A semi-empirical valence bond (VB) method, called VBDFT(s), is described and applied to C\textsubscript{n}H\textsubscript{n+2} conjugated hydrocarbons. The method is a Hückel-type VB scheme with energies scaled to density functional theory energies based on a single parameter; the matrix element \( \lambda \) due to spin transposition between bonded atoms. Total energies, excitation energies, resonance and \( \pi \)-bond energies are presented for the various species. The insight that can be derived from the corresponding wavefunctions is discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The decline of valence bond (VB) theory [1] originated in a complexity of reasons. The foremost among them is the \( N! \) problem which creates implementation difficulties, even in these days with the advent of fast computers. Equally important is the disrepute of VB theory, contributed to by the use of oversimplified models such as resonance theory and perfect pairing [2]. Thus, the failures of the oversimplified models to account for e.g. the antiaromaticity phenomenon and the origins of the triplet ground state for O\textsubscript{2} have cast doubts on VB theory as a ‘correct’ theory and held back the formulation and teaching of new VB insights. This VB situation can be contrasted with that in molecular orbital (MO) theory, which has flourished due to its ease of implementation and to the build-up of insight and MO theoretical wisdom [3], through simple methods such as Hückel and extended Hückel theory.

In view of the renaissance in VB methods [4–10], there is a need to create modern VB tools which may serve to develop a VB thought culture. The great advantage of such a task is that VB theory, with its built-in electron correlation effects, will necessarily lead to tools which anchor the qualitative insight on a physically correct level. A reasonable strategy for the creation of these tools is to incorporate the VB philosophy into density functional theory (DFT) [11], hence VBDFT, and to proceed step-by-step such that each new step refines the previous tools. This Letter makes the first step and introduces a Hückel-type
VB method which uses a single parameter to scale the VB energy to density functional energies. The method described below is applied at present to covalent states of polyene hydrocarbons, but is extendable in principle to other systems and to non-covalent states.

2. Theory and methods

2.1. VB determinant basis functions

VB determinants were used some time ago, in chemistry, as the building blocks for electronic structure [12–17]. Malrieu and co-workers [13–16] have applied the method extensively using an effective Heisenberg Hamiltonian in terms of two parameters, derived from a multi-reference configuration interaction treatment of ethylene and carried over to produce VB states and properties of a variety of hydrocarbons with remarkable beauty. Our approach draws on the work of Malrieu and co-workers [13–16], but differs from it in aspects of formulation, in computational options and in its reliance on DFT [11] to generate all the VB determinants, which are subsequently diagonalized by means of a single parameter matrix element. Thus, in our method the total energies are scaled to match those produced by DFT; hence the name VBDFT(s), where the parenthetical (s) stands for semi-empirical.

The physical idea behind the VBDFT(s) approach is straightforward. Consider a molecular species for which the electrons may be classified into two subgroups; the major one which we call ‘passive’ and is treated as a closed shell of electron pairs and a minor subgroup which we call ‘active’ and which we wish to be treated by VB theory. Such situations are common in chemistry, e.g. conjugated systems with $\sigma$–$\pi$ separation, a reaction which involves reorganization of a small number of electrons, a bond breaking process and so on. In such cases, the fundamental building block of the electronic structure is a VB determinant (VBD), which constitutes a specific alignment of the ‘active’ electrons in the field of the ‘passive’ electrons. The VBDs can be used in two different manners, which together provide a complementary insight. A direct use of VBDs results in VBD-mixing in which the states are described as linear combinations of electron arrangement patterns. Alternatively, the VBDs can be grouped into Rumer

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme1}
\caption{Scheme 1.}
\end{figure}
functions [18], which then mix to form the final states as combinations of chemical structures.

A special class of species, which are the focus of this Letter, are open-chain conjugated molecules with an average of a single ‘active’ electron per site moving in a field of closed-shell ‘passive’ σ-electrons. These species possess a low-energy manifold of covalent VBVs [13–16] well separated from ionic manifolds, as depicted in Scheme 1 for three representative species. Ethylene (Scheme 1, a) has two covalent VBVs, $\langle S_z \rangle = 0$, in which the ‘active’ $p_y$ electrons are arranged in opposite spin situations. In the allyl radical (Scheme 1, b) and butadiene (Scheme 1, c), there are a few stacks of VBVs with $\langle S_z \rangle$ values of 1/2 and 0, respectively. In the lowest-energy stack the active electrons are arranged in a spin-alternant manner; henceforth the ‘spin-alternant’ VBD, which is $\pi$-nonbonding and hence a good reference situation [19]. The allyl radical, which represents an odd-membered species has a single spin-alternant VBD (b-1), while the even-membered species represented by butadiene possess two such spin-alternant VBVs (c-1 and c-I). Above these fundamental determinants, there exist stacks of excited determinants which are generated from the spin-alternant VBD by successive pairwise spin transpositions. Generally, a transposition generates an adjacent triplet pair of electrons and raises the energy due to the corresponding triplet repulsion (overlap repulsion) associated with the Pauli exclusion rule.

In the general case of a $C_nH_{2n+2}$ chain with $n-1$ CC bonds, the number of covalent VBVs with the lowest $\langle S_z \rangle$ value is given by Eq. (1) and is also the dimension ($d_{VBD}$) of the basis functions.

$$d_{VBD} = \binom{n}{p}; \quad p = \text{number of } \beta \text{ electrons}. \quad (1)$$

Thus, there will be one or two spin-alternant VBVs, depending on whether $n$ is odd or even and $n-2$ stacks of VBVs separated from each other by an increment of triplet repulsion on neighbouring atoms. The upper-most stack will have in the general case $n-2$ adjacent triplet pairs and will lie above the spin-alternant VBD by an $(n-2)$-fold pair–triplet repulsion. This manifold of VBVs constitutes the basis set $\Phi_m$ from which we generate the state eigenfunction. Each $\Phi_m$ in the basis set is an eigenfunction of the $S_z$ operator and possesses therefore a definite alignment of spins ($\langle S_z \rangle = 0$ for $n$-even and $\langle S_z \rangle = 1/2$ for $n$-odd). However, the $\Phi_m$s are not eigenfunctions of the $S^2$ operator [13–17], but become so by diagonalization which produces a set of state eigenfunctions for the Hamiltonian and the spin operators.

The Hamiltonian for the problem can most conveniently be expressed as a sum of two parts defined in Eq. (2).

$$H = H^\lambda + H^\nu. \quad (2)$$

$H^\nu$ provides by construction, the diagonal elements of the Hamiltonian, thus accounting for the energy of the ‘passive’ electrons and the unpaired ‘active’ electrons. $H^\lambda$ is specified in Eq. (3a) to give the self-energies ($E_m$) of the $\Phi_m$ VBVs. $H^\lambda$ is the part that gives the off-diagonal elements of the Hamiltonian; thus describing the VB pairing of the ‘active’ electrons in Eqs. (3a) and (3b) by transposing the spins over bonded atoms $a$ and $b$, and thereby mixing different $\Phi_m$s which differ by such a spin transposition.

$$H^\nu = \sum_m E_m|\Phi_m\rangle\langle\Phi_m|, \quad (3a)$$

$$H^\lambda = \sum_{a,b} \lambda_{ab} \left[ |a\bar{b}\rangle\langle\bar{a}b| + |\bar{a}b\rangle\langle a\bar{b}| \right] + \text{higher orders;} \quad a, b – \text{bonded}. \quad (3b)$$

Strictly speaking, VBVs can mix by long-range transpositions. Detailed VB calculations using the ab-initio software TURTLE [6] show that the ‘high-order terms’ in Eq. (3b) are small and can be neglected. Of course, such a neglect has a price and one expects that the cumulative error will increase as the size of the molecule increases. Nevertheless, in view of the prospective lucidity of the tool, the price of the close-neighbor approximation of Eq. (3b) seems worthwhile. Thus, as shown pictorially in Scheme 1, d, two VB determinants will maintain a matrix element $\lambda_{ab}$ if they are mutually related by a spin transposition over the bonded centres $a$ and $b$. Further neglect of overlap between the VBVs leads to a Hückel appearance of the matrix representation of the Hamiltonian.

To exemplify, we show in Eq. (4) a schematic
representation of such a Hamiltonian matrix for ethylene using the VBD basis in Scheme 1, a.

\[
\begin{pmatrix}
\alpha & \lambda \\
\lambda & \alpha
\end{pmatrix}
\]  

(4)

Here $\alpha$ is the energy of the spin-alternant determinants (Scheme 1, a) and the $\lambda$ is their matrix element which has a positive value. The corresponding wavefunctions and energies will be,

\[
\Psi_1 = \frac{1}{\sqrt{2}} \left[ (\ldots \sigma \bar{\sigma}) a \bar{b} - (\ldots \sigma \bar{\sigma}) \bar{a} b \right];
\]

\[
E_1 = \alpha - \lambda,
\]

(5a)

\[
\Psi_2 = \frac{1}{\sqrt{2}} \left[ (\ldots \sigma \bar{\sigma}) a \bar{b} + (\ldots \sigma \bar{\sigma}) \bar{a} b \right];
\]

\[
E_2 = \alpha + \lambda,
\]

(5b)

where Eq. (5a) describes a singlet pair of the $\pi$-bond in the $\langle a|\bar{b} \rangle$ p$_{\sigma}$-atomic orbitals and Eq. (5b) a corresponding triplet pair.

For a C$_2$H$_{n+2}$ species, the diagonalization of the Hamiltonian matrix will generate a spectrum of covalent states which have the same $S$ eigenvalue and all the possible $\langle S^2 \rangle$ eigenvalues, in numbers which can be read from the branching diagram. Each such state eigenfunction will be expressed as a normalised linear combination of the basis VBDs, in Eq. (6).

\[
\Psi_i = \sum_m c_{mi} \Phi_m; \quad \sum_m c_{mi}^2 = 1.
\]

(6)

Electronic structure becomes then a linear combination of spin arrangement patterns, while the respective state energy arises from a balance between the triplet–pair repulsions in the VBDs and their resonance or singlet-pairing energies (in $\lambda$ units) due to the VB mixing.

2.2. Rumer basis functions

An alternative representation of the state eigenfunction of a given spin manifold uses the Rumer functions ($R_i$) which are the chemically familiar structures which endow the VB scheme with a complementary insight on electronic structure. A Rumer function [18] is a product of singlet bond wavefunctions (Eq. (5a)) of all the bonds in the Rumer structure. As such, all the Rumer structures for a given species can be generated from the VBDs by basis set transformation. Thus, each Rumer structure ($R_i$) is a constrained linear combination of a subset ($m'$) of VBDs, which are signed but otherwise appear with equal coefficients, as in Eq. (7),

\[
R_i = N_i \sum_{m'} (-1)^i \Phi_m'; \quad N_i = (2)^{-p/2};
\]

(7)

$p$ = number of $\beta$ electrons, where the sign is determined by the number of spin transpositions ($t$) relative to the spin-alternant VBD. The state eigenfunction is obtained by diagonalizing the Hamiltonian in the Rumer basis set, Eq. (8a).

\[
\Psi_i = \sum_k a_k R_k ,
\]

(8a)

\[
\langle \Psi_i | \Psi_i \rangle = \sum_k a_k^2 + \sum_{k \neq k'} a_k a_{k'} \langle R_k | R_{k'} \rangle .
\]

(8b)

Note that the Rumer structures are not mutually orthogonal since they share common VBDs.

2.3. DFT calibration of self-energies and matrix elements

A convenient way to calculate the self-energies $E_m$ of the determinants, in Eq. (3a), is based on inputting the determinants, into a standard electronic structure calculation software, as guess wavefunctions and then determining the energy of the guess wavefunctions and then determining the energy of the guess [19]. Since each VBD has a definite electron and spin density the densities can be transformed into self-energies of the VBD using the DFT formalism [11] as in Eq. (9).

\[
E_m (\rho_m) = T_m (\rho_m) + V_{ext} (\rho_m) + V_{nuc} (\rho_m) + E_{xc} (\rho_m) ,
\]

(9)

where $\rho_m$ is the density, $T_m$ is the kinetic energy of the noninteracting particles, $V_{ext}$ is the energy of nuclear–electron attraction, $V_{nuc}$ is the Coulomb energy and $E_{xc}$ is the exchange-correlation energy. Since DFT methods involve electron correlation, the energy of a VBD already includes the correlation effect for the ‘passive’ $\sigma$-shell electrons. Some underdground $\pi$-correlation may also enter the VBD energy and lead thereby to double counting of the
correlation effect in the VBDFT(s) energies. However, the virtual independence of the VB matrix element $\lambda$ (see next paragraph) on whether the VBD energy is determined by Hartree–Fock, VBSCF [6], or DFT, as well as the reasonable $\pi$-bond energies, etc., (see later) lead us to believe that the effect is minor.

The value of the matrix element $\lambda$, Eq. (3b), is determined from a calculation on ethylene, as the energy difference between ethylene and the corresponding input VBD (see Eq. (5a)). For the ground-state geometry of ethylene with the D95V basis set [20], the resulting $\lambda$ is $\sim 0.11 \pm 0.01$ au and not sensitive to the changes in the functional or basis set. Further, using ab-initio VBSCF calculations [6] to determine $\lambda$ leads to a virtually identical value.

This $\lambda$ value was carried over to diagonalize the VB states for all the molecules. Thus, the VBDs are generated using all possible spin permutations on the spin-alternant VBD and fed into GAUSSIAN 94 [21], while the corresponding energies are collected and together with the corresponding $\lambda$ values are fed into the diagonalization routine, which provides eigenvectors and energies for all the possible spin eigenstates.

Once the self-energies of the VBDs and their $\lambda$ matrix elements are known, the Rumer structures are constructed and their self-energies are determined by transformation from the VBD basis to the Rumer one. Starting from VBDs, the matrix elements between the Rumers are definable in terms of the $\lambda$ parameter; a valuable facility because matrix elements between Rumers are definable in terms of the $\lambda$ parameter which is optimised for the ground-state geometry to feed bond-specific $\lambda$ values from Eq. (11) into the diagonalization routine of VBDFT(s).

Three points are warranted at this point:

(a) using a standard uniform bond length for all molecules, shows that a single $\lambda$ value is sufficient to fit VBDFT(s) ground-state energies to DFT results. We also found $\lambda$ as a function of the C–C bond length $r$ in Eq. (11).

(b) the parameter $\lambda$, which is determined relative to the total energy of the ethylene involves implicitly the effect of ionic structures. This is in line with the philosophy [5] that ionicity in covalent bonds is a manifestation of the distortion of the atomic orbitals in the molecular environment. While this is certainly not general [7], at least for the class of species investigated here, one could do away with explicit treatment of the ionic structures.

(c) The $\lambda$ parameter which is optimised for the ground state overestimates excitation energies relative to CASPT2 [23,24] results. To obtain good numerical results will require a characteristic $\lambda$ for the excited state, which is a normal situation in electronic calculations that perform state specific optimisations (e.g., in MCSCF [23,24] or VB ab initio [6]). The change of $\lambda$ changes the energy of the excited state, but the form of its wavefunction remains invariant. Consequently, insight on the covalent excited states is still provided from a calculation that uses the $\lambda$ parameter fitted for ground-state energies, as used in the present Letter.
3. Results and discussion

3.1. Ground-state VBDF(s) energies and wavefunctions

The VBDF(s) energies have been scaled against the B3LYP, BHLYP and BLYP functionals in GAUSSIAN 94 [21] for C\textsubscript{n}H\textsubscript{n+2} species where n = 3–10 (there are no methodological problems to exceed n = 10). Fig. 1 shows the correlation of the VBDF(s) ground-state energies plotted against the corresponding B3LYP total energies. The correlation shows that the VBDF(s) and B3LYP total energies are virtually identical with a mean error of 0.0043 au and highest error of 0.0098 au. For the even-membered series the error scales moderately with size. For the odd-membered series, the error is significantly smaller and does not show a clear size dependence.

The VBD makeup of the ground state, shows that the spin-alternant determinant \[16\] possesses the highest coefficient \[c_0\] in the wavefunction, albeit this coefficient diminishes with the increase in the size of the molecule (e.g., in C\textsubscript{5}H\textsubscript{5} \[c_0 = 0.81\], while in C\textsubscript{10}H\textsubscript{12} \[c_0 = 0.41\]). It follows therefore, that the total VB energy mirrors the balance between the tendency to keep an electronic structure that minimises the triplet repulsion, as in the spin-alternant VBD, and the opposing tendency to optimise the singlet spin-pairing by the mixing in of the higher-lying VBDs.

3.2. Excited-state VBDF(s) energies

An added bonus of the VBDF(s) method is the spectrum of covalent excited states, corresponding to the spin manifold due to n-electrons on n-centres. We focus here on the low-lying states; for the even-membered polyenes we consider the \(2^1\text{A}_u\) state also called the ‘hidden’ state and the \(1^3\text{B}_u\) triplet state, while for the odd-membered polyene we focus on the first doublet excited state (\(1^2\text{B}_1\) for C\textsubscript{3}H\textsubscript{4} and C\textsubscript{5}H\textsubscript{6}, \(1^2\text{A}_2\) for C\textsubscript{3}H\textsubscript{7} and C\textsubscript{5}H\textsubscript{11}). As shown in Fig. 2 in all cases the excitation energies fall with the chain length, \(n\), in line with previous VB [15] conclusions and with experimental and CASPT2 results [23,24].

The \(1^3\text{B}_u\) triplet states of the even-membered polyenes are dominated by the two spin-alternant VBDs which appear in an opposite linear combination compared to the singlet ground states. In contrast, the excited states of the same spin multiplicity as the ground state arise from stacks of excited VBDs. Thus, the odd-membered radicals possess \(1^2\text{B}_1\) or \(1^2\text{A}_2\) excited states described by VBDs from the first excited stack and typified by a single triplet–pair repulsion. The ‘hidden’ excited states (\(2^1\text{A}_x\)) of the even-membered polyenes are characterised by a significant contribution from the spin-alternant VBDs and somewhat larger contributions from VBD’s which possess two pairs of triplet repulsion. The relative weights of the two VBD types become closer and closer as the chain size increases. Generally speaking for all the excited-state types, the dominant VBDs of the first excited state mix in a sandwich manner with the spin-alternant VBDs from below and with higher excited VBD stacks from above. The higher excited VBDs become more numerous as the chain size increases, and this is the root cause as to why the excitation energies diminish with the size \(n\) in Fig. 2. Thus, the energies of the low-lying excited states reflect a balance between the tendency to conserve the minimum amount of pair repulsions (which requires high coefficients for the lowest-lying excited determinants) and the opposing tendency to optimise the singlet spin-pairing.
tendency to maximise the number of singlet pairs by mixing with higher-lying VBDs.

3.3. Bonding, delocalisation and resonance energies

Since the spin-alternant VBD is \( \pi \)-nonbonding [19], it may serve as a reference to derive \( \pi \)-bonding and delocalisation energies as the difference between the energy of the ground state (\( \Psi_0 \)) and the energy of the spin-alternant VBD (\( \Phi_{sa} \)). In turn, the resonance energies are determined from the energy difference between the state and a single-reference Rumer structure.

An important quantity is the ground state’s \( \pi \)-energy/electron which converges to a constant value of 31 ± 1 kcal/mol in agreement with the result of the Toulouse group [14]. This constant value allows the total ground state’s \( \pi \)-energy to be expressed as a function of the chain length \( n \) as follows:

\[
E(\Psi_0) \text{ (kcal/mol)} = E(\Phi_{sa}) + 31n. \tag{12}
\]

The largest \( \pi \)-bond energy, 67.1 kcal/mol, belongs to ethylene which possesses the shortest bond, while in the higher homolog even-membered polyenes a single \( \pi \)-bond energy (total \( \pi \)-energy divided by number of bonds) is almost constant, \( \sim 63.1 \pm 1.9 \) kcal/mol. This is in line with the bond additivity attributed to polyenes. A \( \pi \)-bond energy can be derived also for the odd-membered series, by dividing the total \( \pi \)-bonding and delocalisation by the number of bonds in the most stable Rumer structure. The value of 64.7 ± 1.5 kcal/mol is surprisingly close to the even-membered series.

The resonance energies for the ground states are larger for the odd-membered systems as might be expected and have a constant increment as a function of the size \( n \). Resonance energies can be quantitated for excited states as well, relative to the Rumer structure of the highest weight. A crossover was found from negative (destabilising) resonance energies for the short-chain members to positive resonance energies (stabilising) for the longer-chain members.

4. Conclusions

The VBDFT(s) method is a Hückel-type VB scheme, in the philosophical line of earlier treatments [13–17]. The method is scaled to give DFT energies based on a single parameter; the matrix element \( \lambda \) due to spin transposition between bonded atoms. Such an implementation of the VBDFT(s) method ensures that the bulk of the total energy is
the self-energy of the VB determinant and the remaining VB mixing part is a perturbation on the total energy; a sensible feature for a semi-empirical theory. Limitations are expected [16], but it is apparent that irrespective of the eventual quantitative performance of VBDFT(s), its advantage will be the ability to generate lucid physical insight about electronic structure and to develop thereby a VB culture of thought.

The overall performance of the simple semi-empirical scheme generates an incentive for future developments culminating in a non-parametrized VBDFT.

Acknowledgements

This research was sponsored in part by a grant from the ISF, The Israel Science Foundation, established by the Israel Academy of Sciences and Humanities, and in part by the Volkswagen-Stiftung.

References