rated ground state CO molecules. (iii) The linear dissociation of ethylenedione to two molecules of CO is symmetry forbidden and accordingly has a high activation energy. (iv) In contrast, dissociation of trans bent ethylenedione is symmetry allowed; trans bending leads easily to two separated molecules of CO with little or no activation energy. (v) Our results therefore suggest that it is unlikely that singlet ethylenedione will be observed experimentally. There is a somewhat better prospect for generating and observing the triplet.

### References and Notes

(1) Queen Elizabeth II Fellow.
(2) (a) For an early attempt at the synthesis of ethylenedione, see H. Staudinger and H. Anthes, *Chem. Ber.*, **46**, 1426 (1913); (b) J. J. Bloomfield, J. R. S. Irelan, and A. P. Marchand, *Tetrahedron Lett.*, 5647 (1968); (c) J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *ibid.*, 125 (1969); (d) D. Bryce-Smith and A. Gilbert, *Chem. Commun.*, 1319 (1968); (e) D. L. Dean and H. Hart, *J. Amer. Chem. Soc.*, **94**, 687 (1972); (f) H.-D. Scharf and R. Klar, *Tetrahedron Lett.*, 517 (1971); *Chem. Ber.*, **105**, 575 (1972).
(3) (a) D. M. Hirst, J. D. Hopton, and J. W. Linnett, *Tetrahedron, Suppl.*, **2**, 15 (1963); (b) B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970); (c) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970); (d) R. C. Haddon, *Tetrahedron Lett.*, 3897 (1972); (e) J. Fleischhauer, M. Beckers, and H.-D. Scharf, *ibid.*, 4275 (1973); (f) N. H. F. Beebe and J. R. Sabin, *Chem. Phys. Lett.*, **24**, 389 (1974); (g) M. J. S. Dewar, R. C. Haddon, and W. K. Li, manuscript in preparation.
(4) J. M. Landesburg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **93**, 972 (1971).
(5) L. M. Jackman, V. R. Haddon, and R. C. Haddon, unpublished observations, 1971.
(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(7) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).
(8) J. A. Pople, *Int. J. Quantum Chem., Symp.*, **5**, 175 (1971).
(9) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.
(10) G. M. Schwenzer, S. V. O'Nell, H. F. Schaefer, C. P. Baskin, and C. F. Bender, *J. Chem. Phys.*, **60**, 2787 (1974).
(11) (a) C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, **70**, 2675 (1966). For a recent application to methylene, see (b) C. F. Bender, H. F. Schaefer, D. R. Franceschetti, and L. C. Allen, *J. Amer. Chem. Soc.*, **94**, 6888 (1972).
(12) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(13) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(14) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
(15) For a review, see L. Radom and J. A. Pople, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci. Theor. Chem., Ser. One* (1972).
(16) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).
(17) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).
(18) J. E. Del Bene, *J. Amer. Chem. Soc.*, **94**, 3713 (1972); L. Radom, unpublished data.
(19) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 6377 (1971).
(20) P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *Chem. Phys. Lett.*, **13**, 30 (1972); V. Staemmler, *Theor. Chim. Acta*, **31**, 49 (1973); M. J. S. Dewar, R. C. Haddon, and P. K. Weiner, *J. Amer. Chem. Soc.*, **96**, 253 (1974); M. J. S. Dewar, R. C. Haddon, W. K. Li, W. Thiel, and P. K. Weiner, *ibid.*, submitted for publication.
(21) W. L. Hase, R. J. Phillips, and J. W. Simons, *Chem. Phys. Lett.*, **12**, 161 (1971).
(22) Test calculations in which the symmetry was reduced to $C_{\infty v}$ yielded optimized $D_{\infty h}$ structures.
(23) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290, 4291, 4292 (1971). For a discussion of such discontinuities, based on an accurate nonempirical potential energy surface, see C. P. Baskin, C. F. Bender, C. W. Bauschlicher, and H. F. Schaefer, *ibid.*, **96**, 2709 (1974).

# The Generalized Valence Bond Description of Allyl Radical[1a]

### George Levin[1b] and W. A. Goddard III*

*Contribution from the Arthur Amos Noyes Laboratory of Chemical Physics,[1c] California Institute of Technology, Pasadena, California 91109. Received May 1, 1974*

**Abstract:** *Ab initio* generalized valence bond (GVB) and configuration interaction calculations are reported for the ground and low-lying excited states of allyl. The GVB wave functions lead to energies very close to those of the full CI wave functions (0.13 eV error for the ground state) providing a firm basis to the interpretations based on the GVB wave functions. We find that the ground state and first singlet excited state of allyl are well described as the classical resonant and antiresonant combinations of simple valence bond structures. The theoretical value obtained for the allyl resonance energy is 11.4 kcal, in reasonable agreement with thermochemical estimates (11.6 ± 2 kcal).

## I. Introduction

The $\pi$ orbitals of unsaturated organic compounds are chemically the most active part of the molecules and as such have been the subject for much theoretical investigation. In a previous paper,[2] we reported generalized valence bond (GVB) calculations on ethylene and allyl cation, including some excited states. In this paper we report GVB calculations on the ground and excited states of allyl radical, allowing simultaneous optimization of both the spatial orbitals and the spin coupling while generating a spin eigenfunction.[3-5]

The $\pi$-electron system of allyl cation is the smallest $\pi$ system displaying what is known in valence bond (VB) theory as resonance. The GVB approach is well suited to describing resonance since the wave function is sufficiently flexible to describe a linear combination of the two classical resonance forms. However, in the GVB approach the shapes of the orbitals are optimized (rather than assumed to be atomic-like as in VB), and the overall form of the wave function is not restricted to expressions of the resonance form. Even so we find that the ground and first excited states are well described as the resonant and antiresonant states

$$\diagup\!\!\!\diagdown \quad \pm \quad \diagup\!\!\!\diagdown$$
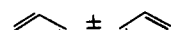
thus providing a rigorous quantum mechanical basis for the concept of resonance.

## II. Calculational Considerations

**A. The Wave Functions. a. Hartree–Fock.** The Hartree–Fock (HF) wave function for the ground state of allyl radical may be written in the form[6]

$$\mathcal{C}[\varphi_1 \alpha \varphi_1 \beta \ldots \varphi_q \alpha \varphi_q \beta \varphi_{\pi_1} \alpha \varphi_{\pi_1} \beta \varphi_{\pi_2} \alpha] \qquad (1)$$

where for allyl radical there are then doubly occupied $\sigma$ orbitals, one doubly occupied $\pi$ orbital, and one singly occupied $\pi$ orbital (here $\sigma$ and $\pi$ indicate orbitals that are symmetric and antisymmetric, respectively, with respect to reflection through the molecular plane). Many low-lying excited states involve excitation of an electron from a $\pi$ orbital to a higher $\pi$ orbital and are described by HF wave functions of the form

$$\alpha[\Phi_\sigma \phi_{\pi_1} \alpha \phi_{\pi_2} \beta \phi_{\pi_2} \alpha] \tag{2a}$$

$$\alpha[\Phi_\sigma \varphi_{\pi_1} \alpha \varphi_{\pi_1} \beta \varphi_{\pi_3} \alpha] \tag{2b}$$

or

$$\alpha[\Phi_\sigma \varphi_{\pi_1} \alpha \varphi_{\pi_2} \beta \varphi_{\pi_3} \alpha] \tag{3}$$

where $\Phi_\sigma$ denotes the product of all of the doubly occupied $\sigma$ orbitals (including spin terms). The electron correlation errors in (1) and (2) are expected to be much larger than for (3) due to the presence of doubly occupied $\pi_1$ or $\pi_2$ orbitals in (1) and (2) but not in (3). In fact we will find that neither (2a) nor (2b) yields a reasonable description of the lowest excited state of allyl.

**b. The Valence Bond Wave Function.** In the valence bond (VB) wave function of allyl there is a singly occupied atomic $\pi$ orbital on each carbon atom. We will denote these orbitals as $\chi_l$, $\chi_c$, and $\chi_r$ as indicated in (4). These orbitals

$$\begin{array}{c} \chi_c \\ \diagdown \\ \chi_l \quad \chi_r \end{array} \tag{4}$$

may be coupled into the two different doublet states indicated in (5) and (6).

$$\diagup\!\!\diagdown \cdot = \boxed{\begin{array}{|c|c|} \hline \chi_l & \chi_c \\ \hline \chi_r & \\ \hline \end{array}} = \Psi_1 \tag{5}$$

$$\cdot\diagup\!\!\diagdown = \boxed{\begin{array}{|c|c|} \hline \chi_r & \chi_c \\ \hline \chi_l & \\ \hline \end{array}} = \Psi_2 \tag{6}$$
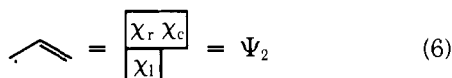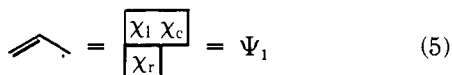
where orbitals in the same row of the tableau in (5) or (6) are singlet paired (i.e., paired in a bonding manner). The wave functions corresponding to (5) and (6) are

$$\begin{aligned} \Psi_1 &= \alpha[\Phi_\sigma(\chi_l\chi_c + \chi_c\chi_l)\chi_r \alpha\beta\alpha] \\ &= \alpha[\Phi_\sigma\chi_l\chi_c\chi_r(\alpha\beta - \beta\alpha)\alpha] \\ &= \alpha[\Phi_\sigma\chi_r\chi_l\chi_c\alpha(\alpha\beta - \beta\alpha)] \end{aligned} \tag{7a}$$

$$\begin{aligned} \Psi_2 &= \alpha[\Phi_\sigma(\chi_r\chi_c + \chi_c\chi_r)\chi_l \alpha\beta\alpha] \\ &= \alpha[\Phi_\sigma\chi_r\chi_c\chi_r(\alpha\beta - \beta\alpha)\alpha] \\ &= \alpha[\Phi_\sigma\chi_r\chi_l\chi_c(\beta\alpha\alpha - \alpha\alpha\beta)] \end{aligned} \tag{7b}$$

These wave functions have the same energy and are referred to as the simple VB wave functions. It is perhaps important to note that the structures in (5) and (6) differ only in the way that the spin functions are coupled. They involve equivalent spatial orbitals.

Allowing the wave function for the system to be a superposition of $\Psi_1$ and $\Psi_2$ leads to an optimum wave function of the form

$$\Psi_a = \Psi_1 - \Psi_2 \equiv \diagup\!\!\diagdown\cdot - \cdot\diagup\!\!\diagdown \tag{8a}$$

with an energy lower than $E_1$ (the energy of $\Psi_1$ or $\Psi_2$), $E_a < E_1$, and a second wave function

$$\Psi_s = \Psi_1 + \Psi_2 \equiv \diagup\!\!\diagdown\cdot + \cdot\diagup\!\!\diagdown \tag{8b}$$

with an energy higher than $E_1$, $E_s > E_1$. $\Psi_a$ and $\Psi_s$ are the antisymmetric and symmetric combinations of the simple VB wave functions in (5) and (6). The energy change

$$E_{res} = E_1 - E_a \tag{9a}$$

resulting from the favorable combinations of the VB states is generally called the *resonance energy*. We will refer to the energy increase

$$E_{antires} = E_s - E_1 \tag{9b}$$

occurring in the unfavorable combination $\Psi_s$ of VB states as the *antiresonance energy*.

From (7) the wave functions in (8) can both be written as

$$\Psi_i = \alpha[\Phi_\sigma\chi_r\chi_l\chi_c\Theta_i] \tag{10}$$

where the spin functions $\Theta_i$ are

$$\Theta_a = 2\alpha\alpha\beta - (\alpha\beta + \beta\alpha)\alpha \tag{11}$$

$$\Theta_s = -(\alpha\beta - \beta\alpha)\alpha \tag{12}$$

Thus proceeding from the simple valence bond wave function as in (5) or (6) to the resonance state in (8a) is equivalent to optimizing the spin function in (10).

**c. The Generalized Valence Bond Wave Function.** The generalized valence bond (GVB) wave function is formally the same as the VB wave function

$$\alpha[\Phi_\sigma\phi_a\phi_b\phi_c\Theta] \tag{13}$$

but the orbitals $\phi_a$, $\phi_b$, and $\phi_c$ and the spin coupling $\Theta$ are all solved for self-consistently[3] (rather than using atomic orbitals as in the VB wave function). Although the GVB orbitals are allowed to have any shape, we will find that they often are each mainly concentrated near a different carbon atom. In such cases the optimum GVB orbitals will be denoted as $\phi_l$, $\phi_c$, $\phi_r$ (indicating the location of the maximum amplitude of each orbital).

There are two linearly independent ways of coupling three electrons into a doublet. For example, the spin functions in (7a) and (7b) or alternatively the spin functions in (11) and (12) may be used. We will find it convenient to use the orthogonal spin functions of (11) and (12), denoting them as

$$\theta_1 = (\alpha\beta - \beta\alpha)\alpha \tag{14}$$
$$\theta_2 = 2\alpha\alpha\beta - (\alpha\beta + \beta\alpha)\alpha$$

referred to as the G1 and G2 (or GF) spin functions.[3] Note that electrons 1 and 2 are coupled into a singlet state in $\theta_1$ and into a triplet state in $\theta_2$. The optimum spin function for (13) is given by

$$\Theta = C_1\theta_1 + C_2\theta_2 \tag{15}$$

In discussing such wave functions it is often convenient to use the diagram

$$\boxed{\begin{array}{|c|} \hline \phi_a \ \phi_b \\ \hline \phi_c \\ \hline \end{array}} \tag{16}$$

to indicate the wave function $\alpha[\Phi_\sigma\phi_a\phi_b\phi_c\theta_1]$ (that is, singlet coupling of $\phi_a$ and $\phi_b$) and

$$\boxed{\begin{array}{|c|c|} \hline \phi_a & \phi_c \\ \hline \phi_b & \\ \hline \end{array}} \tag{17}$$

to indicate the wave function $\alpha[\Phi_\sigma\phi_a\phi_b\phi_c\theta_2]$ (that is, triplet coupling of $\phi_a$ and $\phi_b$).

In terms of these diagrams the resonant VB state in (8a) can be expressed as

$$\boxed{\begin{array}{|c|c|} \hline \chi_r & \chi_c \\ \hline \chi_l & \\ \hline \end{array}} = \boxed{\begin{array}{|c|c|} \hline \chi_l & \chi_c \\ \hline \chi_r & \\ \hline \end{array}} - \boxed{\begin{array}{|c|c|} \hline \chi_r & \chi_c \\ \hline \chi_l & \\ \hline \end{array}} \tag{18}$$

and the antiresonant VB state (8b) can be expressed as

**Table I.** Comparison of Ground-State Energies for Allyl

| | Energy, hartrees | Error eV | Error kcal |
|---|---|---|---|
| VB | −116.35544 | 1.79 | 41.2 |
| HF | −116.377697 | 1.18 | 27.2 |
| GVB–GF[a] | −116.414974 | 0.17 | 3.8 |
| GVB | −116.416438 | 0.13 | 2.9 |
| CI | −116.421089 | 0.00 | 0.0 |

[a] The coefficient $C_1$ in (15) or (30) is restricted to be zero and the orbitals are solved for self-consistently.

$$\boxed{\begin{array}{cc}\chi_r & \chi_1\end{array}} = -\boxed{\begin{array}{cc}\chi_1 & \chi_c\end{array}} - \boxed{\begin{array}{cc}\chi_r & \chi_c\end{array}} \quad (19)$$

(compare with (10) and (11)).

**B. The Variational Equations.** The basic variational equations for GVB wave functions are discussed in ref 3. Our current programs[7,8] solve these variational equations by expanding consistently through first order in the orbital corrections so that within the radius of convergence the iterations converge quadratically (for a fixed spin coupling). The orbitals and spin coupling are then optimized self-consistently iteratively for each state. Thus rather than solving homogeneous equations

$$\mathbf{HC} = \epsilon\mathbf{C}$$

for new orbitals, **C**, we solve an inhomogeneous equation

$$\mathbf{B\Delta} = -\mathbf{X}$$

where $\Delta$ is the correction vector (components corresponding to every basis function of each vector), **X** corresponds closely to the first derivative (of the energy) vector (and goes to zero as convergence is obtained), and **B** corresponds closely to the second derivative matrix.[7–9] (This procedure corresponds to the Newton method of solving for roots of algebraic equations.) The matrix **B** is generally singular since some changes in the orbitals (e.g., renormalization) do not change the energy; however, these variations are easily eliminated, leading to nonsingular **B** matrices to invert.[21,22] For the ground state at convergence the eigenvalues of the (modified) **B** matrix are all positive indicating a real minimum. Excited states have successively one or more negative eigenvalues since there are one or more ways of changing the wave function and leading to a lower energy. For the states considered herein there are no difficulties obtaining multiple roots of the same symmetry and the variational equations ensure rigorous upper bounds for the higher roots.

**C. The Core Hamiltonian.** As discussed elsewhere,[2,10–12] the problem of finding a wave function of the form

$$\mathcal{Q}[\Phi_{core}\Phi_{val}]$$

may be reduced to that of finding the wave function

$$\mathcal{Q}[\Phi_{val}] \quad (20)$$

if (i) the core is a product of doubly occupied orbitals and (ii) if the orbitals of $\Phi_{val}$ are taken to be orthogonal to those of $\Phi_{core}$. In solving for the valence wave function in (20), the Hamiltonian will have the form

$$\mathcal{3C} = \sum_{i=1}^{n_\pi} h_c(i) + \sum_{i>j}^{n_\pi} \frac{1}{r_{ij}} \quad (21)$$

where $n_\pi$ is the number of electrons in $\pi$ orbitals and

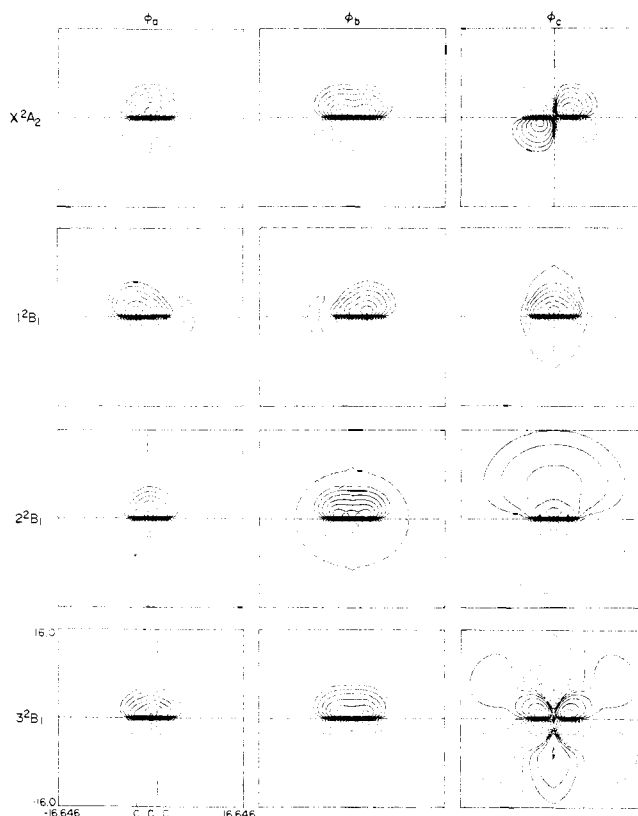$$h_c(i) = h(i) + \sum_{j=1}^{q}(2J_j - K_j) \quad (22)$$



ALLYL RADICAL GVB PI ORBITALS

**Figure 1.** The GVB orbitals of various states of allyl radical. The amplitudes are plotted in two planes perpendicular to the molecular plane. Each plane passes through one terminal carbon atom and through the central carbon atom. These planes are then joined at the central carbon. Long dashes indicate zero amplitude. The most diffuse contour has an amplitude of 0.003, and the amplitude increases by a factor of 2.1544 at each contour, corresponding to a factor of 10 for three contours.

includes the potential due to the $q$ doubly occupied orbitals of the $\sigma$ core in addition to the usual one-electron terms, $h(i)$. This approach is valid for completely general treatments of the valence wave function, including GVB or CI. For allyl radical, the $\sigma$ electron core was formed from an *ab initio* HF calculation on the ground state of allyl cation.

**D. The Basis and Other Details.** 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.[13a] This was contracted to a double $\zeta$ basis (4s, 2p) on each carbon and (2s) on each hydrogen, as suggested by Dunning.[13b] The above basis was supplemented by two additional $\pi$ Gaussian functions[14] on each carbon with orbital exponents of 0.382 and 0.0127. All calculations used the following geometry:[15] $R_{CC} = 1.40$ Å, $R_{CH} = 1.08$ Å, and all bond angles = 120°.

**III. Results**

In Table I we compare the energies obtained for the ground state of allyl from various methods. Comparing in each case with the energy for full CI, the error in the GVB wave function is 0.13 eV = 2.9 kcal, the error in the HF wave function is nine times as great (27.2 kcal) and the error in the VB wave function is 14 times as great (41.2 kcal).

The GVB $\pi$ orbitals for allyl radical are depicted in Figure 1. Included in this figure are the orbitals of the ground state ($1^2A_2$) and of three excited states ($1^2B_1$, $2^2B_1$, and $3^2B_1$) obtained by the excitation of a $\pi$ orbital. The energies for these wave functions are in Table II.

**Table II.** Energy Quantities for the GVB Wave Functions of Allyl Radical (All Using the Same Basis)

| State | Total energy, hartrees | Spin coupling[a] $C_1$ | $C_2$ | Excitation energy, eV |
|---|---|---|---|---|
| $1^2A_2$ | $-116.416438$ | $-0.118^c$ | $0.928$ | $0$ |
| | $-116.414974^b$ | $0.0^c$ | $1.0$ | $(0.039)$ |
| $1^2B_1$ | $-116.297120$ | $1.0^d$ | $0.0$ | $3.247$ |
| $2^2B_1$ | $-116.237380$ | $0.999^d$ | $-0.042$ | $4.872$ |
| $3^2B_1$ | $-116.209966$ | $0.999^d$ | $0.030$ | $5.618$ |

[a] Refer to eq. 15. [b] In this calculation the spin coupling was restricted so that $C_1 = 0$. [c] The orbitals are ordered as $\phi_1\phi_r\phi_c$ or in terms of Figure 1 as $\phi_a\phi_c\phi_b$. [d] The orbitals are ordered as $\phi_a\phi_b\phi_c$.

As can be seen from Figure 1, the lowest two states involve only orbitals with the characteristic extent of atomic 2p orbitals, hence we refer to them as valence-like states. The other two states each contain a very diffuse orbital and will be referred to as Rydberg states.

The first excited state ($1^2B_1$) in Figure 1 contains GVB orbitals each of which is localized near one of the centers. For the ground state, however, the optimum orbitals are found to be delocalized, $\phi_a$ and $\phi_b$ are symmetric ($b_1$), and $\phi_c$ is antisymmetric ($a_2$). We shall consider why this occurs.

**Symmetry and Delocalized Orbitals.** The states in Figure 1 all contain an odd number of electrons in $\pi$ orbitals (i.e., orbitals that are antisymmetric with respect to reflection on the molecular plane). Thus these states must each correspond to either the $B_1$ or $A_2$ representations of the $C_{2v}$ symmetry group of allyl. To determine which we must find how the wave function changes upon reflection in the symmetry plane interchanging the terminal groups of allyl. Denoting this reflection as $\sigma$, then

$$\sigma\Phi_{B_1} = +\Phi_{B_1}$$
$$\sigma\Phi_{A_2} = -\Phi_{A_2} \tag{23}$$

From (18) the VB wave function for the ground state can be written as

$$\boxed{\begin{array}{cc} \chi_l & \chi_c \\ \chi_r & \end{array}} \tag{24}$$

that is, the $\chi_l$ $\chi_r$ orbitals are triplet coupled. Even though these orbitals are not symmetry functions, the total wave function is of $A_2$ symmetry since

$$\sigma\chi_l = \chi_r$$
$$\sigma\chi_c = \chi_c$$
$$\sigma\chi_r = \chi_l$$

and hence

$$\sigma\boxed{\begin{array}{cc} \chi_l & \chi_c \\ \chi_r & \end{array}} = \boxed{\begin{array}{cc} \chi_r & \chi_c \\ \chi_l & \end{array}} = -\boxed{\begin{array}{cc} \chi_l & \chi_c \\ \chi_r & \end{array}} \tag{25}$$

[the sign change for interchange of $\chi_l$ and $\chi_r$ is obvious from (18)]. On the other hand, for the excited VB wave function in (19) we obtain

$$\sigma\boxed{\begin{array}{cc} \chi_l & \chi_r \\ \chi_c & \end{array}} = \boxed{\begin{array}{cc} \chi_r & \chi_l \\ \chi_c & \end{array}} = +\boxed{\begin{array}{cc} \chi_l & \chi_r \\ \chi_c & \end{array}} \tag{26}$$

and hence the wave function has $B_1$ symmetry.

Mixing the $\chi_l$ and $\chi_r$ orbitals as

$$\phi_1 = \cos\theta\chi_l + \sin\theta\chi_r$$
$$\phi_c = \chi_c \tag{27}$$
$$\phi_r = -\sin\theta\chi_l + \cos\theta\chi_r$$

we find that

$$\boxed{\begin{array}{cc} \phi_1 & \phi_c \\ \phi_r & \end{array}} = (\cos^2\theta + \sin^2\theta)\boxed{\begin{array}{cc} \chi_l & \chi_c \\ \chi_r & \end{array}} \tag{28}$$

and hence the wave function and energy for the resonant state in (28) is unchanged by mixing the $\chi_l$ and $\chi_r$ orbitals. Thus even with unsymmetric orbitals of the form (27), the total wave function in (28) has $A_2$ symmetry.

The use of (27) in (26) leads to

$$\boxed{\begin{array}{cc} \phi_1 & \phi_r \\ \phi_c & \end{array}} = -\sin\Theta\cos\Theta\boxed{\begin{array}{cc} \chi_l & \chi_l \\ \chi_c & \end{array}} +$$

$$\sin\Theta\cos\Theta\boxed{\begin{array}{cc} \chi_r & \chi_r \\ \chi_c & \end{array}} + (\cos^2\Theta - \sin^2\Theta)\boxed{\begin{array}{cc} \chi_l & \chi_r \\ \chi_c & \end{array}} \tag{29}$$

and hence a real change in the wave function and hence in the energy. This new wave function (eq 29) has $B_1$ symmetry only if $\sin(2\theta) = 0$.

On the other hand, with a mixture of the two spin couplings

$$C_1\boxed{\begin{array}{cc} \chi_l & \chi_r \\ \chi_c & \end{array}} + C_2\boxed{\begin{array}{cc} \chi_l & \chi_c \\ \chi_r & \end{array}} \tag{30}$$

or

$$C_1\boxed{\begin{array}{cc} \phi_1 & \phi_r \\ \phi_c & \end{array}} + C_2\boxed{\begin{array}{cc} \phi_1 & \phi_c \\ \phi_r & \end{array}} \tag{31}$$

we in general get mixtures of $B_1$ and $A_2$ symmetry. One exception occurs: if (27) is replaced by

$$\phi_u = (1/\sqrt{2})(\chi_l + \chi_r)$$
$$\phi_g = (1/\sqrt{2})(-\chi_l + \chi_r) \tag{32}$$

then the $\phi_u$ and $\phi_c$ orbitals are of $b_1$ symmetry and $\phi_g$ is of $a_2$ symmetry, so that both

$$\boxed{\begin{array}{cc} \phi_u & \phi_c \\ \phi_g & \end{array}} \tag{33a}$$

and

$$\boxed{\begin{array}{cc} \phi_u & \phi_g \\ \phi_c & \end{array}} \tag{33b}$$

are of $^2A_2$ symmetry. Thus for this particular special choice of the coefficients in (27), both spin couplings are allowed without destroying symmetry. Since the wave function in (28) leads to the same energy for all (nonsingular) choices of the coefficients and since the choice of (32) allows an additional term (33b) of proper symmetry

$$\Psi = C_1\boxed{\begin{array}{cc} \phi_u & \phi_g \\ \phi_c & \end{array}} + C_2\boxed{\begin{array}{cc} \phi_u & \phi_c \\ \phi_g & \end{array}} \tag{34}$$

not allowed for other choices of the coefficients, we expect the optimum wave function to involve delocalized orbitals as in (32) and for small admixtures of the second spin coupling (33b) to occur in (34). This is precisely what is found in the GVB wave function for the ground state.[16] The orbitals are shown in Figure 1 and the spin coupling coefficients are $C_1 = -0.118$ and $C_2 = +0.928$.

Restricting the GVB wave function so that $C_1 = 0$ and solving for the optimum orbitals leads to an increase in the energy of 0.91 kcal.[17] However, with $C_1 = 0$ we can recombine the GVB orbitals into localized orbitals, as

$$\phi_1 = (\phi_a - \phi_b)/\sqrt{2}$$
$$\phi_r = (\phi_a + \phi_b)/\sqrt{2} \tag{35}$$

GVB PI ORBITALS FOR THE
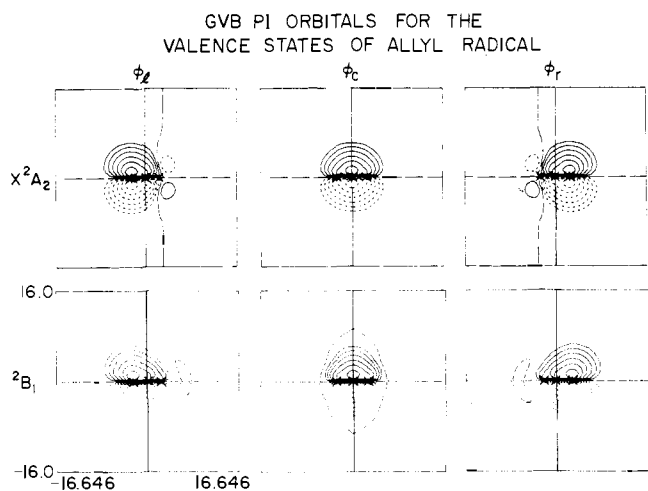VALENCE STATES OF ALLYL RADICAL



Figure 2. The GVB orbitals of the valence states of allyl radical. For $X^2A_1$ those orbitals were obtained using $C_1 = 0$ in eq 34 while optimizing the orbitals and then transforming using eq 35.

leading to the orbitals in Figure 2. Note the close comparison of these orbitals with the GVB orbitals of the first excited state (in Figure 1). In our qualitative discussions of allyl we will use the localized orbitals of (35), although they yield an energy 0.91 kcal higher than the optimum GVB orbitals for the $^2A_2$ state.

## IV. Discussion

**A. Resonance.** As we saw in section IIA, VB considerations indicate that there should be two valence-like states of allyl radical, the classical resonant and antiresonant states, (7) and (8). In accord with the VB picture the GVB results lead to only two valence-like states.

The ground and first excited states of allyl can be described as

$$\boxed{\begin{array}{|c|}\hline \phi_1 \,\, \phi_c \\\hline \phi_r \\\hline\end{array}} \equiv \boxed{\begin{array}{|c|}\hline \phi_c \,\, \phi_1 \\\hline \phi_r \\\hline\end{array}} - \boxed{\begin{array}{|c|}\hline \phi_c \,\, \phi_r \\\hline \phi_1 \\\hline\end{array}} \quad (36)$$

and

$$\boxed{\begin{array}{|c|}\hline \phi_1 \,\, \phi_r \\\hline \phi_c \\\hline\end{array}} \equiv \boxed{\begin{array}{|c|}\hline \phi_c \,\, \phi_1 \\\hline \phi_r \\\hline\end{array}} - \boxed{\begin{array}{|c|}\hline \phi_c \,\, \phi_r \\\hline \phi_1 \\\hline\end{array}} \quad (37)$$

using for $\varphi_1$, $\varphi_c$, and $\varphi_r$ either the atomic orbitals (i.e., VB) or the localized orbitals from self-consistent GVB calculations on either the ground or excited states. From (36) we will define the resonance energy (of the ground state) of allyl as the energy stabilization of the resonant wave function in (36) as compared with the single configuration wave function

$$\boxed{\begin{array}{|c|}\hline \phi_c \,\, \phi_1 \\\hline \phi_r \\\hline\end{array}} \quad (38)$$

using the same orbitals. That is

$$E_{res} = E(\text{\large/\!\!\!\!\!\diagup\!\!\!\diagdown}) - E(\text{\large/\!\!\!\!\!\diagup\!\!\!\diagdown} - \diagup\!\!\!\!\diagdown) \quad (39)$$

Similarly from (37) we define the antiresonance (of the excited state) of allyl as the destabilization energy of the antiresonant wave function in (37) as compared with the same single configuration wave function in (38).

$$E_{antires} = E(\text{\large/\!\!\!\!\!\diagup\!\!\!\diagdown} + \diagup\!\!\!\!\diagdown) - E(\text{\large/\!\!\!\!\!\diagup\!\!\!\diagdown}) \quad (40)$$

Using the atomic $\pi$ orbitals we find that the resonance energy[18] is

$$E_{res} = 15.9 \text{ kcal}$$

**Table III.** The Resonance Energies and Related Quantities for Allyl Radical

| | Atomic (VB) | GVB ($^2A_2$) ground state[a] | GVB ($^2B_1$) excited state |
|---|---|---|---|
| /\ | $-116.33012^c$ | $-116.39681$ | $-116.39579$ |
| /\ $-$ /\ | $-116.35544$ | $-116.41499$ | $-116.41080$ |
| /\ $+$ /\ | $-116.23784$ | $-116.28663$ | $-116.29712$ |
| Resonance energy $^2A_2$, kcal | 15.89 | 11.40 | 9.42 |
| Antiresonance energy $^2B_1$, kcal | 57.93 | 69.16 | 61.94 |
| $\boxed{\begin{array}{|c c|}\hline \phi_1 & \phi_r \\\hline \phi_c & \\\hline\end{array}}{}^b$ | $-116.27173^c$ | $-116.338301$ | $-116.34502$ |
| Destabilization energy $^2B_1$, kcal | 21.27 | 32.44 | 30.07 |

[a] The orbitals used here are the localized orbitals from the GF spin coupling ($C_1 = 0$ in eq 15). This wave function leads to an energy 0.91 kcal above the optimum energy of the $^2A_2$ state. [b] This wave function has orbitals $\phi_1$ and $\phi_c$ coupled into a triplet state and then $\phi_r$ is coupled to yield a doublet. [c] Using ethylene $\pi$ orbitals for $\phi_1$ and $\phi_c$ and the methylene ($^3B_1$) $\pi$ orbital for $\phi_r$ yields energies of $-116.36823$ and $-116.27606$ for the G1' and GF coupled wave functions.

while the antiresonance energy is

$$E_{antires} = 57.9 \text{ kcal}$$

With the optimum localized GVB orbitals from the ground state we find

$$E_{res} = 11.4 \text{ kcal}$$

$$E_{antires} = 69.2 \text{ kcal}$$

and using the optimum GVB orbitals from the excited state leads to

$$E_{res} = 9.4 \text{ kcal}$$

$$E_{antires} = 61.9 \text{ kcal}$$

(See Table III for a tabulation of the energies.) The best estimate of the resonance energy is that using the ground state orbitals, i.e., $E_{res} = 11.4$ kcal; we include the other values partly to indicate how little the resonance energy changes with rather large changes in the orbitals (for example the VB wave function yields a ground state energy 38.3 kcal higher than that of the GVB wave function).

This theoretical estimate of 11.4 kcal for the resonance energy is in reasonable agreement with the value of $11.6 \pm 2$ kcal from thermochemical considerations.[18] Note that the experimental value is obtained by comparing the heat of formation of allyl with that expected for a structure with localized bonds (and hence different bond lengths). To distinguish these quantitites the quantity we report is often called the *vertical* resonance energy.

From Table II we see that the antiresonance energies are much larger than the resonance energies. This arises from the nonorthogonality of the wave functions

$$\text{/\!\!\!\!\!\diagup\!\!\!\diagdown} \quad \text{and} \quad \diagup\!\!\!\!\diagdown \quad (41)$$

Using (36) and (37) the energies are given as

$$E(^2A_2) = \frac{H_{11} + H_{12}}{1 + S} = H_{11} + \frac{(H_{12} - SH_{11})}{(1 + S)}$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (42)$

$$E(^2B_1) = \frac{H_{11} - H_{12}}{1 - S} = H_{11} - \frac{(H_{12} - SH_{11})}{(1 - S)}$$

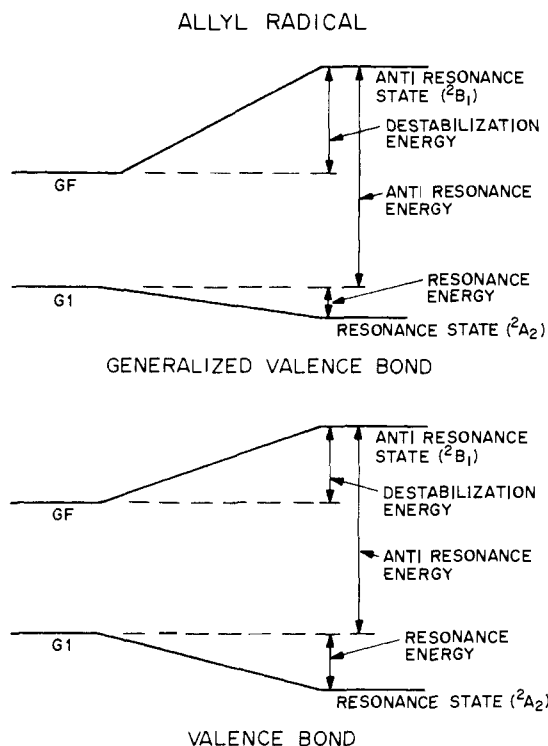where $H_{11}$ is the energy of (the normalized) wave function

ALLYL RADICAL



**Figure 3.** A comparison of the VB and GVB resonance and stabilization energies for the valence state of allyl radical.

38; $S$ is the overlap between the two wave functions of (41) and $H_{12}$ is the Hamiltonian matrix element between these wave functions. From (42) we see that

$$E_{res}/E_{antires} = (1 - S)/(1 + S) \qquad (43)$$

The orbitals of the VB, GVB ($^2A_2$), and GVB ($^2B_1$) wave functions lead to $S = 0.57$, $S = 0.72$, and $S = 0.71$, respectively, suggesting a ratio of $\sim\frac{1}{6}$ for (43).

**B. The Fused Ethylene Model.** An alternative approach to building up the states of allyl is to start with the states of ethylene and to examine how these states are modified by fusing a third $\pi$ orbital onto the ethylene.[19] The GVB description of ethylene[2] yields two valence-like states, the ground (N) state and the first excited triplet (T) state, which can be described as

$$\text{N:} \quad \boxed{\phi_1\,\phi_c} \qquad (44)$$

$$\text{T:} \quad \boxed{\begin{array}{c}\phi_1\\\phi_c\end{array}} \qquad (45)$$

in terms of localized orbitals on the left and center carbons. These states are found to be separated by 4.24 eV = 98 kcal[17] in the GVB description. Fusing on the $\phi_r$ orbital leads then to zero-order (doublet) states of the form

$$\boxed{\begin{array}{c}\phi_1\,\phi_c\\\boxed{\phi_r}\end{array}} \qquad (46)$$

and

$$\boxed{\begin{array}{c}\phi_1\,\boxed{\phi_r}\\\phi_c\end{array}} \qquad (47)$$

Letting the orbitals of (46) and (47) relax, we may consider that the ground state ($^2A_2$) of allyl arises from (46), being stabilized by the amount of the resonance energy, 11.4 kcal. The first excited state of allyl can then be viewed as arising from the excited state (47) of ethylene, with a destabilization energy of
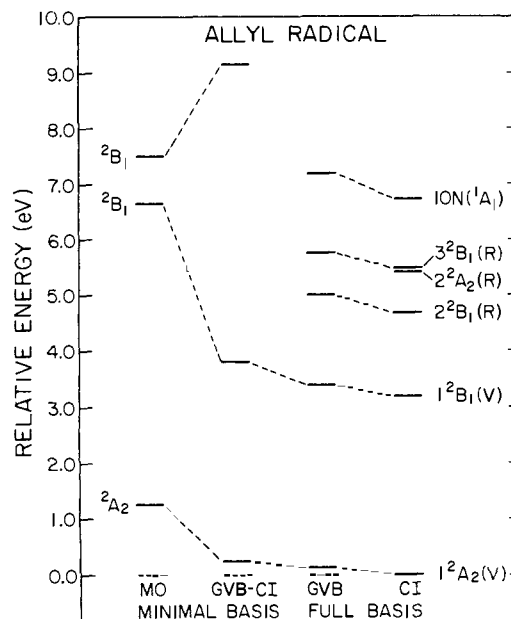


**Figure 4.** The relative energies of the MO, GVB, and CI wave functions. All energies are relative to the full CI wave function.

**Table IV.** Allyl Radical Energies Using a Minimum Basis Set[a] (Energies in Hartrees)

| State | Full CI | —Dominant configurations— | |
|-------|---------|---------------|------------------------|
| | | Configuration | Energy (single config) |
| $1\,^2A_2$ | $-116.411955$ | $(1b_1)^2(1a_2)$ | $-116.375139^c$ |
| | $(-116.421089)^b$ | | |
| $1\,^1B_1$ | $-116.281236$ | $(1b_1)(1a_2)^2$ | $-116.176541$ |
| | $(-116.303426)^b$ | $(1b_1)^2(2b_1)$ | $-116.145339$ |
| $2\,^1B_1$ | $-116.084705$ | $(1b_1)^1(1a_2)^2$ | $-116.176541$ |
| | $(-116.248310)^b$ | $(1b_1)^2(2b_1)$ | $-116.145339$ |
| $3\,^1B_1$ | $-115.835376$ | $(1a_2)^2(2b_1)$ | $-115.817880$ |
| | $(-116.219937)^b$ | $(1b_1)(2b_1)^2$ | $-115.769586$ |

[a] Using the natural orbitals from the GVB wave function. [b] Energies from the full CI calculations using the full basis. [c] Solving self-consistently for the HF wave function in the full basis leads to $-116.377697$.

$$E_{destab} = E(\text{\scriptsize$\nearrow\!\!\diagdown$} + \text{\scriptsize$\diagup\!\!\searrow$}) - E_{(47)} = 30.1 \text{ kcal}$$
$$(48)$$

(using the excited state orbitals). These views are illustrated in Figure 3.

In this view the $^2A_2 \rightarrow {}^2B_1$ excitation energy of allyl should be comparable to the N $\rightarrow$ T excitation energy of ethylene. In fact the numbers are 3.2 eV for allyl and 4.2 eV for ethylene. The basic reason for the decrease in the excitation energy in going from ethylene to allyl is that (46) involves an antibonding interaction between the new orbital $\phi_r$ and the ethylene N state orbitals $\phi_1$ and $\phi_c$ while (47) involves bonding interactions between $\phi_r$ and the ethylene T state orbitals.[20] Thus the energy separation between (46) and (47) is only 2.5 eV. The stabilization and destabilization effects attendant to the relaxation of the wave functions in (46) and (47) to obtain the optimum wave functions then leads to an increase in the energy separation by 0.7 eV yielding the final excitation energy of 3.2 eV.

**C. Comparison of GVB and MO Descriptions.** In the simple MO description of allyl there are three MO's: $1b_1$ is the doubly occupied bonding MO, $1a_2$ is the singly occupied MO, and $2b_1$ is the empty antibonding MO. The ground state is then

$$^2A_2: \quad (1b_1)^2(1a_2) \qquad (49)$$

**Table V.** Energies for Allyl Radical (Hartree Atomic Units)

| State | GVB | CI Full[a] | $E_{CI} - E_{GVB}$ | CI Singles[b] |
|---|---|---|---|---|
| $1\,^2A_2$ | −116.416438 | −116.421089 | −0.004651 | −116.399944 |
| $1\,^2B_1$ | −116.297120 | −116.303426 | −0.006306 | −116.222573 |
| $2\,^2B_1$ | −116.237380 | −116.248310 | −0.010930 | −116.197000 |
| $2\,^2A_2$ | | −116.222188 | | −116.187229 |
| $3\,^2B_1$ | −116.209966 | −116.219937 | −0.009971 | −116.175801 |
| Allyl cation | −116.163675 | −116.173420 | −0.009745 | |

[a] Full CI within $\pi$ space. [b] Only single excitations from dominant configuration allowed.

and excited states are obtained by exciting from $1a_2$ or $1b_1$ to $2b_1$ or $1a_2$.

$$^2B_1: \quad (1b_1)^2(2b_1) \tag{50}$$

$$^2B_1: \quad (1b_1)(1a_2)^2 \tag{51}$$

$$^{4,2}A_2: \quad (1b_1)(1a_2)(2b_1) \tag{52}$$

In this description one would expect either (50) or (51) to be the first excited state, correctly predicting the symmetry of this state.

We now want to compare the MO and GVB descriptions. However, since the model in (49)–(52) is clearly only capable of describing valence excited states, we will compare these methods using wave functions based on just three valence-like orbitals,[21] $1b_1$, $1a_2$, and $2b_1$. The results are indicated in Figure 4 and Table IV.

The MO description leads to the $(1b_1)(1a_2)^2$ state at 5.4 eV excitation energy and the $(1b_1)^2(2b_1)$ state at 6.3 eV. However, in the GVB–CI description the first $^2B_1$ state is at 3.6 eV while the second is at 8.9 eV. The problem here is that to expand the GVB wave function for the antiresonant state in (37) in terms of MO's requires *both* the $(1b_1)(1a_2)^2$ and $(1b_1)^2(2b_1)$ configurations with rougly equal coefficients. The first excited state of allyl is simply not described by either MO configuration.

As a further test of the MO approach we included the full basis (12 functions) and carried out a CI calculation allowing all single excitations from (49). This should closely approximate the HF wave functions for the excited states. As shown in Table V this does not eliminate the problem with the HF description of the first $^2B_1$ state. This difficulty is intrinsic to the single Slater determinant form of the HF wave function and hence is not overcome by carrying out HF calculations with a complete basis.

On the other hand with the GVB description one obtains a quantitatively accurate description of both the ground and first excited state of allyl as simply a recoupling of the spin functions.

As will be reported in later papers we have carried out similar studies on the lower excited states of butadiene[22] and benzene[8] finding exactly the same situation. The valence excited states involve essentially a recoupling of the spin functions and are well described with the GVB wave functions but very poorly described with MO's.

**D. Excitation Energies.** In Table V we present the results of configuration interaction (CI) calculations performed on allyl radical using the identical basis set and $\sigma$ electron core as was used for the GVB calculations. First, we note that there is good agreement between the results of the GVB and full CI calculations. For example, for the ground state the difference between GVB and CI is only 0.00465 hartree = 0.127 eV. This close agreement with the full CI wave function justifies interpreting the wave function in terms of GVB orbitals.

In Table VI, excitation energies from various sources are compared. Experimental results lead to transitions at 3.04 eV[23a] and 5.0 eV[23b] in reasonable agreement with our results of 3.2 eV and 4.9 eV. The best previous theoretical

**Table VI.** Excitation Energies for Allyl Radical (All Values in eV)

| State | —Present work—<br>GVB | Full CI | Peyerimhoff & Buenker (*ab initio* CI)[15] | Hirst and Linnett (semiempirical CI)[a] |
|---|---|---|---|---|
| $^2A_2$ | 0 | 0 | 0 | 0 |
| $^2B_1$ | 3.25 | 3.20 | 3.79 | 2.42 |
| $2\,^2B_1$ | 4.87 | 4.70 | 8.0 | 9.791 |
| $2\,^2A_2$ | | 5.41 | | |
| $3\,^2B_1$ | 5.62 | 5.47 | | |
| Cation | 7.04 | 6.74 | | |

[a] D. M. Hirst and J. W. Linnett, *J. Chem. Soc.*, 1035 (1962).

studies[15] used a less extensive valence basis and omitted diffuse functions. As a result they miss the Rydberg excited states and obtained a $1\,^2B_1 \leftarrow {}^2A_2$ excitation energy 0.7 eV higher than our value.

From Figure 1 we see that the $2\,^2B_1$ and $3\,^2B_1$ states each involve one very diffuse orbital, *i.e.*, a Rydberg orbital. From the shapes of the orbitals the $2\,^2B_1$ state should correspond to a

$$(2\,^2B_1) \quad 1a_2 \longrightarrow 3pb_1 \tag{53}$$
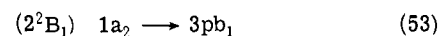
excitation while the $3\,^2B_1$ state should correspond to a

$$(3\,^2B_1) \quad 1a_2 \longrightarrow 3db_1 \tag{54}$$
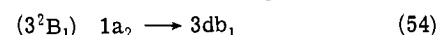
excitation (the $d\pi$ orbital is in the reflection plane perpendicular to the molecule). Although we did not solve for the GVB orbitals of the $^2A_2$ Rydberg states, we found from our CI calculations that a $^2A_2$ state is 0.006 eV lower than the $3\,^2B_1$ state. This is consistent with the description in (54) for $3\,^2B_1$ since

$$(2\,^2A_2) \quad 1a_2 \longrightarrow 3da_2 \tag{55}$$
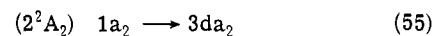
would be expected to be close to (54).

Our calculated quantum defects are $\delta(2\,^2B_1) = 0.40$ and $\delta(3\,^2B_1) = -0.29$. The value for the 3p orbital is consistent with the typical value of 0.50 (*e.g.*, $\delta_{3p} = 0.50$ for butadiene[24]) for np Rydberg orbitals. Usually nd Rydberg orbitals have $\delta \sim 0$. Our negative value reflects the inadequency of our basis for describing d Rydberg states.

### V. Summary

The generalized valence bond description of allyl radical is quantitatively accurate, leading to energies only a few kilocalories from full configuration interaction calculations. Qualitatively the GVB wave functions lead to a description of the ground and first excited states of allyl in close agreement with the usual valence bond idea of resonating structures.
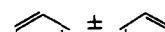


Indeed the calculated resonance energy of 11.4 kcal is in reasonable agreement with thermochemical estimates of the excitation stabilization energy of allyl radical. These results provide a direct rigorous quantum mechanical verification of the validity of the concept of resonance.

## References and Notes

(1) (a) Partially supported by Grants GP-15423 and GP-40783X from the National Science Foundation; (b) NSF Predoctoral Fellow, 1969–1972. (c) Contribution No. 4871.
(2) G. Levin, W. A. Goddard III, and D. L. Huestis, *Chem. Phys.*, **4**, 409 (1974).
(3) R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.*, **51**, 1073 (1969).
(4) W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971).
(5) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Accounts Chem. Res.*, **6**, 368 (1973).
(6) Here $\mathfrak{A}$ indicates the antisymmetrizer or determinant operator. Thus (1) describes a single Slater determinant.
(7) R. C. Ladner, Ph.D. Thesis, California Institute of Technology, November 1971.
(8) G. Levin, Ph.D. Thesis, California Institute of Technology, April 1974.
(9) D. L. Huestis, Ph.D. Thesis, California Institute of Technology, September 1972.
(10) T. H. Dunning, Jr., Ph.D. Thesis, California Institute of Technology, September 1969.
(11) F. E. Harris, *Advan. Quantum Chem.*, **3**, 61 (1967).
(12) T. H. Dunning, Jr., R. P. Hosteny, and I. Shavitt, *J. Amer. Chem. Soc.*, **95**, 5067 (1973).
(13) (a) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); (b) T. H. Dunning, Jr., *ibid.*, **53**, 2823 (1970).
(14) In order to obtain an accurate description of the Rydberg states, a better choice for diffuse exponents would have been 0.0382 and 0.0127. However, the basis used led to an error of only 0.1 eV in describing the $2p \rightarrow 3p$ excitation of C atom.
(15) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).
(16) Since no operator in the wave function ensures that this total wavefunction possesses the proper spatial symmetry, it is possible for the optimum self-consistent orbitals to be asymmetric so as to lead to a total wave function that is neither $A_2$ or $B_1$ symmetry. Using our variational approach we can be sure that the calculated ground state wave function (which is of $^2A_2$ symmetry) is a relative minimum (all variations in orbitals lead to positive curvatures). It is still conceivable that a lower absolute minimum exists. However, we carried out extensive searches and conclude that our wave function is the lowest absolute minimum.
(17) The conversions between various units of energy are 1 hartree = 27.2117 eV = 627.526 kcal and hence 1 kcal = 0.0016 hartree. Note that we use the abbreviation kcal to indicate kilocalories per mole.
(18) A. B. Trenwith, *Int. J. Chem. Kinet.*, **5**, 67 (1973).
(19) This is analogous to the approach suggested by Dr. T. H. Dunning, Jr. (private communication, April, 1971), for considering the excited states of butadiene. See, for example, the discussion in H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules, A Survey of Rigorous Quantum Mechanical Results," Addison-Wesley, Reading, Mass., 1972.
(20) W. A. Goddard III and C. W. Wilson, Jr., *Theor. Chim. Acta*, **26**, 211 (1972).
(21) To provide a convenient valence basis we used the ground state GVB orbitals as the basis. The first $b_1$ orbital was taken as the sum of the two $b_1$-GVB orbitals (this should lead to a close approximation to the first natural orbital), the second $b_1$ orbital for the CI calculation was taken as orthogonal to the first one, and the $a_2$ orbital was taken directly from the VB wave function. The results are summarized in Table V. The energies for the first two states are 0.009 and 0.022 hartree higher than obtained with the full basis and hence these orbitals provide a good description of the valence states. Of course the valence orbitals cannot describe the Rydberg states. Using these orbitals, the energy of the single HF configuration is only 0.0016 hartree (1.0 kcal) higher than the self-consistent HF energy for the full basis (see Table I).
(22) G. Levin and W. A. Goddard III, "The GVB Description of the Low-Lying Electronic States of s-trans-1,3-Butadiene," to be published.
(23) (a) C. L. Currie and D. A. Ramsay, *J. Chem. Phys.*, **45**, 488 (1966); (b) A. B. Callear and H. K. Lee, *Trans. Faraday Soc.*, **64**, 308 (1968).
(24) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Princeton, N.J., 1967.

# A Pseudopotential SCF Method for Valence-Only Molecular Calculations

**Patrick Coffey,\* Carl S. Ewig, and John R. Van Wazer**

*Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. Received June 17, 1974*

**Abstract:** A nonempirical valence-only LCAO–MO–SCF method is presented based on an adaption of the Phillips–Kleinman pseudopotential to replace orthogonality constraints and on representation of the core–valence coulomb and exchange interactions by an exponential screening function. Computation times are greatly reduced compared to full *ab initio* calculations. Results are reported for main-group atoms up to atomic number 36, and for the molecules $C_2$, $Si_2$, $Ge_2$, and $PF_3$. These are compared to conventional SCF results and, for $C_2$ and $PF_3$, with experiment.

Despite rapid advances in computer technology in the last decade, *ab initio* calculations on relatively small molecules containing elements of atomic number greater than 18 (Ar) are still expensive and far from routine. Since the expense of a calculation increases roughly as the fourth power of the number of basis functions, even a 1000-fold increase in computer speed would allow only a six-fold increase in the complexity of a system to be investigated within the same computational time. Thus, investigation of many chemical problems using conventional *ab initio* methods does not seem possible in the near future.

The success of semiempirical MO methods has been largely limited to elements of atomic number less than 10 (Ne), due to lack of reliable spectroscopic data on the heavier elements and to the breakdown of the common approximations for the various integrals. As an example of the latter, most methods take the off-diagonal core-hamiltonian integral $H_{ab}$ as proportional to the overlap integral between orbitals a and b.

$$H_{ab} \sim k S_{ab} \qquad (1)$$

Jug[1] has shown that this approximation is poor for $p_\sigma$–$p_\sigma$ integrals over symmetrically orthogonalized orbitals. Equation 1 constrains $H_{ab}$ to have the same sign as $S_{ab}$, but, according to Jug, this is not necessarily the case at all. This problem is even more severe with integrals over d orbitals. Thus, the prospects for successful simple extension of semiempirical methods to the heavier elements appear dim.

In this paper we will outline a third and potentially much more useful approach for predicting the properties of inorganic compounds. This involves partitioning of the molecule's electronic distribution into "valence" and "core" orbitals. Such a partitioning allows the valence orbitals to be treated by comparatively rigorous *ab initio* techniques, with a minimal amount of labor. The distinction between bonding valence electrons and non-bonding core electrons is widely applied in many fields of chemistry; partitioning techniques use this distinction to its greatest possible computational advantage.

The theory of core–valence separation was widely studied in the early days of quantum chemistry[2-11] and also has been the subject of considerable recent interest.[12-24] In the