Commentationes

Spatially Projected Generalized Valence Bond Description of the pi-States of Allyl Radical*

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Ab initio, spatially projected generalized valence bond [GVB(SP)] calculations are reported for the ground and (pi-electron) excited states of allyl radical. We find that the wavefunctions of the ground and first excited state correspond closely to the classical valence bond description of resonant and anti-resonant states, ⌢ ± ⌢. The higher states involve excitation of Rydberg orbitals, but even here the orbitals of the GVB(SP) wavefunctions are basically localized. The theoretical value obtained for the allyl resonance energy is 14 kcal in good agreement with thermochemical estimates.

Key words: Allyl radical, ground and pi-states of ~

1. Introduction

Previously we reported the generalized valence (GVB) wavefunctions for allyl radical [1] and *s-trans*-1,3-butadiene [2]. In general, the total energies and excitation energies obtained from the GVB wavefunction were in good agreement with full configuration interaction (CI) results. The GVB wavefunction [3] explicitly includes permutation symmetry operators ensuring that the total wavefunction will have the proper spin symmetries and satisfy the Pauli principle for arbitrary shapes of the orbitals. In addition to obtaining good energies the hope here was that with no symmetry induced restrictions on the orbitals, the shapes of the orbitals would have physical significance and thereby lead to useful chemical concepts. This has proved to be the case for most systems; however an examination of the results for allyl radical and butadiene suggested that for some states the individual orbital shapes were being restricted in order to obtain total wavefunctions possessing the correct *spatial* symmetry. This led us to consider generalizing the GVB wavefunction by including a projection operator ensuring that the total wavefunction has the correct spatial symmetry for an *arbitrary* set of spatial orbitals [2]. The resulting wavefunction is denoted as GVB(SP) where SP indicates spatial projection.

In this paper we present the GVB(SP) wavefunctions for the various pi-electron states of allyl radical. As anticipated, the individual orbitals of some states are

very different between the GVB and GVB(SP) wavefunctions, indicating that the GVB orbitals were restricted by spatial symmetry requirements. We find that the GVB(SP) wavefunctions lead to simple chemically reasonable descriptions of the states of allyl radical.

In Section 2, we shall develop the GVB(SP) wavefunction by examining the valence bond (VB) wavefunction and generalizing this wavefunction while retaining the basic form of VB wavefunction. Section 3 presents the results of our calculations. Section 4 includes our interpretations of the results and comparisons with other results.

2. Calculational Considerations

In this section, we shall develop the spatially projected Generalized Valence Bond [GVB(SP)] wavefunction by examining, in turn, the Valence Bond (VB) wavefunction, the Generalized Valence Bond (GVB) wavefunction, and the GVB(SP) wavefunction to demonstrate the successive generalization involved in these wavefunctions. Our discussion will be limited to three electron systems and oriented toward the pi-electron system of allyl radical.

2.1. Valence Bond Wavefunction

The VB wavefunction may be represented as a linear combination of bonding structures formed using atomic orbitals for each electron. Considering only the pi-electron system the three-electron system of allyl radical has two equivalent bonding structures usually represented by the two VB canonical structures

$$\text{(structures)} \qquad (1)$$

These two structures correspond to the two independent ways of coupling three spinorbitals to form a doublet state.

Let χ_r, χ_c, and χ_l denote atomic orbitals located on the right, center, and left centers respectively. The VB wavefunction for a three-electron doublet may be represented as

$$\psi^{VB} = c_1 \psi_1 + c_2 \psi_2 \qquad (2a)$$

$$\psi^{VB} = c_1 \begin{array}{|c c|} \chi_c & \chi_l \\ \hline \chi_r & \\ \hline \end{array} + c_2 \begin{array}{|c c|} \chi_c & \chi_r \\ \hline \chi_l & \\ \hline \end{array} \qquad (2b)$$

where two orbitals in a horizontal box indicates that the orbitals are singlet coupled. In the VB method one optimizes the structure mixing coefficients, c_1 and c_2.

In the allyl radical pi-electron system, the two forms are equivalent; thus the two solutions are

$$c_1 = -c_2 \qquad (3a)$$

$$c_1 = c_2, \qquad (3b)$$

referred to as the resonant and anti-resonant solutions, respectively.

The wavefunction corresponding to the individual terms of (2) are

$$\psi_1 = \mathscr{A}[\Phi_\sigma(\chi_l\chi_c + \chi_c\chi_l)\chi_r\alpha\beta\alpha]$$
$$= \mathscr{A}[\Phi_\sigma\chi_l\chi_c\chi_r(\alpha\beta - \beta\alpha)\alpha] \tag{4a}$$

$$\psi_2 = \mathscr{A}[\Phi_\sigma(\chi_r\chi_c + \chi_c\chi_r)\chi_l\alpha\beta\alpha]$$
$$= \mathscr{A}[\Phi_\sigma\chi_r\chi_c\chi_l(\alpha\beta - \beta\alpha)\alpha] \tag{4b}$$
$$= \mathscr{A}[\Phi_\sigma\chi_l\chi_c\chi_r(\alpha\alpha\beta - \alpha\beta\alpha)]$$

where Φ_σ represents the product of all doubly-occupied sigma orbitals and $\mathscr{A}$ is the antisymmetrizer. Using (4), Eq. (2) can be written as

$$\psi^{VB} = \mathscr{A}[\Phi_\sigma\chi_l\chi_c\chi_r\Theta] \tag{5}$$

where

$$\Theta = c_1(\alpha\beta\alpha - \beta\alpha\alpha) + c_2(\alpha\alpha\beta - \alpha\beta\alpha). \tag{6}$$

2.2. Generalized Valence Bond Wavefunction

The GVB wavefunction is formally the same as the VB wavefunction

$$\mathscr{A}[\Phi_\sigma\varphi_a\varphi_b\varphi_c\Theta] \tag{7}$$

except that the orbitals φ_a, φ_b, and φ_c are solved for self-consistently (rather than being taken as atomic orbitals as in the VB wavefunction) and the spin coupling Θ is simultaneously optimized. Although the GVB orbitals are allowed to have any shape, we find that they typically concentrate each near a different carbon atom. In such cases, we shall denote the optimum GVB orbitals as ϕ_l, ϕ_c, ϕ_r indicating the location of the maximum amplitude of each orbital.

There are two independent ways of coupling three electrons into a doublet. We find it convenient to use orthogonal spin functions denoting them as

$$\theta_1 = (\alpha\beta - \beta\alpha)\alpha$$
$$\theta_2 = 2\alpha\alpha\beta - (\alpha\beta + \beta\alpha)\alpha \tag{8}$$

referred to as the G1 and G2 (or GF) spinfunctions. Note that electrons 1 and 2 are singlet coupled in θ_1 and triplet coupled in θ_2. The spin function for (7) is

$$\Theta = c_1\theta_1 + c_2\theta_2. \tag{9}$$

It is often convenient to use the diagram

$$
\begin{array}{|c c|}
\hline
\varphi_a & \varphi_b \\
\hline
\varphi_c & \\
\hline
\end{array}
\tag{10}
$$

to represent the wavefunction $\mathscr{A}[\Phi_\sigma\varphi_a\varphi_b\varphi_c\theta_1]$ and the diagram

$$
\begin{array}{|c c|}
\hline
\varphi_a & \varphi_c \\
\hline
\varphi_b & \\
\hline
\end{array}
\tag{11}
$$

to represent the wavefunction $\mathscr{A}[\Phi_\sigma\varphi_a\varphi_b\varphi_c\theta_2]$.

2.3. Spatially Projected Generalized Valence Bond Wavefunction

If in the GVB wavefunction we have localized orbitals φ_r, φ_c, φ_l such that φ_r and φ_l are *not identical* in form, then the two VB canonical structures are not equivalent.

In this case the ground state GVB wavefunction will not be an equal mixture of these two structures as in the VB theory. Conversely if the ground state is forced to be an equal mixture of these two structures, the ground state wavefunction will not possess the correct spatial symmetry. In order that the total wavefunction possesses the correct spatial symmetry, with inequivalent orbitals and a general Θ, the individual orbitals must be delocalized symmetry functions, each individually transforming according to a particular representation of the molecular symmetry group. To remove such restrictions upon the shapes of the orbitals and still generate a wavefunction with the correct spatial symmetry we have introduced a spatial projection operator into the GVB wavefunction.

Let $\hat{P}$ be an operator which operates only on spatial coordinates and which generates a state of a definite symmetry. The individual electron orbitals which constitute this state need not possess any particular symmetry and will possess components of all symmetries. The spatially projected GVB wavefunction [2, 4][1] is formed by letting $\hat{P}$ operate on the GVB wavefunction

$$\psi^{GVB(SP)} = \hat{P}\psi^{GVB}. \tag{12}$$

The spatial projection operator does not affect the spin part of the wavefunction.

To determine the effect of introducing a spatial projection operator, we will use as a model the allyl pi-electron system and a spatial symmetry group containing two elements, e the identity and σ the reflection through the plane bisecting the system. Generalization to larger spatial symmetry groups is mathematically straightforward, but interpretations become more complicated.

Let us first consider the effect of spatial projection upon the VB wavefunction (2). Since the individual electron orbitals are identical atomic orbitals, the behavior of the electron orbitals under the spatial symmetry group is

$$e\chi_l = \chi_l \qquad \sigma\chi_l = \chi_r$$

$$e\chi_c = \chi_c \qquad \sigma\chi_c = \chi_c \tag{13}$$

$$e\chi_r = \chi_l \qquad \sigma\chi_r = \chi_l.$$

The states that can be formed with these orbitals can be divided into two groups, those symmetric and those antisymmetric under σ. (Corresponding to the B_1 and A_2, irreducible representations, respectively, of the point group C_{2V} for allyl radical.) The two independent components of the VB wavefunction behave under the symmetry operator σ as

$$\sigma \begin{array}{|c|c|} \hline \chi_c & \chi_r \\ \hline \chi_l \\ \cline{1-1} \end{array} = \begin{array}{|c|c|} \hline \chi_c & \chi_l \\ \hline \chi_r \\ \cline{1-1} \end{array} , \tag{14a}$$

$$\sigma \begin{array}{|c|c|} \hline \chi_c & \chi_l \\ \hline \chi_r \\ \cline{1-1} \end{array} = \begin{array}{|c|c|} \hline \chi_c & \chi_r \\ \hline \chi_l \\ \cline{1-1} \end{array} . \tag{14b}$$

By forming linear combinations of these components, we can generate wavefunctions which are symmetric and antisymmetric under σ.

$$\psi_A^{VB} = \begin{array}{|c|c|} \hline \chi_c & \chi_r \\ \hline \chi_l \\ \cline{1-1} \end{array} - \begin{array}{|c|c|} \hline \chi_c & \chi_l \\ \hline \chi_r \\ \cline{1-1} \end{array} \tag{15}$$

$$\psi_S^{VB} = \begin{array}{|c|c|} \hline \chi_c & \chi_r \\ \hline \chi_l \\ \cline{1-1} \end{array} + \begin{array}{|c|c|} \hline \chi_c & \chi_l \\ \hline \chi_r \\ \cline{1-1} \end{array} \tag{16}$$

Defining two spatial projection operators by

$$\hat{P}_A = e - \sigma \tag{17}$$

$$\hat{P}_S = e + \sigma \tag{18}$$

we see that

$$\psi_A^{VB} = \hat{P}_A \left(\begin{array}{|c|c|} \hline \chi_c & \chi_r \\ \hline \chi_l \\ \cline{1-1} \end{array} \right) \tag{19}$$

$$\psi_S^{VB} = \hat{P}_S \left(\begin{array}{|c|c|} \hline \chi_c & \chi_r \\ \hline \chi_l \\ \cline{1-1} \end{array} \right) \tag{20}$$

The antisymmetric spatially projected VB wavefunction (15) or (19) is identical to the resonant state wavefunction, and the symmetric spatially projected VB wavefunction (16) or (20) is identical to the anti-resonant wavefunction. Thus, for a three-electron doublet system, spatial projection of a VB wavefunction is identical in effect to optimizing the mixing of the two bonding structures.

The GVB(SP) wavefunction is a generalization of the spatially projected VB wavefunction in the same way the GVB wavefunction is a generalization of the VB wavefunction–in lieu of atomic orbitals, the individual electron orbitals are

solved for self-consistently. The GVB(SP) wavefunction for a state of a particular symmetry has the form

$$\Psi^{GVB(SP)} = \hat{P}\psi^{GVB}$$

$$= \hat{P}\left[c_1 \begin{array}{|c|c|} \hline \varphi_a & \varphi_b \\ \hline \varphi_c \\ \hline \end{array} + c_2 \begin{array}{|c|c|} \hline \varphi_a & \varphi_c \\ \hline \varphi_b \\ \hline \end{array} \right]. \tag{21}$$

Frequently the orbitals are found to be localized, and in this case, the wavefunction will have the form

$$\Psi^{GVB(SP)} = \hat{P}\left[c_1 \begin{array}{|c|c|} \hline \varphi_l & \varphi_c \\ \hline \varphi_r \\ \hline \end{array} + c_2 \begin{array}{|c|c|} \hline \varphi_l & \varphi_r \\ \hline \varphi_c \\ \hline \end{array} \right]. \tag{22}$$

Here φ_r is in general not equivalent to φ_l,

$$\sigma\varphi_r \neq \varphi_l$$

in contradistinction to the case for VB (atomic) orbitals [see (13)]. Thus, the two terms in (22) are *not* related by a symmetry operation and both terms must be included in the GVB(SP) wavefunction. For valence states, we expect φ_r and φ_l to be quite similar and one spin coupling component to be the primary component of each wavefunction.

2.4. The Variational Equations

The variational equations for GVB(SP) are derived in a manner analogous to the usual GVB equations [3b] except that there are additional cross terms resulting from the symmetry operators (17) and (18). The program was constructed for general Abelian groups with the basis functions belonging to irreducible representations of the symmetry group. In evaluating the one-, two-, three-, and four-particle density matrix elements occurring in the variational equations, the program expands each GVB(SP) orbital in terms of its symmetry components and combines the integrals corresponding to the particular overall symmetry required[1].

The variational equations were expanded 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 were then iteratively optimized self-consistently for each state. Thus rather than

$$HC = \varepsilon C$$

we solve

$$BA = -X$$

where Δ is the correction 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 [2–4][1]. (This corresponds essentially 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 [2][1]. 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 wavefunction 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 [2][1].

2.5. The Core Hamiltonian

As discussed previously [4], the problem of finding a wavefunction of the form

$$\mathscr{A}\left[\Phi_{\text{core}}\Phi_{\text{val}}\right] \tag{23}$$

may be reduced to finding the wavefunction

$$\mathscr{A}\left[\Phi_{\text{val}}\right] \tag{24}$$

if 1) the core is a product of doubly occupied orbitals and 2) if the orbitals of Φ_{val} are taken to be orthogonal to those of Φ_{core}. The Hamiltonian for the valence orbitals will have the form

$$\mathscr{H} = \sum_{i=1}^{n_\pi} h\,\text{core}\,(i) + \sum_{i>j}^{n_\pi} \frac{1}{r_{ij}} \tag{25}$$

where

$$h\,\text{core}\,(i) = h(i) + \sum_{j=1}^{g} (2J_j - K_j) \tag{26}$$

includes the potential due to the g doubly occupied orbitals of the sigma core,

$$h(i) = \tfrac{1}{2} V_i^2 - \sum_a \frac{Z_a}{r_{ia}} \tag{27}$$

in the usual one-electron Hamiltonian, and n_π is the number of pi-electrons. For allyl radical, the sigma-electron core was formed from an *ab-initio* HF calculation on the ground state of allyl cation.

2.6. 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 [5a]. This was contracted to a double-zeta basis $(4s, 2p)$ on each carbon and $(2s)$ on each hydrogen, as suggested by Dunning [5b]. The above basis was supplemented by two additional pi-Gaussian functions on each carbon with orbital exponents of 0.382 and 0.0127. All calculations used the following geometry: $R_{CC} = 1.40\,\text{Å}$, $R_{CH} = 1.08\,\text{Å}$ and all bond angles $= 120°$.

Table 1. GVB(SP) energies for ground and excited states of ally radical

State	Total energy (h)	Spin coupling coefficients	
		c_1	c_2
$1\,^2A_2$	-116.41861	1.00	0.00
$1\,^2B_1$	-116.30143	-0.938	0.345
$2\,^2B_1$	-116.24590	0.999	-0.027
$2\,^2A_2$	-116.22125	0.999	0.003
$3\,^2B_1$	-116.21743	0.999	-0.032
$4\,^2B_1$	-116.14024	0.089	0.996
$3\,^2A_2$	-116.13617	0.858	0.514
$4\,^2A_2$	-116.13513	0.973	-0.231
Cation $(^1A_1)$[a]	-116.17279	$-$	$-$
$(^3B_2)$	-116.06272	$-$	$-$

[a] Reference [4].
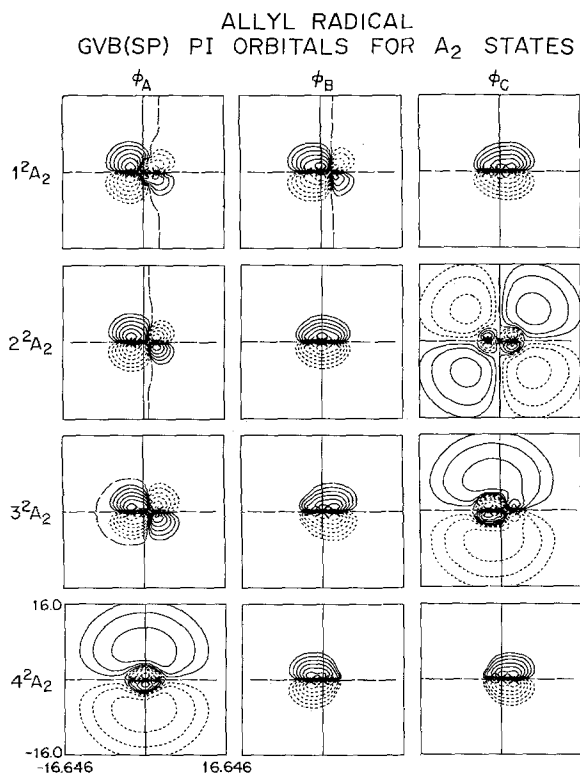
ALLYL RADICAL
GVB(SP) PI ORBITALS FOR A_2 STATES

Fig. 1. The A_2 states of allyl radical. The first two orbitals are singlet coupled in all cases except the $3\,^2A_2$ state in which case the first two orbitals are triplet coupled. The amplitude of the most diffuse contour is 0.003. The amplitude of each succeeding contour is a factor of 2.1544 greater or a factor of 10 for each three contours
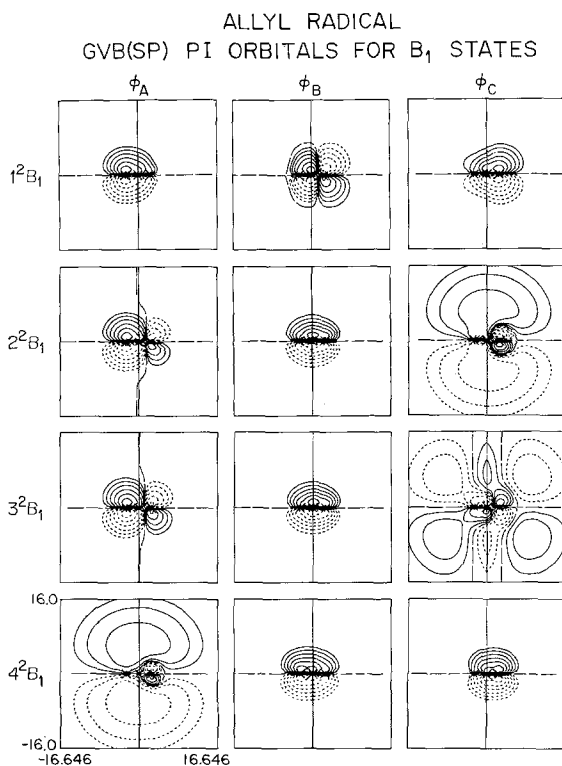
ALLYL RADICAL
GVB(SP) PI ORBITALS FOR B$_1$ STATES

Fig. 2. The B_1 states of allyl radical. The first two orbitals are singlet coupled in all cases except the $4\,{}^2B_1$ state in which case the first two orbitals are triplet coupled. The amplitudes are the same as in Fig. 1

3. Results

The lowest four pi-electron states of both A_2 and B_1 symmetries were examined. The total energies, excitation energies, and spin couplings are summarized in Table 1. Figure 1 depicts the orbitals for the A_2 states and Fig. 2 the orbitals for the B_1 states. In Fig. 1, the orbitals in the first two columns, ϕ_a and ϕ_b, are singlet coupled except for the $3\,{}^2A_2$ state, for which ϕ_a and ϕ_b are triplet coupled. In Fig. 2, the orbitals in the first two columns ϕ_a and ϕ_b are singlet coupled except for the $4\,{}^2B_1$ state, for which ϕ_a and ϕ_b are triplet coupled.

From Figs. 1 and 2, we see that there are only two valence-like states, the $1\,{}^2A_2$ and the $1\,{}^2B_1$ states. These states correspond to the resonant and anti-resonant states of valence bond theory. All of the other states contain one diffuse orbital and are designated as Rydberg-like states. We note the similarity between the orbitals of the $3\,{}^2A_2$ state and orbitals of the $2\,{}^2B_1$ state. These states are the two possible symmetry combinations out these three orbitals, analogously to the orbitals of $1\,{}^2A_2$ and $1\,{}^2B_1$ states, which are also formed using the same orbitals.

4. Discussion

4.1. Resonance Models

In the GVB(SP) description of allyl radical, there are two valence-like states, which we have identified as the resonant and antiresonant states. Examining Figs. 1 and 2 we see that the orbitals for these states are very similar, and from Table 1, these two states have the same spin coupling, both being G1(10). In the GVB(SP) description, spatial symmetry differentiates between these two states.

The ground state of allyl radical is of symmetry $^2A_2$ and is therefore antisymmetric under reflection through a plane passing through the center carbon and bisecting the molecule. If in (21) we imagine that φ_a and φ_c are identical in form but are localized about different centers, then only considering the G1 spin coupling, the wavefunction for the $1\,^2A_2$ state is

$$\Psi = \hat{P}_{A_2}\left(\begin{array}{|c|c|} \hline \varphi_l & \varphi_c \\ \hline \varphi_r & \\ \cline{1-1} \end{array}\right) \tag{28a}$$

or

$$\Psi = \begin{array}{|c|c|} \hline \varphi_l & \varphi_c \\ \hline \varphi_r & \\ \cline{1-1} \end{array} - \begin{array}{|c|c|} \hline \varphi_r & \varphi_c \\ \hline \varphi_l & \\ \cline{1-1} \end{array} \;. \tag{28b}$$

This is the same form as the VB resonance state and the GVB $1\,^2A_2$ (resonance) state [1]. In the GVB(SP) description resonance arises from the symmetry of the state. To the extent φ_l and φ_r differ, the second tableau in (22) is required, but we see from Table 1, that C_2 is very small and the second tableau contributes little.

The first excited state of allyl radical has B_1 symmetry. Again imagining that φ_a and φ_c are identical in form but localized about different centers and considering only the G1 spin coupling in (21), the wavefunction for this state is

$$\Psi = \hat{P}_B\left(\begin{array}{|c|c|} \hline \varphi_l & \varphi_c \\ \hline \varphi_r & \\ \cline{1-1} \end{array}\right) \tag{29a}$$

$$\Psi = \begin{array}{|c|c|} \hline \varphi_l & \varphi_c \\ \hline \varphi_r & \\ \cline{1-1} \end{array} + \begin{array}{|c|c|} \hline \varphi_r & \varphi_c \\ \hline \varphi_l & \\ \cline{1-1} \end{array} \;. \tag{29b}$$

This is the same form as the VB antiresonant state and the GVB $1\,^2B_1$ (antiresonant) state [1]. Antiresonance arises in the GVB(SP) description from the symmetry of the state. In general, φ_l and φ_r will not have the same form and the second (GF) tableau must be included in the wavefunction. From Table 1, we see that the GF contribution for this state is small and (29) is the dominant part of the wavefunction.

Let us examine the VB and GVB descriptions of these two states to compare the different descriptions of resonance. In the VB description there are two valence-like states of allyl radical, the resonant and antiresonant resonant states. These states are described as the antisymmetric and symmetric combinations,

respectively, of the VB canonical structures. The GVB results [1] also indicate that there are only two valence-like states of allyl radical. In fact, the GVB description of these two states is identical to the VB description except that self-consistent orbitals are used in lieu of atomic orbitals. In the GVB *model* the resonance arises from optimization of the spin coupling (given a particular set of orbitals), and the antiresonant state is formed using the same spatial orbitals and the orthogonal spin coupling. The optimum GVB orbitals for the $1\,^2B_1$ state are found to be localized much as in the VB wavefunction and are consistent with the simple GVB model [1]. However, the optimum GVB orbitals for the $1\,^2A_2$ state are delocalized orbitals not the localized orbitals expected in the GVB and VB models. This argues against the simple GVB resonance model for describing the $1\,^2A_2$ and $1\,^2B_1$ states. However we find that using optimal localized orbitals in the $1\,^2A_2$ state leads to an energy only slightly (0.88 kcal) higher in energy than that of the fully optimized GVB wavefunction [1]. Using these localized orbitals for the $1\,^2A_2$ state, the GVB orbitals for the $1\,^2A_2$ and $1\,^2B_1$ states are quite similar in form although not identical.

We thus have arrived at three different qualitative descriptions of the $1\,^2A_2$ and $1\,^2B_1$ states of allyl radical but all have essentially the same form (28 b) and (29 b), respectively. The individual orbitals used in these three sets of wavefunctions differ. The VB wavefunction uses atomic orbitals. The GVB wavefunction uses self-consistent orbitals, but spatial symmetry considerations either restrict the individual orbitals to be delocalized symmetry functions, or if the orbitals are localized, restrict the spin coupling to the resonant (or antiresonant) combinations and require the shapes of φ_r and φ_l to be equivalent [1]. The GVB(SP) wavefunction without restricting the shape of the orbitals or the spin coupling generates the resonant (or antiresonant) combination of structures through a spatial symmetry operator.

By comparing the energy of the GVB(SP) wavefunction for the $1\,^2A_2$ state with the energy resulting from the optimum wavefunction of form (10) [optimum orbitals but the G1 spin coupling] [1], we obtain the GVB(SP) estimate of the resonance energy. This GVB(SP) estimate of the allyl radical resonance energy is 14.3 kcal as compared to 11.4 kcal [1] for the GVB wavefunction and 15.9 kcal [1] for the VB wavefunction, using the same basis set for all computations. The experimental value for the allyl radical resonance energy is 10 ± 1.5 kcal [7]. The antiresonance energy found from the GVB(SP) wavefunction for the $1\,^2B_1$ state is 59.2 kcal as compared to 61.9 kcal for the VB wavefunction and 57.9 kcal for the GVB wavefunction.
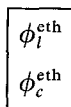
4.2. The Fused Ethylene Model

Dunning [6] has proposed a model for the pi-states of butadiene that treats these states as arising out of combinations of ground and excited states of ethylene. In this model, two ethylenes are fused to form butadiene and the pi-states of butadiene are identified with combinations of ethylene pi-states. We found that this model works well for the valence states of s-trans-1,3-butadiene but were unable to apply this model to Rydberg states as the orbitals were found to be delocalized [2]. Since the GVB(SP) description of allyl radical yields localized

orbitals for all states, we can examine the applicability of fused ethylene to the pi-states of allyl radical. Allyl radical in this model is considered as a combination of ethylene and methylene.

The GVB(SP) description of ethylene [4] yields two valence like states, the grond (N) state

$$\boxed{\phi_l^{eth} \quad \phi_c^{eth}}$$
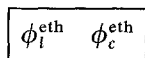
and the lowest triplet (T)

$$\boxed{\begin{array}{c} \phi_l^{eth} \\ \phi_c^{eth} \end{array}}$$

state at 4.2 eV (vertical excitation energy). The $1\,^2A_2$ state of allyl radical may be considered as arising from a combination of an N state of ethylene with a $2p$-like pi-orbital on the third carbon (i.e., a $^3B_1$ methylene).
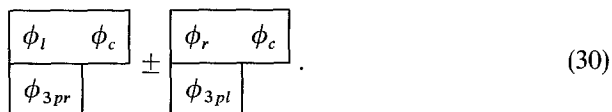
$$\boxed{\begin{array}{cc} \phi_l^{eth} & \phi_c^{eth} \\ \phi_r^{me} & \end{array}} \quad .$$
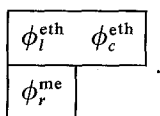
The $1\,^2B_1$ state of allyl radical would then be the combination of the T state of ethylene and the same third orbital,

$$\boxed{\begin{array}{cc} \phi_l^{eth} & \phi_r^{me} \\ \phi_c^{eth} & \end{array}} \quad .$$
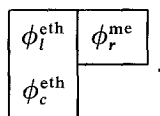
Fusing the methylene and the ethylene to form allyl leads to repulsive interactions for the lower state and attractive interactions for the upper state (decreasing then the excitation energy). Readjustments in the orbitals lead then to the GVB(SP) wavefunction and the final energies with the excitation energy decreasing to 3.2 e.V.

In this model the higher (Rydberg) states arise from combining the N state of ethylene with a $3p$ or $3d$ orbital on the methylene, leading to three excited states (two d orbitals are of π symmetry). Another set of states about 3 eV higher arise from coupling the T state of ethylene with the $3p$ and $3d$ orbitals.

To better visualize the Rydberg states we will consider explicitly the resonance of the above states. Thus $N + 3p$ leads to

$$\boxed{\begin{array}{cc} \phi_l & \phi_c \\ \phi_{3pr} & \end{array}} \pm \boxed{\begin{array}{cc} \phi_r & \phi_c \\ \phi_{3pl} & \end{array}} \quad . \tag{30}$$

Since the $3p$ orbital is diffuse, we can as a first approximation assume that

$$\phi_{3pr} \approx \phi_{3pl} = \phi_{3p} \, . \tag{31}$$

In this case the wavefunction (30) leads to

$$
\begin{array}{|cc|}
\hline
\phi_l & \phi_c \\
\hline
\phi_{3p} \\
\cline{1-1}
\end{array}
\pm
\begin{array}{|cc|}
\hline
\phi_r & \phi_c \\
\hline
\phi_{3p} \\
\cline{1-1}
\end{array} .
\tag{32}
$$

corresponding essentially to an N state core for the $+$ sign and a T state core for the $-$ sign. Thus the third state of allyl is expected to be of the form (30) with a $+$ sign. This conclusion is correct and the orbitals of the $2\ ^2B_1$ state (Fig. 2) correspond to the form expected from (30).

The next excited state would be obtained by combining the N state of ethylene with a $3d$ orbital on the methylene

$$
\begin{array}{|cc|}
\hline
\phi_l & \phi_c \\
\hline
\phi_{3dr} \\
\cline{1-1}
\end{array}
\pm
\begin{array}{|cc|}
\hline
\phi_r & \phi_c \\
\hline
\phi_{3dl} \\
\cline{1-1}
\end{array}
\tag{33}
$$

There are two $3d\pi$ orbitals to be used in (33). For $3d_{xy}$ (taking the molecule to be in the yz plane with z as the symmetry axis) we have

$$
\phi_{3dl} \approx -\phi_{3dr} \approx \phi_{3d}
\tag{34}
$$

and (33) becomes

$$
\begin{array}{|cc|}
\hline
\phi_l & \phi_c \\
\hline
\phi_{3d} \\
\cline{1-1}
\end{array}
\mp
\begin{array}{|cc|}
\hline
\phi_r & \phi_c \\
\hline
\phi_{3d} \\
\cline{1-1}
\end{array} .
\tag{35}
$$

Thus it is the minus combination in (33) that leads to an N-like ethylene state in (35). This wavefunction leads to the $2\ A_2$ state of allyl, the next excited π state. For the other $3d\pi$ orbital ($3d_{xz}$) we have

$$
\phi_{3dl} \approx \phi_{3dr}
$$

so that (33) reduces to

$$
\begin{array}{|cc|}
\hline
\phi_l & \phi_c \\
\hline
\phi_{3d} \\
\cline{1-1}
\end{array}
\pm
\begin{array}{|cc|}
\hline
\phi_r & \phi_c \\
\hline
\phi_{3d} \\
\cline{1-1}
\end{array}
\tag{36}
$$

leading to the $3\ ^2B_1$ state. From Figs. 1 and 2 we see that the $2\ ^2A_2$ and $3\ ^2B_1$ states have these characters.

The higher states shown in Figs. 1 and 2 correspond to the antiresonant combinations of (32), (35), and (36) or equivalently in the fused ethylene model to use of the T state on the ethylene.

In the $3\ ^2A_2$ state, the two tight orbitals are triplet coupled and may be considered as an ethylene T state core. Since the ethylene T state core has A_2 symmetry and the diffuse orbital is almost orthogonal to the tight orbitals, the diffuse orbital must have B_1 symmetry and should be a $3p\pi$ orbital. The difference between the $2\ ^2B_1$ and the $3\ ^2A_2$ states is in the cores, the first being an ethylene N state and the second an ethylene T state. We note that the difference in energy

Table 2. Comparison of GVB, GVB(SP), and CI energies for the ground
and excited states of allyl radical

State	GVB[a,b]		GVB(SP)		Full CI[a,b]	
	Total energy (hartrees)	Excitation energy(eV)[d]	Total energy (hartrees)	Excitation energy(eV)[d]	Total energy (hartrees)	Excitation energy(eV)[d]
$1\,^2A_2$	−116.416438	0.0	−116.418612	0.0	−116.421089	0.0
$1\,^2B_1$	−116.297120	3.249	−116.301432	3.188	−116.303426	3.203
$2\,^2B_1$	−116.237380	4.872	−116.245897	4.702	−116.248310	4.702
$2\,^2A_2$	−	−	−116.221249	5.374	−116.222188	5.412
$3\,^2B_1$	−116.209966	5.610	−116.217433	5.474	−116.219937	5.474
$4\,^2B_1$	−	−	−116.140243	7.575	−116.145124	7.509
$3\,^2A_2$	−	−	−116.136173	7.686	−116.137979	7.709
$4\,^2A_2$	−	−	−116.135127	7.713	−	−
Cation $(^1A_1)$[c]	−116.15790	7.035	−116.17279	6.689	−116.173420	6.740
Cation $(^3B_2)$[c]	−116.06065	9.682	−116.06272	9.684	−116.06273	9.752

[a] Reference [1].
[b] All calculations were performed using the same basis set.
[c] Reference [4].
[d] 1 h = 27.2117 eV.

Table 3. Excitation energies for allyl radical (all values in eV)

State	GVB(SP)	GVB[a]	CI[a]	Peyerimhoff and Buenker[b] (ab initio CI)	Semi-empirical CI[c]
$1\,^2A_2$	0	0	0	0	0
$1\,^2B_1$	3.19	3.25	3.20	3.79	2.43
$2\,^2B_1$	4.70	4.87	4.70	8.0	9.79
$2\,^2A_2$	5.374		5.412	11.66	12.492
$3\,^2B_1$	5.474		5.474		14.35
$3\,^2A_2$	7.686		7.701		12.942

[a] Reference [1].
[b] Reference [10].
[c] Reference [11].

between these two states is 2.99 eV while in allyl cation the excitation energy of
the $^3B_2$ state (corresponding to the ethylene T state) over the $^1A_1$ (corresponding
to the ethylene N state) is 3.00 eV, in excellent agreement.

4.3. Rydberg-Like Excited States

Table 2 contains a comparison of GVB, GVB(SP), and full (or complete
within the basis set) CI calculations on the allyl radical pi-electron system. All
calculations were performed using the same basis set. The agreement among the
three sets of calculations is quite good both with regard to total energies and
excitation energies. We note that for Rydberg states, the difference between the
GVB and GVB(SP) energies is the greatest. The GVB(SP) allows an excitation
to be localized near one center and a description of the state in terms of localized
orbitals. The GVB description is in terms of delocalized symmetry orbitals for
the Rydberg states. The GVB(SP) energy for Rydberg states is in excellent agree-
ment with the full CI results.

The $2\,^2B_1$, $3\,^2B_1$, and $2\,^2A_2$ all have a rather diffuse orbital and have been described as Rydberg states. To test this assignment further, the quantum defects, ζ, for these states were calculated using

$$E_n = A - R/(n - \zeta)^2$$

where E_n is the energy of the state, A is the energy of the ion taken as the GVB(SP) energy from Ref. 1, and ζ the quantum defect. We obtain

$$2\,^2B_1 : \zeta = \quad 0.38 \ (3p\pi)$$
$$3\,^2B_1 : \zeta = -0.35 \ (3d\pi)$$
$$2\,^2A_2 : \zeta = -0.21 \ (3d\pi).$$

For p-like Rydberg states, ζ is typically 0.50 [8] which is consistent with the assignment of $2\,^2B_1$ as the upper state of the $2p\pi \to 3p\pi$ excitation. For d and f-like Rydberg orbitals ζ is typically < 0.10. However our basis set only includes $p\pi$ functions leading to a poor description of the $3d\pi$ orbitals and hence a negative sign of ζ for the $2\,^2A_2$ and $3\,^2B_1$ states.

Ionizing the diffuse orbital from the $3\,^2A_2$ state leads to the $1\,^3B_2$ state of allyl cation since the two orbitals are triplet coupled. Using the GVB(SP) energy for the $1\,^3B_2$ state [1], we obtain a value of 0.39 for the quantum defect (relative to $n = 3$). Thus the $3\,^2A_2$ state corresponds essentially to a $2p\pi \to 3p\pi$ excitation from the $1\,^2B_1$ state. This is the same as the $2\,^2B_1$ state, the difference between these two states being in the spin coupling of the core orbitals. The calculated quantum defects for these states differ by only 0.01.

Table 3 contains a comparison with other results. The GVB(SP) results compare very favorably. The basis set used by Peyerimhoff and Buenker [9] did not contain diffuse function accounting for their poor description of the $2\,^2B_1$ state.

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