

## The valence bond theory applied to the cyclobutadiene molecule

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**Abstract** The valence bond theory is applied here in an *ab initio* calculation of the lowest triplet state of the cyclobutadiene  $\pi$ -electron system. Optimizing a suitable linear combination of atomic orbitals we show that with only a few structure, one capable of obtaining results close enough to those obtained by the full-configuration interaction limit. We will discuss separately the use of the classical and spin-optimized valence bond approaches.

### 1. Introduction

The first quantum-mechanical discussion of how atoms combined to form stable molecular bonds was given by Heitler and London<sup>1</sup> in 1927. Since these early days the theoretical foundations laid by the founders of the field have been considerably extended and many interesting applications of valence bond (VB) theory have been made<sup>2-4</sup>.

Valence bond theory in its modern form<sup>5-7</sup> is capable of giving a good account of both localized and de-localized bonding, using wavefunctions which are compact, accurate, and easy to interpret using the language of classical chemistry. Thus<sup>7</sup> the benzene  $\pi$ -electron system is well described as a mixture of the two Kekule-type structures, provided the  $2p_\pi$  atomic orbitals (AOs) on the six carbon atoms are replaced by slightly modified AOs which, whilst still being localized and equivalent (i.e. permuted under  $D_{6h}$ -symmetry operations), have somewhat stronger overlap with their neighbours.

In the approach used by Gerratt and collaborators<sup>5,7</sup>, the wavefunction is based on a single configuration of different non-orthogonal orbitals but includes all possible spin coupling schemes: both the orbitals and the mixing coefficients for different spin components are simultaneously optimized and the general forms of the orbitals are not constrained in any way. The essentially *atomic* character of the optimal orbitals is thus of real significance and is not merely an artifact of the calculation.

Here we show that, in a VB calculation, the full-configuration interaction (CI) limit of the lowest triplet stat of cyclobutadiene  $\alpha$ -electron system may be quite closely approached, using only two covalent structures, by increasing the mutual overlap of neighbouring orbitals (see refs. 8-10). In the following we will discuss separately the use of classical structures and of spin-optimized theory, due to Gerratt *et al.*. The cyclobutadiene is regarded as a plane square molecule and we take the internuclear distance from the current literature<sup>11</sup>.

Optimization of orbitals in a VB-type wavefunction is not new: it was introduced by Goddard<sup>12</sup>. The Goddard method selects some complete set of functions  $x_\mu$  and expands each atomic orbital  $\phi_i$  in terms of these

$$\phi_i = \sum_{\mu} C_{\mu i} x_{\mu}$$

The resulting finite set of nonlinear algebraic equations for the  $C_{\mu i}$  can be readily solved iteratively, and the resulting wavefunction can probably be made approach the exact solutions by choosing larger and larger basis sets. Further, the orbital exponents are also optimized in this method. This orbital-optimized theory obviously must lead to results of great precision, but it has a very heavy computational penalty. The approach of the present paper, though not leading to wavefunctions of quite such high accuracy, does not suffer from such disadvantage and may have a more direct appeal to the chemist.

## 2. Cyclobutadiene: The classical VB approach

The cyclobutadiene  $\pi$ -electron system is a simple system and has four electrons and four atomic orbitals. The earliest non-empirical VB calculations on this molecule<sup>2b</sup> correctly predicted a lowest triplet state of  ${}^3A_2$ -symmetry for the square planar conformation. If the four AOs are denoted by  $a, b, c, d$ , reading anticlockwise round the square, the Rumer diagrams for the spin couplings are



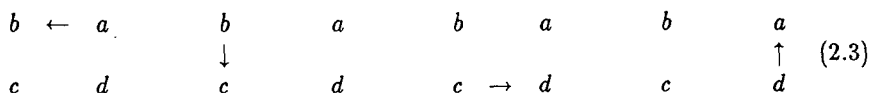
with associated spin functions

$$\begin{aligned}
 \theta_1 &= 1/\sqrt{2}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]\alpha(s_3)\alpha(s_4) \\
 \theta_2 &= 1/\sqrt{2}[\alpha(s_2)\beta(s_3) - \beta(s_2)\alpha(s_3)]\alpha(s_1)\alpha(s_4) \\
 \theta_3 &= 1/\sqrt{2}[\alpha(s_3)\beta(s_4) - \beta(s_3)\alpha(s_4)]\alpha(s_1)\alpha(s_2) \\
 \theta_4 &= 1/\sqrt{2}[\alpha(s_4)\beta(s_1) - \beta(s_4)\alpha(s_1)]\alpha(s_3)\alpha(s_3) \quad (2.1)
 \end{aligned}$$

Of these functions, only three are linearly independent. We can easily show that

$$\theta_4 = -(\theta_1 + \theta_2 + \theta_3) \quad (2.2)$$

The VB structures, represented by



will correspond to the functions

$$\phi_1 = \hat{A}[a \ b \ c \ d \ \theta_1]$$

$$\phi_2 = \hat{A}[a \ b \ c \ d \ \theta_2]$$

$$\phi_3 = \hat{A}[a \ b \ c \ d \ \theta_3]$$

$$\phi_4 = \hat{A}[a \ b \ c \ d \ \theta_4] \tag{2.4}$$

where

$$\phi_4 = -(\phi_1 + \phi_2 + \phi_3)$$

Here  $\hat{A}$  is the antisymmetrizer operator and the functions are not normalized. The orbitals are equivalent, but otherwise arbitrary and non-orthogonal.

The symmetry properties of the classical VB structures constructed in this way are simple and have been fully discussed elsewhere<sup>2b</sup>.

The effect of the spatial symmetry operations of the D<sub>2</sub>-point group on  $\phi_1, \phi_2, \phi_3, \phi_4$  is given below

<i>R</i>	<i>E</i>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>4</sub>	$\bar{C}$ <sub>4</sub>	<i>C</i> <sub>2</sub> <sup>1</sup>	<i>C</i> <sub>2</sub> <sup>2</sup>	<i>C</i> <sub>2</sub> <sup>23</sup>	<i>C</i> <sub>2</sub> <sup>12</sup>
<i>R</i> φ <sub>1</sub>	φ <sub>1</sub>	φ <sub>3</sub>	-φ <sub>4</sub>	-φ <sub>2</sub>	φ <sub>4</sub>	φ <sub>2</sub>	-φ <sub>3</sub>	-φ <sub>1</sub>
<i>R</i> φ <sub>2</sub>	φ <sub>2</sub>	φ <sub>4</sub>	-φ <sub>1</sub>	-φ <sub>3</sub>	φ <sub>3</sub>	φ <sub>1</sub>	-φ <sub>2</sub>	-φ <sub>4</sub>
<i>R</i> φ <sub>3</sub>	φ <sub>3</sub>	φ <sub>1</sub>	-φ <sub>2</sub>	-φ <sub>4</sub>	φ <sub>2</sub>	φ <sub>4</sub>	-φ <sub>1</sub>	-φ <sub>3</sub>
<i>R</i> φ <sub>4</sub>	φ <sub>4</sub>	φ <sub>2</sub>	-φ <sub>3</sub>	-φ <sub>1</sub>	φ <sub>1</sub>	φ <sub>3</sub>	-φ <sub>4</sub>	-φ <sub>2</sub>

there for example *C*<sub>2</sub><sup>1</sup> and *C*<sub>2</sub><sup>12</sup> refer to the two-fold axes through vertices 1 and midway between 1 and 2, respectively. The character operator which produces a function of <sup>9</sup>A<sub>2</sub>-symmetry is

$$\rho = \sum_R \chi(R)R = [E + C_4 + \bar{C}_4 + C_2 - C_2^1 - C_2^2 - C_2^{23} - C_2^{12}]$$

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Making use of this operator we get

$$\rho\phi_1 = \rho\phi_3 = -\rho\phi_2 = -\rho\phi_4 = 2(\phi_1 + \phi_3 - \phi_2 - \phi_4) = 4(\phi_1 + \phi_3) \quad (2.5)$$

The only wavefunction of  ${}^9A_2$ -symmetry, which can be constructed from the covalent structures, is thus (unnormalized)

$$\psi = (\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

and from eq.(2.5) we obtain

$$\psi = (\phi_1 + \phi_3) = \hat{A}[a \ b \ c \ d \ (\theta_1 + \theta_3)] \quad (2.6)$$

The mixing of the two structures is evidently symmetry determined. Polar structures are treated in a similar way.

From eq.(2.6) we can see that the lowest triplet state of the cyclobutadiene  $\pi$ -system depends only on the two linearly independent covalent functions  $\phi_1$  and  $\phi_3$ . As it should be, the numerical result agrees with this theoretical result.

The above argument does not depend on the nature of the orbitals used. The effectiveness of the covalent structures in describing the bonding can be improved by increasing the mutual overlap of neighbouring orbitals<sup>8-10</sup>, in accordance with what used to be called the criterion of maximum *overlap*<sup>13</sup>. In the present context, the appropriate linear combinations of the original AOs will be

$$\begin{aligned} \bar{a} &= a + \lambda(b + d) + \mu c \\ \bar{b} &= b + \lambda(a + c) + \mu d \\ \bar{c} &= c + \lambda(b + d) + \mu a \\ \bar{d} &= d + \lambda(a + c) + \mu b \end{aligned} \quad (2.7)$$

where  $\lambda$  and  $\mu$  are numerical parameters. The parameter values will be chosen to increase the overlap.

Orbitals of this kind (eq.(2.7)) were first used by Coulson and Fisher<sup>14</sup> and later by Mueller and Eyring<sup>15</sup> who described them as *semi-localized*; but they were never widely adopted owing to the chemical difficulties arising from the use of heavily non-orthogonal functions.

A general wavefunction of  ${}^3A_2$ -symmetry, instead of eq.(2.6), will then be

$$\psi = \hat{A}[\bar{a}\bar{b}\bar{c}\bar{d}(\theta_1 + \theta_3)] \quad (2.8)$$

where the two parameters in the orbitals eq. (2.7) may be varied in order to minimize the energy.

To illustrate the results it will be sufficient to perform three calculations: (i) a full Configuration-Interaction (CI) calculation using the basis orbitals ( $a, b, c, d$ ); (ii) a single-configuration calculation (2 covalent structures ( $\phi_1, \phi_3$ )) using the AOs ( $\mathbf{a}, \mathbf{b}, c, d$ ), and (iii) a single-configuration calculation (2 covalent structures ( $\phi_1, \phi_3$ )) using the modified AOs in eq.(2.7). The full-CI calculation (i) yields the basic-set limit and gives a lowest  ${}^3A_2$ -state with energy  $E({}^3A_2) = -3.73054E_h$ .<sup>\*</sup> The single-configuration calculation (ii) gives  $E({}^3A_2) = -3.63680E_h$ .

In the latter case (iii), we take the modified orbitals from eq.(2.7) but with  $\mu = 0$  (for reasons which will be clear presently), then the wavefunction taken from eq. (2.8) will be a one-parameter variation function. Optimization is achieved when  $\lambda = 0.225$  and the resulting energy is found to be  $E({}^3A_2) = -3.72867E_h$ . This constitutes a very good result, differing only about 0.05% from the full 15-structure CI calculation.

It is well known that a complete configuration-interaction calculation in the molecular orbital (MO) framework is equivalent to a complete multi-structure calculation in the valence-bond framework if the same values of the integrals are used. Then the energy obtained from eq.(2.8) is also approximately equal to the energy obtained from a complete MO-SCF-CI.

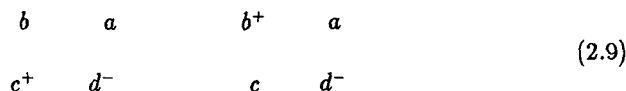
To understand this result it is necessary to consider in more detail the full-CI calculation. There are 15 linearly independent triplet structures: 3 covalent

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<sup>\*</sup> All energies are in units of  $E_h$  (Hartrees).

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(shown above), 8 singly-polar (short-bonded) and 4 singly polar (long-bonded). Typical members of the set are



being respectively, singly-polar short-bonded, and singly-polar long bonded.

By expanding the product  $\bar{a}\bar{b}\bar{c}\bar{d}$  involved in the single-configuration calculation (iii), it is easy to verify that the wave function eq.(2.8) becomes a linear combination of the covalent and singly-polar short-bonded  ${}^3A_2$ -symmetry functions. Making  $\mu = 0$  in eq. (2.7) is the same as eliminating the contribution of the singly-polar long-bonded structures, and we know that the contribution of these structures to the energy is small in general. This was readily verified in our case. This is the reason that the energy obtained with the wavefunction of eq.(2.8) is close to the full-CI energy.

### 3. Cyclobutadiene: the spin-optimized VB approach

In the approach due to Gerratt and collaborators, the wavefunction is taken to be

$$\psi = \hat{A}[\varphi_1\varphi_2\varphi_3\varphi_4(c_1\bar{\theta}_1 + c_2\bar{\theta}_1 + c_3\bar{\theta}_1)] \tag{3.1}$$

where the spin functions correspond to branching diagram paths. The first corresponds to the Rumer function  $\theta_1$ . The orbitals are linear combinations of the localized basis functions  $a, b, c, d$ , and are optimized along with the coefficients  $c_1, c_2$  and  $c_3$ .

The orbitals resulting from the complete optimization program, the lowest triplet state of cyclobutadiene  $\pi$ -system

$$\varphi_1 = a + \lambda(b + d) + \mu c$$

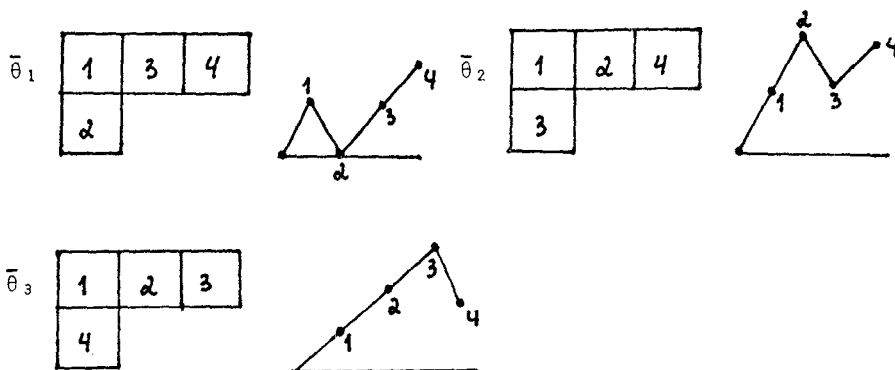
$$\varphi_2 = b + \lambda(a + c) + \mu d$$

$$\varphi_3 = c + \lambda(b + d) + \mu a$$

$$\varphi_4 = d + \lambda(a + c) + \mu b \tag{3.2}$$

coincide with the AOs (normalized) of eq. (2.7). Then, we can see from eq.(2.7) or eq.(3.2) that the atomic orbitals of  $^3A_2$ -state are deformed but remain *localized*. The same occurs with the benzene molecule (see ref.7). In recent calculations of the  $^1B_{2g}$ -ground state of the cyclobutadiene  $\pi$ -electron system, Cooper<sup>16</sup> has shown that there are two equivalent *delocalized* pairs of orbitals, each containing a symmetrical and an antisymmetrical combination of diagonally related AOs.

To reconcile this result with that obtained in the previous section we examine now the spin factor. The branching diagram functions carry standard irreducible representations of the symmetric group and they are associated with standard Young tableaux:



where the first function  $\bar{\theta}_1$  coincides with a single Rumer (spin-paired) function - in this case  $\theta_1$  in eq. (2.1). It is easily verified that the other branching diagram functions ( $\bar{\theta}_1, \bar{\theta}_3$ ) can be written in terms of the linearly independent spin functions of eq.(2.1). The resultant (normalized) functions are

$$\bar{\theta}_2 = 2/\sqrt{3}(1/2 \theta_1 + \theta_2)$$



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$$\bar{\theta}_3 = \left[ \frac{12\sqrt{3}}{10\sqrt{3}-3} \right]^{1/2} \left( \frac{\theta_1}{3} + \frac{2\theta_2}{3} + \theta_3 \right) \quad (3.3)$$

On putting these results in eq.(3.1) we obtain the spin-optimized coefficients. They are

$$c_1 = 1$$

$$c_2 = -\sqrt{3}/3 \quad (3.4)$$

$$c_3 = \left( \frac{12\sqrt{3}}{10\sqrt{3}-3} \right)^{-1/2}$$

When the orbitals are appropriately chosen, the coefficient values thus ensure that the function will have  ${}^3A_1$ -symmetry.

Apart only from normalization, we obtain from the above results that the spin-optimized VB resultant wavefunction, as given below

$$\psi = \hat{A}[\varphi_1\varphi_2\varphi_3\varphi_4(\theta_1 + \theta_3)] \quad (3.5)$$

is identical in form to eq.(2.8). This means that if we made also  $\mu = 0$  in eq.(3.2) we should obtain the same energy from the lowest triplet state of cyclobutadiene  $\pi$ -electron system as obtained by the classical VB approach.

#### 4. Conclusion

The delocalized orbitals, which sometimes result from a fully optimized VB calculation, are not always an essential feature of the wavefunction; for it is sometimes possible to find a transformation which expresses the result in terms of classical structures only. The possibility of obtaining delocalized orbitals depends upon the occurrence of an invariance in the spin factor. In the case of the square planar system, the spin factor for the  ${}^1B_{2g}$ -ground state is invariant under the spin permutations  $P_{13}^1$  and  $P_{24}^1$  ref. 9. The diagonally delocalized pairs may then be eliminated in favour of localized equivalent orbitals (modified AOs) located

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on the four centers, and the wavefunction then becomes a sum of two classical (Kekule-type) structures<sup>6</sup>.

In our case ( $^3A_2$ -state of the cyclobutadiene  $\bar{\alpha}$ -system), the spin factor does not possess this invariant property, but the description in terms of the classical structures remains valid; the localized orbitals (eq.(2.7)) are uniquely determined and the possibility of transforming to delocalized orbitals does *not* exist. This conclusion is consistent with other recent calculations, e.g. on the benzene molecule<sup>7</sup> where the classical structures (Kekule-type) arise naturally from the full optimization and where it is easily demonstrated that the spin function does not possess the symmetry required for passing to an alternative description in terms of delocalized orbitals.

From the above discussion, we conclude that the occurrence of delocalized orbitals depends on the symmetry of the state - the lowest triplet state of the cyclobutadiene  $\pi$ -system has  $^3A_2$ -symmetry (localized orbitals) and the ground state has  $^1B_{2g}$ -symmetry (delocalized orbitals).

From our results we can conclude also that it is possible to generate, in general, an excellent approximation to a full-CI wavefunction with a few structures, using modified AOs as in eq.(2.7).

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**Resumo**

Aplica-se a teoria de ligação de valência, dentro da aproximação *ab initio*, para calcular a energia mais baixa do tripleto da molécula do ciclobutadieno; considera-se somente os elétrons  $\pi$ . Modificando convenientemente os orbitais atômicos do sistema, verifica-se que com poucas estruturas pode-se obter resultados muito próximos a um cálculo completo de interação de configuração. Discute-se separadamente as aproximações clássicas e spin-otimizado da teoria de ligação de valência.