

GENERALIZED VALENCE BOND WAVEFUNCTIONS FOR THE LOW LYING STATES OF METHYLENE*

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Generalized valence bond (GVB) calculations are reported for the 3B_1 , 1A_1 , and 1B_1 states of the CH_2 molecule. The GVB method is discussed and compared with other multi-configuration and separated pair methods. The lowest singlet state (1A_1) is found to lie 0.50 eV about the lowest triplet state (3B_1) and the 1B_1 - 1A_1 separation is found to be 1.40 eV.

I. Method

In the GVB approach [1] we replace the orbitals ϕ_i which are doubly occupied in the Hartree-Fock (HF) wavefunction:

$$\psi_{HF} = \mathcal{A}[\phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta \dots \phi_n\alpha\phi_n\beta] \quad (1)$$

by singlet-coupled pairs of orbitals:

$$\psi_{GVB} = \mathcal{A}[(\phi_{1a}\phi_{1b} + \phi_{1b}\phi_{1a})(\phi_{2a}\phi_{2b} + \phi_{2b}\phi_{2a}) \dots (\phi_{na}\phi_{nb} + \phi_{nb}\phi_{na})\alpha\beta\alpha\beta \dots \alpha\beta]. \quad (2)$$

For a state of spin S the last $2S$ orbitals are usually taken as in HF to be singly occupied with up-spin α . Rather than using atomic orbitals in (2) as in the VB method [2], we solve variationally for the optimum orbitals of (2). In addition to yielding lower energies than HF, the GVB approach also leads to proper treatment of the breaking of bonds and offers the conceptual advantage of leading to localized orbitals in close correspondence to the qualitative ideas of bonding and nonbonding pairs of molecules.

As was originally shown by Hurley et al. [3], each pair in (2) can be represented in terms of two natural orbitals (NO's),

$$\begin{aligned} \phi_{ia}(1)\phi_{ib}(2) + \phi_{ib}(1)\phi_{ia}(2) \\ = C_{1i}\phi_{1i}(1)\phi_{1i}(2) + C_{2i}\phi_{2i}(1)\phi_{2i}(2). \end{aligned} \quad (3)$$

(Coulson and Fischer [4] also discussed GVB-like descriptions for H_2 .) In this representation GVB is seen to be a special case of the separated pair [5-7], strongly orthogonal geminal [8-10], self-consistent group [11, 12], and multi-configuration SCF [13-16] wavefunctions (where in general more than two NO's are used) [17].

In GVB, as in these other methods, the strong orthogonality constraint [18] is imposed, i.e., the NO's of pair i are taken to be orthogonal to each other as well as to the NO's of the other pairs. This means that the GVB orbitals satisfy the relations

$$\begin{aligned} \langle \phi_{ia} | \phi_{ib} \rangle &\neq 0, \\ \langle \phi_i | \phi_j \rangle &= 0 \text{ otherwise.} \end{aligned} \quad (4)$$

Without these orthogonality constraints the optimum wavefunction of the form (2) is the G1 wavefunction [19], and hence GVB is a special case of G1.

As has been shown by Kutzelnigg [7] and by Silver et al. [6], the total electronic energy of (2) has the form

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$$E = \sum_k f_k h_k + \sum_{k,l} a_{kl} J_{kl} + b_{kl} K_{kl}, \quad (5)$$

where h is the one-electron hamiltonian (kinetic energy and nuclear attraction), $h_k = \langle k | h | k \rangle$, J_{kl} and K_{kl} are the usual Coulomb and exchange integrals, and f_k is the occupation number (f_k will be 2 for doubly-occupied orbitals, 1 for singly-occupied open-shell orbitals, and C_i^2 for GVB NO's).

Applying the variational principle to (5) (to obtain the optimum orbital ϕ_k) leads to the variational equations

$$H_k \phi_k = \epsilon_k \phi_k \quad k = 1, 2, \dots, M, \quad (6)$$

$$H_k = f_k \hat{h} + \sum_l a_{kl} \hat{J}_l + b_{kl} \hat{K}_l,$$

where M is the number of distinct orbitals and \hat{J}_l and \hat{K}_l are the Coulomb and exchange operators, respectively. To find the optimum orbitals of (5) the M equations (6) must be solved self consistently. (All doubly occupied orbitals may be taken to be eigenfunctions of the same hamiltonian.) The restriction that the orbitals of each pair be orthogonal to the orbitals of all other pairs leads to Lagrange multipliers in the variational equations (6). Rather than replacing these Lagrange multipliers through use of coupling operators, we use the OCBSE method [20] in which each GVB pair is solved for in the space orthogonal to the other occupied orbitals.

To obtain full optimization of the orbitals, the mixing of all occupied orbitals amongst themselves is optimized each iteration as discussed in ref. [22]. In this way the partition of the basis set is continually changed until self-consistency is attained. With the exceptions of a few strongly orthogonal geminal calculations on small diatomic molecules [6] and several multi-configuration SCF calculations [13–16] previous calculations [11, 23] have not fully optimized the orbitals since the total basis was partitioned into orthogonal sets to be used by the different orbitals and the partition was not iterated.

A good example of the importance of full optimization occurs in the case of ethane molecule where the Hartree–Fock wavefunction leads to a rotational barrier, 3.3 kcal, in good agreement with experiment (2.9 kcal). However, using the GVB form of wave-

function but not optimizing the orbitals fully, Klessinger [12] obtained a barrier of -5.1 kcal (eclipsed form lower rather than staggered). We carried out fully-optimized GVB calculations [1] on ethane and found a barrier of 3.1 kcal, showing the importance of full optimization.

2. The methylene molecule

Despite the great interest in the chemistry of methylene [25] only recently has the geometry of the ground state been firmly established and the separation of the lowest triplet and singlet states is still not known.

There are three important low-lying states of CH_2 , the $^3\text{B}_1$, $^1\text{A}_1$, and $^1\text{B}_1$ states. In the Hartree–Fock description each of these states involves a carbon 1s pair of orbitals ($1a_1$) and two pairs of orbitals ($2a_1$ and $1b_2$) primarily associated with the CH bonds. This leaves two low-lying molecular orbitals, a nonbonding orbital in the molecular plane ($3a_1$) and a π orbital perpendicular to the plane ($1b_1$). The HF states are then described as

$$^3\text{B}_1 : (3a_1)^1 (1b_1)^1,$$

$$^1\text{B}_1 : (3a_1)^1 (1b_1)^1,$$

$$^1\text{A}_1 : (3a_1)^2.$$

All ab initio calculations on CH_2 (dating back to the work by Foster and Boys [26] in 1960) have agreed in predicting the ground state to be a bent $^3\text{B}_1$ state [27, 28]. The best published calculations are those of O'Neil et al. [27] (OSB) which lead to a bond angle (θ) of 135° . The experimental observations on CH_2 by Herzberg [30] were interpreted to indicate that the $^3\text{B}_1$ state is linear (but also mentioned a possible second interpretation leading to $\theta = 140^\circ$). Recent experimental results [31–33] have confirmed the theoretical predictions of $\theta \approx 135^\circ$.

Herzberg and Johns [34] reported an extensive study of the $^1\text{B}_1 \leftarrow ^1\text{A}_1$ spectra of CH_2 . The lowest observed transition was at 1.34 eV; but they deduced that this was a (060) \leftarrow (000) transition and extrapolated their results to obtain a 0–0 singlet to singlet transition energy of 0.88 eV [37]. Although no phos-

phorescence from 1A_1 to 3B_1 was observed, they estimated the (0,0) triplet to singlet energy difference to be < 1.0 eV. The most complete theoretical calculations by OSB [27] lead to 0-0 transition energies[‡] of 0.97 eV (${}^1B_1 \leftarrow {}^1A_1$) and 0.96 eV (${}^1A_1 \leftarrow {}^3B_1$).

The GVB calculations were performed at four HCH angles (90, 105, 135, and 180 degrees), each with a CH bond distance of $2.1a_0 = 1.11$ Å. A bond angle of 105° is near the minimum of the 1A_1 potential curve, and a bond angle of 135° is near the minimum for the 3B_1 and 1B_1 curves. The basis sets employed consisted of a double zeta (DZ) contracted gaussian basis [35] and the same set augmented by a set of uncontracted d functions (with orbital exponent 0.532) on the carbon atom (POL).

The GVB wavefunctions for these states have the form

$${}^3B_1: \alpha(1s_c)^2 [1a,1b] [2a,2b] \{3a,3b\},$$

$${}^1B_1: \alpha(1s_c)^2 [1a,1b] [2a,2b] [3a,3b],$$

$${}^1A_1: \alpha(1s_c)^2 [1a,1b] [2a,2b] \cdot [3a,3b],$$

where each pair $[ia, ib]$ denotes a GVB singlet pair

$$(\phi_{ia}\phi_{ib} + \phi_{ib}\phi_{ia})\alpha\beta,$$

as in (2) and where $\{3a,3b\}$ denotes a triplet-coupled pair. These orbitals are obtained in separate self-consistent calculations for each state, although the 1s orbital remains an essentially unchanged carbon atomic 1s orbital. In all three cases the ϕ_{1a} and ϕ_{1b} orbitals localize in the region of the left CH bond and ϕ_{2a} and ϕ_{2b} are symmetrically related to ϕ_{1a} and ϕ_{1b} and localized in the region of the right CH bond.

For the B_1 states the ϕ_{3a} orbital lies in the molecular plane (a σ -orbital) and the ϕ_{3b} orbital is anti-symmetric with respect to the plane (a π -orbital). For the 1A_1 state, ϕ_{3a} and ϕ_{3b} have the form of sp-hybridized lobe-type orbitals, hybridized to point above and below the molecular plane and bent back from the hydrogens. This splitting of the HF non-

bonding pair leads to a large drop in energy ($0.0214h = 0.48$ eV = 13 kcal) as might be expected from the near degeneracy of the $3a_1$ and $1b_1$ orbitals.

In table 1 we compare the energies of the GVB wavefunctions at the lowest calculated points for each state (in the GVB 1-pair calculation, the 1B_1 and 3B_1 states were treated as in open-shell Hartree-Fock theory and the 1A_1 state was treated by splitting only the sp pair). We note that the 1-pair GVB description is a reasonably consistent description for all states in that each state dropped approximately the same amount (0.0221, 0.0227, and 0.0274 h) in energy when the CH bonding pairs were split. The two configuration wavefunctions of OSB in the table are equivalent to the 1-pair GVB calculation although we used a larger basis set.

We also performed a configuration interaction calculation (denoted as GVB CI) at each point using the six orthogonal GVB natural orbitals as a basis (keeping the 1s pair doubly occupied). This procedure provides a simple means of obtaining the optimum valence natural orbitals and thus forms an alternative to the iterative natural orbital method of Bender and Davidson [16]. As indicated in table 1 the GVB CI led to improvements in energy of 0.0115, 0.0052, and 0.0080 au for the 3B_1 , 1A_1 , and 1B_1 states, respectively. As shall be reported elsewhere in a more comprehensive study of hydrocarbons, the GVB spin coupling is expected to be more appropriate for the 1A_1 than for the 3B_1 and 1B_1 states. The use of GVB CI removes this restriction in the spin-coupling and hence should increase the ${}^3B_1 - {}^1A_1$ splitting (as observed).

As shown in fig. 1 the 3B_1 state is the lowest state for $100^\circ < \theta \leq 180^\circ$, but the 1A_1 state is lower for $\theta < 100^\circ$ (θ is the HCH angle). The 3B_1 and 1B_1 states exhibit shallow minima at approximately $\theta = 135^\circ$ with energies 0.39 eV = 9.0 kcal and 0.28 eV = 6.5 kcal below that of the linear configurations (${}^3\Sigma_g^-$ and ${}^1\Delta_g$). The observed zero-point energy for the bending motion in the 1A_1 state leads to a classically allowed range of bending for the 1A_1 state of approximately 90° to 115° . Since the ${}^3B_1 - {}^1A_1$ crossing occurs at 100° , we would expect the inter-system crossing from the 1A_1 to the triplet manifold to be unusually rapid, perhaps sufficiently so that phosphorescence from 1A_1 to 3B_1 would be difficult to observe. This might also lead to perturbations in the 3B_1 vibrational levels above 0.5 eV.

[‡] All theoretical transition energies reported here (except vertical transition energies) refer to adiabatic differences calculated from the minima of the respective states without zero-point corrections.

Table 1
Energies for the states of CH₂ ($R_{CH} = 2.10 a_0 = 1.11 \text{ \AA}$)

Method	Energy (hartree)		
	³ B ₁ (135°)	¹ A ₁ (105°)	¹ B ₁ (135°)
HF	-38.9202	-38.8821	-38.8544
GVB-1 pair		-38.9035	
GVB-3 pair	-38.9483	-38.9362	-38.8818
GVB CI	-38.9598	-38.9414	-38.8898

From the GVB CI results we predict the ¹A₁ - ³B₁ splitting (see table 2) to be 0.50 eV and the ¹B₁ - ¹A₁ splitting to be 1.40 eV. This is in conflict with both the previously reported CI calculations and the experimental estimates for these quantities. However, the previous CI calculations did not include the 3d polarization functions which we find to be quite important

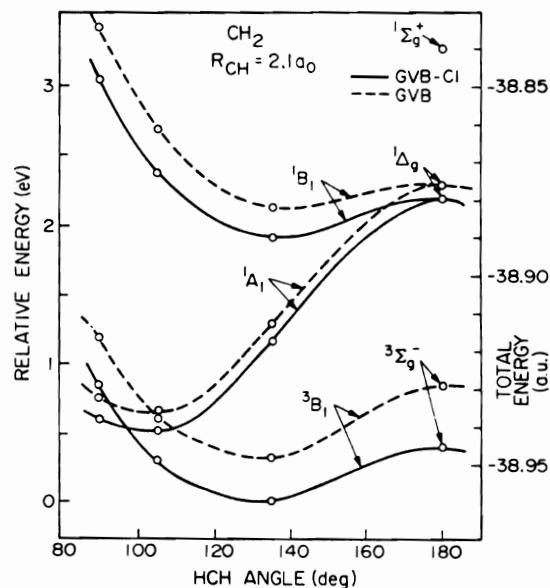


Fig. 1. The potential energy curves for the low-lying states of CH₂ as a function of HCH angle ($R_{CH} = 2.1 \text{ bohr} = 1.11 \text{ \AA}$).

Table 2
Excitation energies for CH₂. Two columns are adiabatic excitation averages (zero-point energies must be included to get 0-0 excitation energies). The vertical excitation energies are given in the last column

References	Method	Total energy ³ B ₁ (hartree)	¹ A ₁ ← ³ B ₁ (eV)	¹ B ₁ ← ¹ A ₁ (eV)	¹ B ₁ ← ¹ A ₁ vertical (eV)
This work	HF	-38.9202	1.03	0.75	1.32
	GVB-1 pair	-38.9202	0.45	1.34	1.91
	GVB-3 pair	-38.9483	0.32	1.49	2.06
	GVB CI ^{a)}	-38.9598	0.50 (0.97) ^{a)}	1.40 (1.11) ^{a)}	1.88 (1.69) ^{a)}
[27]	CI	-38.9826	0.96	0.97	1.56
[29]	VB CI	-38.915	1.39	0.84	1.52
[26]	CI	-38.904	1.06	1.55	
[28]	CI	-38.908	1.04	0.64	1.53
Experimental [32]		-	< 1.0 ^{b)}	0.88 ^{c)} 1.38 ^{d)}	2.06 ^{e)}

a) The quantities in parentheses were obtained by using a DZ basis essentially identical to that used in ref. [27].

b) Estimated upper limit [34].

c) Extrapolated [37].

d) Lowest observed ¹B₁ ← ¹A₁ transition [34]. Since the zero-point energies are 0.04 eV for ¹B₁ and 0.08 eV for ¹A₁, the 0-0 transition energy of 1.34 eV leads to 1.38 eV for the difference between the bottom of the ¹B₁ and ¹A₁ potential curves.

e) Obtained assuming the vertical transition to correspond to the middle of the observed ¹B₁ (0ν0) ← ¹A₁ (000) spectrum and adding 0.08 eV to correct for the zero-point energy of the ¹A₁ state.

for the 1A_1 state. Recently Bender and Schaefer [36] have added d functions to their first order CI wavefunction and find that the $^1A_1-^3B_1$ separation decreases from 0.96 to 0.60 eV.

Correcting for the zero-point energies, our calculations lead to 1.36 eV for the 0-0 singlet to singlet transition, very close to the lowest transition ($10823\text{ cm}^{-1} = 1.34\text{ eV}$) observed by Johns and Herzberg [34]. They assigned this as $(060) \leftarrow (000)$ based on an extrapolation of the isotope shifts for $^{12}\text{CH}_2$ and $^{13}\text{CH}_2$. However, we suspect that their first observed transition is in fact $(000) \leftarrow (000)$ and that the isotope shift extrapolation approach may break down for a transition to a state with a broad shallow double minimum such as 1B_1 . In addition, we find the $^1B_1 \leftarrow ^1A_1$ vertical transition to be at 1.88 eV, which is approximately in the middle of the range of observed transitions (1.34 to 2.52 eV) assigned as $(0v0) \leftarrow (000)$. This also supports the new numbering of the vibrational transitions. Thus, with the renumbering, there is very good agreement between experiment and theory.

From the GVB CI calculations we find a second 1A_1 state which has a minimum at $180^\circ(^1\Sigma_g^+)$ with an energy 3.22 eV above the minimum of the first 1A_1 state. This excitation energy is in good agreement with the band observed at $27586-30035\text{ cm}^{-1}$ (3.42-3.72 eV) [34] which Herzberg and Jones tentatively assigned as a $^1\Sigma^+ \leftarrow ^1A_1$ transition.

We conclude from this work that through the procedure of carrying out GVB calculations and then a CI calculation making use of the GVB orbitals, we can obtain useful interpretations of the wavefunction (in terms of the GVB orbitals) as well as high accuracy and a consistent treatment of different states.

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