

Convergence of valence bond theory in trans-butadiene molecule

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Abstract The valence bond theory, in an *ab initio* approximation, has been used to calculate the π -electron energy of the three lowest states of the trans-butadiene molecule. Using the methods of non-orthogonal orbitals valence bond calculations, bi-orthogonal valence bond basis and the optimized atomic orbital approximation, in each case a comparison of the rate of convergence of the energy to the full configuration interaction limit has been made. It is concluded that, when undertaking an orbital optimization, only the covalent structures can reproduce the results of the full configuration interaction limit.

1. Introduction

The main practical issue which has prevented further development of the valence bond theory of the molecular electronic structure for the past fifty years has been the so-called "non-orthogonality problem". Due to this non-orthogonality, *ab initio* valence bond (VB) calculations have usually been restricted to few electron systems.

Methods have been developed to handle the non-orthogonality problem directly¹⁻⁵. Using VB structures defined in terms of orthogonal orbitals an alternative approach⁶⁻⁸ is to orthogonalize the basis functions. Unfortunately, this orthogonalized valence bond (OVB) procedure converges slowly in the sense that the "multiply-polar" structures must be included in large numbers^{6,8}.

Norbeck and McWeeny⁹ combined the advantages of the VB and OVB approaches by setting up two bases, which are bi-orthogonal in nature, and applying the method of moments, instead of solving the usual variational secular equations.

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When **all** structures are included the basis set limit is reached, but **even** truncated sets give **good** (though non-monotonic) convergence.

Recently, **McWeeny**¹⁰ has shown that the full configuration interaction (**CI**) limit may be closely approached using only a small number of structures by slightly modifying the nearest-neighbour orbitals in order to enhance their mutual overlap. Energies obtained with this approach have been reported for some **molecules**^{10,13}.

In this report we compare the rate of convergence of the energy to the **full**-**CI** limit for the **three** lowest states of the trans-butadiene molecule, obtained with the following methods: the non-orthogonal orbitals **VB** calculation; the bi-orthogonal valence bond (**BOVB**) method⁸ and the optimized atomic orbitals **approximation**¹⁰⁻¹³.

2. Theory: The trans-butadiene molecule

Using the minimal Clementi basis set (**7s 3p/3s**) Gaussian contracted to [**2s 1p/1s**] a standard molecular orbital self-consistent field (**SCF**) calculation **was** performed to describe the electronic structures of trans-butadiene. Next, considering the 26 electrons corresponding to the σ bonds and **1s** shells of the carbon atoms as the core electrons of a set of doubly occupied orbitals, we replace the **1-electron** Hamiltonian for the π electrons by an effective Hamiltonian. The p_z atomic orbitals (**AO**) are orthogonal to the core (see ref. 11 and **references** therein). The total energy in this case is equal to the π electrons' energy plus the core **energy**^{11,14}.

Thus, our **VB** calculation involves only four π electrons and four **non**-orthogonal p_z atomic orbitals. Consequently, there are 20 singlets and 15 **triplets**¹⁵.

Fig. 1 shows the carbon skeleton of the trans-butadiene, where each p_z **non**-orthogonal **AO** is denoted by

$$\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, \mathbf{u}_4 \tag{2.1}$$

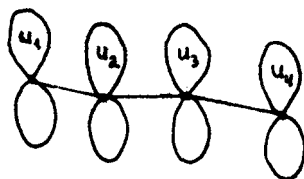


Fig. 1 - Carbon skeleton of the trans-butadiene molecule.

Using the modified orbitals

$$\begin{aligned}
 \bar{u}_1 &= u_1 + \lambda u_2 \\
 \bar{u}_2 &= u_2 + \lambda u_1 + \nu u_3 \\
 \bar{u}_3 &= u_3 + \lambda u_4 + \nu u_2 \\
 \bar{u}_4 &= u_4 + \lambda u_3
 \end{aligned}
 \tag{2.2}$$

where λ, ν are numerical parameters determined by the requirement of a minimum total electronic energy, we will see in the next section that the energy obtained with covalent structures is approximately equal to the energy obtained with the full-CI calculation. Orbitals of this kind were first used by Coulson and Fisher¹⁶, and later by Mueller and Eyring¹⁷ but they have not extensively adopted them, as we do here, owing to technical difficulties arising from the use of heavily non-orthogonal functions.

If $\{u\}$ is a linearly independent set of non-orthogonal atomic orbitals, it is possible to construct another linearly independent set of orbitals $\{\tilde{u}\}$, such that

$$\langle \tilde{u}_i | u_j \rangle = \delta_{ij}$$

The sets $\{u\}$ and $\{\tilde{u}\}$ are sometimes referred to as “bi-orthogonal” and the relationship between them is easily seen to be

$$\tilde{u} = uS^{-1}$$

where S is the overlap matrix of the set $\{u\}$.

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The **1-electron** and **2-electron** integrals were transformed to the **bi-orthogonal** basis using the simple transformation equations .

$$\langle \tilde{u}_i | h | u_j \rangle = \sum_m T_{im}^\dagger \langle u_m | h | u_j \rangle, \quad (2.3)$$

$$\langle \tilde{u}_i \tilde{u}_j | g | u_k u_l \rangle = \sum_{m,n} T_{im}^\dagger T_{jn}^\dagger \langle u_m u_n | g | u_k u_l \rangle$$

where $T = S^{-1}$. The resulting bi-orthogonal VB method does not yield **upper** bounds to the energy levels , **but** as more structures are added it nevertheless converges towards the same "basis set limit" as the conventional **VB** calculation. In addition, it has attractive **computational** features in requiring only the simple **VB** rules for matrix elements , together with a "**2-index**" transformation of **2**-electron integrals rather than the customary (**exceedingly** time-consuming) **4-index** transformation.

In the next section, a comparison is **made** of the rate of convergence of the three lowest states of the trans-butadiene molecule when the three proposed methods are used: i) the **VB** ii) the optimized atomic orbitals and iii) the **BOVB** calculation, eqs. (2.1), (2.2) and (2.3), respectively.

3. Results and Conclusions

To compare the convergence of the different methods, it is helpful to **introduce** an ordered set of approximations whose limit is the complete calculation for a given basis set. In the valence bond formulation, the first level of approximation includes **all** covalent structures (COV). The importance of ionic structures is less than that of covalent structures and decreases as the number of doubly occupied atomic orbitals increases. The singly ionic adjacent (SIA) structures are **some-**what energetically **lower** than the singly ionic non-adjacent (SINA) because in the former the electron-electron repulsion in the doubly occupied orbital is partially compensated by the absence of repulsion from an electron on an adjacent centre. **Doubly** ionic structures (DI) have such a high electron-electron repulsion that they make only minor contributions to the ground and **low-lying** excited states. Tables

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1, 2 and 3 give the approximate levels with the associated number of symmetry-adapted structures in the progression COV, SIA, SINA and DI (where applicable). Since each **level** includes the structures from **all** the precedent ones, the final level represents a complete multi-structure **valence-bond** calculation.

All energies from tables 1, 2 and 3 are in units of E_h (Hartrees), and a **minimal** Clementi basis set (7s 3p/3s) Gaussian-contracted to [2s 1p/1s] **has** been used in these calculations.

Table 1 shows the π electron energies of the ground state of 1A_g symmetry of trans-butadiene molecule, for each level of approximation and the corresponding number of structures used in each level, obtained with the **approaches** described in the **last** section.

Table 1 - Ground state energy of the trans-butadiene molecule (with different approaches).

Level of approximation	Number of structures	π -electron energy (Hartrees)		
		Non-orthogonal basis (eq.(2.1))	Bi-orthogonal basis (eq.(2.3))	Optimized orbitals (eq.(2.2))
COV	2	-3.3762	-3.1271	-3.4612
SIA	8	-3.4545	-3.3967	
SINA	14	-3.4595	-3.4145	
DI	20	-3.4633	-3.4633	

It can be seen from table 1 that the energies obtained with the **bi-orthogonal** basis (eq. (2.3)) in any level of approximation are of lower quality than those from the non-orthogonal basis (eq. (2.1)), that is, the VB approximation converges more rapidly than the BOVB to the full-CI limit. Only when **all** structures are included in the calculation the two methods lead to the same values. On the other hand, we also verify that the computational time to perform the **full-CI** calculation using the bi-orthogonal basis is shorter than that of non-orthogonal basis. Besides, one notes that this computational time difference between the **two** methods increases when the number of structures increases. For example, in the **full-CI** calculation of the singlet state of the benzene molecule (**175-structures**), the computational time using the non-orthogonal basis is about ten times larger than the **BOVB** method. Apart from computational **advantages**, no iterative optimization

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of orbitals is required and the usual 4-index transformation of electron repulsion integrals is replaced by a 2-index transformation (eq. (2.3)).

Using the modified orbitals of eq.(2.2) the covalent structures lead to results close to those obtained by the full-CI limit (Table 1).

In tables 2 and 3, we have the \bar{a} electron energies respectively of the 1A_g and 3B_u excited states of the trans-butadiene molecule. From these tables we can see again that the BOVB approximation converges more slowly than the VB approximation in relation to the full-CI limit, where the two methods give the same results. When the optimized orbitals (eq. (2.2)) are used, only the covalent structures give results which are approximately equal to the full-CI limit.

Table 2 - Excited state energy of the 1A_g symmetry of the trans-butadiene molecule (with different approaches).

Level of approximation	Number of structures	\bar{a} -electron energy (Hartrees)		
		Non-orthogonal basis (eq.(2.1))	Bi-orthogonal basis (eq.(2.3))	Optimized orbitals (eq.(2.2))
COV	2	-3.1353	-3.0807	-3.1744
SIA	8	-3.1711	-3.1605	
SINA	14	-3.1766	-3.1732	
DI	20	-3.1772	-3.1772	

Table 3 - Excited state energy of the 3B_u symmetry of the trans-butadiene molecule (with different approaches).

Level of approximation	Number of structures	\bar{a} -electron energy (Hartrees)		
		Non-orthogonal basis (eq.(2.1))	Bi-orthogonal basis (eq.(2.3))	Optimized orbitals (eq.(2.2))
COV	3	-3.2642	-3.1069	-3.3195
SIA	9	-3.3148	-3.2968	
SINA	15	-3.3219	-3.3219	

The results can be summarized as follows:

The VB method converges more rapidly than the BOVB method to the full-CI limit. In all cases studied in the present report the computational time to make the full-CI calculation in the BOVB approximation is shorter than in the VB approximation. It is also concluded that if the optimized orbitals of eq. (2.2) are used the covalent structures are needed to reproduce the results of the full-CI limit for the three lowest states of trans-butadiene.

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References

1. F. A. Matsen, Adv. Quantum Chem. **1**, 59 (1964).
2. F. Prosser and S. Hagstrom, Int. J. Quantum. Chem. **2**, 89 (1968).
3. G.G. Balint-Kurti and M. Karplus. J. Chem. Phys., **50**, 478 (1969).
4. G. A. Gallup, Int. J. Quantum Chem., **6**, 899 (1972).
5. J. Gerratt, Adv. At. Mol. Phys., **7**, 141 (1971).
6. R. McWeeny, Proc. Roy. Soc., A223 63, 306 (1954).
7. I. L. Cooper and R. McWeeny, J. Chem. Phys., **45**, 226, 3484 (1966).
8. W. Th. A. M. van der Lugt and L. J. Oosterhoff, Mol. Phys., **18**, 177 (1970).
9. J. M. Norbeck and R. McWeeny, Chem. Phys. Letters, **34**, 206 (1975).
10. R. McWeeny, Theoret. Chim. Acta, **73**, 115 (1988).
11. R. McWeeny and F. E. Jorge, J. Mol. Structure (THEOCHEM), **46**, 459 (1988).
12. F. E. Jorge, Rev. Bras. Física, **19**, 281 (1989).
13. F. E. Jorge and R. N. Suave, Rev. Bras. Física, **20**, 84 (1990).
14. R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics*, Academic, London (1969).
15. R. McWeeny, Proc. Roy. Soc., Ser. A, **227**, 228 (1955).
16. C. A. Coulson and I. Fischer, Phil. Mg., **40**, 306 (1949).
17. C. R. Mueller and H. Eyring, J. Chem. Phys., **19**, 1495 (1951).

Resumo

Aplica-se a teoria de ligação de valência para calcular as energias dos elétrons π dos três estados de mais baixa energia da molécula do trans-butadieno. Usando três métodos diferentes, compara-se a taxa de convergência da energia para o limite de um cálculo completo de interação de configurações. Além disso, verifica-se que, quando se faz uma otimização dos orbitais atômicos, somente as estruturas covalentes são capazes de reproduzir os resultados de um cálculo completo de interação de configurações.