **7** according to all resonance energies at the VB-local level. In VB-delocal, however, only the $E_{res}^{\perp}PE$ and the $E_{res}^{\perp m}PE$ show this trend.

Table 6.7: Contribution of different interactions to the $E_{res}^{\perp m}$ (in kcal/mol) for **8**

Structures	**8a**	**8b**	**8c**	**8d**
		VB-local		
8b	-20.97			
8c	-20.97	0.16		
8d	-13.70	-3.88	-3.88	
8e	0.03	-15.54	-15.54	-0.51
		VB-delocal		
8b	-34.42			
8c	-34.42	0.11		
8d	-22.98	-4.18	-4.18	
8e	-0.25	-14.14	-14.14	-0.30

Table 6.8: Contribution of different interactions to the $E_{res}^{\perp m}$ (in kcal/mol) for **9**

Structures	**9a**	**9b**	**9c**	**9d**	**9e**
			VB-local		
9b	-0.09				
9c	-16.97	-16.97			
9d	-16.97	-16.97	0.28		
9e	-9.62	-0.18	-3.15	-3.15	
9f	-0.18	-9.62	-3.15	-3.15	-0.94
			VB-delocal		
9b	-0.58				
9c	-22.01	-22.01			
9d	-22.01	-22.01	0.79		
9e	-13.40	-1.06	-5.79	-5.79	
9f	-1.06	-13.40	-5.79	-5.79	-1.69

The $E_{res}PE$ value for **2** is quite small, especially in VB-delocal. However, the $E_{res}^{\perp}PE$ and the $E_{res}^{\perp m}PE$ are reasonably high both at VB-local and VB-delocal levels. Previous spin-coupled results[81] suggested that **2** is a combination of a distorted benzene ring and an isolated double bond and is a nonaromatic system. The nucleus-independent chemical shift (NICS)[21,82] showed that the 6-membered ring is aromatic while the 4-membered ring is antiaromatic and an overall moderately antiaromatic character was assigned to this system. Based on the perpendicular component of magnetic shielding it was shown[83] that **2** is neither an aromatic nor an antiaromatic system. The 6-membered ring was classified as a nonaromatic while the question of the (anti)aromaticity of the 4-membered ring was left open. Our VBSCF results show that the resonance in the 6-membered ring is of the same magnitude as that in **4**. The $E_{resonance}PE$ shows that **2** is stabilised by resonance to some extent. We, there-

Table 6.9: Resonance energy (in kcal/mol) per π electron for **1-9**

	VB-local			VB-delocal		
System	$E_{res}PE$	$E^{\perp}_{res}PE$	$E^{\perp m}_{res}PE$	$E_{res}PE$	$E^{\perp}_{res}PE$	$E^{\perp m}_{res}PE$
1	-4.62	-7.36	-7.36	-3.33	-10.13	-10.13
2	-1.48	-3.35	-6.17	-0.53	-5.00	-8.68
3	-0.22	-0.63	-1.20	-0.05	-0.86	-1.63
4	-3.19	-6.14	-6.42	-1.34	-8.31	-9.64
5	-1.44	-1.62	-1.62	-1.97	-3.18	-3.18
6	-2.70	-5.22	-7.18	-1.20	-5.65	-8.66
7	-3.02	-5.14	-5.39	-1.90	-7.24	-7.84
8	-3.55	-6.62	-6.77	-1.50	-8.82	-10.02
9	-3.90	-5.96	-6.30	-2.57	-8.39	-8.85

fore, suggest that this system should be considered as nonaromatic if not slightly aromatic. For **3** a resonance energy of -15.79 kcal/mol was reported[84] with the VB-local approach in the D_{2h} geometry and including 4 radical-type structures. But the D_{2h} geometry is a transition state between the two symmetry-equivalent C_{2h} minima. In C_{2h} symmetry, the VB wave function of **3** is completely dominated by a single structure (structure **3a** in Figure 6.2) and results in negligible values for all types of $E_{resonance}PE$. The NICS values suggested that **6** is moderately aromatic[21,82] while **9** is aromatic,[63,85,86] whereas our VBSCF results show that both **6** and **9** have large $E_{resonance}PE$ (nearly of the same magnitude as that of **4**, **7** or **8**) and are as aromatic in nature as **4**, **7** or **8** are.

In VB-local the values for all the $E_{resonance}PE$ of **8** are larger than that of **7** but in VB-delocal the $E_{res}PE$ shows the opposite trend. This change is caused by the larger overlap of structure **8a** (the most stable contributing structure of **8**) with the other structures of **8** compared to the overlap of **7a** or **7b** with the other structures of **7**. As mentioned before, the overlap between the structures (the **S** matrix in Eq. (6.4)) lowers the energies of the contributing structures relative to the total energy of the system. We can calculate this overlap as $\sum_i^n c_i\langle\Phi_i|\Phi_1\rangle$ where $\langle\Phi_i|\Phi_1\rangle$ are elements of the **S** matrix and c_i is the coefficient of ith structure. For **8a** this overlap is 0.7625 in VB-local while it is 0.7683 in case of **7a** or **7b**. In VB-delocal it increases to 0.9328 in case of **8a** compared to 0.8987 in case of **7a** or **7b**. This larger overlap decreases the energy of **8a** compared to the energy of **7a** or **7b** in VB-delocal and results in smaller E_{res} and $E_{res}PE$ for **8** than that for **7**. When the structures are transformed to orthogonal basis the energy of **8a** again becomes higher than the energy of **7a** or **7b** in VB-delocal while the total energy of **8** is lower than that of **7**. Hence, the $E^{\perp}_{res}$ and the $E^{\perp}_{res}PE$ values for **8** again become larger than those for **7**.

Due to the use of strictly atomic orbitals, the VB-local approach is generally considered as providing a clear correspondence between the VB structures (spin-functions) and the Lewis or the Kekulé valence structures. In VB-delocal the orbitals are slightly distorted and have their tails on the neighbouring atoms or beyond. To see how much this distortion of the atomic orbitals change the VB picture of the structures in VB-delocal, we calculated the overlap between the orbitals obtained from VB-local and VB-delocal methods. It has been found that for each system the delocalised atomic orbitals have more than 96% overlap with the strictly atomic orbitals showing that the structures in VB-delocal remain essentially the same as that in VB-local.

6.3.2 Why is Phenanthrene More Stable than Anthracene?

It is well established that the kinked or bent polycyclic benzenoids are more stable than their linear or straight counter parts.[67,87] The case of anthracene and and phenanthrene (compounds 7 and **8**, respectively, in Figure 6.1) is an archetypal representative. Various experimental[88--91] and theoretical[30,92--97] studies have shown that **8** is 4-8 kcal/mol more stable than 7. The question why kinked benzenoids are more stable than linear ones is still a matter of discussion. Gutman and Stanković[98] have found that the greater stability of **8** over 7 is due to the presence of two (symmetry equivalent) disjoint 6π electrons conjugated circuits or Clar's sextets in the former. Bader and co-workers[99] have reported that the H—H bonding interaction in the bay region in **8** is responsible for its extra stability, compared to 7. This proposal of H—H bonding interaction has been challenged both theoretically[100--103] and experimentally[103] and it was shown that, in fact, the H—H interaction in the bay region of **8** is destabilising rather than bonding.

We present further evidence based on our VBSCF study on 7 and **8** that the extra stability of **8** is not due to the H—H interaction in the bay region instead it is a consequence of resonance. The VBSCF calculations on the single most stable structure of 7 (7**a** or 7**b** Figure 6.2) and **8** (**8a** Figure 6.2) were performed and the results are presented in Table 6.10. If there would be a H—H stabilising effect, it should be present in the single structure of **8** at both VB-local and VB-delocal level. In our VBSCF method the σ orbitals for both systems were taken from a preceding RHF and were frozen. So the H—H interaction if present is included in the core. The π system in both 7 and **8** is equally crude in VB-local (atomic *p*-orbitals). If it is assumed that the stability of **8** is due to the H—H bonding interaction, its single structure is expected to be more stable than that of 7. But this is not the case (see Table 6.10). On the other hand **8** is 3.55 kcal/mol more stable than 7 at VB-local level (see Table 6.1) which shows that it is resonance that makes **8** more stable than 7.

When the local restriction is removed from both systems, the single structure of **8** becomes more stable compared to that of 7 (Table 6.10) only by changes in its π electrons system. Note that the energy of the single structure of both systems is lower than the energy of the corresponding structures in the multi-structure wave function. This is because in the

Table 6.10: VBSCF energy (hartree) for the single Kekulé valence structure of 7 and **8**

Method/System	**7a/7b**	**8a**
VB-local	-535.527965	-535.521742
VB-delocal	-535.950550	-535.957943

single structure wave function the orbitals need to minimise the energy of one structure only instead of being a compromise to minimise the total energy at the expense of the energy of individual structures and the structure also uses the space of the other (missing) structures both in VB-local and VB-delocal. This latter effect (which is unavoidable in a single structure calculation) is less prominent in VB-local because the orbitals are not allowed to distort freely. However, in VB-delocal it is quite obvious where it is in favour of **8a** than 7**a** or 7**b** because of the symmetry of the former. Structure **8a** transforms as the totally symmetric representation of **8**, while for 7 only the combination 7**a** + 7**b** transforms as the totally symmetric representation. Therefore, **8a** can adapt the orbitals better than 7**a** or 7**b** to recover the effect of the missing structures although it cannot recover the whole effect of the resonance in the absence of other structures. So the energy of **8a** becomes more negative than that of 7**a** or 7**b** in VB-delocal. The same effect is also present in the multi-structure VB wave function that results in a smaller E_{res} for **8** than for 7. However, in the multi-structure wave function, we can transform the VB structures to orthogonal basis to avoid the overlap between them. After this transformation the energy of **8a** again becomes higher than the energy of 7**a** or 7**b** in VB-delocal (see Tables 6.1 and 6.2) while the total energy of **8** is still lower than that of 7 which again shows that the resonance is the factor which makes **8** more stable than 7.

A comparison of the different contributions to the resonance in both systems (Tables 6.6 and 6.7) shows that all interactions favour 7, except those which result from the resonance in the outer 6-membered rings of **8** and leads to the 6π electron conjugated circuits. The collective contribution of these 6π electron conjugated circuits in **8** dominates all other contributions which favour 7 and makes **8** more stable than 7. These results are in line with Gutman and Stanković's[98] findings. We conclude from these results that the extra stability of **8** over 7 is a consequence of resonance and/or delocalisation in the π-system and not because of the H—H bonding interaction in the bay region.

6.3.3 Resonance Interactions Between Different π Conjugated Circuits

The π electron conjugated circuits theory[27--29] has proven to be very useful in getting insight into aromaticity especially for the big systems which are far beyond the reach of *ab initio* VB methods. The same can be said about Herdon's semi-emprical VB method.[31,32] The Kekulé valence structures are central in both of these approaches and the interactions between these structures are determined empirically to agree with the delocalisation energies

Table 6.11: Values for the resonance interactions (kcal/mol) between different π electron conjugated circuits for **1**- **9**[†]

System/Method	VB-local		VB-delocal	
6 π				
1a ⟷ **1b**	-44.12	(3.93)	-60.74	(4.07)
2a ⟷ **2b**	-39.02	(1.17)	-60.84	(4.17)
4a ⟷ **4b**/**4c**	-40.67	(0.48)	-59.99	(3.32)
6a ⟷ **6b**/**6c**	-43.63	(3.44)	-62.36	(5.69)
6b/**6c** ⟷ **6d**	-38.93	(1.26)	-55.73	(0.94)
7a ⟷ **7b**	-38.03	(2.16)	-48.85	(7.82)
7a ⟷ **7d**, **7b** ⟷ **7c**	-39.91	(0.28)	-56.15	(0.52)
8a ⟷ **8b**/**8c**	-41.28	(1.09)	-59.79	(3.12)
8a ⟷ **8d**	-36.45	(3.74)	-51.88	(4.79)
8b/**8c** ⟷ **8e**	-43.05	(2.86)	-60.91	(4.24)
9a/**9b** ⟷ **9c**/**9d**	-40.78	(0.59)	-56.07	(0.60)
9a ⟷ **9e**, **9b** ⟷ **9f**	-36.46	(3.73)	-46.76	(9.91)
10 π				
4b ⟷ **4c**	-12.76	(0.24)	-23.56	(1.59)
5a ⟷ **5b**	-16.23	(3.23)	-31.81	(9.84)
7a ⟷ **7c**, **7b** ⟷ **7d**	-12.02	(0.98)	-21.87	(0.10)
8b/**8c** ⟷ **8d**	-12.12	(0.88)	-14.90	(7.07)
9c/**9d** ⟷ **9e**/**9f**	-11.86	(1.14)	-17.73	(4.24)
14 π				
7c ⟷ **7d**	-4.29	(1.18)	-12.58	(6.52)
8d ⟷ **8e**	-1.90	(1.21)	-1.67	(4.39)
9a ⟷ **9f**, **9b** ⟷ **9e**	-0.67	(2.44)	-2.66	(3.40)
9e ⟷ **9f**	-5.57	(2.46)	-7.34	(1.28)
4 π				
2b ⟷ **2c**	43.60	(2.98)	43.89	(12.11)
6d ⟷ **6e**	37.63	(2.98)	19.67	(12.11)
8 π				
2a ⟷ **2c**	18.58	(0.65)	32.07	(4.24)
3a ⟷ **3b**	21.62	(2.39)	30.21	(2.38)
6b, **6c** ⟷ **6e**	17.48	(1.75)	21.21	(6.62)
12 π				
6a ⟷ **6d**	-0.08	(0.70)	-0.58	(1.25)
6a ⟷ **6e**	2.42	(1.80)	3.90	(3.23)
6b ⟷ **6c**	1.12	(0.50)	2.79	(2.12)
8a ⟷ **8e**	0.06	(0.56)	-0.67	(1.34)
8b ⟷ **8c**	0.38	(0.24)	0.30	(0.37)
9a ⟷ **9b**	-0.21	(0.83)	-2.31	(2.98)
9c ⟷ **9d**	0.68	(0.06)	1.28	(0.61)

[†] Values in parentheses are the absolute deviations from the corresponding mean values.

Table 6.12: Mean values for the resonance interactions (kcal/mol) between different π electron conjugated circuits

Circuit/Method	VB-local	VB-delocal
6 π	-40.19	-56.67
10 π	-13.00	-21.97
14 π	-3.11	-6.06
4 π	40.62	31.78
8 π	19.23	27.83
12 π	0.62	0.67

derived from the Molecular Orbital Theory-based calculations in the former case and the spectroscopic data in the latter case. The resonance energy and the resonance energy per π electron, calculated by Jiang and Li[104] with their VB approach, have also been used[29] to determine these parameters. However, the parameters derived from these VB results show that the interaction between 14 π electron conjugated circuits is more important than that of 10 π electron conjugated circuits which is counterintuitive.

In the *ab initio* VBSCF method, the resonance (off-diagonal) interactions between the structures, i.e., $\langle \Phi_i | \mathscr{H} | \Phi_j \rangle$ (short $\Phi_a \longleftrightarrow \Phi_b$), in the orthogonalised **H** matrix give a direct measure of these resonance parameters. The values obtained for these interactions in **1-9** and the mean values for each type of interaction (conjugated circuit) are collected, respectively, in Tables 6.11 and 6.12. The mean values show that the interactions in the (4n+2) π electron conjugated circuits have a negative (stabilising) contribution while that in 4n π electron conjugated circuits have a positive (destabilising) contribution. These negative and the positive contributions of, respectively, (4n+2) and 4n π electron conjugated circuits decrease with increasing value of n. Table 6.12 also shows that these values for all interactions are dependent upon the choice of the orbitals and, except for the 4π electron conjugated circuit, increase in VB-delocal compared to those in VB-local. Also these values are substantially higher than those chosen in the Refs. 27--29, 31, 32.

6.4 Conclusion

The resonance energy is a nonobservable property and its calculated value for any system depends upon the underlying method and its definition. Two types of *p*-orbital models (VB-local and VB-delocal) have been used within the framework of the VBSCF method to see their effect on the calculated Pauling-Wheland resonance energies and the total mean resonance energies of cyclic conjugated systems. In VB-local method the variational space of the *p*-orbitals is restricted which has an interpretational advantage but the quality of the VB wave function is not so good. In VB-delocal the wave function is much better due to the distortion of the atomic *p*-orbitals which results in enhanced overlap between the orbitals. It has been found that the choice of these two types of orbitals has a profound effect on the calculated resonance energies and their qualitative trend.

When the contributing structures are nonorthogonal to each other (as in the original Pauling-Wheland definition of the resonance energy), each structure also uses the space of the other structures which are present in the wave function. This overlap increases in VB-delocal compared to that in VB-local. The E_{res} calculated with VB-delocal method is, therefore, generally smaller than that obtained from VB-local for each system studied here, except for compound **5** (azulene).

On transforming the VB wave function to orthogonal basis, the contributing structures are changed and gain some positive energy. In this case the use of the Pauling Wheland definition results in large $E_{res}^{\perp}$ compared to the E_{res} at the corresponding VB-local or VB-delocal level. As the overlap between the contributing structures is larger in the VB-delocal than in the VB-local, orthogonalisation raises the energy of the structures more in the VB-delocal than in the VB-local relative to the total energy at the same level. This results in larger $E_{res}^{\perp}$ in VB-delocal than in VB-local. The same trend is also found for the $E_{res}^{\perp m}$ with the two choices of the *p*-orbitals.

For structural isomers, in general, non of the three different resonance energies are in accordance with the order in their total energies in any of VB-local or VB-delocal method. For structural isomers of benzenoids only, however, the $E_{res}^{\perp}$ and the $E_{res}^{\perp m}$ values are in the same order as their total energies.

The resonance energy in cyclic conjugated systems is a ground state property and the VB-delocal method is much better for calculating the ground states of these systems compared to the VB-local method. It is, therefore, concluded here that the resonance energies calculated using the VB-delocal method are more reliable than those calculated with VB-local method. Although the wave function in the VB-delocal method includes the effect of the ionic and the long-bond (Dewar) structures, the orbitals still remain predominantly atomic orbitals as they have more than 96% overlap with the strictly atomic orbitals in VB-local in all cases studied here thus retaining essentially the same correspondence between the VB spin-functions and the intuitive Lewis or Kekué valence structures as in VB-local. Among the three definitions of the resonance energy, the $E_{res}^{\perp}$ and the $E_{res}^{\perp m}$ (which are close to each other and show similar trends) are more reliable than the E_{res} because the use of nonorthogonal structures in the latter case can create ambiguities in the estimates of the resonance energy.

Table 6.13: List of Abbreviations

E	Total energy of the system
E_{res}	Pauling Wheland resonance energy with nonorthogonal structures
$E_{res}^{\perp}$	Pauling Wheland resonance energy with Löwdin-orthogonalised structures
$E_{res}^{\perp m}$	Total mean resonance energy with Löwdin-orthogonalised structures
$E_{resonance}PE$	Resonance energy per π electron
$E_{res}PE$	Pauling Wheland resonance energy per π electron with nonorthogonal structures
$E_{res}^{\perp}PE$	Pauling Wheland resonance energy per π electron with Löwdin-orthogonalised structures
$E_{res}^{\perp m}PE$	Total mean resonance energy per π electron with Löwdin-orthogonalised structures

References

1. Garratt, P. J. *Aromaticity*; McGraw-Hill: London, New York, **1971**.
2. Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; John Wiley & Sons: New York, **1994**.
3. Krygowski, T. M.; Cyrański, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783--1796.
4. Krygowski, T. M.; Cyrański, M. K. *Chem. Rev.* **2001**, *101*, 1385--1419.
5. Cremer, D. *Tetrahedron* **1988**, *44*, 7427--7454.
6. Schleyer, P. v. R.; Jiao, H. *Pure & Appl. Chem.* **1996**, *68*, 209--218.
7. Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132--136.
8. Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442--447.
9. Hückel, E. *Z. Physik* **1931**, *70*, 204--286.
10. Hückel, E. *Z. Physik* **1931**, *72*, 310--337.
11. Hückel, E. *Z. Physik* **1932**, *76*, 628--648.
12. Pauling, L.; Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 362--374.
13. Wheland, G. W. *The theory of resonance and its application to organic chemistry*; John Wiley & Sons: New York, **1953**.
14. Pauling, L. *The Nature of the chemical Bond*; Cornell University Press: London, **1960**.
15. Pauling, L.; Sherman, J. *J. Chem. Phys.* **1933**, *1*, 606--617.
16. Kistiakowski, B.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 146--153.
17. Bird, C. W. *Tetrahedron* **1985**, *41*, 1409--1414.
18. Bird, C. W. *Tetrahedron* **1986**, *42*, 89--92.
19. London, F. *J. Phys. Radium* **1937**, *8*, 397--409.
20. Pople, J. *J. Chem. Phys.* **1956**, *24*, 1111.

21. Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317--6318.
22. Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789--795.
23. Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305--310.
24. Gutman, I.; Milun, M.; Trinajstic, N. *Match* **1975**, *1*, 171--175.
25. Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692--1704.
26. Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750--2758.
27. Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 68--70.
28. Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444--450.
29. Randić, M. *Tetrahedron* **1977**, *33*, 1905--1920.
30. Randić, M. *Chem. Rev.* **2003**, *103*, 3449--3606.
31. Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404--2406.
32. Herndon, W. C.; Ellzey, M. L. *J. Am. Chem. Soc.* **1974**, *96*, 6631--6642.
33. Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687--1697.
34. Mo, Y. *J. Chem. Phys.* **2003**, *119*, 1300--1306.
35. Mo, Y. *J. Org. Chem.* **2004**, *69*, 5563--5567.
36. Mo, Y. *J. Phys. Chem. A* **2009**, *113*, 5163--5169.
37. Mo, Y.; Hiberty, P. C.; Schleyer, P. v. R. *Theor. Chem. Acc. (Theoretica Chimica Acta)* **2010**, *127*, 27--38.
38. Mo, Y.; Schleyer, P. v. R. *Chem. Eur. J.* **2006**, *12*, 2009--2020.
39. Zielinski, M. L.; van Lenthe, J. H.; Havenith, R. W. A.; Jenneskens, L. W. *Theor. Chem. Acc. (Theoretica Chimica Acta)* **2010**, *127*, 19--25.
40. Truhlar, D. G. *J. Chem. Educ.* **2007**, *84*, 781--782.
41. Hess, B. A., Jr.; Schaad, L. J. *Chem. Rev.* **2001**, *101*, 1465--1476.
42. Hehre, W. J.; Ditchfield, D.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796--4801.
43. Hehre, W. J.; Taylor, R. T.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7162--7163.
44. Radom, L. *J. Chem. Soc., Chem. Commun.* **1974**, 403--404.
45. George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans.* **1977**, *2*, 1036--1047.
46. Cyrański, M. K. *Chem. Rev.* **2005**, *105*, 3773--3811.
47. Heitler, W.; London, F. *Z. Physik* **1927**, *44*, 455--472.
48. Heisenberg, W. *Z. Physik* **1926**, *38*, 411--426.
49. Heisenberg, W. *Z. Physik* **1926**, *39*, 499--518.
50. Heisenberg, W. *Z. Physik* **1927**, *41*, 239--267.

51. van Lenthe, J. H.; Balint-Kurti, G. G. *Chem. Phys. Lett.* **1980**, *76*, 138--142.
52. van Lenthe, J. H.; Balint-Kurti, G. G. *J. Chem. Phys.* **1983**, *78*, 5699--5713.
53. van Lenthe, J. H.; Dijkstra, F.; Havenith, R. W. A. TURTLE - A gradient VBSCF Program Theory and Studies of Aromaticity. In *Theoretical and Computational Chemistry: Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10, pp 79--116.
54. Gerratt, J. General Theory of Spin-Coupled Wave Functions for Atoms and Molecules. In *Advances in Atomic and Molecular Physics*; Bates, D., Esterman, I., Eds.; Academic Press, **1971**; Vol. 7, pp 141--221.
55. Gerratt, J.; Raimondi, M. *Proc. R. Soc.* **1980**, *A371*, 525--552.
56. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Farady Symp. Chem. Soc.* **1984**, *19*, 149--163.
57. Cooper, D. L.; Gerratt, J.; Raimondi, M. Modern Valence Bond Theory. In *Advances in Chemical Physics: Ab intio Methods in Quantum Chemistry -II*; Lawley, K. P., Ed.; John Wiley & Sons: London, **1987**; Vol. LXIX, pp 319--397.
58. Kotani, M.; Amemiya, A.; Ishiguro, E.; Kimura, T. *Tables of molecular integrals*, 2nd ed.; Maruzen Co.: Tokyo, **1963**.
59. Rumer, G. *Nachr. ges. Wiss. Gött. Math. Phys.* **1932**, 337--341.
60. van Lenthe, J. H.; Havenith, R. W. A.; Dijkstra, F.; Jenneskens, L. W. *Chem. Phys. Lett.* **2002**, *361*, 203--208.
61. Dijkstra, F.; van Lenthe, J. H.; Havenith, R. W. A.; Jenneskens, L. W. *Int. J. Quantum Chem.* **2003**, *91*, 566--574.
62. Havenith, R. W. A.; van Lenthe, J. H.; Jenneskens, L. W. *J. Org. Chem.* **2005**, *70*, 4484--4489.
63. Havenith, R. W. A.; van Lenthe, J. H.; Dijkstra, F.; Jenneskens, L. W. *J. Phys. Chem. A.* **2001**, *105*, 3838--3845.
64. Hiberty, P. C.; Humbel, S.; Byrman, C. P.; van Lenthe, J. H. *J. Chem. Phys.* **1994**, *101*, 5969--5976.
65. Gallup, G. A.; Norbeck, J. M. *Chem. Phys. Lett.* **1973**, *21*, 495--500.
66. Löwdin, P. O. *Rev. Mod. Phys.* **1967**, *39*, 259--287.
67. Clar, E. *The Aromatic Sextet*; J. Wiley & Sons: London, **1972**.
68. Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, **1964**; Vol. 1-- 2.
69. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257--2261.
70. Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J. *Mol. Phys.* **2005**, *103*, 719--747.
71. Havenith, R. W. A.; Jenneskens, L. W.; Fowler, P. W.; Steiner, E. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2033--2039.

72. Ciesielski, A.; Krygowski, T. M.; Cyrański, M. K.; Dobrowolski, M. A.; Balaban, A. T. *J. Chem. Inf. Model.* **2009**, *49*, 369--376.
73. Verbeek, J.; Langenberg, J. H.; Byrman, C. P.; Dijkstra, F.; Havenith, R. W. A.; Engelberts, J. J.; Zielinski, M. L.; Rashid, Z.; van Lenthe, J. H. **1988--2012**, TURTLE an *ab initio* VB/VBSCF Program, Theoretical Chemistry Group, Utrecht University, Utrecht.
74. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Nature* **1986**, *323*, 699--701.
75. Rashid, Z.; van Lenthe, J. H. *J. Comput. Chem.* **2011**, *32*, 696--708.
76. Cooper, D. L.; Gerratt, J.; Raimondi, M. The Spin-coupled Valence Bond Description of Benzenoid Aromatic Molecules. In *Topics in Current Chemistry: Advances in the Theory of Benzenoid Hydrocarbons*; Gutman, I., Cyvin, S. J., Eds.; Springer-Verlag: Berlin, **1990**; Vol. 153, pp 41--55.
77. Sironi, M.; Cooper, D. L.; Gerratt, J.; Raimondi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 675--677.
78. Cooper, D. L.; Gerratt, J.; Raimondi, M. The Spin-coupled Description of Aromatic, Antiaromatic and Nonaromatic Systems. In *Pauling's Legacy: Modern Modelling of the Chemical Bond; Theoretical and Computational Chemistry*; Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, **1999**; Vol. 6, pp 503--518.
79. Toblek, H. J.; Bauder, A.; Günthard, H. H. *J. Mol. Spectrosc.* **1965**, *18*, 239--246.
80. Anderson, A. G., Jr.; Steckler, B. M. *J. Am. Chem. Soc.* **1959**, *81*, 4941--4946.
81. Karadakov, P. B.; ; Gerratt, J.; Cooper, D. L.; Raimondi, M.; Sironi, M. *Int. J. Quantum Chem.* **1996**, *60*, 545--552.
82. Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075--7083.
83. Jensen, M. Ø.; Thorsteinsson, T.; Hansen, A. E. *Int. J. Quantum Chem.* **2002**, *90*, 616--628.
84. Havenith, R. W. A.; Engelberts, J. J.; Fowler, P. W.; Steiner, E.; van Lenthe, J. H.; Lazzeretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 289-- 294.
85. Havenith, R. W. A.; Jiao, H.; Jenneskens, L. W.; van Lenthe, J. H.; Sarobe, M.; Schleyer, P. v. R.; Kataoka, M.; Necula, A.; Scott, L. T. *J. Am. Chem. Soc.* **2002**, *124*, 2363--2370.
86. Güell, M.; Poater, J.; Luis, J. M.; Mó, O.; Yáñez, M.; Solà, M. *ChemPhysChem* **2005**, *6*, 2552--2561.
87. Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, **1989**.
88. Colemaann, D. J.; Pilche, D. G. *Trans. Faraday Soc.* **1966**, *62*, 821--827.

89. Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163--3173.
90. Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3173--3181.
91. Dabestani, R.; Ivanov, I. N. *Photochem. Photobiol.* **1999**, *70*, 10--34.
92. Kato, T.; Yoshizawa, K.; Hirao, K. *J. Chem. Phys.* **2002**, *116*, 3420--3429.
93. Balaban, A. T. *Pure & Appl. Chem.* **1980**, *52*, 1409--1429.
94. Behrens, S.; Köster, A. M.; Jug, K. *J. Org. Chem.* **1994**, *59*, 2546--2551.
95. Moyano, A.; Paniagua, J. C. *J. Org. Chem.* **1991**, *56*, 1858--1866.
96. Moyano, A.; Paniagua, J. C. *Trends Org. Chem.* **1993**, *4*, 697--740.
97. Fukui, K. *Science* **1982**, *218*, 747--754.
98. Gutman, I.; Stanković, S. *Maced. J. Chem. Chem. Eng.* **2007**, *26*, 111--114.
99. Matta, C. F.; Hernández-Trujillo, J.; Tang, T.; Bader, R. F. W. *Chem. Eur. J.* **2003**, *9*, 1940--1951.
100. Poater, J.; Visser, R.; Solà, M.; Bickelhaupt, F. M. *J. Org. Chem.* **2007**, *72*, 1134--1142.
101. Poater, J.; Solà, M.; Bickelhaupt, F. M. *Chem. Eur. J.* **2006**, *12*, 2902--2905.
102. Poater, J.; Bickelhaupt, F. M.; Solà, M. *J. Phys. Chem. A* **2007**, *111*, 5063--5070.
103. Grimme, S.; Mück-Lichtenfeld, C.; Erker, G.; Kehr, G.; Wang, H.; Beckers, H.; Willner, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 2592--2595.
104. Jiang, Y.; Li, S. Valence Bond Calculations and Their Applications to Medium-Sized Conjugated Hydrocarbons. In *Theoretical and Computational Chemistry: Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, **2002**; Vol. 10, pp 565--602.

SUMMARY

The aim of this research has been to extend the *ab initio* Valence Bond Self-Consistent Field (VBSCF) methodology and to apply this method to the electronic structure of molecules. The valence bond method directly deals with the chemical structure of molecules in a pictorial language, which chemists are familiar with. One of the problems in this case is the manual generation of the structures where the spin-coupling patterns of the electrons correspond to the classical (Kekulé valence) structures for polycyclic conjugated systems, which is cumbersome because the number of such structures grows very rapidly with the size of the system. To solve this problem, a procedure has been developed which can generate these structures automatically using the geometry (i.e., the coordinates of the atoms) of the molecules. The efficiency of the method has been tested by generation of Kekulé valence structures for selected cases of small as well as giant conjugated systems and it has been shown that the procedure is computationally very efficient and economical (both in memory and time). For cyclic conjugated systems it has also been shown that the consideration of only Kekulé valence structures in the VB wave functions already gives an excellent description of their electronic structure.

Another methodological improvement that has been made in this work is on improving the convergence of the VBSCF wave function. Second-order converging SCF techniques for the optimisation of orthogonal orbitals have made excellent progress in the past few decades, however, not for the optimisation of non-orthogonal orbitals. A second-order converging VBSCF method has been developed in this thesis based on a Newton-Raphson scheme. The convergence of the method has been analysed using two optimisation models, i.e., a restricted optimisation (VB-local) and a full optimisation without any restriction (VB-delocal). The new method shows excellent convergence when the singly occupied orbitals do not mix with each other, which is usually the case in VB-local. When good starting orbitals are available in VB-delocal, the same convergence behaviour has been found in the full optimisation. The convergence efficiency of the method has been compared with the Super-CI method. Finally, a combination of Super-CI and Newton-Raphson methods has been shown to be computationally more efficient than either the Super-CI or the Newton-Raphson method alone, in particular for the initial guess orbitals which are far from convergence. In the combined method the first few iterations are performed with Super-CI until reasonably small orbital gradients or correction vectors, and then the final iterations are performed using the Newton-Raphson method.

Next, the efficiency of two quite different orbital optimisation algorithms in VBSCF methods has been analysed in detail. One of these algorithms is based on an approximate Newton-Raphson (aNR)

method, where the Hessian matrix is approximated by a diagonal matrix to reduce the computational effort. The second algorithm uses a Fock matrix for the orbital optimisation. It has been found that the Fock matrix method is slightly more expensive than the aNR method, although the former does not involve a 4-index transformation of the integrals from atomic orbital to VB orbital basis. This is caused by the fact that the calculation of the matrix elements is often more expensive than the 4-index transformation.

In the last chapter, the VBSCF method has been applied to calculate the resonance energies of some small as well as reasonably large cyclic conjugated molecules using the VB-local and VB-delocal methods. The resonance energy of cyclic conjugated systems is considered as an important measure of their aromaticity. The effect of the choice of the orbitals on the calculated resonance energies has been explored. It has been shown that resonance energies calculated with the VB-delocal method are more reliable than those obtained from the VB-local method. Furthermore, the results for phenanthrene and anthracene show that the extra stability of the kinked or bent benzenoid systems over their linear counterparts is a result of the larger resonance energies in the bent benzenoids. At last, the empirical parameters used in other semi-empirical VB methods and conjugated circuit theory have been quantified with the results of the VBSCF calculations on cyclic conjugated molecules.

SAMENVATTING

Het doel van dit onderzoek was het verbeteren van de *ab initio* Valence Bond Self-Consistent Field (VBSCF) methodologie en de toepassing van de methode op de elektronen structuur van moleculen. De Valence Bond methode heeft rechtstreeks te maken met de chemische structuur van moleculen in een taal die scheikundigen begrijpen. Een van de eerste problemen die is opgepakt, is het handmatig genereren van structuren waarbij de spin koppeling patronen corresponderen met de klassieke (Kekulé valentie) structuren van polycyclische geconjugeerde systemen. Om dit probleem op te oplossen is een procedure ontwikkeld die deze structuren automatisch kan genereren met als invoer de geometrie van de moleculen (nl. de coördinaten van de atomen). De efficiëntie van deze methode is getest door middel van het genereren van Kekulé valentie structuren voor een select aantal gevallen van zowel kleine als zeer grote geconjugeerde systemen en het is aangetoond dat deze procedure computationeel zeer efficiënt en economisch is (zowel in het geheugen als tijd). Tevens bleek de beschouwing van alleen de Kekulé valentie structuren in de VB golffunctie voor polycyclische geconjugeerde systemen een uitstekende beschrijving te geven van de elektronen structuur.

Een andere methodologische verbetering die aangebracht is in dit werk gaat over het verbeteren van de convergentie van VBSCF golffuncties. In de laatste decennia is veel vooruitgang geboekt bij de verbetering van tweede orde convergerende SCF technieken voor de optimalisatie van orthogonale orbitals, echter niet voor de optimalisatie van niet-orthogonale orbitals. In dit proefschrift is de ontwikkeling beschreven van een tweede orde convergerende VBSCF methode, gebaseerd op een Newton-Raphson schema. De convergentie van de methode wordt geanalyseerd met gebruikmaking van twee optimalisatie modellen, nl. een beperkte optimalisatie (VB lokaal) en een volledige optimalisatie zonder beperkingen (VB de-lokaal). De nieuwe methode toont uitstekende convergentie als de enkel bezette orbitals niet met elkaar mengen, zoals bij VB lokaal het geval is. Als er goede start orbitals beschikbaar zijn in VB de-lokaal, wordt hetzelfde convergentiegedrag gevonden bij volledige optimalisatie. De efficiëntie van de methode wordt besproken in vergelijking tot de Super-CI methode. Tenslotte wordt aangetoond dat een combinatie van de methoden, d.w.z. Super-CI en Newton-Raphson, computertechnisch efficiënter is dan alleen Newton-Raphson.

In het volgende hoofdstuk wordt de efficiëntie van twee totaal verschillende orbital optimalisatie algoritmen in VBSCF methoden gedetailleerd geanalyseerd. Een van deze algoritmen is gebaseerd op de benaderde Newton-Raphson (aNR) methode, waarbij de Hessian matrix wordt benaderd middels een diagonale matrix om de rekentijd te beperken. Het tweede algoritme maakt gebruik van een Fock matrix voor de orbital optimalisatie. De Fock matrix methode bleek enigszins duurder te zijn dan de aNR methode, hoewel er bij de eerste geen 4-index transformatie van atomaire orbitals naar VB orbitals vereist is. De reden is dat de berekening van matrix elementen vaak duurder is dan de 4-index transformatie.

In het laatste hoofdstuk, is de VBSCF methode gebruikt om de resonantie energie van zowel enkele kleine als van redelijk grote systemen te berekenen, met gebruikmaking van de VB lokaal en de VB de-lokale methoden. Het effect van de keuze van de orbitals op de berekende resonantie energie werd onderzocht. De resonantie energie van polycyclisch geconjugeerde systemen wordt als een belangrijke maatstaf voor hun aromaticiteit beschouwd. Aangetoond wordt dat de resonantie energieën berekend met de VB de-lokaal methode betrouwbaarder zijn, dan die verkregen met de VB lokaal methode. Bovendien bleek uit de resultaten voor fenantreen en antraceen dat de extra stabiliteit van de geknikte of gebogen benzenoide systemen ten opzichte van hun lineaire tegenhangers een gevolg is van de grotere resonantie-energie in de gebogen benzenoids. Uiteindelijk konden de empirische parameters die bij andere semi-empirische VB methoden gebruikt worden gekwantificeerd worden met de resultaten van de hier verrichtte VBSCF berekeningen aan cyclische geconjugeerde moleculen.

خلاصہ

اس تحقیق کا مقصد اَیب اِنشِیو ویلنس بانڈ سیلف کنسیسٹنٹ فیلڈ (وی بی ایس سی ایف) طریقہ کار کی مزید بہتری اور اس طریقہ کار کا اطلاق مالیکیولوں کی الیکٹرانی ساخت پر کرنا ہے۔ ویلنس بانڈ طریقہ کار مالیکیولوں کی الیکٹرانی ساخت کو براہ راست ایسی تصویری شکل میں بیان کرتا ہے جس سے کیمیادان آشنا ہیں۔ اس سلسلے میں پہلا درپیش مسئلہ کثیر دائروی کانجوگیٹڈ مالیکیولوں کی دستی طریقے سے ایسی ساختیں تشکیل دینا ہے جن میں الیکٹرانوں کے جوڑے گئے اَسپِن اِن مالیکیولوں کی کلاسیکی کیکلے ویلنس ساختوں سے مطابقت رکھتے ہوں، جو کہ ایک ثقیل عمل ہے کیونکہ ایسی ساختوں کی تعداد مالیکیولوں کی جسامت کے ساتھ بڑی تیزی سے بڑھتی ہے۔ اس مسئلے کے حل کے لیے ایک ایسا طریقہ کار وضع کیا گیا ہے جو مالیکیولوں کی جومیٹری (یعنی ایٹموں کے محددات) استعمال کرتے ہوئے یہ ساختیں خودکار بنا دیتا ہے۔ کچھ منتخب شدہ نسبتاً چھوٹے اور خاصے بڑے کانجوگیٹڈ مالیکیولی نظاموں کی کیکلے ویلنس ساختیں بنا کر اس طریقے کی کارکردگی جانچی گئی ہے اور یہ واضح کیا گیا ہے کہ یہ طریقہ کمپیوٹر کی میموری اور حسابی تگ ودو کے لحاظ سے انتہائی مکفی ہے۔ یہ بھی واضح کیا گیا ہے کہ صرف کیکلے ویلنس ساختیں ویلنس بانڈ کے موجی تفاعل میں استعمال کرنے سے دائروی کانجوگیٹڈ مالیکیولوں کی الیکٹرانی ساخت کی بڑے عمدہ طریقے سے وضاحت ہو جاتی ہے۔

ایسی ہی ایک اور بہتری وی بی ایس سی ایف موجی تفاعل کے تقاربی عمل کو بہتر بنانے کے لیے کی گئی ہے۔ آرتھوگونل مدارچوں کو مستحسن بنانے کے لیے ثانوی درجہ کا تقارب رکھنے والی ایس سی ایف تکنیکوں نے پچھلے چند عشروں میں خوب ترقّی کی ہے، تاہم نان آرتھوگونل مدارچوں کو مستحسن بنانے کے لیے ایسا نہیں ہو سکا۔ اس مقالے میں ثانوی درجے کا تقارب رکھنے والا وی بی ایس سی ایف طریقہ وضع کیا گیا ہے جس کی بنیاد نیوٹن-رافسن طریقے پر ہے۔ اس نئے طریقے کی کارکردگی کا تجزیہ مدارچوں کو مستحسن بنانے کے دو نمونے استعمال کرتے ہوئے کیا گیا ہے، پہلے نمونے میں مدارچوں کو ان کے اپنے ایٹموں پر مقید رکھا جاتا ہے، اسے وی بی-لوکل نمونہ کہتے ہیں جبکہ دوسرے نمونے میں اس طرح کی کوئی قید نہیں ہوتی اور اسے وی بی-ڈی لوکل نمونہ کہتے ہیں۔ جب ایک الیکٹران رکھنے والے مدارچے آپس میں مدغم نہ ہوں، جیسا کہ عموماً وی بی-لوکل نمونے میں ہوتا ہے، تو نیا طریقہ بہت اعلیٰ تقارب دکھاتا ہے۔ اگر اچھے ابتدائی مدارچے میّسر ہوں تو اسی طرح کا تقاربی رویّہ وی بی-ڈی لوکل طریقے میں بھی پایا گیا ہے۔ نئے طریقے اور سپر کنفگریشن انٹر ایکشن کی تقاربی کارکردگی کا موازنہ کیا گیا ہے۔ آخر میں یہ واضح کیا گیا ہے کہ کمپیوٹر کی حسابی تگ ودو کے لحاظ سے سپر کنفگریشن انٹر ایکشن اور نیوٹن-رافسن طریقوں کا امتزاج ان دونوں کے الگ الگ استعمال کی نسبت کہیں زیادہ موزوں ہے، خاص طور پر اس وقت جب ابتدائی قیاسی مدارچے تقاربی حل سے بہت دُور ہوں۔ اس امتزاجی طریقے میں ابتدائی سائیکلز سپر کنفگریشن انٹر ایکشن سے حل کیے جاتے ہیں یہاں تک کہ مدارچوں کے تبدیل ہونے کی شرح یا ان کی اصلاح کرنے والا ویکٹر ایک خاص حد تک کم

ہو جائے، اور اختتامی سائیکلز نیوٹن-رافسن طریقے سے حل کیے جاتے ہیں۔

اس کے بعد وی بی ایس سی ایف طریقے میں مدارچوں کو مستحسن بنانے کے دو مختلف الگورتھمز کی کارکردگی کا بڑی تفصیل سے تجزیہ کیا گیا ہے۔ ان الگورتھمز میں سے ایک کی بنیاد ایک تقریبی نیوٹن-رافسن طریقے پر ہے، جس میں کمپیوٹر کی حابی تگ ودو کو کم کرنے کے لیے ہاشیئن قالب کو ایک وتری قالب سے قیاس کر لیا جاتا ہے۔ دوسرے الگورتھم میں مدارچوں کو مستحسن بنانے کے لیے فوک قالب استعمال کیا جاتا ہے۔ کمپیوٹر کی حابی تگ ودو کے حوالے سے یہ معلوم ہوا ہے کہ فوک قالب طریقہ کار تقریبی نیوٹن-رافسن طریقے کی نسبت تھوڑا زیادہ مہنگا ہے اگرچہ اوّل الذکر میں ایٹمی مدارچوں کے چہار درجی تکمیلوں (یعنی فور انڈیکس اِنٹیگرَلز) کو ویلنس بانڈ کے مدارچوں کی اساس میں منتقل کرنے کی ضرورت نہیں ہوتی۔ اس کی وجہ یہ حقیت ہے کہ قالبوں کے ارکان کا حساب کتاب اکثروبیشتر چہار درجی تکمیلوں کے انتقال سے زیادہ وقت طلب ہوتا ہے۔

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LIST OF PUBLICATIONS

1. Zahid Rashid and Joop H. van Lenthe; "Generation of Kekulé Valence Structures and the Corresponding Valence Bond Wave Functions", *J. Comput. Chem.* **2011**, 32, 696-708.

2. Zahid Rashid, Joop H. van Lenthe and Remco W. A. Havenith; "Resonance And Aromaticity: An Ab Initio Valence Bond Approach", *J. Phys. Chem. A*, **2012**, 116, 4778-4788.

3. Joop H. van Lenthe, Ria Broer and Zahid Rashid; "On the Efficiency of VBSCF Algorithms", *J. Comput. Chem.* **2012**, 33, 911-913.

4. Zahid Rashid and Joop H. van Lenthe; "A Quadratically Convergent VBSCF Method", *J. Chem. Phys.* **2012**, *Submitted.*

Outside This Thesis

- Elwin Molenbroek, Natan Straathof, Zahid Rashid, Joop H. van Lenthe, Martin Lutz, Aurore Gandubert, Robertus J. M. Klein Gebbink, Sebastian Dück, Luisa De Cola, Sylvestre Bonnet; "Zinc Coordination to the Bapbpy Ligand and to Bapbpy-functionalized Lipid Vesicles: Free Zinc Detection via Fluorescence Enhancement", *Dalton Trans.* **2012**, *In Press*, doi: 10.1039/c2dt32488a.

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CURRICULUM VITAE

The author was born on 8th of July 1983 in a small village of district Pakpattan in Pakistan. After receiving his early education from a local village school and a nearby city (Arifwala), he got admission in Sahiwal College where he obtained B.Sc. degree in 2003. In the same year he started M.Sc. Chemistry studies at the Institute of Chemistry, University of the Punjab (Pakistan) and graduated in january 2006. In 2007, he obtained a fellowship for M.Sc. leading to Ph.D. from the Higher Education Commission of Pakistan and joined the Theoretical Chemistry Group of Utrecht University as a masters student in 2008. After completing M.Sc. (Chemistry and Physics: Nanomaterials) in January 2009, he started his Ph.D. under the supervision of Dr. Joop van Lenthe. Most of his Ph.D. research is in the area of Valence Bond Self-Consistent Field method which is presented in this thesis and part of this work has been published in peer reviewed scientific journals. During the Ph.D. studies, he also attended several national and international conferences, summer and winter schools and presented his work as oral and poster presentations.