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Classical structures in modern valence bond theory*

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The results of some recent *ab initio* valence bond calculations, in which both structure coefficients and orbital forms are optimized, are analysed. The origin of structures in which the optimum orbitals are no longer "atomic" in character but instead *delocalized*, is traced back to the presence of certain symmetries in the wavefunction. When such symmetries exist it is possible to choose alternative linear combinations of the delocalized orbitals and to rewrite the wavefunction in terms of VB structures of "classical" form. The advantages of the classical structures are discussed in the context of a simple example - a square planar conformation of four hydrogen atoms.

Key words: Valence bond theory — VB structures — Spin eigenfunctions

Valence bond theory in its modern form [3, 6, 13] is capable of giving a good account of both localized and non-localized bonding, using wavefunctions which are compact, accurate, and easy to interpret using the language of classical chemistry. Thus [2] the benzene pi-electron system is well described as a mixture of two Kekule-type structures, provided the $2p_\pi$ AOs on the six carbon atoms are replaced by slightly modified AOs which, whilst still being localized and equivalent (i.e. permuted under the D_{6h} symmetry operations), have somewhat stronger overlap with their neighbours. In fact, the corresponding wavefunction gives a ground-state energy exceedingly close to the full-CI limit obtained using 5 "covalent" and 170 "ionic" or "polar" structures constructed from a minimal basis. This truly remarkable result suggests that, in spite of the well-known technical difficulties of implementing *ab initio* valence bond calculations, many

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

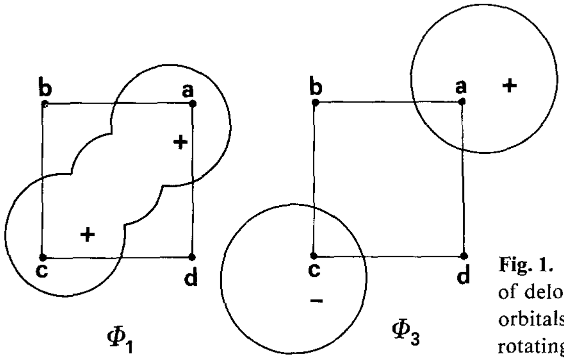

Fig. 1. Schematic representation of one pair of delocalized orbitals in cyclobutadiene. The orbitals of the second pair are obtained on rotating through 90°.

of the concepts introduced by Heitler, London, Pauling and the other pioneers of the 'thirties' were essentially sound and are still of great potential value.

In the approach used by Gerratt and coworkers, 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 simultaneous 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.

When similar calculations are performed on cyclobutadiene, however, the resultant orbitals have a quite unfamiliar form (Fig. 1) and yield structures which bear no resemblance to the "bonded" structures of orthodox VB theory[1]. The object of this note is to show that even in such a situation (which appears to be rather rare) the bonding can be equally well described using only the classical structures. That being so, there are obvious conceptual advantages in transforming to localized orbitals and the chemically meaningful structures to which they lead, whenever possible. To discuss this possibility we shall use the simplest possible 4-electron analogue of the cyclobutadiene π-system, namely the plane square conformation of four hydrogen atoms. In this way we eliminate any complications or uncertainties arising from the presence of a σ-bonded core. It is also convenient to adopt a minimal basis (four 1s orbitals) and to discuss separately the use of classical structures and of the spin-optimized theory due to Gerratt et al.

2. H_4: the classical VB approach

The earliest non-empirical VB calculations on the cyclobutadiene π-electron system [8] correctly predicted a $^1B_{2g}$ ground state for the square planar conformation: attention will therefore be focussed on the corresponding state of H_4. If

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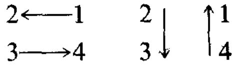
[1] To be referred to as "classical VB structures"

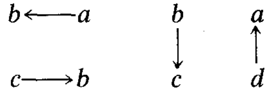
the four AOs are denoted by a, b, c, d, reading anticlockwise round the square, and the Rumer diagrams for the spin couplings are



with associated spin functions

$$\Theta_1 = \theta(1,2)\theta(3,4), \qquad \Theta_2 = \theta(2,3)\theta(1,4),$$
$$\theta(i,j) = 2^{-1/2}[\alpha(i)\beta(j) - \beta(i)\alpha(j)] \tag{2.1}$$

then the VB structures, represented by



(2.2)

will correspond to the functions

$$\Phi_1 = \mathscr{A}[abcd\Theta_1]$$
$$\Phi_2 = \mathscr{A}[abcd\Theta_2]. \tag{2.3}$$

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

The symmetry properties of the classical VB structures constructed in this way are particularly simple and have been fully discussed elsewhere [8]. A symmetry operation sends every structure into another structure, obtained by operating on the diagram and attaching a factor $(-1)^\nu$ where ν is the number of even cycles in the orbital permutation to which the symmetry operation leads; a further factor -1 is included for every arrow reversal that may be needed in making the "image" match one of the original structures. There is then no difficulty, knowing the irreducible representations of the molecular point group, in generating by inspection the linear combinations of structures (covalent, polar, or multiply-polar) that belong to any desired symmetry species.

In the present instance, the effect of the spatial symmetry operations of D_4 on Φ_1 and Φ_2 is very simple:

$\mathscr{R}$	$\mathscr{E}$	$\mathscr{C}_2$	$\mathscr{C}_4$	$\bar{\mathscr{C}}_4$	$\mathscr{C}_2^{(1)}$	$\mathscr{C}_2^{(2)}$	$\mathscr{C}_2^{(23)}$	$\mathscr{C}_2^{(12)}$
$\mathscr{R}\Phi_1$	Φ_1	Φ_1	$-\Phi_2$	$-\Phi_2$	$-\Phi_2$	$-\Phi_2$	Φ_1	Φ_1
$\mathscr{R}\Phi_2$	Φ_2	Φ_2	$-\Phi_1$	$-\Phi_1$	$-\Phi_1$	$-\Phi_1$	Φ_2	Φ_2,

where for example the rotations $\mathscr{C}_2^{(1)}$ and $\mathscr{C}_2^{(12)}$ refer to the two-fold axes through vertices 1 and midway between 1 and 2, respectively. The character operator which produces a function of B_2 symmetry is

$$\rho = \sum_R \chi(\mathscr{R})\mathscr{R} = (\mathscr{E} + \mathscr{C}_2 - \mathscr{C}_4 - \bar{\mathscr{C}}_4 - \mathscr{C}_2^{(1)} - \mathscr{C}_2^{(2)} + \mathscr{C}_2^{(23)} + \mathscr{C}_2^{(12)})$$

and hence $\rho\Phi_1 = \rho\Phi_2 = 4(\Phi_1 + \Phi_2)$. The only wavefunction of this symmetry (B_{2g} when reflection across the molecular plane is taken into account), which can be constructed from the linearly independent covalent structures is thus (unnormalized)

$$\Psi = (\Phi_1 + \Phi_2) = \mathscr{A}[abcd(\Theta_1 + \Theta_2)] \tag{2.4}$$

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

The above argument does not depend on the nature of the orbitals used, as long as they correctly represent the identity of the four atoms by transforming into one another under symmetry operations and are thus "equivalent" in the usual sense. The effectiveness of the covalent structures in describing the bonding can be improved by increasing the mutual overlap of neighbouring orbitals, in accordance with what used to be called (see [4]) "the criterion of maximum overlap". Modified AOs of this kind were first used by Coulson and Fischer [5] and later by Mueller and Eyring [11] who called them "semi-localized" orbitals: their significance has been revealed in a very striking way in the recent work of Cooper et al. [2], which shows that their use drastically reduces the need to include polar structures. In the present context, the appropriate semi-localized combinations of the original AOs will be

$$\begin{aligned} \bar{a} &= a + \lambda(b+d) + \mu c \\ \bar{b} &= b + \lambda(a+c) + \mu d \\ \bar{c} &= c + \lambda(b+d) + \mu a \\ \bar{d} &= d + \lambda(a+c) + \mu b, \end{aligned} \tag{2.5}$$

where λ and μ are numerical parameters. It must be stressed that although these orbitals formally resemble the Löwdin orthogonalized AOs, which were introduced in VB theory (see [7]) in order to eliminate non-orthogonality difficulties, the parameter values will be chosen to *increase* the overlap.

A general one-configuration wavefunction of ${}^1B_{2g}$ symmetry will then be, instead of (2.4),

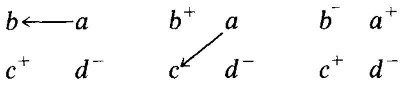
$$\Psi = \mathscr{A}[\bar{a}\bar{b}\bar{c}\bar{d}(\Theta_1 + \Theta_2)], \tag{2.6}$$

where the two parameters in the orbitals (2.5) may be varied in order to minimize the energy.

To illustrate the results it will be sufficient to assume a minimal basis and to perform two calculations: (i) a full-CI calculation using the basis orbitals (a, b, c, d); and (ii) a single-configuration calculation (2 covalent structures), using the modified AOs in (2.5). The full-CI calculation yields the basis-set limit and gives a lowest ${}^1B_{2g}$ state with energy $E({}^1B_{2g}) = -1.64064\mathrm{E_h}$.

The modified orbitals are taken as in (2.5) but with $\mu = 0$ (for reasons which will be clear presently), and the corresponding ${}^1B_{2g}$ combination of Kekulé-type structures in (2.6) will thus be a 1-parameter variation function. Optimization is achieved when $\lambda = 0.116$ and the resultant energy is found to be $E(^1B_{2g}) = -1.64064\mathrm{E_h}$-coincident with the basis-set limit for the full 20-structure CI calculation!

To understand this result it is necessary to consider in more detail the full-CI calculation. There are 20 linearly independent singlet structures: 2 covalent (shown above), 8 singly-polar (short-bonded), 4 singly-polar (long-bonded), and 6 doubly-polar. Typical members of the set are



(2.7)

being respectively singly-polar short-bonded, singly-polar long-bonded, and doubly-polar. The corresponding functions contain orbital products with substitutions (e.g. for the first structure, *abdd*, with *d* in place of *c*) and an appropriate Rumer-type spin factor. By using the rules [8] for constructing the combinations of given point group symmetry it is then easy to show that there is a single unique combination of polar structures of $^1B_{2g}$ type; it contains only the 8 singly-polar[2] short-bonded structures - no $^1B_{2g}$ combinations of the remaining types being found. In other words, the full-CI approximation of $^1B_{2g}$ symmetry is a *one-parameter* variation function. It is not important how this parameter is introduced: in the calculation based on only two Kekulé-type structures it may be introduced by modifying the AOs according to (2.5) and it is easily verified by expanding the product $\bar{a}\bar{b}\bar{c}\bar{d}$ that the wavefunction (2.6) becomes a linear combination of the covalent and singly-polar (short-bonded) $^1B_{2g}$ symmetry functions, the parameter μ being redundant. It is evident that modification of the AOs within a very compact VB function is capable of providing a much more efficient route to an accurate wavefunction than detailed consideration of all the terms in a full-CI calculation.

3. H$_4$: the spin-optimized VB approach

In the approach due to Gerratt and collaborators, the wave-function is taken to be

$$\Psi = \mathscr{A}[\phi_1\phi_2\phi_3\phi_4(c_1\Theta_{tt} + c_2\Theta_{ss})], \tag{3.1}$$

where the spin functions correspond to branching diagram paths, respectively, "up-up-down-down" (triplet/triplet, coupled to singlet) and "up-down-up-down" (singlet/singlet), the latter corresponding to the Rumer function Θ_1. The orbitals (all allowed to be different) are linear combinations of the localized basis functions *a, b, c, d,* and are optimized along with the coefficients c_1, c_2.

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[2] It is noteworthy that a reference function consisting of non-polar structures is not variationally stable against mixing with *singly*-polar (i.e. "mono-excited") functions; a Brillouin-type theorem does not apply and in the present example the stabilization is due *solely* to the admixture of singly-polar structures

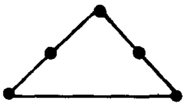
Recent calculations [1] confirm that the orbitals resulting from the complete optimization program, with no constraints whatever, are of the same "diagonal" form as in the case of the cyclobutadiene π-system (Fig. 1). They are

$$\begin{aligned}\phi_1&=(a+c)+\lambda(b+d)\\ \phi_2&=(b+d)+\lambda(a+c)\\ \phi_3&=(a-c)\\ \phi_4&=(b-d).\end{aligned}\tag{3.2}$$

There are thus two equivalent delocalized pairs, each containing a symmetrical and an antisymmetrical combination of diagonally related AOs; and there is no evidence of the short-bonded (Kekulé-type) structures which are a cornerstone of the classical VB theory. The coefficients c_1 and c_2 converge towards values $-1/2$ and $+\sqrt{3}/2$ and thus appear to be symmetry-determined.

To reconcile this result with that obtained in the previous section we first examine the spin factor. The branching diagram functions carry standard irreducible representations of the symmetric group (see, for example [12]) and are associated with standard Young tableaux. In standard order (last-latter sequence) they are

$$\Theta_{tt}: \quad \begin{array}{|c|c|}\hline 1 & 2\\ \hline 3 & 4\\ \hline\end{array}$$



$$\Theta_{ss}: \quad \begin{array}{|c|c|}\hline 1 & 3\\ \hline 2 & 4\\ \hline\end{array}$$

where the last function Θ_{ss}, arising from the bottom path, coincides, as always, with a single Rumer (spin-paired) function - in this case Θ_1 in (2.1). The other branching diagram function, Θ_{tt}, can be obtained (e.g. Ref. [10]) by taking a second Rumer function, Θ_3 with spin pairings $1\rightarrow 3$ and $2\rightarrow 4$ (following the columns in the standard tableau) and Schmidt orthogonalizing against Θ_1. Thus,

$$\Theta_{tt}=M(\Theta_3-\lambda\Theta_1).$$

It is easily verified that $\lambda=\langle\Theta_1|\Theta_3\rangle=1/2$; and the resultant (normalized) function, with standard phase, is

$$\Theta_{tt}=(2/\sqrt{3})(\Theta_3-\tfrac{1}{2}\Theta_1).\tag{3.3}$$

Although Θ_3 corresponds to a non-standard Rumer diagram, with crossed links, it is easily related to the classical structures (2.2) using a well-known identity: in fact $\Theta_3=\Theta_1-\Theta_2$ and hence (3.3) becomes

$$\Theta_{tt}=(2/\sqrt{3})(\tfrac{1}{2}\Theta_1-\Theta_2)\tag{3.4}$$

in terms of the spin functions (2.1) associated with the Kekulé-type structures (2.2). On putting these results in (3.1), with the spin-optimized coefficients, we obtain at once (apart from normalization)

$$\Psi=\mathscr{A}[\phi_1\phi_2\phi_3\phi_4(\Theta_1+\Theta_2)],\tag{3.5}$$

which is identical in form with (2.6); the coefficient values thus ensure that, when the orbitals are appropriately chosen, the function will have ${}^1B_{2g}$ symmetry.

The last step is to account for the unusual form of the orbitals given in (3.2). The possibility of finding such forms arises in fact from a peculiarity of the spin function $\Theta = (\Theta_1 + \Theta_2)$. It is clear, either from the Rumer diagrams or from expansion into primitive spin products, that Θ is invariant under the spin permutations P^s_{13} and P^s_{24}. The antisymmetry of Ψ in (2.6) then implies that the function changes sign under the corresponding transpositions of spatial variables or, equivalently, of *orbitals* $\bar{a}$, $\bar{c}$ and $\bar{b}$, $\bar{d}$. The spatial factors $\bar{a}(\boldsymbol{r}_1)\bar{c}(\boldsymbol{r}_3)$ and $\bar{b}(\boldsymbol{r}_2)\bar{d}(\boldsymbol{r}_4)$ in (2.6) may thus be replaced by (disregarding normalization)

$$\bar{a}(\boldsymbol{r}_1)\bar{c}(\boldsymbol{r}_3) - \bar{c}(\boldsymbol{r}_1)\bar{a}(\boldsymbol{r}_3), \qquad \bar{b}(\boldsymbol{r}_2)\bar{d}(\boldsymbol{r}_4) - \bar{d}(\boldsymbol{r}_3)\bar{b}(\boldsymbol{r}_4)$$

respectively. But such antisymmetrized products (determinants) are left invariant by a linear transformation of orbitals - which may consequently be replaced by their sums and differences, namely, using (2.5),

$$\begin{aligned}
\bar{a} + \bar{c} &= (1+\mu)(a+c) + 2\lambda(b+d) \\
\bar{a} - \bar{c} &= (1-\mu)(a-c) \\
\bar{b} + \bar{d} &= (1+\mu)(b+d) + 2\lambda(a+c) \\
\bar{b} - \bar{d} &= (1-\mu)(b-d).
\end{aligned} \tag{3.6}$$

These orbitals, with renormalization and redefinition of parameters, coincide with those obtained in the fully optimized VB calculations of Cooper [1] for H_4 and Cooper et al (1986), for cyclobutadiene. On replacing $\bar{a}$, $\bar{b}$, $\bar{c}$, $\bar{d}$ in (2.6) by the linear combinations (3.6), the classical two-structure function (2.6) is transformed into (3.1). The redundancy of the parameter μ is obvious, since it affects only the normalization; and with an appropriate choice of the single remaining parameter λ either function is capable of yielding the basis-set limit of $E({}^1B_{2g})$.

4. Conclusion

The delocalized orbitals which sometimes result from a (one-configuration) fully optimized VB calculation, and which are associated with non-classical structures, are not always an esssential feature of the wavefunction; for it may often be possible to find a transformation which expresses the result in terms of classical structures only. In fact, the possibility of obtaining *de*localized orbitals appears to present itself only in exceptional circumstances: it depends upon the occurrence of an invariance in the spin factor of the wave-function (generally a mixture of several branching diagram functions) against one or more subgroups of spin permutations. In the case of the square planar system, considered for here illustration, the spin factor for the ${}^1B_{2g}$ ground state (which is a symmetry-determined mixture) is invariant under two such subgroups. The diagonally delocalized pairs may then be eliminated in favour of localized equivalent orbitals (modified AOs) located on the four centres, and the wavefunction then becomes a sum of two classical (Kekulé-type) structures. In other cases (e.g., *cis*- or *trans*-butadiene, or H_4 in a rectangular conformation), the spin factor does not possess this invariance property; the description in terms of classical structures remains valid; the localized orbitals are uniquely determined; and the possibility of transforming to *de*localized orbitals does not exist. This conclusion is consistent with other recent calculations e.g. on the benzene molecule (Cooper et al. [2]) where the classical structures 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.

Needless to say, the fact that by mixing together a few Kekulé-type structures (embodying all the intuitions and experience of a 100 years of classical chemistry) it is sometimes possible to generate an excellent approximation to a "full-CI" wavefunction has enormous implications for the theory of the chemical bond.

Acknowledgements. Thanks are due to Joseph Gerratt for drawing my attention to the occurrence of delocalized orbitals in spin-coupled VB calculations, and for many stimulating conversations during a recent visit to Pisa; and also to David Cooper for informing me of his results on H_4 and for a lively exchange over the European network. A full account of the method used in this work (McWeeny [9]) will be published elsewhere.

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Note added in proof. A referee has objected that *if* the spin-optimized coefficients in (3.1) do not have *exactly* the values assumed then the argument which shows the equivalence of the two descriptions is invalid and the delocalized description must be the correct one. It is easily shown, however, that when the delocalized orbitals (3.2) are used in (3.5) the resultant *many*-electron function cannot be of pure B_{2g} symmetry unless Θ_1 and Θ_2 appear with *identical* coefficients. In other words, the coefficients c_1 and c_2 in the alternative form (3.5) have values determined, in this case, by *spatial symmetry* rather than by optimization of the energy. The equivalence of the two descriptions is therefore a rigorous result, associated with the invariances referred to in Sect. 4.

The reason that Cooper et al. sometimes obtain delocalized (i.e. MO-type) orbitals, belonging to irreducible representations of the molecular point group, appears to be that they satisfy eigenvalue equations in which the *one*-electron effective Hamiltonian possesses a certain degrees of symmetry. The construction of a *many*-electron wavefunction of pure symmetry species is then a separate, and not always trivial, exercise. One of the great strengths of the classical VB approach, in which not only the orbitals but also the structures are simply permuted under spatial symmetry operations, is the ease with which *many*-electron functions of any desired symmetry species may be constructed.