and away from regions of negative overlap, or transition density.[3] An atom will migrate if a path of positive ρ is available from one site to another. Instead of forbidden and allowed processes, one would find favored and unfavored processes.

In such an analysis, it is important to keep proper phase relationships between the interacting orbitals. The phase of one orbital is not independent of that of the other, as implied by Fukui.[1a] In a recent paper Goddard has shown how favored and unfavored reaction paths can be predicted by following the orbital phases.[25]

Accordingly, symmetry in a molecule is not necessary for making deductions about favorable reaction paths. Its presence does facilitate the task of analysis very markedly. Molecular orbitals built up of atomic s, p, and d orbitals will always have an inherent symmetry that can be used for prediction.

In conclusion, the rule that a reaction is allowed, if the symmetries of the bonds that are made match up with the symmetries of the bonds that are broken, seems to be unusually simple and reliable. While derived above for unimolecular reactions, it clearly is equally valid for ground state reactions of any molecularity. A requirement is that at least one element of symmetry be conserved over the reaction path.

Acknowledgments. The author is grateful to National Sciences Foundation Grant GP-31060X for support of this work.

(25) W. A. Goddard, *J. Amer. Chem. Soc.*, **94**, 793 (1972).

Generalized Valence Bond Description of Simple Alkanes, Ethylene, and Acetylene[1a]

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Abstract: Generalized valence bond wave functions are reported for CH, CH_2, CH_3, CH_4, C_2, C_2H_2, C_2H_4, C_2H_6, and C_3H_6. These wave functions have the form of valence bond wave functions except that the orbitals are solved for self-consistently (as with Hartree–Fock wave functions). General characteristics of these wave functions are discussed.

Considerable progress in the understanding of bonding and molecular structure has been made through the use of both valence bond[2a] and Hartree–Fock wave functions.[2b] In many respects these wave functions lead to different interpretations of the wave functions, but in recent years the emphasis has been on the Hartree–Fock or molecular orbital description, which has also yielded quantitatively useful wave functions. Recently the *ab initio* generalized valence bond (GVB) method[3,4] has been developed which takes the wave function to have the form of a VB function, but which allows all orbitals to be solved for self-consistently (as in Hartree–Fock). Thus in GVB no special hybridization is imposed on the orbitals, and, in addition, the orbitals are permitted to delocalize onto other centers. With this approach one would hope to combine quantitatively useful calculations with the convenient VB oriented interpretations to obtain useful conceptual ideas concerning similarities and differences in bonding for various states and reactions of molecules. Herein are reported the results of GVB calculations on a number of related hydrocarbons (CH, CH_2, CH_3, CH_4, C_2, C_2H_2, C_2H_4, C_2H_6, and C_3H_6).

In the GVB approach the doubly occupied molecular orbitals ϕ_i of the many-electron Hartree–Fock wave function are replaced by two-electron valence bond functions ϕ_{ia} and ϕ_{ib}

$$\phi_i(1)\phi_i(1)\alpha(1)\beta(2) \rightarrow [\phi_{ia}(1)\phi_{ib}(2) + \phi_{ib}(1)\phi_{ia}(2)]\alpha(1)\beta(2)$$

and the optimum orbitals, ϕ_{ia} and ϕ_{ib}, of each pair are solved for variationally, subject only to the restriction that they be orthogonal[5] to the orbitals in other pairs. In addition to yielding an energy lower than the Hartree–Fock energy, this method offers two major conceptual advantages.

(1) The orbitals of each pair turn out to be localized hybrid atomic-like orbitals in close correspondence to chemists' "intuitive" ideas of bonds and lone pairs in molecules. (Note that each orbital contains *one* electron; thus a two-electron bond involves *two* different orbitals, generally one more concentrated on each of the two atoms involved in the bond.)

(1) (a) Partially supported by a grant (GP-15423) from the National Science Foundation; (b) National Science Foundation Predoctoral Fellow; (c) NDEA Predoctoral Fellow.

(2) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; (b) R. S. Mulliken, *Rev. Mod. Phys.*, 41, (1932); A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(3) W. A. Goddard and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971).

(4) (a) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1971); (b) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **56**, 738 (1972).

(5) The restriction that the orbitals of one pair are orthogonal to the orbitals of other pairs is called the strong orthogonality restriction. We have examined this restriction for a number of cases[4b] and find that for ground states of molecules of the type considered herein, this restriction should have only minor effects on the energies and their properties.

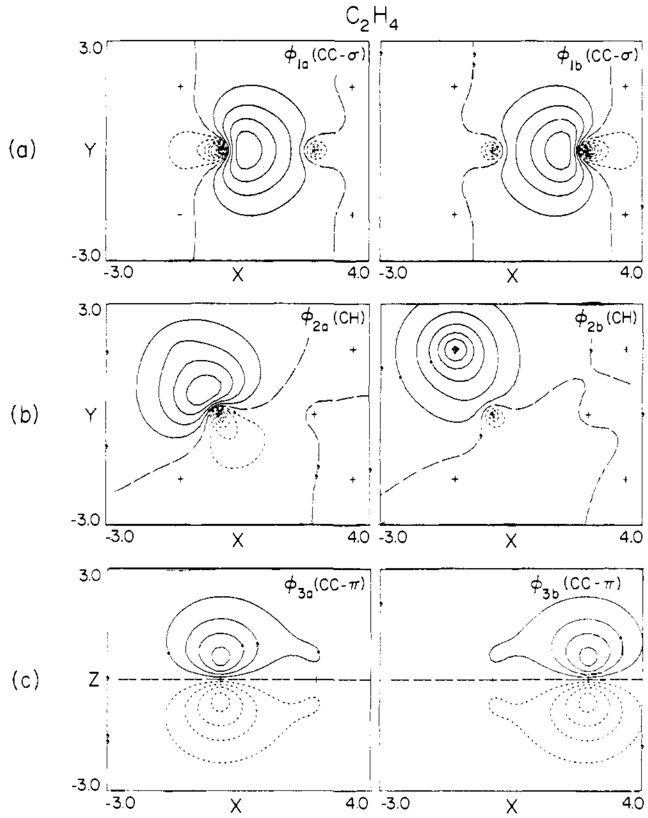

Figure 1. The bonding GVB orbitals of ethylene. Orbitals are shown for only one of the CH bonds (ϕ_{2a} and ϕ_{2b}); the core orbitals are not shown. The contour increments are 0.01 au; the long dashes indicate nodal lines and the solid lines indicate positive contours. All plots are for the MBS wave functions.

(2) The process of breaking chemical bonds is correctly described since the GVB orbitals of the molecule change smoothly into the atomic orbitals of the products.

For example, for ethylene, we find two types of GVB σ bonding pairs as shown in Figure 1. One pair (Figure 1a) is localized mainly in the C–C region and can be considered a CC σ-bonding pair. The other type is localized in one of the CH regions (Figure 1b); there are four equivalent such pairs, one localized in each CH region. These CH bonding pairs are each described by two orbitals: one (ϕ_{2b}) is essentially a hydrogen atomic orbital, and the other (ϕ_{2a}) is a hybrid orbital (74% p character) mainly on the C but oriented toward the H.

The C=C bond is described in terms of two pairs. One of these pairs (ϕ_{1a} and ϕ_{1b}) involves orbitals which are symmetric with respect to the molecular plane (σ orbitals). These orbitals have 68% p character on their main center but are much more delocalized onto the second center than were the orbitals of the CH bonds. The second pair of orbitals (ϕ_{3a} and ϕ_{3b}) of the C=C bond are antisymmetric with respect to the molecular plane (π orbitals) and are very nearly atomic pπ functions on the respective carbon atom. Allowing the σ and π orbitals to split in this way leads to a calculated bond energy 26 kcal greater than for the conventional doubly occupied π orbital. Another result is that the optimum σ,π representation of the bond gives a lower energy than the optimum bent-bond description, whereas in localized MO theory both descriptions would be equivalent in energy.

Calculational Details

Hurley, Lennard-Jones, and Pople[6] pointed out that wave functions of the GVB form

$$\phi_{1a}\phi_{1b} + \phi_{ib}\phi_{ia} \quad (1)$$

may be transformed to an equivalent natural orbital (NO) representation

$$C_{1i}\phi_{1i}\phi_{1i} + C_{2i}\phi_{2i}\phi_{2i} \quad (2)$$

where

$$\langle\phi_{1i}|\phi_{2i}\rangle = 0$$

[Coulson and Fischer[7] had previously pointed out that a two-electron, two basis function CI wave function can be written in the form (1).] When the many-electron wave function is written in this form, one can see that ψ_{GVB} is a special case of a multiconfiguration wave function where all orbitals ϕ_i and configuration interaction (CI) coefficients C_i are optimized. Setting $C_1 = 1$ and $C_2 = 0$ for each pair would result in the Hartree–Fock wave function, except that in HF the orbitals would lose their localized nature and would revert back to become symmetry functions. The relation of GVB to other approaches is discussed more fully in ref 3 and 4b.

As shown in ref 4, the GVB natural orbitals are obtained by solving a set of equations

$$H_i\phi_i = E_i\phi_i \quad (3)$$

and iterating until self-consistency is achieved, analogous to the procedure used in Hartree–Fock calculations. However, we analyze the wave function in terms of the GVB orbitals (1).

There will usually be a separate Hamiltonian H_i for each orbital, except for the doubly occupied orbitals which can all be taken to be eigenfunctions of a single closed-shell Hamiltonian. In addition, such wave functions as open-shell doublets or singlets can be handled easily in this approach. The procedure of handling orthogonality constraints in the GVB equations has been discussed in ref 4.

Just as for Hartree–Fock calculations, the GVB self-consistent variational equations (3) are solved by expanding each orbital in terms of a large basis set and solving for the expansion coefficients.

Three basis sets were used in the present calculations.

(a) MBS—the minimum basis set (STO-4G) of contracted Gaussians developed by Pople.[8]

(b) DZ—the $(9s_c5p_c/4s_H)$ basis of Gaussians contracted to "double zeta" [4s2p/2s] size.[9]

(c) POL—the DZ basis plus 3d polarization functions with exponent 0.532.

A CH distance of 2.1 au was assumed for CH and CH_2, and HCH angles in the range of 90 to 180° were used for CH_2. For CH_3, R(C–H) was 2.039 (from CD_3)[10] while the geometries for other hydrocarbons were taken from experiment.[11]

(6) A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc., Ser. A*, 220, 446 (1953).
(7) C. A. Coulson and I. Fischer, *Phil. Mag.*, 40, 386 (1949).
(8) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(9) (a) S. Huzinaga, *ibid.*, **42**, 1293 (1965); (b) T. H. Dunning, Jr., *ibid.*, **53**, 2823 (1970).
(10) G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, Princeton, N. J.: Vol. II, 1945; Vol. III, 1967.

Configuration interaction (CI) calculations were also performed for CH, CH_2, and C_2H_4 by using all configurations constructed from the orthogonal GVB natural orbitals. The calculations will be referred to as GVB–CI. For excited states the configurations were constructed from the self-consistent orbitals for those states rather than using ground state orbitals.

GVB Description of the CH_n Series

First we will consider the CH_n series of molecules.

C and CH. In the usual HF description of the ground ^3P state of the C atom, the configuration is $(1s)^2(2s)^2(2p_z\alpha)(2p_y\alpha)$ (we will neglect the 1s orbitals in the rest of this discussion). The GVB 2s orbitals of C polarize in opposite directions along the x axis

$$\phi_{sx} = \phi_{2s} + \lambda\phi_{2p_x}$$

$$\phi_{s\bar{x}} = \phi_{2s} - \lambda\phi_{2p_x}$$

to form directed sp lobes sx and s$\bar{x}$.

The wave function then becomes

$$\psi_{\text{GVB}} = \mathcal{A}\{(sxs\bar{x} + s\bar{x}sx)zy\alpha\beta\alpha\alpha\}$$

which is represented in Figure 2a. The sp lobes are shown along the x axis along with two perpendicular orbitals, p_z and p_y, where y is pointing out of the plane and where the arrows denote unpaired electrons. In the diagram at the right of Figure 2, orbitals in the same row are singlet coupled while the z and y orbitals in the same column have maximum (triplet) multiplicity.

Bonding an H atom to the p_z carbon orbital, we obtain the $^2\Pi$ state of CH (Figure 2b). (The bond is denoted by a solid line.) The self-consistent GVB lone pair orbitals [sx, s$\bar{x}$] bend back from the CH bond at an angle of 128° while the z orbital incorporates some s character as the bond is formed (see Figure 3). At large internuclear distance the z and y orbitals are triplet coupled, corresponding to $C(^3P) + H(^2S)$. At this point the GVB coupling is no longer appropriate and one should permit recoupling of the orbitals to attain proper dissociation. Spin-coupling changes, best treated within the SOGI[12] approach, are discussed for CH by Bobrowicz and Goddard.[13]

Bonding an H to the sz lobe of C would yield the $^4\Sigma^-$ state of CH (Figure 2c) which is calculated to be 0.36 eV = 8.2 kcal above the ground $^2\Pi$ state. The self-consistent sx, s$\bar{x}$, and H orbitals are shown in Figure 3. The difference in bonding is dramatically reflected by the p character in the bonding orbital of the $^2\Pi$ (82%) and $^4\Sigma^-$ (35%) states (see Table I).

One can recouple the s$\bar{x}$, z, and y orbitals of the $^4\Sigma^-$ state to form the $^2\Delta$, $^2\Sigma^-$, and $^2\Sigma^+$ states of CH. The GVB and GVB–CI excitation energies are compared with the experimentally observed quantities in Table II.

CH_2. Forming a CH bond with the unpaired p_y orbital of CH ($^2\Pi$) results in the $^1A_1$ state of CH_2, where the sx and s$\bar{x}$ lobes point above and below the HCH plane, respectively. Interaction of the orbitals of the new bond with those of the old one would increase the HCH angle to a value greater than 90° (experimentally the angle is 103.2°).[10]

(11) (a) C_2H_6: G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, 20, 313 (1952); (b) C_3H_6: O. Bastiansen, *Acta Crystallogr.*, 17, 538 (1964).

(12) R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.*, 51, 1073 (1969).

(13) F. Bobrowicz and W. A. Goddard III, submitted for publication.

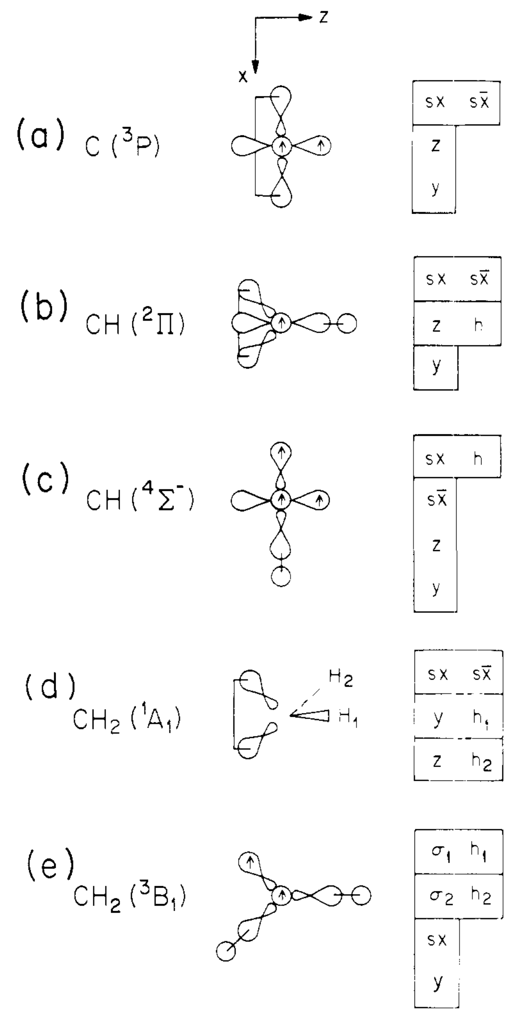

Figure 2. Schematic diagram of bonding in C, CH, and CH_2.

Table I. Hybridization of GVB Orbitals

Molecule	Pair	% p character MBS[a]	DZ[b]
$C(^3P)$	Lone (σ)	13.2	13.2
$CH(^2\Pi)$	Bond	92.8	81.5
	Lone (σ)	21.3	25.7
$CH(^4\Sigma^-)$	Bond	37.6	34.8
	Lone (σ)	37.9	42.0
$CH_2(^1A_1)$	Bond	86.1	78.5
	Lone (sp)	36.1	43.2
$CH_2(^3B_1)$	Bond	51.9	51.5
	Lone (a_1)	70.9	72.4
$CH_2(^1B_1)$	Bond	46.5	47.2
	Lone (a_1)	82.8	83.8
CH_3	Bond	59.8	60.8
CH_4	Bond	67.9	70.3
C_2H_2	CH bond	53.2	
	CC bond	42.9	52.2
C_2H_4	CH bond	74.4	
	CC bond	68.0	
C_2H_6	CH bond	68.5	
	CC bond	66.3	72.0
C_3H_6	CC bond	81.7	

[a] Minimum basis set. [b] Double ζ basis set.

Similarly, bonding to one of the sp lobes would produce the $^3B_1$ state (in CH_2 the two CH bonds become equivalent), as well as the higher $^1B_1$ state (see Figure 2e). Since the initial angle between the sp lobe and the CH bond is 128°, the increase in bond angle due to

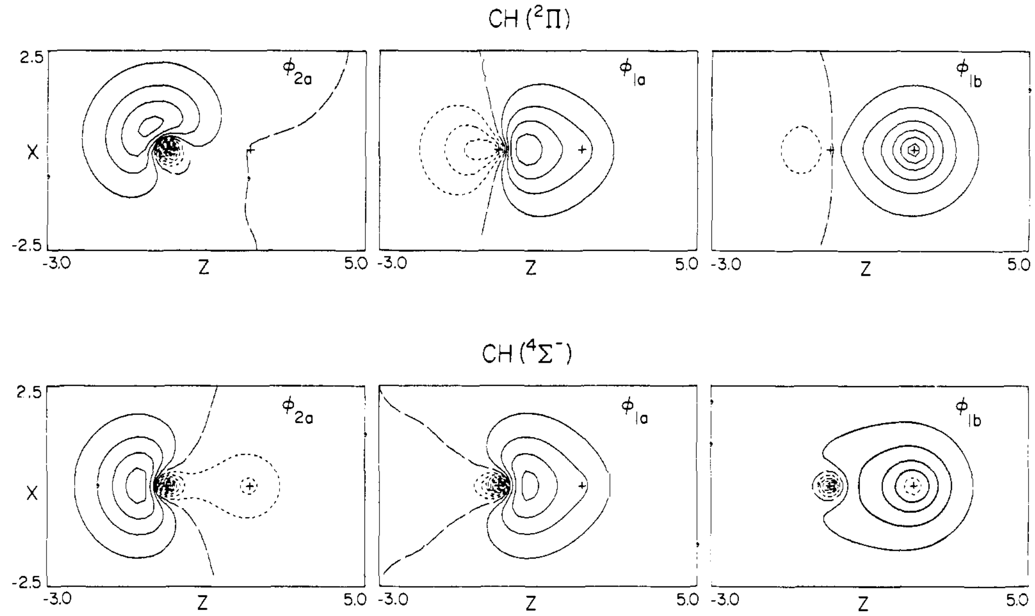

Figure 3. The GVB orbitals of CH ($^2\Pi$ and $^4\Sigma^-$ states). For the $^2\Pi$ state orbital ϕ_{2b} is equivalent to ϕ_{2a} but reflected in the yz plane. For the $^4\Sigma^-$ state ϕ_{2b} is a π orbital and is not shown.

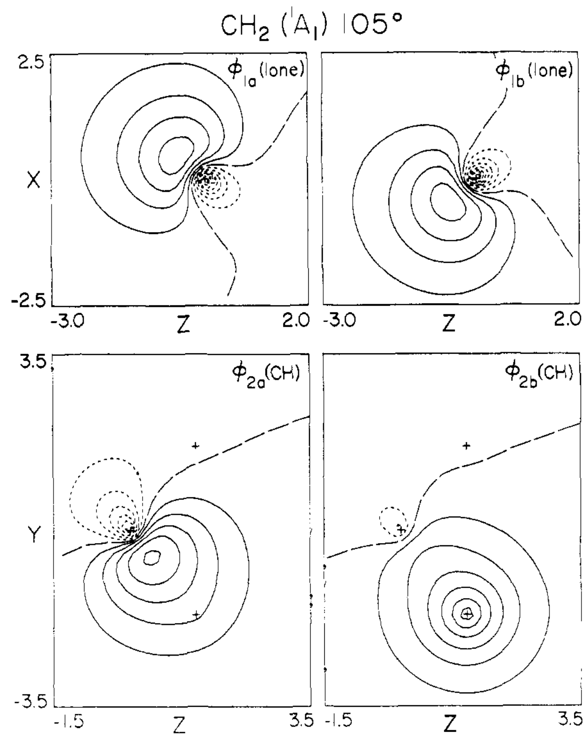

Figure 4. The GVB orbitals of CH_2 ($^1A_1$). The molecule is in the yz plane. Orbitals are shown for only one of the CH bonds (ϕ_{2a} and ϕ_{2b}). Core orbitals are not shown.

formation of the second bond should be less than for the $^1A_1$ state (13°). An angle increase of 8° would lead to agreement with the experimental value of 136 ± 8°[14-16] and recent extensive CI calculations.[17]

Again the hybridization indicates that CH bonds

(14) R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970).
(15) E. Wassermann, W. A. Yager, and V. Kuck, *J. Amer. Chem. Soc.*, **92**, 7491 (1970).
(16) G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).
(17) S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *ibid.*, **55**, 162 (1971).

Table II. Excitation Energies (eV) for CH and CH_2 (POL Basis)

State	HF	GVB	GVB–CI	Exptl
		CH Molecule		
$^4\Sigma^- \leftarrow {}^2\Pi$	−0.28	0.46	0.36	
$^2\Delta \leftarrow {}^2\Pi$	+2.73	3.52	3.43	2.87[a]
$^2\Sigma^- \leftarrow {}^2\Pi$	3.36	4.22	3.81	3.22[a]
$^2\Sigma^+ \leftarrow {}^2\Pi$	4.18	4.97	4.46	3.94[a]
		CH_2 Molecule		
$^1A_1 \leftarrow {}^3B_1$	1.03	0.45	0.50	(<1.0)[b]
$^1B_1 \leftarrow {}^1A_1$	0.75	1.34	1.40	0.88[c] (1.34)[d]
$^1B_1 \leftarrow {}^1A_1$ (vert)	1.32	1.91	1.88	1.98[e]

[a] Reference 22. [b] Estimated upper limit (ref 18). [c] Extrapolated value (ref 18). [d] Lowest observed transition. [e] Obtained from median excitation energy of $^1B_1 \leftarrow {}^1A_1$ band.

in the $^3B_1$ state (47% p) involve less p bonding than the $^1A_1$ state (78%). The bonding orbitals and lone-pair orbitals for the two states are shown in Figures 4 ($^1A_1$) and 5 ($^3B_1$). From Figure 6, where the change in hybridization with angle is shown, it is seen that the $^1A_1$ state contains more p character in the CH bond even at the same HCH angles.

As reported in an earlier communication,[4a] the $^3B_1$ state remains the lowest state for $\theta > 100°$, but near 100° its curve is crossed by the $^1A_1$ state (see Figure 7). The $^1A_1 \rightarrow {}^3B_1$ energy separation is found to be 0.50 eV = 11.5 kcal. This is in good agreement with recent experimental estimates[18a] of ~9 kcal. The $^1B_1 \leftarrow {}^1A_1$ energy separation (1.40 eV) does not agree with the *extrapolated* experimental value (0.88 eV); however, it does agree with the lowest observed transition[18a] (1.34 eV).

CH_3 and CH_4. One of the three equivalent bonding pairs in planar CH_3, obtained from bonding an H to the σ unpaired orbital of CH_2 ($^3B_1$), is shown in Figure 8. In addition, one of the four bonding pairs of CH_4 is also included in Figure 8. These results differ some-

(18) (a) W. L. Hase, R. J. Phillips, and J. W. Simons, *Chem. Phys. Lett.*, **12**, 161 (1971); (b) G. Herzberg and J. W. C. Johns, *Proc. Roy. Soc., Ser. A*, **295**, 107 (1966).

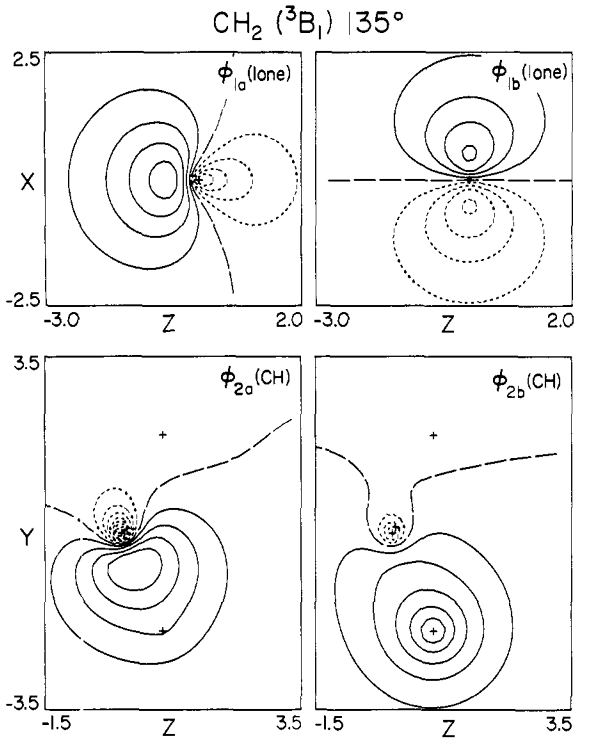

Figure 5. The GVB orbitals of CH_2 ($^3B_1$). See caption of Figure 4.

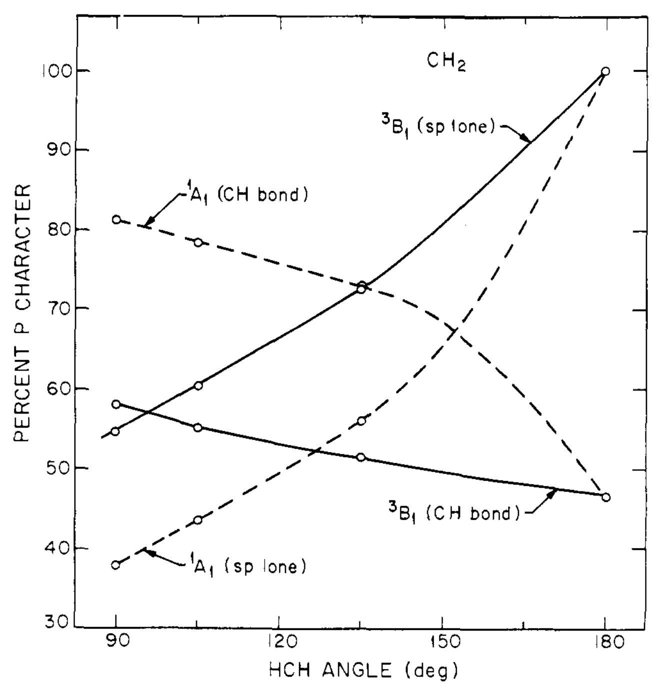

Figure 6. The hybridization of the GVB orbitals of CH_2. sp lone refers to orbitals ϕ_{1a} and ϕ_{1b} for the $^1A_1$ state and orbital ϕ_{1a} for the $^3B_1$ state.

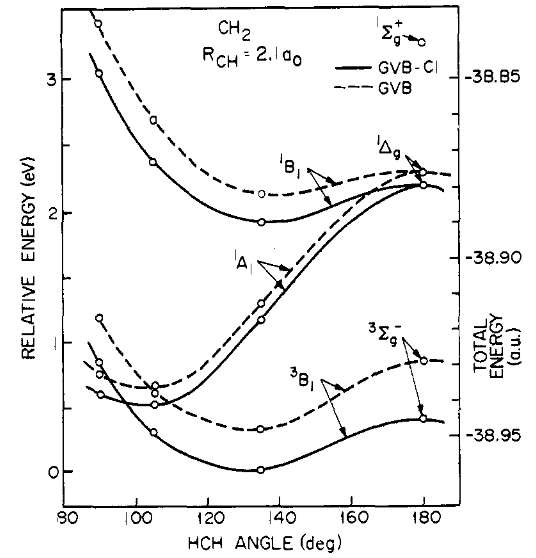

Figure 7. The potential curves of the states of CH_2.

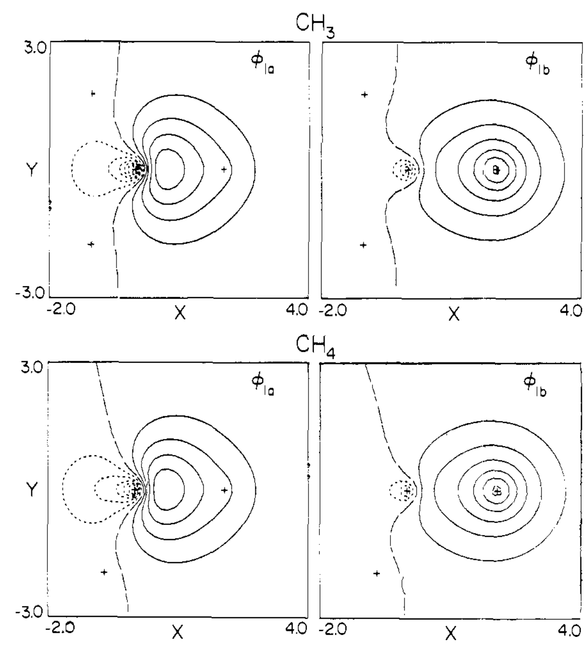

Figure 8. The bonding GVB orbitals of CH_3 and CH_4.

what from the usual notion of hybridized atomic orbitals, since the C bonding orbitals in the MBS basis have $sp^{1.5}$ and $sp^{2.1}$ hybridization, respectively, as compared with the usual sp^2 and sp^3 bonding assumed in the VB description of methyl and methane. Such changes are allowed since the orbitals can now delocalize onto the hydrogen, and hence the atomic orthogonality conditions no longer uniquely fix the hybridization.

C_2H_2, C_2H_4, C_2H_6, and the C_2 Molecule

In the earlier discussion of ethylene, we showed that the GVB orbitals have the form of four equivalent pairs of C–H bonding orbitals, a pair of C–C σ-bonding orbitals, and a pair of nearly atomic-like π-bonding orbitals. For single bonds, one can construct only a σ and σ^* orbital from localized orbitals on each center. By explicitly including the $\sigma^2 \rightarrow \sigma^{*2}$ excitation in the GVB form of the wave function as in (2), GVB recovers much of the additional binding energy left out of a Hartree–Fock MO calculation. In multiple bonds, such as C_2H_4, even though GVB obtains an energy 0.054 hartree (34 kcal) lower than HF in the MBS basis, only a restricted number of excitations are included in GVB because of the "perfect pairing" and "strong orthogonality" assumptions. We can test these assumptions by using the four orbitals in the C=C double bond of ethylene in a CI calculation. For an MBS

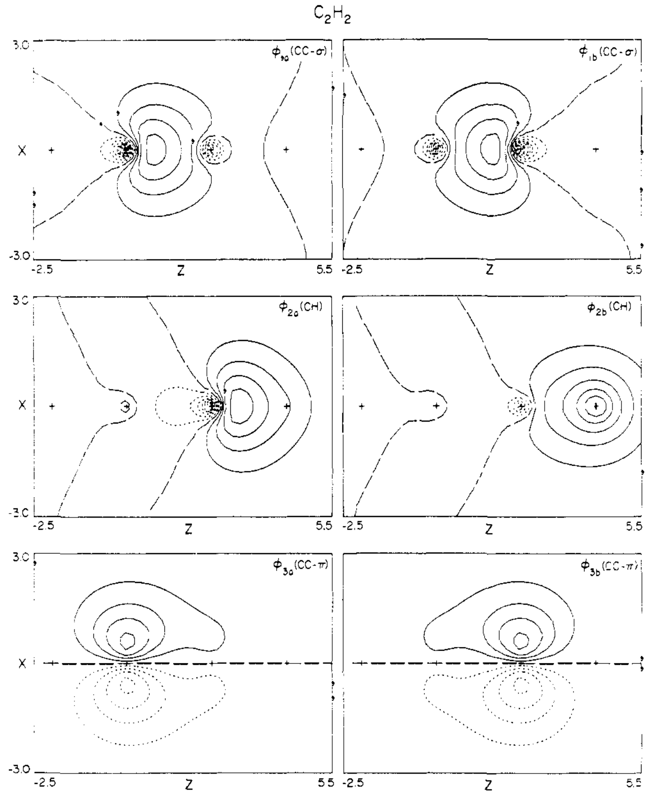

Figure 9. The bonding GVB orbitals of C_2H_2.

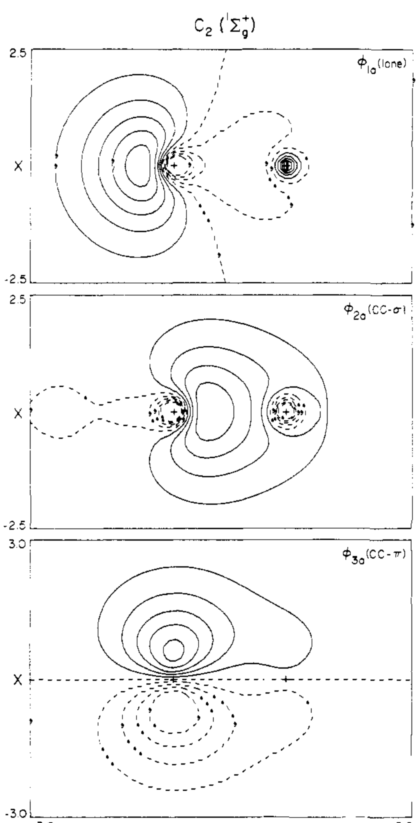

Figure 10. The GVB orbitals of the ${}^1\Sigma_g{}^+$ state of the C_2 molecule. Corresponding to each orbital shown (ϕ_{ia}) is another orbital (ϕ_{ib}) reflected onto the opposite side of the molecule.

basis, this results in an increase of 0.018 hartree (11 kcal) in the binding energy (see Table III), due mainly

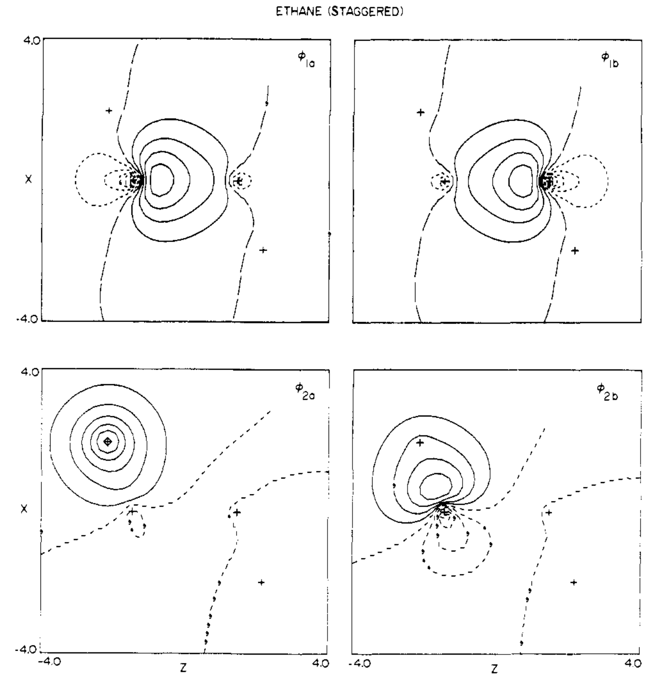

Figure 11. The bonding GVB orbitals of C_2H_6. Orbitals for only one CH bond are shown.

Table III. σ–π Correlation in Ethylene (MBS Basis)

	E, hartrees	$\Delta H[C_2H_4 \rightarrow 2CH_2(^3B_1)]$, kcal
HF	−77.6246	126
GVB (2-pair)	−77.6797	168
GVB–CI	−77.6978	179
Exptl		167[a]

[a] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

to the $\sigma\pi \rightarrow \sigma^*\pi^*$ excitation which is needed to dissociate C_2H_4 into two ground state CH_2 ($^3B_1$) fragments.

A similar descritpion is obtained for acetylene (Figure 9). The C–C triple bond is described by a σ-bonding pair and two equivalent π-bonding pairs. If the bond were described as originating from equivalent tetrahedral lobes on each C, one would have obtained three equivalent bent "banana" bonds. Indeed, certain schemes of localizing HF molecular orbitals[19] suggest that this arrangement minimizes electronic repulsion (although the total HF energy remains the same whether the MO's are localized or not). [Klessinger's[20] group function calculations on C_2H_4 and C_2H_2 found that the $\sigma\pi$ description is lower by about 0.013 and 0.016 au, respectively.] The bent bond solution of the GVB equations is higher than the $\sigma\pi$ solution and only the lower state ($\sigma\pi$) was solved for self-consistently. With the POL basis the GVB and GVB–CI calculations lead to CC bond dissociation energies of 180 and 206 kcal, respectively, in fair agreement with the experimental results of 231 kcal. The difference of 26 kcal between GVB and GVB–CI may indicate that some sort of banana-like description may be appropriate for the triple bond of C_2H_2.

(19) M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).

(20) (a) M. Klessinger, *Int. J. Quant. Chem.*, **4**, 191 (1970); (b) *J. Chem. Phys.*, **53**, 225 (1970).

Table IV. Generalized Valence Bond Results for Hydrocarbons

Molecule	Basis	Energy, hartrees E_{HF}[a]	E_{GVB}	Pair information Pair	Overlap	$\Delta\epsilon_i$, hartree
$C(^3P)$	MBS	−37.50862	−37.52754	Lone	0.732	−0.0189
	DZ	−37.68541	−37.70331	Lone	0.732	−0.0193
$C(^1D)$	MBS	−37.4401	−37.45897	Lone	0.732	−0.0189
	DZ	−37.6268	−37.6463	Lone	0.733	−0.0195
$CH(^2\Pi)$	MBS	−38.0455	−38.0832	Bond	0.812	−0.0173
				Lone	0.717	−0.0204
	DZ	−38.2582	−38.2941	Bond	0.810	−0.0181
				Lone	0.733	−0.0178
	POL	−38.2703	−38.3085	Bond	0.826	−0.0165
				Lone	0.704	−0.0217
$CH(^4\Sigma^-)$	MBS	−38.0581	−38.0685	Bond	0.863	−0.0104
	DZ	−38.2649	−38.2757	Bond	0.863	−0.0108
	POL	−38.2805	−38.2914	Bond	0.864	−0.0109
$CH_2(^1A_1)$	MBS	−38.6491	−38.7015	Bond (2)	0.816	−0.0168
				Lone	0.699	−0.0188
	DZ	−38.8614	−38.9113	Bond (2)	0.816	−0.0173
				Lone	0.734	−0.0153
	POL	−38.8822	−38.9362	Bond (2)	0.826	−0.0163
				Lone	0.683	−0.0214
$CH_2(^3B_1)$	MBS	−38.7065	−38.7337	Bond (2)	0.840	−0.0136
	DZ	−38.9119	−38.9391	Bond (2)	0.840	−0.0136
	POL	−38.9202	−38.9483	Bond (2)	0.843	−0.0140
$CH_2(^1B_1)$	MBS	−38.6244	−38.6375	Bond (2)	0.843	−0.0131
	DZ	−38.8546	−38.8685	Bond (2)	0.842	−0.0139
	POL	−38.8681	−38.8818	Bond (2)	0.845	−0.0137
CH_3	MBS	−39.3529	−39.3959	Bond (3)	0.837	−0.0143
	DZ	−39.5492	−39.5935	Bond (3)	0.839	−0.0147
	POL	−39.5598	−39.6038	Bond (3)	0.841	−0.0147
CH_4	MBS	−40.0071	−40.0691	Bond (4)	0.828	−0.0155
	DZ	−40.1849	−40.2467	Bond (4)	0.832	−0.0154
	POL	−40.1982	−40.2596	Bond (4)	0.834	−0.0153
$C_2(^1\Sigma_g^+)$	MBS	−74.8567	−75.1318	σ	0.940	−0.0030
				$\pi(2)$	0.648	−0.0354
				Lone	0.331	−0.1013
	POL		−75.53000	σ	0.934	−0.0042
				$\pi(2)$	0.698	−0.0254
				Lone	0.303	−0.1049
C_2H_2	MBS	−76.4037	−76.5016	CH(2)	0.841	−0.0138
				CC-σ	0.929	−0.0045
				CC-π(2)	0.664	−0.0329
	DZ	−76.7991	−76.8573[b]	CC-σ	0.908	−0.0070
				CC-π(2)	0.691	−0.0260
	POL	−76.8229	−76.9043	CH(2)	0.847	−0.0141
				CC-σ	0.922	−0.0060
				CC-π(2)	0.701	−0.0241
C_2H_4	MBS	−77.6246	−77.7353	CH(4)	0.839	−0.0142
				CC-σ	0.893	−0.0078
				CC-π	0.578	−0.0462
	DZ	−78.0100	−78.0519[b]	CC-σ	0.875	−0.0102
				CC-π	0.631	−0.0317
	POL	−78.0370	−78.1332	CH(4)	0.842	−0.0147
				CC-σ	0.889	−0.0095
				CC-π	0.644	−0.0293
C_2H_6 (staggered)	MBS	−78.8608	−78.9691	CH(6)	0.826	−0.0157
				CC	0.835	−0.0139
	DZ	−79.2044	−79.2198[b]	CC	0.822	−0.0154
C_2H_6 (eclipsed)	MBS	−78.8555	−78.9641[b]	CH(6)	0.826	−0.0158
				CC	0.836	−0.0139
C_3H_6	MBS	−116.4961	−116.5143[c]	CC(1)	0.790	−0.0183

[a] The "HF" energy is the energy of the principal natural orbital wave function obtained by adding the pair splitting energies to E_{GVB}. [b] In these GVB calculations, only the CC bond pairs were split. [c] In this GVB calculation, only one CC bond pair was split.

Removal of the two H's in C_2H_2 results in the $\cdot C{\equiv}C\cdot$ biradical, whose ground state is found experimentally to be $^1\Sigma_g^+$. The HF wave function should lead to a poor description of this state since the two nonbonding orbitals are required to be in a doubly occupied orbital (the HF configuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2$). In fact, the HF heat of reaction for $C_2 \rightarrow 2C$ was found[21] to be −22.1 kcal as compared with the experimental value of +144 kcal. With the POL basis we find bond dissociation energies of 77 and 122 kcal for GVB and GVB–CI wave functions, respectively, the latter being in good agreement with the experimental result. The two biradical orbitals have an overlap of only 0.303 (one of which is shown in Figure 10) and are localized on the respective carbons.

In ethane, the main property of interest here is the barrier to internal rotation. Since the Hartree–Fock calculations lead to a difference between the eclipsed

(21) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

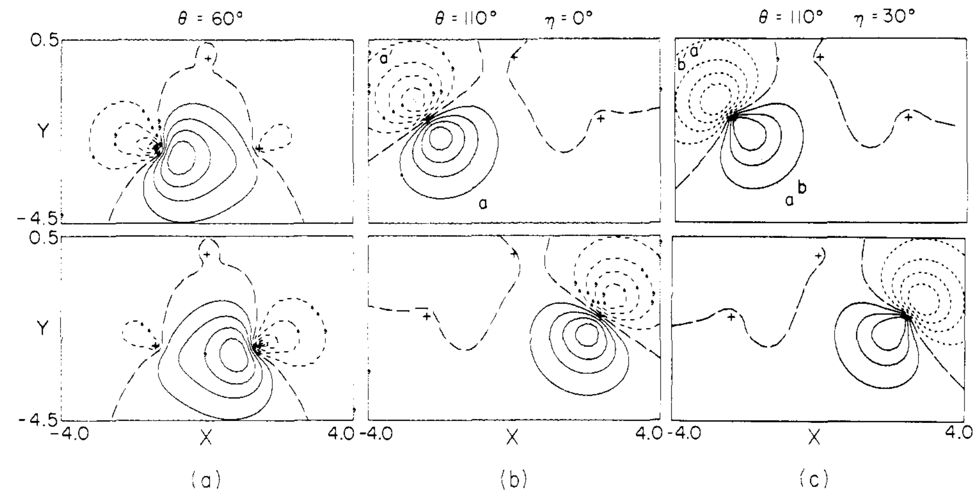

Figure 12. The GVB orbitals for the C–C bond in (a) cyclopropane, (b) trimethylene ($\theta = 110°$) with planar CH_2 groups ($\eta = 0°$), and (c) trimethylene ($\theta = 110°$) with symmetrically canted CH_2 groups ($\eta = 30°$).

Table V. Heats of Reaction (kcal/mol) for Various Simple Hydrocarbons[a]

Reaction	Basis	HF	GVB	GVB–CI	Exptl[b]
$CH \rightarrow C + H$	MBS	23.1	35.0		81
	DZ		68.8		
	POL	54.0	65.8	67.7	
$CH_2 \rightarrow CH + H$	MBS	101.1	94.4		103
	DZ	96.5	91.0		
	POL	94.1	87.8	95.0	
$CH_3 \rightarrow CH_2 + H$	MBS	91.9	101.8		111
	DZ	86.2	96.9		
	POL	87.6	97.6		
$CH_4 \rightarrow CH_3 + H$	MBS	96.8	108.7		103
	DZ	85.2	96.2		
	POL	86.9	97.8		
$C_2 \rightarrow 2C$	MBS	−22.1	72.7		144
	POL		77.0	122.3	
$C_2H_2 \rightarrow 2CH$	MBS	198	210		231
	DZ	178	192		
	POL	177.1	180.2	205.7	
$C_2H_4 \rightarrow 2CH_2$	MBS	126.4	168.4	179	171
	DZ	117	143		
	POL	123.3	147.1		
$C_2H_6 \rightarrow 2CH_3$	MBS	95.5	106.8		87
	DZ	66.5	76.2		
$C(^3P) \rightarrow C(^1D)$	MBS	31.1	31.1		29.1[c]
	DZ	36.1	36.0		
	POL	36.1	36.0		
$C(^3P) \rightarrow C(^5S)$	MBS	49.1	60.9		61.7[c]
	DZ	56.1	68.2		
	POL	56.1	68.2		
$CH(^2\Pi) \rightarrow CH(^4\Sigma^-)$	MBS	−7.9	+9.2		
	DZ	−4.2	+11.5		
	POL	−6.4	+10.7	8.2	
$CH(^2\Pi) \rightarrow CH(^2\Delta)$	MBS	75.5	93.8		66.6[d]
	DZ	58.7	75.4		
	POL	63.0	81.2		
$CH_2(^3B_1) \rightarrow CH_2(^1A_1)$	MBS	36.0	20.2		(<23)[e]
	DZ	31.7	17.5		
	POL	23.9	7.6	11.5	

[a] In each case the ground state of the molecule is understood unless otherwise stated. [b] All experimental references are quoted from ref 21 except as noted. [c] C. E. Moore, *Nat. Bur. Stand. (U. S.), Circ.*, No. 467 (1949). [d] Reference 22. [e] Reference 25.

and staggered forms of 3.3 kcal (in our MBS basis), in good agreement with the value of +2.9 kcal obtained from microwave spectra,[22] one would hope that the GVB description would not reduce the agreement between the theory and experiment. Although the total energy of both the staggered and eclipsed forms drops about 3 eV from HF to GVB, the rotational barrier is essentially unchanged (+3.1 kcal). This contrasts with the group function calculations[20b] on ethane which predict the *eclipsed* form to be lower by 0.5 kcal. In Figure 11 we show one of the six equivalent CH bonding pairs and the CC bonding pair.

The results (from Hunt, Goddard, and Dunning[23]) for ethylene will be discussed in detail elsewhere; however,

(22) S. Weiss and G. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

a summary of results is pertinent here. Using the POL basis, the GVB results lead to a cis–trans barrier of 66.6 kcal for the ground (N) state of ethylene. This is in good agreement with the experimental activation energy of 65 kcal. The $\pi\pi^*$ triplet (T) state is found to have a minimum in energy for the perpendicular geometry with its minimum lying 1.7 kcal lower than the saddle point in the N state. The T state has a cis–trans barrier of 31.4 kcal.

Cyclopropane and the Trimethylene Biradical

We have reported previously[24,25] the results of GVB calculations on cyclopropane and the broken-bond trimethylene intermediate involved in the geometrical and structural isomerizations of C_3H_6. In Figure 12a we note that the orbitals of the C–C bond have essentially sp^4 (82% p) character and are bent outside the ring in agreement with Coulson and Moffitt's earlier VB calculations.[26] As the central CCC angle is increased from 60 to 120° the orbitals change continuously into p orbitals for planar end groups. We found essentially no barrier to ring closure (<1 kcal) for trimethylene and a barrier height of 60.5 kcal in good agreement with the experimental activation energy (64.2 kcal).

(23) W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., submitted for publication; see also W. J. Hunt, Ph.D. Thesis, California Institute of Technology, Sept 1972; T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969).
(24) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 638 (1972).
(25) W. A. Goddard III and P. J. Hay, to be published.
(26) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

General Characteristics of GVB Orbitals

In Table IV we summarize the results of the GVB calculations of hydrocarbons. In addition to the HF and GVB total energies, the overlap $\langle\phi_{ia}|\phi_{ib}\rangle$ and the pair-splitting energy $\Delta\epsilon_i$ (*i.e.*, the energy change due to adding the second natural orbital to the pair) is reported for each pair. To a very good approximation (~0.001 hartree), the total improvement in energy in GVB over HF is given by the sum of the pair splitting energies. In Table V we note that improved agreement with experimental heats of reaction is obtained using GVB functions.

Typically for reactions involving breaking of single bonds, GVB accounts for an improvement of 10–12 kcal in ΔH of the reaction (corresponding to about 10–15% of the total bond strength). For multiple bonds, although the pair lowerings are much larger than for single bonds, these are partially offset by pair lowerings in the molecular fragments with the result that total improvements in heats of reaction are 14–40 kcal.

Ab Initio Study of the Hydrogen Bond in $[H_3N–H\cdots NH_3]^+$

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Abstract: *Ab initio* SCF calculations with varying flexibility in the basis set are reported for the hydrogen-bonded $[H_3N–H\cdots NH_3]^+$ complex. The calculations indicate that the proton transfer between the two nitrogen nuclei occurs with very little adjustment in the magnitudes of the terminal NH distances and HNH angles but is accompanied by a significant decrease (0.25 bohr) in the NN separation in the course of this exchange. An analysis of the charge distribution calculated for this hydrogen-bonded complex is also undertaken and a treatment of the vibrational structure associated with the proton transfer in this system is discussed.

I. Introduction

It is difficult to overestimate the importance of the hydrogen bond in various chemical and biological processes, particularly those which occur routinely in nature. At the same time, however, it would be rather easy to underestimate the difficulties involved in achieving a reliable theoretical description of this phenomenon; the main reason for this complexity is the fact that the characteristics of a given hydrogen bond depend quite strongly upon the properties of the specific electronegative centers involved. As a result, even though the typical hydrogen bond produces a relatively small binding energy (generally somewhat less than 10 kcal/mol), examples of this phenomenon are known with binding energies as great as 50 kcal/mol.[2]

Most theoretical *a priori* investigations on this general subject have dealt with systems containing oxygen,[3]

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(2) A well-known example is the system $[F—H\cdots F]^-$ which has been studied experimentally by (a) S. A. Horrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, **86**, 4497 (1964); (b) T. C. Waddington, *Trans. Faraday Soc.*, **54**, 25 (1958), while theoretical calculations have been carried out by (c) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970); (d) E. Clementi and A. D. McLean, *J. Chem. Phys.*, **36**, 745 (1962); (e) A. D. McLean and M. Yoshimine, *IBM J. Res. Develop.*, **11**, (1967).
(3) More recent examples in the literature are (a) K. Morokuma and J. R. Winick, *J. Chem. Phys.*, **52**, 1301 (1970); (b) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *Chem. Phys. Lett.*, **4**, 527 (1970); (c) G. H. F. Diercksen, *Theor. Chim. Acta*, **21**, 335 (1971); (d) G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.*, **6**, 419 (1970), for $[F–H\cdots OH]^-$; (e) M. Dreyfus, B. Maigret, and A. Pullman, *Theor. Chim. Acta*, **17**, 109 (1970), for formamide dimer; (f) M. Dreyfus and A. Pullman, *ibid.*, **19**, 20 (1970), for formamide dimer; (g) E. Clementi,