

THE GENERALIZED VALENCE BOND π ORBITALS OF ETHYLENE AND ALLYL CATION*

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Using a fixed sigma core obtained from full electron ab initio Hartree–Fock calculations, the spatially projected GVB orbitals for the pi electron systems of ethylene and allyl cation are reported. The GVB(SP) method generates wavefunctions possessing the correct spatial and spin symmetry without restricting the nature of the individual orbitals. The GVB(SP) wavefunction provides a simple interpretation of the molecule in terms of orbitals each containing a single electron. The resulting total energies and excitation energies agree very well with full configuration interaction calculations.

1. Introduction

Since both the thermal and photochemical reactions of unsaturated organic molecules generally involve the pi orbitals of the molecules, the pi-electron systems of unsaturated organic molecules have been the subject of numerous theoretical studies. The simplest such systems are found in the ethylene molecule and the allyl cation, each of which contains two electrons in π orbitals. Ethylene, in particular, has been studied extensively as a prototype of larger non-aromatic, unsaturated molecules.

The usual molecular orbital (MO) or Hartree–Fock (HF) picture of the pi orbitals of the ground state of ethylene or allyl cation involves a single doubly-occupied pi orbital. This orbital transforms according to a particular irreducible representation of the molecular symmetry group and as a result is generally delocalized over the whole molecule. The HF picture for the lowest excited states of the pi-electron system involves two singly-occupied pi orbitals coupled to either a

singlet or triplet. In the Hartree–Fock description of the ground state two electrons move uncorrelated in the same orbital whereas in the excited state these electrons are in different orbitals. As a result the excitation energies should be underestimated.

The Generalized Valence Bond (GVB) description [1] of electronic wavefunctions offers the advantage of allowing a different orbital for each electron, thereby including a more comparable level of electron correlation in all states while retaining a simple orbital interpretation. The wavefunctions reported herein include operators for both spin and spatial projection so that no symmetry restrictions need be placed upon the orbitals.

We report the results of GVB calculations (including spatial projection) ([2–4], see also [5]) of the π -electron orbitals for ethylene and allyl cation. Ground states and low-lying excited states for both systems are included, all with the geometry of the ground state.

2. Computational considerations

2.1. *The Hartree–Fock and generalized valence bond wavefunctions*

The Hartree–Fock wavefunction for the ground

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state of ethylene is of the form:

$$\alpha[\phi_1\alpha\phi_1\beta\dots\phi_q\alpha\phi_q\beta\phi_{\pi_1}\alpha\phi_{\pi_1}\beta] = \alpha[\Phi_\sigma\phi_{\pi_1}\alpha\phi_{\pi_1}\beta], \quad (1)$$

where there are seven doubly-occupied σ orbitals (orbitals that are symmetric under the operation of reflection through the molecular plane) and one doubly-occupied π orbital (orbitals that are antisymmetric under the operation of reflection through the molecular plane). The many-electron product Φ_σ is used here to represent all of the σ orbitals. Some of the important excited states of ethylene are obtained by replacing one π orbital in (1) with an excited π orbital, ϕ_{π_2} . This produces wavefunctions of the form

$$\text{triplet: } \alpha[\Phi_\sigma(\phi_{\pi_1}\phi_{\pi_2} - \phi_{\pi_2}\phi_{\pi_1})\alpha\beta], \quad (2)$$

$$\text{singlet: } \alpha[\Phi_\sigma(\phi_{\pi_1}\phi_{\pi_2} + \phi_{\pi_2}\phi_{\pi_1})\alpha\beta]. \quad (3)$$

In the Hartree–Fock procedure, the orbitals of (1), (2) and (3) are solved for self-consistently. The resulting wavefunctions represent only an approximate description of the molecular states, and for example, provide the correct excitation energies only if similar correlation effects occur in the various states. In (1), both π electrons occupy the same orbital, whereas in an exact description, one expects the electrons to correlate their motions to remain spatially separated. In (2) and (3), each π electron occupies a different orbital and as a result tends to move in different regions of space. Thus, in this description the ground state has a greater (correlation) error than the excited states, resulting in excitation energies that are smaller than the experimental values.

In order to obtain a more consistent description of the various states of ethylene, we replace the doubly-occupied π orbital of (1) with

$$(\phi_{\pi a}\phi_{\pi b} + \phi_{\pi b}\phi_{\pi a}) \quad (4)$$

(the valence bond description of the π orbitals) and solve for these (nonorthogonal) orbitals self-consistently. In this manner, the same correlation effects that have been included in the excited states are also included in the description of the π electrons of the ground state, providing a more consistent description of the ground and excited states. This method of allowing certain Hartree–Fock pairs (i.e., doubly-occupied orbitals) to be described in terms of valence bond pairs [e.g., eq. (4)] which are solved for self-consistently is called the generalized valence bond method [1].

2.2. The core hamiltonians

As demonstrated in the appendix[†], the problem of solving for wavefunctions of the form

$$\alpha[\Phi_{\text{val}}(1, 2)\Phi_\sigma(3, \dots, N)] \quad (5)$$

can be reduced to the two-electron problem of solving for

$$\alpha[\Phi_{\text{val}}(1, 2)] \quad (6)$$

if (i) Φ_σ is a product of doubly-occupied orbitals and (ii) if the orbitals of Φ_{val} are taken to be orthogonal to those of Φ_σ . In this case the two-electron hamiltonian (called the core hamiltonian) for (6) becomes:

$$\mathcal{H}(1, 2) = h^{\text{core}}(1) + h^{\text{core}}(2) + 1/r_{12}, \quad (7)$$

where

$$h^{\text{core}}(i) = h(i) + \sum_{j=1}^q (2J_j - K_j) \quad (8)$$

and h is the usual one-electron operator

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_a Z_a/r_{ia}. \quad (9)$$

Although the eigenfunction Φ_{val} of (7) is a rigorous solution for (5) given a particular Φ_σ , the resulting total wavefunction is useful only if Φ_σ is relatively insensitive to changes in Φ_{val} . In this case a Φ_σ may be found once and then used for various types of descriptions of the valence electrons [e.g., Hartree–Fock (HF), GVB, or configuration interaction (CI)] and for the description of excited states. For ethylene we used in each case the Φ_σ from an ab initio HF calculation on the same state so that Φ_σ should be well described. For allyl cation, we used the Φ_σ from a self-consistent, ab initio HF calculation on the ground state of allyl cation. This Φ_σ should be a good description of the σ orbitals for the GVB and GVB(SP) calculations on the ground state and valence-like excited states. Higher excited states involving a relatively diffuse orbital will not be as well described since the corresponding Φ_σ would contract somewhat if solved for self-consistently. Using the ground state core for these excited states would tend to result in an overestimation of the excitation energies.

[†] Based on unpublished work by W.A. Goddard III, T.H. Dunning and P.J. Hay. See for example ref. [6].

2.3. Spatially projected wavefunctions

The simple valence bond (VB) description of the π electrons of the ground state of ethylene is

$$\boxed{\ell 2p_x \ r 2p_x} = (\phi_{\ell 2p_x} \phi_{r 2p_x} + \phi_{r 2p_x} \phi_{\ell 2p_x})(\alpha\beta - \beta\alpha), \quad (10)$$

where the tableau in (10) denotes singlet-paired orbitals. (Note we use the standard choice of x as the axis perpendicular to the molecular plane.) To describe a π -excited state in this model, we might consider exciting one electron from a $2p_x$ orbital to a $3p_x$ (or $3d_{xz}$) orbital. This results in wavefunctions of the form

$$\boxed{\ell 2p_x \ r 3p_x} \quad (11)$$

or

$$\boxed{\ell 3p_x \ r 2p_x} \quad (12)$$

depending on whether the left or right orbital is excited. Neither (11) nor (12) possesses the correct molecular symmetry, and we expect that a more appropriate description of the excited states would be

$$\begin{aligned} \boxed{\ell 2p_x \ r 3p_x}_s &\equiv \boxed{\ell 2p_x \ r 3p_x} + \boxed{\ell 3p_x \ r 2p_x} \\ &= (\phi_{\ell 2p_x} \phi_{r 3p_x} + \phi_{r 3p_x} \phi_{\ell 2p_x})(\alpha\beta - \beta\alpha) \\ &\quad + (\phi_{\ell 3p_x} \phi_{r 2p_x} + \phi_{r 2p_x} \phi_{\ell 3p_x})(\alpha\beta - \beta\alpha), \end{aligned} \quad (13)$$

or

$$\boxed{\ell 2p_x \ r 3p_x}_a \equiv \boxed{\ell 2p_x \ r 3p_x} - \boxed{\ell 3p_x \ r 2p_x} \quad (14)$$

where the subscripts s or a indicates that the wavefunctions of (11) and (12) have been recombined into a state which is symmetric (13) or antisymmetric (14) with respect to the spatial symmetry operation (reflection) interchanging the ℓ and r centers[†].

We now define a reflection operator which will be used to provide a mathematical formulation of (13) and (14). \hat{R} is defined as the operator which takes

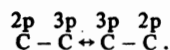
$$x \rightarrow x, \quad y \rightarrow y, \quad z \rightarrow -z,$$

where the z axis is perpendicular to the reflection plane.

Thus

$$\hat{R} \boxed{\ell 3p_x \ r 2p_x} = \boxed{r 3p_x \ \ell 2p_x} = \boxed{\ell 2p_x \ r 3p_x}$$

[†] This is directly analogous to resonance in classical valence bond theory. The two structures would be denoted as



and (13) may be written as

$$\boxed{\ell 2p_x \ r 3p_x}_s = \hat{P}_s \boxed{\ell 2p_x \ r 3p_x} \quad (15)$$

where

$$\hat{P}_s = (1 + \hat{R}). \quad (16)$$

Similarly (14) is

$$\boxed{\ell 2p_x \ r 3p_x}_a = \hat{P}_a \boxed{\ell 2p_x \ r 3p_x} \quad (17)$$

where

$$\hat{P}_a \equiv (1 - \hat{R}). \quad (18)$$

This is analogous to writing the spatial part of (10) as

$$(\phi_{\ell 2p_x} \phi_{r 2p_x} + \phi_{r 2p_x} \phi_{\ell 2p_x}) = (1 + P_{12}) \phi_{\ell 2p_x} \phi_{r 2p_x}, \quad (19)$$

where P_{12} interchanges electrons one and two.

Using spatial projection operators, the spatial parts of the two-electron wavefunctions (13) and (14) have the form

$$(1 \pm \hat{R})(1 + P_{12}) \phi_{\ell a}(1) \phi_{r b}(2), \quad (20)$$

i.e., with one orbital for each electron.

In order to provide a more accurate description than the above simple VB description but without sacrificing the simple model suggested by (20), we will use wavefunctions of the form (20) and solve each orbital selfconsistently. This is called the generalized valence bond (GVB) approach [1-5]. To indicate explicitly that a spatial projection operator has been included [2-5], the notation GVB(SP) will be used. As usual the GVB(SP) wavefunction (20) may be interpreted in terms of one electron in orbital $\phi_{\ell a}$ and the other electron in orbital $\phi_{r b}$ each moving in the average field due to the other electrons.

The details of the self-consistent field equations for GVB(SP) wavefunctions are presented elsewhere [3]. Here we merely summarize the notation to be used. If

$$\hat{R} \phi_{\ell a} = \phi_{r a}, \quad \hat{R} \phi_{r b} = \phi_{\ell b},$$

then the forms of the projected wavefunctions are as in fig. 1 and lead to the total symmetries indicated in fig. 1. For example,

$$\begin{array}{c} \phi_{\ell a} \\ \phi_{r b} \end{array}_a = [(\phi_{\ell a} \phi_{r b} - \phi_{r b} \phi_{\ell a}) - (\phi_{r a} \phi_{\ell b} - \phi_{\ell b} \phi_{r a})] (\alpha\beta + \beta\alpha). \quad (21)$$

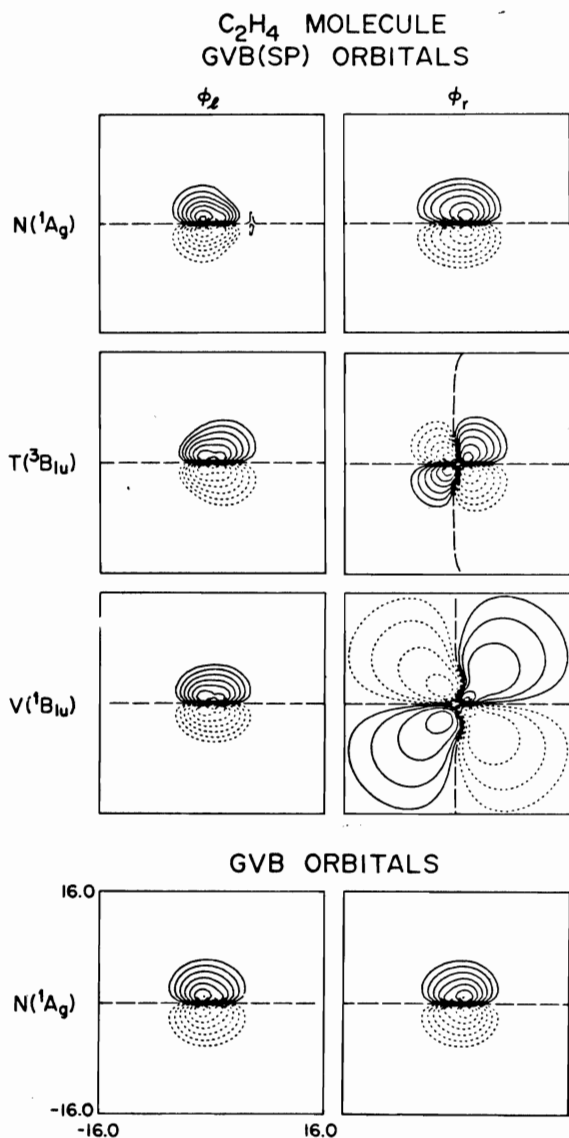


Fig. 1. The GVB(SP) orbitals of ethylene. The nodal line is indicated by long dashes. Positive contours are indicated by solid lines and negative contours by dotted lines. The positive contours correspond to amplitudes of 0.003, 0.00646, 0.0139, 0.03, 0.0646, 0.139 and 0.3; and similarly for the negative amplitudes.

2.4. The basis and other details

For each state of ethylene we used the σ orbitals

from a Hartree–Fock calculation [9] on the same state to define the h^{core} in (7) for use in the π -electron calculations of this state. One Hartree–Fock calculation was performed on allyl cation and the resulting σ orbitals used to define h^{core} in (7) for all of the allyl cation π -electron calculations.

The basis set consisted of a (9s 5p) set of gaussian functions on each carbon and a (4s) set on each hydrogen, as suggested by Huzinaga [7]. This was contracted (as suggested by Dunning [8]) to a (4s 3p) on each carbon and (2s) on each hydrogen for ethylene and to a double-zeta basis (4s 2p) on each carbon and (2s) on each hydrogen for allyl. In order to describe Rydberg-like excited states, it is necessary to also include more diffuse functions, and consequently, the above basis was supplemented by three additional diffuse π gaussian functions (orbital exponents of $\alpha = 0.0365$, 0.0116 and 0.0037) on each carbon for ethylene and by two additional functions ($\alpha = 0.382$ and 0.0127) on each carbon for allyl cation.

3. Results

The GVB orbitals for the π orbitals of ethylene are depicted in fig. 1. Included in this figure are the orbitals for the ground (N) state using both GVB and GVB(SP) wavefunctions, and the GVB(SP) orbitals for the first triplet (T) state and the first excited singlet (V) state. The ground state geometry is used for all three states. Table 1 contains a summary of the calculated energies and includes HF results for comparison.

The allyl cation GVB π orbitals are depicted in fig. 2. This figure includes the GVB and the GVB(SP) orbitals for the ground (1A_1) state and the GVB(SP) orbitals for the next four states (3B_2 , 1B_2 , 3A_1 , 2^1A_1). Table 2 contains a summary of the calculated results.

4. Discussion

4.1. Ethylene

In the HF (or MO) description, the π wavefunctions for the N, T and V states have the following form

$$N: \pi_g \pi_u, \quad T: \pi_g \pi_u - \pi_u \pi_g, \quad V: \pi_g \pi_u + \pi_u \pi_g,$$

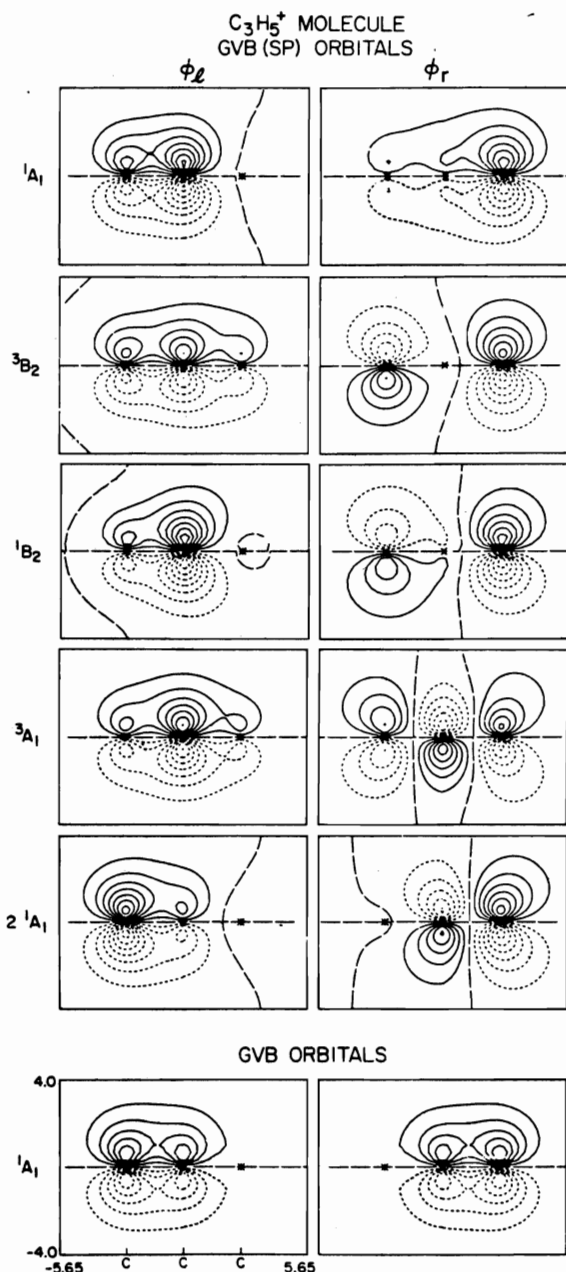


Fig. 2. The GVB(SP) orbitals of allyl cation. The amplitude of the most diffuse contour is 0.05. Each subsequent contour has an amplitude of 0.05 greater than the previous line. The orbital amplitudes are shown in the planes containing the carbon atoms and perpendicular to the molecular plane. Thus, the two halves of each plot are bent to an angle 120° .

where the (occupied) orbitals are (delocalized) symmetry functions.

From fig. 1, we see that the N state GVB π orbitals are relatively localized, much as in the VB description. However, the changes in these orbitals from the atomic form have increased the overlap from 0.34 (for atomic orbitals) to 0.59. Thus one can view the GVB orbitals as

$$\phi_{\pi_L} = N[\phi_{2p_L} + \lambda\phi_{2p_R}] , \quad \phi_{\pi_R} = N[\phi_{2p_R} + \lambda\phi_{2p_L}] ,$$

where λ is approximately 0.14. If one of the π orbitals is ionized, the remaining orbital becomes completely delocalized

$$\phi_{\pi_g} = N(\phi_{2p_L} + \phi_{2p_R})$$

just as in the MO description (if readjustments are allowed in the σ core for the ion state and spatial projection is used for the entire wavefunction, a more localized representation may be obtained).

For the excited states, we find that the excited orbital (ϕ_r) remains close enough to one of the nuclei so that the unexcited orbital (ϕ_L) is still somewhat localized (near the other nucleus); the unexcited orbital is, however, much less localized than in the ground state. Note, in particular, that the unexcited orbitals of the V and T states of ethylene are very similar, but that the excited orbital, although possessing the same nodal structure in both states, is far more diffuse in the V state than in the T state. This same basic character was found earlier in the HF wavefunctions by Dunning et al. [9] and has been discussed in detail elsewhere ([10, 11]; cf. [12]).

In fig. 1, we show the GVB(SP) orbitals for the N state, which should be compared to the GVB orbitals also in fig. 1. The GVB(SP) wavefunctions permits the two orbitals to be inequivalent. As a result, one orbital becomes tighter but more delocalized while the other becomes more diffuse but more localized. The resulting more delocalized orbital is quite similar in form to the unexcited orbitals in the GVB(SP) description of the T and V states.

4.2. Allyl cation

One would expect the allyl cation π orbitals to be rather similar to the ethylene pi orbitals. The major difference in the two systems should result from the fact that the allyl cation has a net positive charge and consists of three centers. The effect of this net positive charge should be to reduce the spatial extent of the orbitals as compared to the analogous ethylene

Table 1
Energy quantities for the GVB wavefunctions of ethylene. All energies in hartrees (1H = 27.2117 eV) unless indicated otherwise

State	Method	Total energy	Orbital energy		Excitation energy (eV)
			ϕ_Q	ϕ_R	
N(1A_g) ¹⁾	GVB	-78.034134	-0.45003	-0.45003	-
	GVB(SP)	-78.046172	-0.48878	-0.44837	0
T($^3B_{1u}$)	GVB(SP)	-77.891962	-0.52368	-0.25306	4.196
V($^1B_{1u}$)	GVB(SP)	-77.742095	-0.59932	-0.07076	8.274

1) The overlap $\langle \phi_Q | \phi_R \rangle$ is 0.632 for GVB and 0.592 for GVB(SP).

Table 2
Energy quantities for allyl cation (all energies in hartrees unless indicated otherwise)

State	Total energy	Orbital energy		Excitation energy (eV)
		ϕ_Q	ϕ_R	
1 1A_1 GVB ¹⁾	-116.163675	-0.712930	-0.712930	-
	-116.172789	-0.787221	-0.704021	0
3B_2 GVB(SP)	-116.062719	-0.809458	-0.573322	2.995
1B_2 GVB(SP)	-115.959400	-0.720730	-0.497721	5.807
3A_1 GVB(SP)	-115.898766	-0.787015	-0.391671	7.457
2 1A_1 GVB(SP)	-115.833770	-0.651677	-0.448324	9.225

1) For the 1A_1 state the overlap $\langle \phi_Q | \phi_R \rangle$ is 0.660 for GVB and 0.549 for GVB(SP). For 2 1A_1 the overlap is 0.380.

Table 3
Comparison of energies obtained from various calculational methods (using the same sigma core and basis set for each comparison). The total energy (hartrees) is given in each case

	State	HF	GVB	GVB(SP)	Full CI
Ethylene	N	-78.014268	-78.034134	-78.046172	-78.046457
	T	-77.891731	-	-77.891962	-77.891971
	V	-77.741542	-	-77.742095	-77.742183
Allyl cation	1 1A_1	-116.145274	-115.157899	-116.172789	-116.173420
	3B_2	-	-116.060646	-116.062719	-116.062725
	1B_2	-	-115.956382	-115.959400	-115.959503
	3A_1	-	-115.898547	-115.898766	-115.898898
	2 1A_1	-	-115.744890	-115.833770	-115.836320

Table 4
The excitation energies of allyl cation (in eV)

State	Present work			Peyerimhoff and Buenker ¹⁾ CI
	GVB	GVB(SP)	Full CI	
1 1A_1	0	0	0	0
3B_2	2.646	2.995	3.012	3.67
1B_2	5.484	5.807	5.821	7.02
3A_1	7.057	7.457	7.470	9.23
2 1A_1	11.239	9.225	9.173	10.89

1) Ref. [13]. The CI energy for the ground state was -116.1300 hartree as compared with -116.1734 hartree for our CI wavefunction.

orbitals. The presence of three centers should result in a delocalization of the orbitals. These expectations are most evident in a comparison of the 1B_2 (first excited singlet) state of allyl cation with the V state of ethylene. In this case both orbitals of the 1B_2 state of allyl cation are quite tight, whereas the excited orbital of the ethylene V state is very diffuse (see fig. 1 and 2).

Further evidence of the similarity of the pi-electron states of ethylene and allyl cation is found in the orbital energies and excitation energies summarized in tables 1 and 2. The excited states in both systems may be best described as one-electron excitations from the ground state, leaving the other orbital essentially unchanged. The excitation energies in the allyl cation system are lower because the net positive charge in this system leads to a greater stabilization of the excited orbitals as compared to the ethylene system. For example, the excitation energy to the V state of ethylene was found to be 8.27 eV while the excitation energy of the 1B_2 state of allyl cation was found to be 5.80 eV.

4.3. Comparison with other methods

In tables 3 and 4 the results of GVB(SP) calculations are compared with those from HF, GVB (without spatial projection), and full configuration interaction (CI) calculations, all performed with the same basis set and σ core.

The agreement between the GVB(SP) and full CI calculations is excellent, the largest disagreement being 0.017 eV (0.4 kcal)* for the allyl cation ground state. In comparison the HF energy for this state is 0.028 hartree (17.5 kcal) above the full CI energy. Thus the GVB(SP) method leads to an energy essentially identical to the full CI energy while providing orbitals useful for qualitative understanding of the system and qualitative extension to larger molecules.

Table 4 contains a comparison of excitation energies for allyl cation as calculated by various methods. Peyerimhoff and Buenker [13] reported CI calculations for allyl cation. They used a [3s 1p/1s] basis contracted from a (10s 5p/5s) primitive basis. Our basis is considerably more extensive, (9s 5p/5s)

* Hartree atomic units are used ($|e| = 1, h = 1, m_e = 1$);
1 hartree = 27.2117 eV = 627.71 kcal.

contracted to [4s 2p/2s] plus a diffuse function, and hence should lead to more reliable excitation energies.

5. Summary

We find that GVB with spatial projection leads to a wavefunction with energies very close to the full CI wavefunction (CI within the π system). The GVB(SP) wavefunction also yields a simple interpretation of the wavefunctions for the various states.

Appendix: The core potential**

Consider a wavefunction of the form

$$\alpha(\phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta\dots\phi_q\alpha\phi_q\beta\phi_v\alpha). \quad (\text{A.1})$$

The variational equation for the optimum orbital ϕ_v is

$$H_v\phi_v = \epsilon_v\phi_v, \quad (\text{A.2})$$

where H_v has the form

$$H_v = h + \sum_{j=1}^q (2J_j - K_j) \quad (\text{A.3})$$

if in solving (A.2) we restrict ϕ_v to be in the space orthogonal to the doubly-occupied orbitals

$$\{\phi_1, \dots, \phi_q\}. \quad (\text{A.4})$$

Now consider the case of a more complicated N -electron wavefunction

$$\alpha(\Phi_{\text{core}}\Phi_{\text{val}}), \quad (\text{A.5})$$

where

$$\Phi_{\text{core}} = \phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta\dots\phi_q\alpha\phi_q\beta \quad (\text{A.6})$$

and Φ_{val} is some ($N' = N - 2q$) many-electron function.

Since each orbital in Φ_{core} is doubly occupied, then in the wavefunction (A.5) it is no restriction to require that Φ_{val} be orthogonal to each orbital of Φ_{core}

$$\int \Phi_{\text{val}}(1, \dots, N') \phi_j(i) d^3r_i = 0, \quad (j = 1, \dots, q). \quad (\text{A.7})$$

As a result if Φ_{val} is solved for within the space orthogonal to the core orbitals (A.4), then the only surviv-

** See footnote on page 410.

ing terms in the energy expression involving both the core and valence orbitals have the form

$$\langle \mu | \sum_j (2J_j - K_j) | \nu \rangle, \quad (\text{A.8})$$

where μ and ν are functions belonging to the valence space, i.e., the space orthogonal to the set (A.4).

Thus in the many-electron space satisfying (A.7), the variational wavefunction Φ_{val} can be obtained by solving for the optimum wavefunction of the form

$$a(\Phi_{\text{val}}) \quad (\text{A.9})$$

using the $N' = N - 2q$ electron hamiltonian

$$\mathcal{H} = \sum_i^{N'} h^{\text{core}}(i) + \sum_{i>j}^{N'} 1/r_{ij}, \quad (\text{A.10})$$

where $h^{\text{core}}(i)$ is given by (A.3). The only restriction made here is that the core orbitals are not reoptimized to reflect changes in the valence orbitals.

However, given the Φ_{core} the use of (A.9) and (A.10) involves no additional approximations, $h^{\text{core}}(i)$ includes all the proper terms that arise from the Pauli principle. The major advantage of the above procedure is that the two-electron integrals involving the core orbitals are processed only once to form the matrices

$$\langle \mu | h^{\text{core}} | \nu \rangle.$$

With these matrices one can carry out various types of calculations (HF, GVB, CI) on the various excited states while working with only a small number of electrons, two in the case of ethylene and allyl cation. In this case the calculations take no longer than if only

two electrons had been present.

The h^{core} forms an effective potential for movement of the valence electrons. This differs from the various pseudopotential methods and usual effective potential methods in that we do *not* approximate the way that the field terms due to Φ^{core} enter the wavefunction.

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